

Chapter 2

Controllable Synthesis of Water-Soluble Pt–Ni Alloys and the Study of Their Catalytic Properties

2.1 Introduction

Noble metal nanoparticles (NPs) (i.e., Pt, Pd, [1–3] etc.) have been widely used as catalysts in many applications such as organic reactions [4], fuel cells [5], and so on, while their properties are closely bound up to well-defined sizes, compositions, and structures [6]. To improve atomic efficiency and sustainability, researchers have studied the Pt-based bimetallic nanostructures in which Pt is partially replaced by cheap 3D-transition metals (i.e., Fe, Co, Ni, etc.) [7, 8]. Considering the limited resource and rising cost of Pt, this bimetallic nanostructures will not only efficiently reduce the consumption of Pt, but also exhibit superior catalytic performances than the single component, possibly due to the different geometric and electronic structures brought by the introduction of the second metal [9, 10].

The hydrogenation reactions of benzalacetone, styrene, and nitrobenzene are important industrial processes [11–13] in which homogeneous catalysts have been widely used, but the recycling of catalysts remains difficult. Owning high selectivity for the desired product without sacrificing activity, heterogeneous catalysts [14] have attracted much attention for the ease of their separation and recycling [15, 16]. Besides, as a favorable heterogeneous catalyst, bimetallic catalysts could have optimized activity, selectivity, and stability due to the possible synergistic effects.

So far, most of the alloys that consist of Pt and 3D-transition metals (i.e., Fe, Co, Ni) have been produced with hydrophobic solvents while few cases are reported to synthesize the materials in a hydrophilic system. In this chapter, we developed a general method for the shape and composition controlled synthesis of a series of water-soluble Pt–Ni alloy utilizing poly(vinylpyrrolidone) as a surfactant. As a complement to the hydrophilic system, the water-soluble catalysts produced by this method are also compatible with hydrophobic solvents through a ligands exchange process. The shapes of octahedral, truncated octahedral, and cubic Pt–Ni alloy were controlled by varying the growth inhibition agents such

as benzoic acid, aniline, carbon monoxide, and potassium bromide. In a preliminary structure-activity study, we found that the rates of hydrogenation reactions were significantly affected by the shape and composition of as-prepared nanocrystals. Besides, we found that the octahedral PtNi₂ alloy exhibited superior reactivity toward both the hydrogenation of the C=C and N=O bonds. On the other hand, the Pt–Ni alloy nanocrystal has much higher catalytic activity than its monometallic counterparts, endowing the hydrogenation of the C=C and N=O bonds a great selectivity and activity at room temperature under atmospheric pressure.

2.2 Experimental Section

2.2.1 Chemicals and Instruments

Chemicals: Analytical grade benzyl alcohol, aniline benzaldehyde, benzoic acid, and salicylic acid were obtained from Beijing Chemical Reagents, P.R. China. Pt(acac)₂ (99 %), Ni(acac)₂ (99 %), and PVP (MW = 8000, AR) were purchased from Alfa Aesar. Oleylamine (80–90 %) was purchased from Acros., Pt/C (10 wt%) was purchased from Sigma Aldrich, activated carbon (Vulcan XC-72) was purchased from Carbot. All of the chemicals were used without further purification.

Instruments: XRD patterns were recorded by Rigaku D/Max 2500Pc X-ray powder diffractometer with CuK α radiation ($\lambda = 1.5418 \text{ \AA}$). TEM images and HRTEM images were recorded by a Hitachi H-800 transmission electron microscope working at 100 kV and a FEI Tecnai G2 F20 S-Twin high-resolution transmission electron microscope working at 200 kV, respectively. Electrochemical measurements were conducted on CHI 660D electrochemical analyzer. X-ray photoelectron spectroscopy (XPS) experiments were performed on a ULVAC PHI Quantera microprobe. Binding energies (BE) were calibrated by setting the measured BE of C1s–284.8 eV. The catalytic reaction results were measured by gas chromatography (GC) (SP-6890) and gas chromatography–mass spectroscopy (GC–MS) (ITQ 700/900/1100) and ¹H NMR. The NMR spectroscopy was conducted on a JEOL JNM-ECX 400 MHz instrument.

2.2.2 Experimental Methods

Preparation of Pt–Ni Octahedral Nanocrystals. In a typical synthesis of PtNi₂ octahedral nanocrystals, Pt(acac)₂, (8.0 mg), poly(vinylpyrrolidone) (PVP, MW = 8000), (80.0 mg), Ni(acac)₂ (10.0 mg), benzoic acid (50 mg), and benzylalcohol, (5 ml) were added to a 12-ml Teflon-lined stainless-steel autoclave, followed by 5–10 min vigorous stirring at room temperature. The sealed vessel was then heated at 150 °C for a 12 h. When it was cooled down to room temperature,

the products were first precipitated by excess acetone, separated via centrifugation, and further purified by an ethanol-acetone mixture for 3 times.

Preparation of Pt–Ni Truncated Octahedral Nanocrystals. In a typical synthesis of PtNi₂ truncated octahedral nanocrystals, Pt(acac)₂, (8.0 mg), poly(vinylpyrrolidone) (PVP, MW = 8000), (80.0 mg), Ni(acac)₂ (10.0 mg), and aniline (0.1 ml), benzylalcohol, (5 ml) were added to a 12-ml Teflon-lined stainless-steel autoclave, followed by 5–10 min vigorous stirring at room temperature. The sealed vessel was then heated at 150 °C for a 12 h. When it was cooled down to room temperature, the products were first precipitated by excess acetone, separated via centrifugation, and further purified by an ethanol-acetone mixture for 3 times.

Preparation of Pt–Ni Cubic Nanocrystals. In a typical synthesis of PtNi₂ cubic nanocrystals, Pt(acac)₂, (8.0 mg), poly(vinylpyrrolidone) (PVP, MW = 8000), (80.0 mg), Ni(acac)₂, (10.0 mg) and potassium bromide (50.0 mg), and benzylalcohol, (5 ml) were added to a 10-ml round-bottom flask equipped with a magnetic stirrer, followed by 5–10 min vigorous stirring at room temperature. After aerating the reaction flask full of carbon monoxide, the flask was then immersed in an oil bath at 150 °C for 4 h under a carbon monoxide balloon. When it was cooled down to room temperature, the products were first precipitated by excess acetone, separated via centrifugation, and further purified by an ethanol-acetone mixture for 3 times.

