Size-Selective Synthesis of Small Silver Clusters with Porous Ionic Crystals based on Keggin-Type Polyoxometalates

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Small silver clusters consisting of a few atoms have unique catalytic and optical properties, which are not observed in the corresponding bulk samples.[1] While the properties of small silver clusters are highly dependent on their size, size-selective synthesis is still challenging because small clusters tend to aggregate. Although we have previously reported size-controlled synthesis of small silver clusters within redox-active porous ionic crystal, improving size-selectivity has remained as our next challenge.[2] In this work, we utilized $[Cr_3O(OOCH)_6L_3]_2[\alpha\text{-}XM_{11}M'O_{40}]$ (L = methylpyridine (mepy) or ethylpyridine (etpy), X = Si orP, M = Mo or W, M' = Mo, W, or V, **L-XMM'**) as scaffold and investigate the effect of POM and crystal structure of size selectivity of small Ag clusters formed in PICs.

Small Ag clusters were synthesized thorough 2 step reaction. In the reaction 1, electrons were stored in the PIC scaffolds by reducing comprising POMs.

$$\textbf{L-XMM'} + Cs^+ + xe^- \rightarrow \textbf{L-XMM'}(\boldsymbol{x}) \quad \ldots\ldots(1)$$

In the reaction 2, Ag introduction was occurred and electrons transferred from POM to Ag^+ followed by aggregation of Ag^0 and Ag^+ to form small Ag clusters in the PIC.

$$\textbf{L-XMM'}(\boldsymbol{x}) + yAg^+ \rightarrow \textbf{L-XMM'}(\boldsymbol{x}, \boldsymbol{y}) + Cs^+ \quad \ldots\ldots(2)$$

X-ray photoelectron spectroscopy (XPS), Photoluminescence spectroscopy (PL), and X-ray absorption fine structure (XAFS) measurements revealed that constituent elements of POMs (X and M) affect the size of Ag clusters initially formed and crystal structure affect the stability of Ag cluster formed inside PICs which results in size-selective formation.

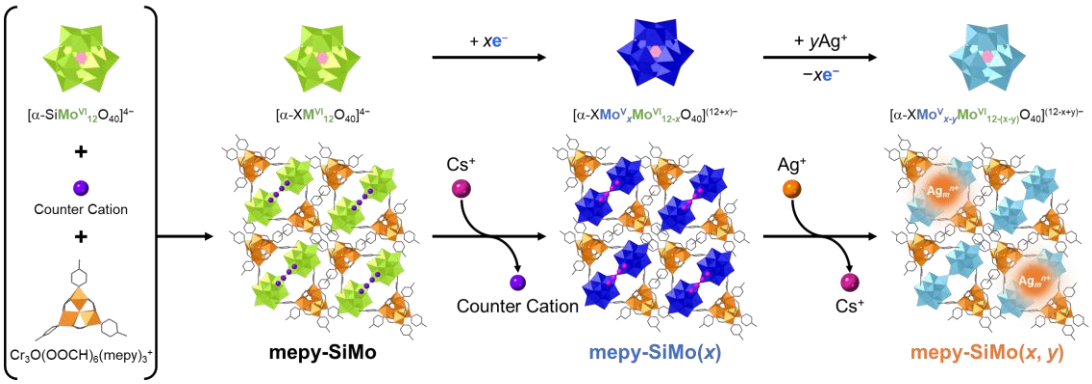

Figure 1 Ag cluster formation in PICs

1) Y. Lei *et al.*, *Science* **2010**, *328*, 224. 2) N. Haraguchi, T. Tachikawa, S. Uchida, et al., Small, 2023, 19, 2300743.