

Shaped Ni Nanoparticles with an Unconventional *hcp* Crystalline Structure

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Experimental procedures

Synthesis of hourglass-shaped Ni nanoparticles with *hcp* structure

Nickel acetylacetonate (Sigma Aldrich, 90%) 81 mg was dissolved in 10 ml of mesitylene (Sigma Aldrich, 98%). The appropriate amount of hexadecylamine (Sigma Aldrich, 90%; 0-30 equivalent relative to the Ni precursor) was dissolved in 10 ml of mesitylene. The hexadecylamine solution was mixed with the metal precursor solution and trioctylphosphine (Sigma Aldrich, 90%; 0-2.67 equivalent relative to the Ni precursor) under vigorous stirring. The mixed solution was placed in a 30 ml Teflon liner and sealed in the bomb of an autoclave that was pressurized to 10 bar with hydrogen gas. The autoclave was held at 140 °C for 24 hrs. The nanoparticle products were washed with toluene and gathered using magnetic force.

Synthesis of spherical Ni nanoparticles with *fcc* structure

Spherical nickel nanoparticles (15±3 nm in size) were synthesized using a literature protocol¹. Briefly, 500 mg of nickel acetylacetonate was mixed with 8 ml of oleylamine (Aldrich, 70%) and 2 ml of trioctylphosphine under vigorous stirring in a round bottom flask. The mixture was degassed at 100 °C and heated to 200 °C under a nitrogen atmosphere. The resultant nanoparticles were cooled to room temperature and centrifuged using acetone as the antisolvent. Spherical Ni nanoparticles with a size of 32±4 nm were synthesized using the same procedure except that 5.5 ml of oleylamine and 0.8 ml of trioctylphosphine were added.

Characterization

The nanoparticle shape was investigated using transmission electron microscope or high resolution transmission electron microscope (JEOL and TECNAI). A powder X-ray diffractometer (Ultima IV, RIGAKU) was used to investigate the crystalline structure of the nanoparticles. An X-ray photoelectron spectrometer (K-alpha, Thermo U. K.) equipped with a monochromatic Al K α X-ray source (12 kV, 3 mA) was used to measure the surface property

of the nanoparticles. Binding energies were calculated using the maximum intensity of the C 1s signal at 285 eV as a reference. Elemental analysis was carried out using an inductively coupled plasma optical emission spectrometer (Thermo, iCAP 6000).

Catalytic activity test (4-nitrophenol hydrogenation)

4-nitrophenol (Aldrich, 99%) was dissolved in isopropyl alcohol (Duksan) to a concentration of 2 mM. Nonpolar solvent didn't show distinct UV peaks when 4-nitrophenol was dissolved. NaBH₄ (Aldrich, 99%) was also dissolved in ethanol (Duksan) to a concentration of 1 M. Ni nanoparticles (1 mg) were dispersed in 5 ml of isopropyl alcohol. Hourglass-shaped *hcp* Ni nanoparticles and spherical *fcc* Ni nanoparticles with a similar size of 32 nm were used as catalysts. A solution of 4-nitrophenol (5 ml) was mixed with the Ni nanoparticle solution and stirred for 5 min. Then, 5 ml of the NaBH₄ solution was added to the 4-nitrophenol solution and stirred for 30 sec ($t = 0$). The reacting solution was sampled every 2 min (0.1 ml), diluted with 2 ml of isopropyl alcohol, and then monitored using UV-Vis spectroscopy. Because the Ni nanoparticles are magnetic, a vortexer rather than a magnetic stir bar was used for stirring.

