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Nanotechnology 25 (2014) 435602 (6pp)

Facile synthesis of Cu-Pd bimetallic multipods for application in cyclohexane oxidation

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Received 29 May 2014, revised 14 August 2014 Accepted for publication 22 August 2014 Published 9 October 2014

Abstract

The synergy between Cu and Pd makes Cu-Pd bimetallic nanocrystals interesting materials for investigation. The scarcity of shapes of Cu-Pd bimetallic nanocrystals motivated us to explore highly branched structures, which may promote a wide range of applications. In this communication, we report a facile synthesis of Cu-Pd bimetallic multipods $(19.2 \pm 1.2 \text{ nm})$, on branches of which some high-index facets were exposed. Modification of reaction parameters concerning capping agents and reductant led to the formation of other shapes, including sphere-like nanocrystals (SNCs). When loaded onto TiO₂, the as-prepared Cu-Pd bimetallic multipods exhibited excellent catalytic activity for the oxidation of cyclohexane by hydrogen peroxide and higher selectivity towards cyclohexanone than monometallic catalysts and SNCs/TiO₂.

S Online supplementary data available from stacks.iop.org/NANO/25/435602/mmedia

Keywords: alloy, nanocatalysts, cyclohexane oxidation

1. Introduction

As a non-noble metal, Cu possesses distinctive and sometimes desirable electrical, optical and catalytic properties, such as high electrical/thermal conductivity, localized surface plasmon resonance in the visible range, catalytic activities for water-gas shift and gas-detoxification reactions, and electrocatalytic activity in solid oxide fuel cells [1–6]. In this sense, Cu nanocrystals have broad potential for applications and to serve as a less expensive alternative to noble metal counterparts. However, owing to their low reduction potential and high susceptibility towards oxidation, Cu nanocrystals are relatively difficult to synthesize in solutions. This reality undoubtedly limits the exploitation and application of Cu nanocrystals. From the perspectives of making better use of Cu and creating synergies, the combination of Cu and a more stable noble metal, e.g. Pd, may be extremely lucrative [7–10]. As a noble metal material to which extensive research has been dedicated, Pd nanocrystals are well-known for their remarkable capability to absorb hydrogen under ambient conditions and high activity to catalyze numerous niche reactions [11–14]. Therefore, developing Cu-Pd bimetallic nanocrystals should provide an expansive dimension to promote overall properties, which has been substantiated by many successful demonstrations [15–23]. For example, the notable synergistic effect between Cu and Pd makes Cu-Pd bimetallic nanocrystals excellent catalysts for hydrogenation, oxygen reduction reaction, CO oxidation and hydration of acrylonitrile, etc [18–21].

In an effort to maximize the bimetallic synergy, however, it is critically important to take the morphology into account, because nearly all physical and chemical properties of nanocrystals are strongly correlated with size and shape [8, 10, 24, 25]. Nevertheless, morphologies of Cu-Pd

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bimetallic nanocrystals are not extensively explored in diversity. Tan et al synthesized tetrapod-like Cu-Pd bimetallic nanocrystals by simultaneously reducing copper acetylacetonate and palladium acetyacetonate with formanilide [18]. However, to our knowledge, no further cases of Cu-Pd nanocrystals with highly branched architectures have been reported in literature. Highly branched nanocrystals, including multipods and nanodendrites, are of particular research interest owing to their unique structures and physicochemical properties [26, 27]. In general, they are characterized by multiple tips or edges, which can serve as inter-particle hotspots for surface-enhanced Raman scattering and are beneficial to a large specific surface area for catalytic applications [26-31]. The possible presence of high-index facets on branches, which relates to reactive atomic steps and kinks, gives rise to substantially greater catalytic activity than lowindex ones [26]. In addition, the polytypism of some multipods makes them prospective building blocks for complicated nanoscale devices [32, 33]. In this regard, the development of highly branched Cu-Pd bimetallic nanocrystals is greatly desired.

Herein, we report a facile aqueous phase synthesis of Cu-Pd bimetallic multipods. The as-prepared multipods were 19.2 ± 1.2 nm (figure S1available at stacks.iop.org/NANO/25/ 435602/mmedia) in size and contained multiple branches on which some {311} high-index facets were exposed. Through adjusting the type of capping agent and the concentrations of the capping agent and reductant, we obtained other shapes, including sphere-like nanocrystals (SNCs). In addition, the absence of Cu or Pd precursors did not lead to monometallic nanocrystals in the shapes of either multipods or SNCs. The oxidation of cyclohexane by hydrogen peroxide was utilized as a probe reaction to test catalytic properties of Cu-Pd bimetallic nanocrystals loaded on TiO₂ supports. Compared to monometallic catalysts and SNCs/TiO₂, multipods/TiO₂ exhibited excellent activity and the highest selectivity towards cyclohexanone.

