A Well-Confined Redox Route to Silver Nanoparticles on the Surface of MoO_3

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The preparation of nanomaterials is a great challenge in the fields of synthetic chemistry and materials science because of the unusual properties that differentiate them from the bulk.[1−13] To utilize and optimize the chemical/physical properties of nanoscale metals, a number of workers have focused on the control of the size and/or shape of nanoparticles as well as their self-assembly into ordered structures by developing effective synthetic techniques. Several techniques, such as gas condensation,[14] irradiation,[15,16] sol−gel,[17,18] sonochemical deposition,[19] and nanostructured templates[20−22] for preventing the nanoparticles from irreversible aggregation, have been reported. Here, we report an effective well-confined redox method to prepare high-quality Ag nanoparticles. Our strategy was based on a self-redox reaction that employed reductive $[Na(H_2O)_2]_{0.25}MoO_3$ bronze and oxidative ion-exchanged silver ions. This in situ redox, at certain temperatures, led to the formation of Ag nanoparticles with tunable size.

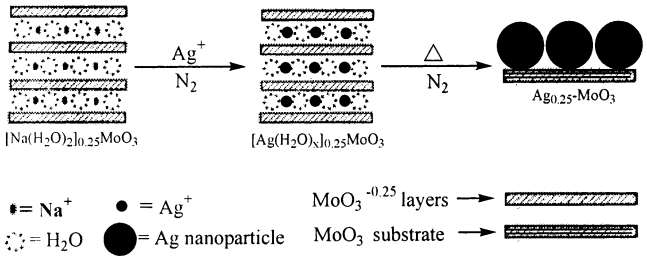

Figure 1. Formation of silver nanoparticles on the surface of the MoO_3 substrate. (Interlayer spacing of $[Na(H_2O)_2]_{0.25}MoO_3$, d_{020} = 9.72 Å, and of $[Ag(H_2O)_x]_{0.25}MoO_3$ (x = 1.5), d_{020} = 9.41 Å, and the size range of Ag nanoparticles is 3−10 nm.)

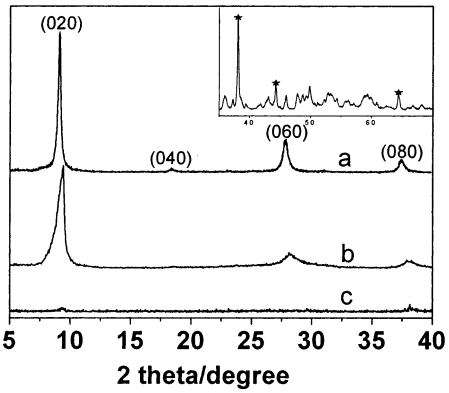

Figure 2. X-ray powder diffraction patterns for $[Na(H_2O)_2]_{0.25}MoO_3$ (a), $[Ag(H_2O)_x]_{0.25}MoO_3$ (b), and $Ag_{0.25}-MoO_3$ treated at 330 °C for 10 min (c). Inset is also for $Ag_{0.25}-MoO_3$ and the star-denoted peaks correspond to the cubic silver.

The synthesis of $[Na(H_2O)_2]_{0.25}MoO_3$ bronze was carried out according to a previously reported method.[23] The reaction of ion exchange of Na^+ by Ag^+ was first carried out in solution and then the self-redox reaction of $[Ag(H_2O)_x]_{0.25}MoO_3$ at 330 °C in N_2 followed. The schematic reactions 1 and 2 are illustrated in Figure 1.

