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Abstract
Surface characterization is crucial for understanding how the atomic-level structure affects the chemical and photophysical properties of semiconducting nanoparticles (NPs). Solid-state nuclear magnetic resonance spectroscopy (NMR) is potentially a powerful technique for the characterization of the surface of NPs, but it is hindered by poor sensitivity. Dynamic nuclear polarization surface enhanced NMR spectroscopy (DNP SENS) has previously been demonstrated to enhance the sensitivity of surface-selective solid-state NMR experiments by one to two orders of magnitude. Established sample preparations for DNP SENS experiments on NPs require the dilution of the NPs on mesoporous silica. Using hexagonal boron nitride (h-BN) to disperse the NPs doubles DNP enhancements and absolute sensitivity as compared to standard protocols with mesoporous silica. Alternatively, precipitating the NPs as powders, mixing them with h-BN, then impregnating the powdered mixture with radical solution leads to further four-fold sensitivity enhancements by increasing the concentration of NPs in the final sample. This modified procedure provides a factor 9 improvement in NMR sensitivity as compared to previously established DNP SENS procedures, enabling challenging homonuclear and heteronuclear 2D NMR experiments on CdS, Si and Cd3P2 NPs. These experiments allow NMR signals from the surface, sub-surface and core sites to be observed and assigned. For example, we demonstrate that the acquisition of DNP-enhanced 2D 113Cd113Cd correlation NMR experiments on CdS NPs and natural isotropic abundance 2D 13C29Si HETCOR of functionalized Si NPs. These experiments provide a critical understanding of NP surface structures.

Keywords
Surface Characterization, Quantum Dots, Solid-State NMR Spectroscopy, Nanoparticles

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KEYWORDS: Surface Characterization, Quantum Dots, Solid-State NMR Spectroscopy, Nanoparticles

ABSTRACT: Surface characterization is crucial for understanding how the atomic-level structure affects the chemical and photophysical properties of semiconducting nanoparticles (NPs). Solid-state nuclear magnetic resonance spectroscopy (NMR) is potentially a powerful technique for the characterization of the surface of NPs, but it is hindered by poor sensitivity. Dynamic nuclear polarization surface enhanced NMR spectroscopy (DNP SENS) has previously been demonstrated to enhance the sensitivity of surface-selective solid-state NMR experiments by one to two orders of magnitude. Established sample preparations for DNP SENS experiments on NPs require the dilution of the NPs on mesoporous silica. Using hexagonal boron nitride (h-BN) to disperse the NPs doubles DNP enhancements and absolute sensitivity as compared to standard protocols with mesoporous silica. Alternatively, precipitating the NPs as powders, mixing them with h-BN, then impregnating the powdered mixture with radical solution leads to further four-fold sensitivity enhancements by increasing the concentration of NPs in the final sample. This modified procedure provides a factor 9 improvement in NMR sensitivity as compared to previously established DNP SENS procedures, enabling challenging homonuclear and heteronuclear 2D NMR experiments on CdS, Si and CdP: NPs. These experiments allow NMR signals from the surface, sub-surface and core sites to be observed and assigned. For example, we demonstrate that the acquisition of DNP-enhanced 2D 110Cd;115Cd correlation NMR experiments on CdS NPs and natural isotopic abundance 2D 13C;29Si HETCOR of functionalized Si NPs. These experiments provide a critical understanding of NP surface structures.

INTRODUCTION

Colloidal semiconducting nanoparticles (NPs), also referred to as quantum dots (QDs), have garnered attention in recent years for their potential in technologies such as optoelectronics,1-2 photovoltaics,3-5 catalysis,6-7 biomedical sensors,8-9 and others.10-12 Many different synthetic methods have been employed to synthesize NPs and in general, these methods are categorized as top-down or bottom-up approaches.13-14 NPs exhibit a wide range of functionality because their optoelectronic properties and chemical reactivity can be easily tuned by changing either the composition,15-16 surface ligands,17-21 and/or their size and morphology.22-25 NPs have a high surface-to-volume ratio where different surface functional groups and surface defects strongly affect their optoelectronic and chemical properties. Therefore, obtaining a molecular level depiction of the surface of NPs is important from both a fundamental and applied perspective.

QDs are typically characterized using a variety of techniques such as Fourier transform infrared spectroscopy (FTIR), absorption and emission spectroscopies, powder X-ray diffraction (pXRD), scanning/transmission electron microscopy (SEM/TEM), and solution/solid-state nuclear magnetic resonance (NMR) spectroscopy. In general, NMR is a powerful technique for structure determination because NMR probes the local chemical environment by measuring chemical shifts or electric field gradients (EFG) and also enables the connectivity/proximity of different chemical sites to be ascertained via scalar couplings or dipolar couplings. Most of the elements found in main group inorganic semiconductors have NMR active nuclei, potentially making solid-state NMR an ideal tool for probing the structure of NPs. Solid-state NMR has previously been applied to a number of different NP systems, such as cadmium chalcogenides (CdX, X = S, Se, Te),3-5 indium phosphide (InP),3-5-3 silicon (Si),3-5-3 to determine both the surface and bulk structure. Direct excitation solid-state NMR experiments mainly probe the bulk of the NPs, although surface NMR signals are visible in small diameter NP NMR spectra.26, 31, 35, 42-43, 45 The chemical shift of the core NMR signals is often correlated to the band gap and particle size of semiconductor NPs.26, 31, 35, 42-43, 45 Solid-state NMR can also selectively probe the surface of inorganic NPs. Polarization transfer from the surface protons of ligands or terminating functional groups (hydride, hydroxide, etc.) to the surface hetero-nuclei enhances surface NMR signals.45-52 Cross-polarization53 magic angle spinning (CPMAS) is the most commonly used method to transfer polarization from protons to surface hetero-nuclei via heteronuclear dipolar couplings. CPMAS NMR spectra of NPs typically show NMR signals from both the surface and the subsurface/core layers,29, 31, 42, 51-52, 54-55 although core NMR signals are often significantly attenuated. Alternatively, scalar polarization transfers by INEPT or J-HMQC enables...
the selective observation of surface atoms directly bonded to H at-
oms41, 56 or surface ligands.32 For example, Noda and co-workers
characterized CdSe NPs capped with 15N-enriched L-cysteine and
demonstrated coordination of the amine group to surface Cd atoms
by measuring nitrogen-cadmium f-coupling constants (JH,N) and
15N-113Cd dipolar couplings.33

While solid-state NMR has many potential advantages for the char-
acterization of NPs, it is hindered by poor sensitivity which arises
from low polarization of the nuclear spins, the low natural abun-
dance of many NMR active isotopes and long longitudinal relaxation
times (T1). Surface-selective NMR experiments are also challenging
because only a small fraction of the atoms constitute the surface.
Consequently, long experimental times, isotopic enrichment,
and/or large sample volumes are often required to obtain solid-state
NMR spectra of reasonable quality that can provide meaningful
structural information. For example, Strouse and co-workers were
able to obtain a 2D 77Se-1H CP heteronuclear correlation
(HETCOR) solid-state NMR spectrum of CdSe NPs that showed
signals from the surface and sub-surface Se sites in close proximity
to the 1H nuclei of capping ligands, but the 2D HETCOR required 11
days of spectrometer time.20

