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Core–shell nanoparticle based SERS from hydrogen adsorbed on a rhodium(111) electrode†

Jian-Feng Li, Jason R. Anema, Ying-Chao Yu, Zhi-Lin Yang, Yi-Fan Huang, Xiao-Shun Zhou, Bin Ren and Zhong-Qun Tian*

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We present the first *in situ* surface Raman spectra of hydrogen on rhodium under electrochemical conditions using gold-core rhodium-shell (Au@Rh) nanoparticles for SERS or gold-core silica-shell (Au@SiO_2) nanoparticles for SHINERS. The advantage of SHINERS lies in the versatility to study single crystal surfaces such as the H–Rh(111) system.

Surface-enhanced Raman scattering (SERS) is a powerful technique for adsorbate detection and characterization because it is sensitive down to the single-molecule regime and because of the rich structural information that it offers.[1] SERS suffers from a lack of substrate generality, however, as a strong enhancement effect can be obtained only from nanostructured free-electron metals (the noble metals Au, Ag and Cu are most commonly used).[1] Our group has sought to expand the substrate–material generality of SERS to include group VIIIB transition metals, both directly[2–5] and through the use of "borrowed SERS" strategies wherein the weak SERS activity of the transition metal is augmented by additional enhancement from a nearby noble metal nanostructure having good surface plasmon resonance (SPR) properties.[6,7] It is the latter of these two approaches that we employ in the present work.

Hydrogen is an important adsorbate in electrochemistry and energy related applications. The evolution of hydrogen gas is a common problem in electrochemical systems when the applied potential is sufficiently negative for the reductive dissociation of water to occur.[8] Also, a hydrogen-based energy economy looks quite promising, therefore surface structures and surface processes involving adsorbed hydrogen are expected to become increasingly important.[9,10] The Raman scattering cross-section of hydrogen is very small however, and surface hydrogen is quite difficult to detect on any substrate.

In this work we present the first SERS (and also the first Raman) spectra of hydrogen adsorbed on Rh *in situ* under electrochemical conditions. This was accomplished by employing two different strategies for borrowing SERS activity.

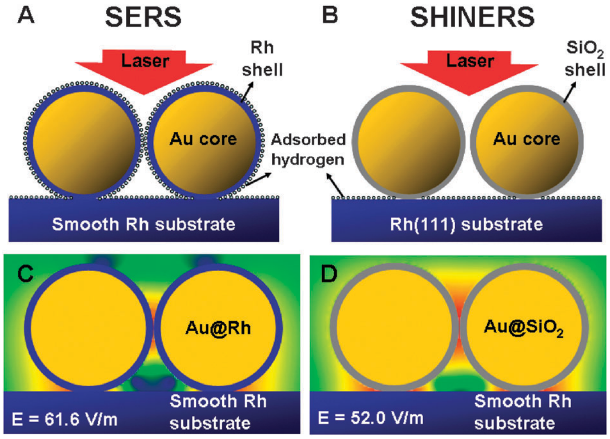

Fig. 1 Two different versions of the "borrowed SERS" strategy were used to obtain signal from hydrogen on Rh. An ultrathin Rh shell was added to a Au core and the resulting NPs were spread over a smooth Rh electrode (A); then an ultrathin SiO_2 shell was added to a Au core and the resulting NPs were spread over a Rh(111) electrode (B). The FDTD method was used to map electric field-strength in the vicinity of a 2 × 2 array of Au@Rh NPs on smooth Rh (C) and a 2 × 2 array Au@SiO_2 NPs on smooth Rh (D).

The first strategy involves adding an ultrathin shell of Rh to a Au nanoparticle (NP) (Fig. 1A). Here, enhanced electromagnetic field-strength extends from the surface of the core to the surface of the shell where it increases the intensity of Raman scattering from hydrogen adsorbed there. The shell must be ultrathin because the enhanced field decays exponentially with distance from the surface of the noble metal.[1] However the shell must be thick enough to possess bulk properties (about 5 atomic layers) if conclusions about the bulk are to be drawn. Electrochemical experiments are carried out by placing the Au@Rh NPs on a smooth Rh electrode, and signal arises from hydrogen on the surface of the electrode in addition to hydrogen on the surface of the NPs. The Rh shell is added by wet chemical methods so it must be polycrystalline, and a polycrystalline electrode is also employed.

The second strategy involves coating a Au NP with an ultrathin SiO_2 shell and again spreading the structure on a bulk sample of Rh (Fig. 1B). The gold core enhances the

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State Key Laboratory of Physical Chemistry of Solid Surfaces and College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, 361005, China. E-mail: zqtian@xmu.edu.cn; Fax: +86 592-2186979; Tel: +86 592-2186979

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incident (and Raman-scattered) radiation as before, but the shell plays a different role. In this case, it prevents the core from perturbing the electronic structure of the underlying Rh substrate. We call this method shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS).[7] The greatest advantage of our SHINERS technique is the versatility it gives to SERS. These NPs can be spread over any surface, and in the present work we add them to a single crystal of Rh.

