Probing the Structure and Composition of Nanomaterials with Optimized DNP SENS Sample Preparations and Fast MAS DNP

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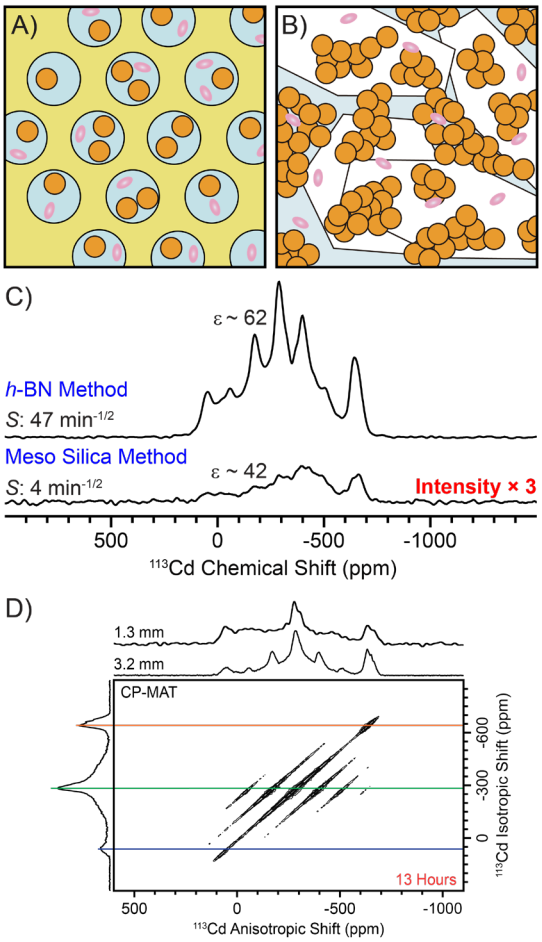

Figure 1. Schematic of DNP QD sample preps: (A) mesoporous silica impregnation method and (B) *h*-BN powder mixing method. (C) DNP enhanced ^{113}Cd CP-CPMG spectra with DNP enhancements and sensitivity indicated. (D) Comparison of ^{113}Cd CP-MAT compared to a fast MAS DNP ^{113}Cd spectrum. The fast MAS DNP ^{113}Cd spectrum eliminates spinning sidebands and the need for MAT experiments to obtain isotropic shifts.

Semiconductor nanoparticles (NPs) have a wide range of potential applications including, but not limited to, LEDs, solar cells, batteries, solid-state lighting, catalysts, bio-sensors, etc.[1] The properties and functionality of NPs are controlled and modified by altering their surface structure. Therefore, the characterization of the surface structure is crucial for the rational design of improved NPs. Solid-state NMR (SSNMR) spectroscopy is an ideal probe of surface structure; however, poor sensitivity makes it challenging to characterize dilute surface sites. DNP surface enhanced NMR spectroscopy (DNP SENS) has emerged as a powerful method to enhance the sensitivity of solid-state NMR experiments on inorganic materials. Previously, DNP SENS was performed on colloidal (NPs) by dispersing them in the pores of silica with polarizing agent solution (Figure 1A).[2] Using this approach, challenging 1D and 2D surface-selective NMR experiments could be performed.[2-3] However, this sample preparation results in dilution of the NPs and silica has unfavorable dielectric properties for DNP.

Here we demonstrate improved sample preparation protocols for DNP SENS experiments on NPs and use them to perform SSNMR experiments that were previously considered challenging or impossible. Using CdS NPs and ^{113}Cd SSNMR experiments we systemically optimized the NP sample preparation for DNP. We first tested several different support materials to disperse the NPs. Hexagonal boron nitride (*h*-BN) yielded 2-4 times higher DNP enhancements than silica. Next, we found that the NPs could be deposited as precipitated solids on *h*-BN or mixed as solids to increase the NP concentration (Figure 1B) while maintaining high DNP enhancements. Our new procedure yields a ca. 10-fold improvement in sensitivity (Figure 1C), enabling challenging 2D correlation experiments such as ^{113}Cd-^{113}Cd CP-INADEQUATE, ^{113}Cd-^{113}Cd CP-MAT (Figure 1D) and ^{113}Cd-^{113}Cd spin diffusion to be performed in hours. These 2D NMR experiments illustrate the symmetry and connectivity of the different Cd surface sites. DNP SSNMR was also applied to dodecyl functionalized Si NPs, which we have previously characterized with fast MAS solid-state NMR.[4] With DNP we obtained a natural abundance 2D ^{13}C-^{29}Si correlation spectrum showing bonding of surface Si and C atoms. We have also investigated the use of fast MAS DNP to further enhance NMR sensitivity. Fast MAS allows DNP enhanced scalar ^{1}H-^{29}Si SSNMR spectra of Si NPs to be obtained and simplifies DNP ^{113}Cd SSNMR spectra by eliminating spinning sidebands.

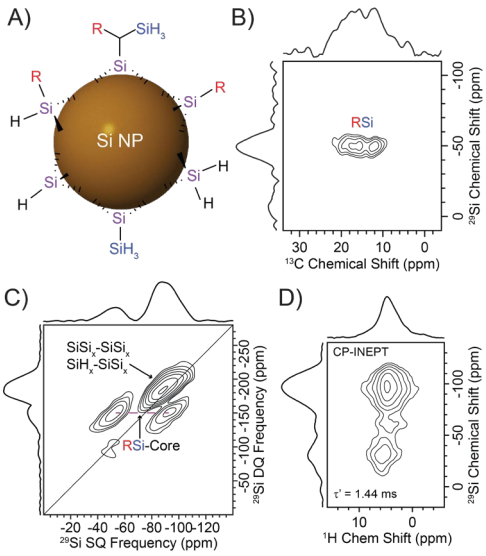

Figure 2. (A) Proposed Si NP surface species. DNP-enhanced 2D (B) ^{13}C-^{29}Si TEDOR, (C) ^{29}Si-^{29}Si INADEQUATE and (D) ^{1}H-^{29}Si scalar INEPT spectra.

References:(1) Kovalenko, M. V. et. al. ACS Nano, **2015**, *9*, 1012-1057. (2) Piveteau, L. et. al. *J. Am. Chem. Soc.* **2015**, *137*, 13964-13971. (3) Piveteau, L. et. al. ACS Central Science **2018**, *4*, 1113-1125. (4) Hanrahan, M. P. et. al. *Chem. Mater.* **2017**, *29*, 10339-10351.