Preparation of Ni Octahedral and Truncated Octahedral Nanocrystals. In a typical synthesis of octahedral Ni nanocrystals, poly(vinylpyrrolidone) [PVP, MW = 8000, (80.0 mg)], Ni(acac)₂ (10 mg), benzaldehyde (0.5 mL), benzoic acid (50.0 mg), and benzyl alcohol (5 mL) were added to a 12-mL Teflon-lined stainless-steel autoclave, followed by 5–10 min vigorous stirring at room temperature. The sealed vessel was then heated at 200 °C for 12 h. When it was cooled down to room temperature, the black nanoparticles were precipitated by acetone, separated via centrifugation, and further purified by an ethanol-acetone mixture for 3 times. The Ni-truncated octahedron was synthesized using the above procedure with aniline (0.1 mL) instead of benzaldehyde and benzoic acid.

Typical Procedure for the Hydrogenation of Benzalacetone, Styrene, and Nitrobenzene. To a 10-mL round-bottom flask was charged a solution of the respective substrate (0.5 mmol benzalacetone, or styrene, or nitrobenzene) in THF (2.5 mL) and the Pt–Ni catalyst (0.01 mmol, 2 mol%). After being purged with H₂, the reaction mixture was stirred in an oil bath at 25 °C under a H₂ balloon. The product was purified by column chromatography and subsequently characterized by ¹H NMR.

Preparation of Oleylamine-Capped Pt–Ni Alloy. In the synthesis of oleylamine-capped Pt–Ni alloy, Pt–Ni catalyst (10.0 mg) and oleylamine (0.1 ml) were mixed together with toluene (5 ml) in a 10-ml round-bottom flask. The resulting mixture was refluxed for 12 h at 100 °C. The products were precipitated by adding ethanol, separated via centrifugation, and further purified by an ethanol-cyclohexane mixture for 3 times.

Preparation of Clean Pt–Ni/C Catalysts. In the synthesis of clean Pt–Ni/C catalysts, activated carbon (100.0 mg) were mixed together with 30 ml of ethanol

in a 100 ml beaker, followed by sonication for 30 min to ensure the activated carbon is adequately dispersed. To this beaker Pt–Ni catalyst (10.0 mg) was then added and then sonicated for 1 h. The resulting black mixture was transferred into a centrifuge tube, separated via centrifugation, and further purified by ethanol-cyclohexane mixture for 3 times. The as-prepared solid was dispersed in 40 ml of acetic acid and heated at 70 °C for 10 h with vigorous stirring. When it was cooled down to room temperature, the resulting black mixture was separated via centrifugation with the dumping of the clear liquid, followed by washing the black solid with ethanol for 3 times and dried in an oven.

Catalyst Recovery. The Pt–Ni catalysts were separated from the reaction mixture by a magnet. After being washed with ethanol for 3 times, the recovered catalysts were directly used in the next cycle of the reaction without further manipulations.

2.3 Results and Discussion

2.3.1 Structural Characterization

The representative transmission electron microscopy (TEM) images (Fig. 2.1) showed that the as-prepared Pt–Ni alloys were all uniform in terms of the narrow size distribution, shape, and exclusively bound by well-defined {111} or {100} facets. The high-resolution TEM (HRTEM) images and fast Fourier transform (FFT) images (Fig. 2.1b, f, j) on single NP both confirmed their single-crystal-line nature. Continuous lattice fringes measurements with an interplanar spacing of 0.213 and 0.186 nm could be assigned to the corresponding {111} facets and {100} facets of fcc Pt–Ni alloy, respectively.

Pt–Ni Octahedrons. The octahedral Pt–Ni particles have an average distance of 11.8 ± 1.2 nm from one apex to the opposite apex and consist of only eight equivalent {111} facets. The high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) micrographs showed that all the surfaces of the octahedrons were smooth without obvious defect throughout the nanocrystal. The corresponding elemental maps of HAADF-STEM (Fig. 2.1c) showed that both Pt and Ni were distributed evenly throughout each individual PtNi₂ alloy octahedral nanocrystal. To realize the formation of Pt–Ni octahedrons preferably, this chapter taken a study on the effect of the amounts of benzoic acid on the shape. Indeed, the yields of octahedrons significantly increased from 40 to 95 % with the amounts of benzoic acid from 0 to 0.04 mmol. In contrast, the yield was almost unaffected by further increasing the amount of benzoic acid. Herein, the usage of benzoic acid was believed to play an important role in the formation of Pt–Ni octahedrons (Fig. 2.2).

Pt–Ni Truncated Octahedrons. By replacing benzoic acid with aniline, we could obtain a series of Pt–Ni alloy with truncated octahedral shape. The truncated