2. Experimental section

2.1. Synthesis and characterization

The standard procedure to synthesize Cu-Pd bimetallic multipods involves CuCl₂ and H₂PdCl₄ as precursors, glucose as the reductant, octadecylamine (ODA) as the capping agent and deionized water as the solvent. Typically, aqueous solutions of CuCl₂ (0.1 M, 0.3 mL) and H₂PdCl₄ (0.1 M, 0.3 mL) were added into a 20 mL glass vial containing a mixture of ODA (100 mg) and deionized water (4.5 mL). After the vial holding the mixture was magnetically stirred at room temperature overnight, it was added with an aqueous solution of glucose (1 M, 0.14 mL) and transferred into an oil bath to be heated at 110 °C for 2 h. The solution changed its color from yellow to deep brown as the reaction proceeded, indicating the formation of Cu-Pd bimetallic nanocrystals. Figure 1(a) shows a typical transmission electron microscopy (TEM) image of mono-dispersed multipods prepared through the



Figure 1. (a) TEM image of a typical sample of Cu-Pd bimetallic multipods that were prepared using the standard procedure. (b) HRTEM image of an individual Cu-Pd bimetallic multipod taken from the sample of (a). The inset shows the corresponding FT pattern. (c)–(f) HRTEM images recorded from branches 1, 3, 4 and 5 marked in (b), respectively. These images reveal the preferential exposure of {111} facets along with some {100}, {110} and high-index {311} facets on branches.

standard procedure. The products contained multiple branches and had an average size of approximately 19.2 ± 1.2 nm. The single crystalline structure of multipods is clearly resolved in the high-resolution TEM (HRTEM) image (figure 1(b)) of an individual nanocrystal, with the electron beam tilted along the $\langle 110 \rangle$ zone axis. This orientation is further substantiated by the corresponding Fourier transform (FT) pattern provided in the inset. HRTEM images of different branches (figures 1(c)–(f)) demonstrate their single crystalline structure with highly ordered continuous fringe patterns. The d-spacing of 2.1 Å and 1.9 Å can be accredited to the {111} and {200} planes, respectively. Most of the exposed facets (marked by black arrows) were found to be {111}, although some {100}, {110} and high-index {311} facets could also be identified.

In order to verify the structure and composition of the asprepared Cu-Pd bimetallic multipods, x-ray diffraction (XRD) and energy dispersive x-ray (EDX) analysis were conducted. As shown in figure 2(a), the XRD peaks of Cu-Pd bimetallic multipods can be indexed as a face-centered cubic (*fcc*) structure, each one of which lies amongst that of pure *fcc* Pd (JCPDS no. 46-1043) and pure *fcc* Cu (JCPDS no. 85-1326). Equivalently, lattice parameters of Cu-Pd bimetallic multipods were between those of the constituent metals, suggesting the possibility of an alloy structure. Based on the hypothesis



Figure 2. (a) XRD pattern of Cu-Pd bimetallic multipods. (b) STEM image of an individual Cu-Pd bimetallic multipod. (c), (d) STEM-EDX elemental mapping images of (c) Cu and (d) Pd. (e) merged image of (b), (c) and (d).

of the alloy structure, the atomic percentages of Cu and Pd were calculated to be 62.5 and 37.5%, respectively, by employing Vegard's law [34]. This result is in accordance with that obtained from inductive coupled plasma-atomic emission spectroscopy (ICP-AES), wherein atomic percentages of Cu and Pd were severally determined to be 57.3 and 42.7%, respectively. Figure S2 shows the EDX spectrum, which confirms the contents of Cu and Pd in the products (Si came from the silicon) and is generally consistent with the results of ICP-AES. The alloy structure was almost proven by scanning transmission electron microscopy-energy dispersive x-ray (STEM-EDX) elemental mapping analysis. A scanning transmission electron microscopy (STEM) image of an individual Cu-Pd bimetallic multipod is provided in figure 2(b). Figures 2(c) and (d) show elemental mapping images of Cu and Pd, respectively; both of which approximate the profile of a multipod. The merged image (figure 2(e)) as a direct view shows the complete overlapping of the two metal components.