Dynamic nuclear polarization (DNP) has been shown to greatly in-
crease the sensitivity of solid-state NMR experiments.57-60 In a typical
DNP solid-state NMR experiment, the large spin polarization of un-
paired electrons, usually from exogenous radical polarizing agents
(PA), is transferred to NMR active nuclei at cryogenic temperatures
(< 120 K) by irradiating the sample at a specific microwave fre-
quency. The theoretical maximum DNP signal enhancement (ε)
is proportional to the gyromagnetic ratio of the electrons and a given
nucleus (maximum ε0 of 6.58 for protons).59, 61 DNP solid-state NMR
has previously been applied to a variety of systems including biomol-
eules62-64 pharmaceuticals,65 polymers,66 heterogeneous catalysts,67-
68 bulk inorganic materials,69-71 battery materials,72 and nanoparti-
cles.51-52, 55, 66, 73-80 DNP surface enhanced NMR spectroscopy (SENS)
has been demonstrated as a general method to enhance NMR signals
from interfaces/surfaces of inorganic materials and heterogeneous
catalysts.65, 67, 81 This technique has been primarily applied to materi-
als such as silica and alumina which find application in heterogene-
ous catalysis. Typically, porous and/or high surface area inorganic
materials are prepared for DNP by impregnating the solid powders
with a minimal volume of solution containing a PA.

DNP SENS has previously been applied only a handful of times to
colloidal semiconductor NPs. DNP was performed on colloidal solu-
tions of metallic tin (Sn) NPs,76 Si NPs68 and clay NPs72 by directly
dissolving the DNP PA in the solution, then freezing the solution in-
side of the DNP probe. However, many colloidal NPs will precipi-
tate when cooled to cryogenic temperatures, leading to phase sepa-
gation of the NPs and PA and poor DNP sample enhancements.51
To address this problem Kovalenko, Copéret, Emsley and co-work-
ers showed that colloidal NPs and PA could be impregnated onto
mesoporous silica32, 55 for DNP experiments (Figure 2A). The NPs
and PA are held in close proximity to one another within the silica
mesopores (or gel matrix),32 preventing separation and resulting in
significant 1H DNP enhancements (ε ≈ 50). However, as is shown
below, there are some clear potential drawbacks of this method.
First, silica is not an ideal material for DNP because it has unfavora-
ble dielectric properties and second, the silica significantly dilutes
the NPs, reducing the absolute NMR sensitivity.

Here, we demonstrate improved methods for preparing NPs for
DNP-enhanced NMR experiments that yield ca. one order of mag-
nitude improvements in absolute sensitivity as compared to estab-
lished DNP sample preparation procedures. First, hexagonal boron
nitride (h-BN) is shown to be an improved support material for dis-
persing NPs for DNP solid-state NMR. h-BN has favorable dielec-
tric properties, (i.e. a large real component of the dielectric constant)
resulting in an approximate doubling of DNP enhancements and
NMR sensitivity, as compared to NP samples dispersed with meso-
porous silica. It is also demonstrated that precipitated NP powders
can be physically mixed with h-BN powder, then impregnated with
PA solution, as is traditionally done for porous materials such as sil-
ica.60 The impregnated powder procedure provides an additional
large gain in sensitivity by increasing the concentration of the NPs,
while still maintaining reasonably high DNP enhancements. Using
these optimized sample preparation protocols, it is possible to per-
form 2D natural isotopic abundance homo- and hetero-nuclear cor-
relation solid-state NMR experiments that would be impossible with
conventional solid-state NMR. For example, acquisition of DNP-
enhanced 2D 13C-13C correlation NMR experiments on CdS
NPs and natural isotopic abundance 2D 1H-1H HETCOR of func-
tionalized silicon NPs is demonstrated. These 2D NMR experi-
ments provide detailed insight into the structure and proximity of
different sites on the NP surface.

RESULTS AND DISCUSSION
Testing DNP Support Materials. First, improved support materials
for DNP experiments on NPs were identified.85-87 In 2014, Kubicki
et al. reported that the addition of materials with large real dielectric
constants (refractive index) such as potassium bromide (KBr) and
sapphire (α-Al2O3) could significantly increase DNP enhancements
by improving the coupling of the microwaves to the sample.88 There-
fore, we hypothesized that DNP enhancements for dispersed NP so-
lutions could be increased by using a support material with more fa-
vorable dielectric properties. For this purpose, materials that are free
of elements typically found in semiconductor NPs were chosen to
avoid introducing large background signals. Powdered hexagonal
boron nitride (h-BN) and α-Al2O3 both have favorable dielectric
constants44 and will not give rise to background NMR signals for
most inorganic semiconductors.

To determine the most effective support material for DNP on NPs,
the proton DNP enhancement of a frozen 16 mM TEKPol 1,1,2,2-
tetachloroethane (TCE) solution was measured for different im-
pregnated support materials. The support materials tested were h-
BN, α-Al2O3, silica gel, MSU-H, and MSU-F. MSU-H and MSU-F
are commercially available mesoporous silica materials with hexago-
nal pores and a foam morphology, respectively. Mesoporous silica
was reported as the original support material for DNP solid-state
NMR experiments on NPs.32 Enough radical solution was added to
each support material by impregnation so that the material appeared
slightly wet.89 A degassing step was also performed on the samples to
eliminate any dissolved oxygen in the solvent and ensure optimal
enhancements were achieved.85 Consistent with previous results, the
degassing step increased the 1H T1 of the radical solution and the
DNP enhancements (Figure S1-S2 and Table S1). All three silica
samples had solvent enhancements less than that reported for bulk
TCE, consistent with previous DNP SENS experiments on silica ma-
terials (Figure 1).90-92 α-Al2O3 and h-BN gave very high solvent
DNP enhancements of εCP = 293 and εCP = 357, respectively (Fig-
ure 1). Powdered α-Al2O3 (sapphire) is known to transmit micro-
waves efficiently and is the material from which DNP rotors are manu-
factured. The εCP of 357 measured for h-BN was the largest en-
hancement measured for all the support materials suggesting that h-
BN could be a better NP support material for DNP in comparison to mesoporous silica.

Figure 1. Comparison of the $^{13}$C CPMAS DNP enhancements measured for a frozen solution of 16 mM TEKPol dissolved in 1,1,2,2-tetrachloroethane (TCE). The enhancement for the bulk frozen TCE solution was taken from Kubicki et al.$^{83}$ Silica gel, mesoporous silicas (MSU-F and MSU-H), alpha alumina ($\alpha$-Al$_2$O$_3$) and hexagonal boron nitride ($h$-BN) were impregnated with a TEKPol TCE solution. All enhancements were determined after performing a freeze-thaw cycle inside the DNP probe, then allowing the sample to rest at the base of the probe for 5 minutes to eliminate dissolved oxygen gas prior to re-insertion.$^{83}$