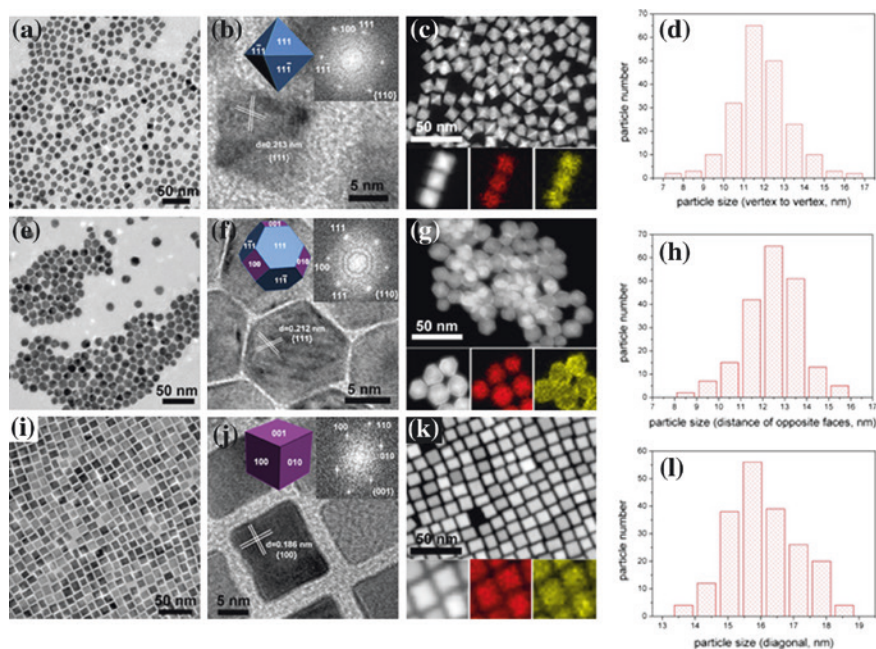


Fig. 2.1 **a** TEM, **b** HRTEM (*Top-right and top-middle* insets show the corresponding FFT pattern and the ideal structure model), and **c** HAADF-STEM images of PtNi₂ octahedrons, corresponding element maps showing the distribution of Pt (*yellow*) and Ni (*red*). **d** Size distribution of octahedral particles (average size: 11.8 ± 1.2 nm, 95 % octahedrons and 5 % irregular shapes). **e** TEM, **f** HRTEM, and **g** HAADF-STEM images of PtNi₂-truncated octahedrons. **h** Size distribution of truncated octahedral particles (average size: 12.5 ± 1.1 nm, 90 % truncated octahedrons and 10 % irregular shapes). **i** TEM, **j** HRTEM, and **k** HAADF-STEM images of PtNi₂ cubes. **l** Size distribution of cubic particles (average size: 16.1 ± 1.7 nm, 95 % octahedrons and 5 % irregular shapes). Reprinted with the permission from Ref. [17]. Copyright 2012 American Chemical Society

octahedrons consisted of both {100} and {111} facets and the average distance of two opposite faces was 12.5 ± 1.1 nm (Fig. 2.1e). In our synthetic method, the benzoic alcohol was used as solvent and reductant; however, the addition of aniline was believed to add as coreductant and affect the reaction kinetics of the reduction of the nanocrystals [18]. The sizes of truncated octahedral Pt–Ni alloy could be tuned from 16.0 to 12.5 nm, 7.2 nm, and 4.8 nm by varying the quantity of aniline. Herein, the nucleation process could be facilitated by the addition of aniline, and the fleetly and largely increase of these nuclei densities significantly helps to reduce the size of the truncated octahedrons while the aniline was added as a strong reductant. The Fig. 2.3 showed that a truncated octahedron can be generated by cutting off six vertices from octahedron, where *a* was the distance from the vertex to the body center, then *b* was the height of each square pyramid, so the degree of truncation can be defined as *b/a*.

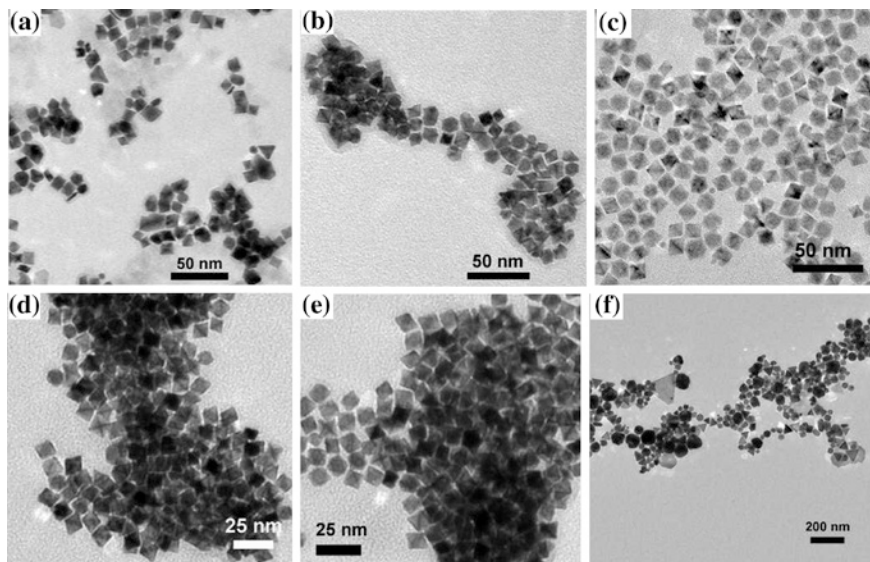


Fig. 2.2 TEM images show the effect of benzoic acid amounts on the formation of PtNi₂ octahedral nanocrystals. The amounts of benzoic acid used were **a** without adding any benzoic acid (40 % octahedrons and 60 % irregular shapes), **b** 0.005 g (0.04 mmol) (70 % octahedrons and 30 % irregular shapes) and **c** 0.25 g (2.0 mmol) (95 % octahedrons and 5 % irregular shapes). TEM images of PtNi₂ octahedrons prepared by replacing benzoic acid with **d** salicylic acid and **e** sodium benzoate. **f** TEM image of nanocrystals collected from the reaction with the same conditions used in the synthesis of octahedral Ni but without adding any benzoic acid (15 % octahedrons and 85 % irregular shapes). Reprinted with the permission from Ref. [17]. Copyright 2012 American Chemical Society

Fig. 2.3 Schematic structure of truncated octahedron. Reprinted with the permission from Ref. [17]. Copyright 2012 American Chemical Society

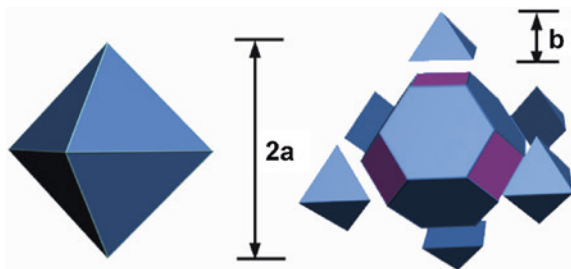


Figure 2.4 showed that the degree of truncation of the as-prepared truncated octahedron depended on the molar ratio between benzoic acid and aniline, a higher molar ratio yielded products with a much greater degree of truncation.