$$[Na(H_2O)_2]_{0.25}MoO_3 + Ag^+ \rightarrow [Ag(H_2O)_x]_{0.25}MoO_3 + Na^+ \quad (1)$$

$$[Ag(H_2O)_x]_{0.25}MoO_3 \rightarrow Ag_{0.25}-MoO_3 + xH_2O \quad (2)$$

The identification of $[Ag(H_2O)_x]_{0.25}MoO_3$ was carried out by X-ray powder diffraction (XRD). Typical layered structures of $[Na(H_2O)_2]_{0.25}MoO_3$ (Figure 2a) and $[Ag(H_2O)_x]_{0.25}MoO_3$ (Figure 2b) showed similar diffractions and the difference in their structures was only due to the sizes of the hydrated ions within the layers as the d spacing in the 0l0 direction was modified. Since the hydrated ionic radius of Ag^+ ion is smaller than that of Na^+, the interlayer space of $[Ag(H_2O)_x]_{0.25}MoO_3$ becomes smaller than that of $[Na(H_2O)_2]_{0.25}MoO_3$. The diffraction

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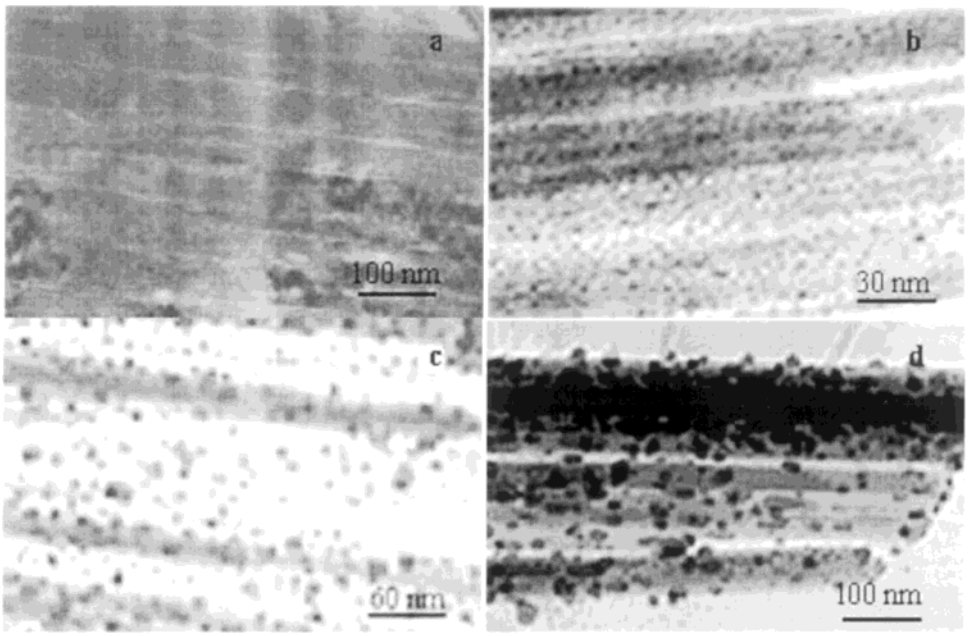

Figure 3. TEM images of layered $[Na(H_2O)_2]_{0.25}MoO_3$ (a); Ag nanoparticles on MoO_3 substrate formed at 330 °C for 10 min, particle size = 3 ± 0.5 nm (b); 30 min, particle size = 5 ± 1 nm (c) and 60 min, particle size = 10 ± 5 nm (d).

of $Ag_{0.25}-MoO_3$ (Figure 2c) indicates the formation of the cubic structure of Ag by its characteristic peaks (insert XRD pattern) and that of the disordered and exfoliated layers of MoO_3.

To confirm that the redox reaction had occurred, X-ray photoelectron spectroscopy (XPS) was used to identify the change in oxidation states for Mo and Ag atoms before and after the reaction. In the XPS spectra of Mo in the product ($Ag_{0.25}-MoO_3$) and the starting material ($[Na(H_2O)_2]_{0.25}MoO_3$), a peak shift of 1.4 eV of Mo $2P_{5/2}$ from lower (234.6 eV) to higher binding energies (236.0 eV) clearly indicated oxidization from $Mo^{5.75+}$ to Mo^{6+}.[24] The XPS spectra of Ag $2P_{3/2}$ in $[Ag(H_2O)_x]_{0.25}MoO_3$ and $Ag_{0.25}-MoO_3$ showed a reduction from Ag^+ to Ag^0, by indicating an energy shift from 368.5 eV (Ag^+) to 367.9 eV (Ag^0). The Ag $3d_{5/2}$ peak at a binding energy of 367.9 eV with its fwhm of 1.9 eV showed a splitting of the 3d doublet of ca. 6.0 eV. All experimental values compare well with the reference values for Ag^0 and MoO_3.[24,25]

