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COMMUNICATION

Designing axial growth of Co-Ni bimetallic nanowires with hexagon-like caps and their catalytic hydrogenation for nitrobenzene

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Co-Ni bimetal nanocrystals, which are constructed with long wires and hexagon-like caps, were synthesized through supersaturation, precipitation, and axial growth from the prenucleated bimetal seeds. These Co-Ni bimetallic nanowires with hexagonal caps are more effective than corresponding nanoparticles for the catalytic hydrogenation of nitrobenzene to produce aniline.

Binary metal nanocrystals with precisely defined topologies and geometries have attracted much attention because of their potential applications in catalysis^{1,2}, photonics^{3,4}, electronics⁵, and magnetic^{6,7}. Well-defined bimetal nanocrystals are mostly focused on the noble-noble metals^{8,9}, or extensively on noble-non-noble metals¹⁰, in that noble metals are easy to be nucleation and growth into an uniform structure, and further to induce non-noble metals to nucleate in the crystal structure of noble metals¹¹. It is a challenge to direct the heterogeneous nucleation and growth of two alien non-noble metal atoms to finally determine the shape or morphology of bimetal nanocrystals. Currently, many binary non-noble metals are synthesized through coprecipitation, impregnation, solvothermal or seed-induced methods, and the obtained products are particles in the majority¹²⁻¹⁵. Several synthetic methods concerned the binary non-noble metal alloy have been pursued such as flower-like, handkerchief structure, icosahedral shape and even nanowires and nanodumbbells¹⁶⁻²¹, however, the yield and uniformity of each shape are often not well controlled and the real growth mechanism is incompletely well understood. Drawing inspiration from vapor-liquid-solid (VLS) and solution-liquid-solid (SLS) mechanism which have been widely used to synthesize semiconductor nanowires²²⁻²⁴, our effort is attempted to make an efficient metal feedstock that can provide sufficient metal species, further leading to the supersaturation, precipitation, and axial

growth of a wire.

We show here that high-quality of Co-Ni bimetallic nanowires with hexagonal caps are synthesized by solvothermal growth with long-chain fatty acid as surfactant and propylene glycol as reducing agent at a moderate temperature. The amorphous particles of cobalt stearate mixed with nickel were formed at the initial stage, and then continuous Co feeding these particles resulted in the further increase in the Co concentration, and when the particles became supersaturated, the incoming Co species preferred to precipitate at the existing solid/liquid interfaces and then the interfaces were pushed backward to form nanowires. The nanowires were elongated until the temperature cooled down, meanwhile the particles located on the terminals of wires became the hexagonal structure. Further we show that such novel structure of Co-Ni screw-like nanocrystals gave rise to higher catalytic activity for nitrobenzene hydrogenation toward aniline, compared to corresponding nanoparticles. The synthetic strategy of Co-Ni bimetallic nanowires with hexagonal caps may prove a vital route to the preparation of binary non-noble metals with novel structure suited to the catalytic application.

Fig. 1a-b shows representative Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM) images of Co-Ni (5 wt% Ni) nanocrystals taken from the synthesis with stearic acid acting as a surfactant in the propylene glycol at 160°C for 15 h. These Co-Ni nanocrystals look like screw-shaped with 500-800 nm in length and about 10-50 nm in diameter, as well as 20-120 nm size of screw-caps. Energy-dispersive spectrometry (EDS) of the nanocrystals (inset of Fig. 1b) points to the existence of Co and Ni. The high-resolution TEM image in Fig. 1c shows the different lattice fringes between wire and cap. The inset on the lower right corner of Fig. 1c marked section by a square box indicates that the crystal lattice fringes are 0.191 and 0.217 nm apart, which agree with the d value of (101) and (100) lattice planes of hexagonal Co with growth along the [002] direction, which is also indicated by a fast Fourier transform analysis (top right inset of Fig. 1c). The inset of top left corner of Fig. 1c from the region circled by a ring presents that the crystal lattice fringe is 0.217 nm apart, which agree with the d value of (100) lattice plane of hexagonal Co. It has to point out that the interplanar spacings of 0.398 nm on the inset of lower right corner

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and 0.412 nm on the inset of top left corner of Fig. 1c have lattice fringe direction attributed to (002) of hexagonal Co on the fast Fourier transform analysis. The broadening of the interplanar spacing of (002) plane might be associated to the Ni introduction which is also revealed by Energy-dispersive X-ray spectroscopy mapping analysis indicating the coexistence of Co and Ni in nanowires (Fig. 1e-g). As shown in Fig. 1d, XRD (X-ray diffraction) pattern presents that as-synthesized Co-Ni bimetallic nanocrystals at 15 h reaction are typically indexed as the (100), (002), (101) and (110) diffractions, matching well with Co. Of note, the diffraction peak intensity at $2\theta = 44.6^\circ$ is stronger than others, which might be due to overlap between the (002) planes of hexagonal-packed Co phase (JCPDS No.05-0727) and the (111) planes of cubic Ni phase (JCPDS No.65-2865).