Unlike the typical octahedral Pt–Ni alloy, the elemental map of the truncated octahedral Pt–Ni alloy showed that a greater quantity of Pt segregated at the edges of the particles and Ni appeared more centrally located (Fig. 2.1g), which was

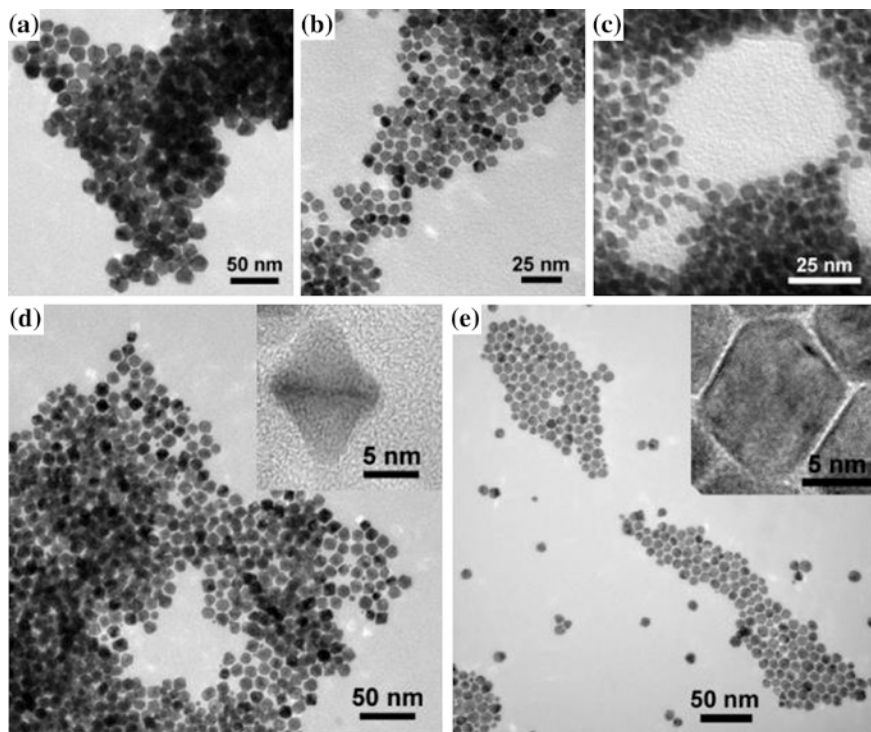


Fig. 2.4 TEM images show the effect of aniline amounts on the shape of Pt–Ni alloy. The amounts of aniline and benzoic alcohol used were **a** 20 μl aniline + 5 ml benzoic alcohol (average distance between two opposite faces is 16.0 nm), **b** 500 μl aniline + 5 ml benzoic alcohol (average distance between two opposite faces is 7.3 nm) and **c** 5 ml aniline (average distance between two opposite faces is 7.3 nm). TEM images of Pt–Ni alloy prepared by varying the molar ratio between benzoic acid and aniline **d** 0.15 g benzoic acid + 50 μl aniline (truncation degree is 0.28) **e** 0.017 g benzoic acid + 300 μl aniline (truncation degree is 0.32). Reprinted with the permission from Ref. [17]. Copyright 2012 American Chemical Society

similar to the core-shell structure. This structure of uneven distribution was further verified by the following line scan of an individual particle (Fig. 2.5).

Pt–Ni Cube. Previous studies have revealed that the carbon monoxide and bromide species could be selectively adsorbed onto Pt {100} crystal faces and induce the formation of nanocubes [19, 20]. Here, we successfully extended this method to the preparation of well-defined Pt–Ni alloy nanocubes. The as-prepared cubic particles had an average diagonal length of 16.1 ± 1.7 nm and were surrounded by six equivalent {100} facets. To better understand the role of CO and KBr in the formation of our Pt–Ni nanocubes, we carried out a series of control experiments. Figure 2.6 showed that the yield of nanocube decreased from 95 to 60 % with the absence of KBr. However, in the absence of CO, mixed morphologies (30 % nanorods, 40 % nanocubes, and 30 % irregular shapes) were observed.

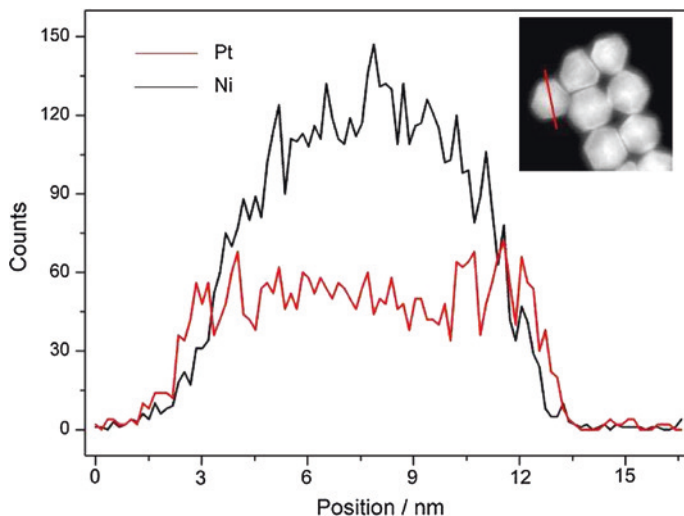


Fig. 2.5 Cross-sectional compositional line profiles of a truncated octahedral PtNi₂ alloy. Reprinted with the permission from Ref. [17]. Copyright 2012 American Chemical Society

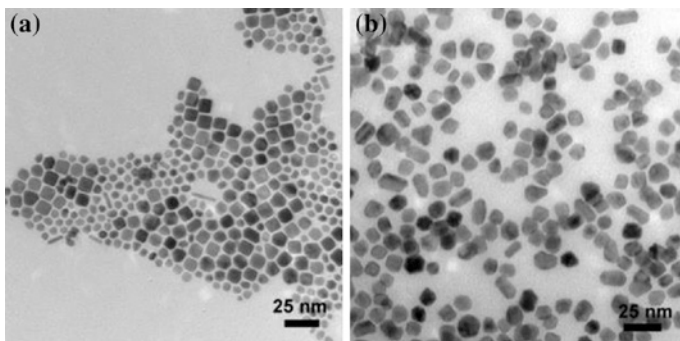


Fig. 2.6 TEM images of nanocrystals collected from the reaction with the same conditions used in the synthesis of cubic PtNi₂ but **a** without adding KBr (60 % octahedrons and 40 % irregular shapes) or **b** without adding CO (30 % nanorods, 40 % nanocubes, and 30 % irregular shapes). Reprinted with the permission from Ref. [17]. Copyright 2012 American Chemical Society

