Nanostructured semiconducting, ferroelectric, and multiferroic crystals: synthesis, characterization and energy application

Jun Wang
Iowa State University

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Nanostructured semiconducting, ferroelectric, and multiferroic crystals: synthesis, characterization and energy application

By

Jun Wang

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Program of Study Committee:
Zhiqun Lin, Major Professor
Michael Kessler
Surya K. Mallapragada
Victor Shang-Yi Lin
Malika Jeffries-EL

Iowa State University

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Dedications

I would like to dedicate this work to Mowen Li, and my parents.
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Abstract

Organic solar cells (e.g., dye sensitized solar cells and organic-inorganic bulk heterojunction cells) are attracting considerable attention due to their low cost, easy processibility, and large scale fabrication capability. However, the solar energy conversion efficiency of these cells is low due to significant charge recombination and inefficient charge separation at the organic/inorganic interface. Thus, further improvement on the efficiency is necessary for the creation of low-cost devices.

In this context, we focus on the synthesis of highly ordered TiO$_2$ nanotube arrays, which was subsequently utilized as photoanode in dye sensitized solar cells and quantum dot solar cells. The highly ordered TiO$_2$ nanotube arrays not only provide a large interface area where excitons, the bound electron-hole pairs, may effectively dissociate, but also have two separate channels for efficient electron and hole transport. Surface engineering, i.e., TiCl$_4$ treatment and oxygen plasma exposure, was combined in the first time to improve the solar energy conversion efficiency of dye sensitized TiO$_2$ nanotube solar cells. With a nanotube film thickness of 14 µm and optimized surface treatment, an overall power conversion efficiency of 7.37 % were obtained when a ruthenium dye N-719 was used as photosensitizer; this performance is among the best for TiO$_2$ nanotube based solar cells. In addition, a number of functional nanocrystals, including semiconducting CdSe quantum dots, ferroelectric BaTiO$_3$ and PbTiO$_3$ nanocrystals, multiferroic BiFeO$_3$ nanocrystals were synthesized and characterized, which possess potential applications in solar cells, light emitting diodes, biosensors, thin-film capacitors, pyroelectric detectors, electrooptic modulators, transducers, actuators, and magnetically recorded ferroelectric memory.
Chapter 1. General Introduction

1.1 Dye sensitized solar cells (DSSCs)

Since first reported in 1991 by Oregan and Gratzel, ruthenium dye sensitized titania nanocrystal solar cells with power conversion efficiency about 10% have received considerable attention.\(^1\) These cells are extremely promising because they are made of low-cost materials and do not need elaborate apparatus to manufacture. The cells have a simple structure that consists of two electrodes and an iodide-containing electrolyte. One electrode is dye-absorbed highly porous nanocrystalline titanium dioxide (TiO\(_2\)) deposited on a transparent electrically conducting substrate (e.g., indium-tin oxide (ITO) or fluorine doped tin oxide (FTO) coated glass). The other is a transparent electrically conducting substrate only (e.g., semi transparent platinum coated conductive glass\(^2,3\)). It is expected that the energy conversion efficiency of DSSC can rise to 33%, which is the ideal value for a single exciton generation system as predicted by Shockley and Queisser in 1961.\(^4\) The working principle of DSSC is illustrated in Figure 1-1.\(^1\)
Unlike the conventional semiconductor devices, DSSCs separate the function of light absorption from charge carrier transport. Current is generated when a photon absorbed by a dye molecule giving rise to electron injection into the conduction band of semiconductor, e.g., TiO$_2$. The dye must be regenerated to complete the circuit, which is accomplished by electron transfer from a redox species in solution. The monochromatic current yield can be illustrated as

$$\eta_l(\lambda) = LHE(\lambda) \times \phi_{\text{inj}} \times \eta_e$$  \hspace{1cm} (1)$$

where $LHE$ is light harvest efficiency (the fraction of incident photons that are absorbed by the dye), $\phi_{\text{inj}}$ is the quantum yield for charge injection, and $\eta_e$ represents the charge collection efficiency at the back contact. This equation expresses the ratio of measured current to the incident photon flux at a given wavelength.$^1$ The TiO$_2$ nanocrystal film
used in the DSSC system is deposited on a conductive glass from colloidal solution. The TiO$_2$ nanoparticle can be obtained by hydrolysis of titanium tetra-isopropoxide, followed by autoclaving for 12 h at 200°C.\textsuperscript{1,5,6} By adjusting the TiO$_2$ nanocrystal film thickness and internal surface area while ensuring the pore size is large enough for redox electrolyte to diffuse, efficient light harvesting can be obtained to achieve maximum device performance.

Later on, anodic TiO$_2$ nanotube arrays were used to substitute the TiO$_2$ nanoparticle system for dye sensitized solar cells.\textsuperscript{7-10} The anatase anodic TiO$_2$ nanotubes have the vertical nanocrystal array, which gives the excellent pathway for electron transport to the anode. A systematic study of TiO$_2$ nanotube for DSSC, compared to the conventional TiO$_2$ nanoparticle system, showed an enhanced charge collection efficiency and light scattering at a certain thickness, the nanotubes have the same dye molecule absorption capability as TiO$_2$ nanoparticle film.\textsuperscript{8} This offers the possibility to improve the device efficiency to 33% if the thickness of TiO$_2$ nanotube grown on conductive glass can be further improved, which is currently limited by the quality of titanium deposited on the conductive glass.\textsuperscript{10} The highest efficiency form dye sensitized anodic TiO$_2$ nanotube is 6.9% as recently reported by Mor et al using a 20 μm thick TiO$_2$ nanotube array in the backside illumination mode.\textsuperscript{9}

Quantum dots, for example, CdS, CdSe, CdTe, InAs, InP and PbSe, which absorb visible light and inject electrons to large bandgap semiconductor, e.g., TiO$_2$, have shown promising potential as a substitute for ruthenium dye used in conventional DSSCs.\textsuperscript{3,11-14} Quantum dots carry the advantages of tunable band gap, efficient visible absorption, and multi-exciton generation capability.\textsuperscript{13,15-22} Both theoretical study and experimental results
have shown the possibility to use quantum dots for solar cells. Although it is currently under debate, theoretical calculation showed that as many as seven exciton can be generated when PbSe quantum dot absorbed one photon at a certain energy level, and an ideal power conversion efficiency of about 42% can be expected, which is one third higher than the 33%, due to Shockley-Queisser limit for one exciton generation system. Thus, quantum dots with multi-exciton generation capability show tremendous potential as sensitizers for a new generation solar energy conversion device and may further increase the power conversion efficiency. Moreover, the optical properties of quantum dots can be tailored to maximize solar photon absorption. Yu et al have reported the highest efficiency of 1.7% under 5 mw/cm² illumination using InAs quantum dots to sensitize TiO₂ nanoparticle film. However, at higher intensity illumination, the efficiency reduced because of the enhance charge recombination. Further work is necessary to improve the quantum dot sensitized solar cell (QDSSC) efficiency through rational design of device structures, modification of the redox electrolyte, molecular linkage of quantum dots to TiO₂, etc.

As described above, in the DSSC device, liquid redox electrolyte was used, which makes it not convenient and unsafe to store and transport the device as the iodide base electrolyte is highly corrosive. Thus, solid state solar cell device is highly desirable. The commonly used method is to use conjugated polymers to substitute the iodide redox electrolyte. Prene et al have spin cast a layer of hole conducting poly (3-octylthiophene) (P3OT) on the dye soaked TiO₂ nanoparticle film to fabricate the all-solid-state DSSC, as shown in Figure 1-2.
Kroeze et al and Schmidt-Mende et al also infiltrated hole conducting conjugated polymer in the porous TiO$_2$ film to yield solid state DSSC.\textsuperscript{24, 25} However, the infiltration degree of hole conducting polymer was limited and cannot reach high occupancy as liquid electrolyte. Therefore the efficiency of solid state dye sensitized solar cell was always lower compared with the devices using liquid redox electrolyte.

Figure 1-2. A schematic of the all-solid-state DSSC.

Other methods have also been introduced to make all-solid-state DSSC devices. Schmidt-Mende et al used organic dye to substitute the conventionally used ruthenium dye for solid state solar cell and achieved an efficiency that was comparable to the ruthenium dye sensitized solar cell.\textsuperscript{26}

In order to obtain high efficiency solid state DSSC, the infiltration of hole conducting polymer is a key step. Further study is required, including filling more polymers into nanopores, improving the interface between polymer and dye, and the optimization of device parameters.

To obtain high power conversion efficiency from quantum dots sensitized solar cells, first of all, the device composition should be optimized. For example, unlike the
porous TiO$_2$ nanoparticle system in which the cross linked nanopores give the pathway for air to escape, infiltration of CdSe quantum dots and electrolyte into the one side open anodic TiO$_2$ nanotube arrays may be difficult due to the air is trapped within the tubes.\textsuperscript{9,27} Applying proper solvents that can easily wet TiO$_2$ nanotubes, in conjunction with vacuum, may be helpful for the infiltration of quantum dots and electrolytes.\textsuperscript{9} The electrolyte is also important in the final device performance. For CdSe quantum dots used as sensitizer, iodide redox electrolyte can easily destroy CdSe, resulting in an unstable device.\textsuperscript{3} Polysulfide aqueous electrolyte has been proved to be suitable for CdSe quantum dots,\textsuperscript{12} meanwhile the anatase TiO$_2$ nanotubes have been found to be super hydrophilic.\textsuperscript{28} Therefore, polysulfide would be a better choice of electrolyte for preparing quantum dot solar cell devices, in which CdSe quantum dots are used as sensitizer. In order to produce high efficiency quantum dots sensitized TiO$_2$ nanotube solar cells, transparent titania nanotubes grown on conductive glass are required.\textsuperscript{10,29} However, it is very difficult to deposit high-quality titanium layer on substrate. Moreover, the thickness of titanium that can be deposited is limited.\textsuperscript{29} Molecular linkage of quantum dots to inner walls of titania is also an important means of enhancing the charge separation,\textsuperscript{12} which, in turn, improve the efficiency of QDSSC devices. In order to molecularly link quantum dots to the TiO$_2$ surface, two approaches can be used. First, the TiO$_2$ nanotubes are functionalized using bifunctional molecules (e.g., 3-mercaptopropionic acid (MPA)). The nanotubes are then soaked in the quantum dot suspension, during which quantum dots would tether to inner walls of TiO$_2$ via the ligand exchange process. The carboxylic group at one end of MPA chemically links to TiO$_2$, while the thiol group on the other end preferentially anchors to quantum dots. The other approach involves the modification of quantum dot surface first
using MPA via ligand exchange in the solution, followed by soaking the anatase TiO₂ nanotubes in the MPA functionalized quantum dot suspensions. In either approach, removal of trapped air in TiO₂ nanotubes is critical in order to achieve high degree of filling of quantum dots.

1.2 Highly order nanoporous alumina membrane (PAM)

Highly ordered porous alumina membrane (PAM) obtained via self-organization during electrochemical anodization of an aluminum foil in acidic electrolyte has been studied extensively for more than a decade due to its intriguing application as a starting structure for fabrication of ordered nanodevices. Since Masuda et al first introduced the two-step procedure to fabricate well ordered porous alumina in 1995, the mechanism of nanopores formation in PAM and its application has been widely studied. Porous alumina membrane with different pore size, thickness, and pore shape were successfully fabricated. The well ordered structures have been widely used to produce optical devices, fabricate nanodevices, serve as sensor template, and provide as intriguing nanoscopic geometry to study the confinement effect. Porous alumina thin film with good contact to substrates (e.g., silicon wafer and glass) was also fabricated by electrochemically anodizing aluminum deposited on the substrate. Systematic studies of the fabrication of PAM suggested that the interpore distance increased with the anodization voltage (Figure 1-3), while the thickness of membrane was dictated by anodization time.

In order to obtain PAM with well ordered porous arrays, certain anodization conditions should be met: 1) sulphuric acid at 25 V, with interpore distance of 63 nm,
2) oxalic acid at 40 V, with interpore distance of 100 nm; and 3) phosphoric acid at 195 V with interpore distance of 500 nm. By taking advantage of nanoimprinting instead of the abovementioned self-organizing pore-forming procedure, it became more feasible to tune the pore size, interpore distance, and even the pore shape. Figure 1-4 illustrates a typical nanoimprinting scheme. Lee et al fabricated a long range ordered PAM with interpore distance of 200 nm ~ 300 nm using hard anodization; Masuda et al reported the fabrication of PAM with pores interval of 13 nm and pore diameter of 7 nm using monodisperse nanoparticles as template and anodized at 16 °C in 0.3 M sulfuric acid with a constant potential of 3 V; Peng et al fabricated PAM with ideally ordered 10 nm channels by anodization of focused-ion-beam patterned aluminum; Masuda et al demonstrated the preparation of square and triangular nanohole array architectures in anodic alumina. These extensive studies make it possible to utilize the porous alumina more widely in many nanotechnology related applications.
Figure 1-3. Interpore distance in PAM as a function of anodization potential.

Figure 1-4. A typical schematic illustration of the formation of order PAM. (a) texturing on the aluminum surface; (b) ordered PAM after anodization.
A typical procedure to prepare PAM with diameter, $D = 60$ nm and interpore distance, $\lambda = 110$ nm via two-step anodization process is described as follows. First, high purity aluminum foil was degreased by sonicating in a mixture of ethanol, chloroform, and acetone at a volume ratio of 1:2:1. The foil was then washed thoroughly using DI-water and dried with $\text{N}_2$. The degreased aluminum foil was first anodized in 0.3 M oxalic acid at 0 °C with an anodization potential of 42 V for 3 h. A platinum foil was used as the counter electrode; the first anodized alumina was selectively dissolved in a mixture of phosphoric acid and chromic acid at 60 °C for 6 h, resulting in concave patterns on the aluminum foil, which subsequently acted as the template for well ordered structure growth. The foil was then washed thoroughly with DI-water, dried, and anodized under the same condition as in the first anodization. By adjusting the second anodization time, different thickness can be achieved, typically from several hundred nanometers to tens of micrometers. Selective removal of the backside aluminum using saturated copper chloride resulted in PAM with one side pore open, while the other blocked by a barrier layer of $\text{Al}_2\text{O}_3$. In order to obtain PAM with two sides pore open, 5 wt% phosphoric acid was subsequently used to remove the $\text{Al}_2\text{O}_3$ barrier layer. The formation of porous alumina via electrochemical anodization involved the competition of several spontaneous processes: electrochemical oxidation of aluminum to form alumina; electrochemical forced dissolution of formed alumina; and chemical dissolution of alumina in acidic electrolytes. The formation mechanism of PAM is shown in Figure 1-5. It has been suggested that it was the larger electric filed, due to an increased curvature, at the bottom of pores caused the increased oxidation growth and oxide dissolution, thus contributing to the pore growth.
Recently, Lee et al reported the fast fabrication of long-range ordered PAM by hard anodization, in which the anodization current was much higher than conventional mild anodization, thereby dramatically enhancing the alumina growth speed. At higher anodization potential, PAM with large interpore distance and significant thickness can be obtained in a relatively short time. This method largely expanded the pore array morphology in PAM, giving more choice where the nanopores of PAM was used and tremendously reduced the PAM preparation time.

![Formation mechanism of PAM](image)

Figure 1-5. Formation mechanism of PAM.

The as-prepared PAM consists of highly ordered hexagonal arrays of straight, cylindrical nanopores throughout the whole membrane. Thus, it is an ideal structure for fabricating nanodevices, sensor templates, and optical devices. It is also well suited for study of nano confinement effects, for example, crystallization kinetics of semicrystalline polymer in PAM as a function of pore size. By controlling the second anodization,
PAM with tunable thickness can be obtained and can be used as a mask for thermal evaporation, electro-deposition or sputtering to deposit nanodots, nanowires, and nanotubes. For example, Lee et al produced silver nanowire bundles via electrochemical deposition using PAM as mask, and, subsequently, used the nanowire bundles for surface enhanced Raman spectroscopy.\textsuperscript{61} Masuda et al fabricated gold nanodots using thin PAM as thermal evaporation mask.\textsuperscript{31} Lei et al obtained the semiconductor nanoparticle arrays on silicon wafer using ultra-thin PAM as evaporation mask.\textsuperscript{62, 63} Masuda et al also employed PAM for lasing and photonic crystals.\textsuperscript{38, 53} Coakley et al infiltrated semi-conducting conjugated polymer into the nanopores of PAM and suggested enhance hole mobility in the conjugated polymer.\textsuperscript{45} Dotzauer et al used PAM as a template to prepare catalytic membrane composed of nanoparticles absorbed at the inner wall of PAM.\textsuperscript{64} Lahav et al employed PAM as support and prepared nanoparticle nanotubes by absorption of gold nanoparticle in the nanopores.\textsuperscript{65} PAM was also used as the biosensor substrate by monitoring the absorption, emission, and scattering spectra when bonded with biological specimens. In summary, PAM possesses well ordered, straight nanopores throughout the whole membrane. The pore size, thickness, and shape can be readily tuned by varying the anodization conditions. This makes it promising to be used in the fabrication of nanodevices, photonic devices, biosensors, solar energy conversion devices, etc. By incorporating with the surface functionalization of the inner walls, the application of PAM can be further expanded.\textsuperscript{64, 65} The –OH group at the alumina surface can readily react with functional groups, e.g. carboxylic group,\textsuperscript{66} silane\textsuperscript{67} etc. Figure 1-6 shows the examples for the functionalization of the inner walls of PAM.\textsuperscript{66, 67}
Figure 1- 6. Examples of surface functionalization of the inner wall of PAM. (a) PAM reacts with carboxylic acid, and (b) PAM reacts with silane.

1.3 Highly order anodic titania nanotube array

Similar to the electrochemical anodization of aluminum to form nanoporous alumina, TiO$_2$ nanotubes were obtained via the electrochemical anodization of titanium in the fluorine containing electrolytes, and exhibited the most remarkable properties among all the nanostructured TiO$_2$ from other procedures. Zhu et al systematically studied the application of anodic TiO$_2$ nanotubes for dye sensitized solar cells (DSSCs) and suggested enhanced charge collection efficiency and light scattering in the nanotube compared with the conventionally used TiO$_2$ nanoparticle system. The TiO$_2$ nanotubes
have also been used as hydrogen sensor and showed an extreme change of electrical resistance when exposed to a small amount of hydrogen.$^{71}$

In 1999, Zwilling et al reported the porous structure formation in titanium via electrochemical anodization in the fluorine containing electrolytes.$^{72}$ Years later, Gong et al first demonstrated the fabrication of uniform TiO$_2$ nanotube via electrochemical anodization of titanium in the hydrofluoric acid containing solution.$^{68}$ Since then, numerous researches have been carried out in regard of the fabrication and application of TiO$_2$ nanotubes. Fabrication of TiO$_2$ nanotubes with various pore size (20 ~ 110 nm), thickness (200 nm ~ 1000 µm) and wall thickness (7 ~ 34 nm) have been reported in recent years.$^9, 73$ TiO$_2$ nanotubes were obtained by anodizing high purity titanium in the fluorine containing electrolytes, sharing the similar nanostructure formation mechanism as the anodization of aluminum, including electrochemical oxidation of titanium, electrochemical dissolution of TiO$_2$, and chemical dissolution of TiO$_2$ by fluorine ions. However, the fluorine ion in aqueous electrolytes can dissolve TiO$_2$ in significant speed, resulting in the nanotube structure with limited nanotube array thickness, e.g., several hundred nanometers thick when anodizing titanium in the 0.5 wt% hydrofluoric acid.$^{68}$ Later on, by adjusting the pH of electrolyte, using fluorine containing the buffer solution, or applying nonaqueous electrolyte, TiO$_2$ nanotubes with thickness up to 220 µm was achieved.$^{73}$ In general, three generation of electrolytes have been developed for the anodization growth of titania nanotubes. The first generation of electrolyte is hydrofluoric acid (HF) aqueous solution, in which only several hundred nanometer thick titania nanotubes can be obtained. When the anodization time was long, the fast dissolution of TiO$_2$ in HF aqueous solution significantly competed with the electrochemical oxidation
of titanium. Thus, after a certain thickness of TiO₂ nanotubes were achieved, there was a balance between these two speeds. As a result, the thickness cannot increase further. However, the application of TiO₂ nanotubes in the fields of solar cells, gas sensors, etc. requires improved thickness for more efficient absorption of incident light or gas residue to ensure better performance. One of the methods is to decrease the chemical dissolution speed of TiO₂ during anodization. The PH of the electrolyte was found to affect the dissolution speed, which was significantly reduced at higher pH. The second generation of fluorine containing electrolyte has a relatively higher PH, indicating slower chemical dissolution of TiO₂. Using this kind of electrolyte, TiO₂ nanotubes with thickness of several micrometers were successfully prepared and exhibited a considerable improved performance in gas sensors, etc. The third generation of electrolyte, using nonaqueous solvent containing ammonium fluoride,⁶⁹, ⁷³, ⁷⁴ was then introduced and further reduced the dissolution speed by reducing the water content in the electrolyte, thereby largely reducing the chemical dissolution of TiO₂ by fluorine ion. TiO₂ nanotubes with thickness up to 220 µm have recently been reported by Shankar et al., ⁷³ using ethylene glycol containing ammonium fluoride as the electrolyte. It should be noted that TiO₂ has very poor mechanical property. Thus, it is difficult to obtain the freestanding TiO₂ nanotube arrays as PAM, which, to some extent, limits its applications. Recently, Mor et al reported the fabrication of transparent TiO₂ nanotubes via anodization of titanium pre-deposited on the substrate, and successfully applied it for the high-performance DSSCs and hydrogen sensors.¹⁰, ²⁹, ⁷⁵ However, the thickness of nanotubes was only at several hundred nanometers due to the limited ability of depositing thicker and high-quality titanium on the substrate.⁷³ TiO₂ nanotubes directly after anodization are amorphous and
not photoactive, therefore, high temperature annealing is necessary to induce the formation of photoactive anatase crystalline without destroying the nanotube structure.\textsuperscript{76}

The as-anodized TiO\textsubscript{2} nanotubes are amorphous. Their morphologies can be transformed to anatase or rutile after the high temperature annealing. The TiO\textsubscript{2} nanotubes have large surface area and possess unique electrical and optical properties. They show enhanced performance in photocatalysis, gas sensors, hydrogen generation, and photovoltaics.

Mor et al studied the hydrogen generation capability of anodic TiO\textsubscript{2} nanotubes and suggested that the wall thickness of nanotubes, controlled by the electrolyte temperature, was a key parameter of the photoanodic response and the overall efficiency of the water-splitting reaction.\textsuperscript{77} The thicker the wall of nanotubes, the higher photoanodic response can be obtained. For example, for a certain diameter of 22 nm of the nanotubes, the TiO\textsubscript{2} nanotubes with 224 nm long and 34 nm wall thickness anodized at 5 °C produced a photoanodic response that was twice that of the nanotubes with 120 nm long and 9 nm wall thickness anodized at 50 °C. Using the TiO\textsubscript{2} nanotubes with 22 nm in diameter and 34 nm wall thickness, a hydrogen generation rate of 960 µmol/h W, upon illumination at 320-400 nm with an intensity of 100 mw/cm\textsuperscript{2}, has been obtained. The overall conversion efficiency was 6.8%. This technology suggests an intriguing energy source that is efficient, renewable, nonpolluting, and readily portable.

Many researches have been carried out on the application of self-organized TiO\textsubscript{2} nanotube arrays for highly sensitive hydrogen sensor,\textsuperscript{71, 75, 78} which can be used to monitor the hydrogen level where it is needed, such as in food production plants, pollution monitoring in engines, monitoring the hydrogen level in premature baby body
in case of infection, etc. Varghese et al first reported the highly sensitive hydrogen sensor based on the electrical resistance change of anodic TiO$_2$ nanotubes. The TiO$_2$ nanotubes with 22 nm inner diameter demonstrated a change up to $10^4$ in electrical conductance upon exposure to 1000 ppm hydrogen at 290$^\circ$C. The mechanism of hydrogen sensing was suggested as follows: the hydrogen molecules dissociated at the titania surface, diffusing into the TiO$_2$ lattice, and acted as electron donors, thereby significantly increasing the conductance of TiO$_2$ nanotubes. The hydrogen sensitivity is highly dependent on the nanotubes diameter. The nanotubes morphology and wall thickness are found to evoke the unique conductance response, as the wall thickness is on the order of Debye length. Later on, Mor et al demonstrated the room-temperature TiO$_2$ nanotube hydrogen sensor, in which a 10 nm thick non-continuous palladium layer was coated. The TiO$_2$ nanotubes used had an inner diameter of 22 nm, wall thickness of 13.5 nm, and nanotubes length 400 nm. The non-continuous palladium layers facilitated the breakage of hydrogen molecules into atomic forms and diffuse into the nanotubes. A change in electrical resistance of 175000% was obtained at 24$^\circ$C. A higher performance hydrogen sensor has been recently documented using transparent TiO$_2$ nanotubes on transparent substrate. More intriguingly, due to the outstanding photocatalytic properties of TiO$_2$ nanotubes, TiO$_2$ nanotubes were able to self-clean through a photocatalytic oxidation process when exposed to UV illumination after contamination, for example, motor oil contamination, during the application for hydrogen sensor. Thus, anodic TiO$_2$ nanotubes are expected to have promising applications in highly efficient self-cleaning photocatalytic surfaces. It may also be used to detect other chemicals by doping with other metals, like tin, gold, silver, copper, or niobium. However, the
hydrogen sensor cannot self-clean from contaminations which contain salts, the salts in
the contamination may degrade the photocatalytic properties of TiO$_2$ nanotubes.