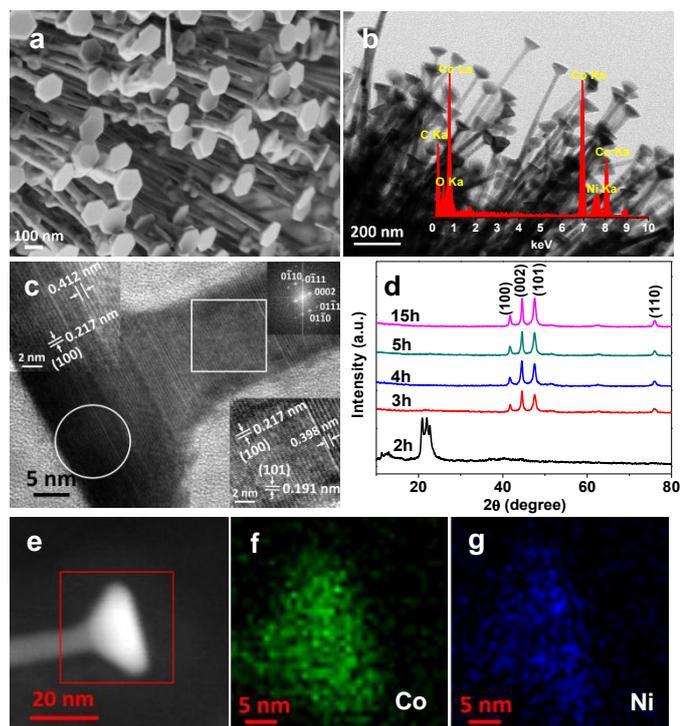


Fig. 1 (a) SEM and (b) TEM images of Co-Ni nanocrystals prepared at 15 h. Inset is EDS spectrum of Co-Ni nanocrystals. (c) HRTEM image of an individual screw-like nanocrystal. Insets are expansion of marked sections and Fourier transform analysis from HRTEM. (d) XRD patterns of Co-Ni nanocrystals made in different time. (e) STEM image of Co-Ni nanowires with caps and (f-g) EDS elemental mapping of Co (green) and Ni (blue) taken from a circled area of (e).

To determine the growth mechanism of these nanowires with hexagonal caps, above all we set to study the time-sequential evolution experiment, which will give us insight into the morphological variation of Co-Ni bimetallic nanowires with hexagonal caps. If no surfactant was introduced at the initial process of reaction system, 2 μm microspheres were observed in the Fig. 2a. When the stearic acid was added in the synthetic system under otherwise identical experimental condition for 2 hours, only hump domains can be observed and no 1D structure was found in Fig. 2b. The deposition at 2 hours reaction has been demonstrated as cobalt stearate by XRD (Fig. 1d). When the reaction time was extended to 3 hours, the spherical screw-caps and the short rods were present and these short rods pointed out of the centres (Fig.

2c). Notably, these depositions after 2-hour reaction are Co-Ni nanocrystals reflected by XRD (Fig. 1d). As the reaction time was longer than 3 hours, screw-caps on the end of wires started to transform from small sphere to large hexagon shape, meanwhile the nanowires became longer gradually (Fig. 2d-f). These phenomena evidently imply that the formation of the caps is prior to that of the wires, and these preformed caps might induce the axial growth of wires under the direction of surfactant. These observations suggest that the synthesis of the high-quality screw-like structure of Co-Ni bimetallic nanocrystals might go through the supersaturation of bimetal, precipitation of Co, and axial growth of a wire in turn. Thus the mechanism of the formation of Co-Ni nanowires with hexagonal caps seems to be similar to VLS or SLS, and cobalt stearate serves as a reservoir to control the liberation of Co species in the solution. The liberated Co species favored the combination with Ni to form the Co-Ni particles, that is, the predecessor of these caps. When the preformed particles became supersaturated, the incoming Co species that were liberated from cobalt stearate preferred to precipitate at the existing solid/liquid interfaces, and the interfaces were pushed backward to yield nanowires.