DNP Sample Preparation with h-BN Support Material. To determine the optimal NP DNP sample preparation technique, DNP-enhanced $^{13}$C and $^{113}$Cd solid-state NMR experiments were performed on n-decanoate capped cadmium sulfide (CdS) NPs with an average diameter of 3.1 nm determined from absorption spectroscopy$^{8}$ and TEM images (Figure S3-S4). CdS NPs were chosen for initial experiments because they are easily synthesized and air stable,$^{9}$ and the $^{13}$C NMR signals of the surface ligands and $^{113}$Cd NMR signals of the surface and core cadmium nuclei can be easily observed with DNP.$^{52}$ The first DNP NP sample preparation method tested was the previously reported impregnated support procedure,$^{50}$ but, with some slight modifications. First, 7 mg of MSU-F or 30 mg of h-BN were impregnated with 100 $\mu$L of a 50 mg/mL CdS NP solution in TCE. The impregnation step was performed on a balance in a fume hood and the sample mass afterward was monitored until ca. 85 $\mu$L of the TCE CdS NP solution had evaporated. The TCE was removed by evaporation to increase the concentration of NPs on the support material; if the NPs are not concentrated by evaporation of the solvent, then only ca. 1 mg of NPs will typically make it into the rotor. After evaporation, 12.5 $\mu$L of a 40 mM TEKPol TCE solution was then added to the wet powders to achieve a final radical concentration of ca. 16 mM within the TCE (Scheme S1). The impregnated MSU-F or h-BN powders were then transferred to the rotor. Note that the addition of about 100 $\mu$L of a 50 mg/mL CdS NP solution implies that ca. 2 - 4 mg of CdS NPs end up in the rotor; most of the rotor volume (~ 20 $\mu$L) is occupied by the solvent and support material.

$^1$H DNP enhancements were measured for the solvent and the NP surface by acquiring $^{13}$C CPMAS NMR spectra with and without microwave irradiation. The DNP-enhanced $^{13}$C CPMAS NMR spectra show one main observable NMR signal at 75 ppm, attributed to TCE, and signals in the at 180 ppm and the region of 30 ppm are attributed to the carbonyl and the methylene carbons of the decanoate capping ligands (Figure 2 and Figure S5). The additional two $^{13}$C NMR signals at ca. 115 and 140 ppm are attributed to ligands from the cadmium precursor (Cd(9-deceny1-xanthinate)). With h-BN as the support material, the TCE DNP enhancement ($\epsilon_{CP, sub}$) was double that of MSU-F, and the DNP enhancement of the NP ligand signals ($\epsilon_{CP, samp}$) was almost six times greater with h-BN (Figure S5 and Table 1). DNP-enhanced $^1$H-$^{113}$Cd CP Carr-Purcell-Meiboom-Gill (CPMG) solid-state NMR spectra were also obtained for both samples to assess the absolute $^{113}$Cd NMR sensitivity obtained with both support materials. All $^{113}$Cd solid-state NMR spectra show three $^{113}$Cd NMR signals which are attributed to the core of the CdS NP (Cd$_x$S$_{1-x}$ sites), the surface of the CdS NP (Cd$_x$S$_{1-x}$ sites) and a molecular cadmium oxide impurity (likely CdO or CdO$_2$ sites, see detailed assignments below). The signal-to-noise ratio (SNR) of the $^{113}$Cd NMR spectra and experiment time ($t$) were used to calculate absolute sensitivity ($S$, $S = SNR \times t^{-1/2}$). Using h-BN as a support provides a 50% improvement in the $^{113}$Cd NMR absolute sensitivity as compared to MSU-F as a support material (Table 1 and Figure 2). Clearly h-BN is a superior support material for dispersing NPs because it provides better DNP enhancements and absolute sensitivity. Alternative sample preparation procedures were then tested to see if the concentration of NPs and absolute NMR sensitivity could be further improved. This was accomplished with a powder impregnation procedure,$^{50}$ similar to that used for DNP experiments on porous materials or microcrystalline organic solids. In the powder impregnation procedure, the NPs were first precipitated as a powder by evaporation of the colloidal solution. Then, 20 mg of precipitated NP powder was mixed with an equivalent mass of h-BN powder. The powders were lightly ground by hand in a mortar and pestle for less than 1 minute to evenly mix the precipitated NPs and h-BN. 30 mg of the mixed powder was then impregnated with 20 $\mu$L of 16 mM TEKPol TCE solution and then transferred to a sapphire rotor. The powder impregnation procedure should result in a large increase in NP concentration in the final sample as compared to the impregnated support procedure. For samples prepared with a 1:1 mass ratio of NP:h-BN ca. 10–15 mg of NP will make it into the rotor, corresponding to a 5-fold increase in NP concentration. However, note that the NPs are likely aggregated in the impregnated powder procedure and are likely not well dispersed in the TCE or on the support (Figure 2C). If the NPs form large aggregates, then $^1$H spin diffusion amongst the ligand hydrogen spins is likely required to distribute the DNP-enhanced $^1$H polarization over the aggregated NPs. Consequently, the impregnated powder method is only likely to work for NPs capped with organic ligands. The presence of CdS NP aggregates on h-BN was confirmed with TEM of the CdS NPs prepared using the impregnated powder procedure with h-BN (Figure S4).

Comparing the powder impregnation and impregnated support procedures using h-BN as the support material, both $\epsilon_{CP, samp}$ and $\epsilon_{CP, sub}$ decrease by a factor 2 for the impregnated powders (Figure 2).
Figure 2. General schemes of the different sample preparation methods for DNP-enhanced solid-state NMR experiments on CdS NPs. The impregnated support procedure with CdS NPs and PA solution (A) dispersed inside the mesopores of silica (MSU-F) or (B) dispersed on h-BN. (C) The impregnated powder procedure where a mixture of CdS NP and h-BN were impregnated with radical solution. Yellow spheres represent CdS NPs and the orange ovals represent the radical PA. (D-F) Corresponding DNP-enhanced $^{13}$C CPMAS spectra and (G-I) $^{113}$Cd CP-CPMG solid-state NMR spectra of the CdS NPs showing both surface and core $^{113}$Cd signals. Experiment times were between 5 and 15 min. All sample preparation methods used a final radical concentration of 16 mM TEKPol TCE and all NMR spectra were acquired with $\nu_{\text{rot}} = 10 \text{ kHz}$. $^1H$ DNP enhancements measured via $^1H-^{13}$C CPMAS are indicated for the solvent ($S_{\text{CP}, \text{solv}}$) and surface ligands ($S_{\text{CP}, \text{sample}}$). Signal-to-noise ratio (SNR), experiment time ($t$) and sensitivity ($S = SNR \times t^{-1/2}$) are indicated. The sample preparation schemes (A-C) are not drawn to scale and a legend for the schemes is located in the bottom right corner of A.

However, the $^{13}$C and $^{113}$Cd absolute NMR sensitivity increased by a factor of 7 and 4, respectively, for powder impregnation in comparison to the impregnated support procedure (Figure 2 and Table 1). It should also be noted that the $^{113}$Cd NMR spectra of NPs prepared by the impregnated powder procedure show slightly sharper $^{113}$Cd NMR signals than samples prepared by the impregnated support procedure. This improvement in resolution could occur because the precipitated NPs may form partially ordered aggregates while in the impregnated sample the NPs will be dispersed in the frozen, amorphous solvent. Precipitation of the NPs may also produce changes in surface ligand concentration. In 2012 Hens and coworkers reported that 4 cycles of purification of NPs with short chain alcohols (methanol, ethanol, etc.) the surface ligand concentration went from 4.1 to 3.2 ligands•nm$^{-2}$, which corresponds to a 22% reduction in ligand concentration. The CdS NP sample used for this study was only purified three times with a minimal amount ethanol to limit the loss of surface ligands.

