Photoinduced electron transfer reactions at silver electrodes

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Hung Tian

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To Yongjun and Mimi
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GENERAL INTRODUCTION

Dissertation Organization

This dissertation contains two chapters that are in the format of published papers. Preceding the chapters, brief reviews of plasmon excitation, photoelectrochemistry and photosynthesis are given. Following the chapters, a General Summary concludes the dissertation.

Introduction

In the past four years, my research has focused on the construction of photosynthetic model systems on silver electrodes, studying the electron transfer mechanisms of these systems and thereby attempting to mimic the electron transfer aspects of the photosynthetic process. The research areas included plasmon absorption by the silver electrode surface, photosynthesis and photoelectrochemistry. The chemical substances involved in these studies are: carbon dioxide, viologens and chlorophylls (Chl).

In this introduction section, a general review is given concerning the above three categories. First, plasmon excitation in silver electrodes is discussed. Next, in the photoelectrochemistry part, the basic concepts of this technique are summarized together with research progress in the field of photoelectrochemical reduction of carbon dioxide and viologens. Finally, the electron transfer reactions in photosynthesis and the properties of chlorophylls are also discussed.
Plasmon Excitation at Silver Electrodes

In recent years, the study of the interaction of light with silver has received considerable attention, both for its own merit and also with respect to investigations of the mechanisms responsible for surface-enhanced Raman scattering (SERS). Silver is an exceptional material because it exhibits pronounced plasmon excitation in the near UV region.

Generally, for a metal, there are two plasmon oscillation modes. The first arises due to the Coulomb interaction of the electron gas with the positive lattice ions, and the necessary and sufficient condition for its occurrence is given by

$$\varepsilon(\omega_p) = 0 \quad (1)$$

where $\varepsilon$ is the complex dielectric constant of the metal and $\omega_p$ is the volume plasmon frequency. The second mode arises due to the fact that the surface electronic properties differ from those of the bulk [1]. The additional mode of plasmon oscillations will occur when

$$\varepsilon_{metal}(\omega_s) + \varepsilon_{medium}(\omega_s) = 0 \quad (2)$$

where $\varepsilon_{metal}$ and $\varepsilon_{medium}$ are the complex dielectric constants of the metal and the medium with which the metal is in contact, respectively. The second kind of oscillation is called the surface plasmon oscillation which propagates parallel to the surface as a surface plasmon wave, its quantum of energy is given by $E = h\nu_{plasma}$. The existence of both volume and surface plasmon oscillations has been verified by electron energy loss experiments [2]. Silver manifests its intense bulk and surface plasmons around 3.6 eV. However, the maximum of the intense surface plasmon excitation and emission varies according to
experimental conditions. The following parameters can affect the intensity of surface plasmons dramatically.

- **Variation of the work function of metals.** An elegant way of achieving this is to use a metal-solution interface in an electrochemical cell. The work function of the electrons is considerably lowered through the interaction with the optically dense electrolyte solution as compared to a vacuum.

- **Variation of the electrode potential.** Because the electron emission depends on the electrode potential, the peak of photoemission can be changed continuously within an appreciable range by varying the electrode potential. Gerischer et al [3] investigated this situation carefully, and pointed out that the quantum yield at the surface plasmon energy and maximum position of plasmon emission increase with negative electrode potential. A model for the production of plasmon oscillation at a metal-electrolyte interface was also proposed.

- **Polar adsorbates.** Polar adsorbates which are aligned on a metal surface, generate an electric field that shifts the photothermal for plasmon emission in a way that has been known for decades. In choosing adsorbate molecules for threshold reduction, a molecule containing a dipole is required. At the same time, however, the dipole should be oriented more or less perpendicular to the surface, if the moment is to be effective. Thus, a molecule, like benzene, is ineffective because it lacks of a dipole moment and acetonitrile is ineffective because its large moment is aligned parallel to the surface in the adsorbed state. However, pyridine and related molecules are effective because they orient at a right
angle to the surface [4]. The electric field associated with a layer of oriented polar molecules is enhanced by the same mechanism that enhances Raman scattering and should further reduce the photothreshold. Thompson et al. [5] have investigated the effect of various surface treatments on the photothreshold shifts produced by a variety of polar molecules. They found that a nitrogen lone pair electronic orbital is essential for a large threshold shift. Other molecular properties, such as the dipole moment and polarizability have a smaller effect.

An understanding of the nature of surface plasmons is essential for future studies in a numbers of areas. These include, for example, determination of the highest enhancement (resonant enhancement) at silver surface, an understanding of the electron transfer mechanism at a solution/film/metal interface, and construction of a photosynthetic model system on a metal electrode surface. In the first Chapter of the dissertation, the concept of surface plasmon excitation is employed in the development of a possible mechanism of carbon dioxide photoreduction at the silver film electrode.

The possibility of a dramatic increase in the rate of photoinduced reactions of adsorbates on metal surfaces has been hypothesized to result from the large enhancement of many optical processes (including Raman scattering) on certain structured metal surfaces [6]. Harris reported the first observation of an enhanced photoreaction rate for the fragmentation of a number of molecules on roughened silver substrates using near-UV irradiation [7]. Other reports of enhanced decomposition rates have subsequently appeared including the decomposition of rhodamine-6G on a silver island film [8] and the photodissociation of
dimethylcadmium on cadmium island films [9]. In these studies it was determined that the photochemistry apparently occurs directly from the first excited singlet state following one-photon absorption. Distance-dependence studies of photofragmentation rates by use of an inert spacer layer to separate the molecule undergoing photochemistry from the surface indicate that energy transfer to the metal surface is important in determining the reaction rate. A maximum decomposition rate observed for pyridine is between 15-20 Å from the surface, as a result of the different distance dependencies of enhanced molecular absorption at the rough silver surface and damping by energy transfer to the surface. These competing processes produce a maximum photochemical rate when surface enhanced absorption is still present but the energy damping rate has been decreased substantially.

It is well known that the electrochemical reduction of carbon dioxide is a thermodynamically difficult process. If surface plasmon excitation can serve as an extra energy source, this reaction may be facilitated. It has already been reported that large photocurrents occur at a polycrystalline silver electrode during cathodic reduction of carbon dioxide [40]. The sharp peak in the photocurrent as a function of excitation wavelength suggests that surface plasmon excitation plays an important role in the reduction process. However, these authors did not show whether carbon dioxide reduction was really enhanced. During the past two years, we have studied carbon dioxide reduction on roughened silver film electrodes and observed the reduction potential is shifted about 200 mV more positive relative to a smooth electrode due to the plasmon enhancement. Evidence of plasmon enhancement was also obtained, which is in a good agreement with other researchers’
results [10].

Photoelectrochemistry

*What is Photoelectrochemistry?*

The conversion of radiant energy to electrical or chemical energy by molecules is a result of the intramolecular “pumping” of electrons upon absorption of light in the visible or UV regions to higher energy levels (i.e. molecular excitation). Intermolecular electron transfer from these excited molecules, either directly or via an external circuit in an electrochemical cell, provides the basis for the energy conversion process. Efficient utilization of the radiant energy requires a separation of the photogenerated electron-hole pair before recombination, and this has been found to occur quite effectively in the electric field present at the interface between a electrode and an electrolyte solution.

In photoelectrochemistry, semiconducting solids have been intensively studied for their interaction with electrolyte solutions, and the theory of interaction of illuminated semiconductors with electrolytes has been reviewed [11]. In a photoelectrochemical cell, a semiconductor electrode immersed in a electrolyte is connected through an external circuit to a counter electrode. In a p-type semiconductor in the dark, there are many holes in the valence band, but only a small number of electrons in the conduction band. Under illumination with light more energetic than the band gap, the number of electrons in the conduction band increase. This increase in electron density in the conduction band results in
a cathodic current [12], when the electrons are transferred to a suitable acceptor in the solution.

Many studies have been focused on photoelectrochemical effects at the semiconductor-liquid interface. Bard divided the progress of this research field into three areas [13]. The earliest work, beginning with the observations of Becquerel, dealt mainly with the rather small photoeffects observed with metal electrodes (probably covered with thin layers of semiconducting material). The rather extensive work (1839-1955) has been well reviewed [14]. Extensive investigations of electrochemistry of the semiconductor materials and photoeffects, between 1955 and 1971, led to models for the semiconductor-liquid interface and provided mechanisms for electrode reactions. Although possible applications to energy conversion were considered rather early, serious interest in the construction of liquid junction photovoltaic cells and especially in the photoelectrolysis of water at semiconductor electrodes, began in about 1971, with the publications of Fujishima and Honda [15]. Reviews of this more recent work and the principles of semiconductor photoelectrochemistry have appeared [16].

Some researchers have used the combination of n- and p-type semiconductors such as n-TiO₂ and p-GaP, and illuminated both electrodes, which results in "self-driven" photoelectrolysis cells not requiring an external bias [17].
**Photoelectrochemical Reduction of Carbon Dioxide**

The photoreduction chemistry of carbon dioxide has received substantial attention only during the last decade. Carbon dioxide photoreduction is of interest with respect to understanding the behavior of the natural photosynthetic process and for developing artificial photosynthetic energy conversion schemes. The extremely negative one-electron redox potential for carbon dioxide reduction indicates that substantial energy input is required to achieve direct carbon dioxide activation. Most systems investigated to date are very inefficient on an absolute energy conversion efficiency basis. However, the fundamental chemistry involved in photochemical carbon dioxide reduction schemes is essential to advancing our understanding of multi-electron transfer catalysis.

The carbon dioxide photoreduction schemes developed to date can be divided into two conceptually different categories, depending on the type of photosensitizer used in the process. Homogeneous systems are entirely molecular based, and rely on dissolved molecules to absorb the photons, prevent nonproductive thermalization and back-electron transfer reactions, and catalyze the necessary chemical steps that lead to the ultimate reduced carbon containing products. The other type of system utilizes a semiconductor electrode or semiconductor colloid to accomplish the initial light absorption and charge separation steps, and then relies on either homogenous or heterogeneous catalysts to yield the ultimate chemical products of the system. Both types of systems have some unique properties, and neither has yet been proven to be clearly superior. In this part, the second type is reviewed.
Most researchers construct carbon dioxide photoreduction systems on semiconductor electrodes or use semiconductor powder suspensions. Manassen et al. [18] achieved heterogeneous photoassisted reduction of carbon dioxide in an aqueous solution by using semiconductor powders, with either a high-pressure Hg-lamp or sunlight as the energy sources. The products were methanol, formaldehyde and methane. Honda et al. [19] described the photoelectrocatalytic reduction of carbon dioxide to formic acid, formaldehyde, methanol and methane, in the presence of photosensitive semiconductor powders suspended in water as catalysts. The photocatalytic reaction kinetics were elucidated by reference to the theory of charge transfer at photoexcited semiconductors. The photocatalytic reactions are considered to follow the schemes.

\[
\begin{align*}
\text{CO}_2 \text{(aq)} + 2\text{H}^+ + 2e_{\text{cond}}^- & \rightarrow \text{HCOOH} \\
\text{HCOOH} + 2\text{H}^+ + 2e_{\text{cond}}^- & \rightarrow \text{HCHO} + \text{H}_2\text{O} \\
\text{HCHO} + 2\text{H}^+ + 2e_{\text{cond}}^- & \rightarrow \text{CH}_3\text{OH} \\
\text{CH}_3\text{OH} + 2\text{H}^+ + 2e_{\text{cond}}^- & \rightarrow \text{CH}_4 + \text{H}_2\text{O}
\end{align*}
\]

where \(2e_{\text{cond}}^-\) denotes an electron in the conduction band of a semiconductor.