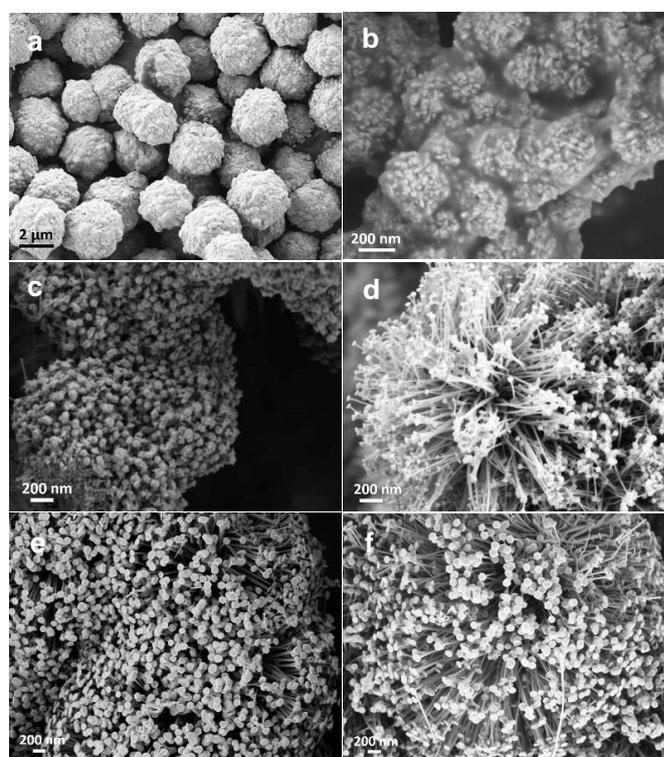


Fig. 2 (a) SEM image of Co-Ni particles synthesized without a surfactant. SEM images of the morphologic evolution of Co-Ni nanocrystals with stearic acid as a surfactant with reaction time. The reaction time was (b) 2 h, (c) 3 h, (d) 4 h, (e) 5 h, and (f) 15 h.

A series of experimental conditions were carried out to gain deeper insight into how the screw-like structure of Co-Ni nanocrystals formed. Firstly, it is worth to note that the reaction temperature is key to the preparation of screw-like structure. When the temperature was below 120°C , no deposition was collected; when the temperature was fixed at a range of $120\text{--}130^\circ\text{C}$, there was one-dimensional structure without caps obtained in the deposition (Fig. S1a-b); as the temperature was 140°C , caps started to appear

on the end of nanowires (Fig. S1c); while the temperature was above 160°C, the needle-like structure was observed (Fig. S1d-e). The optimum temperature thus for the growth of screw-like nanocrystals was 160°C. In addition, the content of Ni and the different surfactants have effect on the yield of screw-like structure. The Ni weight content in Co-Ni should be less than 10 %, but these caps on the end of nanowires otherwise was absent (Fig. S2). The carboxylic acids with different carbon numbers serving as surfactants, such as salicylic acid, lauric acid, myristic acid, citric acid, and cinnamic acid were tried to induce the growth of wires, and it is found that long-chain fatty acids as surfactants are effective for the axial growth of Co-Ni to form the one-dimensional structure with caps (Fig. S3). One reason is that the complexes of metals and acids in the system controlled the content of free metal ions in solution, which might modify the nucleation and growth steps during crystal synthesis^{25,26}. Nevertheless, the interactions between the metal ions and surfactants are rather intricate. These results are inspiring and further work will be performed full density functional theory calculations incorporating metal ions and carboxylic acids to find out more details on the relative rates of atom deposition and surface diffusion of two alien metals induced by surfactants.

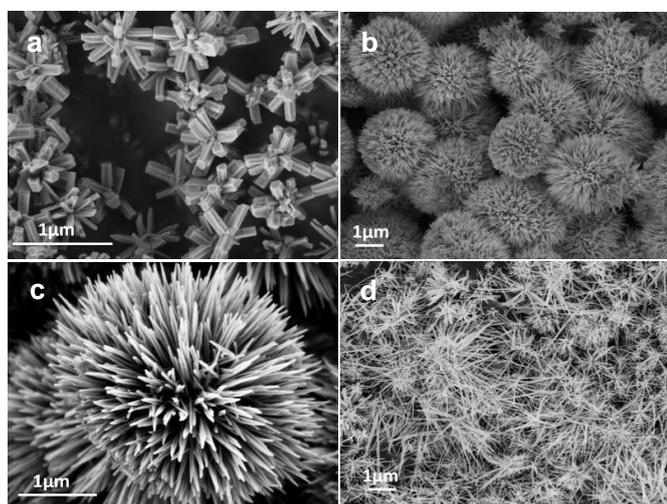


Fig. 3 SEM images of (a) Co-Ru nanocrystals, (b) Co-Pd nanocrystals, (c) Co-Au nanocrystals, and (d) Co-Cu nanocrystals. (Note: the content of Ru, Pd, Au, and Cu in Co-based nanocrystals is 1 wt%, respectively.)