The mass ratio of NP:h-BN used for powder impregnation was varied from 1:0 to 1:1 to determine the ideal ratio of NPs to h-BN that provides the best NMR sensitivity (Figure S7). A 1:1 mass ratio of NP:h-BN provided better absolute NMR sensitivity than a 3:1 NP:h-BN mass ratio or impregnation of the pure precipitated powdered NPs (1:0 CdS:h-BN) (Figure S7). The 1:1 sample gave 2.5 times higher DNP enhancement and 1.5 times better $^{13}$C NMR sensitivity than the 1:0 sample. For comparison, the impregnated support procedure described above produces a sample which has an approximate composition of 1:5 NP:h-BN mass ratio. The increase in DNP enhancement with added h-BN could occur because h-BN has better dielectric characteristics and/or the h-BN may help reduce the size of NP aggregates. However, the increase in DNP enhancement is accompanied by dilution of the sample. Therefore, the 1:1...
ratio of NP: h-BN likely provides the best tradeoff between DNP enhancement and NP concentration.  

**2D Solid-State NMR Experiments on CdS NPs.** With optimal DNP sample preparation methods in hand, we were able to perform more challenging 2D correlation experiments to characterize the surface of the CdS NPs. Recently, Emsley and co-workers used DNP and 2D phase adjusted spinning sidebands enhanced by phase-incremented echo-train acquisition (2D PASS-PIETA) experiments to correlate anisotropic $^{113}$Cd spinning sidebands manifolds to isotropic $^{113}$Cd chemical shifts for CdSe and CdS NPs and nanoplatelets. The isotropic dimension of the 2D PASS-PIETA NMR spectrum resolves the different NMR signals associated with the surface, shell and core. With this in mind, the first challenging NMR experiment performed on the CdS NPs was a $^{113}$Cd 2D CP magic-angle-turning (CP-MAT),89-90 which gives similar information to a PASS-PIETA experiment (Figure 2I and Figure 3A). Note that CPMG/PIETA acquisition of the direct dimension signal was not required because of the high $^{113}$Cd NMR sensitivity provided by the impregnated powder procedure. The increased sensitivity would be especially useful in cases where the transverse relaxation time is too short for CPMG/PIETA acquisition.

The 2D CP-MAT spectrum correlates the spinning sideband manifolds to the isotropic peaks in the indirect dimension. The indirect dimension shows three distinct isotropic NMR signals. The first signal occurs at an isotropic chemical shift of 52 ppm which matches the previously reported chemical shift for bulk CdS.55, 62 Therefore, this signal corresponds to CdS, sites residing in the sub-surface or core regions of the CdS NPs. As expected, this site has a small chemical shift anisotropy (CSA) ($\Omega < 250$ ppm) consistent with the highly symmetric, tetrahedral Cd coordination in the core. The second site centered at $–283$ ppm is assigned to the surface Cd atoms that are coordinated by the capping carboxylate ligands, in agreement with previous observations.55 The $^{113}$Cd isotropic shift of $–283$ ppm is intermediate between the chemical shifts of CdS (52 ppm) and molecular cadmium oxide impurity ($–631$ ppm), consistent with a CdS$_2$O$_2$ coordination environment. Because of the asymmetric CdS$_2$O$_2$ coordination environment, there is a large CSA of 487 ppm for this site. The $^{113}$Cd chemical shift and large CSA are consistent with previously reported values for both CdS and CdSe NPs.55, 65 Note that there is a large distribution of isotropic chemical shifts in the range of 0 to $–555$ ppm centered around the surface NMR signal at $–283$ ppm. The breadth of this distribution likely reflects the disordered nature of the surface and suggests that there could be minor numbers of Cd atoms coordinated by 1 or 3 oxygen and sulfur atoms (CdS$_2$O$_2$ and CdS$_3$O$_2$ sites). Alternatively, these signals could also arise from Cd nuclei in the sub-surface layers because bulk-like sites in the sub-surface regions may exhibit chemical shifts distinct from either surface or core NMR signals. A third signal at an isotropic chemical shift of $–631$ ppm is also visible. This shift should correspond to Cd coordinated by 4 to 7 oxygen atoms (denoted as CdOx sites). This site also has minimal CSA ($\Omega < 250$ ppm), suggesting that the cadmium coordination is symmetric and possibly tetrahedral or octahedral. We hypothesize that this signal arises from a molecular cadmium impurity formed as a byproduct during the synthesis of the CdS NPs (see below).

Having identified the different Cd coordination environments present in the CdS NPs, additional 2D NMR experiments were then performed to probe the proximity/connectivity of the Cd sites. A refocused incredible natural abundance double resonance transfer experiment (refocused INADEQUATE)90 experiment was performed to observe the connectivity of Cd species linked by bridging sulfide or oxide atoms. The INADEQUATE experiment utilizes homonuclear $^{113}$Cd scalar couplings ($J$ couplings) to generate double quantum (DQ) coherences and selectively observe $^{113}$Cd spin pairs that are linked by a bridging sulfide or oxide. DQ correlations will appear in the indirect dimension at the sum of their single quantum (SQ) chemical shifts. The 2D $^{113}$Cd-$^{113}$Cd INADEQUATECPMG spectrum was obtained with a $J_{evolution}$ time ($\tau$) of 2 ms, which approximately corresponds to a two-bound homonuclear cadmium $J$-coupling ($J_{CC}$) of ca. 125 Hz (Figures 3 and S8-S9). Previously, a $J_{CC}$ of 82 Hz was measured for cadmium thiolate molecular clusters with bridging sulfide ligands. The $^{113}$Cd-$^{113}$Cd 2D INADEQUATE spectrum shows a clear auto-correlation at 52 ppm in direct dimension and 104 ppm in the indirect dimension, which arises from correlations between Cd spins in the core of the CdS NPs (Figure 3). Correlations between core and surface or sub-surface Cd atoms results in a broad signal in the indirect dimension that covers a shift range of ca. 0 to $–555$ ppm. The broad range of chemical shifts in the indirect dimension could arise from the CSA of surface sites and/or the large range of isotropic shifts associated with surface sites. The observation of this correlation confirms the proximity of the surface and core Cd atoms. A second 2D $^{113}$Cd-$^{113}$Cd INADEQUATECPMG spectrum was obtained with a mixing time of 16 ms, which approximately corresponds to a $J_{CC}$ of ca. 15 Hz. This spectrum shows a single auto-correlation for the $^{113}$Cd peak at $–650$ ppm corresponding to connections between CdOx species, suggesting that the CdOx impurity does not correspond to isolated molecular carboxylate compounds (Figure S9).

<table>
<thead>
<tr>
<th>Sample Preparation Method</th>
<th>Impregnated Support - MSU- F</th>
<th>Impregnated Support - h-BN</th>
<th>Impregnated Powder</th>
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<td>EC CP, samp</td>
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<td>128</td>
<td>62</td>
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<td>EC CP, solr</td>
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<td>201</td>
<td>92</td>
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<td>$^{13}$C Exp. Time (min.)</td>
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<tr>
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<td>48</td>
<td>87</td>
<td>637</td>
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<td>$^{13}$Cd $S'(min^{-1/2})$</td>
<td>6</td>
<td>13</td>
<td>54</td>
</tr>
</tbody>
</table>

The sensitivity ($S$) was calculated by dividing the signal to noise ratio by the square root of the total experiment time, $S = \frac{SNR}{\tau^{1/2}}$. 

