

Spectroscopic and computational study of BPE adsorption on Ag/SiO₂ as a function of silver oxidation and adsorbate coverage

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Adsorption of a commonly used spectroscopic probe molecule BPE, trans-1,2-bis(4-pyridyl)ethylene, which consists of two pyridine rings joined by a CH=CH link (Figure 3), was studied on monodispersed Ag nanoparticles as a function of the adsorbate surface coverage and the extent of Ag oxidation. Monodispersed Ag nanoparticles with a diameter of ~50 nm supported on silica (Figure 1) were synthesized using a colloidal solution. The extent of Ag oxidation was varied with a time-controlled exposure to ozone and monitored with X-ray photoelectron spectroscopic (XPS) measurements.

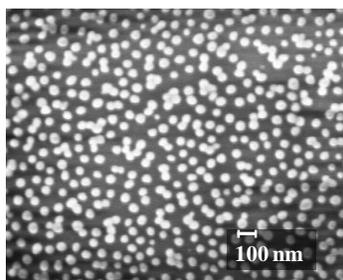


Figure 1. SEM image of monodispersed Ag particles supported on silica

Surface-enhanced Raman spectra (SERS) of adsorbed BPE exhibit two prominent peaks at 1590 and 1620 cm⁻¹ (Figure 2), which are assigned, respectively, to the pyridyl ring breathing and bridging C=C stretch based on DFT calculations. The relative intensity of these two peaks was found to change with the BPE surface coverage and also with the extent of Ag oxidation. The observed changes in Raman peak intensities are attributed to differences in BPE adsorption modes. DFT calculations suggest that BPE can adsorb in two configurations: vertical and horizontal (Figure 3). Although both adsorption modes are energetically similar at low coverage on metallic Ag, the vertical configuration becomes more preferable with increasing coverage due to lateral interactions. The opposite effect is predicted based on DFT calculations for the increase in the extent of Ag oxidation due to the greater stability of the horizontal BPE on oxidized Ag surfaces.

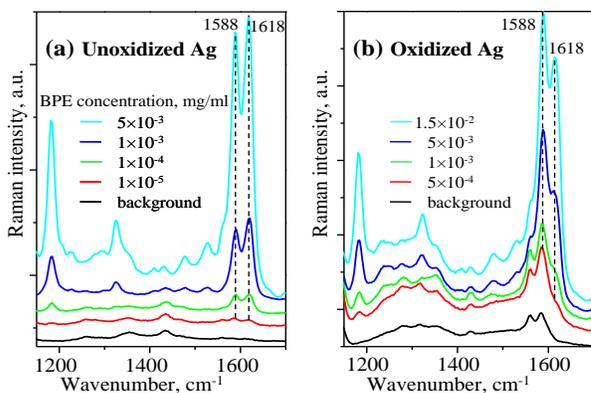


Figure 2. Surface-enhanced Raman spectra (SERS) of BPE as a function of solution concentration measured on (a) unoxidized and (b) oxidized Ag nanoparticles.

The closely integrated experimental-theoretical study for the first time identified at the molecular level the adsorption modes and energetics of BPE on silver surfaces and the effects of the adsorbate coverage and the extent of Ag oxidation.

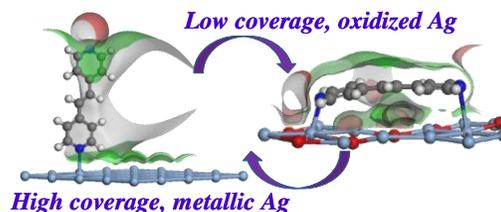


Figure 3. DFT models of BPE adsorbed in horizontal and vertical orientations with visualization of the electrostatic potential.