The morphology and size distribution of Ag nanoparticles were observed on a Hitachi-8100IV transition electronic microscope (TEM). Figure 3a shows the typical layered structure of the starting material, $[Na(H_2O)_2]_{0.25}MoO_3$. Figure 3b shows the Ag nanoparticle morphology of a sample obtained at 330 °C after a 10-min heating treatment in which Ag nanoparticles were formed on the surface of the MoO_3 substrate. TEM imaging showed the spherical Ag nanoparticles ca. 3 nm in diameter and with a narrow particle size distribution. Additionally, the particles were inhibited from gradual aggregation and dispersed on the surface of the MoO_3 substrate. Due to the thermodynamic aggregation, the average size of the Ag particles increased with an increase in the heating time. For example, Ag particles with an average size of ca. 6 nm were obtained after a 30-min heating treatment (Figure 3c), while ca. 10-nm Ag particles were obtained by further extending the reaction time to 60 min (Figure 3d). The structure of the MoO_3 substrate became disordered as the Ag particles formed on the surface of the MoO_3 substrate at relatively low temperatures such as 300 °C, whereas the pure MoO_3 is stable up to 400 °C. Accordingly, in the initial stage of the redox reaction, the formed Ag atoms must be transferred from the interlayers onto the surface of the MoO_3, on which they were further aggregated into nanoparticles.

The thermal gravimetric and differential thermal analysis (TG-DTA) obtained in nitrogen gas provided additional evidence for the relationship between the redox reaction and structural stability. As expected, the TG-DTA of $[Na(H_2O)_2]_{0.25}MoO_3$ showed two stages of weight loss with distinct endothermic peaks at 100 and 240 °C, which were assigned to the dehydration on the external surface and the interlayer. The TG-DTA curves of $[Ag(H_2O)_x]_{0.25}MoO_3$ can be divided into three corresponding stages: in the first stage, the endotherm accompanied by two steps of weight loss occurred at 100 and 240 °C, which is attributed to dehydration; in the second stage, the exotherm in the range of 300−330 °C is attributed to the self-redox reaction: $Ag^+ + MoO_3^{0.25-} \rightarrow Ag_{0.25}-MoO_3$; in the third stage, an endotherm at ca. 500 °C is due to the melting of the Ag nanoparticles. Moreover, when TG-DTA was carried out in the air, an endotherm at ca. 500 °C with a weight gain of 1% was observed, due to the oxidization of the Ag nanoparticles, in accordance with the calculated value of 1.1%.

A UV−vis absorption spectral peak at 345 nm for 3-nm $Ag_{0.25}-MoO_3$ was observed. It is attributed to the surface plasmon absorption of the silver clusters.[26−28] The electronic energy levels and optical transitions in the silver surface were extensively studied and it was confirmed that the transition from 4d to 5sp generally

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occurred at around 320 nm.[27,28] The absorption of our well-dispersed Ag nanoparticles supported the formation of "quantum-dots".[29]

In summary, we have demonstrated that Ag nanoparticles with controlled size could be fabricated based on multilayer MoO_3. The flexibility of the silver ion exchange and the well-confined redox reaction greatly facilitate the fabrication of Ag nanoparticles on the surface of MoO_3. Moreover, this well-confined preparation route for silver nanoparticles can be readily generalized to other systems.

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Supporting Information Available: Experimental details, XPS spectra, TG-DTA, and UV−vis spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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