Ni Nanocrystals. This general method could also be applied to the synthesis of Ni octahedrons with an average size of 40 ± 4.5 nm, albeit at an elevated temperature of 200 °C when benzaldehyde was used as an extra reductant (Fig. 2.7a). Similarly, the truncated octahedral Ni with an average size of 25.2 ± 4.3 nm was synthesized when aniline replaced benzoic acid and benzaldehyde. Unfortunately, this route could not be extended to the synthesis of Ni nanocubes. It is intriguing that these magnetic Ni octahedrons spontaneously assembled into large-scale one-dimensional nanostructures on copper grid after ethanol was evaporated (Fig. 2.7b–d). The self-assemble behavior of the magnetic nanoparticles was

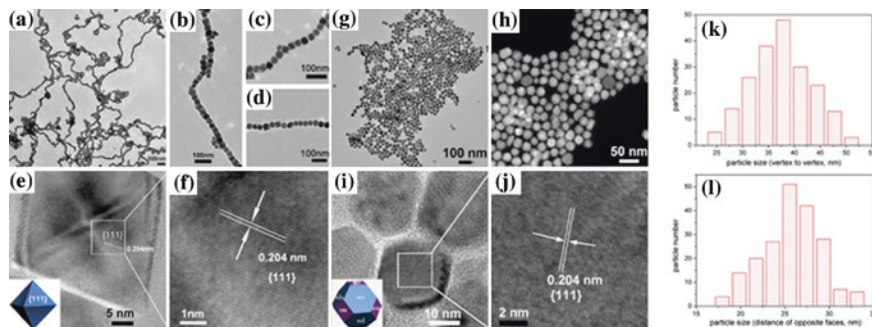


Fig. 2.7 **a** TEM image of Ni octahedrons **b–d** Magnified TEM images of Ni 1D structures with different orientation **e** HRTEM image of Ni octahedron; the inset is the scheme of the structure of octahedron; **f** Magnified images of the lattice fringe of the Ni octahedron. **g** TEM, **h** HAADF-STEM, and **i** images of Ni-truncated octahedrons; **j** magnified images of the lattice fringe of the Ni-truncated octahedron size distribution of **k** octahedral Ni nanoparticles (average size: 40.0 ± 5.1 nm, 90 % octahedrons, and 5 % irregular shapes) and **l** truncated octahedral Ni nanoparticles (average size: 25.2 ± 4.3 nm, 80 % octahedrons, 15 % nanoplate, and 5 % irregular shapes). Reprinted with the permission from Ref. [17]. Copyright 2012 American Chemical Society

corresponding to the Stoner–Wohlfarth model, [21] which was believed to be a result of their magnetic anisotropy [22–24]. The HRTEM of as-synthesized Ni NPs showed lattice fringes of 0.204 nm, which could be assigned to {111} planes of Ni in face-centered cubic (fcc) phase (Fig. 2.7e, f, i, j).

Importantly, our method is found to be generally applicable to the synthesis of other water-soluble bimetallic nanocrystals such as RhNi, PdNi, PdCu, and PtCu with excellent monodispersity and crystallization (Fig. 2.8).

The Fig. 2.9 showed that the X-ray diffraction (XRD) patterns of all these Pt–Ni nanocrystals could be indexed to {111}, {200}, and {220} diffractions of fcc metal with the peak positioned between those of Pt (JCPD-04–0802) and Ni (JCPD-04–0850) standard peak. We noted that the peaks continuously shifted from the Pt standard peaks to Ni standard ones when the content of Ni increases. Besides, the composition of the Pt–Ni alloy could be effectively controlled by choice of ratios between the two precursors, which was further verified by Energy-dispersive X-ray spectroscopy (EDX) and ICP-AES.

It is believed that the formation of the bimetallic alloy in the synthesis system developed in this chapter is the result of a noble-metal-induced-reduction process [25]. That is the Pt (0) species would perform to facilitate the reduction of Ni (II) to Ni (0) in the growth of Pt–Ni nanocrystals.

2.3.2 Surface Modification of Water-Soluble Pt–Ni Alloy

It is important to note two features of our method: the use of alcohol with high boiling point as solvents, phenyl organic molecules as growth inhibition agents,

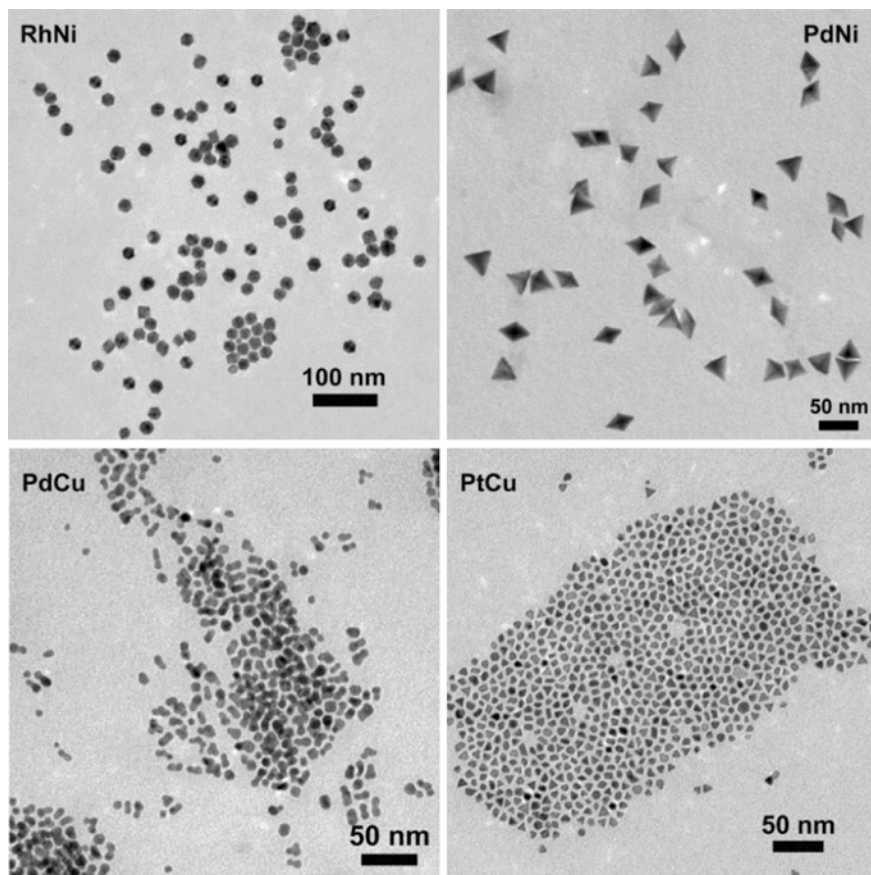


Fig. 2.8 TEM images of different water-soluble nanoalloy particles. Reprinted with the permission from Ref. [17]. Copyright 2012 American Chemical Society

