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A seed-mediated approach to the morphology-controlled synthesis of bimetallic copper–platinum alloy nanoparticles with enhanced electrocatalytic performance for the methanol oxidation reaction

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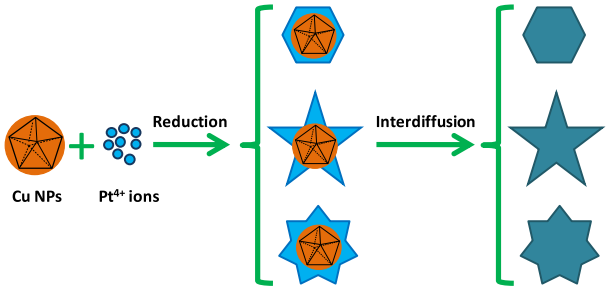
HIGHLIGHTS

- Bimetallic CuPt alloy nanoparticles with different morphologies have been prepared.
- The seed-mediated growth is used as synthetic approach.
- The morphology and electronic coupling have effect on the electrochemical property.
- The dendritic CuPt alloy nanoparticles display superior electrocatalytic activity.

GRAPHICAL ABSTRACT



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ABSTRACT

Mastery over the morphology of nanomaterials usually enables control of their properties and enhancement of their usefulness for a given application. Herein, we report a seed-mediated approach for the fabrication of bimetallic copper–platinum (CuPt) alloy nanoparticles with different morphologies. This strategy involves the first synthesis of Cu seed particles with multiple twins, and subsequent nucleation and growth of Pt metal. Then upon the Cu/Pt molar ratios in the synthesis, the rapid interdiffusion of Cu and Pt atoms results in the formation of bimetallic CuPt alloy nanoparticles with polyhedral, stellated, or dendritic morphologies. It has been found that both the morphology and electronic coupling effect between Cu and Pt components have significant effect on the electrochemical property of the alloy particles. In particular, the dendritic CuPt alloy nanoparticles display the highest specific activity for methanol oxidation reaction (MOR) due to their abundant atomic steps, edges, and corner atoms in the dendritic structure, while the polyhedral CuPt alloy particles show best carbon monoxide (CO) tolerant behavior due to the strong electronic donation effect from Cu to Pt atoms.

1. Introduction

Platinum (Pt) nanoparticles are catalytically active for the anodic (methanol oxidation reaction, MOR) reaction of the direct methanol fuel cell (DMFC) [1–3]. It is commonly accepted that the electrocatalytic activity of nanosized Pt particles strongly depend on their sizes and morphologies [4–11]. The former is capable of

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providing more surface-to-volume ratio, which usually translates to the high specific surface area for the fuel cell reactions, while the latter could significantly enhance the catalytic activity due to an increased number of active sites [8]. In comparison with the pure Pt nanoparticles, which are susceptible to carbon monoxide (CO) poisoning in the MOR [12–14], the Pt-based bimetallic nanoparticles, that is, Pt alloys with secondary metals with well defined morphologies, have attracted considerable attention for the past few years [15–22]. The incorporation of secondary metal, particularly the less expensive transition metals, would dramatically reduce the amount of valuable Pt used in the electrode. In addition, the adjuvant metal in the bimetallic alloy nanoparticles could alter the surface electronic structure of Pt and modify its *d*-band center position. As a result, the interaction between the Pt surface atoms and poisonous intermediate (e.g. CO) is weakened and the resistance to poisonous substance is therefore improved [23–25].

In comparison with the abundant routes based on altering of capping agent, controlling of reaction kinetics, overgrowth on polyhedral seeds, and electrochemical synthesis for the shape-control of single Pt nanocrystals [8], the strategies reported on the synthesis of Pt-based binary nanoparticles with well-defined morphologies are still very limited due to the lack of synthetic inaccessibility. The most commonly used co-reduction of two different metal precursors often fails to good shape control of the final alloy products. Considering the further exploration of the shape-dependent properties and their consequent applications, the development of more effective approaches for the production of Pt-based bimetallic alloys with a wide spectrum of well-defined morphologies would be undoubtedly important and pose significant challenges.

In this work, we report a seed-mediated approach for the fabrication of bimetallic CuPt alloy nanodendrites with polyhedral, stellated, or dendritic morphologies. In this newly developed strategy, the Cu nanoparticles with multiple twins are formed firstly, and served as seeds for the subsequent nucleation and growth of Pt metal. Then the rapid interdiffusion of Cu and Pt atoms results in the formation of bimetallic CuPt alloy metal nanoparticles with different morphologies (upon the Cu and Pt precursor ratios in the synthesis). In particular, as we will see, the dendritic CuPt alloy nanoparticles display superior catalytic activity toward MOR as compared with the CuPt alloys with polyhedral or stellated morphologies and commercial Pt/C catalysts due to their abundant atomic steps, edges, and corner atoms. This study offers an example to demonstrate the tuning of alloy particle morphology by an alternative to the co-reduction method, and the concept of this strategy might be extended to design and fabricate other bimetallic alloy nanoparticles with well defined morphologies for a given technological application.