Fig. 1C and D show the distribution of electric field-strength surrounding a 2 × 2 array of Au@Rh NPs and a 2 × 2 array of SHINERS NPs, each placed on a smooth Rh surface, as calculated by the finite-difference time-domain (FDTD) method.[11] In a first approximation, SERS intensity scales with the fourth power of electric field-strength,[1] so the "hottest" regions in Fig. 1C and D (red) are expected to be most SERS-active.

55 nm Au NPs were synthesized according to Frens' method[12] for use as the core. In order to add a 1–2 nm Rh shell, 1 mL of 39 mM sodium citrate and 2 mL of 1.0 mM $RhCl_3$ were added to 30 mL of the Au NP sol. The resulting mixture was refluxed for 3 hours to ensure complete reduction of $RhCl_3$ on the surface of the Au NPs by sodium citrate. The NPs were then washed and concentrated using a centrifuge.

The final diameter (D) of our Au@Rh core–shell NPs may be calculated according to the relation

$$D = D_{\mathrm{Au}}\left(1 + \frac{V_{\mathrm{M,Rh}}N_{\mathrm{Rh}}}{V_{\mathrm{M,Au}}N_{\mathrm{Au}}}\right)^{1/3}$$

where D_{Au} is the experimentally-measured average diameter of the Au seeds, $V_{\mathrm{M,Rh}}$, $V_{\mathrm{M,Au}}$, N_{Rh} and N_{Au} are the molar volumes and molar number of Rh and Au, respectively. Therefore, shell thickness can be estimated by $(D - D_{\mathrm{Au}})/2$ and we obtained a value of 1.6 nm. In order to verify this number we dissolved our Au@Rh NPs with aqua regia, measured the relative amounts of Au and Rh present by atomic emission spectroscopy (AES), and calculated a Rh shell thickness of 1.7 nm.

SHINERS NPs were prepared by a method that is based on those of Frens[12] (Au core) and Liz-Marzán *et al.*[13] (SiO_2 shell). A detailed description of the method used to prepare them will be given in a couple of forthcoming articles.[14,15] Since the Raman scattering cross-section of hydrogen is very small and field-strength decays exponentially with distance from the noble metal core, it may be desirable to use a 1 nm SiO_2 shell with pinholes instead of a 2 nm shell without pinholes. It should be pointed out that this can be done because pinholes are of no consequence for the H–Rh system. First, the shell will keep the Au core from making electrical contact with the Rh surface, perturbing its electronic structure and causing an additional Stark effect, provided the pinholes are small. Second, hydrogen is not strongly adsorbed on Au so a H–Au peak will not appear in the H–Rh spectrum. The actual thickness used was between 1 and 2 nm, likely having some pinholes.

Scanning electron microscope (SEM) images of the Au@Rh and Au@SiO_2 NPs are provided in Fig. 2A and B respectively. The absorption spectra of a 55 nm bare Au NP sol, a 55 nm Au@1–2 nm Rh NP sol and a 55 nm Au@1–2 nm SiO_2 NP sol are provided in Fig. 2C. It may be seen that neither the 1–2 nm Rh shell nor the 1–2 nm SiO_2 shell have a significant effect on the surface plasmon resonance of the underlying Au core.

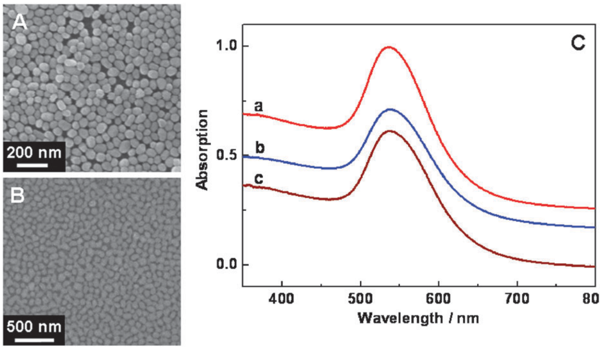

Fig. 2 SEM images of Au@Rh NPs and Au@SiO_2 NPs appear in A and B. Absorption spectra for bare Au NPs (red curve, a), Au@Rh NPs (blue curve, b) and Au@SiO_2 NPs (brown curve, c) are given in C.

Electrochemical SERS measurements were performed using a LabRam I confocal microprobe Raman system (Jobin-Yvon, France) and a home-built electrochemical cell. A 2 mm diameter Rh electrode was polished consecutively with 3, 1, 0.3 and 0.05 μm mesh alumina powder, then 15 μL of clean concentrated Au@Rh NP sol were added to the surface. A Rh(111) electrode was prepared by flame-annealing the end of a 1 mm diameter Rh wire to create a 3 mm diameter bead, then 3 μL of clean concentrated SHINERS NP sol were added. A Pt wire was used as the counter electrode and a saturated calomel electrode (SCE) was used as the reference. The electrolyte solution employed was 0.1 M in sodium perchlorate. The excitation wavelength was 633 nm.

