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Bimetallic nanocrystals with tailored morphologies for electrocatalytic applications

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ABSTRACT

The catalytic activity and selectivity of nanocrystals (NCs) can be tuned by controlling their morphology, because the exposed surfaces of the NCs have distinct crystallographic planes that can determine their overall catalytic properties. However, the control of the size, shape, and composition of NCs has been limited due to the complex kinetics in the reduction of cationic metal precursors and to the difficulty in finding suitable stabilizing agents. Therefore, development of an efficient synthesis route for the preparation of monodisperse bimetallic NCs is still a radical issue to study their properties and applications such as polymer electrolyte and proton exchange membrane fuel cells (PEMFCs). Herein we report facile wet-chemical synthesis routes to prepare bimetallic NCs with well-defined morphologies including Au@Pd octahedra, Au-Pd alloy octahedra, Au-Pd rhombic dodecahedra, Au-Pd hexoctahedra, and Au-Pd nanodendrites, and their electrocatalytic performances toward ethanol and formic acid oxidation.

1. INTRODUCTION

The shape-controlled synthesis of metal nanocrystals (NCs) has received increasing attention in recent years because NC shape has a profound influence on the optical, magnetic, and catalytic properties of NCs. In particular, the catalytic activities and stabilities of NCs in numerous chemical reactions significantly depend on NC shape. This could be due to specific combinations of the facet types on the NC surface and the overall shape of the NC. Accordingly, various shapes of mono- or multi-metallic NCs have been synthesized in the past decade. Despite the great advances in this field, the control of the size, shape, and composition of NCs has been limited due to the complex kinetics in the reduction of cationic metal precursors and to the difficulty in finding suitable stabilizing agents. In this regard, development of an efficient synthesis method for the preparation of monodisperse bimetallic NCs is still a radical issue to study their properties and applications such as polymer electrolyte and proton exchange membrane fuel cells (PEMFCs).

Here, facile wet-chemical synthesis routes to prepare bimetallic NCs with well-defined morphologies, such as Au@Pd octahedra, Au-Pd alloy octahedra, Au-Pd rhombic dodecahedra, Au-Pd hexoctahedra, and Au-Pd nanodendrites, and their enhanced electrocatalytic activity and stability toward small organic molecule oxidation are reported.

2. SYNTHESIS OF BIMETALLIC NANOCRYSTALS WITH TAILORED MORPHOLOGIES FOR ELECTROCATALYTIC APPLICATIONS

We found that maneuvering the nucleation/growth kinetics of NCs could lead to the formation of Au-Pd NCs having distinctly different morphologies.[1-8] For instance, co-reduction of $AuCl_4^-$ and $PdCl_4^{2-}$ precursors with cetyltrimethylammonium chloride (CTAC) in the absence of ascorbic acid (AA) yielded Au@Pd core-shell NCs with an octahedral shape.[2] The evolution of NCs took about 48 h at 90 °C. This result indicates that the slow reaction kinetics could promote the thermodynamically-favored growth of NCs. That is, due to the higher reduction potential of $AuCl_4^-$ in comparison to $PdCl_4^{2-}$, Au precursors were reduced first to form octahedral Au NC cores enclosed by stable {111} facets. This was followed by the epitaxial growth of Pd layers onto the Au cores, producing the Au@Pd core-shell NCs. On the other hand, co-reduction of both metal precursors in the presence of AA in an amount relative to the metal precursors ([AA]/[M]) of 0.75 generated Au-Pd alloy NCs with a {111}-faceted octahedral morphology.[7] When we further increased the relative amount of AA so that the [AA]/[M] ratio was 1, we produced rhombic dodecahedral (RD) Au-Pd alloy NCs exclusively bound by {110} facets, which has the highest surface energy among the three low-index ones.[6] Transmission electron microscopy (TEM) monitoring of the evolution of RD Au-Pd NCs demonstrated that Au-Pd alloy NCs with the RD morphology appeared at a very early stage of the reaction and then acted as seeds for the further growth of NCs. Meanwhile, AA was increased to a greater amount in the synthesis than that used in the preparation of RD NCs to have a [AA]/[M] ratio of 4, leading to the growth of hexoctahedral (HOH) Au-Pd alloy NCs predominantly bound by high-index {541} facets.[8] Interestingly, the co-reduction of Au and Pd precursors using a significantly large relative amount of AA with a [AA]/[M] ratio of 20 or using hydrazine as a reductant, which has a higher reducing capability than AA, generated, respectively, flower-like or dendritic Au-Pd alloy NCs instead of polyhedral NCs with a well-defined morphology.[1,3] These results and observations collectively indicate that manipulating the NC growth kinetics via control of the relative amount of AA is the key synthetic lever to control the morphology of Au-Pd NCs. Our findings suggest that faster reduction kinetics can drive more kinetically-controlled growth of NCs, facilitating the formation of NC seeds enclosed by facets with higher surface energy. The subsequent growth of NCs with the reduction of the remaining metal precursors on the surface of these NC seeds results in the formation of NCs with high-energy facets. Fig. 1 summarizes the correlation between NC morphology and the NC growth kinetics proposed above.