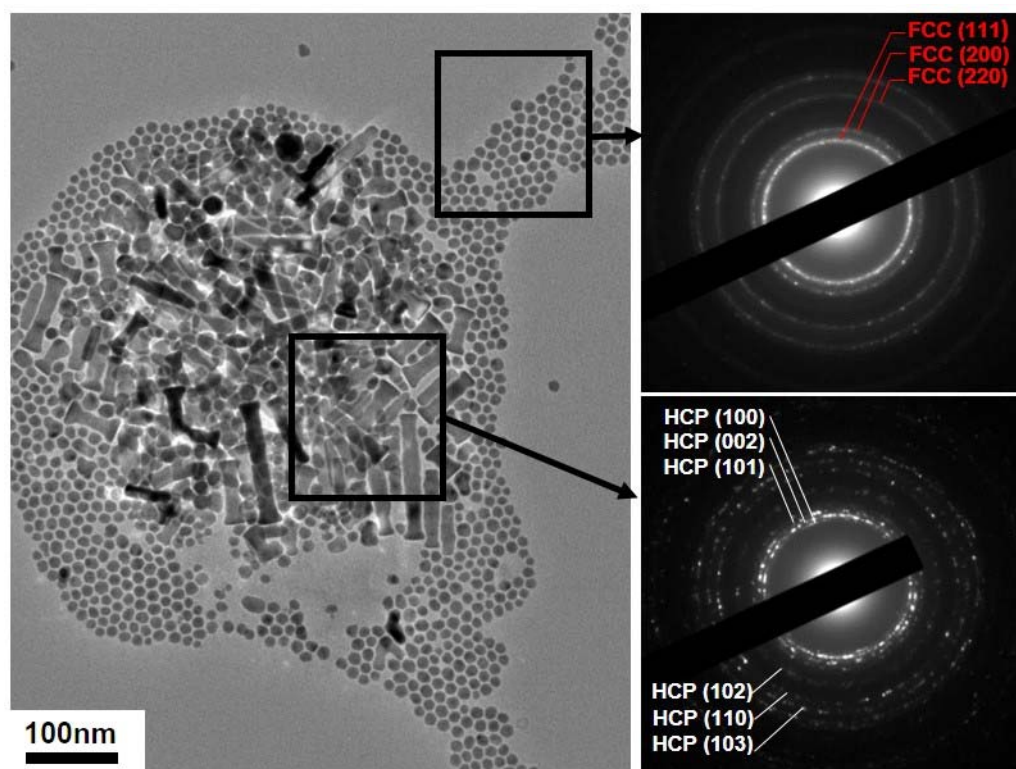


Figure S1. TEM images of the as-prepared Ni nanoparticles prior to the magnetic separation step. Hourglass-shaped *hcp* Ni nanoparticles are mixed with smaller spherical *fcc* Ni nanoparticles. These nanoparticles were synthesized using 0.3 mmol of Ni precursor, 30 equivalent of HDA and 1.67 equivalent of TOP (relative to the Ni precursor) under 10 bar of H₂ gas.