and hydrophilic PVP as the capping agent. On the one hand, several groups have reported the shape control synthesis of Pt-based alloys, [26–28] which usually involved the use of reductants and growth inhibition agents such as $W(CO)_6$ [29] or CO [30]. In these methods, the use of reagents was mainly credited to the selective binding of CO [31] or bromide anion to Pt. Similarly, in our method, benzoic acid and aniline played a crucial role in the growth of Pt–Ni alloy, probably due to the selective adsorption effect that suppresses crystal growth in certain direction. However, the selective adsorption effect of phenyl organic molecules were well documented, such as on metal (Au, [32] Pt, [33] Ni [34]), on oxides [35] and on carbon materials [36]. This controlling effect of the phenyl organic molecules was substantiated by the fact that substituting benzoic acid with salicylic acid or sodium benzoate also resulted in the controlled synthesis of the Pt–Ni alloy.

On the other hand, the commonly used surfactants such as oleylamine, oleic acid in hydrophobic solvents usually resulted in catalysts of low activity and

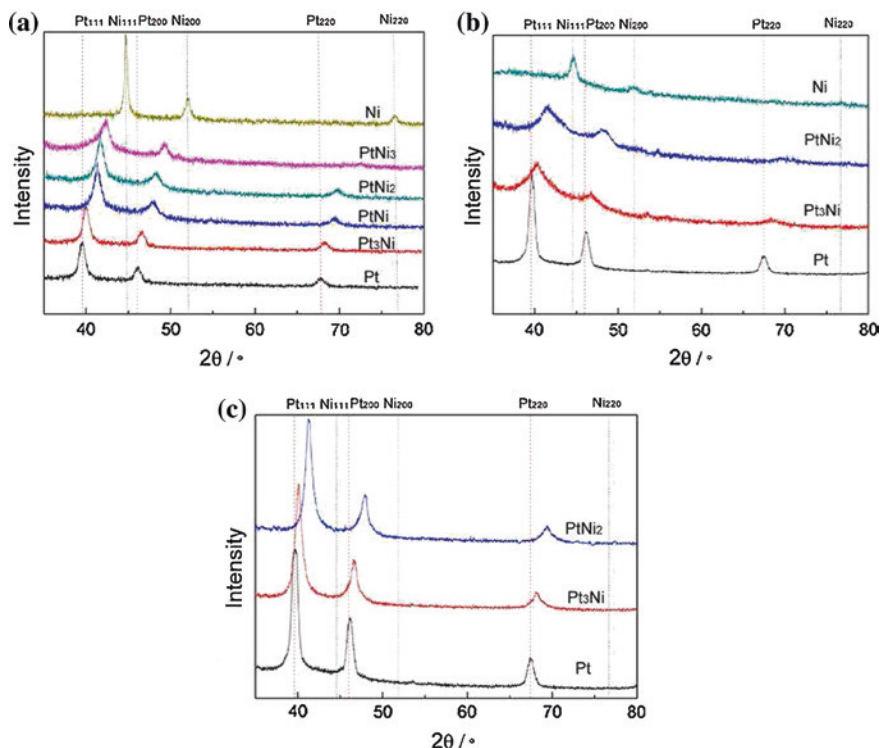


Fig. 2.9 XRD patterns of as-prepared Pt, Pt–Ni and Ni **a** octahedral nanocrystals, **b** truncated octahedral nanocrystals and **c** cubic nanocrystals. Reprinted with the permission from Ref. [17]. Copyright 2012 American Chemical Society

selectivity, possibly due to the strong chemical bonds on the catalysts' surface [37]. Herein, there must be a post treatment for these catalysts to obtain a desired higher catalytic activity while our Pt–Ni nanocrystals prepared in the presence of PVP could be used without any post treatment. Furthermore, we can modify the surface of these water-soluble nanoparticles with hydrophobic species by a simple process of exchanging the ligands, which could make the prepared catalysts a great ability to adapt to the complex reaction situation (Fig. 2.10).

2.3.3 Catalytic Performance of Pt–Ni Alloy in the Hydrogenation Reactions

We chose hydrogenation of benzalacetone, styrene, and nitrobenzene as the laboratory test reactions to probe our nanocrystals' structure–activity relationship, which would shed light on further application of the water-soluble Pt–Ni alloy. Notably, bimetallic catalysts are inspiring for possible synergistic effects that offer a higher catalytic activity for these hydrogenation (Fig. 2.11).

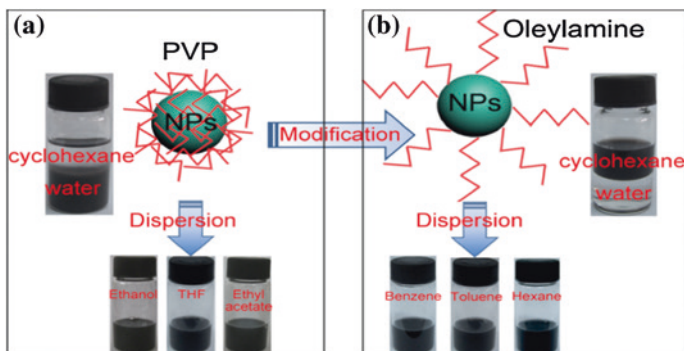


Fig. 2.10 Surface modification of Pt–Ni alloy. Reprinted with the permission from Ref. [17]. Copyright 2012 American Chemical Society

