



Shape-controlled synthesis of Cu-Ni nanocrystals

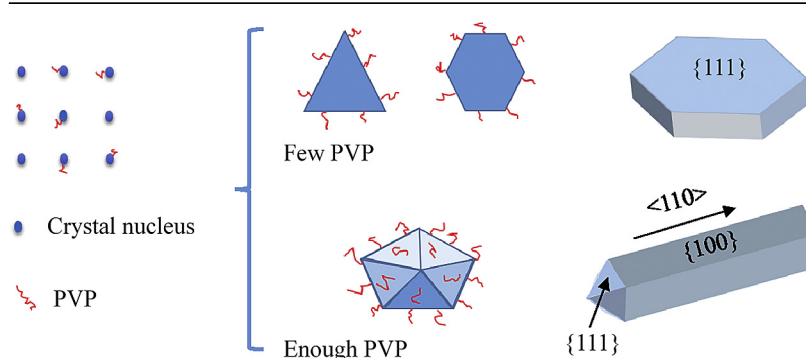
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HIGHLIGHTS

- A highly selective morphology formation of Cu-Ni nanocrystals is developed.
- Nanocrystals evolve from nanoplates to nanowires with increasing PVP amount.
- Nanoplates/nanowires are well dispersed and have high crystallinity and uniformity.
- A mechanism is proposed for the formation of Cu-Ni nanocrystals.
- Nanoplates/nanowires show better catalytic activities than conventional catalyst.

GRAPHICAL ABSTRACT



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ABSTRACT

A highly selective morphology formation of Cu-Ni bimetallic nanocrystals is developed with a solvothermal method, using poly(vinylpyrrolidone) (PVP) as capping agent and aniline as reducing agent in benzyl alcohol. It is shown that temperature is crucial to the controlled synthesis of nanocrystals, and that Cu-Ni nanoparticles evolve from hexagonal nanoplates to nanowires with increasing the concentration of pyrrolidone unit. The synthetic Cu-Ni hexagonal nanoplates and nanowires are well dispersed and have high crystallinity, purity, uniformity of shape and size, and face-centered cubic lattice structure. Furthermore, a mechanism of the formation of Cu-Ni nanocrystals is proposed, and the functions of capping agent, reducing agent, solvent, etc. are discussed. It is also found that both nanoplates and nanowires show better catalytic activities in *o*-xylene combustion than the conventional catalyst. Especially, the Cu-Ni nanowire catalyst exhibits the most excellent catalytic performance due to the formation of durian-like surface structure.

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1. Introduction

Nanocrystals (NCs) composed of two different metals have received extensive attention because of their excellent chemical-physical properties and low costs. Considering the common energy bands of binary systems of bimetal, it is possible to

continuously alter the electronic structure and geometry of nanocrystal surfaces by changing the bimetal composition, further converting the adsorption capacity of nanoparticles for reactants and products [1]. Therefore, bimetallic nanocrystals with outstanding performances can be applied in many areas such as catalysis [2–4], electronic industry [5,6] and biotechnology [7]. Up to now, remarkable progress has been achieved in the shape-controlled synthesis and forming mechanism of bimetallic nanocrystals. However, most of researches focused on the controllable synthesis of precious metal-based nanocrystals. For example, Niu

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and his co-workers [8] successfully synthesized highly branched Pt-Ni bimetallic nanobundles (NBs) with stepped surfaces, which have an outstanding catalytic activity and durability. Guo et al. [9] reported that FePt and CoPt alloy nanowires (NWs) showed excellent catalytic performances in oxidation-reduction reaction. Furthermore, Pt-M (M = Au, Ni, Pd) icosahedrons [10], Pt-Ni octahedrons, truncated octahedrons and nanocubes [11], Au-Cu nanocubes and octahedrons [12], Au@Pd [13] and Au@Ag [14] core-shell structures, and PdPt [15] and CoPt [16] nanowires have been successfully synthesized, and tested to certify their catalytic performances in hydrogenation reactions, electrocatalytic and heterogeneous catalytic reactions.

Similarly, the catalytic properties of non-noble bimetallic nanostructures are also strongly determined by their shapes and compositions. For example, with the sheet structure, Cu-Ni nanocrystals exhibited high catalytic performance in the catalytic reduction of methylene blue in water [17]. By using the as-prepared rough Cu wires as the “substrate”, Sun and co-workers [18] prepared Cu nanowire-Ag nanocrystals heterostructures which exposed better electrocatalytic performance than that of pure Cu nanowires or Ag nanocrystals. However, the preparation methods of non-noble bimetallic NCs with special shapes have few descriptions. The major reason is that non-noble metal ions with low electrode potential are difficult to be reduced into zero-valence monomers by common reducing agents in their nucleation and growth processes. Moreover, if strong reducing agents are introduced, reduction kinetics will be unable to be in a controllable state. Therefore, special reducing agents and capping agents should be used in the facile and reliable synthetic procedure to achieve shape- and morphology-controlled non-noble bimetallic NCs with high catalytic activities [2,19]. Recently, Gou et al. [20] reported that Cu@Cu-Ni five-fold twined pentagonal nanowires and nanocubes were synthesized in oleylamine in the presence of capping agent, Cl^- , and reducing agent, trioctylphosphine (TOP). In a previous article, Zeng and his co-workers [21] demonstrated that Cl^- ion could coat the surface of seeds in the growth step of crystalline and promote the Cu-ZnO nanorods growth.

