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Polyamine-assisted hydrothermal synthesis of bimetallic Pd\textsubscript{1}Cu\textsubscript{3} multipods and their high catalytic ability in 4-nitrophenol reduction

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Bimetallic Pd\textsubscript{1}Cu\textsubscript{3} multipod nanocrystals (Pd\textsubscript{1}Cu\textsubscript{3}-MNCs) are synthesized by a facile hydrothermal method. The catalytic reduction of Cu\textsuperscript{II} by Pd crystal nuclei is critical for the formation of Pd\textsubscript{1}Cu\textsubscript{3}-MNCs. Pd\textsubscript{1}Cu\textsubscript{3}-MNCs show remarkably enhanced catalytic activity for the hydrogenation reduction of nitro functional groups compared to the commercial Pd black.

Pd-based bimetallic nanocrystals have been intensively explored as effectively catalytic materials in the field of organic synthesis and electrocatalysis. Compared to single-component Pd nanocrystals, Pd-based bimetallic nanocrystals generally displayed superior catalytic/electrocatalytic activities because of the geometric effect, electronic effect and synergistic effect between different components.\textsuperscript{1-6} Meanwhile, the morphologies of Pd nanocrystals affected their catalytic/electrocatalytic activities and stability because of structure effect. For example, highly branched Pd multipod nanocrystals with structural anisotropy exhibited remarkably improved electrocatalytic/catalytic activities and stabilities owing to high density of low-coordinated atoms (such as steps, kinks, terraces, islands and vacancies) and particular self-supported structure that could effectively suppresses Ostwald ripening or grain growth.\textsuperscript{6-10}

Recently, Pd-Cu alloy nanocrystals have been widely used as effective catalysts for the methanol oxidation reaction, nitrate electroreduction, oxygen reduction reaction, formic acid oxidation reaction, \emph{etc.}, which not only exhibited higher catalytic activities compared with monometallic Pd nanocrystals but also reduced the cost significantly.\textsuperscript{3, 11-16} Nielsenite (Pd\textsubscript{1}Cu\textsubscript{3}), a palladium-group bimetallic mineral material, was discovered and named by Nielsen.\textsuperscript{17} Although various Pd-Cu alloy nanocrystals with various elemental compositions have been synthesized, Pd\textsubscript{1}Cu\textsubscript{3} nanocrystals were rarely synthesized and investigated. Maybe, the different reduction kinetics of Pd\textsuperscript{II} and Cu\textsuperscript{II} precursors resulted in difficulty in the formation of Pd-Cu alloy because of their distinct standard reduction potentials (Pd\textsuperscript{II}/Pd\textsuperscript{0}: 0.915 V vs. RHE; Cu\textsuperscript{II}/Cu\textsuperscript{0}: 0.342 V vs. RHE). In this work, we demonstrated a one-pot hydrothermal method to synthesize bimetallic Pd\textsubscript{1}Cu\textsubscript{3} multipod nanocrystals (Pd\textsubscript{1}Cu\textsubscript{3}-MNCs) based on catalytic growth mechanism. To the best of our knowledge, there is no report on the synthesis of bimetallic Pd\textsubscript{1}Cu\textsubscript{3} nanomaterials. The as-prepared Pd\textsubscript{1}Cu\textsubscript{3}-MNCs exhibited remarkably enhanced catalytic activity for the hydrogenation reduction of nitro functional groups over commercially available Pd black.