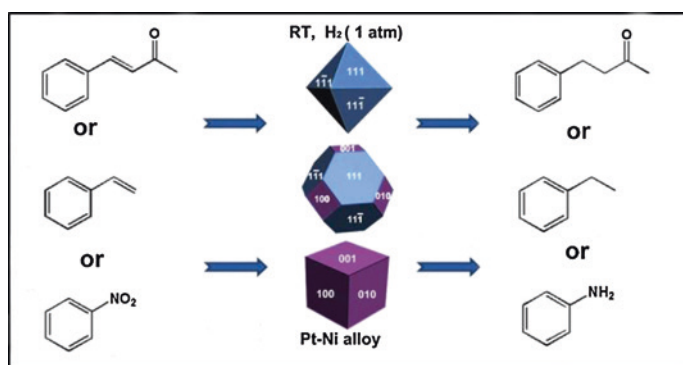


Fig. 2.11 Hydrogenation of Benzalacetone, Styrene, and Nitrobenzene. Reprinted with the permission from Ref. [17]. Copyright 2012 American Chemical Society

We first studied the effects of solvents, which showed that the use of hydrophilic solvents such as ethanol and ethyl acetate could also obtain excellent catalytic activity with the exception of THF. To this end, three types of catalyst [i.e., Ni, Pt, and Pt_xNi_{1-x} (0 < x < 1)] with comparable composition and different shapes were tested to ensure a meaningful comparison. It is interesting to note that the catalyst activity in hydrogenation of benzalacetone increase with the increased percentage of {111} facets [38]. Next, we examined the composition-activity dependence using octahedral Pt–Ni catalysts of different Pt/Ni ratios. Overall, bimetallic nanoalloy catalysts are more active than their monometallic counterparts, in the order of PtNi₂ > PtNi ≈ PtNi₃ > Pt₃Ni > PtNi₁₀ > Pt > Ni. The same trend was also observed in the hydrogenation of styrene with these Pt–Ni octahedrons. The Turnover frequencies (TOF) measured using octahedral PtNi₂ was up to 6-times higher than that measured using octahedral Pt catalyst. It was very satisfying to see that the best catalyst achieved 100 % conversion with nearly 100 %

Table 2.1 Solvent effect of catalytic reactions^a

Entry	Substrate	Solvent	Temp. (°C)	t. (h)	Conversion ^b (%)	Selectivity ^c (%)
1	benzalacetone	CH ₃ OH	25	2	90	>99
2	benzalacetone	AcOEt	25	2	95	>99
3 ^d	benzalacetone	THF	0	2	76	97
4	styrene	CH ₃ OH	25	2	99	>99
5	styrene	AcOEt	25	2	99	>99
6 ^d	styrene	THF	0	2	85	>99

^aConditions: substrate (0.5 mmol), 2 mol% catalyst with respect to the substrate and THF solvent (2.5 ml) were stirred under hydrogenation balloon/room temperature conditions

^bDetermined by GC using n-tridecane as an internal standard

^cSelectivity (%) = [(GC peak area of desired product)/(GC peak area of total products)] × 100

^dReaction temperature: 273.15 K

Table 2.2 Turnover Frequencies [TOFs (h⁻¹)] of the Hydrogenation of Benzalacetone Catalyzed by Various Catalysts^a

Entry	Catalyst	Average size. (nm)	Composition ^b	TOFs [h ⁻¹]
1	Pt octahedron	11.9	—	23
2	PtNi ₂ octahedron	11.8	0.37:0.63	139
3	Ni octahedron ^c	40.0	—	—
4	PtNi ₂ truncated octahedron	12.5	0.36:0.64	114
5	PtNi ₂ cube	11.2	0.35:0.65	95

^aConditions: substrate (0.5 mmol), 2 mol% catalyst with respect to the substrate and THF solvent (2.5 mL) were stirred under hydrogenation balloon/room temperature conditions

^bThe compositions were measured by ICP-AES

^cConsidering the ratio between surface area and volume, the amounts of Ni was 4 mol% respect to the substrate

selectivity in 2 h at room temperature under atmospheric H₂ pressure, which could effect both hydrogenation reactions 0 °C albeit at a slightly decreased rate (Tables 2.1 and 2.2).

We then evaluated PtNi₂ octahedron in the hydrogenation reactions of nitrobenzene, a more challenging reaction and important industrial process. It was again to our delight that nitrobenzene was quantitatively converted to aniline in 24 h, and the nanocrystals are substantially more active than the monometallic Pt and Ni nanocrystals (Fig. 2.12). The oxidation state of octahedral PtNi₂ and octahedral Ni nanocrystals were measured by XPS. The surface information about PtNi₂ alloy revealed the Pt 4f_{7/2} and 4f_{5/2} had a binding energy of 71.3 and 74.6 eV, characteristic of Pt (0). The Ni 2p_{1/2} and 2p_{3/2} were 869.9 and 852.8 eV, respectively, which corresponded to the Ni (0) (Fig. 2.13). In contrast, the XPS results showed that the oxidation state of Ni on the surfaces of octahedral Ni nanocrystals was mainly corresponded to Ni(II), which indicated the surfaces of octahedral Ni nanocrystals were dominated by a thin layer of oxidized Ni. Furthermore, the low activity of octahedral Ni catalyst could be contributed to the inertness of this thin

