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SERS Not To Be Taken for Granted in the Presence of Oxygen

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Surface-enhanced Raman spectroscopy (SERS) has been widely explored by the broader scientific research community for chemical and biological sensing and measurements, as it combines the capability of molecular fingerprinting (i.e., the capability to differentiate between various molecular vibrations) with ultrahigh, sometimes single-molecule sensitivity.[1,2] Such a combination is unique and cannot be achieved with other spectroscopic techniques. A convenient way to build SERS-active nanostructures is to use Ag or Au nanoparticles as building blocks, either through aggregation of such particles in solution[1a] or immobilization of these particles at surfaces.[1b,3] Ag is generally preferred over Au as SERS-active element because of the up to 2 orders of magnitude greater enhancement factor. Ag is, however, prone to oxidation in air or water.[4] There is a dearth of knowledge about the effect of oxidation of the Ag surface on the SERS activity of Ag nanostructured substrates.

In this communication, we report that oxidation of the Ag nanoparticle (Ag NP) surface under ambient conditions has a dramatic effect on the adsorption and SERS detection limit of nitroaromatic molecules in aqueous solutions. We show for the first time that oxidation of the Ag NP surface hinders charge transfer from Ag to the aromatic ring and drastically decreases the detection sensitivity by ~5 orders of magnitude. We reveal that ultrasensitive SERS detection of nitroaromatic compounds can be achieved when oxidation of the surface-immobilized Ag NPs is inhibited by using argon gas.

Ag NPs with sizes of 45 ± 8 nm and a ζ potential of -35 mV (due to loosely bound citrate ions) were synthesized by a modified version of the Lee and Meisel method,[5] as described in the Supporting Information (SI). The Ag NPs were immobilized on the surface of glass coverslips attached as the bottom of custom-made sample cuvettes with a capacity of ~0.22 mL (for SERS experiments) or on the surface of silicon wafers (for XPS experiments) using an adsorbed polycation, poly(allylamine hydrochloride) [mass-average molecular mass (M_w) of 70 000 g/mol (Sigma-Aldrich)] as an intermediate layer. Substrates with a layer of densely immobilized Ag NPs (~135 nanoparticles/μm^2) were used in all experiments. Substrates used for XPS and SERS were kept under Milli-Q-purified water that was purged with either argon gas (Ar-purged substrates) or oxygen (O_2-purged substrates) for 3 to 5 min. XPS data suggest that slight oxidation of the Ag NP surface occurred when the substrates were kept in water purged with oxygen (see the SI). This was inferred from the shifts in the Ag 3d peak position toward lower binding energies.[6] Importantly, less oxidation was observed for substrates kept in Ar-purged water.

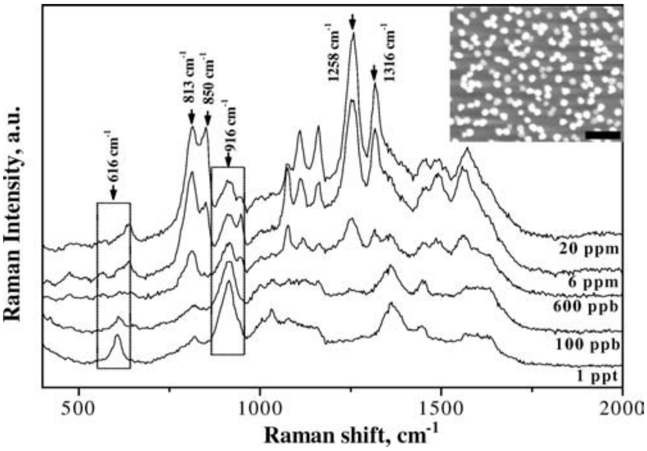

Figure 1. SERS spectra of *p*-nitrophenol (PNP) adsorbed at the surface of immobilized Ag NPs (shown in the inset, scale bar = 0.1 μm) obtained using Ar-purged aqueous solutions. Spectra were acquired using a laser power of ~1.8 mW at 532 nm excitation for 20 s. To evade the problem of spot-to-spot variability of the SERS signal,[7] the laser beam was defocused using a Nikon CFI60 10× objective (spot size ≈ 1 mm).

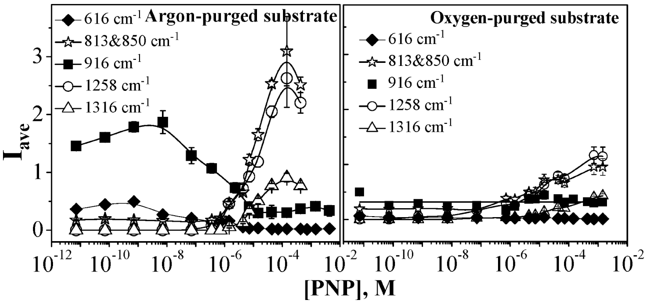

Figure 2. Integrated intensities of SERS out-of plane (616 and 916 cm^{-1}) and in-plane (813, 850, 1258, and 1316 cm^{-1}) bands of PNP observed for (left) Ar-purged and (right) O_2-purged substrates. Error bars show standard deviations calculated using five data points taken at different illumination spots.