Transition metal-based catalysts are widely used to manipulate the electron transfer kinetics and lessen the voltage required for carbon dioxide reduction. Tetra-azamacrocyclic metal complexes were used to catalyze the electrochemical reduction of carbon dioxide at illuminated p-Si at potentials approaching the thermodynamic values [20]. Halmann [21] reported photoelectrochemical reduction of aqueous carbon dioxide on p-type gallium phosphate in a liquid junction solar cell. Photoelectrochemical reduction of aqueous carbon
dioxide in an acidic aqueous medium of V(II)-V(III) chloride was carried out on a p-type
gallium single crystal electrode by illumination with visible light. The Faradaic yields of
formic acid, formaldehyde and methanol were 1.5, 0.3 and 0.14%, respectively [22].

In general, formic acid is the predominant product in the electrochemical reduction of
carbon dioxide in aqueous media on metal electrodes [23,24]. This process was shown to
involve two electron transfer steps, producing as the initial intermediate the COO− radical
anion, which then undergoes protonation to the formyl radical HCOO, followed by a further
electron capture to produce the formate anion.

\[
\begin{align*}
\text{CO}_2 + e^- & = \text{COO}^- \\
\text{COO}^- + H^+ & = \text{HCOO} \\
\text{HCOO}^- + e^- & = \text{HCOO}^-
\end{align*}
\]

In the photoelectrochemical reduction of carbon dioxide on a semiconductor
electrode, the products observed also include formaldehyde and methanol—in contrast to the
reduction on metal electrodes, which in aqueous media yield only formic acid. However,
some researchers found carbon monoxide is also a possible product. For example, the use of
surface modified metallic and semiconducting electrodes for the electrocatalytic and
photoelectrocatalytic reduction of carbon dioxide was demonstrated by using
electropolymerized films of [Re(CO)\textsubscript{3} (v-bpy)\textsubscript{Cl}] [25]. Large turnovers (ca. 600) were
obtained for a film on metallic electrodes (e.g. Pt). On semiconductor electrodes (p-Si and
polycrystalline thin film of p-WSe\textsubscript{2} ) somewhat lower (450) turnovers were obtained. In both
cases CO was the predominant reduction product with essentially unit current efficiency. The different products may be due to a different reduction mechanism.

**Photoelectrochemical Properties of Viologens**

Photoelectrochemical systems have been developed which show respectable solar efficiencies for the production of electrical power [26,27], for the generation of hydrogen from water [28,29], and for the photoelectrolysis of haloacids [30]. Recently, Vermeulen and Thompson described a halide-viologen complex trapped in an inorganic matrix which can store solar optical energy indefinitely [37].

A common aspect of these types of studies is that many investigators used viologens as electron acceptor in above reactions. Viologens, 1,1'-disubstituted-4,4'-bipyridinium dication (V$^{2+}$), constitute interesting and versatile redox systems with three oxidation states, as shown below:

\[ V^{2+} - e^- \rightarrow V^{+} + e^- \rightarrow V \]

namely the colorless dication, violet cation radical and yellow-to-brown neutral form.

Typically, investigations start with the colorless dication, which is observed to undergo a reversible one-electron reduction to the radical cation, that may be soluble (small substituents and/or organic solvents) or form a deposit on the electrode (larger substituents and aqueous solutions). There is a second stage of reduction in which the cation is reduced to the neutral form that is almost always insoluble in aqueous solutions.
Tsuchida et al. [31] observed electrocatalysis of oxygen reduction at a pyrolytic graphite electrode coated with an intermolecular complex of poly(xylyviologen)-poly(sulfonate). The reduction potential of oxygen molecules at the polymer-coated electrode was more positive than that obtained at a bare electrode by 350 mV (maximum). Wohrel et al. [32] reported that the electrochemically formed viologen radical can produce a photogalvanic effect on the surface of an indium tin oxide (ITO)-coated electrode dipped in an aqueous electrolyte in presence of oxygen. They proposed that the mechanism involves the reaction of the photoexcited cation radical with oxygen. Weaver et al. [66] reported a novel approach for the fixation of carbon dioxide which combines a semiconductor photoelectrode (p-type indium phosphate, p-InP) with a biological catalyst (a formate dehydrogenase enzyme) to affect the first step of the two electron reduction of carbon dioxide to formic acid. The photogenerated electrons in the semiconductor, which are coupled to the enzyme through a mediator (methylviologen), can be produced with light of wavelength shorter than 900 nm (> 1.35 eV), so that much of the solar energy is captured by this process. Mohammad [67] reported that the formation of neutral methylviologen can catalyze carbon dioxide reduction. However, due to the reaction between neutral methyl viologen and carbon dioxide, the reduction product is not formic acid or methanol etc. He proposed that it was a compound formed between neutral methyl viologen and carbon dioxide.

Dutta et al. [33] studied the photoinduced redox reaction between Ru(bpy)₃²⁻ and methylviologen. They examined the photoinduced electron transfer between Ru(bpy)₃²⁻ and
methylviologen in the supercage of hydrated zeolite Y. The size of the Ru(bpy)$_3^{2-}$ molecules ensures that it is trapped within the supercages, yet it can interact with molecules in the neighboring cages through the 7-Å ring openings. Methylviologen, on the other hand, can migrate through the zeolite network, and evidence for photoelectron transfer from entrapped Ru(bpy)$_3^{2-}$ to methylviologen in neighboring cages is provided by time-resolved resonance Raman spectroscopy. Two pathways are observed for the fate of the transferred electron. Rapid back electron transfer from methylviologen radical to Ru(bpy)$_3^{3-}$ is observed via a second order process on the microsecond time scale. A slow process, that occurs on a longer time scale and is observed by steady-state photolysis, leads to charge separation and stabilization of the redox pairs for an extended period. These researchers proposed that methylviologen diffuses through the cages, and particular orientations are established which lead to electron hopping along adjacent molecules resulting in charge separation. Miyashita et al. [34] reported that stearylviologen can quench electron transfer from a photoexcited ruthenium complex in barium stearate Langmuir Blogett (LB) films. Kevan et al. [35] reported the photoreduction yield of methylviologen in the presence of a wide variety of counterions in frozen aqueous solution as measured using ESR at 77 K. The signal intensity was also measured in frozen micelles and vesicular suspensions. By precipitating the chloride counterions with silver perchlorate, it was shown that methylviologen appeared to engage in photoinduced electron transfer with the surfactant headgroups.

A new application of viologens is the reversible labeling of DNA. Takagi et al. [36] reported that a new synthetic bis-9-acridinyl derivative containing a viologen linker chain
binds strongly to DNA and shows a typical cyclic voltammogram, indicating a potential for use as a reversible electrochemical labeling agent for DNA.

**Photosynthesis**

Photosynthesis is the most important processes responsible for the development and maintenance of our environment. As such, it has served as a major source of inspiration for photochemical research [38]. Photosynthetic organisms provide paradigms for many of the most basic photochemical and photophysical processes. For example, the central event of photosynthesis, the conversion of light energy to chemical potential energy in the reaction center, is achieved via photointiated electron transfer which yields long-lived, energetic charge-separated states [39,40]. The sunlight which drives the electron transfer process is collected by antenna systems and its energy is transferred to the reaction center by singlet-singlet energy transfer.

There are many valid approaches to the preparation and study of man-made systems which mimic some aspects of natural photosynthesis. In this part, a brief description of natural photosynthetic electron transfer is given followed by a discussion of some of the artificial devices which have been constructed in attempts to mimic this process. Some of the criteria for creating a successful artificial systems will be described. Finally, several commonly used model systems will be introduced.
Description of Natural Photosynthetic Electron Transfer

Photosynthesis, the process by which light from the sun is converted into the energy necessary for the vital functions of living organisms, is the cornerstone of life on the earth. How does photosynthesis work? At the molecular level, what are the interactions that capture the energy of sunlight and turn it into the energy of life? What is the architecture – the organization in space – of the molecules involved? And how does the particular architecture give rise to the speed and efficiency of the photosynthetic process?

These fundamental questions are now yielding answers. Through the separate efforts in such disparate fields as spectroscopy, X-ray crystallography and molecular genetics, the molecular mechanism of one type of photosynthesis - the photosynthesis of certain bacteria - has been pictured in great detail.

At the start of the light reactions of photosynthesis, a photon strikes the end of the photosynthetic reaction center nearest to the inner surface of the membrane. An electron in the special pair bacteriachlorophylls of the reaction center becomes excited and carries the energy of the photon to the other end of the reaction center (the end near the outer surface of the membrane) by means of a series of chemical intermediates. A second photon causes another electron to follow the same route. These interactions produce a separation of charge with the negatively charged electrons near the outer surface of the membrane, and the molecules bearing excess positive charge are left near the inner surface of the membrane. The separation of charge represents stored energy, because energy would be released if the electrons and the positively charged molecules were able to recombine. Later the charge
separation drives chemical reactions that are coupled to, and provide the energy for, certain processes of bacterial metabolism [41].

**Construction of Artificial Photosynthetic Model Systems**

Artificial photosynthetic systems are designed to mimic the natural photoinitiated electron transfer process to some degree, and thus to use light energy to produce energetic, long-lived charge separated states. An approach to this problem which is used in many laboratories is to prepare biomimetic systems which use pigments, electron donors, and electron acceptors that are related to those found in natural reaction centers.

Seibert et al. [42] attached bacterial photosynthetic reaction centers directly to a SnO$_2$ electrode. The light induced, primary charge separation processes which occurs across the reaction center macromolecule was coupled to the electrode, and in a two electrode configuration photovoltages of 70 mV and photocurrents of 0.3 $\mu$A cm$^{-2}$ were observed in an external circuit.