**Table 1.** DNP enhancements, experimental times, and sample sensitivities for the different DNP sample preparation procedures shown in Figure 2.
Figure 3. DNP-enhanced $^{113}\text{Cd}$ 2D solid-state NMR correlation spectra of CdS NPs acquired with a spinning frequency of 10 kHz. (A) 2D $^{113}\text{Cd}$-$^{113}\text{Cd}$ magic-angle turning (MAT) spectrum where the solid lines indicate distinct $^{113}\text{Cd}$ NMR signals. (B) Individual rows extracted from the CP-MAT 2D spectrum showing $^{113}\text{Cd}$ sideband manifolds associated with the core, surface and an impurity. The chemical shift tensor parameters are indicated. (C) $^{113}\text{Cd}$-$^{113}\text{Cd}$ refocused-INADEQUATE-CPMG spectrum showing correlations between core and surface $^{113}\text{Cd}$ sites. The diagonal line indicates autocorrelations. (D) $^1\text{H}$ spin diffusion $^{113}\text{Cd}$-$^1\text{H}$ CP-HETCOR acquired with 20 ms for $^1\text{H}$ spin diffusion. The CdS NP sample was prepared using the wetness impregnation sample preparation procedure.

was acquired. The spin diffusion CP-HETCOR spectrum, shows two distinct groups of $^1\text{H}$ correlations. The $^{113}\text{Cd}$ NMR signals from the core and surface CdS sites correlate to $^1\text{H}$ NMR signals at 2 ppm. This $^1\text{H}$ chemical shift likely corresponds to the $^1\text{H}$ spins of the decanoate capping ligands. The second correlation demonstrates that $^{113}\text{Cd}$ signal from the CdO, NMR signal only correlates to a $^1\text{H}$ signal at 6.2 ppm, which likely corresponds to the $^1\text{H}$ spins of solvent (TCE). Therefore, the $^1\text{H}$ spin diffusion CP-HETCOR experiment suggests that the $^{113}\text{Cd}$ NMR signals arises from a spatially segregated byproduct such as carboxylic acid hydrate compounds with bridging oxide, carboxylate or water ligands. In addition to the solid-state NMR spectroscopy, traditional NP characterization methods including transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDX, Figure S4) and X-ray photoelectron spectroscopy (XPS) were also applied (Figure S10 and Table S3). The EDX spectrum confirmed the presence of Cd, S, C and O within the CdS NP sample. The Cd 3$d$ XPS peak position and shape confirms most Cd are in CdS and suggests the presence of cadmium coordinated by oxygen. However, since the CdS NPs are passivated with oxygen containing decanoic acid, EDX or XPS were unable to confirm domain segregations between the CdOx and CdS particles. These results highlight the utility of solid-state NMR spectroscopy. Finally, the proximity and ordering of the different Cd sites was also probed with $^{113}\text{Cd}$ spin diffusion experiments. Emsley and co-workers recently showed that homonuclear spin diffusion amongst moderate-$\gamma$ nuclei such as $^{31}\text{P}$, $^{119}\text{Sn}$, $^{113}\text{Cd}$, and $^{28}\text{Si}$ can relay DNP.
fusion time. In part B, the highlighted portions of the $^{113}$Cd NMR pulse was then used to selectively store the magnetization associated with $^{113}$Cd magnetization is generated by CP. A frequency-selective spin diffusion experiment is shown in Figure 4A. In this experiment, $^{113}$Cd spins within the CdS NPs. The pulse sequence for the $^{113}$Cd $^{113}$Cd spin diffusion should be observable between dipolar coupled $^{113}$Cd spins, provided the two $^{113}$Cd spins have similar chemical shifts or overlapping sidebands to permit spin diffusion.99,100 The $^{113}$Cd spin diffusion experiment clearly shows that the surface $^{113}$Cd magnetization is transferred to core sites by $^{113}$Cd spin diffusion (Figure 4C). No spin diffusion was observed between the surface CdS and CdOx NMR signals, again suggesting that these sites are spatially separated. To confirm this, a second $^{113}$Cd spin diffusion experiment was performed with the selective $\pi/2$ flip-back pulse applied on resonance with the CdOx peak (Figure S11). There is no evidence of spin diffusion to the CdS surface or core NMR signals in this $^{113}$Cd spin diffusion experiment. However, it is important to keep in mind that the absence of $^{113}$Cd spin diffusion does not directly confirm spatial separation because overlap of $^{113}$Cd NMR signals/sidebands is likely required to enable spin diffusion between different sites. Note that the 2D CP-MAT spectrum shows overlap between the CdOx, NMR signal and the last sideband associated with the CdS surface sites, suggesting spin diffusion could occur if these sites were proximate.

Cadmium Phosphide NPs. To demonstrate the generality of the improved DNP sample preparation technique it was applied to characterize other NP materials. DNP NMR was applied to characterize oleate capped cadmium phosphide NPs (Cd$_3$P$_2$) with an average diameter of 2.1 nm as measured by TEM (Figure S12). Quantum dots have been demonstrated to have high photoluminescence (PL) quantum yields and a size tunable PL over the visible and NIR spectrum, making this material ideal for LEDs and other optical applications.98-100 The Cd$_3$P$_2$ sample was prepared with the impregnated powder method by mixing equivalent weights of h-BN and precipitated Cd$_3$P$_2$ NPs. Then 30 mg of the powdered mixture was impregnated with a 16 mM TEKPol TCE solution. This sample preparation gave $\varepsilon_{\text{CP}} \approx 46$ (Figure 5A). All manipulations were performed in a glovebox to prevent surface oxidation. The lack of surface oxidation is confirmed by the absence of intense phosphate signals that normally appear at 0 ppm in the $^{31}$P CPMAS spectrum.37,52,101

The $^{31}$P CPMAS solid-state NMR spectrum of Cd$_3$P$_2$ yielded a broad $^{31}$P signal centered at –300 ppm, consistent with previous reports (Figure 5A, top spectrum).99,102 Acquisition of a $^{31}$P CPMAS solid-state NMR spectrum with up to 100 s of spin diffusion time leads to the appearance of a narrower $^{31}$P NMR signal at –225 ppm that is attributed to core phosphides (Figure 5A, lower spectrum). The chemical shift of the core phosphides is slightly more negative than the previously reported $^{31}$P chemical shift of bulk Cd$_3$P$_2$ (peaks between –125 ppm and –175 ppm).103 The decreased $^{31}$P shift of the Cd$_3$P$_2$ NPs as compared to bulk Cd$_3$P$_2$ likely reflects the increased band gap of the NPs.26,35,45

The $^{113}$Cd CP-MAT NMR spectrum of the Cd$_3$P$_2$ shows an extremely broad NMR signal that spans 1300 ppm. Ratcliffe and co-workers previously observed that the $^{113}$Cd solid-state NMR spectra of Cd$_3$P$_2$ magic-sized NPs exhibited broad spinning sideband manifolds which covered a similar chemical shift range.44 They observed $^{113}$Cd isotropic chemical shifts at +140 ppm, –243 ppm and –360 ppm. The first signal was observed in a direct excitation spectrum and was attributed to core Cd NMR signals; the latter two were evident in CPMAS NMR spectra, suggesting these two NMR signals correspond to ligand coordinated surface Cd atoms.44 A DNP-enhanced 1D CP total sideband suppression (TOSS)104 $^{113}$Cd NMR spectrum shows two very broad $^{113}$Cd NMR signals centered at +220