In previous studies, bimetallic nanocrystals were usually synthesized in the presence of metal halide (Cl^- , Br^-) or metal carbonyl ($\text{W}(\text{CO})_6$), indicating the growth of nanocrystals was primarily attributed to the strong binding of Cl^- ion or CO. These syntheses were commonly performed in oleylamine [22,23], oleic acid [24] or 1-octadecene [25], which often resulted in nanocrystals with undesirable performance in catalytic selectivity. The main deficiency is that these chemicals with long chains have strong chemical bonds to adsorb the face of nanocrystals. Consequently, it is essential to wash the post-synthetic long chains or to load the synthesized nanocrystals on supports for outstanding performances when they are used as catalysts [26]. Usually, the role of benzoic acid and aniline is their adsorption effect instead of strong binding, and NCs prepared with poly(vinylpyrrolidone) (PVP) are dissolved in organic solvents, resulting in nanocrystals without need for any special post processing. Herein, we develop an alternative non-aqueous method to synthesize Cu-Ni nanoplates and nanowires with good morphologies by utilizing PVP as capping agent and aniline as reducing agent.

2. Experimental

2.1. Chemicals

Nickel (II) acetylacetonate ($\text{Ni}(\text{acac})_2$, 98%), copper (II) acetylacetonate ($\text{Cu}(\text{acac})_2$, 98%), and PVP ($M_w = 40000$) were supplied by Aladdin Chemical Reagent Co., Ltd. (Shanghai, China). Nickel nitrate, copper nitrate, benzyl alcohol and aniline were received from

Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All chemicals were of analytical-reagent (AR) grade and were used as received without further purification.

2.2. Synthesis of Cu-Ni nanocrystals

0.1 mmol $\text{Cu}(\text{acac})_2$, 0.1 mmol $\text{Ni}(\text{acac})_2$, 0.5 ml aniline and an appropriate amount of PVP were dissolved in 15 mL of benzyl alcohol, followed by vigorous stirring for 10 min and sonication for 10 min. Then the mixture was transferred into a Teflon-lined autoclave. The sealed vessel was heated to a specific reaction temperature and kept for 720 min, and then cooled down to ambient temperature. The product was washed by acetone, centrifuged at 10000 rpm for 8 min, and then purified by a mixed solution of ethanol and acetone for several times. Finally, the product was dried in a vacuum oven at 60 °C for 480 min. Cu-Ni nanocrystals with different morphologies were obtained by changing PVP concentration (0.1, 0.2, 0.3, or 0.4 mM) and reaction temperature (200 or 220 °C).

2.3. Characterization

Powder X-ray diffraction (XRD) patterns of nanocrystals were measured by a Bruker D8 Advance Diffractometer (Germany) with $\text{CuK}\alpha$ radiation ($\lambda = 0.15406$ nm) operated at 40 kV and 30 mA. The angular scan was performed from 10 to 80° (2θ), at a scanning speed of 2° min⁻¹. The crystalline phases were identified by reference to powder diffraction data (JCPDS-ICDD). The morphology and structure were observed by a Hitachi S-3400N scanning electron microscope (SEM) operated at an accelerating voltage of 20 kV, equipped with secondary electron (SE) detector and Horiba EX-250 energy-dispersive X-ray spectroscopy (EDS). Sample was coated with gold to create contrast. Transmission electron microscope (TEM) images were obtained on a JEOL JEM-1230 microscope operated at 100 kV. The chemical compositions of nanocrystals were obtained by EDS analysis. The samples for the TEM measurements were prepared by dispersing the as-prepared nanocrystal powder in ethanol, dropping the sample suspension on the TEM copper grid coated with carbon film, and then drying at room temperature.

3. Results and discussion

3.1. Effect of PVP concentration

In Fig. 1, SEM images of the four samples prepared at 200 °C using different concentrations of PVP are shown. It can be seen that the nanocrystal morphology varies significantly with the amount of PVP. Fig. 1(A) presents that the nanocrystals prepared at 0.1 mM PVP are spherical or elliptical in shape, without uniform particle size. The low concentration of PVP leads to the lack of adequate PVP to coat the abundant smaller particles. With the fast formation of seeds, nanocrystals, therefore, grow into disorderly nanospheres with different diameters. Fig. 1(A) suggests that Cu-Ni nanocrystals with a well-defined and uniform shape cannot be formed at a relatively low concentration of PVP. While the concentration of PVP is increased to 0.2 mM, the well-defined Cu-Ni hexagonal nanoplates (hereinafter referred to as sample B) are formed with plate size of about 70–100 nm, as shown in Fig. 1(B). Furthermore, the dispersion of the nanocrystal particles is quite good, which may be attributed to the chemical adsorption of PVP on the particle surfaces. A similar functional mechanism of PVP was also reported in a previous paper by Sun et al. [27].

As seen in Fig. 1(C), the morphology of nanowires occurs by increasing the concentration of PVP to 0.3 mM. Obviously, the

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