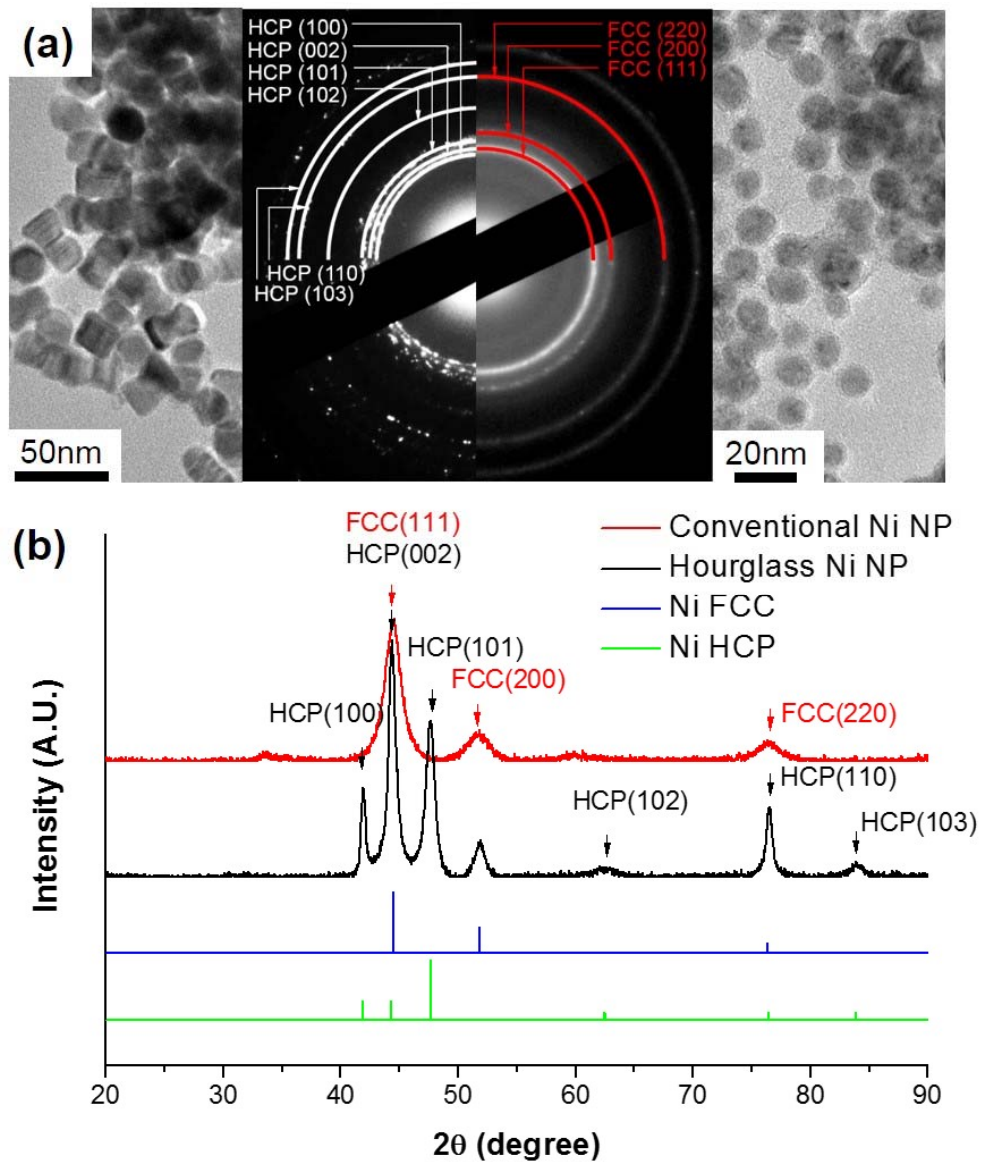


Figure S2. (a) Selected area electron diffraction patterns showing the different crystalline structures of the hourglass-shaped Ni nanoparticles (left) and conventional spherical Ni nanoparticles (15 ± 3 nm in size) (right). (b) X-ray diffraction patterns.

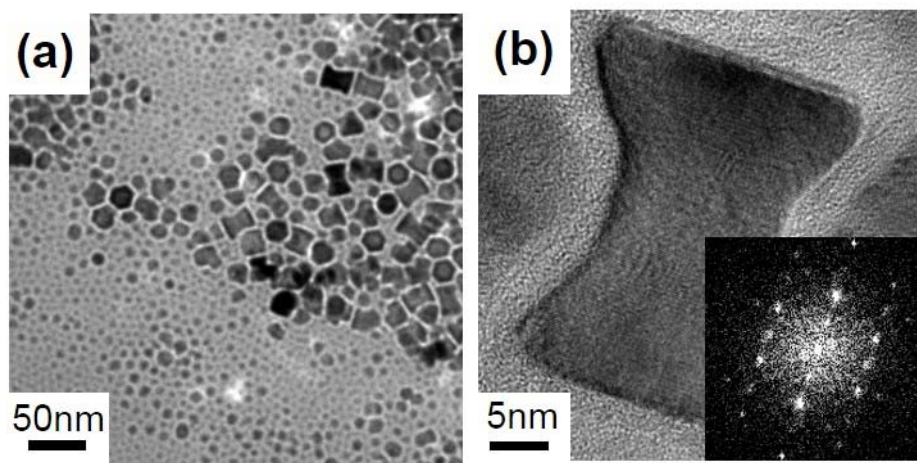


Figure S3. (a) TEM image of as-synthesized Ni nanoparticles after 6 hrs of synthesis without magnetic separation, and (b) HR-TEM image of the obtained hourglass-shaped Ni nanoparticle. Its FFT pattern (inset) shows *hcp* structure for a zone axis of [010].

Table S1. Yields of the hourglass-shaped nanoparticles obtained after magnetic separation for various synthesis time. 0.3 mmol of Ni precursor, 0.5 mmol (1.67 equiv.) of TOP, and 6 mmol (20 equiv.) of HDA were used in all cases at 10 bar H₂ pressure.

Synthesis Time	Mass of Ni NP ^a (Yield ^b) Try 1	Mass of Ni NP ^a (Yield ^b) Try 2	Average Yield
6 hrs	0.61 mg (3.3%)	0.86 mg (4.6%)	4%
9 hrs	6.1 mg (33%)	5.6 mg (30%)	32%
12 hrs	6.7 mg (36%)	7.3 mg (39%)	38%
18 hrs	7.9 mg (43%)	7.8 mg (42%)	42%
24 hrs	8.2 mg (44%)	8.7 mg (47%)	46%

^aMass of the obtained hourglass-shaped Ni NP after magnetic separation, measured by inductively coupled plasma elemental analysis.