The photosensitization of wide bandgap semiconductors such as TiO$_2$ by adsorbed dyes has become more practical for solar cell application recently with the development of porous films of very high surface area [43]. Only the first monolayer of adsorbed dye results in efficient electron injection into the semiconductor, but the light harvesting efficiency of a single dye monolayer is very small, due to limited surface area. In a porous film consisting of nanometer-sized TiO$_2$ particles, the effective surface area can be enhanced 100-fold, thus, making light absorption efficient even with only a dye monolayer on each particle. Nature.
in fact, uses a similar means of absorption enhancement by stacking the chlorophyll-containing thylakoid membranes of the chloroplast to form the grana structures.

The photosensitization of a wide band gap semiconductor (ZnO) by chlorophylls was first investigated by Calvin et al. [44]. Chlorophyll monolayers were also deposited on a SnO₂ optically transparent electrode by means of the Langmuir-Blodgett (LB) technique, and the effect of different metal centers was investigated [45]. Up to 0.3 quantum efficiencies were reported for the systems. The photosensitization of TiO₂ solar cells with chlorophyll derivatives and related natural porphyrins were demonstrated by Kay and Graetzel [46]. Incident photon to current efficiency of up to 83% was reached by excitation into the Soret peak at 400 nm with a 12-um-thick TiO₂ film sensitized by copper mesoporphyrin IX. which corresponded to nearly unity quantum efficiency of charge separation when light reflection losses are taken into account.

Fujihira has reviewed similar research accomplished in his group [47]. This group used a newly synthesized linear electron acceptor-sensitizer-electron donor (A-S-D) triad as a charge separation unit and an antenna pigment for light harvesting. The synthetic amphiphilic triad molecule has three functional moieties within a molecule, e.g., a hydrophilic electron acceptor viologen (A), a hydrophobic sensitizer perylene (S) and a hydrophobic electron donor ferrocene (D) moiety. Because of the overlap of the emission spectrum of the antenna pyrene and the absorption spectrum of the sensitizer perylene moiety of the triad, the thermodynamic driving force was minimized and the electronic coupling was maximized. Light energy harvested by the antenna molecules was efficiently transferred to the
sensitizer moiety of the triad. Conversion to electrical energy was accomplished via multistep electron transfer across the monolayer through the charge separation unit of the triad molecule in the highly oriented monolayer assembly.

The Photoelectrochemical Behavior of Chlorophyll Monolayers on Metal Electrode

The design of electronic components with molecular dimensions is an area of active research and speculation. The reaction centers of photosynthetic organisms are in fact photovoltaic devices at the molecular level [48].

During the last decade, an increasing number of studies have appeared on the photoelectrical and photoelectrochemical behavior of chlorophyll in the form of solid layers coated on metal electrodes [49,50,51]. In photoelectrochemical cells employing metal electrodes (usually platinum) coated with various forms of chlorophyll films, cathodic photocurrent has usually been obtained, presumably reflecting the p-type semiconductor properties of the bulk chlorophyll layer.

Honda et al. [52] studied the photoelectrochemical behavior of a chlorophyll a-lipid film on a platinum electrode in an aqueous electrolyte. It was demonstrated that under illumination, cathodic photocurrents were observed at electrodes coated with a sufficient number of monolayers. The quantum efficiency of the photocurrent was estimated to be about $10^{-4}$, much lower than that obtainable for dye-sensitized photocurrent on semiconductor electrodes. The low energy conversion efficiency may due to the rapid energy quenching of chlorophyll excited states by free electrons in the metal.
To slow down the energy quenching rate, researchers usually add a spacer between the metal electrode and chlorophyll monolayer. Tarasevich et al. [53] reported that the insertion of a dielectric interlayer (cetyl alcohol) between a metal and a pigment can slow down electron exchange between the excited pigment and the metal. This increases the lifetime of the excited state and other non-equilibrium states, thereby permitting primary charge separation and subsequent involvement of components in the solution.

**Light Induced Electron Transfer in Model Systems**

As mentioned above, the basic process of photosynthesis involves the absorption of sunlight and the conversion of the resulting singlet excitation energy into chemical potential energy in the form of long-lived transmembrane charge separation. The rate constant for photoinitiated electron transfer is strongly dependent upon the donor-acceptor separation. A schematic description of this process is as shown below:

\[
A + D \rightarrow A - D^* \rightarrow A^- + D^* \rightarrow A + D
\]

The photoexcited donor molecules \(D^*\) must react with the acceptor (A) to form the redox products. and the energy wasting back reaction must be prevented. Since the photoproducts store a considerable amount of energy, the back reaction is strongly thermodynamically allowed and is the major obstacle to achieving efficient energy conversion. To overcome this problem and realize the charge separated state \((A^- - D^-)\), a variety of artificial photosynthetic reaction systems have been designed to prolong the charge separated state and accomplish the photoreactions.
Intramolecular electron transfer reactions have been studied intensively in connection with photosynthesis. In general, molecules that possess more well-defined structural relationship between the donor and acceptor yield more subtle insights into electron-transfer reactions. For the efficient charge separation, the present theory of electron transfer predicts that the distance, the orientation, and the energy gaps are the most important factors determining the electron transfer rates. The dependence of the rates on the distance has been studied with chemically modified electrodes, (LB) films and intramolecular A-D systems with rigid hydrocarbon spacers. The rates for all cases decreased exponentially with an increase in spacer distances.

There are two major aspects to the design of artificial reaction centers. The first consideration is the choice of pigments and electron donors and acceptors. Especially critical are excited state energy levels and photophysical parameters, and the redox properties of all relevant states. The second is the selection of an organizing principle that will control the interactions among these components.

Supramolecular systems synthesized to model the photosynthetic reaction center are designed to mimic several key properties of the reaction center protein. (1) multistep electron transfer to increase the life time of the radical pair product; (2) high quantum yield, fast formation, and slow recombination of the singlet-initiated charge separation; (3) temperature independent electron transfer rate; and (4) spin polarization of the radical pair states. Thus far, most reaction center models fulfill only a subset of these criteria. A breakthrough was made by Wasielewski et al. by using time-resolved electron paramagnetic
resonance spectroscopy (TREPR) in a nematic liquid crystal [64, 65]. The anisotropic properties of liquid crystal are the key factor in reducing photoinduced intramolecular electron transfer rate in donor-spacer-acceptor systems. A rate reduction by 3-4 orders of magnitude in liquid crystals as compared to normal isotropic liquids, enables submicrosecond EPR spectroscopy to be applied to these reactions.

In conclusion, significant advances have occurred in understanding and designing photosynthetic model systems. The structure of natural reaction centers coupled with fundamental theories of electron and energy transfer provide a framework for the initial design and fine-tuning of the molecular devices. A key feature in the mimicry of natural photosynthesis is the exploitation of multistep electron and energy transfer strategies, which are a function of the supramolecular architecture of the device, rather than simple pairwise interactions of linked donors and acceptors [48].

References


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CHAPTER I

EFFECT OF SURFACE PLASMON EXCITATION ON PHOTOELECTROCHEMICAL REDUCTION OF CARBON DIOXIDE

A paper to be submitted to the Journal of Physical Chemistry

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Abstract

Surface plasmon enhanced carbon dioxide photoreduction has been investigated. Under laser illumination and when the electrode polarization potential is more negative than -1000 mV, the carbon dioxide anion radical is produced and chemisorbed on the silver electrode surface as a monolayer. The surface adsorbed carbon dioxide radical can be oxidized and the peak potential is near -680 mV. It was confirmed that surface plasmon excitation enhances the production of the carbon dioxide radical and hence catalyzes carbon dioxide reduction. With laser illumination, the reduction potential is shifted positively by ca. 200 mV. The major carbon dioxide reduction products are formic acid and methanol. The mechanism of the plasmon enhanced carbon dioxide reduction is discussed.

1. Introduction

Since the discovery of surface enhanced Raman scattering (SERS), theoretical and experimental studies have been focused on developing an understanding of the mechanism of enhancement and possible applications of this phenomenon. In the past decade, the possibility of achieving dramatic increases in the rate of photoinduced reactions of adsorbates
on metal surfaces has been hypothesized [1] in addition to the large enhancement of many processes (Raman scattering, IR absorption, fluorescence, and second harmonic generation) on certain structured metal surfaces. Harris et al. [2] reported the first observation of an enhanced photoreaction rate for the fragmentation of a number of molecules on a roughened silver substrate using near-UV radiation. These researchers concluded that the photochemistry apparently occurs directly from the first excited singlet state following one-photon absorption. It was further concluded that the enhanced photochemistry is due to surface-enhanced molecular absorption.

In this paper, the possible enhanced photoelectrochemical reduction of carbon dioxide on a silver electrode surface is investigated. For almost a half century, the photoelectrochemical reduction of CO\textsubscript{2} has been extensively studied [3, 30]. In most cases, semiconductor electrodes were used, but metals have been used to a more limited extent. Recently, unusually large steady state photocurrents (0.9 mA/cm\textsuperscript{2}) were reported at a polycrystalline silver electrode immersed in an aqueous solution containing dissolved CO\textsubscript{2} [4]. The photoelectric effect or ejection of photoexcited electrons from a cathodically polarized metal electrode usually produces currents that are only in the \(\mu\text{A/cm}^2\) range. The increase in photoemissive yield was attributed to energy transfer from decomposing plasmons to a single electron, as described by previous researchers [5]. It was proposed that CO\textsubscript{2} or one of its reduction intermediates functions as a scavenger for the photoejected electrons and produces CO:

\[
\text{CO}_2 + \text{H}_2\text{O} + 2e^- \rightarrow \text{CO} + 2\text{OH}^-
\]
The quantum yield for this reaction was shown to maximize at an excitation wavelength of 360 nm (3.6 eV) or close to the surface plasmon resonance of Ag in a vacuum. Moreover, the quantum yield increased from about $3.2 \times 10^{-3}$ to $7.0 \times 10^{-3}$ with roughening of the silver electrode by 900 oxidation-reduction cycles. Both observations support the role of surface plasmons in this effect.

Generally, there are two distinct types of photoeffects which can be observed during electrochemical polarization of an illuminated metal electrode in a solution of an electrolyte[6]. The first one usually arises during (or following) the anodic polarization of the metal electrode and results in the formation of a semiconducting surface film. In this case, the observed photocurrent is the consequence of electron-hole pair formation. Another type of photoeffect arises at a clean metal surface and is associated with the photoemission of electrons from the metal into the solution. This second type of photoeffect is responsible for catalyzing the formation of the CO$_2$ reduction intermediate (possibly the carbon dioxide radical anion) on a silver electrode and shifting the CO$_2$ reduction potential to a more positive value.

