Characterization of surface water on Au core Pt-group metal shell nanoparticles coated electrodes by surface-enhanced Raman spectroscopy

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We utilized the strategy of 'borrowing SERS activity', by chemically coating several atomic layers of a Pt-group metal on highly SERS-active Au nanoparticles, to obtain the first SERS (also Raman) spectra of surface water on Pt and Pd metals, and propose conceptual models for water adsorbed on Pt and Pd metal surfaces.

Water is the commonest solvent and plays vital roles in life and many chemical processes. For instance, in electrochemistry the configuration and orientation of water in regions immediately adjacent to the metal surface can directly affect the electrode/aqueous solution interface reactions.[1–3] Unfortunately, detailed information on water molecules lodged on the interface collected by conventional electrochemical methods has not been straightforward and uncontroversial.[4,5] Therefore, clarifying the structure and orientation of interfacial water at microscopic-level can greatly improve our fundamental understanding of the electrode/electrolyte interface phenomena, which is still an ongoing issue in surface chemistry.

A variety of *in-situ* spectroscopic techniques developed recently have provided new information about the microscopic structure and dynamics of interfacial water molecules.[6–11] However, the interactions between water molecules and electrolyte ions as well as those between water and electrode surfaces are very complex, and a detailed insight on interfacial water has remained elusive. Surface-enhanced Raman scattering (SERS), as a highly sensitive tool for investigating vibrational characteristics of surface species,[12–14] not only can avoid extensive interference from enormous bulk water but also tremendously enhance Raman signals of surface molecules. There have been some interesting SERS studies revealing the dependency of the structure of surface water on potentials, ions, and pH.[15,16] However, all these studies are limited to coinage metals (*i.e.*, silver, gold and copper) that are known to show a large surface enhancement factor up to 10^5 or more. Although our group has confirmed that many transition metals (VIII B group elements) of practical and fundamental importance can directly generate reasonable SERS activities as revealed by many adsorbed labels, there has been no report so far on SERS of interfacial water on transition metals.[17,18] This absence mainly arises from the fact that water has a very small scattering cross section. It is therefore highly desirable to seek an alternative way to overcome this obstacle.

Recently, we utilized the strategy of 'borrowing the SERS activity'[19–21] by chemically coating several layers of a transition metal on highly SERS-active Au nanoparticles. Through long-range effects of the electromagnetic enhancement created by the highly SERS-active core underneath, good-quality SERS spectra of adsorbates on transition metal surfaces have been obtained.[22] These core–shell nanoparticles have the chemical properties of the shell but show the enhancement of the core provided mainly through surface plasmon resonance. Therefore, their SERS signals can be significantly enhanced in comparison to those from pure transition metal nanoparticles.[22,23] This strategy is appreciably advantageous to investigate some molecules with a low Raman cross section that were impractical to study in the past. Accordingly, we have successfully extended the SERS study of water to several transition metals. In this communication, we present SERS of water on two typical Pt-group metals, platinum and palladium, in the potential region of hydrogen evolution, wherein the hydrogen is adsorbed at the Pt surface while absorbed inside Pd bulk. The SERS spectra thus obtained allow us to scrutinize the interfacial structure of water on these two surfaces and also to compare the results with those on a gold surface as a typical SERS active substrate.

We first synthesized gold particles with about 55 nm diameter as cores, onto which 4–5 monolayers (corresponding to around 1.4 nm) of either platinum or palladium were coated to form core–shell nanoparticles.[23] The Au@Pt nanoparticle sol was prepared according to the following protocol: a freshly prepared 55 nm gold seed sol was added into 1.0 mM H_2PtCl_6 solution, and the mixture was heated up to 80 °C. Under the conditions, one half volume of 10 mM ascorbic acid to that of the H_2PtCl_6 solution was slowly injected into the above mixture through a step motor controlled syringe. Stirring was continued for another 30 min to ensure a complete reduction of H_2PtCl_6 and deposition of platinum metal. The mixture turned from red brown to dark brown indicating a reaction has occurred for the formation of products (*i.e.* Au@Pt). The thickness of the Pt shell was controlled simply by changing the concentration ratio of H_2PtCl_6 to Au sols. The method for preparing a Au@Pd nanoparticle modified Pd electrode is similar except that a much lower temperature at around 4 °C was used during the preparation of Au@Pd nanoparticles. After several rounds of cleaning and concentration by centrifugation, Au@Pt or Au@Pd core–shell nanoparticles were coated on smooth Pt or Pd electrode surfaces, respectively, and were dried in vacuum.

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Henceforth, in this report Pt and Pd represent the Au@Pt and Au@Pd core–shell nanoparticle modified electrodes, respectively.