Anodic TiO$_2$ nanotubes have also been used for producing DSSCs. The highly
oriented nanostructures make TiO$_2$ nanotubes as an excellent pathway for electron
transport. Thus it is expected to increase the power conversion efficiency of DSSC
compared with the conventional TiO$_2$ nanoparticle-based systems. In 2006, Mor et al first
introduced the DSSC using transparent anodic TiO$_2$ nanotubes to substitute the titania
nanoparticle system, and a power conversion of 2.9% was achieved using only 350 nm
thick titania nanotubes grown on conductive substrate. A performance that reaches the
ideal limit of 33% by increasing the thickness of the transparent titania nanotubes was
envisioned. However, fabrication of thicker TiO$_2$ nanotube on top of conductive glass
was constrained by the quality and thickness of titanium deposited on the substrate. As an
alternative, backside illumination type device was proposed and recently a power
conversion efficiency of 6.9% was reported using a 20 µm thick TiO$_2$ nanotubes grown
on titanium foil. For the transparent TiO$_2$ nanotubes in the front side illumination mode
and TiO$_2$nanotubes on titanium foil in backside illumination mode, different cell
structures were used as shown in Figure 1-7. An advantage of the front side
illumination is that the incident light can directly reach the photoactive TiO$_2$ nanotubes
without energy loss when passing through the semi-transparent electrode.

Zhu et al carried out an systematic study on the dye sensitized anodic
TiO$_2$nanotube by comparing with the conventional TiO$_2$ nanoparticle-based systems. The results suggested the enhanced charge collection efficiency and light scattering in the
TiO$_2$ nanotube with same thickness and same dye molecule absorption efficiency as that
of the titania nanoparticle films. By optimizing the device parameters, higher performance of DSSCs based on anodic TiO$_2$ nanotube is expected.

Figure 1-7. Device structure of transparent titania nanotube and TiO$_2$ nanotube on titanium foil. (a) Front side illumination mode for the transparent TiO$_2$ nanotube grown on the transparent conductive glass; (b) Backside illumination mode for the TiO$_2$ nanotube that grown on the titanium foil.
1.4 Quantum dots

A quantum dot (QD) is a semiconductor nanostructure that confines the motion of conduction band electrons, valence band holes, or excitons (pairs of conduction band electrons and valence band holes) in all three spatial directions. The confinement can be due to electrostatic potentials, the presence of an interface between different semiconductor materials (e.g., in the case of self-assembled QDs), the presence of the semiconductor surface (e.g., in the case of a semiconductor nanocrystal), or a combination of these. A QD has a discrete quantized energy spectrum. Small QDs, such as colloidal semiconductor nanocrystals (e.g., CdSe, CdTe, CdS, PbSe, InAs, etc.), usually with size of 2 to 10 nm, have received considerable attention over the past years. QDs have high efficiency visual absorption, high efficient and tunable emission, high charge transfer efficiency, and multiple exciton generation capability, making them promising for applications in light emitting diodes (LED), photovoltaic cells, bioimaging, biosensors, etc. One of the intrinsic properties of QD is size dependent emission under ultraviolet illumination, due to the quantum confinement effect as shown in Figure 1-8.
The band gap of the QDs is mostly determined by the core materials and its diameter. Due to different core materials, QDs may exhibit different band gaps, which in turn different emission wavelength. The size of QD determines its band gap: the smaller size results in higher band gap, in respect to shorter emission wavelength. Figure 1-9 shows the emission wavelength of several typical QDs.\(^8\)

![Figure 1-8](image1.png)

Figure 1-8. Size dependent photoluminescence of QDs.

![Figure 1-9](image2.png)

Figure 1-9. Representative of QD core materials as a function of their emission wavelength superimposed over the spectrum.
The best available QD fluorophores for biological application are made of CdSe cores overcoated with a layer of high band gap ZnS because of the most refined chemistry. The ZnS shell layer passivates the CdSe surface, protecting it from oxidation and leaching of CdSe to the surrounding solution, thereby improving the photoluminescence of QDs.

Recent research on QD has shown that the multiple exciton generation capability of QDs when absorbing only one high energy photon from the sun light, although this is currently under debate. Shaller et al reported the highest of seven excitons formed one absorbed photon from PbSe nanocrystal. This contrast with the up-to-date solar cells in which only one electron was generated upon absorption of one photon of the sun light. This indicates that using QDs for solar cells may enhance the power conversion efficiency of panels. Theoretical study has suggested that QD-based solar cells have an ideal power conversion efficiency of 42%, while in the one exciton generation system 33% is the ideal value according to Shockley-Queisser limit.

Due to high efficient emission and specific Gaussian distributed light emitting, QDs have potential to be used in the application of light emitting and display. Bowers et al have recently reported the white light emitting of magic-sized CdSe nanocrystals.

The breakthrough in preparing high quality colloidal QDs (e.g., CdSe) was accomplished by Murray et al in 1993 using high temperature growth solvent/ligand, combined with pyrolysis of organometallic precursors. QDs prepared using this method have narrow size distribution, e.g., 8–11%. They were passivated by hydrophobic ligand and can be changed to hydrophilic via ligand exchange process using hydrophilic
ligand. Later on, Peng et al systematically studied the synthesis of III-VI semiconductor nanocrystals, the shape control, and the solubility.

1.4 Functional nanocrystals

**Iron oxide nanoparticles.** Iron oxide, as one of the most attractive magnetic materials, has been extensively studied in recent years. Iron oxide nanoparticles are excellent candidates for study of nanoscale magnetic properties, drug delivery, magnetic resonance imaging (MRI), biocatalyst, battery materials, cell separation, and building block for nanodevices. The wide range of applications using iron oxide nanoparticles requires delicate control over their size, shape, and composition. There has been impressive work carried out on the synthesis of various iron oxide nanoparticles, including FeO, γ-Fe₂O₃, and Fe₃O₄.

**Ferroelectric nanocrystals.** Perovskite-type mixed metal oxide with the general formula of ABO₃ have received much attention in the past decades due to their unique ferroelectric, catalytic, sensing, superconducting, and optical properties for applications in thin-film capacitors, pyroelectric detectors, electrooptic modulators, transducers, actuators, optical memories, and nonlinear optics. Typical perovskite metal oxides include barium titanate (BaTiO₃), strontium titanate (SrTiO₃), barium-strontium titanate ((Ba, Sr)TiO₃), lead titanate (PbTiO₃), lead zirconate titanate (PZT, Pb(Zr, Ti)O₃), etc., among which the BaTiO₃ has been most extensively studied. Following a similar trend to miniaturization as conventional semiconductors, for the fabrication of nanodevices based on BaTiO₃ nanocrystal building blocks with outstanding physical properties and durability at the nanoscale, it is necessary to control the size and shape of BaTiO₃.
The nanostructured BaTiO$_3$ provides the module for the fundamental study of its size dependent properties. In this context, much research has been carried out on the synthesis of BaTiO$_3$ nanocrystals of various shapes (e.g., nanoparticles, nanorods, and nanowires). The commonly used synthetic approaches include the sol-gel process, hydrothermal process, high temperature decomposition of bimetallic precursors, and bioenabled formation, leading to BaTiO$_3$ nanocrystals with the size ranging from several to a few hundred nanometers. Another important ferroelectric material, lead titanate has also gained considerable research interests in recent years due to its broad application in various electronics, such as multilayer capacitors, nonvolatile memories, resonators, and ultrasonic transducers, due to its large pyroelectric coefficient and relatively low permittivity.$^{114,115}$

**Multiferroic nanocrystals.** Multiferroic materials that couple ferroic order parameters are quite promising due to their potential application in various fields, for example, magnetically recorded ferroelectric memory, thus attracting dramatically increasing research focus in the past five years.$^{116,117}$ Among which, Bismuth ferrite (BiFeO$_3$) has been extensively studied as one of the most important multiferroic compounds in past years.$^{117-125}$

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Chapter 2. Anodic Formation of Metal Oxide Nanostructures

2.1 Nanoporous alumina membrane

Introduction

Highly ordered porous alumina membrane (PAM) obtained via self-organization during electrochemical anodization of an aluminum foil in acidic electrolyte has been studied extensively for more than a decade due to its intriguing application as a starting structure for fabrication of ordered nanodevices. Since Masuda et al first introduced the two-step procedure to fabricate well ordered porous alumina in 1995, the mechanism of nanopores formation in PAM and its application has been widely studied. Porous alumina membrane with different pore size, thickness, and pore shape were successfully fabricated. The well ordered structures have been widely used to produce optical devices, fabricate nanodevices, serve as sensor template, and provide as intriguing nanoscopic geometry to study the confinement effect. Porous alumina thin film with good contact to substrates (e.g., silicon wafer and glass) was also fabricated by electrochemically anodizing aluminum deposited on the substrate. Systematic studies of the fabrication of PAM suggested that the interpore distance increased with the anodization voltage, while the thickness of the membrane was dictated by anodization time.

In order to obtain PAM with well ordered porous arrays, certain anodization conditions should be met: 1) sulphuric acid at 25 V, with interpore distance of 63 nm; 2) oxalic acid at 40 V, with interpore distance of 100 nm; and 3) phosphoric acid at 195 V with interpore distance of 500 nm. By taking advantage of nanoimprinting instead of the abovementioned self-organizing pore-forming procedure, it became more feasible to
tune the pore size, interpore distance, and even the pore shape. Lee et al fabricated a long range ordered PAM with interpore distance of 200 nm ~ 300 nm using hard anodization; Masuda et al reported the fabrication of PAM with pores interval of 13 nm and pore diameter of 7 nm using monodisperse nanoparticles as template and anodized at 16°C in 0.3 M sulfuric acid with a constant potential of 3 V; Peng et al fabricated PAM with ideally ordered 10 nm channels by anodization of focused-ion-beam patterned aluminum; Masuda et al demonstrated the preparation of square and triangular nanohole array architectures in anodic alumina. These extensive studies make it possible to utilize the porous alumina more widely in many nanotechnology related applications.

A typical procedure to prepare PAM with diameter, \(D = 60\) nm and interpore distance, \(\lambda = 110\) nm via two-step anodization process is described as follows. First, high purity aluminum foil was degreased by sonicating in a mixture of ethanol, chloroform, and acetone at a volume ratio of 1:2:1. The foil was then washed thoroughly using DI-water and dried with \(N_2\). The degreased aluminum foil was first anodized in 0.3 M oxalic acid at 0°C with an anodization potential of 42 V for 3 h. A platinum foil was used as the counter electrode; the first anodized alumina was selectively dissolved in a mixture of phosphoric acid and chromic acid at 60°C for 6 h, resulting in concave patterns on the aluminum foil, which subsequently acted as the template for well ordered structure growth. The foil was then washed thoroughly with DI-water, dried, and anodized under the same condition as in the first anodization. By adjusting the second anodization time, different thickness can be achieved, typically from several hundred nanometers to tens of micrometers. Selective removal of the backside aluminum using saturated copper chloride resulted in PAM with one side pore open, while the other blocked by a barrier.
layer of Al$_2$O$_3$. In order to obtain PAM with two sides pore open, 5 wt% phosphoric acid was subsequently used to remove the Al$_2$O$_3$ barrier layer. The formation of porous alumina via electrochemical anodization involved the competition of several spontaneous processes: electrochemical oxidation of aluminum to form alumina; electrochemical forced dissolution of formed alumina; and chemical dissolution of alumina in acidic electrolytes. The formation mechanism of PAM is shown in Figure 1-5. It has been suggested that it was the larger electric filed, due to an increased curvature, at the bottom of pores caused the increased oxidation growth and increased oxide dissolution, thus contributing to the pore growth.$^{29}$

Recently, Lee et al reported the fast fabrication of long-range ordered PAM by hard anodization,$^{20}$ in which the anodization current is much higher that conventional mild anodization, thereby dramatically enhancing the alumina growth speed. At higher anodization potential, PAM with large interpore distance and significant thickness can be obtained in a relatively short time. This method largely expanded the pore array morphology in PAM, giving more choice where the nanopores of PAM was used and tremendously reduced the PAM preparation time.

**Experimental**

Porous alumina membrane was fabricated by two-step anodization of high purity aluminum foil (99.99%) in acidic electrolyte. A platinum foil was used as the counter electrode. The aluminum foil (250 µm thick) was firstly degreased by sonicating in a mixture of methanol, chloroform, and acetone at a volume ratio of 1:2:1. The foil was then washed thoroughly using DI-water and dried by N$_2$. The degreased aluminum foil
was first anodized in 0.3 M oxalic acid at 0°C with an anodization potential of 42 V for 3 h. After first anodization, the resulting alumina was selectively dissolved in a mixture of 6 wt% phosphoric acid and 1.8 wt% chromic acid at 60°C for 6 h, forming concave patterns on the aluminum foil, which subsequently acted as the template for well-ordered structure growth. The foil was then washed thoroughly with DI water, dried, and anodized for the second time under the same conditions as those in the first anodization. To obtain two-side open PAM, the aluminum underneath the porous alumina was removed in saturated cupric chloride aqueous solution. The barrier Al₂O₃ layer at backside was removed with 5 wt% phosphoric acid. The thickness of PAM was determined by the second anodization time. Typically, several hundred nanometers to tens of micrometers thick PAM can be obtained. The pore size of PAM was dependent on the anodization potential and the electrolyte. PAM with smaller pore size was also fabricated by anodization in the electrolyte containing 0.2 wt% sulfuric acid at the anodization potential of 20 V, while PAM with larger pore size was produced in the electrolyte containing 0.3 M phosphoric acid at 100 V, 120 V and 140 V at 0°C. At higher voltage (V > 140 V), local heating at the interface of the aluminum, electrolyte, and air quickly damaged the aluminum foil.

Results and Discussion

PAM with different pore diameter and thickness was fabricated in different electrolyte system with different anodization potential. In order to obtain high quality membrane, the electrochemical polishing before anodization is necessary. By adjusting the temperature of polishing solution and polishing time, a mirror like surface can be
obtained, e.g., after 3 h polishing. After the second anodization, the backside aluminum was dissolved using saturated copper chloride aqueous solution, resulting in a freestanding one-side open PAM. Figure 2-1 shows an AFM image of the backside of an as-obtained PAM (i.e., the Al₂O₃ barrier layer) fabricated in 0.3 M oxalic acid at 42 V at 0°C.

The PAM was then placed in 0.5 wt% phosphoric acid for pore opening and pore size adjusting at room temperature for 1 h (i.e., second anodization), resulting in two-side open PAM. Typical SEM images of two-side open PAM are shown in Figure 2-2. A hexagonal array of nanopores with pore diameter (D) of 60 nm and interpore distance (λₖ₋ₖ) of 110 nm is clearly evident (Figure 2-2a). The cross-sectional SEM image confirmed a hexagonal array of nanoscopic porous structures with a high aspect ratio going through the whole membrane (Figure 2-2b). The porosity p of the PAM is ~27% as determined by

\[
p = \frac{2\pi}{\sqrt{3}} \left( \frac{r}{\lambda_{C-C}} \right)^2
\]

(5)

Where \( r \) is the radius of the nanopores and \( \lambda_{C-C} \) is the interpore distance.
Figure 2-1. AFM image of the barrier layer on the backside of PAM before the pore opening. *Left:* height image; *right:* phase image.

Figure 2-2. SEM images of PAM fabricated by a two-step electrochemical anodization process: (a) top view and (b) cross section; Scale bar = 1 µm

PAM with smaller pore diameter can be prepared by anodizing aluminum foil in dilute sulfuric acid at lower anodization potential. As shown in Figure 2-3, the PAM, fabricated via anodization in 2.0 wt% sulfuric acid at 0°C at 25 V, has a pore diameter of 30 nm. Also, the smaller pore size
PAMs with larger pore size \( (D > 60 \text{ nm}) \) were fabricated in an electrolyte containing 0.3 M phosphoric acid at 100 V, 120 V and 140 V at 0°C, resulting in irregular pores array as shown in Figure 2-4. The interpore distance, \( \lambda_{c-c} \) was found not to change linearly. For example, PAM obtained from anodization at 120 V had a smaller \( \lambda_{c-c} \) than that at 100 V. This may be due to the variation (e.g., temperature and local heating) during the anodization process. The PAM with bigger pore size was found to be a soft film and break easily, which may be attributed to increased porosity as compared to the 60 nm PAM. It is worth noting that it is impossible to increase anodization potential higher than 140 V due to the limitation of the cooling system.

In addition to the micrometers thick PAM, ultrathin PAM as thin as 350 nm was also successfully obtained after a 30 s second step anodization in 0.3 M oxalic acid at 42 V at 0°C. The ultrathin PAM was soft and fragile, and could only suspend in solvents (e.g.,
ethanol and acetone). The film was then transferred to Si substrate, followed by the thermal evaporation of gold. Upon removal of thin PAM by floating with solvent, gold nanodots were, thus, obtained on Si substrate. Figure 2-5 shows the SEM images of the ultrathin PAM and the gold nanodots obtained using PAM as deposition mask. We note the gold nanodot arrays can be utilized in surface enhanced Raman scattering measurements. This work is currently under investigation.
Figure 2- 4. SEM images of PAMs with larger pore size fabricated in 0.3 M phosphoric acid at higher potentials at 0°C. (a) 100 V, $D = 270$ nm, $\lambda_{C\cdot C} = 360$ nm; (b) 120 V, $D = 200$ nm, $\lambda_{C\cdot C} = 300$ nm; (c) 140 V, $D = 300$ nm, $\lambda_{C\cdot C} = 400$ nm. Scale bar = 2 µm.
Figure 2-5. SEM images of ultrathin PAM and gold nanodot array obtained using PAM as template. (a) Top view of the ultrathin PAM; (b) and (c) gold nanodots. The brighter part on the lower left of the SEM image in (b) was from unremoved PAM on Si substrate, scale bar = 1 µm in (b); (d) gold nanodots obtained by thermal evaporation of gold through two overlaid thin PAMs.

As discussed in Section 1.2, the pore diameter of PAM increases (from 30 nm to 300 nm) with the increase in anodization potential, which is in good agreement with reported values. However, PAM with regular array of pores can only be obtained at a certain anodization condition, e.g. in 2.0 wt% sulfuric acid at 25 V at 0°C or in 0.3 M oxalic acid at 42 V at 0°C. Due to the constraint of the cooling system, we were unable to conduct anodization at 195 V to produce PAM with pore size larger than 300 nm.

The thickness of the PAM is determined by the second anodization time. The ultrathin PAM with thickness of 350 nm was obtained after 30 s second anodization, while a thicker membrane was obtained with a longer anodization time (i.e., 6 hr second anodization results in PAM thickness of 30 µm)
Alumina surface bears –OH groups. Thus it can readily react with functional groups, such as carboxylic group, silane, etc. To modify the inner wall surface of PAM, PAM was first cleaned with acetone, ethanol, and DI-water, and dried. Subsequently, it was immersed in solutions of molecules that contains reactive functional end groups for several hours, followed by washing with large amount of solvent and storing in inert atmosphere.

**Conclusion**

In summary, nanoporous alumina membrane with hexagonally packed nanopores could be fabricated by two-step anodization under optimized electrochemical conditions. The nanopores diameters, interpore distance and film thickness were readily controlled by tuning the anodization conditions (e.g. potential, time etc.). The obtained porous alumina membrane can be used as template for the preparation of functional nanodevices, such as surface enhance raman scattering substrate, polymeric nanorods, and semiconducting nanowires etc.

**References**


2.2 Highly ordered TiO$_2$ nanotube arrays


**Introduction**

Since Zwilling et al reported the porous structure formation in Ti via electrochemical anodization in fluorine containing electrolytes in 1999,$^1$,$^2$ tremendous
Research efforts have been made to fabricate TiO$_2$ nanostructures by anodization. Gong et al were the first to demonstrate the fabrication of uniform TiO$_2$ nanotube arrays by electrochemically anodizing Ti in the hydrofluoric acid aqueous solution. In anodic TiO$_2$ nanotube arrays, each individual tube is perpendicular to the membrane surface, thereby providing larger surface areas and being an excellent module for use in optical and electronic devices (e.g., dye sensitized solar cells, DSSC, gas sensors, hydrogen generators, etc.). For example, in DSSCs, the highly ordered nanotube arrays provide two separate channels for efficient electron and hole transport from interfaces to electrodes. This is in sharp contrast with electron “hopping” as in TiO$_2$ nanoparticles, which was widely used as electron-accepting species in DSSCs.

Recently, much work has been carried out on the synthesis and applications of ordered anodic TiO$_2$ nanotube arrays. Advance in synthetic techniques made it possible to prepare TiO$_2$ nanotube arrays with various pore diameters (10 ~ 110 nm), thickness (200 nm ~ 1000 µm), and wall thickness (7 ~ 34 nm). Fluorine containing electrolytes have been considered as the best electrolyte for anodic growth of TiO$_2$ nanotubes. In this context, three generations of electrolytes have been developed, i.e. hydrofluoric acid aqueous solution, fluorine containing buffer solution, and non-aqueous electrolyte containing fluorine salt. The formation of TiO$_2$ nanotube arrays is a direct consequence of competition between electrochemical oxidation of Ti and electrical field induced etching of TiO$_2$ as well as chemical etching of TiO$_2$ by fluorine ion.

It is noteworthy that TiO$_2$ has rather poor mechanical strength; thus, it is difficult to obtain the freestanding TiO$_2$ nanotube, which, to some extent, limits its applications in certain fields where the nanotube arrays are required to be in intimate
contact with other substrates. Recently, Mor et al reported the fabrication of transparent TiO$_2$ nanotube arrays by anodizing Ti that was predeposited on a transparent substrate, and then successfully utilized the arrays for high performance DSSCs and hydrogen sensors.$^5, 10, 24$ For example, An overall efficiency of 2.9% was obtained with only 360-nm thick TiO$_2$ nanotubes on the FTO-coated glass.$^{14, 25}$ We note that the thickness of the nanotubes was only on the order of several hundred nanometers due to the limited ability of depositing thicker high-quality Ti on the substrate;$^5$ it was suggested that the quality of predeposited Ti film is key to producing highly ordered TiO$_2$ nanotube arrays.$^5, 24, 26, 27$

The ability to grow TiO$_2$ nanotube arrays directly on substrates other than Ti foil not only shows the flexibility of electrochemical anodization process, but also facilitates the extension of their promising applications. Herein we report the study on electrochemical anodization of high purity Ti in both aqueous and non-aqueous electrolytes, with main focus on the effects of electrolyte temperature and anodization potential on the formation of TiO$_2$ nanotube arrays. The study showed that, in aqueous electrolyte (i.e., dilute hydrofluoric acid), formation of TiO$_2$ nanotube arrays was sensitive to the anodization potential, while in viscous non-aqueous electrolyte (i.e., glycerol), the electrolyte temperature was found to exert significant influence on the nanotube dimension. Both 0.25 mm thick Ti foil and 500 nm Ti coated indium tin oxide (ITO) glass were used for the growth of TiO$_2$ nanotube arrays. The as-prepared TiO$_2$ nanotube arrays were amorphous and converted into anatase phase via high temperature annealing; the crystalline transformation was confirmed by Raman spectroscopy measurement. To the best of our knowledge, this is the first report on the effect of electrolyte temperature on anodic formation of TiO$_2$ nanotube arrays.
Very recently, self-organized, freestanding TiO$_2$ nanotube arrays have been fabricated for flow through photocatalytic application.\textsuperscript{28} To obtain freestanding TiO$_2$ membrane, a corrosive bromine-containing methanol solution was employed for selective chemical etching of the metallic Ti substrate.\textsuperscript{28} It will be quite promising if free-standing thicker TiO$_2$ nanotube arrays could be transferred on top of transparent, conductive substrate for use in the front-side-illuminated DSSCs. To this end, it is desirable to develop an approach to produce a freestanding, much thicker TiO$_2$ nanotube membrane in a simple manner. Herein we report a simple and safe method to achieve self-organized, freestanding, ultrahigh-aspect-ratio TiO$_2$ nanotube arrays without the need for corrosive etching process to separate TiO$_2$ nanotubes from the metallic Ti substrate. TiO$_2$ nanotube arrays with the aspect ratio of length to diameter \( \sim 1500 \) was first grown on Ti foil by electrochemically anodizing Ti foil in a fluorine-containing nonaqueous electrolyte (i.e., ammonia fluoride, NH$_4$F in ethylene glycol). The anodized Ti foil was rinsed extensively with DI water and methanol. Subsequent evaporation of methanol led to the delamination of thin “barrier layer” of TiO$_2$, which was formed between the TiO$_2$ membrane and Ti foil during anodization. A gentle mechanical bending of anodized Ti foil may be applied to facilitate complete detachment of membrane if necessary.

It is noteworthy that the freestanding TiO$_2$ nanotube arrays may then be anchored to conductive glass by using a transparent conductive glue\textsuperscript{29} to provide better interfacial electronic contact between nanotubes and conductive glass for use in front-side-illuminated DSSCs.\textsuperscript{14} The thickness of freestanding TiO$_2$ nanotube arrays more than 100 \( \mu \)m can be readily fabricated, thus an enhanced incident light absorption efficiency is expected. Furthermore, the vertically aligned nanotube geometry not only provides a
large interfacial area where excitons, that is the bound electron-hole pairs, may effectively dissociate, but also have two separate channels for efficient electron and hole transport from interface to contacts. Finally, the absence of “barrier layer” between the nanotubes and electrode imparts an enhanced charge collection at the electrode.\textsuperscript{14} Taken together, we envision that by exploiting these freestanding TiO$_2$ nanotube arrays with ultrahigh aspect ratio fabricated in the present study in the front-side-illuminated DSSCs, an improved device performance may be anticipated.

