

DETECTION OF MONO AND SUB-MONOLAYER MOLECULES ADSORBED ON NANO-PARTICLES BY SETS AND PROTON SOLID STATE NMR

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Introduction

The discovery of surface enhanced Raman scattering (SERS) impacted surface science and spectroscopy because of its extremely high surface sensitivity[1]. However, SERS had not developed as many people had hoped to be a powerful surface diagnostic technique that can be widely used because of some obstacles. First, only noble metals Au, Ag, and Cu, and a few transition metals could provide large enhancement. Second, even for the above SERS-active metals, limited kinds of adsorbates were found to give enhanced Raman spectra of high quality. These obstacles severely limit the widespread applications of SERS involving probing molecular vibrations at the interfaces of composites of both fundamental and practical importance[2].

^{13}C solid-state NMR (SSNMR) is a powerful method for structural analysis of bulk solid molecules[3]. However, the poor sensitivity of ^{13}C SSNMR has required larger amount of sample and longer measuring time, because of the low abundance of ^{13}C . For surface studies, ^{13}C SSNMR requires larger surface area such as Au nanoparticles with diameters of 2 – 4 nm. Proton solid state NMR (^1H SSNMR) is an attractive alternative to ^{13}C , particularly for unlabeled systems and samples in limited quantities because of its high sensitivity[3,4]. However, the strong ^1H - ^1H dipolar interaction veils many important information and limits the use of ^1H SSNMR.

In this abstract we introduce a new analytical strategy for nano-particle surface chemistry using ^1H SSNMR spectroscopy with enhanced resolution under very fast magic angle spinning. The ^1H SSNMR spectroscopy with enhanced resolution can not only provide spectra of high quality for the monolayer or sub-monolayer of adsorbed molecules on nano-particles, but also provide information of affinity and dynamics of the surface species.

Experimental

Materials

Octadecene (ODE, 90%), oleylamine (OLA, 70%) and 4-aminophenyl disulfide (APDS, reagent grade) were purchased from Aldrich. $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ (99.9%+) was from Shangjuly Chemical Co., Ltd., China.

Specimen preparation

Gold nano-particles adsorbed with OLA were prepared as follows. In a 30 mL Schlenk flask, 5 mL of ODE and 0.5 mL of OLA, under vigorous stirring, was heated to 220 °C under Ar flow with a heating mantle. A 0.3 mL methanol solution of 56.3 mM HAuCl_4 was injected rapidly. The appearance of the mixture changed from yellow to colorless immediately. After this, the mixture underwent a sequential color change from slightly red, to red, to deep red, and finally turned blackish blue within 1 min. The reaction mixture was then quenched in an ice bath for 20 min, whereby a solidified chunk was formed. The solid mixture was then put into a 40 °C water bath for 5 min, allowing complete melting of the ODE/OLA mixture, and was then transferred to a 10 mL vial. Upon standing overnight, a blackish blue precipitate was formed at the bottom of the vial (total mixture volume 5.2 mL), and the supernatant turned colorless. The mixture was placed in a 40 °C water bath for 1 min and shaken thoroughly to generate a homogeneous mixture. After 4 mL of the mixture was centrifuged at 4500 rpm for 3 min, the colorless supernatant was decanted, and the precipitate was rinsed with 4 mL of ethanol/toluene (20:1, v/v) mixed solvent thoroughly three times, followed by centrifugation at 4000 rpm for 3 min. The obtained precipitate was allowed to dry under ambient conditions.

Gold nano-particles adsorbed with OLA were put into 1 mM ethanol solution of APDS to proceed the replacement, and then the resultant nano-particles were allowed to dry overnight.

Apparatus and procedures

SERS spectroscopy was performed on a Bruke Multi RAM FT-Raman spectrometer. The ^1H SSNMR of the adsorbed molecules on nano-particles were measured on a Varian UNITYplus-400 NMR spectrometer. We define very fast MAS as above because MAS at about 25 kHz induces crucial changes in spin dynamics for organic solids by eliminating the majority of ^1H - ^1H and ^1H - ^{13}C dipolar couplings.

