

Control of charge state and reactivity of single-sized silver nanoclusters supported on organic substrates

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Silver (Ag) is widely used in industrially essential catalytic reactions, such as Ullmann-type coupling reactions. Nanoclusters (NCs), composed of dozens of atoms, can design a variety of electronic states and high reactivity by atomically defining their size and by controlling their charge states. Developing NC-based catalysts requires a chemically stable surface support that prevents poisoning and degradation caused by reactions with unwanted gas molecules. An example of poisoning is the reaction with molecular oxygen (O₂), the most common active gas in the atmosphere. In this study, single-sized Ag₂₁ NCs were deposited on *p*-type hexa-*tert*-butyl-hexa-*peri*-hexabenzocoronene (C₆₆H₆₆: HB-HBC) modified substrates¹, and their charge states and reactivity at room temperature with O₂ were measured by ultraviolet/X-ray photoelectron spectroscopy (UPS/XPS).

Cationic Ag NCs synthesized in the gas phase by magnetron sputtering were size-selected using a quadrupole mass spectrometer and deposited under soft landing conditions. 0.6 monolayer (ML) of Ag₂₁⁺ was deposited on graphite substrates modified with a 2 nm thick HB-HBC layer. The samples were transported to a photoelectron spectrometer while maintaining ultra-high vacuum (~10⁻⁸ Pa) to investigate the charge and chemical state of the NCs by UPS/XPS measurements (He I α : $h\nu$ = 21.22 eV, Mg K α : $h\nu$ = 1253.6 eV). The sample was exposed to O₂ molecules defined in Langmuir (10⁻⁶ Torr · s) units at room temperature, and the reactivity of the surface-supported Ag₂₁ was evaluated using XPS measurements. Figure 1(a) shows the UPS spectra before and after Ag₂₁ deposition on the HB-HBC substrate. The peak position of the HOMO-2 of Ag₂₁/HB-HBC is about 0.7 eV larger than the 3.31 eV of the HB-HBC⁺ substrate (green line) where the HB-HBC is +1-valent. This suggests that the Ag₂₁

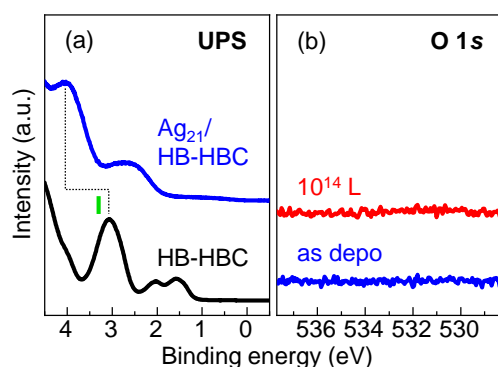


Fig. 1. (a) UPS spectra for an HB-HBC substrate before and after 0.6 ML of Ag₂₁ deposition. (b) XPS spectra of O 1s core levels for Ag₂₁/HB-HBC (0.6 ML) before and after 10¹⁴ L of O₂ exposure.

deposited HB-HBC substrate is strongly positively charged, while the Ag₂₁ takes on a large negative charge, forming a multivalent charge transfer state in Ag₂₁/HB-HBC. Figure 1(b) shows the XPS spectra around O 1s core levels before and after exposing 10¹⁴ L of O₂ to Ag₂₁/HB-HBC. There is almost no difference in intensity before and after exposure. Therefore, by using an HB-HBC modified substrate, we achieved a surface-supporting method that controls the charge state and suppresses poisoning by O₂. These results are promising for the development of nanocatalysts based on nanoclusters that can be used under atmospheric pressure.

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