In principle, it is possible that if the molecular excited state survives long enough on a silver surface for a reaction to occur, an enhancement of reaction rate for surface-adsorbed species as compared to free molecules may be expected. A theoretical treatment of silver spheroids on a conducting half-plane indicates that [7] an enhanced local field is experienced by molecules near a rough silver surface at frequencies near the plasmon resonance of the spheroids. Experimental confirmation of the existence of these enhanced fields has been
provided by a variety of experiments including surface enhanced Raman scattering and the observation of efficient second harmonic generation on rough silver surfaces [8]. Enhancement of the local surface field yields enhanced absorption by molecules at the surface and, hence, an increase in photoreaction rate.

In the following section the surface photoelectrochemical behavior of carbon dioxide on a roughened silver surface is discussed, together with relevant reference data. The dependence of the carbon dioxide reduction efficiency on the electrode surface condition and excitation wavelength are then presented by comparing data obtained from both smooth and roughened silver surfaces. Finally, a mechanism for plasmon enhanced carbon dioxide photoreduction is proposed.

2. Experimental

2.1. Silver film electrode preparation

Silver foil (5×15×1 mm) or vacuum deposited silver films were used as working electrodes. The silver film electrode preparation procedure was as follows: thin glass plates were cut into rectangular pieces (5×20 mm), placed in a Teflon holder and immersed in Chromix solution overnight. The glass was then washed thoroughly with distilled water and placed into saturated KOH/EtOH solution for 6 hours. The pieces were washed with distilled water, neutralized by 6 M HCl solution and then washed with distilled water again. Finally, the cleaned glass pieces were placed in concentrated ammonium hydroxide solution for about 30 minutes, removed and dried at room temperature and heated in an oven at 100°C.
overnight. The cleaned and dried glass pieces were removed from the holder and placed in
an E306A Edward Coating Vacuum Deposition System, and a 1μm thick silver film was
deposited on the glass at the rate of 5 Å/sec. The coated slides were stored in a dessicator to
avoid contamination of the surface. Before each experiment the silver film was washed with
chloroform and placed in an electrode holder.

The roughening processes were different for silver foil and silver film electrodes.
Silver foils were simply dipped into 30% (by volume) nitric acid aqueous solution for about
90 seconds, then washed copiously with distilled water. In the case of the silver film
electrode, an oxidation-reduction cycle (ORC) [9] was used. The ORC can cause changes in
surface morphology at the atomic or nanometer scale.

2.2. Electrochemical cell

The cell consisted of a platinum mesh cylinder as the counter electrode, which was
placed in a glass tube containing a fine silica frit. The reference electrode was a Saturated
Calomel Electrode (SCE). The electrolyte was 0.5 M NaClO₄ aqueous solution. Carbon
dioxide was obtained from a high pressure cylinder (99.99%) and was purified by passing
through a gas filter (Balston, grade BK). The gas was bubbled through the electrolyte
solution in the electrochemical cell at atmospheric pressure. Electrochemistry was performed
using an EG&G 173 potentiostat/Galvanostat and 175 Universal Programmer. All the signals
were recorded by an HP chart recorder.
In most cathodic polarization experiments, the polarization potential was -1100 mV (vs. SCE). This potential was chosen because it was reported that at this value, the selectivity for CO₂ verses H⁻ reduction is 4 as compared to 0.15 at -1350 mV and 0.05 at -1550 mV [10].

2.3. Irradiation of the electrode

A Coherent Ar⁻ 200 series laser and a Coherent Kr⁻ 100 series laser were used as the excitation sources. The laser power at the electrode was varied from 20 mW to 50 mW. The laser beam was directed by mirrors to the working electrode surface. The irradiation area was about 25 mm².

2.4. Identification of the carbon dioxide photoelectrochemical reduction products

During the photoelectrochemical reaction, 0.5 M NaClO₃ aqueous solution was used. It is very difficult to detect the low concentrations of the suspected reaction products (small organic molecules) due to interference from the salt and solvent. Using headspace technology, the organic molecules are evaporated from the reaction matrix until gas/liquid equilibrium is reached in a gas tight container. The upper gas sample can be injected directly into an GC column via a syringe and analyzed by a mass spectrometer.

The three electrode system was used in the photoelectrochemical reduction as described in section 2.1 and 2.2. The reaction cell was sealed tightly with parafilm. Before the reaction, the solution (10 ml 0.5 M NaClO₃) was saturated with carbon dioxide, and during the reaction, a very slow gas flow rate (about 1 ml/min.) was maintained. The
electrode surface was irradiated with 413 nm light (50 mW). The electrode polarization potential was -1.1 V (vs. SCE). The reaction time was 6 hours.

After the reaction, the sealed container was placed into a 65°C water bath for about 30 minutes. The gas sample was injected into a Finnigan TSG 700 GC/MS system (Finnigan Corp., San Jose, CA). An DB1, 3 um film, coated GC column was used. Electron impact ionization with 70 eV electron energy provided in the ionization source. A triple Quadruple mass analyzer was used for detection. Temperature programming was used in the GC-MS analysis. The initial temperature was 40 °C. The temperature was ramped at 5 °C/sec to the final temperature of 80 °C. During the experiment, the first part (about 2 feet) of the GC column was placed into liquid nitrogen to get rid of air and condense the small organic compounds. The injection volume was 2.0 ml. The reaction products were identified as formic acid, methanol and a small amount of formaldehyde.

3. Results and discussion

3.1. Cyclic voltammetry (CV) of the carbon dioxide photoreduction product

Figure 1a illustrates the cyclic voltammogram obtained from a thin silver film in a nitrogen purged 0.5 M NaClO₄ aqueous solution. Only charging current is observed in the voltammogram. When the solution was saturated with CO₂, a cathodic peak was observed at ca. -1050 mV. This is due to the adsorption of the carbon dioxide reduction product [11]. If under the latter conditions, the electrode was polarized at -1100 mV and illuminated with
Fig. 1 Cyclic Voltammogram of a roughened silver film electrode after photoassisted cathodic polarization. Electrolyte, 0.5 M NaClO₄ (pH ca. 5); polarization potential -1100 mV; laser wavelength, 488 nm; laser power, 50 mW; laser spot area on the electrode surface, 0.25 cm; scan rate, 200 mV/sec.

a). in nitrogen purged solution, before and after photoassisted cathodic polarization.

b). in carbon dioxide saturated solution after photoassisted cathodic polarization.
488 nm light (50 mW) for ca. 3 minutes, in addition to the cathodic peak, an anodic peak is observed at about -680 mV (Figure 1b), which gradually disappears on repeated cycling of the potential between -1200 and -400 mV. No significant anodic peak was observed at -680 mV in the cyclic voltammogram if the electrode was polarized at potentials more positive than -1000 mV under laser illumination or at any potential in the absence of laser illumination.

The dependence of the anodic peak height on polarization time and with irradiation by the 488 nm light (50 mW) of the Ar⁺ laser is shown in Figure 2. The peak height increased until ca. 6 minutes, after which it remained constant. The fact that the current reaches a limit suggests that the product of the reaction is adsorbed. By integrating the peak area after 6 minutes of photoassisted polarization and using Faraday’s law (Q = nF), the product density at silver surface was calculated as 4×10¹⁴ molecules/cm² (n = 1). This value is near the expected surface coverage for a monolayer of small molecules (1×10¹⁵ molecules/cm²). Thus, it is proposed that approximately one monolayer of product is formed on the silver electrode surface.

If the photo electrochemical reaction involves a single electron transfer process, the product is the carbon dioxide anion radical (CO₂⁻). Photoemission studies of CO₂ reduction on Hg electrodes showed that a potential of -1.6 V vs. NHE was required for this process. However, it has been noted that adsorption of the radical anion on an electrode surface should lower the required cathodic overpotential [12]. Subsequent reduction processes have been shown to lead to the formation of formic acid, methanol and methane. A detailed reaction
Fig. 2 The dependence of peak height on the time of photoassisted cathodic polarization.

The experimental conditions were the same as the Figure 1.
mechanism has been proposed [14]. However, the products and their mechanism of formation at other metal electrodes may be quite different.

The identity of the polarization product formed upon photoassisted cathodic polarization of saturated carbon dioxide solutions was reportedly by several investigators. J. Giner [13] found carbon dioxide reacts with chemisorbed hydrogen on platinum to form a chemisorption product of reduced carbon dioxide, and this product can be oxidized at a potential of ca. -600 mV (vs. SCE). Barker [14] also observed a similar product on a mercury electrode. He described this product as the carbon dioxide radical. By combining the theoretical prediction and a comparison of the properties of the reduction intermediate in our system with Barker's description of the carbon dioxide radical, it is concluded that the intermediate in our system is also the carbon dioxide radical. It is largely produced by photoassisted cathodic polarization (more negative than -1000 mV) on a silver electrode and oxidized at -680 mV in consecutive CV cycles.

Carbon dioxide reduction at a metal electrode requires a very negative potential (-1900 mV). Generally, there are two ways to decrease the very negative potential requirement and make carbon dioxide reduction easier. The first is to provide an extra energy source other than electrochemical energy: the second is to find an approach (including new electrodes or chemically modified electrodes) which can stabilize the carbon dioxide radical.

In our photoelectrochemical system, the carbon dioxide radical can be efficiently produced at a potential that is several hundred milivolts more positive than the
thermodynamically predicted value. One reason for this is the photon energy serves as an additional energy source (plasmon resonance enhancement is also included and will be discussed in later sections). During carbon dioxide photoreduction, photons interact with the silver electrode surface, and the silver is photooxidized [15]:

\[ \text{Ag} \rightarrow \text{Ag}^+ + e^- \]

Thus, the electrons required for carbon dioxide reduction are greater than that provided by electrochemical polarization. A second reason is that the carbon dioxide radical is stabilized on the electrode surface (This will be further discussed in the next section).

3.2. Photocurrent production in the CO$_2$/Ag system

Gerischer[16] proposed that photoexcited electrons, having sufficient energy and appropriate momentum direction, tunnel through the surface barrier and escape into the solution as quasi-free electrons. They are then thermalized and form solvated electrons in a very fast process. These solvated electrons can either be transferred back to the electrode or react with some species in solution. If this latter process takes place irreversibly, the respective species is called an electron scavenger, and only in the presence of such scavenger molecules, will the system produce a net photocurrent. In our system, surface adsorbed carbon dioxide can act as a scavenger molecule.

