Sequential Synthesis and Structural Transformation of Silver Nanoclusters within a Ring-shaped Polyoxometalate

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Atomically precise silver (Ag) nanoclusters have attracted great interest in diverse fields due to their unique structures, electronic states, and physicochemical properties.[1] In particular, Ag nanoclusters supported on metal oxides are attractive catalysts due to the cooperative catalysis of the Ag nanoclusters and metal oxides. We have recently reported that polyoxometalates (POMs) act as inorganic multidentate ligands that enable the synthesis of ultrastable Ag nanoclusters with unique structures and electronic states.[2] Herein, we report sequential synthesis and structural transformation of the uncovered Ag nanoclusters using a ring-shaped POM that possesses a large cavity (ca. 1 nm in a diameter).[3]

We first synthesized an Ag^+-containing ring-shaped POM (**I**) by the reaction of $[P_8W_{48}O_{184}]^{40-}$ and silver acetate in acetone. Second, the silver nanocluster (**II**) was successfully synthesized within the ring-shaped POM by the reaction of **I**, silver acetate, and a reductant (Figure 1). Furthermore, the reaction of **II** with an additional reductant led the structural transformation into another Ag nanocluster (**III**) in which the Ag atoms were arranged in face-centered-cubic packing. The X-ray absorption near edge structure (XANES) spectra of **II** and **III** revealed that the structural transformation was induced by the reduction of the Ag nanoclusters. The UV-Vis spectrum of **III** exhibited unique absorptions in the visible light region. Although **III** possessed the uncovered Ag surface, **III** exhibited high stability in an organic solvent and the UV-Vis spectrum of the solution remained almost unchanged for about 1 week.

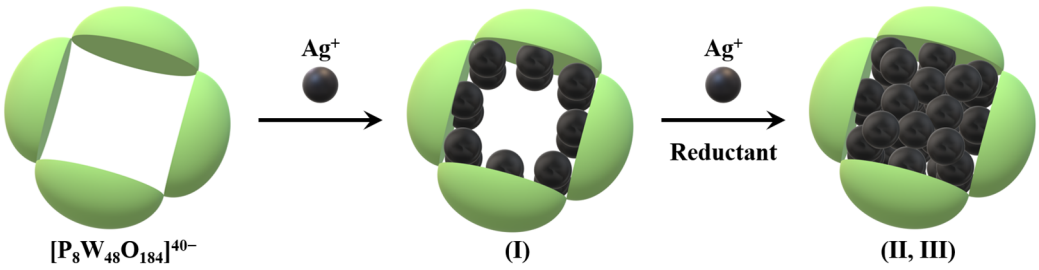

Figure 1. Schematic of sequential synthesis of Ag nanocluster within ring-shaped POM.

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