Result and discussion

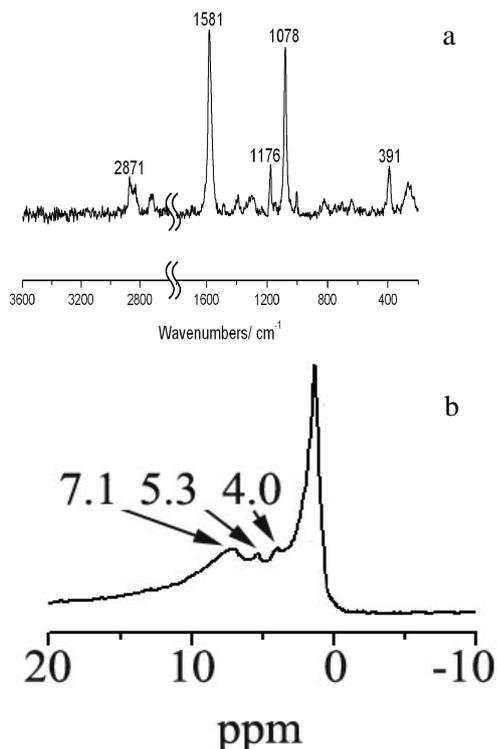


Fig.1: SERS (a) and ¹H SS NMR (b) spectra for 4-APDS replaced OLA on Au (15 nm).

Figure 1 shows SERS and proton solid state NMR spectra of replacement reaction of 4-aminophenyl disulfide (4-APDS) and oleylamine (OLA) on Au (15 nm). SERS spectrum provide information of the molecular orientation of 4-APDS. But SERS does not quantitatively tell us the remaining of OLA. NMR spectrum provide rich information about proton-containing groups, such as CH, NH, aromatic H as well as water. About 11 wt% of OLA remained on Au after the reaction, no matter how long the reaction ran and how high the reaction temperature was.

A multi-pulse (*N*cycles) dipolar filter ¹H experiment was used to select the ¹H magnetization with a weak dipole-dipole interaction. This method has also been applied to distinguish a “mobile” component from a multiphase composite. As *N*cycles increased in the dipolar filter experiment, the signals of the “rigid” parts were suppressed, while the mobile components show an isolated signal.

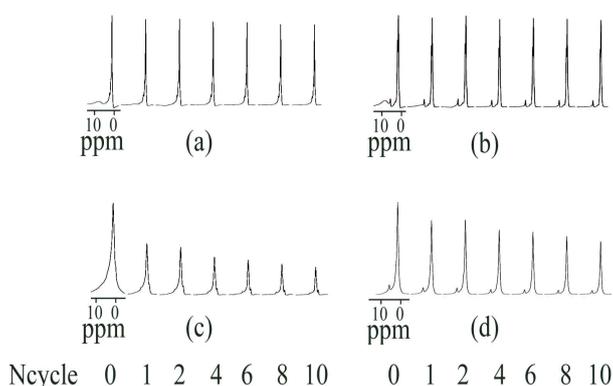


Figure 2. The 10-pulse dipolar filtered ¹H SSNMR spectra for (a) bulk octadecanethiol, (b) OLA, (c) Octadecanethiol on Au and OLA on Au.

Figure 2 shows ¹H SSNMR spectra for bulk octadecanethiol and OLA, and their monolayer adsorbates on Au nano-particles. The reduction in NMR intensities for the adsorbed thiol and OLA as *N*cycles increased indicates that the surface species are restricted in molecular motion. One can also conclude that octadecanethiol has a stronger affinity on Au than OLA since the peak intensities changed faster and greater for the adsorbed thiol than OLA. It is known that thiol can chemically reacted with gold and NH₂ can only physically adsorbed on its surface. Here we demonstrate an unique application for NMR experiments in studying chemically and physically adsorptions on surfaces.

Conclusion

We demonstrate that ¹H SSNMR can easily detect monolayer or sub-monolayer adsorbed molecules on nano-particles. This combination of SERS and NMR opens many opportunities for scientists in various disciplines such as analytical chemistry, molecular biology, and nano-structured materials.

References

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