Figure 3 illustrates the photocurrent response obtained from a roughened silver film electrode following cathodization at -1100 mV in a nitrogen purged and CO$_2$ saturated 0.5 M
Fig. 3  Photocurrent of a roughened silver film electrode. Polarization potential. -1100 mV; laser illumination wavelength. 488 nm; laser power. 50 mW; electrolyte was the same as in Figure 1.

a). in nitrogen purged solution.

b). in carbon dioxide purged solution.
NaClO₄ aqueous solution. As can be seen, irradiation of the electrode in the absence of CO₂ (Fig. 4a) produces no observable photocurrent, but in the presence of CO₂ (Fig. 4b) approximately 1.5 μA of cathodic photocurrent is produced. Considering that only a 0.25 cm² area of the electrode was illuminated by the laser light, about 6 μA/cm² photocurrent was produced in the CO₂/Ag system. The current is not as large as that reported previously, but the potential is not as negative (0.9 mA at -1.64V) either.

In Figure 3, immediately upon illumination of the electrode surface, a cathodic photocurrent grows in and after ca. 40 second, the current reaches a steady state (charge separated state [17]). This state does not change with time as long as the electrode is illuminated. When irradiation is ceased, the cathodic photocurrent gradually decays back to the background level. This process takes about 80 seconds. To examining whether the photocurrent has any thing to do with the anodic peak (Eₚ = 680 mV) in the CV experiments, it was observed that after blocking the laser light, the anodic peak also disappears in about 80-90 seconds. This is the further conformation that the reaction is occurring during illumination (the formation of the charge separated state).

Cathodic photocurrent is expected based on the electron donor properties of the silver electrode surface (Fig. 4). Cathodically polarized silver electrode serves as an electron donor, and carbon dioxide serves as an electron acceptor. When the electrode surface is illuminated with laser light, the charge separated state is produced at the electrode surface, as illustrated in Figure 4.
Fig. 4 A schematic of carbon dioxide and carbon dioxide radical adsorbed on the silver electrode (Ref. 18).
It is well known that surface-induced damping of the excited state is extremely rapid for the first monolayer of molecules on metal surfaces (about $10^{15}$/s for allowed molecular transitions) and most photochemical process will not proceed during this short time [2]. Because of this damping, the initial photoreaction step must occur very rapidly to compete with quenching of the excited state by energy transfer to the surface. This is a serious drawback in the use of metal electrodes for the study of photochemical events as compared to semiconductor electrodes. Although metals can perform the initial light absorption step, they cannot stabilize the charge separated state, which is also crucial for photoreactions, due to the fast surface-damping rate.

In carbon dioxide saturated solutions, a significant photocurrent was observed with the silver electrode. This might be because the silver electrode surface was made inert by adsorbed carbon dioxide molecules or the reduction product. Based on electrochemistry and IR spectroscopy studies, Bockris [18] proposed that in aqueous solution, carbon dioxide and the carbon dioxide radical can adsorb on the electrode surfaces as shown in Figure 4. As the silver electrode surface is modified with a layer of molecules, the surface energy damping speed is not as fast as for clean metals, and the charge separated state is achieved.

3.3. Photocatalyzed carbon dioxide reduction

The standard $\Delta G^0$ (25°C; pH = 0) and corresponding $E^0$ values for the two-, four-, six-, and eight-electron reductions of carbon dioxide in aqueous solution may be calculated [34] to give the values shown below:
<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta G^\circ$ (kJ mol$^{-1}$)</th>
<th>$E^\circ$ (Volts vs. NHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CO}_2(g) + 2\text{H}^+ + 2e^- \rightarrow \text{HCOOH(aq)}$</td>
<td>+38.4</td>
<td>-0.199</td>
</tr>
<tr>
<td>$\text{CO}_2(g) + 4\text{H}^+ + 4e^- \rightarrow \text{HCHO(aq)} + \text{H}_2\text{O}$</td>
<td>+27.5</td>
<td>-0.071</td>
</tr>
<tr>
<td>$\text{CO}_2(g) + 6\text{H}^+ + 6e^- \rightarrow \text{CH}_3\text{OH(aq)} + \text{H}_2\text{O}$</td>
<td>-17.3</td>
<td>+0.030</td>
</tr>
<tr>
<td>$\text{CO}_2(g) + 8\text{H}^+ + 8e^- \rightarrow \text{CH}_4(g) + 2\text{H}_2\text{O}$</td>
<td>-130.8</td>
<td>+0.169</td>
</tr>
</tbody>
</table>

Even though the various reductions are accessible at reasonable potentials, their kinetic barriers can be quite severe, consequently, substantial overpotentials can be incurred at the electrode surface. A number of electrochemical studies at metal surfaces or carbon electrodes have documented the large over potential required for carbon dioxide reduction, both for aqueous and non-aqueous media [35]. A typical reduction potential required at either Pt or Hg working electrode in an aqueous solution is -2.16 V (pH 7). The carbon dioxide anion radical is the initial reaction product, and once formed, is exceedingly reactive [36].

Evidence was obtained in our system that the pre-formation of the carbon dioxide radicals at -1100 mV during laser irradiation enhanced the reduction of bulk CO$_2$, as shown from studies of the effect of light on the onset potential for CO$_2$ reduction. The cyclic voltammogram for the reduction of water in a 0.5 M NaClO$_4$ solution is shown in Figure 5a. Hydrogen evolution is the dominant reaction at about -1900 mV, which is similar to previously reported values [19,32]. If the solution is saturated with CO$_2$, the onset potential is shifted to about -1500 mV (Figure 5b). One reason for this shift might be the change in pH
value of the electrolyte following bubbling with carbon dioxide. By saturating 0.5 M NaClO₄ aqueous solution with carbon dioxide, the pH value decreased about 2 units. According to Hori's calculation [20], the hydrogen reduction potential shifts 125 mV/pH unit. So as the solution pH value is decreased 2 units, the hydrogen reduction potential should shift 250 mV more positive, as measured in our system. However, the involvement of carbon dioxide reduction could also influence the onset potential. The pre-formation of the intermediate (carbon dioxide radical) by illumination of the electrode (maintained at -1100 mV) with 50 mW of 488 nm light for 3 minutes shifted the onset potential to ca. -1250 mV in the CV experiment (Figure 5c). The control experiment, maintaining the electrode at -1100 mV without illumination, did not produce a change in the CV as compared to figure 5b (no pretreatment at -1100 mV). Thus, light is essential for the formation of the carbon dioxide radical at -1100 mV (thermodynamically, this species requires a potential at ca. -1900 mV for formation).

An attempt was made to determine the nature of products formed under continued illumination. The potential of a Ag electrode was maintained at -1100 mV in a CO₂ saturated solution for 6 hours while illuminating with 50 mW of 488 nm light from an Ar⁺ laser. The solution was analyzed with headspace GC-MS. The major components were identified as formic acid, and methanol, together with a trace amount of formaldehyde. Those products are in agreement with previous reports [20,21].
Fig. 5 The cyclic Voltammogram of carbon dioxide reduction on a roughened silver electrode. The experimental conditions were the same as in Figure 1.

a). in nitrogen purged solution before and (or) after photoassisted cathodic polarization.

b). in carbon dioxide saturated solution before photoassisted polarization.

c). in carbon dioxide saturated solution after 3 minutes photoassisted cathodic polarization.
3.4. Dependence of quantum yield on excitation wavelength  

Two types of photoelectrochemical experiments were performed in the carbon dioxide/silver system to determine the wavelength dependence of the reaction efficiency. The production of carbon dioxide radical at different wavelengths was determined using a smooth silver film electrode and an electrochemically roughened silver film electrode. The formation of the carbon dioxide radicals was initiated by maintaining the electrode at -1100 mV under irradiation with 50 mW of 488 nm laser light for a fixed time interval (usually, about 2 to 6 minutes). The cyclic voltammograms which were measured after the photoassisted polarization are shown in Figure 6. Based upon Faraday’s law and an integration of the anodic peak, the amount of product formed in the photoelectrochemical process can be calculated. By measuring the laser power, wavelength and illumination time, the number of photons reaching the electrode surface can also be calculated. The photoelectrochemical quantum efficiency $\eta$ equals the ratio of product formed divided by the number of photons. 

In a photoelectrochemical process, the irradiation wavelength is one of the major factors influencing the $\eta$ values. The dependence of reaction efficiency on irradiation wavelength was determined by using different laser lines to irradiate the electrode surface and measuring the yield of carbon dioxide radicals. As expected, the photoreaction efficiency varied with irradiation wavelength and the reaction efficiencies of the roughened electrode were larger than that of the smooth electrode at all the wavelengths, and especially, at 514 nm. where the reaction efficiency of the roughened electrode was 7 times that of the
Fig. 6 Cyclic Voltammogram of the silver films. The experimental conditions were the same as in Figure 1.

a). a smooth silver film electrode.

b) a roughened silver film electrode.
smooth one (Fig. 7). The highest quantum efficiency for a smooth electrode is about $3 \times 10^{-4}$
and about $2 \times 10^{-3}$ for a roughened electrode, both of which are in good agreement with
previously obtained values [4, 22]. It is apparent that the photoelectrochemical reduction of
carbon dioxide is enhanced at the roughened silver electrode.

The photochemical enhancement can be caused by three factors. First, the roughened
electrode may absorb light more efficiently due to decreased reflection; second, the
roughened electrode has a larger surface area: third, the interaction of light with the
roughened electrode can excite surface plasmons.

In order to determine if plasmon enhancement is involved in the carbon dioxide
photoreduction, it is necessary to predict whether or not the other two factors will contribute
to the enhancement. It is known that normal bulk excitation of electrons or holes occurs in a
region determined by the penetration depth of the light. The excited charge carrier undergoes
inelastic collisions on traveling to the surface which reduces the number of available
electrons or holes with the sufficient energy to undergo charge transfer at the interface. If the
penetration depth of the light is large compared to the inelastic scattering length of the
excited electrons, only a small fraction of the electrons will reach the surface without energy
loss. The surface plasmon excitation, on the other hand, involves light absorption very close
to the surface, with subsequent generation of excited electrons and holes near the surface.
Energy losses due to scattering will be considerably smaller and a large fraction of excited
charge carriers with sufficient energy will be available at the interface. Thus, the scattering
factor is excluded [23]. Usually after a roughening process, the surface area of an electrode
can be increased 3-5 times. By a chronoamperometric technique, we found out that the average surface area of the electrode was increased three fold after one cycle of the ORC roughening process. However, from experimental results, the reaction efficiency can be enhanced as high as 7 times, so in addition to the surface area increment, plasmon enhancement is probably involved in the reaction process.