Compared to the bulk counterparts, nanostructured TiO$_2$ with controlled dimensions, including nanoparticles, nanowires, nanotubes, and mesoporous films, possesses much larger surface area to volume ratio, thereby providing additional reactive sites for catalyzing, sensing, and miscibility with other materials. They exhibit promising performance and have been widely exploited for use in the areas of gas sensors,\textsuperscript{9-11, 30} hydrogen generation,\textsuperscript{13, 31} photocatalyst,\textsuperscript{23, 32} cell separation,\textsuperscript{33} and dye sensitized solar cells (DSSC).\textsuperscript{4-8, 13-15, 34-36} In the latter context, rather than sintered TiO$_2$ nanoparticle films in which electrons hop between nanoparticles,\textsuperscript{15, 16} self-organized TiO$_2$ nanotube arrays provide a direct pathway for efficient electron transport from interface to electrode. These TiO$_2$ nanotube arrays are prepared by electrochemical anodization of Ti in fluorine-containing electrolyte and employed as the photoanode, where each individual TiO$_2$ nanotube is perpendicular to the membrane surface.\textsuperscript{14}

Since the as-prepared anodic TiO$_2$ nanotube arrays are amorphous, high temperature annealing is necessary to convert them into crystalline forms for high performance applications. However, to the best of our knowledge, little work was
done on the systematic studies of temperature dependent crystalline evolution in anodic TiO$_2$ nanotube arrays. Herein, we described the fabrication of various TiO$_2$ nanostructures, including nanowires, highly ordered nanotube arrays, and single crystalline nanoplates, from electrochemically anodized Ti foil. The TiO$_2$ nanowires, which were formed due to the electric field induced chemical splitting of TiO$_2$ nanotubes by fluorine ions upon the lengthy anodization, can be isolated from the nanotube arrays by mild ultrasonication. The highly ordered TiO$_2$ nanotube arrays buried underneath are thus exposed. The transformation of as-prepared amorphous TiO$_2$ nanotubes into anatase or rutile phase as a function of annealing temperature was systematically scrutinized by Raman spectroscopy measurement in conjunction with TEM imaging. In the latter study, the ultramicrotomed sections of samples clearly exhibited the formation of highly crystalline TiO$_2$. More importantly, crystalline TiO$_2$ nanotubes were mechanically broken into intriguing single crystalline TiO$_2$ nanoplates as a result of ultramicrotoming.

**Experimental**

**Chemicals.** All chemicals were used as received without further purification. Ti foil (99.7 % purity, 0.25 mm thick), hydrofluoric acid (48 wt% in water), and ammonium fluoride (reagent, 98%) were purchased from Sigma-Aldrich. Acetic acid, glycerol, and ethylene glycol were purchased from Fisher Scientific. Ti coated ITO glass was prepared by depositing 500 nm thick Ti using an e-beam evaporator. Before deposition, the ITO glass was cleaned by ultrasonicating in acetone, isopropanol, and methanol sequentially.
Anodization of Ti foil. Ti foil was cut into 1 x 0.5 inch\(^2\) pieces. Before electrochemical anodization, Ti foil was degreased by ultrasonication in a mixture of acetone, methanol, and methylene chloride for 30 min, followed by washing with a large amount of DI-water and drying with N\(_2\). Electrochemical anodization was carried out in a two-electrode cell using a power source EC570-90 (Thermo Electron Corporation), where the Ti foil was used as anode and a thin platinum foil was used as the counter electrode. The anodization was performed either at room temperature (298 K) or in an ice bath. After a certain period of anodization (i.e., 4 hr), the Ti foil was immediately washed with a large amount of DI water, subsequently dried with N\(_2\) gas. To induce crystalline phase, the anodized Ti foil was annealed in a furnace.

Anodization of Ti coated ITO glass. 500 nm Ti coated ITO glass was washed with acetone and isopropanol. Electrochemical anodization was performed in a two-electrode cell using a platinum foil as the counter electrode. Hydrofluoric acid aqueous solution (0.5 wt%, with acetic acid added in volume ratio of 1:7) and glycerol solution containing 0.25 wt% of ammonium fluoride were used as electrolytes. The anodization was stopped when the current dropped to zero, which was indicative of complete anodization of Ti thin film. After anodization, the ITO glass was immediately washed with a large amount of DI water and dried with N\(_2\). To induce crystalline phase, the anodized Ti coated ITO glass was annealed in a furnace.
Fabrication of Freestanding TiO$_2$ Nanotube Arrays. TiO$_2$ nanotube arrays with ultrahigh aspect ratio were grown on a Ti foil according to a modified procedure.$^{37}$ Briefly, Ti foil (Sigma-Aldrich; 250 µm thick, 99.7% purity) was cut into a 2.5 cm * 1.0 cm piece. It was degreased by ultrasonication for 30 min in a mixture of acetone, methanol, and methylene chloride, followed by a thorough rinse with DI water and blow dried with N$_2$. Ethylene glycol (Fisher Scientific) was used as the electrolyte. A small amount of ammonium fluoride (Sigma-Aldrich) was added into the ethylene glycol electrolyte. All chemicals and materials in the experiment were used as received without further purification. Electrochemical anodization of Ti foil was carried out in a two-electrode cell at room temperature using a power source EC570-90 (Thermo Electron Corporation), in which a platinum foil was used as the counter electrode. The backside of Ti foil was protected by coating a layer of nail polish. Anodization was conducted at a constant potential of 60 V for a period of time until a desired thickness was reached (e.g., TiO$_2$ membrane with a thickness of ~135 µm was obtained after anodization for 60 h). After anodization the Ti foil with the TiO$_2$ nanotubes grown on one side of its surfaces was thoroughly washed with a large amount of DI water and methanol, and kept in methanol bath overnight.

In order to achieve a freestanding membrane, the grown TiO$_2$ membrane was detached from the metallic Ti substrate as described in the following. The anodized Ti foil was taken out from methanol bath and washed again with a large amount of methanol; then the foil was placed at the bottom of a big box with the anodized surface facing up. The brownish membrane (Figure 1) gradually separated from the Ti foil during the course of methanol evaporation. In our experiment the freestanding TiO$_2$ membrane
can be successfully achieved upon evaporation of methanol once or twice. A possible mechanism of methanol-evaporation induced membrane detachment can be rationalized as follows. A thin layer of TiO$_2$, known as “barrier layer”, was formed between the TiO$_2$ nanotube array and Ti foil during anodization. After anodization, although the Ti foil was thoroughly washed and kept in methanol bath overnight, a small amount of H$^+$ and F$^-$ may still present in the regions between adjacent nanotubes (i.e., the interpore regions). Thus, there existed a slow etching of the “barrier layer” and led to the formation of defects. On the other hand, methanol has low surface tension$^{38}$ (i.e. $\gamma_{\text{CH}_3\text{OH}} = 22.1$ dynes/cm at 20 $^\circ$C), which makes it easy to infiltrate the interpore regions and wet the defects. Subsequent slow evaporation of methanol in the defect areas caused the delamination of the TiO$_2$ “barrier layer” driven by the surface tension. A slight mechanical bending of the foil may be applied if the membrane cannot separate completely after several repeated wetting and evaporation of methanol. The mechanical strength of TiO$_2$ is weak as compared to Ti, thus, the “barrier layer” can be easily delaminated upon methanol evaporation and/or destroyed by a gentle mechanical bending, resulting in a freestanding TiO$_2$ nanotube membrane. It is worth noting that the process is simple, safe, and without the use of corrosive etching solution.$^{28}$

**Formation of TiO$_2$ Nanowires via Ultrasonication.** Close examination of freestanding TiO$_2$ nanotubes right after separated from the Ti foil revealed that a layer of TiO$_2$ nanowires was covered on their top. A mild ultrasonication of membrane in methanol was thus conducted for a few minutes, during which a very thin layer on top of
membrane was gradually broken and dispersed into methanol, thereby exposing the underlying TiO$_2$ nanotubes in membrane. This very thin layer was examined by SEM.

**Formation of TiO$_2$ Nanoplates via Ultramicrotome.** Freestanding TiO$_2$ nanotube arrays annealed at different temperatures were embedded in Spurr’s resin, followed by curing at 60 °C for 48 hr. Ultramicrotome of the embedded TiO$_2$ nanotubes were performed on a Leica Reichert Ultracut using a freshly made glass knife. Thin sections with thickness of 70 nm were collected on carbon coated copper grids (400 mesh) for TEM characterization. For comparison, thin sections of amorphous TiO$_2$ nanotube arrays were also prepared. The TEM sample preparation method was maintained for all annealed samples.

**Characterization.** All anodized Ti (both Ti foil and Ti coated ITO glass) were characterized using a JEOL 5800 LV scanning electron microscopy (SEM). The crystalline nature of both as-prepared and annealed TiO$_2$ nanotube arrays were examined using a Renishaw inVia Raman Microscopy equipped with an Ar laser (488 nm wavelength). TEM and high resolution TEM (HRTEM) were performed on a JEOL 2100 scanning transmission electron microscopy (STEM), operated at 200 kV.

**Results and Discussion**

1. TiO$_2$ nanotube arrays obtained from aqueous electrolyte

   Fluorine containing electrolyte has been recognized as the most efficient electrolyte for anodic formation of TiO$_2$ nanotube arrays. In an electrochemical
anodization process, TiO$_2$ nanotube arrays were formed via self-organizing of TiO$_2$ as a result of delicate balance of electrochemical oxidation of Ti into TiO$_2$, electrical field induced dissolution of TiO$_2$, and the chemical dissolution of TiO$_2$ by fluorine ion. In aqueous electrolyte, the chemical dissolution of TiO$_2$ due to the presence of fluorine ion dominated over other two processes; the anodization process reached equilibrium in a very short time, therefore the film thickness was limited. It was found that only within a certain anodization potential range, ordered TiO$_2$ nanotube arrays were formed.$^3$ In the present study, the effects of both electrolyte temperature and the anodization potential (especially at high voltage) on the formation of TiO$_2$ nanotube arrays were investigated. Figure 2-6 shows surface topologies of TiO$_2$ nanotube arrays obtained by anodizing 0.25 mm thick Ti foil in 0.5 wt% hydrofluoric acid at room temperature (Figure 2-6a) and in an ice bath (Figure 2-6b) for 1 hr. The anodization was performed at 20 V. The nanotubes formed at room temperature had an average inner diameter of 50 nm and outer diameter of 110 nm; while the nanotubes obtained in the ice bath possessed an average inner diameter of 60 nm and outer diameter of 110 nm. At both anodization temperatures, there was slight difference in the inner diameter while the outer diameter was same. This observation may be because, at room temperature, the TiO$_2$ formation rate was higher than that in the ice bath, while the etching of TiO$_2$ induced by electric field and fluorine ion remained similar at both temperatures.
It has been reported that a certain anodization potential is necessary to yield ordered TiO$_2$ nanotube arrays, and 10V was suggested as the lowest required potential.$^3$ In this study, we applied much higher anodization potential with expectation of control over nanotube size. The surface topologies of Ti foil anodized at different potential, i.e., 20 V, 60 V, 80 V, and 100 V for 1 hr are shown in Figure 2-7. The anodization was conducted in an ice bath. As evidenced in the SEM images, at elevated anodization potential, i.e., 60 V and 80 V, the anodized Ti foil did not exhibit nanotubular structures; instead, a sponge-like TiO$_2$ film with nanoholes were formed on the surface (Figure 2-7b and 2-7c). The formation of nanosponges instead of nanotubes may be due to the largely enhanced electrical field induced etching of TiO$_2$ at elevated anodization potential, although the electrochemical oxidation speed was also increased at higher anodization potential. The TiO$_2$ nanotubes formed by electrochemical oxidation of Ti was dissolved by both the chemical etching and the enhanced electrical field induced etching of TiO$_2$, resulting in the sponge-like thin film of ~ 100 nm based on the cross sectional SEM imaging (data not shown). As the anodization potential was further increased to 100 V,
only a dense film of TiO$_2$ was seen on top of the Ti foil (Figure 2-7d), which can be attributed to the even faster etching speed of TiO$_2$, that is, the formed TiO$_2$ via electrochemical oxidation was dissolved immediately in the electrolyte.

Figure 2-7. SEM topology of Ti foil anodized in 0.5 wt% hydrofluoric acid in an ice bath at various anodization potential (a) 20V, (b) 60 V, (c) 80 V, and (d) 100 V. Scale bar = 1 µm in all images.

To demonstrate the flexibility of electrochemical anodization of Ti, rather than Ti foil, the Ti coated ITO glass was employed to grow TiO$_2$ nanotube arrays directly on the ITO glass surface. The ability to produce TiO$_2$ nanotube arrays on transparent substrates other than Ti foil renders semiconductor TiO$_2$ nanotubes for various applications, for example, DSSC in a front–side illumination mode.$^5$ The use of TiO$_2$ nanotube arrays grown on fluorine-doped tin oxide (FTO) glass for DSSCs was reported to yield a power conversion efficiency of 2.9 % with film thickness of only 360 nm;$^{14}$ this is due to
increased incident light harvesting efficiency as compared to the TiO₂ film grown on Ti foil, where the incident light was lost when passing through the top electrode and electrolyte. In the present study, a 500 nm thick Ti film was deposited on cleaned ITO glass using e-beam evaporator, followed by electrochemical anodization in 0.5 wt% hydrofluoric acid aqueous electrolyte (acetic acid was added with volume ratio of 1:7). The anodization was performed in an ice bath at 12 V. Digital images in Figure 2-8 clearly show the change of Ti coated ITO glass before anodization, after anodization, and after subsequent thermal annealing. Initially, the Ti coated glass was dark. After anodization, the anodized area became semi-transparent; upon subsequent thermal annealing at 500 °C, the anodized area changed to be optically transparent. Figure 2-9 shows the SEM images of TiO₂ nanotube arrays formed on ITO glass. Compared to the Ti foil anodized under the same conditions (inset in Figure 2-9a), the nanotube arrays formed on the ITO glass were less ordered and had thicker tube wall. This can be attributed to the short anodization time, which was limited by the original Ti film thickness predeposited. With short anodization time, the self organization process was not complete, leading to less ordered nanotube arrays.

![Figure 2-8](image_url)

Figure 2-8. Digital images of Ti-coated ITO glass before anodization (left panel), after anodization (center panel), and after thermal annealing (right panel).
Figure 2-9. SEM images of electrochemically anodized Ti-coated ITO glass. (a) Surface topology; inset shows the topology of 0.25 mm Ti foil electrochemically anodized under the same condition as the Ti-coated ITO glass; (b) Cross section of the Ti thin film on ITO glass after anodization. Scale bar = 500 nm in all images.

It is important to note that the quality of Ti film is critical to obtain highly ordered TiO$_2$ nanotube arrays, and the quality of Ti thin film prepared by e-beam evaporation in the present study may not be as high as those deposited by radio frequency sputtering at high temperature. Nonetheless, the TiO$_2$ nanotube arrays showed an average inner diameter of 30 nm and film thickness of 300 nm (Figure 2-9).

2. TiO$_2$ nanotube arrays obtained from non-aqueous electrolyte

Non-aqueous electrolytes (e.g., glycerol, ethylene glycol, etc.) containing fluorine ion have been used to fabricate highly ordered TiO$_2$ nanotube arrays with significantly increased film thickness (e.g., nanotubes more than 100 µm in length have been successfully achieved). This is because, in the non-aqueous electrolyte, the mobility of fluorine ion was largely suppressed; thus, the chemical dissolution of TiO$_2$ was reduced. Similar to the anodization of Ti in aqueous electrolyte, we investigated the effect of electrolyte temperature and anodization potential using a non-aqueous
electrolyte, namely, glycerol containing a small amount of ammonium fluoride. Ti foil with thickness of 0.25 mm and 500 nm Ti coated ITO glass were anodized in the non-aqueous electrolyte. Figure 2-10 shows the SEM images of Ti foil anodized in glycerol containing 0.25 wt% of ammonium fluoride at 40 V. The anodization was carried out either at room temperature (Figure 2-10a and 2-10b) or in an ice bath (Figure 2-10c and 2-10d). In both case, highly ordered TiO$_2$ nanotube arrays with regular pore size and smooth tube wall were achieved, and the film thickness were several micrometers (e.g., a 5.5 µm thick film was obtained after 12 hr anodization at room temperature). The TiO$_2$ nanotube arrays obtained at room temperature exhibited an average inner diameter of 90 nm and outer diameter of 110 nm (Figure 2-10a), and the regularity of nanotubes were much better than those produced in an aqueous electrolyte (Figure 2-6). When anodizing in an ice bath, the nanotube size was found to be largely reduced, having an average inner diameter of 20 nm and outer diameter of 50 nm (Figure 2-10c). When comparing with TiO$_2$ nanotubes obtained in aqueous electrolyte (i.e., hydrofluoric acid) where only a margin difference in nanotube diameter was observed (Figure 2-6a vs. 2-6b), it was found that in non-aqueous electrolyte (i.e., glycerol), the nanotube diameter was markedly affected by the electrolyte temperature (Figure 2-10a vs. Figure 2-10c). This can be understood as follows. At lower temperature (i.e., in the ice bath), the fluorine ion mobility in the viscous glycerol electrolyte was further suppressed, resulting in much slower etching of formed TiO$_2$, which in turn, led to smaller nanotube diameter. To the best of our knowledge, this is the first report on the effect of electrolyte temperature in the anodic formation of TiO$_2$ nanotube arrays.
Figure 2-10. SEM images of TiO$_2$ nanotube arrays obtained by anodizing Ti foil in glycerol electrolyte at 40 V. (a) and (b) at room temperature, scale bar = 2 µm for (a) and 5 µm for (b), respectively; (c) and (d) in an ice bath, scale bar = 500 nm for (c) and 1 µm for (d), respectively.
When performing anodization in the ice bath, different anodization potential ranging from 20 V to 100 V was applied. At all applied potentials, highly ordered TiO$_2$ nanotube arrays were yielded, while the nanotube inner diameter did not change much. The SEM images of Ti foil anodized at different potential in glycerol electrolyte (0.25 wt% ammonium fluoride) are shown in Figure 2-11. At 20 V, the nanotubes had an average inner diameter of 20 nm, yet not uniform along the nanotube (Figure 2-11a); this is because during the anodization, the current was so low (less than 1 mA) that the anodization potential automatically increased in order to continue the anodization (i.e.,
increased to 30 V after 2 hr anodization as compared to originally applied 20 V). With increased anodization potential, TiO\(_2\) nanotube arrays with slightly increased inner diameter were obtained (i.e., 25 nm at 80 V and 40 nm at 100 V), indicating that although the anodization potential was increased, the chemical etching of TiO\(_2\) by fluorine ion was still very low in the viscous electrolyte at low temperature; therefore, only small difference in nanotube diameter was observed.

By anodizing Ti coated ITO glass in non-aqueous electrolyte (i.e., glycerol), rather than nanotube arrays, nanoporous TiO\(_2\) film was obtained. Digital images of Ti coated ITO glass before anodization, after anodization, and after subsequent thermal annealing are shown in Figure 2-12. Unlike the semi-transparent film observed in aqueous electrolyte (hydrofluoric acid) (center panel in Figure 2-8), a completely transparent film on ITO glass was seen after anodizing in non-aqueous electrolyte (glycerol). Figure 2-13 shows the SEM images of the Ti coated ITO glass anodized in glycerol at 60 V at room temperature. A 1 \(\mu\)m thick nanoporous film were grown from the 500 nm predeposited Ti (Figure 2-13b). The formation of nanoporous film may be due to a combination of the reduced etching speed of TiO\(_2\) in non-aqueous electrolyte and the incomplete self-organization process as a result of short anodization time (i.e., due to limited Ti film thickness). The increase film thickness (i.e., from original 500 nm Ti to 1 \(\mu\)m TiO\(_2\)) could be resulted from both reduced etching of TiO\(_2\) and volume expansion due to the conversion from metallic Ti to porous TiO\(_2\) upon the anodization. The obtained nanoporous film had an average pore diameter of 35 nm as evidenced in the SEM image (Figure 2-13a).
Figure 2-12. Digital images of 500 nm thick Ti-coated ITO glass before anodization (left panel), after anodization (center panel), and after thermal annealing (right panel).

Figure 2-13. SEM images of Ti-coated ITO glass anodized in glycerol at 60 V at room temperature. (a) Surface topology, scale bar = 500 nm; (b) Cross-sectional view, scale bar = 1 μm; a closeup of the cross-section is shown in inset, scale bar = 250 nm.

3. Free-standing TiO2 nanotube arrays

Figure 2-14 shows a digital image of a brownish freestanding TiO2 nanotube membrane obtained directly after the electrochemical anodization in the NH4F/ethylene glycol electrolyte. The lateral dimension of membrane is ~ 1.0 x 1.0 cm². The top surface of the freestanding TiO2 membrane was covered by a layer of TiO2 nanowires (~ 100 nm) as revealed by SEM (Figure 2-15a). The layer of TiO2 nanowires was formed possibly
due to electric-field-induced chemical etching of TiO$_2$ nanotubes in a “bamboo-splitting” mode (i.e., vertical splitting of anodically grown nanotubes during anodization).$^{39}$ In some region, that is, around the cracks of nanowires, TiO$_2$ nanotubes buried beneath nanowires were observed (Figure 2-15b). The cracks may be resulted from slow but long period time of chemical dissolution of the TiO$_2$ nanowires,$^{39}$ and/or damage during the membrane transferring process. To utilize the freestanding TiO$_2$ nanotubes for a variety of applications, e.g., DSSCs, this 100-nm top layer should be removed in order to infiltrate dye molecules and redox electrolytes into nanotubes in DSSCs.$^{14}$ Attempts to selectively chemical etch the top TiO$_2$ nanowires with HF aqueous solution, which was placed closely below the membrane, were unsuccessful (see Supporting Information, Figure 2-25). The HF treatment etched away not only the top nanowires, but also the buried nanotubes (Figure 2-25). Microscopic holes were formed, leaving behind highly rough membrane (Figure 2-25).

![Figure 2-14](image)

Figure 2-14. Digital image of a freestanding TiO$_2$ nanotube membrane in brown (right). The lateral dimension of the membrane is comparable to a dime shown in the left.
Figure 2-15. SEM images of the freestanding TiO$_2$ nanotube membrane right after anodization (top view). (a) A thin layer of TiO$_2$ nanowires formed due to chemical dissolution of TiO$_2$, and covered on top of nanotubes; scale bar = 2 µm. (b) In some regions (e.g., around the cracks of nanowires) TiO$_2$ nanotubes were revealed. The TiO$_2$ nanowires can be seen on the left of image; scale bar = 5 µm.
Figure 2-16. SEM images of the freestanding TiO$_2$ nanotube arrays after mild ultrasonication treatment to remove the top TiO$_2$ nanowires (top view). The average diameter is 90 nm with wall thickness of 15 nm; the average interpore distance is 120 nm. Scale bar = 2 µm.

Figure 2-17. SEM image of the freestanding TiO$_2$ nanotube arrays (side view). The closed end of nanotube bottoms is clearly evident. The nanotubes are perpendicular to the membrane surface. Scale bar = 2 µm.
Thus, as an alternative approach, mild ultrasonication of the freestanding TiO$_2$ nanotube membrane in methanol was performed for a few minutes. A very thin grey layer on top of the membrane was seen to gradually break and disperse into methanol during ultrasonication. The process was repeated for several times to ensure complete removal of top TiO$_2$ nanowire layer. Figure 2-16 shows topological SEM image of sonicated freestanding TiO$_2$ membrane. Highly ordered arrays of nanotubes are clearly evident. The average tube diameter, D is 90 nm with an average wall thickness of 15 nm; the average interpore distance, $\lambda_{C.C}$ is 120 nm. The cross-sectional SEM image confirms closely packed arrays of nanotubes perpendicular to the membrane surface. The bottom of nanotubes was closed (Figure 2-17). The nanotube arrays go straightly from the top to bottom of the membrane as shown in Figure 2-18. The vertically oriented, close-packed
morphology of nanotubes provides a direct pathway for electron transport at the nanotube walls as compared to the “electron-hopping” in TiO₂ nanoparticles that are commonly used in DSSCs. The thickness of freestanding membrane is ~ 135 µm after 60 h anodization.

The as-prepared TiO₂ nanotube membrane was amorphous, as revealed by Raman spectroscopy, in which broad spectra ranging from 100 to 1000 cm⁻¹ is clearly evident (black curve in Figure 2-19). In order to take advantage of nanotubular structures of TiO₂ for use in DSSCs, the initially amorphous TiO₂ nanotubes should be converted into photoactive anatase or rutile phase.⁴⁰ Thus, thermal annealing of the membrane was carried out at 500 °C in air for 3 h to induce crystalline. Raman spectrum of the annealed membrane (red curve in Figure 2-19) shows the specific peaks of anatase TiO₂ at 145 cm⁻¹, 198 cm⁻¹, 399 cm⁻¹, 516 cm⁻¹, and 640 cm⁻¹.⁴¹, ⁴² The nanotubular structures were retained after high-temperature annealing, as evidenced in SEM measurement (see Supporting Information, Figure 2-26).
4. Crystalline evolution in TiO$_2$ nanotube arrays

Systematic Raman scattering measurements on freestanding TiO$_2$ nanotube arrays annealed at different temperatures were carried out to monitor the high temperature annealing-induced crystalline phase formation. Each sample was scanned at least three times with the average intensity shown in Figure 2-20. Amorphous TiO$_2$ had a broad spectrum ranging from 100 cm$^{-1}$ to 1000 cm$^{-1}$ (black curve in Figure 2-20a). Annealing nanotubes at 200°C did not induce the formation of crystalline phase (red curve in Figure 2-20a where a broad spectrum was still observed). By contrast, anatase TiO$_2$ started to emerge when annealed at 300°C, as
evidenced by the specific peaks at 145 cm$^{-1}$, 198 cm$^{-1}$, 399 cm$^{-1}$, 516 cm$^{-1}$, and 640 cm$^{-1}$ that can be assigned to anatase phase (blue curve in Figure 2-20a); a strong background superimposed on the spectrum might be due to the co-existence of amorphous and crystalline TiO$_2$. 
Figure 2-20. (a-b): Raman spectra of TiO$_2$ nanotube arrays annealed at different temperature. (c): Peak intensity as a function of annealing temperature at specific peak positions, i.e., 399 cm$^{-1}$, 516 cm$^{-1}$, and 640 cm$^{-1}$ for the anatase TiO$_2$. 
The Raman spectra of TiO\textsubscript{2} nanotubes annealed at temperature higher than 400\degree C were shown in Figure 2-20b. As the annealing temperature increased, the Raman intensity increased and reached the maximum at 700\degree C (Figure 2-20b). The peak intensity at 399 cm\textsuperscript{-1}, 516 cm\textsuperscript{-1}, and 640 cm\textsuperscript{-1} as a function of annealing temperature is summarized in Figure 2-20c, clearly suggesting that when the annealing temperature was higher than 600\degree C, the crystallization of nanotubes was complete, in other words, complete transformation from amorphous TiO\textsubscript{2} to anatase TiO\textsubscript{2} was achieved at 600\degree C. When the annealing temperature was higher than 700\degree C, a transition from anatase to rutile phase occurred. For the sample annealed at 800\degree C, specific Raman peaks at 240 cm\textsuperscript{-1}, 447 cm\textsuperscript{-1} and 612 cm\textsuperscript{-1} can be assigned to rutile TiO\textsubscript{2} (orange curve in Figure 2-20b).\textsuperscript{41,42}

It is noteworthy that the anatase to rutile transition temperature is much higher than the reported 620\degree C value,\textsuperscript{11} where the TiO\textsubscript{2} nanotubes situated on Ti foil was used directly and Ti was found to promote the anatase to rutile transition. In the present study, however, freestanding TiO\textsubscript{2} nanotube arrays were used; there was no catalyzing effect from Ti on the crystalline transition. As a result, a higher transition temperature was observed. We also note that the nanotubular structures were retained with annealing temperature up to 600\degree C, which is in agreement with results in literature.\textsuperscript{40,43} When the annealing temperature was further increased (e.g. 700\degree C and 800\degree C), the nanotubular structure corrupted, which can be attributed to the expansion of crystalline grain as shown from SEM images (Figure 2-21).
Figure 2-21. SEM images of TiO$_2$ nanotubes annealed at high temperature. (a) 600°C, (b) 700°C and (c) 800°C. Black arrows indicate the direction that is perpendicular to the TiO2 nanotube arrays film. Scale bar = 1 µm.