Fig. 1 shows potential-dependent SERS spectra (recorded by a LabRam I with a He–Ne laser of about ~8 mW, as well as the spectral acquisition time of 30 s with averaging 10 times) of water adsorbed on Pt, Pd and Au surfaces in 0.1 M $NaClO_4$ in the potential region of the hydrogen evolution reaction (HER), wherein bands at around 1615 cm^{-1} and 3400 cm^{-1} are bending and stretching vibrations, respectively, of water molecules. It should be emphasized, firstly, that the SERS intensity of the bending vibration is just about the same as that of the stretching one. This is in clear contrast to the fact that the Raman intensity of the bending band is normally about 20 and 100 times lower than that of the stretching band for bulk and gaseous water, respectively.[17] Secondly, the broad band at around 2000 cm^{-1} observable only on the Pt surface is ascribable to the Pt–H stretching vibration mode.[24,25] To our knowledge, this is the first recorded Raman spectrum of surface hydrogen together with water.

In order to confirm our assignment, we have examined isotopic effects under comparable conditions. Fig. 2 shows a series of potential-dependent SERS spectra of deuterated water on the Pt electrode. In this case, the bending and stretching bands of normal water (1615 and 3421 cm^{-1}) observed in Fig. 1 are replaced by peaks around 1187 cm^{-1} and 2490 cm^{-1} corresponding to D_2O adsorbed on the Pt electrode surface.[26] Accordingly, the peak at *ca.* 1419 cm^{-1} must correspond to that at 1984 cm^{-1} in Fig. 1 and thus can be safely assigned to the stretching of Pt–D,[26] thus confirming the SERS band assignment.

The strong potential-dependence in the spectral frequency and intensity clearly and characteristically demonstrates that these signals must be derived from the surface water molecules but not from the bulk water for which the Raman bands can be observed at 1641, 3224 and 3434 cm^{-1} for the H–O–H bending and O–H stretching vibrations.[17] Fig. 3 shows that for the water stretching frequencies, the extent of the frequency shifts corresponding to pplied potentials (*i.e.*, vibrational Stark effects) on Pt (*ca.* 14 cm^{-1}/V) is significantly less than those on the Au and Pd electrodes (64 cm^{-1}/V and 76 cm^{-1}/V, respectively), whereas their frequencies decrease in the order of Pt, Pd, and Au (see Fig. 1).

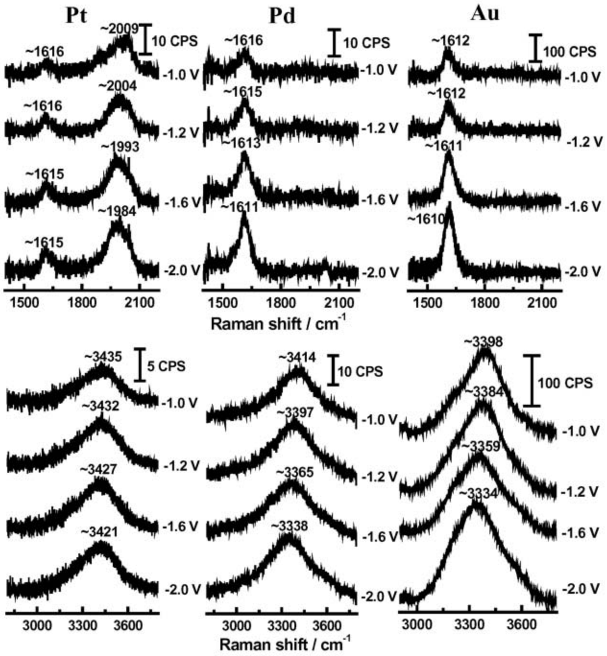

Fig. 1 SERS of water adsorbed on Pt, Pd and Au at different potentials in 0.1 M $NaClO_4$ by excitation at 632.8 nm.

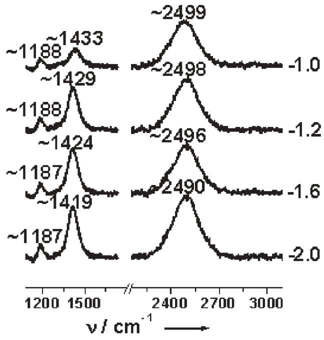

Fig. 2 SERS of deuterated water adsorbed on Pt at different potentials in 0.1 M $NaClO_4$ by excitation at 632.8 nm.

It should be noted that Stark tuning rates depend not only on the electric field strength across interfaces but also on the nature of chemical interactions of an adsorbate with surfaces. Because both the concentration of electrolyte solutions and the geometry of nanoparticles are almost the same for these three interfaces, we believe that the vibrational Stark effects from the electric field of double layers should be similar in the present systems. Therefore, the Stark tuning rate difference should arise primarily from different chemical interactions of interfacial water molecules with surfaces.