To determine further whether surface plasmons play a role in carbon dioxide photoreduction on silver surface, the dependence of $\eta_{\text{roughened}}/\eta_{\text{smooth}}$ ratios on the excitation wavelength was examined (Figure 7). After a 2 minute photoassisted anodic polarization, between 446-514 nm, the $\eta_{\text{roughen}}/\eta_{\text{smooth}}$ ratio increased as the wavelength increased, but the ratio at 647 is low, as shown in Figure 7. For comparison, Table I shows the relative Raman enhancement as a function of wavelength [23].

Not surprisingly, the wavelength dependence of Raman enhancement is very similar to that observed in photoassisted carbon dioxide reduction (Figure 7a). In the majority of current theories [24], the Raman enhancement is ascribed to an increase of the electromagnetic field near the surface resulting from excitation of surface plasmons. So it appears that plasmon enhancement has played a major role in enhanced photoelectrochemical reduction of carbon dioxide.

In the present system, surface plasmon enhancement of the photochemistry is only a factor of 2.5 (after subtracting the surface area enhancement from 7). Thus, it is low in comparison to the $10^5$ enhancement for normal Raman scattering from molecules on island
Fid. 7  The wavelength dependence of reaction efficiency ratio ($\eta_{\text{roughened}}/\eta_{\text{smooth}}$) The experimental conditions were the same as in Figure 1.
TABLE I: Relative Raman Enhancement and surface Heating Rates as a Function of Wavelength (Ref. 24)

<table>
<thead>
<tr>
<th>( \lambda ) (nm)</th>
<th>Raman Enhancement</th>
<th>Surface Heating Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>350.7</td>
<td>0.014</td>
<td>4.5</td>
</tr>
<tr>
<td>363.8</td>
<td>0.055</td>
<td>2.9</td>
</tr>
<tr>
<td>406.7</td>
<td>0.13</td>
<td>1.6</td>
</tr>
<tr>
<td>457.9</td>
<td>0.43</td>
<td>1.0</td>
</tr>
<tr>
<td>514.4</td>
<td>1.00</td>
<td>1.0</td>
</tr>
<tr>
<td>647.1</td>
<td>0.11</td>
<td>1.0</td>
</tr>
</tbody>
</table>
films or electrodes. The smaller enhancement (10^3) measured for resonant Raman scattering from adsorbates shows that the surface-induced broadening of the vibrational levels to which the system is initially pumped reduces the effects of the local field enhancement by a factor of 10, resulting in a net enhancement of about 30. In addition, the new surface induced decay channel of the excited vibrational state reduces the efficiency for populating the thermalized excited electronic level by a factor of 10. Thus, the rate of preparation of the photochemically reactive state is only enhanced by a factor of \( \approx 3 \) [25]. Also it was predicted that the net result for molecules near the islands, the rapid, surface-induced nonradiative damping dominates the photochemical decay and can easily counterbalance the small enhancement in the pumping rate of the photochemical reactive state [26]. So the plasmon enhancement factor (about 2) observed here is reasonable and is in good agreement with the theoretical predictions.

3.5. Mechanism for the carbon dioxide photoreduction on the silver electrode

The formation of the adsorbed carbon dioxide radical is known to be the rate controlling step for carbon dioxide reduction under certain conditions [27]. The very slow self-exchange rate for the \( \text{CO}_2/\text{CO}_2^- \) couple and the large overpotential required for the initial reduction step is due to the change in geometry from a linear to bent structure in the radical anion [28]. Thermodynamically, the electron affinity of carbon dioxide to produce carbon dioxide radical with a bond angle 134°, taken from SCF ab initio calculations[29] of the ground state energy surfaces of \( \text{CO}_2 \) and \( \text{CO}_2^- \) is -0.36 eV, indicating an unstable gaseous
ion. In an electrolyte, however, the anion is stabilized by solvation in a liquid electrolyte and the overall process is as follow:

\[ \text{CO}_2\text{g} + e^- = \text{CO}_2\text{aq}^- + 2.92 \text{ eV} \]

The standard electrode potential (unit photon activity) was calculated by assigning the electron an energy equal to the Fermi level of a Pt electrode in equilibrium with 1 atm hydrogen and unit activity protons. The potential of a hypothetical electrode in equilibrium with 1 atm carbon dioxide and unit activity of carbon dioxide radical would be -1.81V vs. SCE [27]. If solvated CO$_2$ is taken as the reactant, the corresponding value is -1.89V vs. SCE. On a metal surface, overpotential may also be present, so the real reduction potential of CO$_2$ can be even more negative.

However, if a silver electrode is illuminated with a beam of laser light, surface plasmons can enhance the carbon dioxide reduction. As previously discussed, the carbon dioxide radical was produced at -1100 mV with laser illumination, which is about 700 mV more positive than the theoretical prediction. It appears that surface plasmon plays a crucial role in the carbon dioxide reduction at silver electrode. It is proposed that, in our system, surface plasmon not only provide an extra energy source to the reaction, but the carbon dioxide radical is stabilized on the silver surface.

How does surface plasmon excitation enhance the carbon dioxide reduction? Further investigation revealed an interesting fact.

It is known that surface plasmon energy of silver in contact with vacuum is 3.6 eV. Usually, this is the peak value of the photoemissive event. However, if the silver surface is
in contact with electrolyte, the peak position can be at even lower energies. This is because the work function of the electrons at the silver surface is lowered considerably through the interaction with the optically dense electrolyte compared to vacuum. In addition, by varying the electrode potential the work function can be changed continuously within an appreciable range [30]. Brodskiy and Gurevich [33] have developed a theoretical model for the dependence of the photoemissive yield at a metal-electrolyte interface as a function of the photon energy and the work function

$$h\omega_M = \frac{1}{(n+1)} [nh\omega - h\omega(\theta U) + e\Delta U]$$

(2)

where $h\omega_M$ is the position of the maximum photoemission yield, $h\omega$ is surface plasmon energy, $h\omega(\theta U)$ is the electron barrier with respect to a standard potential $\theta U$ and $\Delta U$ is the applied potential. From the Equation, it is obvious that $h\omega_M$ shifts to lower energy levels with increasingly negative electrode potentials. According to Gerischer’s calculation [26], the photoemission peak position can be estimated as 3.1 eV when the applied potential is -1100 mV.

The intriguing point is that the difference in the ground state energy surface of carbon dioxide and that of the solvated carbon dioxide radical results in a value of ca. 3 eV [27]. This value is very close to the maximum photoemission peak position (3.1 eV). So it is possible that a resonance effect maybe involved in the plasmon enhanced carbon dioxide reduction. However, further experimental confirmation is needed.
4. Conclusions

Plasmon enhanced photoelectrochemical reduction of carbon dioxide was demonstrated on a silver film electrode. To the best of our knowledge, this is the first evidence of plasmon enhanced carbon dioxide photoreduction. A significant photocurrent was observed in the system. Cyclic voltammetry confirmed the existence of a charge separated state produced by adsorption of the carbon dioxide radical on the photooxidized silver electrode surface. Also, a possible mechanism was discussed for carbon dioxide photoreduction. A resonance effect may be involved in the carbon dioxide reduction on a silver electrode with laser illumination.

Although in this work, the plasmon enhanced photoreduction was discussed for a bare silver electrode, this enhancement may also be expected in the photosynthetic model systems, which are constructed on silver electrodes.

References


Abstract No. 897.


CHAPTER II

PHOTOINDUCED ELECTRON TRANSFER REACTIONS AT A METHYLVIOLOGEN/SILVER INTERFACE

A paper to be submitted to the Journal of Physical Chemistry

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Abstract

Results obtained from electrochemical, photoelectrochemical and Surface Enhanced Raman Scattering (SERS) investigations of the methylviologen/silver system in the presence as well as the absence of carbon dioxide are presented in this paper. The cyclic voltammogram for methylviologen was observed to shift with irradiation as in the presence of carbon dioxide. A significant photocurrent (about 16 μA/cm²) was obtained in the carbon dioxide/viologen/silver system. It was confirmed that only the methylviologen radical layer which is nearest to the silver surface is photoactive. SERS experiments showed that the methylviologen radical serves as an electron relay between Ag electrode and carbon dioxide. Hence, it photoelectrochemically catalyzes carbon dioxide reduction. The role of the neutral viologen in carbon dioxide reduction was also investigated. A reduction mechanism is discussed.

1. Introduction

Photoinduced electron-transfer in reaction centers of photosynthetic organisms is a highly efficient process with a quantum yield near 1 [1]. The mechanistic aspects of the
primary and secondary electron transfer reactions have been under intense scrutiny for some time. An understanding of the photoelectrochemical process is challenging not only because it is of fundamental biological importance, but also because such knowledge could provide insights regarding the development of efficient artificial photoelectrochemical devices.

A major goal of this research is to model a simple electron transfer system on a silver electrode and understand its photoelectrochemical behavior. In future studies, more components will be added to construct a photosynthetic model system.

Methylviologen was chosen as the electron relay in the system. Viologens, 1,1'-disubstituted-4,4'-bipyridinium dications (MV'), constitute interesting and versatile redox systems with three oxidation states, namely the colorless dication, violet cation radical and yellow-to-brown neutral form. Typically, investigations begin with the colorless dication, which is observed to undergo a reversible one-electron reduction to the radical cation. The latter may be soluble (small substituents and/or organic solvents) or can form a deposit on the electrode (larger substituents and aqueous solutions). There is a second stage of reduction in which the cation is reduced to the neutral form which is almost always insoluble in aqueous solutions.

Methylviologen is the simplest molecule of the viologen family. One application of methylviologen is the catalysis of photoreduction processes in aqueous solutions. Grazel et al. reported that methylviologen is one of the most efficient electron relays used in water photolysis [2]. A common scheme for this process is the production of the blue-colored cation radical by electron transfer from an excited state of a photosensitizer to
methylviologen dication. The back-conversion of the reduced form MV\(^+\) of the relay to its initial state MV\(^{2-}\) through water reduction to hydrogen is greatly enhanced by the presence of a noble metal catalyst [3]. Kaneko et al. [4] reported the cation radical of methylviologen formed on the surface of an Indium Tin Oxide (ITO) electrode gave photogalvanic currents in the presence of oxygen. The mechanism is attributed to the reaction of the photoexcited methylviologen cation radical with oxygen.