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**Figure 4.** DNP-enhanced $^{113}$Cd spin diffusion MAS NMR experiments. (A) CP spin diffusion pulse sequence with a selective $\pi/2$ flip-back pulse followed by a variable $^{113}$Cd spin diffusion period and CPMG signal detection. (B) $^{113}$Cd CP-CPMG spin diffusion spectra with spin diffusion times of 0 s, 50 s and 600 s. (C) Intensity comparison between $^{113}$Cd NMR signals for core CdS$_4$ (blue), surface CdS$_2$O$_2$ (green), and CdOx (orange) as a function of $^{113}$Cd spin diffusion times of 0 s, 50 s and 600 s. (C) Intensity comparison between $^{113}$Cd NMR signals for core CdS$_4$ (blue), surface CdS$_2$O$_2$ (green), and CdOx (orange) as a function of $^{113}$Cd spin diffusion times of 0 s, 50 s and 600 s. Note that the 2D CP-MAT spectrum shows overlap between the CdOx, NMR signal and the last sideband associated with the CdS surface sites, suggesting spin diffusion could occur if these sites were proximate.
Figure 5. DNP-enhanced solid-state NMR spectra of Cd3P2 (A) 31P CP spin echo with 31P spin diffusion times from top to bottom of 0 s, 1 s, 10 s, 25 s and 100 s. (B) (top) 113Cd CP-CPMG, (middle) 113Cd CP-TOSS and (bottom) 113Cd projection from the 31P{113Cd} D-HMQC. (C) 2D 31P{113Cd} constant time D-HMQC. All NMR spectra were acquired with a spinning frequency of 10 kHz. The highlighted regions correspond to the assigned chemical shifts of the different NMR signals: blue is assigned to the core, green is assigned to the subsurface, and orange is assigned to the surface.

ppm and –200 ppm (Figure S8B). SIMPSON simulations confirm the sideband suppression with TOSS was sufficient for 113Cd NMR signals with large CSA (Figure S13). Note that the conventional 113Cd solid-state NMR spectra obtained by Ratcliffe required 4–5 days of signal averaging.44 Here, DNP-enhanced 113Cd NMR spectra were obtained in only 20 minutes. In order to definitively assign the 31P and 113Cd NMR signals a 31P{113Cd} 2D dipolar heteronuclear multiple quantum correlation (D-HMQC) experiment was performed (Figure SC). The 31P{113Cd} 2D D-HMQC spectrum shows a correlation between the core 31P NMR signal at –220 ppm and 113Cd NMR signal at +460 ppm that was not visible in the 113Cd CP-CPMG spectrum. This 113Cd NMR signal associated with the core was likely not observed in the 113Cd CP-CPMG spectrum because 113Cd spin diffusion is slow and thus unlikely to efficiently polarize core 113Cd spins that are distant from surface 1H spins. In the 31P{113Cd} D-HMQC experiment, 31P is first polarized by CP with a 9 ms contact pulse. 31P spin diffusion during the long CP contact pulse is likely fast enough to transport 31P magnetization to core sites. The correlation at –350 ppm 31P chemical shift and –200 ppm 113Cd shift likely corresponds to surface sites since this 113Cd NMR signal has the highest intensity in the surface-weighted 113Cd CP-CPMG spectrum. The reduced shift of the Cd surface sites likely arises due to coordination by the carboxylate groups of the oleate capping ligands (i.e., CdO2P2 sites), as was observed for CdS NPs. Therefore, the remaining correlation at ~280 ppm 31P chemical shift and +220 113Cd chemical shift should correspond to subsurface 113Cd sites.

Silicon Nanoparticles. Finally, DNP-NMR was also applied to characterize the surface of partially oxidized dodecyl functionalized silicon NPs. A particle diameter of 6.4 nm was determined from a true 1H NMR spectrum corrected for 29Si transverse relaxation).108 Here, optimal 29Si-29Si INADEQUATE experiments and observed optimal DQ NMR signals with large CSA (Figure S13). Note that the conventional 29Si solid-state NMR spectra obtained by Ratcliffe required 4–5 days of signal averaging.44 Here, DNP-enhanced 29Si-29Si INADEQUATE spectra of alkyl functionalized silica nanoparticles.108 They measured two bond Si–O–C bonds;41 a surface silicon atom attached to an alkyl chain (*SiHR), a surface silicon monohydride with an attached alkyl chain (*SiHx) or quaternary bulk-like silicon (SiSi4), respectively. There are three probable surface species that have Si–C bonds;41 a surface silicon atom attached to an alkyl chain (*SiHR), a surface silicon monohydride with an attached alkyl chain (*SiHx) or a trihydride species (RSiH3) that is transferred to the alkyl chain during surface silylsilation with alkynes.41
Figure 6. DNP-enhanced $^{13}\text{C}$ and $^{29}\text{Si}$ solid-state NMR spectra of air-exposed, dodecyl functionalized silicon nanocrystals at a spinning frequency of 10 kHz. (A) $^{13}\text{C}$ CPMAS spectra acquired with (black) and without microwave irradiation (blue). The measured DNP enhancement for the surface ligands was $\varepsilon_{\text{C CP}} \sim 74$. (B) $^{29}\text{Si}$ CP-CPMG spectrum. (C) 2D $^{29}\text{Si}$-2$^{29}\text{Si}$ refocused INADEQUATE-CPMG homonuclear correlation spectrum. The diagonal line indicates autocorrelations. (D) DNP-enhanced $^{13}\text{C}$-$^{29}\text{Si}$ CP-TEDOR acquired with 3 rotor cycles of REDOR recoupling to show chemical bonded species. (E) Cartoon illustration of the different surface species and their connections. The colored bonds (purple, red and blue) indicate the different correlations observed in the 2D NMR spectra shown in (C) and (D). The sample was prepared with a 16 mM TEKPol deuterated TCE solution.

The observed $J_{\text{Si-Si}}$ couplings reported for small molecule silanes,109 The observed $J_{\text{Si-Si}}$ of ca. 45 Hz therefore confirms that observed $^{29}\text{Si}$ NMR signals arise from directly bonded silicon atoms, suggesting minimal oxidation of the surface.

The $^{29}\text{Si}$ INADEQUATE spectrum illustrates the structure of the Si NP (Figure 6E). The main correlation centered at $-90$ ppm and $-175$ ppm corresponds to correlations between surface hydrides ($^{*}\text{SiH}_x-^{*}\text{SiH}_y$) or between surface silicon hydrides and quaternary, bulk-like silicon ($^{*}\text{SiH}-^{\text{SiSi}_3}$). Correlations at $-50$ and $-100$ ppm in the direct dimension and $-150$ ppm in the indirect dimension arise from correlations between silicon atoms bonded to carbon and bulk-like silicon or surface silicon hydrides ($^{*}\text{SiR}-^{*}\text{SiH}_x$, $^{*}\text{SiR-}\text{SiSi}_3$, $^{*}\text{SiH}_x-^{*}\text{SiH}_y$, $^{*}\text{SiH}_x-^{*}\text{SiSi}_3$). Due to the overlap and similarity in the isotropic chemical shifts between $^{*}\text{SiH}_x$ and the subsurface atoms it is currently not possible to differentiate these possible correlations.