In a typical synthesis, Pd\textsubscript{1}Cu\textsubscript{3}-MNCs were prepared by reducing PdCl\textsubscript{2} and CuCl\textsubscript{2} precursors with HCHO in aqueous PAH solution at 120 °C for 6 h (see Experimental section for details). The morphology and size of products were firstly investigated by transmission electron microscopy (TEM). Tetrapods, pentapods, hexapods and other multipods are observed from the same mixture (Fig. 1A-B). The particle size of whole multipods is 30±10 nm whereas the length of each pod is 15±5 nm. Energy dispersive X-ray spectroscopy (EDX) analysis indicates that the average composition of multipods is Pd\textsubscript{27}Cu\textsubscript{73} (Fig. 1C), which is consistent with the PdCl\textsubscript{2}/CuCl\textsubscript{2} feeding ratio. In XPS spectrum of Pd 3d, the most intense doublet of peaks (3d\textsubscript{5/2} = 334.98 eV; 3d\textsubscript{3/2} = 340.22 eV) are ascribed to the metallic Pd, while the weaker doublet of peaks (3d\textsubscript{5/2} = 336.35 eV; 3d\textsubscript{3/2} = 341.98 eV) are assigned to PdO (Fig. 1D). By measuring the relative peak areas, the percentage of metallic Pd\textsuperscript{0} is calculated to be 93.1%. Meanwhile, XPS spectrum of Cu 2p displays a doublet of peaks (2p\textsubscript{3/2}=932.4 eV; 2p\textsubscript{1/2}=952.4 eV), which is indicative of metallic Cu (Fig. 1F). Thus, XPS measurements demonstrate that Pd\textsuperscript{0} and Cu\textsuperscript{II} precursors are reduced successfully. X-ray diffraction (XRD) pattern demonstrates that Pd\textsubscript{1}Cu\textsubscript{3} multipods can be identified as face-centered cubic (fcc) structure (Figure 1G). The diffraction peaks of Pd\textsubscript{1}Cu\textsubscript{3} multipods are located...
between those of pure fcc Pd (PDF#46-1043) and Cu (PDF#04-0836) crystal phases, indicating that Pd$_3$Cu$_3$ multipods are indeed alloys. The lattice parameter value (a) of Pd$_3$Cu$_3$ multipods is calculated to be 0.3783 nm based on Scherrer’s formula, in consistent with that of Pd$_3$Cu$_3$ intermetallic mineral material reported by McDonald, indicating that Pd$_3$Cu$_3$ multipods may be intermetallic compound.

As observed, Pd and Cu multiple electron diffraction (SAED) image demonstrates that Pd$_3$Cu$_3$ crystal phases, indicating that Pd$_3$Cu$_3$ imaging reveals that bimetallic Pd$_3$Cu$_3$ Highbangle annular dark-field scanning TEM (HAADF-STEM) (Fig. 2C), which is typical characteristic of metal multipods. obvious pods with ca. 15 nm length (Fig. 2A). The fringes with an interplanar spacing of 0.185 nm are observed at most region of the pod (Fig. 2B), very close to the {200} interplanar spacing on a pod (Fig. 2B), which is typical characteristic of metal multipods. High-angle annular dark-field scanning TEM (HAADF-STEM) image reveals that bimetallic Pd$_3$Cu$_3$ tetrapods possess the same luminance (Fig. 2D), indicating bimetallic Pd$_3$Cu$_3$ tetrapods have an alloy structure rather than a core–shell structure. EDX elemental mapping (Fig. 2E) and EDX line scanning profile (Fig. 2F) clearly show the distribution of Pd atoms is completely consistent with that of Cu atoms, confirming an alloy structure.

The detailed structure of Pd$_3$Cu$_3$-MNCs was investigated by selecting bimetallic Pd$_3$Cu$_3$ tetrapod as representative sample. As observed, Pd$_3$Cu$_3$ tetrapods in TEM image have four obvious pods with ca. 15 nm length (Fig. 2A). The fringes with an interplanar spacing of 0.185 nm are observed at most region of the pod (Fig. 2B), very close to the (200) interplanar spacing of the fcc bimetallic Pd$_3$Cu$_3$ material (0.186 nm). Selected-area electron diffraction (SAED) image demonstrates that bimetallic Pd$_3$Cu$_3$ tetrapods have a polycrystalline structure (Fig. 2C), which is typical characteristic of metal multipods. High-angle annular dark-field scanning TEM (HAADF-STEM) image reveals that bimetallic Pd$_3$Cu$_3$ tetrapods possess the same luminance (Fig. 2D), indicating bimetallic Pd$_3$Cu$_3$ tetrapods have an alloy structure rather than a core–shell structure. EDX elemental mapping (Fig. 2E) and EDX line scanning profile (Fig. 2F) clearly show the distribution of Pd atoms is completely consistent with that of Cu atoms, confirming an alloy structure.
under the present experimental conditions. Surprisingly, PdCu-MNCs are achieved in the present synthesis. Indeed, the single-component Cu ion precursor can’t be reduced under the present experimental conditions, indicating that the reduction of Cu ion is facilitated by the preformed Pd crystal nuclei. It is well known that Cu can take place underpotential deposition (UPD, a phenomenon of electrodeposition of a metal ion at a potential less negative than the Nernst equilibrium potential for the reduction of this metal) on Pd surface.20, 21 Thus, catalytic reduction of Cu ion by Pd crystal nuclei can be ascribed to UPD effect because of the change in thermodynamics energy. Meanwhile, similar to case of Pd-Ni and Pt-Ni alloy nanocrystals,22-25 the deposited surface Cu atoms are then mixed with Pd atoms through an interdiffusion process because of thermal energy, accompanying the simultaneously direct reduction of Pd precursor, and bimetallic PdCu alloy nanocrystals ultimately forms.