Carbon dioxide is attracting attention in conjunction with the natural photosynthetic process. Actually, the natural photosynthesis process can be regarded as a series of oxidation-reduction reactions. The overall equation can be written as:

\[
\text{CO}_2 + 2\text{H}_2\text{O} \rightarrow (\text{CH}_2\text{O}) + \text{H}_2\text{O} + \text{O}_2
\]

Where (CH\(_2\)O) represents the raw organic materials which are produced in the process. However, it is apparent that the carbon dioxide reduction in an electrochemical cell cannot occur as easily as in a natural photosynthetic reaction center. The thermodynamic reduction potential is about -1890 mV (vs. SCE). It has already been confirmed that laser induced surface plasmon excitation of a silver electrode can catalyze the reduction reaction and shift the reduction potential ca. 200 mV more positive [5]. The future goal is to construct an artificial photosynthetic model system which can further catalyze carbon dioxide reduction. However, first, it is necessary to understand the electrochemical and photoelectrochemical behavior of carbon dioxide at a simple modified silver system which is the immediate goal of this paper.
In this study, the electrochemical as well as photoelectrochemical behavior of carbon dioxide/methylviologen/Ag system were investigated. The different roles of the methylviologen radical cation and neutral methylviologen in carbon dioxide reduction were examined. An energy diagram is employed to support the electron transfer mechanism proposed for the system.

2. Experimental

2.1. Photoelectrochemical cell

The cell consisted of a silver film electrode (the fabrication process was described in a previous paper [5]) as the working electrode. A platinum mesh cylinder served as the counter electrode, which was placed in a glass tube containing a fine silica frit. The reference electrode was a Saturated Calomel Electrode (SCE) and the electrolyte was 0.5 M NaClO₄ aqueous solution (pH = 5.5). Carbon dioxide was obtained from a high pressure cylinder and purified by passing through a gas filter (Balston, grade BK). Commercially available methylviologen (1,1'-dimethyl-4,4'-bipyridinium dichloride, from Adrich Chemical Co.) was used without further purification. A methylviologen monolayer was used in most photoelectrochemistry and Raman experiments. The methylviologen self-assembled layer was prepared by the following procedure. First, the electrode was washed carefully with chloroform, and placed in a 1×10⁻³ M methylviologen water/methanol (50:50, v/v) solution for 1-2 hours. Then, the electrode was removed from the solution and the excess liquid on the electrode surface was discarded by rotating the electrode on a motor. Finally, the
electrode was carefully rinse with water. An EG&G 173 Potentialstat/Galvanostat and Universal Programmer were used in electrochemical and photoelectrochemical measurement. All the signals were recorded by a HP chart recorder.

2.2. Irradiation of the electrode

Coherent Ar\textsuperscript{+} 200 series and Coherent Kr\textsuperscript{+} 100 series lasers were used as the excitation sources. The laser power at the electrode ranged from 10 mW to 80 mW. The laser beam was directed by mirrors to the working electrode surface. The illumination area was about 25 mm\textsuperscript{2}.

2.3. SERS spectrometry

An Innova 100 Kr\textsuperscript{+} laser was used as excitation source for Raman measurements. The scattered light was collected in a back scattering geometry by an f/1.2 camera lens and focused onto the slit of a Spex 1807 triple spectrometer. A Princeton Applied Research Model 1420 photodiode array and Princeton Instrument CCD LN152 were used for detection. The laser power at the sample was 50 mW. The spectra were calibrated using indene. The spectra resolution was 5 cm\textsuperscript{-1}.

3. Results and discussion

3.1. Photoelectrochemistry of carbon dioxide/methylviologen/silver system

Cyclic Voltammograms (CV) of 10\textsuperscript{-6} M methylviologen (MV\textsuperscript{2+}) solution at a silver electrode in the dark and under illuminated conditions as well as in the absence (nitrogen
atmosphere) and presence of carbon dioxide are shown in Figure 1. In the dark, the presence of carbon dioxide does not affect the CV, which shows a typical CV for a low concentration of methylviologen. The irradiation of the silver film electrode in the absence of carbon dioxide does not affect the CV either. However, irradiation of the silver film electrode in the presence of carbon dioxide shifts the CV current markedly in comparison with that observed under nitrogen. Such a shift in the CV curves induced by switching the irradiation on and off in the presence of carbon dioxide was reversible and reproducible.

The time-dependent current changes at a methylviologen/silver interface induced by switching the irradiation on and off in the presence and absence of methylviologen as well as carbon dioxide are shown in Figure 2. The measurement was carried out at an applied potential of -1100 mV. In the absence of carbon dioxide and methylviologen, no photocurrent was observed at the instrument sensitivity used here. If only methylviologen was present, a small current fluctuation was observed, which may due to some diffusion processes involving the reactant or product formed during the photoelectrochemical event. Since it is well known that methylviologen is photoelectrochemically active, why then was no significant photocurrent observed? In fact, this observation is in a good agreement with the observations made on other dye molecules' (e.g. chlorophylls) on metal electrodes[6]. Honda et al. pointed out that the photoactive molecules adsorbed on a metal electrode should be much less efficient in a photochemical event as compared to those on a semiconductor electrode, owing mainly to the rapid energy quenching of the dye excited states by free electrons in the metal.
Fig. 1  Cyclic Voltammogram of $\text{MV}^- (10^{-6} \text{ M})$ on a silver film electrode. Electrolyte, 0.5 M NaClO$_4$ (pH ca. 5); scan rate, 200 mV/sec; laser wavelength, 488 nm; laser power, 50 mW.

(---) In a nitrogen purged solution in the dark, no changes are observed in the light, nor in the presence of carbon dioxide in the dark.

(---) In the presence of carbon dioxide under laser illumination.
Fig. 2  Time dependence of the photocurrents at a roughened silver electrode induced by
switching the irradiation on and off. Polarization potential. -1100 mV; electrolyte.
0.5 M KClO₄; laser wavelength. 488 nm; laser power. 50 mW; laser spot area on the
electrode surface. 0.25 cm².

a) A silver film in a nitrogen purged solution.

b) MV⁻ coated silver film electrode in a nitrogen purged solution.

c) MV⁻ coated silver film electrode in a carbon dioxide saturated solution.
One way to increase the photoelectrochemical efficiency is to deposit a spacer layer on the electrode to quench the relaxation rate of the molecular excited state, as reported by Fjihara [7]. Another way is to introduce an efficient electron scavenger into the solution to compete with the electron damping process, as reported by Wohrel [4]. In the present system, when carbon dioxide was introduced into the electrolyte solution, a significant photocurrent was obtained (Figure 2c). It was believed that carbon dioxide molecules serve as scavengers. The possible mechanism of the photocurrent generation might be similar to that ascribed to the methylviologen reaction in an oxygen saturated solution [4]. The excited methylviologen cation radical (MV⁺) reacts rapidly with carbon dioxide to produce a photoelectric response at the silver electrode. The schematic description of the photogalvanic effect is represented in Figure 3, which shows a potential energy diagram of the photoelectrochemical process. The methylviologen cation radical is formed on the silver electrode surface under negative potentials (usually more negative than -600 mV vs. SCE). Without laser illumination, electron transfer from ground state MV⁻ to CO₂ cannot occur, because the energy level of the CO₂/CO₂⁻ pair is higher than the ground state of the MV²⁻⁻⁻ pair. However, when MV⁻ is formed on the silver electrode under irradiation, especially with surface plasmon enhancement (strong photoelectron emission), some fraction of MV⁻ ground state electrons are promoted to the excited state. A rapid electron transfer (ν₁) from the cation radical excited state to CO₂ occurs resulting in the reoxidation of methylviologen cation radical to methylviologen dication, and the reduction of carbon dioxide to the carbon...
Fig. 3 A schematic representation of the photogalvanic effect.
dioxide anion radical. SERS spectra strongly supports this mechanism (the Raman result will be discussed in the later section).

Although the redox energy level of the excited MV\(^{-}\) for the reaction with CO\(_2\) is not known, based on the excitation energy of MV\(^{+}\) (\(\lambda_{\text{max}}\) 550 nm, ca. 2.25 eV), the redox level should be around -2.63 V (vs. SHE) [4]. Since, the redox potential of CO\(_2\)/CO\(_2\)^{-} is ca. -1.65 [15], and taking the potential difference into account, the excited state MV\(^{-}\) could have a much higher reactivity toward CO\(_2\), as compared with the ground state MV\(^{+}\) with a redox level of -0.38 V.

3.2. Potential dependence of the photocurrent

The dependence of photocurrent on applied potential is shown in Figure 4. The potential at which the photocurrent starts to increase (about -600 mV) corresponding to the potential below which blue colored methylviologen radical is observed. As the potential was changed between -800 to -1100 mV, no significant photocurrent increase was observed. It is known that this potential region corresponds to the range where methylviologen radical is stabilized and that among the three oxidation states of methylviologen, only the viologen radical is photoactive[8]. Meanwhile, it has been established that the reactivity of methylviologen radical formed in the solid phase or on a solid surface is very low and only the radical layer nearest to the electrode is photoactive [8]. So the plateau observed in Figure 4 maybe due to a saturation effect. That is, when the applied potential is -800 mV the photoelectrochemical energy is sufficient to form a monolayer of viologen radical and
Fig. 4 Polarization potential dependence of the photocurrent generated in a CO₂/MV⁻/Ag system. Other experimental conditions were the same as in Figure 2.
produces the highest photocurrent. As the applied potential is made increasingly more negative, there is no more viologen radicals formed, and no additional photocurrent increment is expected.

As potentials lower than -1100 mV, the photocurrent begin to increase again. It is known that at potential lower than -1100 mV neutral viologen is produced [9], and neutral methylviologen can react with carbon dioxide radicals [10]. Therefore, this current increment may result from carbon dioxide photoreduction. This observation will be further discussed in the carbon dioxide reduction section.

3.3. Irradiation energy dependence of the photocurrent

The photocurrent increased almost linearly with the light intensity between of 0 to 80 mW (Figure 5) and the photocurrent tends to saturate at about 80 mW. No threshold in the light intensity necessary to generate a photocurrent was observed in the system. It is known that light intensity represents the photoelectric system's response to the quantity of a transient change that occurs from an ambient intensity. The lowest intensity of the linear correlation corresponds to a sensitivity limit for light detection. The upper limit of intensity, on the other hand, shows the saturation effect of the system [16].

The observation which was obtained in the present system is different from that reported for the methylviologen/oxygen semiconductor system [4]. In that system, the threshold of light intensity to generate a photocurrent was 50 mW. It was proposed that this threshold was due to the so called filter effect of the cation radical. The authors presumed
Fig. 5 Irradiation power dependence of the photocurrent in a CO$_2$/MV$^{--}$/Ag system. The other experimental conditions were the same as in Figure 2.
that only the excited methylviologen radicals very close to the electrode or even adsorbed on
the electrode surface can give a photogalvanic response at the electrode. When the light
intensity is weak, all the light does not reach the inner part of the methylviologen layer, thus
producing no excited methylviologen radical near the electrode surface since the
irradiation is produced from the front side of the electrode. A photocurrent cannot be
generated under these conditions. The lowest limiting light intensity required to generate a
photocurrent is determined by the thickness and the concentration of the methylviologen
radical layer formed on the electrode surface. If this assumption is true, the lack of a
threshold in our system is also understandable. First, in the system, a laser was used, which
can provide a much higher density of light and thus the beam can penetrate deeper. Second,
since an adsorbed methylviologen layer (not solution) was used, it is impossible to form a
thick viologen radical layer. Thus, in our system, even low intensity light (10 mW) can
penetrate the viologen radical layer to reach the electrode surface and allow the photoelectric
reaction to occur.