5. Formation of TiO$_2$ Nanoplates

To better understand the crystalline formation in freestanding TiO$_2$ nanotubes induced by high temperature annealing, ultramicrotome was performed. Namely, TiO$_2$ nanotube arrays, after annealed at different temperatures, were embedded in Spurr’s resin and thin sectioned. Subsequently, they were imaged by TEM. In the control experiment, amorphous TiO$_2$ nanotube arrays exhibited a featureless selected area electron diffraction (SEAD) pattern (inset in Figure 2-22a) as expected. For the TiO$_2$ nanotube arrays annealed at 200°C, the SEAD pattern indicated that the nanotubes were still amorphous (inset in Figure 2-22b). For the 300°C annealed TiO$_2$ sample, TEM image showed a majority of the nanotubular morphology (Figure
2-22c), while the nanoplates can be seen in some location. The SAED in the inset implied the crystalline formation in nanotubes. Quite intriguingly, as the annealing temperature further increased to 400°C and above, plate-like nanostructures are evident (Figure 2-22d-h), with the SAED patterns shown in insets clearly demonstrating the crystalline nature of these samples. The nanoplates were believed to be broken from the crystalline TiO$_2$ nanotube arrays (Figure 2-22f and 2-23 in which nanoplates were seen to reside within the nanotube, packed along its long axis, and be about to disassemble from nanotubes). The breakage was driven by the mechanical stress during microtome using a freshly made glass knife. The formation mechanism of TiO$_2$ nanoplates from crystalline TiO$_2$ nanotube arrays is depicted in Scheme 2-1 in which the microtoming direction was perpendicular to the nanotube walls. The high resolution TEM (HRTEM) images on a single TiO$_2$ nanoplate from the samples annealed at different temperature (i.e., 400°C, 500°C, and 600°C) are shown in Figure 2-24, where all nanoplates possessed the [101] crystalline lattice, suggesting that they were single crystalline. Given the 50-nm lateral dimension (Figure 2-23 and 2-24) and the 15-nm wall thickness (Figure 2-16), they are thin plate-like in shape.
Figure 2-22. TEM images of TiO$_2$ nanotube arrays annealed at different temperatures in air for 3 hr. Ultra thin sections were obtained by microtoming the freestanding TiO$_2$ membrane embedded in Spur’s Resin. (a) Amorphous TiO$_2$, scale bar = 500 nm; (b) TiO$_2$ annealed at 200°C, scale bar = 200 nm. (c) TiO$_2$ annealed at 300°C, scale bar = 100 nm. (d) low magnification (scale bar = 200 nm) and (e) high magnification (scale bar = 50 nm) TEM images of TiO$_2$ annealed at 400°C; (f) low magnification (scale bar = 200 nm) and (g) high magnification (scale bar = 50 nm) TEM images of TiO$_2$ annealed at 500°C. (h)
TiO$_2$ annealed at 600°C, scale bar = 100 nm. The corresponding selected area electron diffraction (SAED) patterns are shown in insets.

Figure 2-23. TEM image of TiO$_2$ nanoplates obtained from ultramicrotoming TiO$_2$ nanotubes that were annealed at 500°C, scale bar = 500 nm.

Figure 2-24. HRTEM images of single crystalline TiO$_2$ nanoplates obtained from ultramicrotome of TiO$_2$ nanotubes. (a) annealed at 400°C, scale bar = 2 nm; (b) annealed at 500°C, scale bar = 5 nm; (c) annealed at 600°C, scale bar = 2 nm.
On the basis of the Raman spectra on the TiO$_2$ nanotubes and the TEM results on microtomed thin sections (Figure 2-20 and 2-22), the formation of crystalline TiO$_2$ nanotubes and the subsequent formation of nanoplates can be rationalized as follows. For the amorphous and low temperature annealed nanotubes, no specific Raman peaks of crystalline TiO$_2$ were observed (Figure 2-20a), and no diffraction associated with the crystalline phase was seen (Figure 2-22a-b), confirming that the nanotubes were amorphous. Higher temperature annealing induced the crystalline formation in the nanotube walls. With increased annealing temperature ($T \geq 300^\circ$C), the crystalline domain increased in size and reached the maximum that was dictated by the nanotube wall thickness, annealing temperature, and crystalline stability. At these temperatures, specific Raman peaks of anatase or rutile TiO$_2$ appeared (Figure 2-20b), with the TiO$_2$ nanotube arrays maintaining their tubular morphology after annealing.$^{19}$ When subjected to the ultramicrotome, the crystalline domains in the nanotube walls were broken and separated from one another (Scheme 2-1), thereby forming TiO$_2$ nanoplates as seen in the TEM images and the corresponding SEAD patterns (Figure 2-22d-h and 2-23).

Scheme 2- 1. Schematic illustration on the formation of TiO$_2$ nanoplates from nanotubes during ultramicrotoming crystalline TiO$_2$ nanotube arrays embedded in Spur’s resin.
Conclusion

In summary, high purity Ti foil and Ti thin film coated ITO glass were electrochemically anodized. The effects of electrolyte temperature and anodization potential on the formation of TiO$_2$ nanotube arrays were studied in both aqueous and non-aqueous electrolytes. In aqueous electrolyte, the anodization potential exerted significant influence on the formation of highly ordered TiO$_2$ nanotube arrays, while little effect from the electrolyte temperature was observed. In non-aqueous electrolyte, the electrolyte temperature markedly affected the TiO$_2$ nanotube dimensions, while, unlike in the aqueous electrolyte, anodization potential exhibited slight influence in this regard. To the best of our knowledge, this is the first report on the effect of electrolyte temperature.

We reported a simple and safe method to obtain self-organized, freestanding TiO$_2$ nanotube arrays with ultrahigh aspect ratio of the diameter to length (~1500) by simply utilizing solvent-evaporation induced delamination of the TiO$_2$ “barrier layer”, which was formed between the TiO$_2$ membrane and Ti foil during anodization. A gentle mechanical bending of anodized Ti foil may be applied to facilitate complete detachment of the membrane from the metallic substrate if necessary. As-grown TiO$_2$ nanotubes were amorphous and transformed into photoactive anatase form after annealed at high temperature in air. The amorphous-to-anatase transformation of TiO$_2$ nanotubes was verified by confocal Raman spectroscopy. The nanotubular structures of freestanding TiO$_2$ membrane were retained after annealing. Currently, we are constructing quantum dot sensitized nanostructured solar cells (QDSNSC) in a front-side-illuminated mode by utilizing quantum dots$^{44-48}$ as sensitizers and impregnating them into these vertically
aligned, ultrahigh-aspect-ratio TiO$_2$ nanotubes. The use of TiO$_2$ nanotubes with ultrahigh aspect ratio improves the incident light absorption efficiency. Moreover, the vertically aligned nanotubes not only offer a large interfacial area for excitons to effectively dissociate, but also facilitate efficient electron transports from the tube walls to electrodes. Thus, enhanced photoconversion efficiency may result in.

We also reported the formation of TiO$_2$ nanowires, highly ordered TiO$_2$ nanotube arrays, and single crystalline TiO$_2$ nanoplates from the electrochemically anodized Ti foil. Self organized, highly ordered TiO$_2$ nanotube arrays were fabricated by electrochemical anodization of Ti foil using fluorine-containing ethylene glycol as the electrolyte. Freestanding TiO$_2$ nanotube arrays can be readily obtained by mechanically detaching the formed membrane from the metallic Ti foil. Subsequently, TiO$_2$ nanowires formed in a “bamboo-splitting” fashion due to the electric field induced chemical etching of TiO$_2$ nanotubes can be isolated from the nanotubes buried underneath by mild ultrasonication in methanol. High temperature annealing transformed the as-prepared amorphous TiO$_2$ nanotube arrays into anatase or rutile phase. The crystalline formation in nanotubes as a function of annealing temperature was systematically explored by Raman spectroscopy and TEM measurements. Finally, ultramicrotoming annealed TiO$_2$ nanotube arrays broke the crystalline domains in the tube and yielded single crystalline TiO$_2$ nanoplates as revealed by HRTEM and corresponding SEAD characterizations. To the best of our knowledge, this is the first report on disintegrating anodic TiO$_2$ nanotubes into single crystalline TiO$_2$ nanoplates. The present study not only demonstrated a simple route to producing various TiO$_2$ nanostructures that may further extend the
high performance applications of semiconductor TiO$_2$, but also provided valuable insights into the temperature dependent crystalline transformation in anodic TiO$_2$ nanotube arrays.

**Supporting information**

Figure 2-25. SEM images of the freestanding TiO$_2$ nanotubes obtained after treated with concentrated HF solution to chemically etch the top TiO$_2$ nanowires that were formed by chemical dissolution of TiO$_2$ during electrochemical anodization.$^{39}$ (a) Topology of the chemically etched nanotube arrays; scale bar = 5 µm. (b) Cross section; scale bar = 5 µm.
Figure 2-26. SEM images of the freestanding TiO$_2$ nanotubes after thermal annealing at 500 °C in air. The integrity of nanotubes was retained after annealing. (a) Top of TiO$_2$ nanotubes (top view with a slight tilt). (b) Bottom of TiO$_2$ nanotubes (top view). The scale bars are 1 µm in (a) and (b).
References


Chapter 3. Semiconducting Nanocrystals

3.1 CdSe quantum dots


This work was featured on Inside Front Cover of Journal of Materials Chemistry (issue 27)
Introduction

Quantum dots (QDs) are highly emissive spherical nanoparticles with a few nanometers in diameter.\(^1\)\(^,\)\(^2\) They provide a functional platform for a new class of materials for use in solar cells,\(^3\)\(^-\)\(^5\) LEDs,\(^6\)\(^,\)\(^7\) tunable lasers,\(^8\) optical storage media,\(^9\) nonradiative energy transfer,\(^10\)\(^,\)\(^11\) biosensors,\(^12\)\(^-\)\(^16\) and bioimaging systems.\(^17\)\(^-\)\(^19\) For QDs such as cadmium selenide (CdSe),\(^1\)\(^,\)\(^20\) variation of particle size provides continuous and predictable changes in optical absorption and fluorescence due to their quantum-confined nature. An appropriate surface passivation with a monolayer of coordinating ligands is crucial to ensuring the solubility and miscibility of QDs with the host environment, and to retaining the spectroscopic properties of the materials by preventing QDs from aggregation. Ligand exchange permits derivatization with a broad range of functional groups.

QDs synthesized through a conventional organometallic high temperature growth procedure are functionalized with hydrophobic ligands (e.g., trioctylphosphine oxide (TOPO)).\(^21\)\(^,\)\(^22\) However, on many occasions, it is desirable to prepare water soluble QDs for bioimaging, biosensor, and QD-sensitized TiO\(_2\) nanocrystal solar cells (QDSSCs). In the latter context, due to the size-dependent optical properties and multiple exciton generation capability,\(^23\)\(^-\)\(^27\) QDs can be exploited as the sensitizer in QDSSC. Placing the water soluble QDs in intimate direct contact with the hydrophilic TiO\(_2\) nanocrystals is expected to facilitate efficient charge transfer from the QDs to the TiO\(_2\). This can be realized by functionalizing both the QDs (e.g., dithiocarbamate functionalized QDs with the carboxyl group on the surface) and the TiO\(_2\) (e.g., the hydroxyl group on the TiO\(_2\)
surface\textsuperscript{28-30}) with compatible functional groups, which allow them to react with each other under mild conditions.

Bifunctional molecules with thiol and carboxyl groups at each end (e.g., mercaptopropionic acid (MPA)\textsuperscript{30,31}) have been used as effective ligands to prepare water dispersible QDs. The thiol group provides the chemical affinity to QDs, while the carboxyl group imparts the water solubility. However, the use of monothiol ligands makes QDs susceptible to oxidation.\textsuperscript{32-34} This drawback was recently overcome by using dithiocarbamate moieties as ligands due to their strong chelate-type binding to metal atoms.\textsuperscript{35,36} The resulting dithiocarbamate functionalized QDs exhibited improved resistance to photooxidation. However, to obtain the dithiocarbamate ligand, a multi-step synthesis was needed. Later, a spontaneous assembly of dithiocarbamate on the gold surface was demonstrated by simply exposing gold to carbon disulfide (CS\textsubscript{2}) and a secondary amine.\textsuperscript{37} This approach was then successfully extended to CdSe/ZnS core/shell QDs to tune the surface properties of QDs. Basically, TOPO functionalized CdSe/ZnS QDs were added to the solution containing equivalent amounts of CS\textsubscript{2} and glycine (an amino acid-based ligand), followed by stirring at room temperature for several hours to convert CdSe/ZnS-TOPO to dithiocarbamate functionalized CdSe/ZnS.\textsuperscript{32} Glycine, dissolved in the mixture of chloroform and methanol (1:1 = CHCl\textsubscript{3} : MeOH), provided both a source of amine groups for the formation of dithiocarbamate via its reaction with CS\textsubscript{2} and a source of carboxyl groups for aqueous solubility. It is noteworthy that only very dilute CdSe-TOPO QD dispersions (i.e., 10\textsuperscript{-3} M) were used in the ligand exchange due to the limited solubility of glycine in the CHCl\textsubscript{3}/MeOH mixture.\textsuperscript{32} Thus, the yield of D-CdSe QDs was rather low. However, for applications of water soluble QDs
to bioimaging and QDSSCs, and also from cost considerations, a route to high yield (i.e., large scale preparation) is desirable. Furthermore, the dithiocarbamate functionalized CdSe/ZnS QDs were formed via the ligand exchange in a single phase (i.e., in the 1:1 CHCl₃/MeOH mixture). Thus additional steps (i.e., precipitation and redissolution) were necessary to achieve the CdSe/ZnS QD aqueous solution.³²

Herein, we describe a simple yet novel biphasic ligand exchange method to transfer original hydrophobic CdSe-TOPO QDs into hydrophilic dithiocarbamate functionalized CdSe (D-CdSe) QDs in one step. The D-CdSe QDs were produced with high yield (i.e., a very high concentration (for example, c = 1 mg/ml or higher) of CdSe-TOPO could be used in the reaction, which in turn led to the production of a large scale of D-CdSe QDs via ligand exchange). ³¹P NMR measurements confirmed the ligand exchange by detecting the existence of free TOPO in the chloroform-d phase after the exchange. The resulting water dispersible D-CdSe QDs exhibited an increased photoluminescence (PL) quantum yield as compared to the original CdSe-TOPO QDs, suggesting an effective passivation of dithiocarbamate ligands on the QD surface. The D-CdSe QDs were then mixed with the hydroxyl terminated TiO₂ nanoparticles. Photoluminescence (PL) measurements on the mixture showed a significant emission quenching of D-CdSe, indicating an efficient charge transfer from the D-CdSe QDs to the TiO₂ nanoparticles. The reaction of the carboxyl group on the D-CdSe surface with the hydroxyl group on the TiO₂ rendered QDs in intimate contact with TiO₂, thereby facilitating the electronic interaction between them. The present biphasic ligand exchange method has several advantages over the previously reported ligand exchange processes. First, the reaction is simple and one-step. By mixing CS₂ and glycine in DI
water, and adding them in the CdSe-TOPO chloroform solution, the red-emitting CdSe QDs were directly transferred from the chloroform phase to the water phase after vigorous stirring at room temperature (i.e., interfacial reaction at the chloroform/water interface). Thus, no further precipitation and redissolution were needed to obtain the D-CdSe QD water solution. Second, glycine has excellent solubility in water (e.g., 25 g glycine can be readily dissolved in 100 ml water at room temperature) as compared to its limited solubility in CHCl₃/MeOH mixtures, thereby a large quantity of D-CdSe can ultimately be obtained by increasing the reaction volume and the concentration of CdSe-TOPO QDs. Finally, in comparison to monothiol counterparts, due to the strong chelate-type binding characteristic of dithiocarbamate, the resulting D-CdSe QDs exhibited improved resistance against photooxidation.

Experimental

Synthesis of CdSe-TOPO. TOPO-functionalized CdSe (CdSe-TOPO) QDs were synthesized via an organometallic high temperature growth approach described elsewhere. Briefly, 100 mg of cadmium oxide (CdO, Sigma-Aldrich) and 900 mg of stearic acid (Fisher Scientific) were loaded in an Argon-protected 50 ml three neck flask. They were heated to 170 °C, resulting in a transparent liquid. The liquid was cooled to room temperature, followed by adding 4 g trioctylphosphine oxide (TOPO, Sigma-Aldrich) and 4 g hexadecylamine (Sigma-Aldrich), and degassing under Argon flow for 30 min. The liquid was then heated to 290 °C, followed by the injection of a selenium stock solution containing 60 mg selenium (Sigma-Aldrich), 1.6 ml tributylphosphine (TBP, Sigma-Aldrich), and 4 ml dioctylamine (Sigma-Aldrich). The size of CdSe QDs
was readily controlled by altering the growth time. After the desired size was reached, 10 ml chloroform was injected to the reaction mixture to terminate the QD growth. This solution was finally collected and stored in the dark. All the chemicals were used as received without further purification.

**Biphasic Ligand Exchange.** 5 ml of 1 mg/ml as-synthesized CdSe-TOPO chloroform solution was precipitated by methanol for three times to remove the excess TOPO, and redissolved in 5 ml chloroform. 0.5 g glycine was dissolved in 5 ml DI water followed by adding 0.4 ml CS₂. Glycine was chosen as the source for the amine group and the carboxyl group. The glycine/CS₂ DI water mixture was then added into the CdSe-TOPO chloroform solution. The resulting mixture was vigorously stirred at room temperature for 24 h. To purify the resulting dithiocarbamate functionalized CdSe (D-CdSe) QDs, the excess amount of free dithiocarbamate ligands was removed by either ultracentrifugation or dialysis against the DI water with a 3,500 MWCO SnakeSkin™ Pleated Dialysis Tubing.

**Synthesis of TiO₂ nanoparticles.** TiO₂ nanoparticles were prepared according to the literature. Briefly, titanium isopropoxide was slowly dropped into ethanol and the solution was vigorously stirred for 2 h to hydrolyze titanium isopropoxide.

**Characterization.** The diameter of the CdSe-TOPO QDs was determined by transmission electron microscopy (TEM; JEOL 1200EX scanning/TEM (STEM), operated at 80 kV). The absorption and emission spectra, the latter excited at 365 nm,
were recorded with a home-made UV-vis spectrometer. The success of the biphasic ligand exchange process was verified by $^{31}$P-NMR spectroscopy (Varian VXR-400). Glycine was dissolved in deuterium oxide (D$_2$O). Deuterochloroform (chloroform-d) was used in the $^{31}$P-NMR measurements to dissolve pure TOPO and CdSe-TOPO. The absolute PL quantum yield (PLQY) measurements on the CdSe-TOPO chloroform solution and the D-CdSe ethanol solution were carried out according to a well-established procedure,$^{45}$ using an integrating sphere and UV laser. The measurement involved three consecutive steps: first, the emission from the empty sphere; second, the emission with the sample in place and the laser beam directed to the wall of the sphere; finally, emission of the sample with the laser beam directed to the sample.

**Results and Discussion**

Figure 3-1a shows the TEM image of 4 nm diameter CdSe-TOPO QDs. The absorption and PL spectra of the CdSe-TOPO chloroform solution are shown in Figure 1b (black curves). The absorption and PL maxima were at 599 nm and 612 nm, respectively. Subsequently, the glycine/CS$_2$ DI water mixture was added in the CdSe-TOPO chloroform solution. The resulting biphasic mixture was vigorously stirred at room temperature for 24 h. Glycine provided a source of the carboxyl group and the amine group at each end. The carboxyl group offered the aqueous solubility, while the amine group served as an anchoring moiety through its reaction with CS$_2$ (i.e., formation of the dithiocarbamate ligands, and subsequent attachment to the CdSe surface via biphasic ligand exchange with the original TOPO ligand at the CHCl$_3$/water interface as
schematically illustrated in *Scheme 3-1*). The red-emitting CdSe QDs were found to be successfully transferred from the chloroform phase in the bottom (left image in Figure 3-2) to the water phase on the top (right image in Figure 3-2), as shown by the digital images of the strong emission excited at 365 nm. As a result, water soluble, dithiocarbamate functionalized CdSe QDs (D-CdSe) were obtained. Since glycine has excellent solubility in DI water (for example, 25 g glycine can easily dissolved in 100 ml DI water at room temperature), a large quantity of D-CdSe can be obtained by using high concentration CdSe-TOPO chloroform solution (\( c = 1 \text{ mg/ml} \)) in the exchange as compared to \( c = 10^{-3} \text{ M} \) when glycine was dissolved in the CHCl\(_3\)/MeOH mixture.\(^{32}\) The shape of the absorption and PL spectra of D-CdSe in water were the same as those of CdSe-TOPO in chloroform (Figure 3-1b), signifying that the photophysical properties of the CdSe QDs were retained after the biphasic ligand exchange. The spectra of D-CdSe were slightly red-shifted. This may be due to the change of dielectric environment (i.e., rather than chloroform, D-CdSe is dissolved in water) (Figure 3-1b).
Figure 3-1. (a) TEM image of CdSe-TOPO. Scale bar = 40 nm; (b) The absorption and photoluminescence (PL) spectra of CdSe-TOPO in chloroform (black curves), and the absorption and PL spectra of D-CdSe in water (red curves). The PL spectrum was obtained under UV excitation at the wavelength of 365 nm.

Figure 3-2. Digital camera images of emission under UV excitation at the wavelength of 365 nm, demonstrating the transformation of hydrophobic CdSe-TOPO QDs from chloroform phase (bottom in the left image) into hydrophilic D-CdSe QDs in water (top in the right image) after the biphasic ligand exchange at room temperature.
Scheme 3- 1. Schematic illustration of biphasic ligand exchange for the preparation of hydrophilic, dithiocarbamate functionalized CdSe QDs (i.e., D-CdSe) by replacing the original ligand, TOPO on the CdSe surface.

To verify the success of the biphasic ligand exchange process, $^{31}$P NMR measurements were carried out. Deuterochloroform (chloroform-d) and deuterium oxide were used in the biphasic ligand exchange process. For comparison, pure TOPO in chloroform-d was examined and showed a typical $^{31}$P NMR signal at ~50 ppm (Figure 3-3a). In contrast, no obvious signals were observed for the CdSe-TOPO QDs in chloroform-d within the same scanning time (Figure 3-3b). This can be attributed to the fact that most of free TOPO was removed, and the broadening of the NMR signal due to the inhomogeneous distribution of magnetic environments. After the completion of the ligand exchange, the $^{31}$P NMR on the chloroform-d phase showed a sharp peak at 52 ppm (Figure 3-3c), indicating that TOPO was released from the original CdSe-TOPO surface during the ligand exchange with dithiocarbamate. It is worth noting that when either CS$_2$ or glycine solely was added to the CdSe-TOPO/chloroform/water system, no phase transfer shown in Figure 3-2 was observed.

The PLQY was measured to be 2.4% for the CdSe-TOPO in chloroform, and 15% for the D-CdSe in ethanol, i.e., over six times higher. The increase in the PLQY indicated improved passivation with the dithiocarbamate ligands on the CdSe QD
surface. This is in sharp contrast to the decreased PLQY when monothiol ligands were used for ligand exchange to obtain water soluble QDs.\textsuperscript{46, 47} We note that a complete quenching or strong decrease in emission was recently reported when TOPO-functionalized CdSe or QDs coated with a thin layer of ZnS in CHCl\textsubscript{3}/MeOH mixtures were ligand-exchanged with dithiocarbamate in the same mixture of solvents (i.e., single-phase ligand exchange).\textsuperscript{32} Hence, our method based on the biphasic ligand exchange offers better surface passivation of dithiocarbamate, thereby resulting in a higher PLQY. In addition, the excellent solubility of glycine in DI water may also partially contribute to the increased PLQY. It is worth noting that an increase in PLQY in the water soluble QDs was also recently obtained by replacing the original TOPO with polyelectrolyte (i.e., poly allylamine),\textsuperscript{48} which is consistent with our observation.
Figure 3-3. $^{31}$P NMR of (a) pure TOPO in chloroform-d, (b) CdSe-TOPO in chloroform-d, and (c) free TOPO in chloroform-d phase; the free TOPO was released from original CdSe-TOPO as a result of the biphasic ligand exchange. All the $^{31}$P NMR measurements were performed in chloroform-d for the same period of time.