2.2. Growth mechanism

To investigate the mechanism of growth, we conducted a set of experiments following the standard procedure, with the exception that reaction parameters concerning the capping agent or reductant were modified. Figures 3(a) and (b) show Cu-Pd bimetallic nanocrystals in two different shapes, i.e. multipods and polyhedral nanocrystals, which were obtained through using less (80 mg) or more (300 mg) ODA than the standard measure (100 mg). To comprehend the different growth modes, it is necessary to take into account the decisive Z-Q Zhang et al



- 20 nm

Figure 3. (a), (b) TEM images of Cu-Pd bimetallic nanocrystals that were prepared using the standard procedure, with the exception of the addition of different amounts of capping agent. For (a) and (b), the amount of ODA added was 80 and 300 mg, respectively. (c)–(f) TEM images of Cu-Pd alloy nanocrystals prepared using the standard procedure, with the exception of the different types of capping agents listed as below: (c) ODA, (d) HDA, (e) DDA and (f) DA. The amounts of ODA, HDA, DDA and DA added were 100, 90, 69 and 61 mg, respectively.

processes that were involved in the growth. In general, once seeds form via homogeneous nucleation, they grow in size through the deposition of metal atoms onto them, preferably to active sites where unsaturated atoms reside. However, the diffusion of adsorbed atoms (adatoms) or atomic clusters on the surface takes place in the meantime [35]. From a simplified point of view, the migration of adatoms naturally follows a trend to reduce total surface energy. In our experiments, when the concentration of ODA was lowered, the rate of atomic deposition further increased due to less capping. Anisotropic overgrowth could occur because the rate of atomic addition is even higher than that of adatom diffusion, with high-energy facets growing more quickly than lowenergy ones. Therefore, the formation of Cu-Pd multipods was likely to occur with a lower concentration of ODA (figure 3(a)). In contrast, with an increased concentration of ODA, atomic deposition was slowed down to a level which could be evidently modulated by adatom diffusion. To be precise, the seeds may undergo a relaxation process, during the progress of which adatoms could diffuse on the seed's surface to reduce surface area and high-energy facets. Accordingly, polyhedral nanocrystals covered by low-index



Figure 4. (a), (b) TEM images of Cu-Pd bimetallic nanocrystals that were prepared using the standard procedure with the exception that different concentrations of glucose were used: (a) 2 M and (b) 0.5 M. (c), (d) TEM images of the products obtained under the standard conditions, with the exception that only (c) Cu precursors and (d) Pd precursors were used as the metal precursors.

facets were observed (figure 3(b)). In addition, products obtained at different reaction time points were analyzed to verify the growth mechanism. As shown in figure S3(a), polyhedrons were formed due to a homogeneous nucleation in the initial stage (t = 20 min). As the reaction proceeded to 30 min, protrusion structures started to appear due to the higher deposition rate than diffusion rate at active sites (figure S3(b)). The protrusions of products tended to be more obvious during the prolonged growth process, indicating a diffusion-deposition-based procedure involved in the reaction (figure S3(c)).

The aforementioned analysis was further substantiated by extended experimental results. As shown in figures 3(c)-(f), when hexadecylamine (HDA), decadecylamine (DDA) and decylamine (DA) served as the capping agent instead of ODA (figure 3(c), multipods (figure 3(d)), polyhedrons (figure 3(e)) and SNCs (figure 3(f)) were acquired, respectively. It should be noted that all capping agents added were identical in the number of moles. In this case, the larger size and thus stronger steric effect of HDA made the binding force towards Cu-Pd bimetallic nanocrystals weaker than that of DDA and DA, giving rise to the higher deposition rate [36]. As a consequence, the seeds experienced a growth mode similar to the aforementioned one to form multipods. On the contrary, because of the relatively low level of deposition induced by DDA and DA, nearly isotropic polyhedrons and SNCs were produced. This mechanistic understanding was also justifiable in another case of altering the concentration of the reductant. As shown in the TEM image (figure 4(a)) of the products, anisotropic structures that resembled multipods were preferred when the concentration of glucose in the reaction was increased. This result follows the reasoning that



Figure 5. (a) Chemical equation for the oxidation of cyclohexane by hydrogen peroxide. Time-activity profile for the oxidation of cyclohexane using different shapes of Cu-Pd bimetallic nanocrystals as catalysts: (b) multipods and (c) SNCs.

more abundant reductant around the seeds created an even higher rate of deposition, leading the growth to proceed along specific directions. On the other hand, SNCs (figure 4(b)) were obtained with weaker reduction power due to dominant diffusion. In addition, it was discovered that, when just one of $CuCl_2$ and H_2PdCl_4 was used as the precursor, the shape of the multipods or SNCs (figures 4(c) and (d)) could not be sustained.