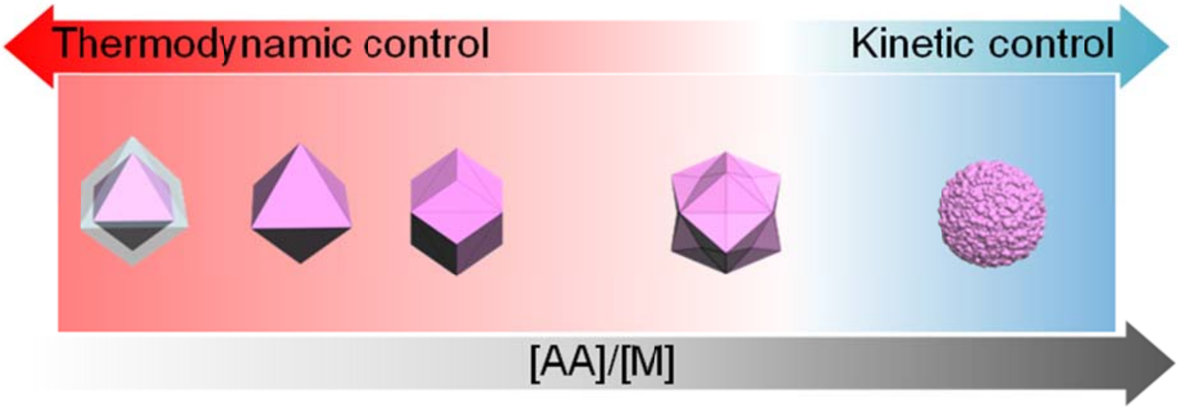

Fig. 1. Scheme for the correlation between the morphology of Au-Pd NCs and the NC growth kinetics.

To investigate the catalytic performance of the prepared Au-Pd NCs with various morphologies, their electrocatalytic activities and stabilities toward ethanol and formic acid oxidation were tested. The experimental results showed that they have higher catalytic performance toward the electro-oxidation of ethanol and formic acid than commercial catalysts.

3. CONCLUSIONS

Au@Pd octahedra, Au-Pd alloy octahedra, Au-Pd rhombic dodecahedra, Au-Pd hexoctahedra, and Au-Pd nanodendrites were prepared through a facile one-pot aqueous synthesis method. These unique structures were produced by the co-reduction of Au and Pd precursors under kinetically-controlled nucleation and growth conditions without any seeds or additional structure-regulating metal ions. The prepared Au-Pd NCs exhibited higher catalytic performance toward the electro-oxidation of ethanol and formic acid than commercial catalysts. We expect that the present work can be extended to the synthesis of other multi-component NCs with precisely-tuned morphologies and crystallographic planes. It can also benefit a number of potential applications in developing catalysts with unprecedented activity.

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