Selective Hydroperoxygenation of Olefin Realized by Coinage Multimetallic Sub-nanocatalyst

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Keywords: Dendrimer; Sub-nanoparticle; Coinage Metal; Hydroperoxygenation Reaction; Catalyst

Although particles on a sub-nanometer (~ 1 nm) scale have attracted worldwide attention, precise synthesis of them has been difficult especially for multimetallic sub-nanoparticles (SNPs). For this obstacle, we recently developed the 'atom-hybridization method (AHM)' using the 4th generation phenylazomethine dendrimer (DPA G4) as a multiligand template[1]. This macromolecule possesses the unique intramolecular potential gradient, thereby accumulates metal salts into its imine units from the inner layer stepwise. Subsequently, synthesis of SNPs with a controlled size is achieved by chemical reduction of metal salts assembled on the DPA G4. The synthesis of multimetallic SNPs is also realized by co-accumulation of various metal salts to each layer of the DPA G4.

In this study, we focused on exploring the reactivity of SNPs through a catalytic reaction[2]. First, three types of coinage metals (Au, Ag, and Cu) were precisely co-accumulated to the DPA G4. Then, we succeeded in the synthesis of mono-, bi-, trimetallic SNPs with desired sizes and compositions (Fig. 1a and b). Finally, the catalytic activity of SNPs was systematically evaluated through the cyclohexene oxidation. As a result, Cu SNPs showed high catalytic performance even under the mild condition in contrast to conventional Cu catalysts (Fig. 1c). Moreover, the hybridization of Au and Ag to the Cu SNPs remarkably activated the catalytic activity, realizing the high selective hydroperoxygenation of the cyclohexene. In conclusion, the unique chemical reactivity of 1-nm catalysts was revealed by the bottom-up synthetic approach applying dendrimer.

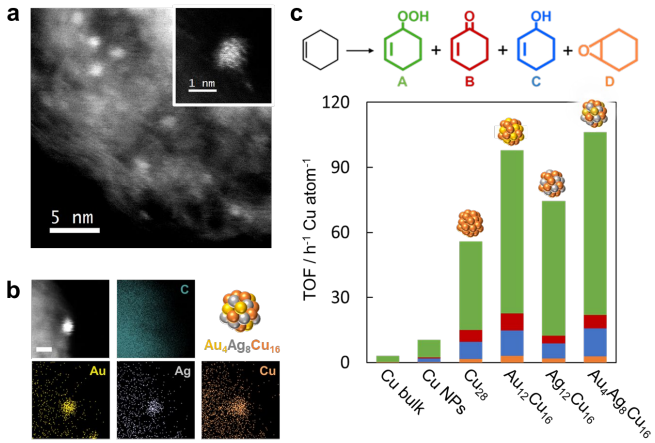

Fig. 1. **a** STEM images and **b** STEM/EDS mapping (scale bar: 2 nm) of the $Au_4Ag_8Cu_{16}$ SNPs supported on carbon. **c** Reaction products and TOFs per Cu atom of SNP catalysts obtained from the cyclohexene oxidation.

1) T. Tsukamoto, T. Kambe, A. Nakao, T. Imaoka, K. Yamamoto, *Nature Commun.* **2018**, *9*, 3873.
2) T. Moriai, T. Tsukamoto, M. Tanabe, T. Kambe, K. Yamamoto, *Angew. Chem. Int. Ed.* **2020**, *59*, 23051–23055.