The method was extended to other Co-based bimetallic nanocrystals, such as Co-Ru, Co-Pd, Co-Au, and Co-Cu, however, the introduction of these metals was not effective to create screw-like structure. As presented in Fig. 3a, Co-Ru nanocrystals took on a new look, in which every nanoflower was self assembled by one-dimensional columnar structure. Co-Pd nanocrystals looked like urchins, which were constructed with one-dimensional needles in Fig. 3b. Co-Au nanocrystals were architected with one-dimensional rods in Fig. 3c. If the second element was cheap metal like copper, the shape of Co-Cu nanocrystals was like needle from Fig. 3d. These discrepant phenomena indicate that the interactions between the metal ions and surfactants probably vary with the nature of metal ion, leading to the various morphologies.

Fig. 4 displays the catalytic results of these Co-Ni bimetallic catalysts for nitrobenzene hydrogenation to creat aniline. It is found that Co-Ni nanowires with hexagonal caps exhibited the higher catalytic activity, compared to corresponding Co-Ni nanoparticles (~15 nm size observed in Fig. S4). From Fig. 4a, Co-Ni (5 wt% Ni)

nanowires achieved the 100 % conversion of nitrobenzene with a selectivity of almost 100 % towards aniline at 6 hours reaction, whereas Co-Ni (5 wt% Ni) nanoparticles gave an incomplete conversion of nitrobenzene towards aniline. Co-Ni (1 wt% Ni) nanowires gave 89 % conversion of nitrobenzene under otherwise identical hydrogenation condition, which was more effective than Co-Ni nanoparticles (1 wt% Ni) for the catalytic hydrogenation of nitrobenzene (Fig. S5), that is, 60 % nitrobenzene conversion for Co-Ni nanoparticles, when the reaction time was up to 6 h. A distinct contrast emerges by comparing catalytic activity per unit surface area of Co-Ni nanowires with hexagonal caps with conventional nanoparticles. As revealed in Fig. 4b, the more apparent difference of activity between nanowires with hexagonal caps and nanoparticles of Co-Ni catalysts was noted. Although Co-Ni nanowires with hexagonal caps have smaller surface areas (e.g. 26.5 m²/g for nanowires; 85.8 m²/g for nanoparticles), as shown in Fig. 5a, they have higher ability for catalytic hydrogenation of nitrobenzene than those nanoparticles. Hence the higher catalytic activity of Co-Ni nanowires could not be ascribed to their specific surface area.

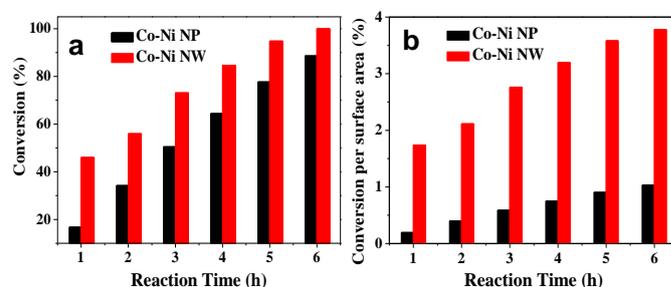


Fig. 4 (a) Catalytic performance of Co-Ni (5 wt% Ni) catalysts for nitrobenzene hydrogenation. (b) Catalytic performance per unit surface area of Co-Ni (5 wt% Ni) catalysts for nitrobenzene hydrogenation. (Reaction conditions: 30 mg catalyst and 1 mL nitrobenzene in 30 mL ethanol at 120°C under 3 MPa H₂. NP: nanoparticles; NW: nanowires with hexagonal caps)