One important conclusion can be reached, which is that the linear light flux
dependence of the cathodic photocurrents indicates that the primary stage of electron
injection from excited methylviologen cation radical to carbon dioxide obeys a simple one-
photon process [6]. This result also supports the electron transfer mechanism which is
proposed based on the potential energy diagram (Figure 3).
3.4. Wavelength dependence of the photocurrent

The wavelength dependence was obtained by keeping the polarization potential at -700 mV. and the laser power at -30 mW. The photocurrent was measured upon changing the irradiation wavelength.

For evaluating the wavelength effect on a photoreaction, the amplitude of photocurrents cannot simply be compared at different irradiation wavelengths. For different wavelengths, although the laser beam powers are the same, the energies of their respective photons are different \( (E = h\nu) \). A more appropriate way is to evaluate them by calculating the photochemical reaction efficiency as a function of the irradiation wavelength (The details of this method was explained in the previous paper) [5]. The photocurrent efficiency gives an indication of the quantum efficiency of the charge separation step. However, it does not contain information concerning the energy conversion. For this information, the electric power output given by the product of photocurrent and photovoltage must be compared with the light power input [11].

Figure 6 shows the action spectrum of the photoreaction efficiency coincides with the broad absorption spectrum of the methylviologen radical (from 450 to 650 nm). This indicates that the origin of photoresponse is the methylviologen radical. This result is in good agreement with previous studies [12].
Fig. 6 Irradiation wavelength dependence of the photoelectric reaction efficiency in a CO$_2$/MV$^{--}$/Ag system. The other experimental conditions were the same as in Figure 2.
3.5. The role of the methylviologen radical and the neutral methylviologen in the reduction of carbon dioxide

Methylviologen can form a very stable self-assembled monolayer in NaClO₄ aqueous solution. The CVs of the methylviologen monolayer at a silver electrode are shown in Figure 7. The peak height is proportional to the scan rate, which is a characteristic of electrochemical reactions for surface adsorbed substances.

3.5.1. Electron relay — methylviologen radical

SERS spectrometry was used in studying the role of methylviologen radical in carbon dioxide reduction. The SERS spectra of the methylviologen monolayer at different polarization potentials in 0.5 M NaClO₄ aqueous solution bubbled with nitrogen is shown in Figure 8. The spectrum obtained at -0.2 V corresponding to the dication form of methylviologen. At -0.6 V, bands height begin to increase at about 1530 and 1350 cm⁻¹; the typical methylviologen radical spectrum is shown at -0.8 V. As the potential is decreased to -1.2 V, the neutral methylviologen spectrum is obtained. This series of SERS spectra clearly represent the three different oxidation states of methylviologen. However, when carbon dioxide is bubbled into the solution, dication spectra are obtained when the polarization potential is lower than -0.8 V (Figure 9). The abnormal Raman spectra of methylviologen under these conditions can be caused either by the solvation of the viologen monolayer, or by the reaction between methylviologen radical and carbon dioxide molecules.
Fig. 7  Cyclic voltammograms of a CO\textsubscript{3}/MV\textsuperscript{-} monolayer/Ag system at different scan rates (500, 200, 100, 50, 20 mV/sec.). Electrolyte composition was the same as Figure 1.
Fig. 8 Polarization potential dependence of the SERS spectra of the methylviologen monolayer on a roughened Ag electrode in the solution saturated with nitrogen. The spectra were measured with 413 nm excitation at the applied potentials shown in the Figure.
Fig. 9  Polarization potential dependence of the SERS spectra of the methylviologen monolayer on a roughened Ag electrode in the solution saturated with carbon dioxide. The spectra were measured with 413 nm excitation at the applied potentials shown in the Figure.
The first possibility is eliminated as the CV peak height is proportional to the scan rate in a solution saturated with carbon dioxide. This indicates that the methylviologen monolayer is still adsorbed on the silver electrode surface. Thus, it is believed that the excited state methylviologen radical does indeed act as an electron relay to donate an electron to carbon dioxide at the silver electrode surface. To further confirm this mechanism, additional SERS experiments were performed. At -0.8 V, in a solution saturated with nitrogen, a strong Raman spectrum of the methylviologen cation radical was obtained. However, at the same potential, if carbon dioxide was bubbled into the solution, the viologen cation radical spectrum disappeared in a second (Figure 10). If nitrogen was once again used to purge carbon dioxide from the solution, the cation radical spectrum returned immediately.

3.3.2. Chemical catalyst — neutral methylviologen

Neutral methylviologen is a powerful reducing agent. Crumbliss et al. used it as a mediator to catalyze CH₃I reduction [13]. Mohammad [10] proposed that neutral methylviologen reacts with carbon dioxide chemically, and the reaction between methylviologen radical and carbon dioxide is catalytic and very slow. The overall reactions of carbon dioxide with neutral methylviologen and viologen radical has been given as:

(i) \( MV^- + CO_2 \rightarrow MV^{2-} + CO_2^- \) very slow

(ii) \( MV^0 + CO_2(\text{+ solvent?}) \rightarrow \text{Product} \)

However, he did not characterize the product formed.
Fig. 10 The SERS spectra of methylviologen monolayer on roughened Ag in the solution saturated with either nitrogen or carbon dioxide. The spectra were measured with 413 nm excitation at the applied potential of -0.8 V.
In our system, in the absence of laser illumination, when a potential between -500 mV and -800 mV was applied to the silver electrode, a blue color was observed on the silver surface. This color was also observed on the silver surface in the presence of carbon dioxide. No significant reaction between the viologen radical and carbon dioxide was observed in the dark.

As applied potentials more negative than -1.0 V, a brownish color appeared on the electrode surface in the presence of carbon dioxide with laser illumination. This product is soluble both in water and methanol. The UV-visible spectrum of the colored compound in methanol was measured and is shown in Figure 11. The compound has a strong absorption band at 393 nm, but no peaks near 600, 540, and 500 nm, which are characteristics for viologen radical. This spectrum is more like the pure neutral viologen absorption spectrum which has absorption at 396 and 370 nm in MeCN [14]. However, it is certain that the product is not neutral viologen, because the neutral viologen is air sensitive and not water soluble. It appears that this product is a salt produced by a rapid reaction between neutral methylviologen and the carbon dioxide. The neutral viologen catalyzed carbon dioxide reaction can also be observed by SERS. At the polarization potential -1.2 V, neutral viologen is the only product. However, in Figure 12, as the solution is saturated with carbon dioxide, the methylviologen dication spectrum is obtained instead of the neutral viologen spectrum. Similar to the results at -0.8 V, if carbon dioxide was removed with nitrogen, a typical neutral viologen spectrum returned.
Fig 11 The UV-vis absorption spectrum of the product produced by the reaction between neutral methylviologen and the carbon dioxide radical. Solvent: methanol.
Fig. 12 The SERS spectra of methylviologen monolayer on roughened Ag in the solution saturated with either nitrogen or carbon dioxide. The spectra were measured with 413 nm excitation at the applied potential of -1.2 V.
Fig. 13 A schematic description of carbon dioxide reduction in the methylviologen monolayer/Ag system.
From above studies, the carbon dioxide reduction mechanism at methylviologen and silver interface can be drawn as shown in Figure 13.

4. Conclusion

Methylviologen has been studied intensively as an electron acceptor or electron carrier in a number of photochemical and electrochemical reactions. However, its photoelectric behavior in a carbon dioxide saturated aqueous solution has not been studied. It was found that the methylviologen cation radical formed electrochemically on the surface of a silver film electrode, can be photoexcited and it can then transfer an electron to carbon dioxide. The potential energy diagram presented in the paper clearly supports the electron transfer process.

In addition, the different roles of viologen cation radical and neutral methylviologen in carbon dioxide reduction were also investigated. It is apparent that the cation radical serves as an electron relay with laser illumination. and the neutral methylviologen serves as a chemical catalyst in carbon dioxide reduction.

References


GENERAL SUMMARY

Surface plasmon enhanced carbon dioxide photoreduction has been investigated. Under laser illumination and when the electrode polarization potential is more negative than -1000 mV, the carbon dioxide anion radical is produced and chemisorbed on the silver electrode surface as a monolayer. The surface adsorbed carbon dioxide radical can be oxidized and the peak potential is near -680 mV. It was confirmed that surface plasmon excitation enhances the production of the carbon dioxide radical and hence catalyzes carbon dioxide reduction. With laser illumination, the reduction potential is shifted positively by ca. 200 mV. The mechanism of the plasma enhanced carbon dioxide reduction is discussed.

Methyl viologen has been studied intensively as an electron acceptor or electron carrier in a number of photochemical and electrochemical reactions. However, its photoelectric behavior in a carbon dioxide saturated aqueous solution has not been studied. It was observed that the methyl viologen cation radical formed electrochemically on the surface of a silver film electrode, can be photoexcited to its excited state, and transfers an electron to carbon dioxide. The mechanism has been confirmed by SERRS data. The energy diagram presented in this paper illustrates the photoreaction mechanism.

In addition, the role of neutral methyl viologen in carbon dioxide reduction was also investigated. In this study, it is apparent that the neutral methyl viologen can catalyze the carbon dioxide reduction process. However, further studies are needed to fully understand the mechanisms involved.
OUTLOOK

As mentioned in the Introduction, the construction of purposely designed monolayer assemblies has a long term aim and more direct goals. Basic to both aspects is the aim to develop the planned artificial photosynthetic model systems and to obtain a deep understanding of the mechanisms involved in natural photosynthetic reaction centers.

Continuing development of artificial photosynthetic model systems should provide future progress. Questions arising are: How can the complicated molecular devices be constructed, what design principles can be imagined, how can the reproducibility and stability problems in an artificial model system be overcome, how can biosystems be understood from the chemistry point of view, how can these model systems be applied to carbon dioxide reduction and water oxidation in the real world?

LB and self-assembled monolayer techniques provide a method to test theoretical models and a means to answer above questions. The results should help in future attempts to make use of inexhaustible materials like carbon dioxide and water that nature provides.
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