2.3. Catalytic application in cyclohexane oxidation

Stimulated by the possible synergy of Cu and Pd in catalytic reactions, we took the cyclohexane oxidation reaction (figure 5(a)) as an example to evaluate the catalytic properties of the two shapes (multipods and SNCs in figure 3(b)) of Cu-Pd bimetallic nanocrystals. This reaction has attracted the

Table 1. Oxidation of cyclohexane by hydrogen peroxide with different types of catalysts. Conv., conversion. Sel., selectivity. SNCs, sphere-like nanocrystals. T, temperature.

					Sel. (%)		
Entry	Catalyst ^a	$T(^{\circ}C)$	Time (hours)	Conv. (%)	Cyclohexanol	Cyclohexanone	TON ^b
1	None	50	12	0			0
2	TiO ₂	50	12	0	_	_	0
3	Multipods ^c /TiO ₂	50	12	78	26	74	228.7
4	SNCs ^c /TiO ₂	50	12	88	39	61	258.7
5	Cu/TiO ₂	50	12	87	47	53	196.6
6	Pd/TiO ₂	50	12	5.2	35	65	19.7

Reagents: acetonitrile (1.5 mL, as the solvent), cyclohexane (0.15 mL, as the substrate), hydrogen peroxide (0.6 mL, 30%, as the oxidant), catalyst (10% mass loading of 4 mg, or only 4 mg TiO₂ as in entry 2).

TON = mole of product per mole of catalyst.

Multipods and SNCs represent Cu-Pd bimetallic multipods and Cu-Pd bimetallic SNCs, respectively.

attention of many researchers because of the significant commercial values of cyclohexanol and cyclohexanone [37-39]. The atomic ratios of Cu and Pd in SNCs were determined to be 55.5 and 44.5% by ICP-AES, values which were found to be close to those of multipods. The corresponding EDX analysis (figure S4) also supported the results of ICP-AES. To make a comparison, monometallic nanocrystals in figures 4(c) and (d) were also tested as catalysts. All catalysts were loaded onto TiO₂ supports. As shown in table 1, no products could be obtained in the blank test (entry 1) or when using TiO2 supports alone (entry 2). It can be derived from the conversions in entries 5 and 6 that, interestingly, Pd was not active for this reaction by itself, while Cu took on the vast majority of catalytic behaviors. According to entries 3-6, bimetallic catalysts generally exhibited a higher turnover number (TON) and thus a higher activity than any of the monometallic counterparts. Among the two bimetallic catalysts, a slightly higher conversion (entries 3 and 4; figures 5(b) and (c)) of cyclohexane was attained after 12 h when SNCs/TiO2 were used as catalysts. Although benefiting from multiple branches and high-index facets, multipods/TiO₂ (78%) did not exceed SNCs/TiO₂ (88%) in conversion, as a consequence of the larger size of multipods $(19.2 \pm 1.2 \text{ nm})$ than SNCs (~8 nm). For all reactions in table 1, only cyclohexanol and cyclohexanone were attained as products. As shown in entries 3-6, multipods/TiO₂ gave the highest selectivity towards cyclohexanone (74%) among all the tested catalysts. The selectivities along with time in figures 5(b) and (c) illustrate that the selectivity to cyclohexanone for multipods/TiO₂ remained higher than that for SNCs/TiO₂ throughout the reaction. These interesting results probably arose from the dominantly high activity of high-index facets.

3. Conclusions

In summary, we demonstrated a facile aqueous synthesis of Cu-Pd multipods through the reduction of CuCl₂ and H_2PdCl_4 by glucose, with ODA as the capping agent. The asprepared multipods were 19.2 ± 1.2 nm in size, with many enclosed by a mixture of low-index and {311} high-index

facets. We investigated the growth mechanism through varying reaction conditions to obtain different shapes. It was found that weaker capping or increased reduction power led to anisotropic structures such as multipods, whereas nearly isotropic structures such as polyhedrons and SNCs appeared when stronger capping or slowed-down reduction were introduced. These results could be mechanistically understood as the contention between atomic deposition and adatom diffusion. Due to the large surface area and the exposure of high-index facets, Cu-Pd multipods/TiO2 exhibited prominent catalytic activity for the oxidation of cyclohexane by hydrogen peroxide. Notably, multipods/TiO₂ were more selective towards cyclohexanone than SNCs and monometallic (Cu or Pd) catalysts. We believe that our simple synthetic strategy based on kinetic control can promote the design of novel highly branched nanostructures with controllable properties for further applications.

Acknowledgements

This work was supported by MOST of China (2014CB932700 and 2011CB921403), NSFC under Grant Nos. 21203173, 51371164 and J1030412, Strategic Priority Research Program B of the CAS under Grant No. XDB01020000, and Fundamental Research Funds for the Central Universities (WK2340000050 and WK2060190025).

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