In future experiments, $^{1}\text{H}$-$^{29}\text{Si}$ f- or dipole-filters will be incorporated into INADEQUATE experiments to differentiate these signals. The presence of a crystalline core of the Si NPs was confirmed with a CP spin diffusion experiment (Figure S18), which showed a sharp $^{29}\text{Si}$ NMR signal at chemical shift of ca. $-83$ ppm, consistent with prior studies.40, 42

DNP SENS also enabled the acquisition of a natural isotopic abundance 2D $^{13}\text{C}$-$^{29}\text{Si}$ HETCOR solid-state NMR spectrum in only 22 h (Figure 6D). To the best of our knowledge, this is the first time a $^{13}\text{C}$-$^{29}\text{Si}$ HETCOR solid-state NMR spectrum has been recorded with natural isotopic abundance. $^{13}\text{C}$-$^{29}\text{Si}$ coherence transfer was performed with the transferred-echo double resonance (TEDOR) block (Figure S19). The TEDOR NMR experiment was performed with only three-rotor cycles of rotational echo double resonance (REDOR) per recoupling block. This mixing time should selectively transfer coherence between $^{13}\text{C}$ bonded to $^{29}\text{Si}$ and suppress coherence transfer between non-bonded $^{13}\text{C}$ and $^{29}\text{Si}$ (Figure S20). The 2D $^{13}\text{C}$-$^{29}\text{Si}$ HETCOR spectrum shows correlations between the $^{29}\text{Si}$ signal at $-50$ ppm, attributed to $^{*}\text{SiHR}$, $^{*}\text{SiR}$ and $^{*}\text{RSH}_3$, and a broad range of $^{13}\text{C}$ NMR signals from 20 ppm to 10 ppm. Lee et al. previously obtained the $^{13}\text{C}$ CPMAS spectrum of Si NPs functionalized 1-
\(^{13}\)C labelled dodecene and observed similarly broad \(^{13}\)C NMR signals.\(^{40}\) The signal broadening of the 1-\(^{13}\)C signal was attributed to bonding of the alkyl chain to different facets on the Si NP surface.\(^{40}\) The broad range of \(^{13}\)C chemical shifts observed in the TEDOR spectrum could also arise because there should be carbon atoms bonded to surface silicon atoms (\(^{8}\)SiR or \(^{8}\)SiHR) and to silyl groups (\(^{8}\)SiH).\(^{41}\)

**CONCLUSIONS**

In summary, we have demonstrated improved DNP NP sample preparation procedures for DNP SENS experiments on NPs. First, for DNP NMR experiments on frozen colloidal NP solutions \(h\)-BN was found to be superior to silica materials. Second, the NP concentration and absolute NMR sensitivity could be substantially increased by performing experiments on precipitated NPs that were mixed with \(h\)-BN, then impregnated with minimal volumes of radiolysis solution. However, as discussed above, precipitation of NPs will cause aggregation of the NPs and may alter the surface ligand concentration and/or surface structure. If aggregation is a concern then the impregnated support procedure with \(h\)-BN can still be used for experiments on dispersed NPs.

The improved NMR sensitivity enabled the acquisition of challenging 2D solid-state NMR experiments that can be used to resolve and assign the surface and core NMR signals in NPs. For CdS NPs three distinct Cd environments were observed with DNP-enhanced NMR experiments. \(^{11}\)Cd homonuclear correlation and spin diffusion NMR experiments were used to demonstrate the proximity of the surface and core cadmium atoms in the CdS NPs and showed that a CdO\(_x\) impurity was present and separated from the CdS surface. \(^{13}\)P spin diffusion and a \(^{13}\)P\(^{115}\)Cd\(^{1}\)HMQC spectrum resolved distinct NMR signals associated with surface, sub-surface and core Cd and P sites within CdP\(_x\)_NP's. Finally, DNP enabled acquisition of \(^{28}\)Si\(^{-}\)\(^{30}\)Si INADEQUATE and a \(^{13}\)C\(^{-}\)\(^{29}\)Si correlation spectra of functionnalized Si NPs that allow the surface bonding network to be partially resolved. We are currently using these approaches to correlate the effects of ligand exchange and other surface treatment procedures with molecular structure and photophysical properties of nanomaterials.

**EXPERIMENTAL**

*Materials.* Decanoic acid (\(\geq 98\%\), Aldrich), potassium tertiary butoxide (t-BuOK, 95%, Aldrich), 9-decen-1-ol (\(\geq 90\%\), Alfa Aesar), phenyl ether (Ph\(_2\)O, 99%, Acros), carbon disulfide (CS\(_2\), \(99.9\%\), Fisher), cadmium chloride (CdCl\(_2\), anhydrous, 99.995%, Strem), methanol (\(\geq 99.9\%\), Fisher), chloroform (CHCl\(_3\), \(99.9\%\), Fisher), tetrahydrofuran (THF, \(\geq 99.9\%\), Fisher), diethyl ether (\(\geq 99.5\%\), Fisher), 1-octadecene (Aldrich), toluene (anhydrous, Aldrich), oleic acid (\(\geq 99\%\), Aldrich), Bio-Bead S-X1 (Bio-Rad Labs), Chloroform-d (CDCl\(_3\), Cambridge Isotopes Laboratories), dimethylsulfoxide-d\(_6\) (DMSO-d\(_6\), Cambridge Isotopes Laboratories), TEKPol biradical (Cortecnet), h-BN (98%, Aldrich) (Figure S21), \(\alpha\)-Al\(_2\)O\(_3\) (99.99%, 0.3µm grain size Aldrich), MSU-F (15 nm cell window size, Aldrich), MSU-F (7 nm pore size, Aldrich), silica gel (SiO\(_2\), Aldrich), 1,1,2,2-tetrachloroethane (99%, Acros) and d: 1,1,2,2-tetrachloroethane (99%, Euroisotop) were obtained from commercial suppliers and used without further purification.

*Synthesis of NPs. CdS NPs.* All synthesis steps were reported by Tavasoli et al. Specifically, 9-decen-1-ol was used as linear C10 alcohol for synthesis of xanthate precursors and decaonic acid was used as the carboxylic acid surface ligand.\(^{31}\) After cooling the reaction to room temperature and dilution with chloroform (5 mL) CdS NPs were precipitated by adding a minimal amount of ethanol followed by centrifugation (4500 rpm for 10 min). The yellow residue was redissolved in a minimal amount of hexane and precipitated by ethanol and followed by centrifugation, this process was repeated once more, and the final precipitate was dried under vacuum overnight. The as-synthesized CdS NPs were precipitated without further surface modification (Figures S3 and S22-S23). The size of the CdS NPs was determined from measuring the wavelength of the first excitonic absorption peak (Figure S3) and confirmed with TEM images (Figure S4) and compared to previous TEM images in which the size distribution was measured.\(^{31}\) CdP\(_x\)_NP's. All reactions for precursor and nanocrystal synthesis were run under an inert atmosphere of nitrogen using a glovebox or standard Schlenk techniques. Warning: dimethyl cadmium is a volatile and extremely toxic material and should be handled with care within a nitrogen glovebox. Both dimethyl cadmium and P(SiMe\(_3\)_2) are pyrophoric, extremely reactive, and should be handled with caution. Cadmium oleate and P(SiMe\(_3\)_2) were prepared following literature procedures.\(^{10}\) All solvents were dried over Ca\(_2\)H\(_2\), distilled, and stored over 4 Å molecular sieves in the nitrogen-filled glovebox. Cadmium phosphide NPs were synthesized following a modified preparation of Jehnsmüller et al.\(^{39}\) Cadmium oleate (0.55 g, 0.8 mmol), oleic acid (0.5 mL, 1.58 mmol), and 10 mL of 1-octadecene (ODE) were combined in a 25 mL 3-neck round-bottom flask under nitrogen flow on a Schlenk line and heated to 150 °C while stirring, P(SiMe\(_3\)_2) (60 μL, 0.2 mmol) in 1 mL of ODE was rapidly injected into the flask. After 3 min, the solution was cooled down by placing the flask in an oil bath. Particles were isolated by first removing the ODE through distillation under reduced pressure, resuspending the resulting paste in 2 mL of toluene, and centrifuging for 10 min at 7,000 rpm. Insoluble products were removed, and the NP solution was purified by gel permeation chromatography to remove excess free ligand (Figure S24). Powdered NP samples were obtained by removing the toluene under a vacuum. Si NPs. Powdered alkyl-functionalized Si NPs (from radical-initiated reaction of hydride-terminated Si NPs with 1-dodecene) were prepared following our established procedures\(^{41, 111-112}\) and exposed to air for several days prior to preparing the sample for DNP (Figure S16). The Si NP particle diameter was estimated to be 6.4 nm from pXRD (Figure S14), consistent with our prior extensive characterization of particle size by TEM and correlation with emission peak energy.\(^{111}\)