Compared to monothiol ligands, dithiocarbamates are bidentate chelating ligands and have stronger affinity for metal atoms. Thus, an increased photostability of the resulting QDs is expected. The D-CdSe QDs exhibit excellent stability under ambient condition, as the strong emission is retained without any change in the absorbance for over 10 months (data not shown).

Scheme 3-2. Schematic illustration of covalent linkage of dithiocarbamate functionalized CdSe QDs to native hydroxyl terminated TiO$_2$ nanoparticles.
To explore the possibility of utilizing the D-CdSe QDs for use in photovoltaic devices (for example, QD-sensitized TiO₂ solar cells), PL studies were performed on the mixture of D-CdSe QDs and TiO₂ nanoparticles. The TiO₂ nanoparticles were prepared according to the literature. Since they were prepared in ethanol, a new batch of D-CdSe QDs in the same solvent was also prepared (i.e., precipitation of D-CdSe QDs in DI water at pH = 7, followed by redissolution in ethanol) and mixed with the TiO₂ nanoparticles at the 5:1 volume ratio. The mixture was allowed to react under vigorous stirring for different periods. Compared to the PL of pure D-CdSe in ethanol (black curve in Figure 4; the emission peak was at 625 nm), a 65% reduction in emission after 2 h stirring was observed (red curve). It further dropped to 6% (i.e., 94% reduction) after 24 h stirring, at which the reaction between functionalized QDs and TiO₂ was expected to be complete. The decrease in the PL indicated a possible charge transfer from QDs to TiO₂. The reaction of the carboxyl group on the D-CdSe surface and the native hydroxyl group on the TiO₂ brought the QDs in direct contact with the TiO₂ nanoparticles as depicted in Scheme 3-2, thereby facilitating the electronic interaction between them. Furthermore, the polar solvent solubility of D-CdSe QDs enabled them to wet the hydrophilic TiO₂ nanoparticles easily, leading to a high adsorption efficiency of QDs on the TiO₂ nanoparticles. Taken together, the D-CdSe QDs can be exploited as intriguing sensitizers for use in QD-sensitized TiO₂ solar cells. Further investigations on the charge transfer using ultrafast transient absorption and fluorescence lifetime measurements are currently underway.
Conclusion

We have reported a simple yet novel route to hydrophilic dithiocarbamate-functionalized CdSe QDs (D-CdSe) via the biphasic ligand exchange process in one step. The resulting water-dispersible D-CdSe QDs exhibited an increased PLQY as compared to the original CdSe-TOPO QDs. The D-CdSe QDs also exhibited excellent stability under ambient conditions. The mixture of D-CdSe QDs and hydroxyl terminated TiO$_2$ nanoparticles showed an almost complete quenching of the emission from D-CdSe, suggesting an efficient charge transfer from QDs to TiO$_2$. This was likely due to the reaction of the carboxyl group on the D-CdSe surface and the native hydroxyl group on the TiO$_2$, placing the QDs in direct contact with TiO$_2$ and thereby facilitating the electronic interaction between them. This opens up an avenue for use of D-CdSe in QD-
sensitized TiO$_2$ solar cells. We envisage that, due to the presence of carboxyl group on the D-CdSe QD surface, further control over the surface property of QDs is possible. For example, positively charged QDs can be readily produced via the amidation of a diamine molecule with the carboxyl group of D-CdSe QDs.$^{42}$

References

3.2 Magnetic luminescent nanocomposites

Introduction

Application of quantum dots in solar energy conversion has recently received considerable attention. Instead of using ruthenium dye as sensitizer in DSSCs, other materials were explored for sensitizing photoanode, for example conjugated polymers\textsuperscript{1,2} and semiconductor quantum dots.\textsuperscript{3-6} Quantum dots (e.g., CdSe, CdS, CdTe, InAs, InP, and PbSe), which absorb visible light and inject electron to large bandgap semiconductor (e.g., TiO\textsubscript{2}\textsuperscript{11-17} and ZnO\textsuperscript{11-17}), have shown promising potential as a substitute for ruthenium
Quantum dots carry the advantages of tunable band gap, efficient visible absorption, and multi-exciton generation capability. Transient absorption experiment on PbSe quantum dots has shown that as many as seven excitons can be generated when PbSe quantum dot absorbed one photon at a certain energy level, and an ideal power conversion efficiency of about 42% can be expected, which is one third higher than the Shockley-Queisser limit 33% in the single exciton generating system. Thus, quantum dots with multi-exciton generation capability show tremendous potential as the sensitizers for a new generation solar energy conversion device and are expected to be able to further increase the power conversion efficiency. Moreover, the optical properties of quantum dots can be tailored to maximize solar photon absorption. Yu et al have reported the highest efficiency of 1.7% under 5 mw/cm² illumination using InAs quantum dots to sensitize titania nanoparticle film.

Infiltration of CdSe quantum dots into nanoporous TiO₂ has not been quite successful due to the aggregation of CdSe quantum dots at top surface of film. Therefore, we are motivated to prepare magnetic quantum dots for better infiltration with assistance of external magnetic field. Fluorescent magnetic nanoparticle nanocomposites have been recently reported and successfully used for bio-detecting. Herein, we reported our recent work on the preparation and characterization of iron oxide-CdSe quantum dots nanocomposites. Both seeded growth and co-decomposition approaches were explored, and the approach using CdSe quantum dots as seeds was found to be most successful. A CdSe core and iron oxide shell nanocomposites were obtained, and the shell thickness was readily controlled by the amount of iron precursor. The obtained nanocomposites exhibit the characteristic optical properties of CdSe quantum dots, as well as the
superparamagnetic properties of iron oxide. These magnetic CdSe nanocomposites should have potential application in quantum dots solar cells as well as bio-detecting.

Experimental

Preparation of iron oleate. Iron oleate was used as the iron precursor and prepared by reported method. Briefly, a certain amount of iron chloride and sodium oleate (TCI chemicals) were dissolved in the mixture of DI-water, ethanol and hexane at the volume ratio of 4:3:7, and heated to 70 ºC for 4 h. The upper organic phase was extracted using a separation funnel and washed with DI-water for 3 times. The obtained iron-oleate was sealed and stored in a dedicnator.

Synthesis of CdSe quantum dots. TOPO functionalized CdSe (CdSe-TOPO) QDs were synthesized via an organometallic high temperature growth approach according to the literatures. Briefly, 100 mg of cadmium oxide (CdO, Sigma-Aldrich) and 900 mg of stearic acid (Fisher Scientific) were loaded in an Argon protected 50 ml flask. They were heated to 170 ºC, resulting in a transparent liquid. The liquid was cooled to room temperature, followed by adding 4 g trioctylphosphine oxide (TOPO, Sigma-Aldrich) and 4 g hexadecylamine (Sigma-Aldrich), degassing under Argon flow for 30 min. The liquid was then heated to 290 ºC, followed by the injection of a selenium stock solution containing 60 mg selenium (Sigma-Aldrich), 1.6 ml tributylphosphine (TBP, Sigma-Aldrich), and 4 ml dioctylamine (Sigma-Aldrich). The size of CdSe QDs was readily controlled by altering the growth time. After the desirable size was reached, 10 ml chloroform was injected to the reaction mixture to terminate the growth of nanocrystals.
This solution was finally collected and stored in the dark. All the chemicals were used as received without further purification.

**Synthesis of CdSe core-iron oxide shell.** CdSe-TOPO quantum dots were purified using chloroform/methanol three times to remove any unreacted residue, and mixed with excess amount of TOPO and hexyldeceneamine (HAD). Fe-oleate dissolved in 1-octadecene was injected at room temperature, molar ratio between Fe and CdSe was controlled. Reaction solution was maintained at 300°C for 30 min under argon protection. After reaction, chloroform was injected to prevent solidification. Control experiment was carried out using CdSe-TOPO without addition of iron oleate while all other steps were the same. The obtained samples were purified using mixture of chloroform and methanol for three times, and finally dissolved in toluene or chloroform.

**Characterization.** All these samples were examined by transmission electron microscopy (TEM) on a JEOL JSM 2100 STEM operating at 200 KV. The UV-vis absorption spectra were recorded with a home-made UV-vis spectrometer.

**Results and Discussion**

Figure 3-5a shows the TEM image of as-prepared CdSe-TOPO seeds, which have near monodisperse size distribution and the average size nanoparticles is measured to be 3.5 nm. These monodisperse CdSe quantum dots were then used as the seeds for growth of CdSe core-iron oxide shell nanocomposites. By controlling the molar ratio between CdSe and iron, the obtained hybrid nanoparticles size varied, while the estimated CdSe
core size changed little (Table 3-1). The estimation of CdSe core size is based on its size dependent optical properties according to the literature. Figure 3-5b-d show the TEM images of as-prepared hybrid nanoparticles with CdSe to iron molar ratio of 1:1 (sample A), 2:1 (sample B), and 5:1 (sample C), respectively. All these hybrid nanoparticles exhibit near monodisperse size distribution. It is worth noting that all these nanoparticles show superparamagnetic characteristics, i.e. they can be extracted from the solution with a magnetic bar and redissolved with removal of external magnetic field. Figure 3-6 show the TEM images of as-prepared CdSe seeds and control sample of CdSe. After heat treatment at 300°C for 30 min, the CdSe nanoparticles size was found to increase almost double (from 3.5 nm to 6.4 nm), while the size distribution was remained near monodispersed. This size expansion is believed to be due to the melt diffusion of CdSe at elevated temperature.

UV-vis absorption of above prepared samples was measured to examine the size dependent optical properties (Figure 3-7). Figure 3-7a shows the absorption spectrum of CdSe seeds and CdSe after controlled heat treatment. The heat treated sample exhibited a red shift of 76 nm from the characteristic absorption maximum, which indicated the increased size of CdSe quantum dots; this is in good agreement with TEM observation (Figure 3-6). According to the estimation, the size of CdSe seeds is 3.6 nm and the size of heat treated CdSe is 6.2 nm, which agree well with the size measured from TEM images in Figure 3-6, 3.5 nm and 6.4 nm, respectively.
Figure 3-5. TEM images of (a) CdSe-TOPO seeds; (b) CdSe-iron oxide, ratio 1:1; (c) CdSe-iron oxide, ratio 2:1; (d) CdSe-iron oxide, ratio 5:1. Scale bar = 20 nm.

Figure 3-6. TEM images of CdSe-TOPO under controlled conditions. (a) CdSe-TOPO seeds; (b) CdSe-TOPO after heat treating at 300°C for 30 min. Scale bar = 20 nm.
Figure 3-7. UV-vis absorption spectrums of (a) CdSe-TOPO seeds and heat treated CdSe-TOPO nanoparticles; (b) CdSe-iron oxide with different CdSe : Fe ratio.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CdSe-TOPO</th>
<th>CdSe-TOPO controlled</th>
<th>Fe-CdSe A</th>
<th>Fe-CdSe B</th>
<th>Fe-CdSe C</th>
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<td>Measured size (nm)</td>
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<td>6.4</td>
<td>7.3</td>
<td>6.3</td>
<td>5.7</td>
</tr>
<tr>
<td>Estimated size (nm)</td>
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<td>6.2</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 3-1. A summary of CdSe-TOPO, CdSe-iron oxide: absorption peak positions, estimated particle size, and particle size measured from TEM images.

Figure 3-7b shows the UV-vis absorption spectrums of CdSe core-iron oxide shell nanoparticles. All three samples exhibit similar characteristic absorption peaks, indicating the similar size of CdSe cores. It is worth noting that the molar ratio between CdSe and iron was varied in these samples, also the measured nanoparticle size varied (Figure 3-5); thus the unchanged CdSe core size indicates the change in iron oxide shell thickness with different molar ratio between CdSe and iron oleate. The estimated CdSe core size for
these three samples is 4 nm (slightly larger than the CdSe seeds, which may be understood as there still exist unreacted Cd and Se precursor in the samples), and the measure size are 7.3 nm, 6.3 nm, and 5.7 nm, respectively (Table 3-1); from which the iron oxide shell thickness can be estimated to be 1.7 nm, 1.2 nm, and 0.8 nm, respectively. The consistence between TEM measurement and UV-vis absorption confirm the CdSe core – iron oxide shell structure of these hybrid nanoparticles. HR-TEM characterization shows that these iron oxide shells are amorphous (results not shown). Further investigation of the core-shell structure will be carried out using techniques such as XPS, and this work is currently undergoing.

Figure 3-8. TEM images of iron oxide nanoparticles that were used as seeds. Scale bar = 5 nm.

In addition to the approach using CdSe quantum dots as seeds, we also tried to use iron oxide nanoparticles as seeds, as well as co-decomposition of CdSe and iron oxide in one reaction. However, either of them offered good quality of hybrid nanoparticles.
Figure 3-8 shows the TEM images of as-prepared iron oxide nanoparticles with average size of 4 nm, which were obtained from iron acetylacetonate according to the literature. Figure 3-9 shows the TEM images from the iron oxide seeded growth sample, near monodisperse nanoparticles were observed (Figure 3-9a), however many ultralong CdSe nanowires were also observed (Figure 3-9b). The formation of CdSe nanowires is believed to be catalyzed by iron oxide nanoparticles seeds. Similar results were also observed when using co-decomposition approach (Figure 3-10), in which the CdSe precursor and iron precursor were mixed together and heated. CdSe nanowires with length more than 10 µm were observed from this sample, and these nanowires exhibit single crystalline nature throughout the whole length according to the HR-TEM images (Figure 3-10). A systematic study of the iron oxide catalyzed formation of CdSe nanowires is currently under investigation.

Figure 3- 9 TEM images of CdSe-iron oxide using small iron oxide nanoparticles as seeds. (a) monodisperse nanoparticles, scale bar = 50 nm; (b) ultralong CdSe nanowires, scale bar = 1 µm.
Figure 3-10. TEM images of CdSe-iron oxide using co-decomposition approach. Scale bar = 500 nm in the low magnification image; scale bar = 2 nm in all three HR-TEM images.

Conclusion

In summary, CdSe core–iron oxide shell nanoparticles were synthesized using CdSe quantum dots as seeds followed by deposition of iron oxide on the CdSe surface. According to the TEM and UV-vis studies, the CdSe core size changed little during the iron oxide deposition process, while the shell thickness of iron oxide can be readily controlled by the ratio between CdSe and iron precursor. The obtained hybrid nanoparticles exhibited superparamagnetic properties of iron oxide and characteristic
optical properties of CdSe quantum dots, making them attractive candidates for potential applications in quantum dots solar cells and bio-detecting. Further investigation, including the XPS study and the iron oxide catalyzed formation of CdSe nanowires, are currently underway.

References


Chapter 4. TiO$_2$ Nanotube Arrays Based Solar Cells

4.1 Dye sensitized solar cells (DSSCs)

(modified from a manuscript that has been accepted for publishing in Chemistry of Materials – Jun Wang, and Zhiqun Lin)

Introduction

As one of the major renewable energy sources, solar energy has the potential to become an essential component of future global energy production. Dye-sensitized solar cells (DSSCs),$^1$ is one of the most promising of several alternative, cost-effective concepts for solar-to-electric energy conversion that has been offered to challenge conventional Si solar cells over the past decade. The configuration of a DSSC consists of a sintered, wide bandgap semiconductor TiO$_2$ nanoparticle network film, a ruthenium-based dye (i.e., sensitizer), and an electrolyte. Upon the absorption of photons, the dye generates excitons (i.e., electron-hole pairs). Subsequently, the electrons inject into the TiO$_2$ photoanode to generate photocurrent; scavenged by a redox couple, holes transport to the cathode. The performance of a DSSC can be improved by optimizing the semiconductor TiO$_2$ nanoparticle film, sensitizer, and electrolyte. The overall power conversion efficiency, PCE of a DSSC up to 11%, which is dictated by its light harvest efficiency, the quantum yield for charge injection, and the charge collection efficiency at the electrodes,$^2$ has been demonstrated. However, much research remains to be done to improve the efficiency and remove the practical problems related to DSSCs. For example, typically a 10µm-thick mesoporous TiO$_2$ (anatase nanocrystals) film with a porosity of 50% is employed as an electron-accepting species in a DSSC. The film is prepared by
dispersing 15-30 nm colloidal TiO\textsubscript{2} particles on a conductive glass support consisting of a network of randomly dispersed nanocrystals.\textsuperscript{3} While versatile and robust, these sintered three-dimensional TiO\textsubscript{2} nanoparticle films lead to enhanced scattering of free electrons and electron trapping at the interfaces, thereby reducing electron mobility and exhibiting slow electron transport. The electron and hole transport across several ill-defined, heterogeneous interfaces in TiO\textsubscript{2} nanoparticle films is very complex.\textsuperscript{4}

In this context, highly ordered, vertically oriented TiO\textsubscript{2} nanotube arrays of different aspect ratios and surface qualities have recently been fabricated as alternative nanoscale architectures to substitute the sintered TiO\textsubscript{2} nanoparticle films in DSSC. They are produced by potentiostatic anodization of titanium (Ti) foil\textsuperscript{5,12} or Ti thin films that have been sputtered using radio frequency (RF) sputter deposition on a variety of substrates with fluorine-containing electrolytes (e.g., fluorine-doped tin oxide (FTO)-coated glass).\textsuperscript{6,13,14} The nanotubular morphology of these arrays offers a large internal surface area with no concomitant decrease in geometric and structural order.\textsuperscript{7} The vertical orientation of the crystalline nanotube arrays after annealing makes them excellent electron percolation pathways for efficient, vectorial charge transport along the nanotube axis.\textsuperscript{7} A \textit{PCE} of 2.9\% was achieved using a 360 nm thick transparent TiO\textsubscript{2} nanotube membrane to assemble DSSC in a \textit{front side illumination mode}.\textsuperscript{15} A \textit{PCE} of 6.89\% has been obtained using 20 µm thick TiO\textsubscript{2} nanotube arrays that were grown on Ti foil in a \textit{backside illumination mode}.\textsuperscript{16} Recently, an improved \textit{PCE} in quantum dot sensitized solar cells was achieved by facilitating the charge transport through TiO\textsubscript{2} nanotube architecture (\textit{PCE} \leq 1\%) rather than sintered TiO\textsubscript{2} nanoparticle film.\textsuperscript{17-19} Comparing solar cells produced from TiO\textsubscript{2} nanotube arrays with that from sintered TiO\textsubscript{2} nanoparticle films,
enhanced charge collection efficiency and enhanced light scattering in TiO$_2$ nanotube-based DSSC was observed. The use of TiO$_2$ nanotubes reduced carrier scattering loss and non-radiative recombination by eliminating unnecessary lateral transport (i.e., hopping between TiO$_2$ nanoparticles) and its resulting recombination loss. It is noteworthy that the dye absorption on TiO$_2$ nanotubes was found to be similar to that on TiO$_2$ nanoparticle films of identical film thickness according to the dye loading measurement.

Surface treatment on TiO$_2$ photoanode not only increased the loading of sensitizers on the TiO$_2$ surface but also improved the electronic interaction between the sensitizer (i.e., dye) and the TiO$_2$ surface, thereby yielding improved device performance. For example, an increased $PCE$ of DSSC was obtained by exposing the TiO$_2$ nanoparticle film to O$_2$ plasma. The O$_2$ plasma treatment promoted the hydrophilicity on the TiO$_2$ surface, leading to the increased dye adsorption. It has been demonstrated that by exposing ZnO nanowires to O$_2$ plasma, the grafting density of CdSe quantum dots on the ZnO nanowire surface increased dramatically, resulting in an improved $PCE$. Notably, the treatment of TiO$_2$ nanotubes with O$_2$ plasma has yet been studied. On the other hand, immersing photoanodes (e.g., TiO$_2$ or ZnO) in titanium tetrachloride (TiCl$_4$) solution led to the formation of a very thin TiO$_2$ blocking layer. As a result, the amount of dye adsorption was increased and the charge transfer from dye molecules to photoanodes was facilitated, and ultimately, an enhanced $PCE$ was readily obtained.

In this letter, we report dye sensitized TiO$_2$ nanotube solar cells with enhanced performance based on highly ordered, vertically oriented TiO$_2$ nanotube arrays after
rational surface engineering, i.e., the TiCl₄ processing followed by O₂ plasma exposure. The TiO₂ nanotube arrays were fabricated by electrochemical anodization; subsequently, they were impregnated with ruthenium dye N-719 that was used as sensitizer and chemically anchored to the surface of TiO₂ nanotubes via the reaction of carboxylate moieties on N-719 surface with complementary hydroxyl groups on the TiO₂ surface. The PCE of solar cells produced using 14 µm thick TiO₂ nanotube arrays under simulated AM 1.5 G irradiation of 100 mW/cm² in backside illumination mode raised from 4.34% to 7.37% after immersion in the TiCl₄ solution followed by exposure to O₂ plasma. The TiCl₄ and O₂ plasma exposure processes led to increased photogenerated current and fill factor, ultimately, a higher PCE. To the best of our knowledge, the PCE of 7.37% is the highest reported efficiency for dye sensitized anodic TiO₂ nanotube solar cell in backside illumination mode, thereby offering an avenue in developing high-efficiency solar cells for renewable energy production.

**Experimental**

Highly ordered TiO₂ nanotube arrays were fabricated according to our previously reported procedure.²⁴-²⁶ Briefly, high purity Ti foil (250 µm thick, 99.7% purity, Sigma-Aldrich) was cut into pieces with each of 1 x 0.5 inch² and degreased by ultrasonication for 30 min in a mixture of acetone, methanol and methylene chloride, followed by a thorough rinse with DI water and blow dried with N₂. Ethylene glycol (Fisher Scientific) was used as the electrolyte in which a small amount of ammonium fluoride (Sigma-Aldrich) was added. Electrochemical anodization of Ti was carried out in a two-electrode cell at room temperature using EC570-90 power source (Thermo Electron Corporation) at 60 V. A platinum foil was employed as the counter electrode. After anodization, the Ti foil with TiO₂ nanotubes grown on one side of its surface was
extensively washed with DI water and dried with N₂ (the backside of Ti foil was protected with a layer of insulate resin to prevent oxidation during the anodization process). The SEM images (JEOL 5800 LV Scanning Electron Microscopy) of as-prepared TiO₂ nanotube arrays are shown in Figure 4-1a-c. The nanotubes had average inner diameter of 90 nm and interpore distance of 120 nm (Figure 4-1a and 4-1c). The membrane thickness can be readily controlled by the anodization time; the cross-section of a 14 µm thick TiO₂ membrane obtained after 2 hr anodization is shown in Figure 1b. We note that TiO₂ nanotube arrays with thickness of 22 µm and 29 µm were obtained after 3hr and 4hr anodization, respectively. The as-prepared TiO₂ nanotubes were amorphous. In order to take advantage of nanotubular structures for use in solar cells, they should be converted into crystalline forms i.e., anatase or rutile phase. The crystalline phase, induced by thermal annealing at 500 °C in air for 3 hr, was confirmed by Raman spectroscopy (Renishaw inVia Raman microscope excited with a 488 nm Ar+ laser at 5 mW with a 10 s acquisition time). A broad spectrum was seen on amorphous TiO₂ nanotubes. By contrast, specific Raman peaks at 145, 196, 399, 516 and 640 cm⁻¹ were observed from annealed TiO₂ nanotube arrays, signifying the formation of anatase TiO₂ (Figure 4-1d). The TiO₂ nanotubular structures were maintained after high temperature annealing.
Figure 4-1. Structural characterization of highly ordered TiO$_2$ nanotube arrays. (a) SEM topology, scale bar = 1μm; (b) SEM cross-sectional view, scale bar = 10 μm; (c) SEM cross-sectional view, scale bar = 1μm; and (d) Raman spectra of amorphous (black curve) and crystalline (red curve) TiO$_2$ nanotube arrays; Raman peaks at 145 cm$^{-1}$, 196 cm$^{-1}$, 399 cm$^{-1}$, 516 cm$^{-1}$ and 640 cm$^{-1}$ suggest the formation of anatase TiO$_2$.