^bYield of the hourglass-shaped NPs = mass of the hourglass-shaped Ni NP / mass of nickel in Ni precursors used for the synthesis.

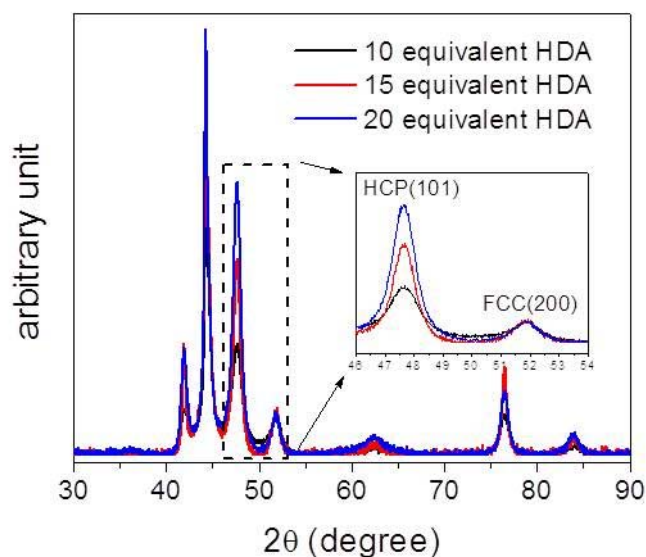


Figure S4. Powder X-ray diffraction patterns of Ni nanoparticles synthesized using 10, 15, and 20 equivalents of HDA relative to the Ni precursor. The XRD patterns were normalized to the peak centered at 51.8° , which corresponds only to *fcc* Ni. The peak centered at 47.7° corresponds to *hcp* Ni only, and its intensity increases when increasing amounts of HDA are added to the reaction solution.

Table S2. Yields of the hourglass-shaped nanoparticles obtained after magnetic separation for various amounts of HDA. 0.3 mmol of Ni precursor and 0.5 mmol (1.67 equiv.) of TOP were used in all cases at 10 bar H_2 pressure.

HDA	Mass of obtained hourglass-shaped Ni NP after magnetic separation	Yields of the shaped NPs based on the amount of Ni precursors
3 mmol (10 equiv.)	2.2 mg	12%
6 mmol (20 equiv.)	8.3 mg	45%
9 mmol (30 equiv.)	11.3 mg	61%

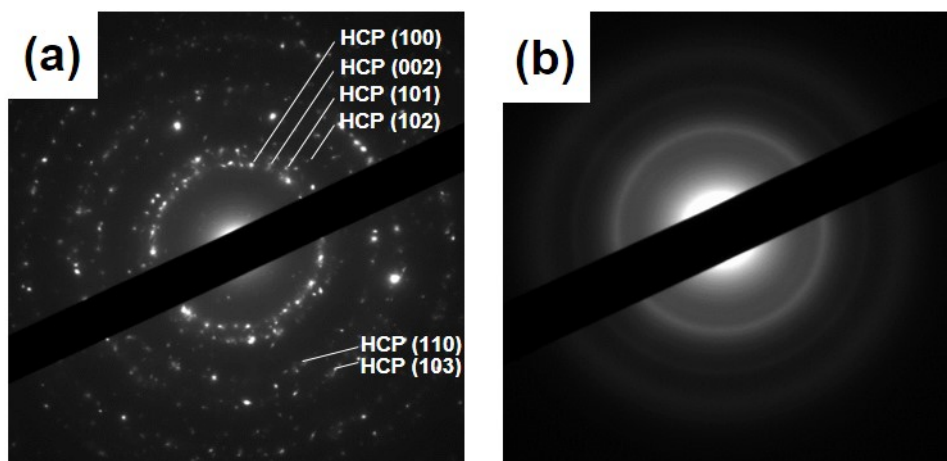


Figure S5. SAED patterns of Ni nanoparticles synthesized (a) without TOP and (b) using 2.67 equivalents of TOP (relative to the Ni precursors). Each case corresponds to Figure 3(a) and (f), respectively.