2. Experimental

2.1. General materials

Copper(II) acetylacetonate ($Cu(acac)_2$, 97%) and chloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$, ACS reagent, ≥37.5% Pt basis) from Aldrich, oleylamine (70%, technical grade), aqueous $HClO_4$ solution (70%, ACS reagent) and Nafion 117 solution (5% in a mixture of lower aliphatic alcohols and water) from Aladdin Reagents, methanol (99%), ethanol (99.5%) and toluene (99.5%) from Beijing Chemical Works, commercial Pt/C catalysts (20 wt% 3.2 nm Pt nanoparticles on Vulcan XC-72 carbon support) from E-TEK, and Vulcan XC-72 carbon powders (XC-72C) with BET surface area of 250 $m^2\ g^{-1}$ and average particle size of 40–50 nm from Cabot Corporation, were used as received. All glassware and Teflon-coated magnetic stir bars were cleaned with *aqua regia*, followed by copious rinsing with de-ionized water before drying in an oven.

2.2. Synthesis of Cu seed particles

In a typical synthesis of Cu seed particles, 26.2 mg (0.1 mmol) of $Cu(acac)_2$ was dissolved in 10 mL of oleylamine placed in a three-necked flask equipped with a condenser and a stir bar. The solution was heated to 180 °C under flowing N_2 and kept at this condition for 2 h for the reduction of Cu^{2+} ions by oleylamine, which also severs as the capping agent. No additional reducing agent and stabilizer were used to form the Cu nanoparticles. After reaction, the solution was cooled down to room temperature and the Cu nanoparticles were purified by precipitation with methanol, followed by centrifugation and washing with methanol, and then re-dispersed in 10 mL of toluene.

2.3. Synthesis of bimetallic CuPt alloy nanoparticles with different morphologies

The seed-mediated growth was applied for the formation of bimetallic CuPt alloy nanoparticles with different morphologies. Typically, 26.2 mg (0.1 mmol) of $Cu(acac)_2$ was added to 10 mL of oleylamine placed in a three-necked flask equipped with a condenser and a stir bar. The solution was heated to 180 °C under flowing N_2 and kept at this condition for 2 h to obtain the Cu seed particles. Subsequently, the $H_2PtCl_6 \cdot 6H_2O$ of 15.5 mg (0.03 mmol), 51.8 mg (0.1 mmol), or 155.4 mg (0.3 mmol) was added to the Cu colloidal solution in oleylamine. The mixture was then heated to 200 °C and kept for another 2 h to obtain the bimetallic CuPt alloy nanoparticles with polyhedral, stellated, or dendritic morphologies. After reaction, the bimetallic CuPt alloy nanoparticles were purified by precipitation with methanol, followed by centrifugation and washing with methanol, and then re-dispersed in 10 mL of toluene.

2.4. Particle characterizations

Transmission electron microscopy (TEM), high resolution TEM (HRTEM), and scanning TEM (STEM) were performed on the JEOL JEM-2100 and FEI Tecnai G^2 F20 electron microscope operating at 200 kV with the supplied software for automated electron tomography. For the TEM measurements, a drop of the nanoparticle solution was dispensed onto a 3-mm carbon-coated molybdenum (Mo) grid. Excessive solution was removed by an absorbent paper, and the sample was dried under vacuum at room temperature. An energy dispersive X-ray spectroscopy (EDX) analyzer attached to the TEM operating in the scanning transmission electron microscopy (STEM) mode was used to analyze the chemical compositions of the synthesized nanoparticles. X-ray photoelectron spectroscopy (XPS) was conducted on a VG ESCALAB MKII spectrometer. Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max-3B diffractometer, using Cu K_α radiation ($\lambda = 1.54056$ Å). Samples for XPS and XRD analyses were concentrated from the toluene solution of nanoparticles to 0.5 mL using flowing N_2. 10 ml of methanol was then added to precipitate the nanoparticles, which were recovered by centrifugation, washed with methanol several times, and then dried at room temperature in vacuum.

2.5. Electrochemical measurements

Electrochemical measurements were performed in a standard three-electrode cell connected to a Bio-logic VMP3 (with EC-lab software version 9.56) potentiostat. A leak-free Ag/AgCl (saturated with KCl) electrode was used as the reference electrode. The counter electrode was a platinum mesh ($1 \times 1\ cm^2$) attached to a platinum wire.

For the loading of the bimetallic CuPt alloy nanoparticles on Vulcan XC-72 carbon support, a calculated amount of carbon