Anatase TiO$_2$ nanotube arrays were then utilized as photoanode to assemble dye sensitized nanostructured solar cells (Scheme 4-1). Prior to dye adsorption, the nanotubes were processed with TiCl$_4$ by immersing them in 50 ml of 0.2 M TiCl$_4$ aqueous solution in a beaker sealed with parafilm and kept in a 60 °C oil bath for 1 hr, followed by rinsing with ethanol and annealed at 500 °C in air for 30 min. Subsequently, the TiCl$_4$-treated TiO$_2$ nanotube arrays were exposed to O$_2$ plasma for different time, and then immediately
soaked in a 0.2 mM dye/ethanol solution for 24 hr to allow complete dye adsorption. The dye used in the study was cis-diisothiocyanato-bis(2,2’-bipyridyl-4,4’-dicarboxylato) ruthenium(II) bis(tetrabutylammonium) (N-719, Solaronix). A semi-transparent platinum (Pt) coated ITO glass was used as the counter electrode, prepared by placing a drop of 0.5 mM chloroplatinic acid (H₂PtCl₆)/isopropanol solution on ITO glass and subsequently fired at 380 °C for 20 min. The dye sensitized TiO₂ nanotube arrays were sandwiched between the Ti foil (anode) and the Pt-coated ITO glass (cathode) by applying a 25 µm thick hot-melt sealing foil as the spacer (SX1170-25, Solaronix). An ionic liquid electrolyte containing 0.60 M BMIM-I, 0.03 M I₂, 0.50 M TBP und 0.10 M GTC in acetonitril/valeronitril 85/15 (v/v) (ES-0004, purchased from io.li.tec, Germany) was injected between two electrodes driven by capillary force through holes on the hot-melt sealing foil. The ionic liquid possesses high thermal stability, negligible vapor pressure, and low toxicity. The backside of Ti foil was then scratched using a sand paper to remove the thin oxide layer, thereby exposing the underlying Ti that serves as the electrode. The current–voltage (I–V) curves were measured using a Keithley 2400 multisource meter illuminated with a solar simulator (AM 1.5G illumination with irradiation of 100 mW/cm²). The active area for all solar cells was 0.125 cm².
Results and Discussion

Figure 4-2 shows the effects of TiCl₄ treatment on I–V characteristics of dye sensitized TiO₂ nanotube solar cells. The thickness of TiO₂ nanotube arrays was 14 µm. For solar cell without subjecting to TiCl₄ processing, the measurement yielded open circuit voltage, $V_{OC} = 0.70$ V, short circuit current density, $J_{SC} = 12.16$ mA/cm², fill factor, $FF = 0.51$, thereby power conversion efficiency, $PCE = \frac{J_{SC}V_{OC}FF}{P_{inc}} = 4.34\%$ (curve b). By contrast, when TiCl₄-treated TiO₂ nanotube arrays were used, the performance sharply increased, yielding $V_{OC} = 0.75$ V, $J_{SC} = 12.48$ mA/cm², $FF = 0.68$, and $PCE = 6.36\%$ (curve c), a 47% increase in $PCE$ when comparing with non-TiCl₄-treated counterpart (curve b). The performance improvement can be rationalized as follows. Upon high temperature annealing, there existed structural defects and cracks on the nanotubes (i.e. structural disorders), which made it possible for the electrolyte to have direct contact
with the Ti electrode on the bottom, leading to decreased shunt resistance and higher chance for charge recombination. By contrast, with TiCl₄ treatment, a thin blocking layer of TiO₂ can be formed on the uncovered region of Ti foil, thus reducing or eliminating the structural disorders. As a consequence, the shunt resistance increased and series resistance decreased; this improved FF, ultimately, a higher PCE. With TiCl₄ treatment, the increased electron transport through TiO₂ nanotube wall to the bottom Ti electrode by decreasing the surface charge recombination as well as the increased dye adsorption by facilitating improved bonding between TiO₂ and dye molecules may also contribute to the enhanced performance.

Figure 4-2. I-V characteristics of dye sensitized TiO₂ nanotube solar cells. The thickness of TiO₂ nanotube membrane was 14 µm. (a) the device in the dark; anatase TiO₂ nanotube arrays were not treated with TiCl₄ (the devices with and without TiCl₄ treatment were indistinguishable in the dark); (b) the device made of anatase TiO₂ nanotube arrays without TiCl₄ treatment under AM 1.5 G illumination, yielding fill factor, FF of 51% and power conversion efficiency, PCE of 4.34%; and (c) the device made of
the TiCl$_4$-treated TiO$_2$ nanotube arrays under AM 1.5 G illumination, yielding $FF$ of 68% and $PCE$ of 6.36%.

O$_2$ plasma treatment has been demonstrated as an effective approach to saturate the metal oxide surface with hydroxyl group,$^{28}$ which increases both the hydrophilicity at the metal oxide surface.$^{23}$ In this regard, to further improve the performance of dye sensitized nanostructured solar cell, O$_2$ plasma exposure was performed on the TiCl$_4$-treated TiO$_2$ nanotubes prior to infiltration of dye N-719. Specifically, the aforementioned TiCl$_4$-treated, 14 µm thick TiO$_2$ nanotube arrays were placed in O$_2$ plasma cleaner (Harrick Plasma PDC-001, a PlasmaFlo gas meter was used to control the O$_2$ flow in the reaction chamber). The plasma condition was optimized by tuning the O$_2$ flow and vacuum until the brightest fluorescence was observed, i.e., with the O$_2$ flow of 1 SCFH and vacuum of 500 mTorr. After plasma exposure for different period of time, TiO$_2$ nanotubes were immersed in the 0.2 mM N-719/ethanol solution for 24 hr. All other steps for the construction of solar cells and the performance measurements were maintained the same. The I–V curves of resulting solar cells are shown in Figure 4-3. In comparison to curve $c$ in Figure 4-2 in which TiO$_2$ nanotubes were not experienced to O$_2$ plasma ($PCE = 6.36\%$), the $PCE$ increased to 6.48% after 1 min O$_2$ plasma treatment. With longer time exposure to O$_2$ plasma, the $PCE$ increased; the highest $PCE = 7.37\%$ was achieved from 10 min O$_2$ plasma-treated sample (see Table 4-1 in Supporting Information for complete device characterization). The enhancement in $PCE$ can be attributed to a large increase in the photocurrent density, $J_{SC}$, while the photovoltage, $V_{OC}$ did not change much and the fill factor, $FF$ slightly decreased. Upon O$_2$ plasma treatment, the hydroxyl group on the TiO$_2$ surface increased and eventually saturated; this promoted
the adsorption of the N-719 dye by forming interfacial bonding between N-719 and the TiO$_2$ via the coupling reaction of terminal carboxylic acid groups on N-791 with complementary hydroxyl groups on the TiO$_2$ surface, thereby substantially regulating the interfacial charge transfer from N-719 dye to TiO$_2$ and, therefore, the ultimate photophysical properties at the nanoscale.

Figure 4-3. I–V characteristics of dye sensitized TiO$_2$ nanotube arrays assembled using TiCl$_4$- and oxygen plasma-treated, 14 µm thick TiO$_2$ nanotube arrays. (a) 1 min oxygen plasma exposure; (b) 2 min oxygen plasma exposure; (c) 10 min oxygen plasma exposure; and (d) 20 min oxygen plasma exposure.

It is worth noting that upon lengthy O$_2$ plasma exposure (e.g., 20 min; Figure 4-3d and Table 4-1), the device performance decreased, exhibiting a largely reduced $J_{SC}$ compared to the sample after 10 min O$_2$ plasma exposure (Figure 4-3c and Table 4-1). The exact reason for this observation is not clear. It may be because the TiO$_2$ surface
became less hydrophilic after longer time plasma exposure than that under the optimized condition. Consequently, the dye loading was reduced, which in turn the decreased device performance. Similar trends were seen in solar cells assembled using 22 µm and 29 µm thick TiO\textsubscript{2} nanotube arrays, that is, the \textit{PCE} increased with time when nanotubes were subjected to O\textsubscript{2} plasma for less than 10 min; otherwise, the \textit{PCE} reduced (see Table 4-1 and Figure 4-5 in Supporting Information).

![Figure 4-4](image)

Figure 4-4. Effects of thickness, $h$ of TiO\textsubscript{2} nanotube arrays on I-V characteristics of dye sensitized TiO\textsubscript{2} nanotube solar cells. All the TiO\textsubscript{2} nanotubes were treated with TiCl\textsubscript{4} and 10 min O\textsubscript{2} plasma exposure prior to N-719 dye adsorption. (a) $h = 14$ µm and \textit{PCE} = 7.37%; (b) $h = 22$ µm and \textit{PCE} = 6.29%; and (c) $h = 29$ µm and \textit{PCE} = 6.05%.

We note that increasing thickness of TiO\textsubscript{2} nanotube arrays may be a good strategy to improve the performance of solar cells by allowing more dye molecules to be adsorbed on TiO\textsubscript{2} nanotube surface, and thus a higher light harvesting efficiency. To this end,
thicker TiO$_2$ nanotube arrays with 22 µm and 29 µm in thickness were prepared and used to fabricate solar cells; they were processed with TiCl$_4$ and oxygen plasma. Quite intriguingly, the use of thicker TiO$_2$ nanotube arrays yielded progressively decreased performance ($PCE = 6.29\%$ for 22 µm thick nanotubes and $PCE = 6.05\%$ for 29 µm thick nanotubes; see Table 4-1 in Supporting Information) compared to the device produced using 14 µm thick nanotubes ($PCE = 7.37\%$). The I–V characteristics of solar cells assembled using 14 µm, 22 µm, and 29 µm thick TiO$_2$ nanotubes are shown in Figure 4a, 4b, and 4c, respectively. For the 22 µm thick TiO$_2$ nanotube arrays, although the device performance increased as a function of O$_2$ plasma exposure time (Figure 4-5 and Table 4-1 in Supporting Information), the $PCE$ was lower than that using 14 µm thick TiO$_2$ nanotubes. When even thicker TiO$_2$ nanotube arrays were used (i.e., 29 µm), the $PCE$ further fell off. The decrease in $PCE$ with increased TiO$_2$ thickness may be likely due to the limitation of current device configuration as depicted in Scheme 1. In the backside illumination mode, the incident photons had to pass through semitransparent Pt-coated ITO glass and the ionic liquid electrolyte (i.e., ES-0004). Thus, a portion of incident photons was lost before reaching the sensitizer N-719 dye and the photoanode TiO$_2$ nanotube arrays. Therefore, as the thickness of nanotubes increased, the remaining photons may be fully absorbed by the dyes that were anchored on the top part of TiO$_2$ nanotube; however, the dyes on the bottom part of nanotubes will not be excited. A solution to this problem may be the use of freestanding TiO$_2$ nanotube arrays (i.e., detached from Ti foil after anodization)$^{24}$ or TiO$_2$ nanotubes directly grown on transparent conductive substrate$^{6, 22}$ in a front-side illumination mode, where the dye adsorbed TiO$_2$ nanotube arrays are directly illuminated from the TiO$_2$ nanotube arrays...
before incident photons encounter the electrolyte and the counter electrode, thereby ensuring good light harvesting efficiency. It is noteworthy that currently both transferring mechanically brittle freestanding TiO$_2$ nanotube arrays to solid transparent substrates by detaching them from Ti foil and directly growing thick TiO$_2$ nanotube arrays on transparent substrates remain challenging for us. In the later context, the direct growth of TiO$_2$ nanotubes on transparent substrate was hindered by the difficulty in depositing thick, highly quality Ti films at the moment. In addition to the constraint imposed by the device configuration, the one-side open nature of TiO$_2$ nanotubes may cause air to be trapped inside, making it, probably, less accessible by the dye and the electrolyte; moreover, with the increased thickness of nanotubes, longer pathways for electron and hole transport to electrodes may result in a higher chance for charge recombination. These compensate the advantage of using O$_2$ plasma to increase the surface hydrophilicity of TiO$_2$ nanotubes and facilitate the infiltration of dyes and electrolytes. Taken together, the device performance decreased with increased nanotube thickness.

**Conclusion**

In summary, we have assembled ruthenium dye N-719 sensitized nanostructured solar cells by using highly ordered anodic TiO$_2$ nanotube arrays as photoanode. Rational surface engineering on TiO$_2$ nanotubes with TiCl$_4$ treatment together with O$_2$ plasma activation under optimized condition dramatically enhanced the performance of resulting devices. A solar cell in backside illumination mode produced using 14 µm thick TiO$_2$ nanotube arrays after surface treatments with TiCl$_4$ and O$_2$ plasma yielded a PCE of 7.37%, which is the highest promising efficiency for solar cells made of TiO$_2$ nanotube
arrays reported in the literature. The use of thicker TiO$_2$ nanotube arrays did not give rise to higher performance as expected. We attribute this observation to the limitation of current device configuration as well as the possible air trapped in one-side open nanotubes. In addition to ruthenium-based organic dyes, in principle, conjugated homopolymers (e.g., regioregular poly(3-hexyl thiophene)), conjugated block copolymers, and semiconducting nanocrystals (e.g., quantum dots) can be employed as alternative photo sensitizers to create a variety of dye sensitized TiO$_2$ nanotube solar cells. This work is currently under investigation. Such rational design and materials engineering of dye sensitized TiO$_2$ nanotube solar cells create new opportunities for understanding and manipulating the molecular and electronic pathways of solar energy conversion.

Supporting information

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<th>Thickness of TiO$_2$ nanotubes</th>
<th>TiCl$_4$ O$_2$ plasma exposure time</th>
<th>$Voc$ (V)</th>
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<th>$FF$</th>
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Table 4-1. Summary of the device performance of dye sensitized TiO$_2$ nanotube solar cells.

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<th>Open Circuit Voltage (V)</th>
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<td>6.05</td>
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Figure 4-5. I-V characteristics of dye sensitized TiO$_2$ nanotube solar cells in which the thickness of nanotubes was 22 µm. All the nanotube arrays were treated with TiCl$_4$ before exposure to O$_2$ plasma for different period of time: (a) 0 min; (b) 1 min; (c) 2 min; (d) 5 min; (e) 10 min, and (f) 20 min.

References
4.2 Quantum dots sensitized solar cells

Introduction

Solar energy has been attracting tremendous research interests due to its impacts on environmental health, unlimited resource and worldwide applications. However, current low power conversion efficiency has largely prevented its wider application. Many efforts have been focused on employing nanostructured semiconductors, conjugate polymers, carbon nanotube, and quantum dots for the next generation high efficiency solar energy conversion devices. For example, by using ruthenium dye to sensitize titania nanoparticulate film, a power conversion efficiency higher than 10% has been achieved;\textsuperscript{1} K. M. Coakley et al studied the organic-inorganic bulk heterojunction photovoltaic cells by infiltrating semiconducting conjugated polymer, poly(3-hexylthiophene) (P3HT), into mesoporous titania film with perpendicular pores throughout the film;\textsuperscript{2-4} A. P. Alivisatos et al made the hybrid solar cell by spin coating thin film of a mixture of CdSe nanocrystal and semiconducting conjugated polymer, and studied the different nanocrystal shape, film morphology, and post treatment on the cell performance.\textsuperscript{5-10} Advincula R. C.\textsuperscript{11} and Skaff H et al grafted semiconducting conjugated polymer directly on the quantum dot, showing enhanced charge transfer.\textsuperscript{12} W. L. Ma et al\textsuperscript{13}, J. G. Xue et al\textsuperscript{14, 15} and K. L. Mutolo et al\textsuperscript{16} studied the photovoltaic cells based on semiconducting conjugated polymer and fullerene. However, to date, the power conversion efficiency of
photovoltaic cells is still not high enough as demand, due to the inefficient charge transport to the electrode and significant charge recombination before reaching the electrode. Improvement of the solar energy conversion efficiency is one of the biggest issues in solar energy research.

Anodic TiO$_2$ nanotube which is obtained via anodization of high purity titanium in fluorine containing electrolyte$^{17, 18}$ has been attracting more and more research attention because of its significant optical-electrical properties compared with conventional used TiO$_2$ nanoparticles$^1$ and sol-gel process generated TiO$_2$.$^{19}$ After high temperature annealing, the anodic TiO$_2$ nanotube exhibits anatase phase, and the well oriented crystalline along the tube makes it excellent pathway for electron transport,$^{20, 21}$ which is promising to improve the device performance if used as electron conductor in solar cell. It has been used to fabricate high efficiency hydrogen sensor$^{22-24}$ and for hydrogen generation through photo-splitting of water.$^{25, 26}$ Recently, anodic TiO$_2$ nanotube arrays have been used to substitute TiO$_2$ nanoparticle film in conventional ruthenium dye sensitized solar cell (DSSC). G. K. Mor et al obtained a photocurrent efficiency of 2.9% using ruthenium dye to sensitize transparent TiO$_2$ nanotube array that was only 360nm in thickness;$^{20}$ later an overall conversion efficiency up to 6.89% was achieved by K. Shankar and G. K. Mor et al using ruthenium dye to sensitize a 20µm thick TiO$_2$ nanotube array; and an efficiency close to the ideal limit (Shockley-Queisser limit of 32%$^{27}$) was expected with increased TiO$_2$ nanotube length and optimized device structure;$^{21}$ K. Zhu et al. compared the anodic TiO$_2$ nanotube arrays and conventional used TiO$_2$ particulate film for ruthenium dye sensitized solar cell by carrying out systematical study on the charge transport and recombination of anodic titania nanotube
array using intensity modulated photocurrent spectroscopy (IMPS) and intensity modulated photovoltage spectroscopy (IMVS),\textsuperscript{29, 30} suggesting enhanced charge collection efficiency and light scattering when the anodic TiO\textsubscript{2} nanotube array is sensitized by ruthenium dye.\textsuperscript{28}

Semiconducting quantum dots, e.g., CdSe, CdS, CdTe, InAs, InP, and PbSe, which absorb visible light and inject electron to large bandgap semiconductor, e.g., TiO\textsubscript{2}, has shown promising potential as a substitute for ruthenium dye in conventional DSSCs.\textsuperscript{31-35} Quantum dots possess many unique properties, including tunable band edge, efficient visible absorption, and multi-exciton generation capability,\textsuperscript{34, 36-43} and has thus been studied both theoretically and experimentally for its potential applications in solar energy conversion. Theoretical calculation shows that as many as seven exciton can be generated when QDs absorb one photon at an energy level that is sufficiently higher than their bandgap,\textsuperscript{39} and an ideal power conversion efficiency limit higher than 40\% is expected.\textsuperscript{31, 34} Thus, quantum dots with multi-exciton generating capability have tremendous potential as sensitizers for next generation solar energy conversion device and is expected to further increase the power conversion efficiency.

Herein, we deposited CdSe in anodic anatase TiO\textsubscript{2} nanotube arrays to produce CdSe sensitized TiO\textsubscript{2} nanotube solar cells, and studied the performance of the resulting device under a 1.5AM simulated sun light illumination. The anodic TiO\textsubscript{2} nanotube array with thickness varying from several hundred nanometers to several micrometers was grown on the high purity titanium foil in the fluorine containing electrolyte, and subsequently annealing at 500\^\circ C in air to form anatase crystalline. The titanium foil at bottom of nanotube then worked as the cathode for the photovoltaic device (as shown in
scheme 4-2 for the device structure) together with a semi-transparent platinum coated conductive glass as counter electrode. In order to achieve good interfacial interaction between CdSe nanocrystal and TiO$_2$, bifunctional molecules were used.\textsuperscript{33} However, the performance of the CdSe sensitized anodic TiO$_2$ nanotube is not promising in current work, due to several problems, including the backside illumination mode, meaning that the platinum electrode and redox electrolyte absorb part of the incident light; insufficient CdSe nanocrystal absorption inside nanotubes due to the possible air trapped inside that prevents complete filling of solvent; relatively short TiO$_2$ nanotube can not efficiently absorb incident light. Future work, including device structure optimization, surface functionalized CdSe nanocrystal, efficient nanotube filling, etc., is currently undergoing, which expects to further improve the power conversion efficiency of semiconducting nanocrystal sensitized anodic TiO$_2$ nanotube.

**Results and discussion**

CdSe nanocrystal was synthesized using a modified procedure according to the method reported in literatures.\textsuperscript{44-46} Typically, 50mg of cadmium oxide (Sigma-Aldrich) and 450mg stearic acid (Fisher Scientific) were placed in a 25ml flask and heated to melt under Ar flow, a transparent solution was thus obtained. The solution was then cooled to room temperature (forming white solid), then ~2g trioctylphosphine oxide (TOPO) (Sigma-Aldrich) and ~2g hexadecylamine (Sigma-Aldrich) was added and degassed under Ar flow for 30 min and heated to 290$^\circ$C, followed by injecting a selenium stock solution containing 30mg selenium (Sigma Aldrich), 0.8ml trioctylphosphine (Sigma-Aldrich) and 2ml dioctylamine (Sigma-Aldrich). 10ml chloroform (Fisher Scientific) was
injected when desired size of nanocrystal was reached, which can be controlled by the reaction time. The CdSe nanocrystals have a diameter of 4 nm, as revealed by the TEM measurement, and very narrow size distribution (Figure 4-6a), which is also supported by the presence of sharp emission peak as shown in Figure 4-6b. Figure 4-6b shows the UV-vis absorption and photoluminescence spectrum of the as-prepared CdSe nanocrystals. Before used to fabricate solar cells, the as-prepared CdSe nanocrystals were washed using methanol for three times in order to remove excess organic ligands, followed by ligand exchange using pyridine (Fisher Scientific) and precipitate in hexane (Fisher Scientific). The pyridine passivated CdSe nanocrystals were dissolved in a mixture of pyridine and acetonitrile at the volume ratio of 1:3.
Anodic TiO$_2$ nanotube arrays were prepared via electrochemical anodization of high purity titanium foil (99.7%, from Sigma-Aldrich) in fluorine containing electrolyte.$^{17,47}$ Two kinds of titania nanotube with different thickness were prepared in aqueous electrolyte and nonaqueous electrolyte. Titanium foil with a size of 0.5 inch x 1 inch was first degreased in acetone, chloroform and methanol with sonication,$^{47,48}$ then washed thoroughly with DI-water and dried under the N$_2$ flow. Anodization was carried out in DI-water containing 0.5wt% hydrofluoric acid (~48wt% in water, from Sigma-Aldrich) at about 0°C with anodization potential of 20 V for 1 h, the nanotube prepared in aqueous electrolyte only had thickness of several hundred nanometers;$^{17}$ A thicker
nanotube array was prepared via anodization of Ti foil in glycerol (Fisher Scientific) containing 0.5 wt % ammonium fluoride\textsuperscript{47} (Sigma-Aldrich) at 100V at 0°C for hours. The as-anodized TiO\textsubscript{2} nanotube was immediately washed using a large amount of DI-water and dried with nitrogen gas flow. SEM measurements show the nanotubular structures of anodized TiO\textsubscript{2}, with a tube diameter of ~60nm and thickness of several hundred nanometers to several micrometers (Figure 4-7). High temperature annealing was subsequently carried out at 500°C in air for 3 hours to transform the amorphous TiO\textsubscript{2} into anatase phase. Amorphous and anatase TiO\textsubscript{2} nanotubes were characterized by Raman spectroscopy shown in Figure 4-8. Anatase TiO\textsubscript{2} has specific raman peaks at 144 cm\textsuperscript{-1}, 198 cm\textsuperscript{-1}, 399 cm\textsuperscript{-1}, 516 cm\textsuperscript{-1} and 640 cm\textsuperscript{-1}, while as-anodized amorphous TiO\textsubscript{2} has a broad spectrum from 420 cm\textsuperscript{-1} to 600 cm\textsuperscript{-1}\textsuperscript{49,51} The Raman spectra showed that after high temperature annealing, the anodic TiO\textsubscript{2} nanotubes exhibited an anatase phase, which possesses excellent optic-electrical properties.
Figure 4- 7. SEM image of TiO$_2$ nanotube arrays on top of Ti foil. a) Top of TiO$_2$ nanotube arrays obtained from anodization of Ti in 0.25 wt % HF electrolyte at 12 V in ice bath, acetic acid was added in ratio of 1:7, scale bar = 1 µm; b) Top view of TiO$_2$ nanotube arrays obtained from anodization of Ti foil in DI-water containing 0.5 wt% HF, 20V, ice bath, scale bar = 1 µm; c) Top view of TiO$_2$ nanotube arrays obtained from a two-step anodization of Ti foil in fluorine containing electrolyte in an ice bath, first anodization in glycerol containing 0.5 wt % ammonium fluoride at 100 V then in 0.5 wt % HF aqueous electrolyte at 20 V, scale bar = 1 µm; d) top view of TiO$_2$ nanotube array obtained via anodization in glycerol containing 0.5 wt% ammonium fluoride, 100 V, ice bath, scale bar = 400 nm; e) a side view of TiO$_2$ nanotube array obtained via anodization in glycerol containing 0.5 wt% ammonium fluoride, 100 V, ice bath, scale bar = 1 µm.
Figure 4-8. Crystalline structure characterization of TiO₂ nanotube array using Raman spectroscopy. Black line corresponds to the Raman spectrum of amorphous TiO₂ nanotube after anodization; red line represents the anatase crystal type of TiO₂ nanotubes after annealed at 450°C for 3 h in air. TiO₂ nanotubes were fabricated in HF (0.5 wt %) aqueous electrolyte with anodization potential of 20 V in ice bath. The specific Raman peaks of anatase TiO₂ are at 144 cm⁻¹, 198 cm⁻¹, 399 cm⁻¹, 516 cm⁻¹, and 640 cm⁻¹. The measurement was carried out using a 488nm wavelength laser with power intensity of 50mw and acquisition time of 10s.

Quantum dots sensitized TiO₂ nanotube solar cells were assembled according to Scheme 4-2. Before introducing CdSe nanocrystals into the nanotubes, the inner wall of anatase TiO₂ nanotube arrays was first functionalized using bifunctional molecule, which has thiol group at one end and carboxylic group at the other end. It has been well studied that thiol group can chemically tethered to CdSe nanocrystal surface while carboxylic group has good binding with TiO₂. Anatase TiO₂ nanotube kept in oven at 100°C was soaked in acetonitrile containing 1mM
3-Mercaptopropionic acid (MPA) for 24 h under vacuum; the TiO$_2$ nanotubes were then washed with a large amount of acetonitrile to remove unabsorbed MPA and subsequently placed in a 25ml flask containing CdSe nanocrystal dispersed in 1: 3 pyridine: acetonitrile under partial vacuum$^{31,52}$ controlled by a flow control adaptor overnight. The excess nanocrystals were washed away using large amount of acetonitrile; in order to reduce the influence of passivate ligand on the efficient charge separation, the nanotube linked with CdSe nanocrystal was placed in a small flask under vacuum and heated to remove pyridine on the nanocrystal surface. The semitransparent platinum coated electrode was prepared by placing one drop of isopropanol containing 5mM platinum chloride on conductive glass slide followed by heat to 350$^\circ$C for 20 min.$^{30,31}$ A 25 µm self sealing hot melt spacer (Solaronix) was placed between the two electrodes; Electrolyte, acetonitrile containing 15 mM potassium iodide and 1.5 mM iodine was introduced into the space between two electrodes by capillary force via two holes on the spacer under partial vacuum, subsequently the two holes were sealed.