The formation of PdCu-MNCs depends on the experimental parameters, including reaction temperature and the feeding ratio of precursors. When reaction temperature fixed at 100 °C, both PAH–Pd and PAH–Cu complexes couldn’t be reduced. Our previous work indicated the Pd icosahedra could be obtained when single-component Pd precursor was used.26 When the feeding ratio of Pd/Cu precursors was fixed at 1:1, only PdCu nanoflowers were obtained (Fig. S2, ESI†). These facts indicate the addition of high-content Cu precursor favors the formation of bimetallic Pd-Cu multipods. During the synthesis, the adsorption of Cu on the surface of the preformed Pd crystal nuclei may change the growth direction of Pd crystal nuclei. Meanwhile, it is clear that the dissolved O2 can result in the selective oxidative etching of Cu atoms on the preformed noble metal crystal nuclei surface.27 Thus, Pd-Cu bimetallic nanocrystals with higher Cu content are more vulnerable to the selective oxidative etching, which facilitates the formation of multipod nanocrystals.

It is clear that the reduction of 4-nitrophenol (4-NP) by NaBH4 occurred directly on the metallic surface. Therefore, the reduction of 4-NP had become one of the model reactions for evaluating the catalytic activity of noble metal nanomaterials.28-30 The catalytic mechanism can be explained as follows. 4-NP is electrophilic and BH4− is nucleophilic with respect to noble metal nanomaterials. The nucleophile BH4− can donate electrons to noble metal nanomaterials, and the electrophile 4-NP can capture electrons from the noble metal nanomaterials. Thus, noble metal nanomaterials can serve as catalytic electron relays for the 4-NP reduction in a NaBH4 solution. The reduction process of 4-NP was monitored using time-resolved UV-vis. Upon the introduction of the PdCu-MNCs into the reaction solution, the peak of 4-NP at 400 nm decreases rapidly with time, accompanying with the gradual emergence of a new peak at 300 nm corresponding to the formation of 4-aminophenol (Fig. 5A). After 19 min, the peak of 4-NP at 400 nm completely vanish, indicating the conversion of 4-NP is nearly 100%. For comparison, the catalytic activities of the commercial Pd black and for the 4-NP reduction were also investigated under same experimental conditions. As observed, the reduction of 4-NP to 4-AP is finished within 34 min using the commercial Pd black as catalyst (Fig. 5B), respectively Reaction rate constant κ is calculated from the slope of the linear section of the plots of ln(C0/Ct) versus t (inserts in Fig. 5A-B). Compared with the commercial Pd black (κ: 0.1 min−1), PdCu-MNCs exhibit improved catalytic activity for the 4-AP reduction (κ: 0.174 min−1). The improved catalytic activity of PdCu-MNCs may originate from the following reasons: (i) Metal multipods generally have abundant defect atoms with low-coordination number, which is highly active for catalytic reaction. (ii) Similar to the case of other alloy,31 synergistic effect between Pd and Cu atoms (such as electronic effect and geometric effect) also contribute to the enhancement in catalytic activity. Under the same total mass conditions, the catalytic activity of the PdCu-MNCs with low Pd content is superior to PdCu nanoflowers with high Pd content (Fig. S3, ESI†), further exhibiting PdCu-MNCs have wide actual application perspective.

In summary, we reported a simple and green co-chemical reduction route to synthesize PdCu-MNCs in aqueous PAH solution. The formation of bimetallic PdCu nanocrystals was attributed to the catalytic growth mechanism, which was supported by the fact that Cu ion couldn’t be solely reduced under the same experimental conditions. In nature, the multipod morphology and high Cu content of PdCu-MNCs were favourable for providing high surface area, enhancing catalytic activity, and reducing the Pd consumption. Indeed, PdCu-MNCs exhibited higher catalytic activity for the reduction of 4-NP than the commercial Pd black, indicating that PdCu-MNCs might have wide potential applications in...
water-based heterogeneous catalytic systems.

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Bimetallic Pd\textsubscript{1}Cu\textsubscript{3} nanomultipods exhibited excellent catalytic activity for the 4-nitrophenol reduction.