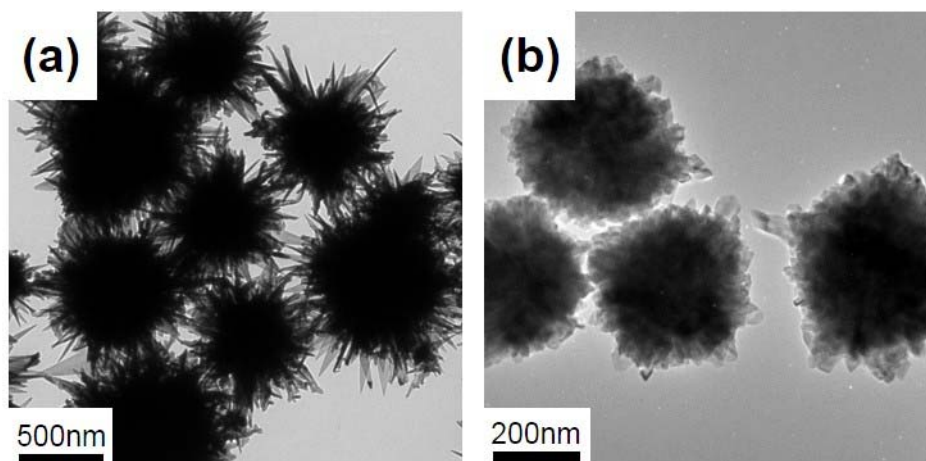


Figure S6. TEM images of Ni nanoparticles synthesized at ambient hydrogen pressure (1 bar). When the amount of TOP was increased from (a) 0.5 equivalents to (b) 1 equivalent (relative to the Ni precursor), the length of the thorny tips decreased.

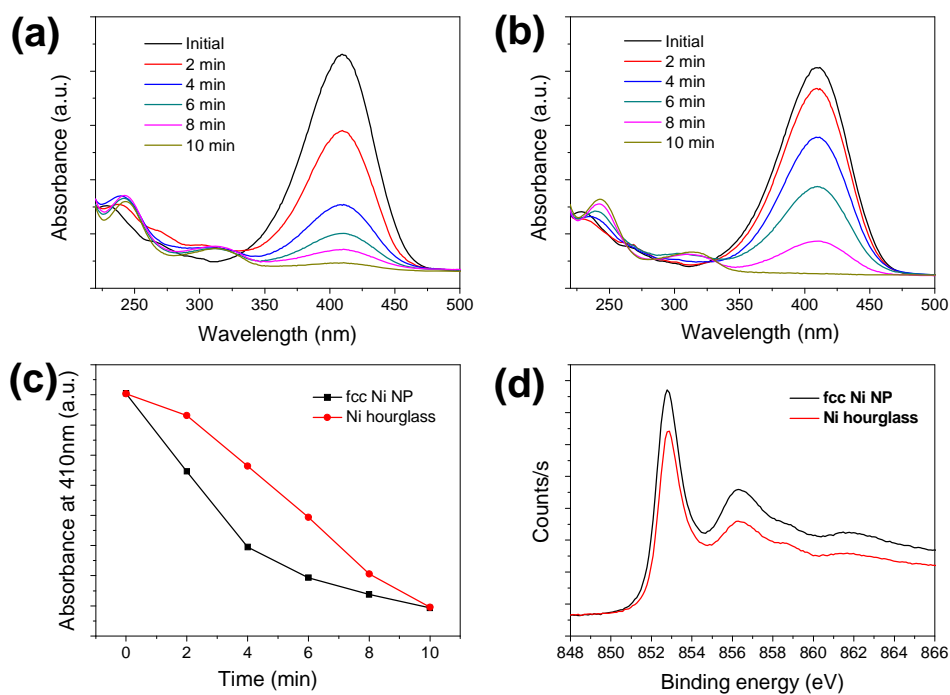


Figure S7. Hydrogenation of 4-nitrophenol using (a) *fcc* Ni nanoparticles (32 nm in size) and (b) *hcp* hourglass-shaped Ni nanoparticles as catalysts. (c) The changes in absorbance of the peak centered at 410 nm over time. (d) XPS data for both types of Ni nanoparticles.

Reference

1. S. Carenco, C. Boissière, L. Nicole, C. Sanchez, P. Le Floch and N. Mézailles, *Chem. Mater.*, 2010, **22**, 1340-1349.