Scheme 4-2. Schematic illustration of the solar cells using CdSe to sensitize TiO$_2$ nanotube arrays.
Figure 4-9. I-V characteristics of quantum dots sensitized TiO$_2$ nanotube solar cells with different nanotube thickness.

As the TiO$_2$ nanotube used here was only one size open, when infiltrating the CdSe nanocrystal and electrolyte the air trapped in the nanotube was not easy to be removed as in the conventional TiO$_2$ nanoparticle film, where the interconnected pores make it easy for air to escape; thus the amount of CdSe nanocrystal within the nanotube was largely reduced, according to the pure performance of solar cell device (results not shown). In order to infiltrate more nanocrystals in the nanotube, partial vacuum and heat were used when soaking the nanotube array in CdSe nanocrystal solution. However, limited improvement was obtained due to the difficulty to remove the trapped air in the nanotube.$^{53}$

Conclusion

In summary, we used CdSe nanocrystals to sensitize anodic TiO$_2$ nanotube array for preparing QDSSCs. However, currently, the performance of solar cells was not promising. The main reason for the low performance was attributed to only small amount
of CdSe nanocrystal adsorbed in the nanotubes. This is due to the difficulty removing the trapped air in one side open nanotube. A possible approach to get more nanocrystals inside nanotubes will be the in situ growth of nanocrystals in the nanotube,\textsuperscript{54} which is currently under investigation. Furthermore, the strong recombination at high illumination might be another reason for the low performance as suggested by P. R. Yu et al.\textsuperscript{31} Future work, including the choice of CdSe nanocrystal with more suitable size, electrolyte with better redox capability, rational design of device structure, etc. are also being conducted to improve the device performance.

**References**

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Chapter 5. Ferroelectric Nanocrystals

5.1 Barium titanate nanocrystals

Introduction

Perovskite-type mixed metal oxide with general formula of \( \text{ABO}_3 \) have received much attention in the past decades due to their unique ferroelectric, catalytic, sensing, superconducting, and optical properties for use in thin-film capacitors, pyroelectric detectors, electrooptic modulators, transducers, actuators, optical memories, and nonlinear optics.\(^1\)\(^-\)\(^3\) Following a similar trend to miniaturization as conventional semiconductors, for the fabrication of nanodevices based on ferroelectric \( \text{BaTiO}_3 \) nanocrystal building blocks with outstanding physical properties and durability at the nanoscale, it is necessary to control the size and shape of \( \text{BaTiO}_3 \) nanostructures.\(^3\)\(^,\)\(^4\) In this context, much research has been carried out on the synthesis protocols of \( \text{BaTiO}_3 \) nanocrystals of various size and shapes (e.g., nanoparticles, nanorods, and nanowires). S. O’Brien et al synthesized monodisperse \( \text{BaTiO}_3 \) nanocrystals using a injection-hydrolysis approach, with nanoparticles size ranging from 4 to 12 nm;\(^4\) H. Park et al prepared single crystalline \( \text{BaTiO}_3 \) nanowires with diameter from 5 to 70 nm and length up to more than 10 \( \mu \text{m} \), in addition they carried out scanning probe microscopy measurement on a single \( \text{BaTiO}_3 \) nanowires to study the nanoscale ferroelectricity of \( \text{BaTiO}_3 \);\(^5\)\(^-\)\(^7\) M. Niederberger et al developed a non-aqueous, non-hydrolytic, non-hydrothermal, and halide-free route for the preparation of size-tunable \( \text{BaTiO}_3 \) nanocrystals capped with surface ligands;\(^3\)\(^,\)\(^8\) G. Ahmad et al reported the rapid bioenabled formation of \( \text{BaTiO}_3 \) nanocrystals at room temperature from an aqueous salt solution, using an appropriate peptide as the precipitating agent for \( \text{BaTiO}_3 \) nanocrystals.\(^9\) However, few work has been done on the
well control of the BaTiO$_3$ nanocrystals size and morphology, while these are of great importance for both fundamental study and engineering applications.

Here in this report, we introduced a non-aqueous high temperature thermal decomposition approach for the synthesis of BaTiO$_3$ nanocrystals with coordinating surface capping ligands, control over the BaTiO$_3$ size and morphology were achieved in this method. High temperature thermal decomposition approach has been widely adopted for the synthesis of various functional nanocrystals, including quantum dots,$^{10-13}$ iron oxide nanoparticles$^{14,15}$ etc., providing well control of nanocrystals size and shape. In our synthesis of BaTiO$_3$ nanocrystals, a commercially available Ba-Ti precursor was thermally decomposed in a high boiling point solvent with the existence of surface capping ligand. By adjusting the reaction conditions, size and morphology control on the BaTiO$_3$ nanocrystals were achieved, with products including BaTiO$_3$ nanoparticles, nanorods and nanowires. The appropriate conditions for the formation of single crystalline BaTiO$_3$ nanocrystals were also concluded from systematic studies. X-ray powder diffraction (XRD), transmission electron microscopy (TEM) and Energy dispersive X-ray microanalysis (EDX) were used to characterize the obtained BaTiO$_3$ nanocrystals.

**Experimental**

In a typical synthesis, 1.6 mM oleic acid (Tech. 90%, Alfa Aesar) and 10 ml of 1-Octadecene (Tech. 90%, Sigma Aldrich) were mixed under magnetic stirring in a three-neck flask and heated to 100°C for 30 min, vacuum was applied to remove trace water and the system were protected by dry Ar. The solution was cool down to 80°C and 1 ml
of barium titanium ethyl hexano-isopropoxide (13% isopropanol solution; equals to about 0.4 mM of metal ions (Ba and Ti)) was injected quickly, followed by heating to 100°C and the isopropanol was removed by vacuum. All chemicals were used as received without further purification. Under Ar protection, the transparent reaction solution (light yellowish) was heated to refluxing for 24 h, resulting in a turbid solution (see supporting information Figure 5-3). Large amount of ethanol was added to the turbid solution, and the precipitates were re-dissolved in toluene. BaTiO₃ nanocrystals with morphology of nanorods and nanowires were obtained by varying the amount of oleic acid, i.e., 3.2 mM of oleic acid for nanorods and 6.4 mM of oleic acid for nanowires while all other conditions remained same.

**Results and Discussion**

Figure 5-1 shows the TEM images of as-synthesized BaTiO₃ nanocrystals (a, b, and c) and XRD spectrum (d); insets are the corresponding selected area electron diffraction (SAED) patterns, indicating that the as-synthesized BaTiO₃ nanocrystals are highly crystalline. Individual BaTiO₃ nanocrystals were clearly observed in the TEM images, with which the analysis statistics on the size and morphology of nanocrystal were summarized in Table 5-1. Under the same experiment conditions, the amount of surface capping ligand (i.e., oleic acid) was found to dictate the morphology of BaTiO₃. When the amount of oleic acid was 4 times higher than metal ions, nanoparticles were obtained; nanorods were obtained when oleic acid was 8 times more, and nanowires were yielded when the ratio of the ligand : metal ions was extremely high (i.e., 16 : 1). The correlation between ligand: metal ions ratio and nanocrystal morphology was found be in good
agreement with Peng’s observation for iron oxide nanocrystals. With extremely high ligand/metal ions ratio, BaTiO$_3$ nanowires with length more than 1000 nm could be obtained (Figure 5-1c). EDX on the BaTiO$_3$ nanocrystals confirmed the chemical composition of the as-synthesized nanocrystals, the Ba/Ti ratio is close to 1. (see supporting information Figure 5-4).

Figure 5-1. Characterization of as-synthesized barium titanate (BaTiO$_3$) nanocrystals: (a) TEM image of BaTiO$_3$ nanoparticles, scale bar = 200 nm; (b) TEM image of BaTiO$_3$ nanorods, scale bar = 100 nm; and (c) TEM image of BaTiO$_3$ nanowires, 200 nm; insets show the corresponding selected area electron diffraction (SAED) patterns. Shown in (d)
are the X-ray powder diffraction spectrum of BaTiO$_3$ nanoparticles (Red), nanorods (Blue) and Nanowires (Green); As a control experiment, the XRD pattern of Si (111) substrate is also shown (Black).

<table>
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<tr>
<th>BaTiO$_3$ nanocrystals</th>
<th>Nanoparticles</th>
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<td>8 : 1</td>
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<tr>
<td>Aspect ratio (L/D)</td>
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<td>7</td>
<td>43</td>
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</table>

Table 5-1. Analysis on the average size and morphology evolution of BaTiO$_3$ nanocrystals, and their dependence on the ligand to metal ions ratio. These data were obtained by analyzing the corresponding TEM images.

Figure 5-2. High resolution TEM images show the highly crystalline nature of as-synthesized BaTiO$_3$ nanoparticles (a), nanorods (b), and nanowires (c). Scale bar = 2 nm.

The crystalline nature of as-synthesized BaTiO$_3$ nanocrystals was examined by XRD and high resolution TEM (HR-TEM). XRD was performed with Cu Kα radiation.
(λ = 1.54056 Å), and the samples were prepared by drop casting concentrated BaTiO$_3$ toluene solution on Si (111) substrate. Figure 5-1d shows the XRD spectrum of BaTiO$_3$ nanocrystals which can be well indexed as cubic BaTiO$_3$ (PDF # 00-005-0626). The crystalline lattice of BaTiO$_3$ nanocrystals was well revealed by HR-TEM measurement (Figure 5-2).

The appropriate conditions for the formation of highly crystalline BaTiO$_3$ were concluded by systematic studies on the refluxing time and the amount of surface capping ligand. Time-dependent study showed that a certain length of refluxing period was required for the formation of BaTiO$_3$ nanocrystals, i.e., 12 h (see supporting information Figure 5-5). This may be because the present method is absolutely water free since the precursor is highly moisture sensitive, and the thermal decomposition rate of the Ba-Ti precursor is slow under current conditions. However, we found that a much longer reaction time did not seem to obviously increase the size of nanoparticles. The same case was observed when synthesizing BaTiO$_3$ nanorods and nanowires. To study the effect of ligand amount, a series of reactions were carried out with the amount of oleic acid ranging from 0.05 mM to 6.4 mM while the Ba and Ti ions were maintained as 0.4 mM. We found that a minimum of 1.2 mM of oleic acid was required for the formation of BaTiO$_3$ nanocrystals (see supporting information Figure 5-6), indicating a ligand to metal ions ratio of 3. When the ligand to metal ions ratio was less than 3, the reaction solution remained transparent after a long period refluxing and no particles could be found when imaging with TEM. When the ligand amount was higher than 1.2 mM, highly crystalline BaTiO$_3$ nanocrystals started to form and the morphology was well controlled (Figure 5-1).
Conclusion

In summary, we reported a non-aqueous high temperature thermal decomposition approach for the synthesis of highly crystalline BaTiO$_3$ nanocrystals. The amount of surface capping ligand (i.e., oleic acid) was found to determine the morphology of BaTiO$_3$ nanocrystals, by varying the ligand to metal ions ratio, BaTiO$_3$ nanoparticles, nanorods and nanowires could be obtained. EDX characterization confirmed the chemistry composition of as-synthesized BaTiO$_3$ nanocrystals; and the highly crystalline nature of these nanocrystals was revealed by XRD, HR-TEM, and selected area electron diffraction (SAED). This approach is simple and can be easily scaled up and extended to the synthesis of other ABO$_3$ type nanocrystals, e.g. SrTiO$_3$. Future work includes the optimization of experiment conditions to obtain BaTiO$_3$ nanocrystals with uniform morphology and better size distribution, and the nanocrystals surface properties control for engineering application; these are currently underway.

Supporting information

Figure 5- 3. Digital camera images show the color change of reaction solution. (a) Transparent, light yellowish solution before refluxing; (b) After 24 h refluxing under Ar,
the reaction solution changed to turbid and brown. The gradual change on solution color and the formation of turbidity was observed during the refluxing process, i.e., after 6 h refluxing, the solution color changed to deep yellow, and after 12 h refluxing, we were able to see the solution change to turbid; this observation is correlated well with the TEM results shown in Figure 5-5.

Figure 5-4. Energy dispersive X-ray spectroscopy (EDS) characterization on the BaTiO$_3$ nanocrystals. (a) EDS spectrum on the BaTiO$_3$ nanoparticles; and (b) EDS elements mapping on the BaTiO$_3$ nanoparticles.
Figure 5-5. TEM images of BaTiO$_3$ nanoparticles obtained at different refluxing periods. (a) 2 h refluxing, scale bar = 50 nm; (b) 6 h refluxing, scale bar = 50 nm; (c) 6 h refluxing, scale bar = 100 nm; (d) 12 h refluxing, scale bar = 100 nm. In the case of nanorods and nanowires, the similar length of refluxing period is necessary for the formation of BaTiO$_3$ nanocrystals according to TEM observation (results not shown here).
Figure 5-6. TEM images of BaTiO$_3$ nanocrystals obtained with 1.2 mM oleic acid as surface capping ligand: (a) a low magnification TEM images, scale bar = 500 nm; (b) a high magnification TEM image, scale bar = 100 nm. In other control experiments where oleic acid was less than 1.2 mM, no nanocrystals were observed. All the experiment parameters, except the amount of oleic acid, were kept as the same for all reactions.

References


5.2 Lead titanate (PbTiO₃) with solution processibility

Introduction

Lead titanate (PbTiO₃), owing to its large pyroelectric coefficient and low permittivity, has been widely used in various electronic devices and received tremendous research attention.¹⁻³ 1-D nanoparticles have been attracted tremendous research interest due to the unconventional physical and chemical properties at nanoscale, such as the size dependent optical properties of quantum dots⁴⁻⁶ and the size dependent properties of multiferroic nanocrystals.⁷⁻⁸ In addition, 1-D nanoparticles could be idea building blocks for the assembly of electronic devices in a low cost manner. However, there exists few
report on the synthesis of lead titanate nanoparticles; several approaches have been reported for the synthesis of PbTiO$_3$ particles, including sol-gel process,$^9$ hydrothermal method,$^{10}$ lithography technique,$^{11}$ and solid-state mixing method.$^{12}$ Unfortunately, the size of lead titanate particles were barely controlled or strict experiment conditions were required.$^9$ Also, the lack of solvent solubility prevents the potential use of low cost solution processed techniques, such as spin coating and evaporation induced self assembly.$^{13}$ Therefore, it is of great importance to develop a facile synthetic approach for high quality lead titanate nanoparticles with good solvent solubility. With this regard, we reported here a non-aqueous route for the synthesis of lead titanate nanoparticles with good solvent solubility. Common chemicals were used in this approach, and there is no need for extremely high temperature and long reaction time,$^3$ making it feasible for large scale synthesis.

**Experimental**

In an argon protected glove box, 1 mmol of lead acetate (99.99%, Sigma Aldrich) was first dissolved in 10 ml of anhydrous benzyl alcohol (Sigma Aldrich) to form a transparent solution, to which 1 mmol of titanium isoproponoxide (97%, Sigma Aldrich) was added and the mixture was magnetically stirred for 30 min to form a uniform solution; consequently, 0.3 ml of oleic acid (technical grade, Sigma Aldrich) was added and after another 10 min stirring the mixture was transferred to a Teflon lined autoclave (45 ml, Parr Instrument). The autoclave was then taken out from glove box and heated in an oven at 200$^\circ$C for 2 hr. After cooling down to room temperature, the white jelly-like product was collected (Figure 5-10a) and purified through a precipitating-redissolving process using ethanol and toluene. The purification process was carried out for three
times and the final product was dried at elevated temperature in air, yielding yellow powder as shown in Figure 5-10d, which is the typical color of lead titanate. Transmission electron microscopy (TEM) and X-ray powder diffraction (XRD) were used to characterize the obtained lead titanate nanoparticles. To prepare TEM samples, a drop of dilute lead titanate nanoparticles in toluene was drop casted on a carbon coated copper TEM grid (400 mesh) and allowed to dry in air. For XRD samples, concentrate suspension of lead titanate nanoparticles in toluene was drop casted on Si wafer and dried to form a yellowish thin film.

Results and Discussion

Figure 5-7 shows the TEM images of as synthesized lead titanate nanoparticles. Nanoparticles with average diameter of 4 nm were obtained (Figure 5-7a); high resolution TEM (HR-TEM) of an individual nanoparticle reveals the crystalline nature, with lattice spacing of 0.276 nm and 0.229 nm (Figure 5-7b) that could be indexed as <110> and <111> of tetragonal lead titanate. Figure 5-8 shows the XRD spectrums of fresh lead titanate nanoparticles (black) and those after annealing at 600°C for 10 min (red). For the as-synthesized nanoparticles, no any specific XRD peaks were observed except a broad peak around 2θ = 30°, this might be because the nanoparticles size is quite small (4 nm) and the lead titanate nanoparticles were not completely crystallized, as revealed by HR-TEM (Figure 5-12). High temperature annealing could promote the crystallization of nanoparticles, resulting in the characteristic XRD peaks. The clear emergence of XRD peaks, which could be indexed to tetragonal lead titanate, is believe to be due to the aggregation of nanoparticles as well as increased crystallization of the nanoparticles. The aggregation of nanoparticles was confirmed by TEM characterization
on the annealed lead titanate solid powders (Figure 5-15a), nanoparticles with average size of 60 nm were observed from the sample that was annealed at 500°C for 10 min. Different annealing temperature were examined and it was found that the characteristic peaks of tetragonal lead titanate start to emerge from annealing temperature of 400°C (Figure 5-11).

Figure 5-7. TEM images of PTO nanoparticles obtained after heating at 200°C for 2 hr, with oleic acid added as surfactant. (a) A low-resolution TEM image of lead titanate nanoparticles, scale bar =20 nm; (b) HR-TEM of an individual lead titanate nanoparticles exhibits the crystalline lattice, scale bar = 5 nm.
Figure 5-8. X-ray powder diffraction spectrums of lead titanate nanoparticles obtained after 2 hr heating, with oleic acid added as surfactant. Black curve show the XRD spectrum of fresh lead titanate nanoparticles while red curved shows the XRD spectrum of lead titanate nanoparticles annealed at 600°C for 10 min, the characteristic peaks could be indexed to tetragonal lead titanate (PDF # 06-0452).

With purpose to increase the crystallization degree in fresh lead titanate nanoparticles, longer time heating at 200°C was carried out. However, the XRD of fresh nanoparticles from longer time reaction did not give any promising information, the crystallization remained as low as those from 2 hr heating (Figure 5-14). Similarly, after annealing at 600°C, the nanoparticles aggregated and the crystallization was promoted, yielding a XRD spectrum that could be indexed to tetragonal lead titanate. Figure 3a shows the TEM of lead titanate nanoparticles obtained after heating at 200°C for 6 hr, the obtained nanoparticles have an average diameter of 4 nm. It is worth noting that a reaction time as long as 48 hr did not make any changes to the nanoparticles size (results not shown), suggesting that a short reaction time of 2 hr is enough in the present method.
An interesting observation is that lead titanate nanoparticles could also be obtained without adding oleic acid into the reaction mixture (Figure 5-9b). The obtained nanoparticles have diameter of 4 nm, similar to the nanoparticles protected by oleic acid. However, these nanoparticles tends to aggregate in both polar and non-polar solvent (i.e., ethanol and toluene) due to the lack of surfactant, which has been considered as essential for providing solvent solubility to nanoparticles. The aggregation of nanoparticles is also revealed by TEM characterization (Figure 5-9b), indicating poor disperse on the carbon coated TEM grids. XRD spectrums of this sample are shown in Figure 5-13; unlike the lead titanate nanoparticles with passivation of oleic acid, an annealing temperature of 500°C was found to be necessary for the emergency of specific XRD peaks. Figure 5-15b shows the TEM image of lead titanate nanoparticles from the sample annealed at 500°C, the size of nanocrystals aggregation is larger than 100 nm, indicating higher aggregation of nanoparticles compared to where protection from oleic acid existed.
(Figure 5-15a). The passivation of oleic acid on the nanoparticles surface was further proved by thermogravimetric analysis (TGA), as shown in Figure 5-16 (d and e). Under both air and nitrogen atmosphere, a difference in mass loss was observed from lead titanate nanoparticles with/without oleic acid passivation, which is believed to be from the oleic acid attached to nanoparticles surface. According to the TGA curves in Figure 5-16 a-c, neglectable difference in mass loss was observed from the analysis carried out under air flow and nitrogen gas flow; this confirmed that the fresh nanoparticles have the same chemical composition as the annealed samples (i.e., PbTiO$_3$), although the obvious difference in XRD spectrums was observed.

**Conclusion**

In conclusion, lead titanate nanoparticles with good solvent solubility were synthesized through a non-aqueous route. The obtained nanoparticles have an average size of 4 nm, and could be well dispersed in non-polar solvent (i.e., toluene and hexane); thus providing good solution processibility. In addition, water soluble lead titanate nanoparticles could be prepared by using Polyvinylpyrrolidone (PVP) as surfactant instead of oleic acid. The crystallization of fresh lead titanate nanoparticles is low as revealed by XRD and HR-TEM; subsequent high temperature annealing lead to promoted crystallization and aggregation of nanoparticles, as revealed by the emergency of characteristic XRD peaks and TEM characterization on annealed nanoparticles. These lead titanate nanoparticles could be used as building blocks for assembly of nanodevices, as well as for studying the fundamental nanoscale properties of lead titanate, which has
not been well investigate so far. In addition, this method could be scaled up, providing practical potential.

Supporting information

Figure 5-10. Digital camera images of lead titanate nanoparticles dispersed in corresponding solvent, i.e., toluene in (a) and (b), ethanol in (c); and the lead titanate nanoparticles after purification and dried in air (d)-(f). (a) and (d) lead titanate nanoparticles obtained after 2 hr heating at 200°C with oleic acid added, the obtained nanoparticles were dispersed in toluene; (b) and (e) lead titanate nanoparticles obtained after 6 hr heating at 200°C with oleic acid added, the obtained nanoparticles were dispersed in toluene; (c) and (f) lead titanate nanoparticles obtained after 2 hr heating at 200°C without oleic acid added, the obtained nanoparticles were dispersed in toluene.
Figure 5-11. XRD spectrum of lead titanate nanoparticles annealed at different temperature ranging from 200°C to 500°C. Lead titanate nanoparticles were obtained after 2 hr heating at 200°C with oleic acid added.

Figure 5-12. HR-TEM. (a) Lead titanate nanoparticles obtained after heating at 200°C for 6 hr with oleic acid added; (b) Lead titanate nanoparticles obtained after heating at 200°C for 2 hr without oleic acid added. Scale bars = 5 nm.
Figure 5-13. X-ray powder diffraction spectrum of fresh lead nanoparticles (black curve) and the samples annealed at different temperature ranging from 200°C to 600°C, the characteristic peaks were found to match well with lead titanate crystal (PDF # 06-0452). Lead titanate nanoparticles were obtained after heating at 200°C for 2 hr without oleic acid added.
Figure 5-14. X-ray powder diffraction spectrum of fresh lead nanoparticles (black curve) and the sample annealed at 600°C (red curve), which is found to match well with lead titanate crystal (PDF # 06-0452). Lead titanate nanoparticles were obtained after heating at 200°C for 6 hr with oleic acid added.

Figure 5-15. TEM images of lead titanate nanoparticles annealed at 500°C for 10 min. (a) lead titanate nanoparticles obtained after heating at 200°C for 2 hr with oleic acid added; (b) lead titanate nanoparticles obtained after heating at 200°C for 2 hr without oleic acid added. Scale bars = 200 nm. To prepare samples for TEM characterization, annealed lead
titanate nanoparticles were dispersed in ethanol under ultrasonication, followed by drop casting one drop of the suspension on carbon coated copper TEM grid and allowed to dry in air.
Figure 5-16. TGA analysis on fresh lead titanate nanoparticles with both air flow (back curves) and nitrogen gas flow (red curves). (a) lead titanate nanoparticles obtained after heating at 200°C for 2 hr with oleic acid added; (b) lead titanate nanoparticles obtained after heating at 200°C for 6 hr with oleic acid added; (c) lead titanate nanoparticles obtained after heating at 200°C for 2 hr without oleic acid added; (d) TGA curves of lead titanate nanoparticles under air flow; and (e) TGA curves of lead titanate nanoparticles under nitrogen gas flow.

References


Chapter 6. Multiferroic Nanocrystals

Introduction

Multiferroic materials that have coupled ferroic order parameters are quite promising due to their potential application in various field, for example magnetically recorded ferroelectric memory, thus attracting dramatically increased research attention in the past five years.\textsuperscript{1, 2}

Nanocrystals, usually with size from 1 to 100 nm, display properties that are found to be significantly different from the bulk materials from which they are drived. One of the examples is semiconductor nanocrystals, also called quantum dots, which have been extensively studied in the past decade in various research areas including solar engery generation, light emitting, and bio-labeling due to the size dependent optical properties.\textsuperscript{3-26} The fundamental properties study and application of nanoscale materials require the facile preparation strategies for high quality samples, i.e., monodisperse nanocrystals with tunable size and morphologies. Therefore several approaches have been developed in the past years for the preparation of high quality nanocrystals, including thermal decomposition, hydrothermal, templated growth approach, etc., to yield high quality nanocrystals. Bismuth ferrite (BiFeO$_3$) has been extensively studied as one of the most important multiferroic compounds in recent years.\textsuperscript{1, 2, 27-34} However, studies are mostly limited to BiFeO$_3$ bulk or thin film. Study on the nanoscale multiferroic properties are promising, however it is limited by the lack of facile synthetic approaches for highly quality multiferroic nanocrystals. This motivates us to develop a facile stratage to fabricate BiFeO$_3$ nanocrystals with tunable size down to several nanometers and controlled morphologies (e.g., nanoparticles, nanorods, and nanowires).
Thermal decomposition has been considered as one of the most efficient approaches for preparing monodisperse nanocrystals. With the addition of surface capping ligand, the obtained nanocrystals are separated from each other and readily dispersed in various solvents; this provides good processibility for devices fabrication. We have extensively worked on the thermal decomposition approaches and synthesized various nanocrystals in the past years, including semiconductor quantum dots (e.g., CdSe, CdTe, etc.), superparamagnetic nanoparticles (e.g. $\gamma$-Fe$_2$O$_3$, Fe$_3$O$_4$, etc.), ferroelectric barium titanate nanocrystals (i.e., BaTiO$_3$), catalytic bismuth nanoparticles (i.e., Bi).