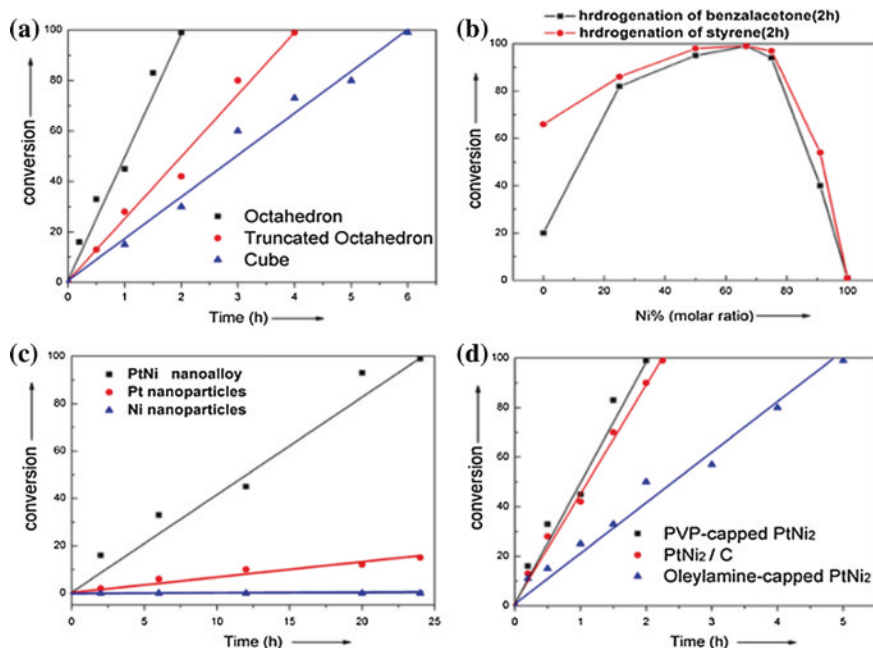


Fig. 2.12 **a** Conversion % as a function of time in hydrogenation of benzalacetone with PtNi₂ octahedral, truncated octahedral, and cubic nanocrystals. **b** Conversion % in a 2 h time of hydrogenation reactions of benzalacetone and styrene at r.t. under 1 atm H₂ pressure with octahedral NPs of different compositions. **c** Conversion % as a function of time in hydrogenation of nitrobenzene with PtNi₂, Ni, and Pt octahedrons. **d** Conversion % as a function of time in hydrogenation of benzalacetone with PVP-capped PtNi₂, "cleaned" PtNi₂/C and oleylamine-capped PtNi₂ octahedrons. Reprinted with the permission from Ref. [17]. Copyright 2012 American Chemical Society

layer of Ni (II). These data collectively suggest that shape, composition, and structure indeed play an important role in dictating the catalysts' activity and selectivity in the catalytic reactions.

One of the major goals in current heterogeneous catalyst research is to design nanocatalysts with good compatibility with complex reaction systems. We prepared the oleylamine-capped PtNi₂ nanocrystals through a ligand exchange process and a "cleaned" PtNi₂/C (10 % loading) catalyst by the washing with ethylic acid. In contrast, the oleylamine-capped nanocrystals are much less active toward hydrogenation of benzalacetone, while the PVP-capped nanocrystals show similar activity to that of the "cleaned" PtNi₂/C catalyst, underlying the superiority of PVP as the capping agent that exempted the catalyst from postsynthesis treatment [39]. Ecologically friendly catalysts, especially those involving precious metals, underscore the emphasis of green chemistry. Unlike the organic syntheses that are routinely performed in nonaqueous solution, nature carries out most of the chemical reactions in water [40]. Owing to their excellent biocompatibility and

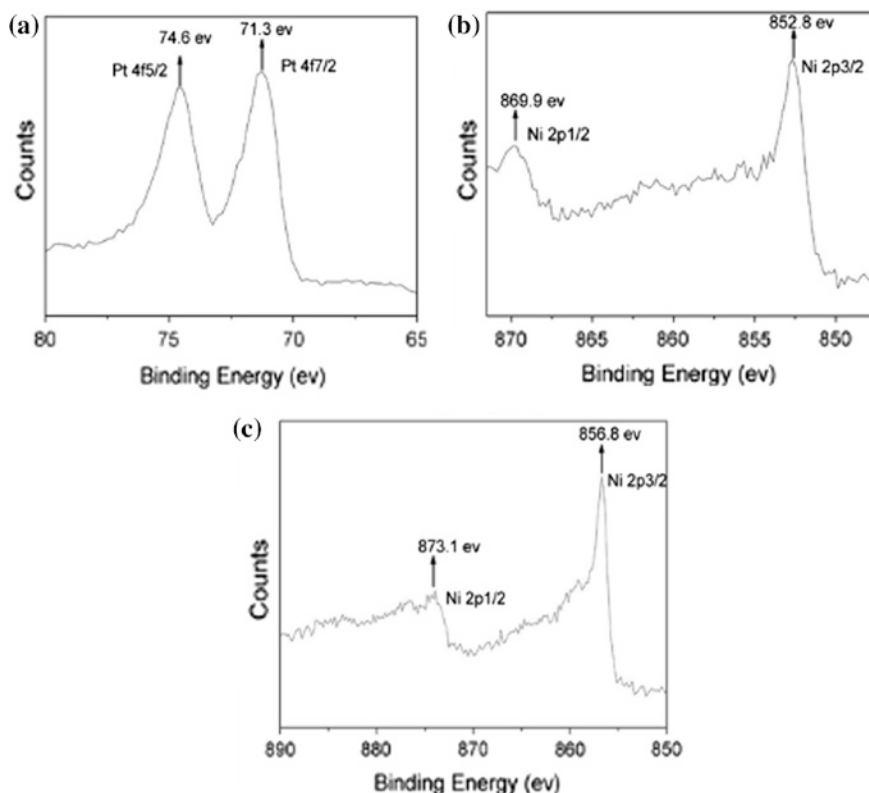


Fig. 2.13 XPS data for the octahedral PtNi_2 nanocrystals: high-resolution scans of the **a** Pt 4f and **b** Ni 2p. XPS data for the octahedral Ni nanocrystals: high-resolution scans of the **c** Ni 2p. Reprinted with the permission from Ref. [17]. Copyright 2012 American Chemical Society

hydrophilicity, the as-prepared water-soluble catalysts could find important applications in green chemistry and biology.

Importantly, the catalysts could be recycled at least five times without observable decay of activity. TEM study of all spent catalysts found no obvious aggregation or shape change, suggesting excellent stabilities of our nanocrystals under these reaction conditions (Table 2.3).

Table 2.3 Recycle of Catalysts

Entry	Catalyst	Temp. [°C]	t. [h]	Conversion [%]	Selectivity [%]
1	PtNi_2	25	2	>99	>99
2	1 recycle	25	2	>99	>99
3	2 recycle	25	2	>99	>99
4	3 recycle	25	2	>99	>99
5	4 recycle	25	2	>99	>99

2.4 Conclusions

In this chapter, we have developed a general method to synthesize water-soluble Pt, $\text{Pt}_x\text{Ni}_{1-x}$ ($0 < x < 1$), and Ni nanocrystals with uniformly controlled shapes and compositions. Through a series of model hydrogenation reactions, we performed a systemic evaluation of structure-activity relationship of the catalysts. Bimetallic nanoalloy catalysts are more active than their monometallic counterparts possibly due to a synergistic effect between the two metals. Using hydrophilic and green PVP as the capping agent could exempt the catalyst from postsynthesis treatment with great enhancement of catalyst's biocompatibility. Overall, this general method could be an effective tool for us to screen efficient catalyst in the future.

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