Accordingly, we propose three adsorption models in Fig. 4 to account for the observed spectral behavior of water in the potential region studied. On Pt, there is a full monolayer of on-top adsorbed hydrogen (that accounts for the strong band at 1984–2009 cm^{-1}),[25] above which water molecules are located as the second outer layer. The very small Stark tuning rate on Pt in Fig. 3 has led us to propose an adsorption model as illustrated in Fig. 4. Water molecules interact with the Pt surface through a chemically

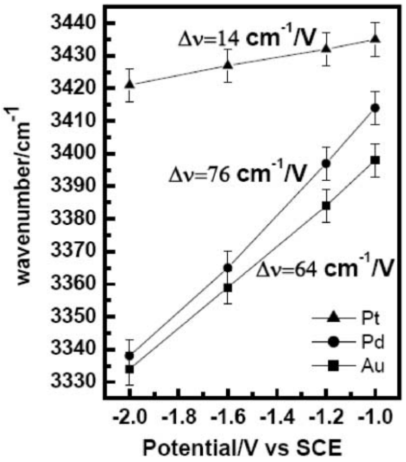

Fig. 3 Plots of stretching frequencies *versus* applied potentials for the O–H bonds of water adsorbed on Pt, Pd and Au electrodes in 0.1 M $NaClO_4$.

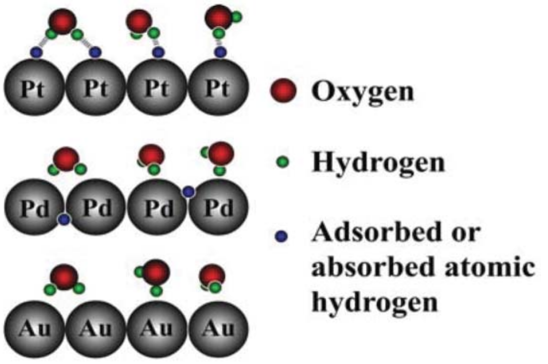

Fig. 4 Suggested models of interfacial water adsorbed on Pt, Pd and Au electrode surfaces.

adsorbed hydrogen monolayer. Since the water molecules are not directly in contact with the Pt surface, the effect of the applied potential on their vibration spectra must be small. Indeed, the O–H stretching vibrational frequency is close to that observed in the bulk solution.

Whereas it is widely accepted that Pd interacts strongly with H, we do not observe bands corresponding to a Pd–H vibration. The main reason may be that hydrogen atoms sit in hollow sites of the Pd surface, and may even be absorbed inside bulk Pd.[24] Such hydrogen atoms immersed in the sub-surface of Pd nanoparticles, as shown in Fig. 4, may have extremely low Raman cross sections for the Pd–H vibration, which is beyond the sensitivity of our instrument. On the other hand, water molecules can adhere onto the bare Pd surface as implied by the larger frequency shifts with applied potentials, *i.e.*, a larger vibrational Stark tuning rate. In contrast to the Pt and Pd metals, the interaction of Au with H atoms is very feeble.[27] Therefore, water molecules can be directly adsorbed on the Au surface through their hydrogen atoms (see Fig. 4), which also leads to a larger Stark tuning rate.

In order to understand the origin of enhanced Raman signals with core–shell structures, it is necessary to discuss the influence of the electromagnetic field enhancement and the chemical enhancement on Raman signals of interfacial water adsorbed on these core–shell nanoparticle coated electrodes. Based on the finite difference time domain method,[22] we simulated our experimental conditions. It was found that the core–shell nanoparticles can provide an enhancement of two orders of magnitude larger than the pure transition metal nanoparticles,[21,22] which is essential to detect the extremely weak SERS signals of water. Furthermore, it is of interest that the strong signals of interfacial water are only observed at more negative potentials than the potential of zero charge and further enhanced with negatively moving potentials, as seen in Fig. 1. Under this variation, the surface electronic tail penetrates into the solution to a distance of 1–3 Å with the more negatively moving potential.[28] It is also known that the metal conduction electron has high polarizability,[29] resulting in an enhancement of the local optical electric field at an adsorbed molecule on the surface of the metal cluster.[30] This effect could further contribute to the SERS enhancement of interfacial water.

In conclusion, using the high electromagnetic enhancement of the Au core to effectively boost the surface Raman signal on the shell metals, we have successfully obtained the first SERS (also the first Raman) spectra of surface water on Pt-group metals. On the basis of the SERS results, we propose conceptual models for water adsorbed on Pt and Pd surfaces in comparison to that on Au surfaces. This work may shed light and open new initiatives on complicated structures of interfacial water. Consequently, the core–shell nanoparticles can be used as a universal substrate with their high SERS activity, improving generality and broadening applicability of SERS. This special nanostructure may also be used as a substrate for surface-enhanced infrared spectroscopy and sum frequency generation spectroscopy. We are optimistic that surface vibrational spectroscopy will become an increasingly versatile and indispensable tool in fundamental and applied studies of interfacial structures and surface processes involving water molecules.

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