We chose to study a series of nitroaromatic compounds because they are important materials in the production of drugs, dyes, explosives, and pesticides. *p*-Nitrophenol (PNP) is also the end product of the enzymatic reaction of acetylcholinesterase and paraoxon. Figure 1 shows SERS spectra collected using Ar-purged PNP solutions. Figure 2 quantitatively compares the SERS bands of PNP for Ar-purged and O_2-purged substrates. A striking observation is that with the Ar-purged substrates, two bands attributed to out-of-plane vibrations (at ~916 and 616 cm^{-1}, assigned to C−H out-of-plane bending and C═O out-of-plane

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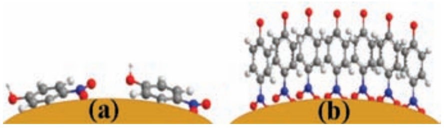
vibrations of the aromatic ring, respectively), dominated the SERS spectra in a range of ultralow concentrations of 1 ppt to 1 ppb (7.19×10^{-12} to 7.19×10^{-9} mol/L). These bands were shifted by 18−37 cm^{-1} to lower energies relative to the normal Raman PNP peaks[8] and were significantly broadened to widths of 40−50 cm^{-1}, indicating strong charge-transfer interactions between PNP and the Ag surface.[9] The presence of 616 and 916 cm^{-1} bands at ultralow PNP concentrations reflects the flat orientation of PNP molecules at Ag NPs. The latter reflects the selective enhancement of SERS bands whose transitions are normal to a metal surface.[2a] Remarkably, with the use of Ar-purged substrates, the limit of detection (LOD) of 1 ppt for PNP (two PNP molecules per Ag NP in this nonresonant SERS experiment) was easily achieved. At higher concentrations, the intensities of the in-plane PNP vibrational bands at 813, 850, 1110, 1163, 1258, 1316, 1486, 1450, and 1570 cm^{-1} increased at the expense of the out-of-plane 616 and 916 cm^{-1} band intensities (see Table 1 in the SI for a complete list of PNP peak assignments). This reflected the more vertical orientation of PNP as a result of surface crowding. During such reorientation, PNP remained attached to the Ag NP surface through the NO_2 group (Scheme 1).[8] It should be noted that molecular reorientations at Ag surfaces have been reported previously.[10] However, unlike in our case, such reorientations were thermally stimulated.

Scheme 1. Orientation of PNP Molecules at (a) Low and (b) High Analyte Concentrations on the Surface of Unoxidized Ag Nanoparticles



Strikingly, with O_2-purged substrates, the situation was dramatically different in two aspects: (1) at all PNP concentrations, the 616 and 916 cm^{-1} bands remained negligibly small in intensity (signal to-noise ratio ≈ 6), and (2) at saturation coverage (corresponding to a PNP solution concentration higher than 10^{-4} mol/L), the SERS intensities of all in-plane PNP bands were ~3 times lower than for the Ar-purged substrates. These results reflect the replacement of Ag−aromatic with silver oxide−aromatic contacts as SERS-inactive silver oxide[11] covered the surface of metallic silver. The effect of surface oxidation on the SERS activity of PNP might be twofold: (1) a decrease of the PNP−surface binding energy, and (2) suppression of the chemical-enhancement contribution, which is attributed to metal-to-molecule charge transfer, to the overall SERS activity (a factor of 3, as estimated from Figure 2). The oxidation effect on the LOD of PNP was dramatic, as shown by the LOD values of ~1 ppt (7.19×10^{-12} mol/L) and ~106 ppb (7.6×10^{-7} mol/L) for the Ar-purged and oxidized Ag surfaces, respectively.

Seeking to understand the generality of our findings, we also studied the binding of 2,4-dinitrophenol (DNP) and 2,4,6-trinitrophenol (TNP) to Ar-purged and O_2-purged substrates (data not shown). These results were very similar to those for PNP. First, as in the case of PNP, the intensities of the in-plane bands increased with increasing DNP and TNP concentration, indicating molecular reorientation at the nonoxidized Ag NP surface. Second, the out-of-plane vibrations remained pronounced down to ultralow (~1 ppt) concentrations of DNP and TNP.

In summary, we found that oxidation of Ag NPs in an aqueous environment drastically affects the SERS activity of Ag NPs and the LOD values for adsorbed nitroaromatic molecules. Although the oxidation of Ag metal under ambient conditions is widely known and reorientation of aromatic compounds on Ag surfaces triggered by increasing analyte coverage,[12] pH changes,[13] or applied potential[14] have been observed previously, this is to our knowledge the first report of the effects of Ag NP oxidation on the adsorption and LOD of aromatic molecules. As SERS-based environmental, chemical, and biological detection is usually conducted under ambient conditions in which Ag is oxidized by air or by water-dissolved O_2, understanding the effect of such oxidation on the SERS sensitivity is crucial for the development of ultrasensitive SERS-based chemical detection. Our findings will be applicable to broader and related fields of research, such as the case of self-assembly of a variety of low-molecular compounds or polymers (which often contain aromatic groups) with metal nanoparticles in aqueous environments, where binding affinity and orientation of the adsorbate may well be affected by metal oxidation.

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Supporting Information Available: Experimental details concerning Ag nanoparticle synthesis, SERS substrate preparation, and SERS and XPS measurements and a table of PNP peak assignments. This material is available free of charge via the Internet at http://pubs.acs.org.

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