**DNP sample preparations. Impregnated support procedure.** 30 mg of h-BN, or 7 mg of MSU-F were massed out on a balance. The difference in the required amount of h-BN or MSU-F reflects differences in density and surface areas. The support materials were then impregnated with 100 μL of a 50 mg/mL concentration of CdS NPs (in TCE) in the fume hood. The NP solution was then evaporated down to 20 μL on the balance in the fume hood. Next 10 μL of 40 mM TEKPol TCE solution was added to achieve a final radical concentration of ca. 16 mM. Once the radical solution was added to the sample it was then packed into a DNP 3.2 mm sapphire rotor (Scheme S1).

**Incipient wetness impregnation procedure.** 20 mg of h-BN and 20 mg of powdered NPs (CdS or CdP\(_x\)) were weighed out and added to a mortar and pestle and were gently ground for ca. 1 min to mix the NPs and support material. 30 mg of the powder mixture was then added to a watch glass where 20 μL of a 16 mM TEKPol TCE solution was added. After the addition of the radical solution the sample was then packed into a DNP 3.2 mm sapphire rotor (Scheme S2). The sample preparation for the Si NPs was similar to the above method however 10 mg of h-BN and 30 mg of Si NPs was used to.
make the powder mixture and 16 mM TEKPol in deuterated TCE was used for the impregnation step. The Cd,P, NPs were prepared in glovebox to prevent oxidation.

**Optical Absorption Characterization of CdS NPs.** Absorption spectra were measured with a photodiode-array Agilent 8453 UV-vis spectrophotometer. Solvent absorption was subtracted from all spectra. Steady-state photoluminescence (PL) spectra were measured with a Horiba-Jobin Yvon Nanolog scanning spectrofluorometer equipped with a photomultiplier detector. Cd,P, NPs. Absorption spectra were collected in a quartz cuvette using a Cary 5000 UV-Vis spectrometer from Agilent. Fluorescence measurements were taken on a Horiba Jobin Yvon FluoroMax-4 fluorescence spectrometer.

**CdS solution NMR.** Solution 1H NMR spectra were obtained with a 9.4 T Varian MR-400 spectrometer equipped with a OneNMR pulse-field-gradient probe. All solution 1H NMR spectra were obtained using a pulse-acquire pulse sequence, with 32 transients and a recycle delay of 1 s.

**TEM and EDX.** Cd,P, TEM and EDX point analysis was performed on carbon coated copper grids using a FEI Tecnai G2-F20 scanning transmission electron microscope (STEM) at the Ames Laboratory Sensitive Instrument Facility. Cd,P, NPs. TEM characterization was performed on a FEI Tecnai G2 F20 microscope at an accelerating voltage of 200 kV at the Molecular Engineering and Sciences Institute (University of Washington, Seattle). The size distributions of the NPs were determined by manual measurement of TEM images using the software ImageJ.

**XPS characterization of CdS NPs.** XPS measurements were performed using a Kratos Amicus/ESCA 3400 instrument. The sample was irradiated with 240 W unmonochromated Mg Kα X-rays, and photoelectrons emitted at 0° from the surface normal were energy analyzed using a DuPont type analyzer. The pass energy was set at 80 eV. CasaXPS was used to process raw data files. XPS spectra were energy calibrated to the C 1s peak position at 284.6 eV.

**FTIR characterization of Si NPs.** FTIR absorbance measurements were made on a Bruker Alpha FTIR spectrometer using a diffuse reflectance infrared Fourier transform spectrometer (DRIFTS) attachment with a resolution of 4 cm⁻¹. Reflective gold-coated polycrystalline Si wafers were used as the substrate for the measurement. A background measurement was taken using a bare substrate and then the Si NPs were deposited by drop casting from toluene. Samples were dried on a hotplate at 100°C in an Ar atmosphere for 10 min. Spectra were baseline-corrected using the concave rubberband correction method (2 iterations).

**DNP solid-state NMR measurements.** DNP NMR experiments were acquired on a Bruker 9.4 T 400 MHz/263 GHz Bruker solid-state NMR/gyrotron equipped with an AVANCE III console. A Bruker 3.2 mm triple resonance probe was configured in 1H-X mode capable of tuning from 13C to 113Cd for CdPs NPs. For the Si NPs the DNP 3.2 mm triple resonance probe was configured to 1H-13C-29Si and for the Cd,P, NPs the probe was configured to 1H-203P-113Cd.

The radiofrequency (rf) pulses for 1H and 13C were calibrated using 1H NMR spectra NMR. Solution 1H NMR spectra were obtained with a Bruker 9.4 T 400 MHz/263 GHz Bruker solid-state NMR/gyrotron equipped with an AVANCE III console. A Bruker 3.2 mm triple resonance probe was configured in 1H-X mode capable of tuning from 13C to 113Cd for CdPs NPs. For the Si NPs the DNP 3.2 mm triple resonance probe was configured to 1H-13C-29Si and for the Cd,P, NPs the probe was configured to 1H-203P-113Cd.

In both CP-D-HMQC and INEPT HETCOR experiments inhibitor diffusion, CP-CPMG,114 CP-MAT,89 refocused-INADEQUATE92 and CP spin diffusion,70 CP-TEDOR,115 constant time116 CP-D-HMQC117 and INEPT HETCOR118 experiments were performed with previously published pulse sequences. The refocused-INADEQUATE pulse sequence was modified to incorporate CPMG signal detection. In both CP-TEDOR and CP-D-HMQC pulse sequences dipolar recoupling was performed with a REDOR scheme119 where recoupling pulses were centered at one-quarter and three-quarters of the rotor cycle. The REDOR recoupling pulses were phase cycled with the XY-8 scheme120 to compensate for offsets and pulse imperfections. During acquisition all experiments utilized SPINAL-64121 for 1H heteronuclear decoupling with a 100 kHz 1H rf field. For a more detailed explanation of the solid-state NMR experiments performed please see the SI.
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REFERENCES