Herein, we investigate the solution based thermal decomposition approach for the synthesis of BiFeO$_3$ nanoparticles. To synthesize high quality monodisperse BiFeO$_3$ nanocrystals based on this approach, bismuth salt and ferric salt will be used as the metals source, surface capping ligand such as oleic acid and oleyamine will be used to prevent aggregation of nanocrystals and provide solubility of the resulting BiFeO$_3$ nanocrystals in non-polar solvent. Non-coordinating solvent with different boiling points from 100°C to more than 300°C will be examined. Under controlled thermal decomposition conditions, the metal salts will decompose and form Bi-Fe complex, which will be oxidized into BiFeO$_3$ with addition of oxidant. By tuning the reaction conditions (i.e., temperature, ligand, reaction time, etc.), control over size and shape of BiFeO$_3$ nanocrystals is possible. TEM and XRD studies were performed to characterize the resulting BiFeO$_3$. Thermal annealing after synthesis was found to be a necessary step for the complete crystalline formation of BiFeO$_3$. It is noteworthy that The thermal decomposition approach can be easily scaled up; the obtained nanocrystals surface are capped by ligand, thus they can be readily dispersed in various non-polar solvent such as toluene, hexane, etc. Hydrophilic
ligand can also be introduced by surface ligand exchange, which has been successfully applied to prepare water soluble quantum dots. These BiFeO$_3$ nanoparticles will then be used as the modules for the study of nanoscale multiferroic properties (i.e. ferroelectricity and magnetic properties) and for possible application in microelectronic devices.

**Experimental**

Bismuth acetate (Sigma Aldrich) and iron acetylacetonate (Sigma Aldrich) with molar ratio of 1:1 were added to oleylamine in a three-neck flask; oleic acid (Sigma Aldrich) was added as the surface protecting agent. The above mixture was degassed, purged with dry Ar, and heated to 100°C until a transparent solution was obtained. This red transparent solution was then heated and allowed to reflux for 1 hr, followed by cooling down to room temperature to obtain a black solution. As-prepared nanoparticles were washed three times by precipitating with a large amount of ethanol, centrifuging, and re-dissolving in toluene. Transmission electron microscopy (TEM) and X-ray powder diffraction (XRD) were used to characterize BiFeO$_3$ nanoparticles. To prepare sample for X-ray powder diffraction, the nanoparticles dispersed in toluene were drop casted on Si wafer and dried. Thermal treatment was carried out in a high temperature furnace in air.

**Results and Discussion**

Control experiments were carried out by decomposing bismuth acetate and iron acetylacetonate under the same conditions. Figure 6-1 shows the characterizations of nanoparticles obtained by decomposing bismuth acetate in oleylamine with existence of
oleic acid. TEM image shows that the obtained nanoparticles have broad size distribution from 20 nm to 70 nm (Figure 6-1a). X-ray powder diffraction spectrum on the obtained nanoparticles can be attributed to bismuth (PDF # 001-0699). Since bismuth nanoparticles has low melting point (i.e. 150 °C), the nanoparticles size can be easily expanded through melt diffusion at elevated reaction temperature (i.e., 320 °C in the present study). Figure 6-2 shows the TEM images of iron oxide nanoparticles prepared from control experiment. Near monodisperse nanoparticles with average diameter of 8 nm were obtained (Figure 6-2a); The obtained iron oxide nanoparticles have low crystalline based on the HR-TEM imaging (Figure 6-2b).

Figure 6-1. Characterization of bismuth nanoparticles. (a) TEM image, scale bar = 50 nm; (b) X-ray powder diffraction of bismuth nanoparticles film deposited on Si (111) substrate (PDF # 001-0699).
Figure 6-2. Characterization of as-prepared iron oxide nanoparticles. (a) low magnification image, scale bar = 10 nm; (b) low magnification image, indicating low crystallinity, scale bar = 2 nm.

Figure 6-3. Characterization of BiFeO$_3$ nanoparticles. (a) low magnification TEM image showing core/shell structure, scale bar = 200 nm; (b) a close-up of a BiFeO$_3$ core/shell nanoparticle, scale bar = 20 nm.
To prepare BiFeO₃ nanoparticles through the thermal decomposition approach, bismuth acetate and iron acetylacetonate with equivalent molar ratio were mixed together in oleylamine with oleic acid added as the surface capping ligand. It is worth noting that the as-prepared black nanoparticles can be retracted from solution using a magnetic bar and redissolved with removal of external magnetic field, indicating the superparamagnetic behavior. TEM images of the as-prepared nanoparticles show a core/shell structure (Figure 6-3). X-ray powder diffraction on the sample shows characteristic peaks of bismuth crystal (Figure 6-4a). In addition, HR-TEM characterization of the core/shell nanostructure shows that the black core is crystallized while those small satellite nanoparticles are amorphous. Therefore, we conclude that the obtained nanoparticles are composed of bismuth core and amorphous iron oxide shell. Thermal annealing was carried out on the obtained nanoparticles film deposited on Si
wafer. After annealed at 600 °C, the sample exhibited characteristic XRD peaks of BiFeO₃ (PDF # 020-0169) (Figure 6-4b).

**Conclusion**

In summary, we used the solution based thermal decomposition approach to prepare BiFeO₃ nanoparticles. The as-prepared nanoparticles showed a crystalline bismuth core and amorphous iron oxide shell nanostructure. Upon thermal annealing, the as-prepared sample was transformed into highly crystalline BiFeO₃. Further studies, including the size control and crystalline formation in solution, are currently undergoing.

**References**

Chapter 7. Polymer Dispersed Liquid Crystals (PDLCs)

Modified from a paper published in *Langmuir*, 23, 7411 (2007)—Jun Wang, Jianfeng Xia, Suck Won Hong, Feng Qiu, Yuliang Yang, and Zhiqun Lin

This work was featured on Cover Image in the July 3, 2007 issue of *Langmuir*.

Introduction

Polymer dispersed liquid crystals (PDLCs) are an important new class of materials for potential applications in the areas of light shutters, flat panel displays, privacy windows, microlens, etc.\(^1\)\(^2\) Such devices require no additional optical elements (i.e., polarizers) for operation, which, otherwise, place limits on device weight and
flexibility. They are prepared by demixing polymer and LC, including thermally induced and polymerization induced phase separation. The performance of PDLC strongly depends on the final morphology of LC domains in polymer matrix. The size, shape, and distribution of LC domains are generally not only dictated by thermodynamic phase equilibria but also strongly depend on phase separation kinetics and anisotropic ordering of LC as most polymer systems hardly reach a thermodynamic equilibrium state. Thus, the fundamental understanding of the phase equilibrium and phase separation kinetics of mixtures of polymer/LC is of crucial importance for optimizing the performance of PDLC materials.

Several PDLCs with controlled LC domain size and distribution have been produced, including holographic PDLC (H-PDLC) formed by pattern photopolymerization using two or more interfering laser beams for use in electrically switchable diffraction grating, photo-enhanced stratification liquid crystal display (PES-LCD) formed by photo-enforced stratification, and phase-separated composite film (PSCOF) based on anisotropic photo polymerization for liquid crystal display (LCD). From a technological viewpoint, a low cost, reliable method is always in demand. Surface-induced structure formation in polymer blends has been widely recognized as an inexpensive, highly reproducible way to deliver polymers to specified regions via selective polymer/substrate interaction. Here, we report the chemically-patterned-surface-induced phase separation of PDLC. Concentric gold (Au) rings on ITO substrate were prepared from polymeric templates formed by evaporation induced self assembly of a polymer solution in a sphere-on-flat geometry. The surface-induced phase separation kinetics of PDLC film made of monodispersed polystyrene (PS) and 4-
cynao-4'-n-pentylbiphenyl (5CB) was investigated by cross-polarized optical microscopy and confocal Raman spectroscopy. The LC domains were preferentially segregated to Au rings due to favorable interfacial interaction between Au and nitrile (CN) group of 5CB, thereby creating a PDLC film with alternating 5CB-rich phase on Au rings and PS-rich phase on ITO rings. The present experiments are considered to represent the first study of surface-induced phase separation of PDLC. The key difference from the other methods (e.g., pattern photopolymerization) of preparing highly structured PDLC is that the structure formation was guided through use of a chemically-patterned substrate, rather than created by introducing two or multiple interference laser beams.

**Materials and Methods**

Polystyrene (PS; weight average molecular weight, $M_w = 5,100$ g/mol and polydispersity, $PDI = 1.07$) was purchased from Polymer Source Inc. A thermotropic liquid crystal (LC), 4-n-pentyl-4'-cyanobiphenyl (5CB; the nematic phase exists at the temperature between 18 °C and 35 °C) was purchased from Sigma-Aldrich. The aspect ratio of the length (~ 16 Å) to the diameter (~ 4.3 Å) of 5CB is 3.7, indicating a rod-like molecule. Its director is the long axis of the cyanobiphenyl moiety. PS and 5CB with 50:50 in weight were dissolved in a common solvent toluene at a concentration, $c = 2$ wt%, resulting in a homogeneous solution. The concentric Au rings patterned ITO substrate (i.e., chemically patterned) was fabricated using the methods introduced previously by us (Figure 7-1). The PDLC film was prepared as follows. A small amount of 2 wt% PS/5CB (50:50) toluene solution (~ 20µl) was drop-cast on the center of Au rings patterned ITO substrate at room temperature, covering both the patterned substrate and
outer bare ITO surface. The sample was left in air for 2 h to allow for a complete evaporation of toluene, which was determined by the stability of the focus with optical microscope (OM) as well as the constant weight of the sample. A uniform PDLC film on the top of the patterned substrate was resulted, while a thinner film was found at outer bare ITO surface (Figure 7-1S in Supporting Information). The thickness of PDLC film on the Au rings patterned ITO substrate, $h$, was ~1 µm as calculated based on the relation of $h = \frac{m}{\rho S}$, where $m$, $S$, and $\rho$ are the mass of the PS/5CB mixture, the area of the PDLC film formed on the substrate, and the density of the film, respectively. $h$ was thinner than the spinodal wavelength of the bulk PDLC phase separation process, which was ~3 µm as measured by small angle laser light scattering.39 The glass transition temperature, $T_g$, of the resulting PDLC film was ~18 °C.40 The decrease of $T_g$ (from $T_g$ of 64 °C for pure PS ($M_w = 5,100$)) was due to the fact that the LC plays the role of plasticizer for the polymer.40-43 After complete evaporation of toluene, the phase separation kinetics of PDLC film on chemically patterned substrate at the room temperature (~ 25 °C) was monitored in-situ by polarized OM (Olympus BX51 equipped with a CCD camera; polarizer $\perp$ analyzer) in transmission mode. It should be noted that the focus and the light intensity were not changed throughout the real-time measurement. The phase separation was complete within 1500 min. After that, the chemical composition of PDLC film on the patterned substrate was identified with spatially-resolved Raman spectroscopy (Renishaw inVia Raman microscopy; excited with a 488-nm Ar$^+$ laser at 10 mW) by examining the characteristic CN stretch vibration spectrum of 5CB in the range of 2210 cm$^{-1}$ to 2250 cm$^{-1}$ with a peak at 2228 cm$^{-1}$. The CN stretching possesses strong Raman cross section. The Raman line scanning was performed in the direction perpendicular to the Au rings.
The spectra from four different spots on each Au ring and ITO ring were acquired only after 10 sec exposure to the laser beam.

Results and Discussion

Preparation of patterned substrate with chemical heterogeneity

The fabrication of chemically patterned ITO substrate consisting of concentric Au rings of high regularity (Figure 7-1a) is briefly described as follows. A very thin layer of gold (Au; 6 nm) was thermally deposited on a precleaned ITO glass (Figure 7-1b). Then, a drop of poly(methyl methacrylate) (PMMA; $M_n = 534$ kg/mol and $PDI = 1.57$) toluene solution ($c = 0.25$ mg/ml) was confined between the spherical lens and the Au-coated ITO substrate (i.e., a sphere-on-flat geometry). The concentric PMMA rings were produced on both the sphere and the ITO substrate within 30 min via the controlled, repetitive “stick-slip” motion of contact line due to irreversible evaporation of toluene. Subsequently, the PMMA rings were utilized as templates to prepare the Au ring replica by removing Au between the PMMA rings with aqueous solution of the mixture of potassium iodide/iodide, followed by eliminating the PMMA rings selectively with acetone (Figure 7-1b; locally, the Au rings appeared as periodic parallel stripes). The patterned substrate was rinsed with toluene thoroughly and blow-dried with N$_2$ before the immediate drop-casting of PS/5CB toluene solution.

Figure 7-1c shows a typical optical micrograph of Au rings patterned ITO substrate used in the studies. The width of Au rings, $w_{Au}$ and the center-to-center distance between Au rings, $\lambda_{Au}$ are $\sim 10$ µm and $\sim 20$ µm, respectively. Only a small zone of the entire Au ring patterns was shown (Figure 7-1c). The overall patterns was $\sim 1$ cm in
diameter governed by the diameter of upper sphere used in the experiment. The use of transparent ITO glass with only 6-nm thick periodic Au rings on the top renders the optical imaging in transmission mode (Figure 7-1c). Moreover, the effect of physical heterogeneity can be neglected due to very thin layer of Au rings (i.e., 6nm). This represents a simple and robust way to produce chemically periodic surfaces with no need for soft lithography (i.e., using PDMS elastomer stamps for micro-contact printing the self-assembled monolayer onto Au surface) or photolithography where a mask was employed.
Figure 7-1. (a) Schematic representation of concentric gold rings patterned ITO. (b) Schematic illustration of the polymeric template assisted formation of gradient concentric...
Au rings. Locally, the Au rings appeared as periodic parallel stripes. The ITO substrate, PMMA rings, and Au rings are shown in gray, green, and yellow, respectively. (c) Typical optical micrograph of the resulting Au rings on an ITO substrate. The brown and yellow curves correspond to Au rings and rings without a Au coating (i.e. ITO rings), respectively. The thickness and width of the AU rings are 6 nm and ~ 10 µmm respectively. The center-to-center distance between adjacent rings is ~ 20 µm. The scale bar is 70 µm.

**Surface-induced phase separation kinetics of PDLC on chemically patterned substrate**

A drop of PS/5CB toluene solution was cast on the Au rings patterned ITO substrate. As PS and 5CB are incompatible,

demixing between them took place during the solvent evaporation. After toluene completely evaporated, a layer of 1 µm thick PDLC film resulted in. Subsequently, the time evolution of PDLC morphology at the room temperature (~ 25 °C) was monitored *in-situ* by polarized OM (Figure 7-2). Generally, the LC droplets in PDLC film are optically birefringent under cross-polarized, transmitted light condition. They convert linearly polarized light to an elliptical state.

The optical micrograph right after complete solvent evaporation is shown in Figure 7-2a ($t = t_0$). The 5CB droplets (i.e. bright domains) randomly distributed on the patterned substrate. The deep green and dark stripes correspond to the ITO rings and the Au rings, respectively. Locally, they appeared as parallel stripes.
Figure 7-2. Time evolution of morphologies of PS/5CB (PS : 5CB = 50 : 50 by weight) on concentric Au rings patterned ITO substrate. The optical micrographs were taken under crossed polarizer and analyzer in transmission mode at room temperature. (a) time
at which toluene evaporated completely was taken as \( t_0 \), (b) \( t_0 + 191 \) min, (c) \( t_0 + 501 \) min, (d) \( t_0 + 791 \) min, and (e) \( t_0 + 1492 \) min. Scale bar = 35 µm.

Since the glass transition temperature of PS/5CB mixture, \( T_g \), \( PS/5CB \) was 18 °C, both 5CB and PS phases were mobile, facilitating the phase separation. At \( t = t_0 + 191 \) min, the size of randomly dispersed 5CB domains increased and the number of domains decreased (Figure 7-2b). As time progressed, 5CB domains were seen to preferentially segregate to the Au rings and grow into bigger droplets (\( t = t_0 + 501 \) min in Figure 7-2c and \( t = t_0 + 791 \) min in Figure 7-2d). It has been demonstrated that 5CB absorbed on Au surface to form a self-assembled monolayer through the interaction between the cyanide group, CN in 5CB and Au, and a tilted orientation on Au nanoparticle surface was observed. In the present study, the strong affinity of 5CB to the Au rings displaced the PS phase towards the ITO parts of the patterned substrate. Thus, the 5CB domains originally located on the Au rings grew bigger by accumulation of 5CB nearby, while the domains on ITO rings gradually disappeared (i.e., transported to Au rings) in a process analogous to evaporation-condensation mechanism in polymer blends. The phase separation completed at \( t = t_0 + 1492 \) min as shown in Figure 7-2e, where the intensity fluctuation of 5CB domains may be attributed to (i) the diffusion of 5CB in PS matrix since the focus and the illumination were not changed throughout the real-time measurement, (ii) the change of the orientation of 5CB). As a result, a thin microstructured PDLC film on chemically patterned substrate was formed, that is, 5CB-rich phase on Au rings alternating periodically with PS-rich phase on ITO rings. This is analogous to thick films (i.e., H-PDLC) formed by photopolymerization of a homogenous
mixture of monomeric precursor, LC, and photoinitiator using an optical grating produced by two interfering laser beams.\textsuperscript{11-20}

It is noteworthy that a layer of PDLC film covered on the patterned ITO substrate was clearly evident in both digital image and optical micrograph (unpolarized) (see Figure 7-5 in Supporting Information). Moreover, the thickness of PDLC film was 1 µm. Taken together, the observed structures was produced by surface-induced phase separation of the PS/5CB mixture, rather than induced by dewetting. The surface-induced structure formation of PDLC in the present study is similar to the case in PES-LCD formed by photo-enforced stratification.\textsuperscript{21} However, the average size of LC droplets in our study was \(~10\) µm, which was dictated by the width of Au rings (Figure 7-1c). This is much smaller than the 500 µm sized boxes used in PES-LCD.\textsuperscript{21} We expect that by using a lower concentration of PMMA toluene solution, PMMA rings with reduced width and periodicity can be readily obtained.\textsuperscript{31, 32} Thus, smaller LC domains on Au rings would result in.

\textit{Evolution of LC domains and chemical composition of PDLC on chemically patterned substrate}

The time evolution of the average size (in terms of LC domain area), number, and total area of 5CB droplets on Au rings were quantified using software \textit{Image J} (Figure 7-3). The initial diameter of the droplets was much less than half of the Au ring width, \(w\) (\(w = \sim10\) µm) \((t = t_0 = 0\) min and \(t = 191\) min in Figure 7-2a and 7-2b, respectively). As time progressed, the droplets on Au rings condensed together and increased successively in
size, forming domains of 5-10 µm in diameter ($t = 501$ min and $t = 791$ min in Figure 7-2c and 7-2d, respectively). The final size of the domains was determined by the Au ring width ($t = 1592$ min in Figure 7-2e). The number of droplets on the Au rings decreased with time (Figure 7-3b), while the total area covered by the 5CB droplets on the Au rings increased with time (Figure 7-3c). It is clear that a longer time was needed for the large 5CB domains on the Au rings to merge (and on the ITO rings to transport to the Au rings) due to a longer distance of movement.
Figure 7-3. Time evolution of (a) average domain size (in terms of LC domain area), (b) the number, and (c) the total area of 5CB droplets on Au rings. The data was obtained by analyzing the cross-polarized optical micrograph in Figure 2. The time $t_0$ was set to 0 min.
Figure 7-4. (a) Raman spectrum of pure 5CB. The vibrational frequencies at 1607 cm\(^{-1}\) and 2228 cm\(^{-1}\) correspond to the ring stretch from benzene derivative (doublets) and CN.
stretch, respectively. The chemical structure of 5CB is shown as an inset. (b) The CN stretch peak (i.e., at 2228 cm\(^{-1}\)) intensity of the PDLC film on Au rings patterned ITO substrate at \(t = t_0 + 1592\) min. The Raman measurements were performed under line canning mode in the direction perpendicular to the ring patterns as indicated by the line in the optical image taken directly using Raman microscope (inset).

As noted above that the resulting PDLC film comprised of alternating stripes of 5CB rich phase and PS rich phase, to confirm that, the chemical imaging was performed by confocal Raman microscope. The Raman spectrum of pure 5CB is shown in Figure 7-4a. The vibrational frequencies at 1607 cm\(^{-1}\) and 2228 cm\(^{-1}\) correspond to the ring stretch from benzene derivative (doublets) and CN stretch, respectively. The chemical structure of 5CB is shown as inset. The CN group in 5CB is unique as compared to PS. Thus, the Raman line scanning was conducted in the direction perpendicular to the Au rings as indicated by a line in the inset (Figure 7-4b) by focusing on the CN stretch vibration spectrum in the frequency region from 2210 cm\(^{-1}\) to 2250 cm\(^{-1}\). The CN stretch peak intensity at 2228 cm\(^{-1}\) along the scanning direction is shown in Figure 7-4b. The width and the periodicity of the Au rings were \(\sim 10\) µm and \(\sim 20\) µm, respectively, as clearly evident in Figure 7-4b. The peak intensity of CN stretch on the Au rings is about 5 times higher than that on the ITO rings (i.e., \(I_{CN, Au} / I_{CN, ITO} = 5\)), which was consistent with optical microscopy observation where the majority of 5CB were deposited on Au rings (Figures 7-2 and 7-3). The low value of the intensity difference \(I_{CN, Au} / I_{CN, ITO}\) may also be partially attributed to the fact that a small amount of 5CB were resided in PS matrix on ITO rings (i.e., 5CB in the PS-rich phase). Our control experiment, in which a drop of the low MW PS toluene solution (\(M_w = 5,100\)) was drop-cast on a bare ITO surface, showed
that PS covered the ITO surface completely. However, PS was found to dewet from the homogeneous Au surface (data not shown). Therefore, the preferential adsorption of PS to the ITO part of the patterned substrate would be expected. This was in line with the observations that 5CB and PS were rich on the Au rings and ITO rings, respectively (Figures 7-2, 7-3, and 7-4).

**Conclusion**

In summary, we have demonstrated that chemically-patterned-surface-induced phase separation of PDLC could afford a unique means to control the distribution of LC and organize micrometer-sized LC in a well-ordered fashion in polymer matrix over a large area with no need for photo irradiation. The LC droplets grow through coalescing preferentially along the Au rings. The patterns on the substrate were transferred to the PDLC film as a direct consequence of the incompatibility of PS and 5CB, the preferential interaction between 5CB and Au, and the comparable pattern size to the length of the domain morphology on the homogeneous substrate. The preferential affinity of 5CB to the Au rings induced a surface spinodal wave that suppressed spinodal decomposition of the bulk due to the fact that the thickness of PDLC film was smaller than the spinodal wavelength, enabling the transfer of surface patterns to the PDLC film in a way similar to the case of polymer blends. The present results may provide new insights into the structure control of PDLC film for potential applications in electro-optical devices. The film thickness, the molecular weight of polymer, and the variation of width and periodicity of the Au rings are expected to influence the structure formation of PDLC
on the patterned substrate. These experimental parameters are currently under investigation and will be optimized to yield ideal pattern transfers of PDLC.

**Supporting information**

![Figure 7-5](image.png)

(a) PDLC film on the Au rings patterned ITO substrate. (b) PDLC film in the area away from concentric Au rings (i.e., the bare ITO region)

Figure 7-5. (a) Digital camera image and (b) optical micrograph of PDLC film on the Au rings patterned ITO substrate. The concentric Au rings appeared in light purple on ITO glass in (a). Scale bar = 35 µm.

**References**

Chapter 8. General Conclusions

Highly ordered nanoporous metal oxide films were successfully synthesized via electrochemical anodization. Under optimized anodization conditions, porous alumina membrane (PAM) with highly ordered hexagonal arrays of nanopores were obtained. Anodic TiO$_2$ nanotube arrays with different tube size, film thickness, and wall thickness, were prepared by anodizing Ti in fluorine containing electrolyte. Ultrahigh aspect ratio, freestanding TiO$_2$ nanotube arrays were fabricated by a simple detaching approach. Systematic studies were conducted to investigate the crystalline formation and transformation on TiO$_2$ nanotube arrays by combining the transmission electron microscopy and Raman scattering studies. Highly ordered TiO$_2$ nanotube arrays were used as photoanode in dye sensitized TiO$_2$ nanotube solar cells. Upon rational surface engineering on TiO$_2$ surface, a markedly improved power conversion efficiency of 7.37% was obtained when a 14 µm thick TiO$_2$ nanotube arrays was sensitized with ruthenium dye N-719.

Functional nanocrystals, including semiconducting CdSe quantum dots, ferroelectric BaTiO$_3$ and PbTiO$_3$ nanocrystals, and multifunctional multiferroic BiFeO$_3$ nanoparticles were also synthesized and characterized. Notably, a simple biphasic ligand exchange process was developed to prepare water soluble CdSe quantum dots, which have potential applications in solar energy conversion and bio-detecting.

Phase separation kinetics of polymer dispersed liquid crystals (PDLCs) on a chemically patterned substrate was also explored as a side project.
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Publications

1. **J. Wang** and Z. Lin*, “Solution based synthesis of monodisperse lead titanate (PbTiO$_3$) nanoparticles”, (in preparation)

2. **J. Wang** and Z. Lin*, “Shape controlled synthesis of barium titanate (BaTiO$_3$) nanocrystals via a non-aqueous thermal decomposition approach”, (in preparation)