SERS spectra of hydrogen on Au@Rh/smooth Rh are presented in Fig. 3A. The potential was stepped in the negative direction, and hydrogen was generated by the reductive dissociation of water at potentials more negative than about −1.0 V. The spectra in Fig. 3B are analogous to those in Fig. 3A, except that deuterium was generated from D_2O. We use Fig. 3B to confirm assignment of the band in Fig. 3A: a H–Rh/D–Rh frequency ratio of 1.4 is observed, and this value is characteristic of a H-surface *vs.* D-surface stretching frequency shift.[16]

SHINERS spectra of hydrogen on Rh(111) are presented in Fig. 4. Again, the potential was stepped in the negative

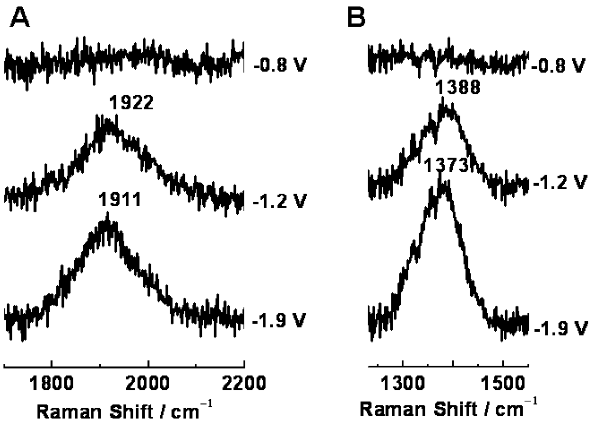

Fig. 3 SERS spectra of hydrogen (A) and deuterium (B) adsorbed on Au@Rh/smooth Rh under electrochemical conditions.

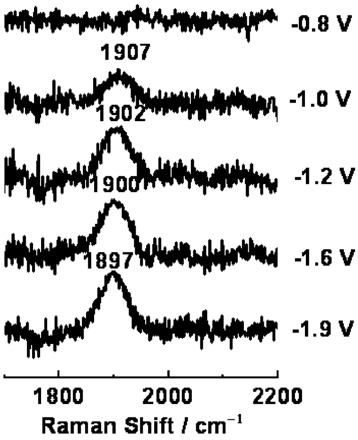

Fig. 4 SHINERS spectra of hydrogen on Rh(111).

direction and the onset of hydrogen adsorption was observed at about −1.0 V. A shift in the frequency of the H–Rh stretching band with applied potential (an electrochemical Stark effect) is seen in all of Fig. 3A, B and 4.

Spectral peaks are much sharper in Fig. 4 than they are in Fig. 3A. In the SHINERS spectra obtained from hydrogen on the atomically flat surface of Rh(111), peak width is about half of what is seen in the SERS spectra of hydrogen on Au@Rh/smooth polycrystalline Rh. This is because single crystal surfaces are well defined and structurally simple whereas polycrystalline ones are ill defined and consist of many different facets. Each facet may yield a slightly different position for a given adsorbate vibrational band due to small differences in adsorption energy. These facet-induced differences cannot be resolved spectrally, and a single broad peak is observed. When a single facet is dominant in the sample, however, a considerably narrower band will be present in the spectrum. Thus, our comparative study illustrates the advantage of SHINERS over conventional SERS as the former can be used to examine single crystal surfaces whereas the latter cannot.

It may also be seen that peak intensity increases as the potential is stepped to more negative values. We have observed this phenomenon before, while examining potential-dependent SERS from water at the surface of Au, Au@Pd and Au@Pt NP coated electrodes.[17] We attribute it to increasing electron spillover, from the metal into the electrolyte solution, with progressively more negative potential. Based on a related phenomenon called electron-enhanced Raman scattering (EERS),[18,19] we propose that this electron tail increases the polarizability of the H–Rh bond and therefore also the Raman scattering cross-section of its stretching vibration.

To summarize, the adsorption of hydrogen on Rh was observed *in situ* under electrochemical conditions using two different versions of the borrowed SERS strategy. These results are significant because the Raman scattering cross-section of hydrogen is so small, surface-enhancement from Rh is so weak, and submersion of the probed surface in an electrolyte solution causes a further decrease in signal intensity due to absorption of light by the aqueous solvent and scattering of light at the air/water interface. The greatest advantage offered by our SHINERS technique lies in the versatility it bestows upon SERS. In the present work, this is exemplified by the fact that a single crystal could be examined by SHINERS, whereas only polycrystalline Rh could be examined using the Au@Rh core–shell NP method.

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