The porous characteristics of the Co-Ni nanocrystals are also shown in Fig. 5b. The pore volumes of Co-Ni nanowires are rather small, as compared to those of nanoparticles. The enhanced catalytic activity of Co-Ni nanowires therefore led us believe that the structural and electronic properties of Co-Ni nanowires with hexagonal caps should play an important role in catalytic hydrogenation of nitrobenzene toward aniline. The X-ray photoelectron spectroscopy (XPS) is used to study the electronic structure of these Co-Ni catalysts. The occurrence of satellite structure results in the deconvolution of Co 2p excitations. The peak at 777.8 eV is assigned to Co⁰, the peak at 779.2 eV is associated with Co³⁺, and the peak at 781.6 eV belongs to Co²⁺, which indicates that Co⁰, Co²⁺, and Co³⁺ are present in Co 2p spectra of Co-Ni nanowires and positive cobalt ions dominates the surface, as shown in Fig. 5c. It is noted that Co³⁺ dominates the surface of nanoparticles. The shift toward higher binding energy is found for Co-Ni nanowires, compared to nanoparticles, that is, Co 2p_{3/2} electron binding energy of Co-Ni nanowires is 1.2 eV higher than the value characteristic of nanoparticles. The shift toward high binding energy reflects the fact that the electron transfers across interface of Co and Ni atoms, which enhanced the catalytic activity of Co-Ni nanowires¹¹. Ni 2p spectra were also recorded and can be decomposed into two Ni species (Ni²⁺ and Ni⁰). Ni 2p_{3/2} electron binding energy of Co-Ni nanowires is 0.8 eV higher than that of Co-

Ni nanoparticles (Fig. 5d). Therefore, taken into considering these above shifts, the influence of Ni on electronic properties of Co-Ni nanowires is stronger than that of nanoparticles, providing an evidence that high activity can be obtained over nanowires catalyst. Moreover, Co-Ni nanowires with caps exhibited better reactivity for hydrogenation of nitrobenzene than Co-Ni nanowires without caps, as presented in Fig. S6. The result is much interesting and the further work is in progress.

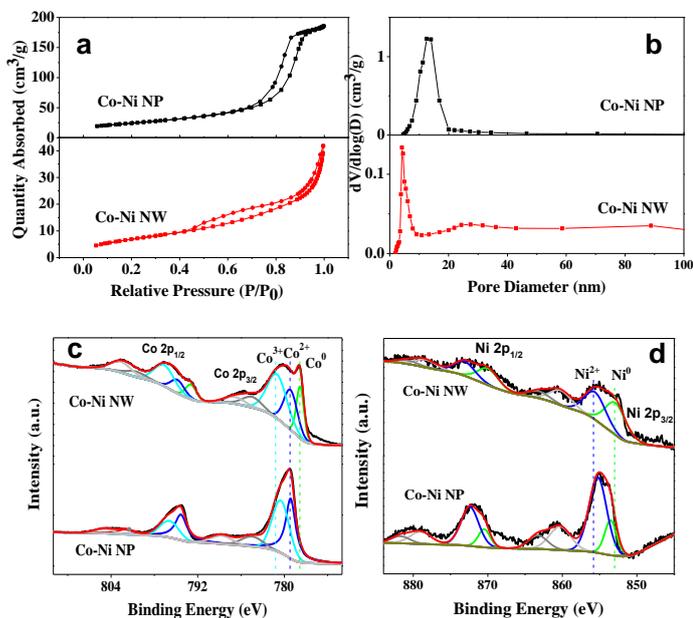


Fig. 5 (a) Nitrogen absorption isotherms of Co-Ni (5 wt% Ni) nanocatalysts measured at 77 K. (b) Corresponding pore size distribution curve determined by the BJH method from the desorption isotherm and (V=pore volume, D=pore width). (c) Co 2p electron region of XPS profiles of Co-Ni (5 wt% Ni) nanocatalysts. (d) Ni 2p electron region of XPS profiles of Co-Ni (5 wt% Ni) nanocatalysts.

In summary, we have synthesized Co-Ni bimetallic nanowires with hexagonal caps via solvothermal growth with long-chain fatty acids serving as surfactants at a moderate temperature. Initially prenucleated Co-Ni particles served as Co and Ni feedstock to provide the growth of Co and Ni species along one-dimensional direction, eventually forming one-dimensional wires, and screw-caps of Co-Ni bimetallic occurred reconstructing from particles to hexagonal nanosheets. The Co-Ni bimetallic nanowires with hexagonal caps exhibited higher catalytic activity for nitrobenzene hydrogenation to yield aniline, compared to Co-Ni spherical nanoparticles. The method could potentially be valuable even for the design and synthesis of binary non-noble metals catalysts to study the shape-dependent chemical behaviour, which is critical for enhancing the activity of some catalytic reactions.

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