

Supplementary Data

Kinetically Controlled Synthesis of Nickel Tetrahedron Nanocrystals for High Performance on Catalytic Hydrogenation

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1. Experimental section

Ni tetrahedrons: All chemicals used in this experiment were analytical grade and were without further purification. In a typical synthesis, 0.595 g NiCl₂·6H₂O, a certain amount of sodium citrate and 75 mL ethylene glycol were mixed in a three-necked bottle, and magnetically stirred at room temperature overnight. Then, 20 mL ethylene glycol (EG) solution of 2 mol sodium hydroxide was added to the above solution drop by drop, followed by adding 10 mL EG solution of 1 mol sodium formate. The mixture was then transferred into an oil bath and heated at 210 °C for 20 h under vigorously magnetic stirring. As the reaction proceeded, the solution gradually changed its color from green to dark, implying the formation of metallic Ni species. The dark precipitate was washed by nanopure water and ethanol and collected.

Ni nanoflowers: 0.237 g NiCl₂·6H₂O, 1.765 g sodium citrate, and 0.32 g sodium hydroxide were dissolved in 30 mL EG, followed by 1 hour vigorous stirring in an oil bath at 35 °C. Then, 10 mL EG solution of sodium formate (1.0 g) was added to the

above solution drop by drop. After that, the resulting homogeneous green solution was transferred into a 100-mL Teflon-lined stainless-steel autoclave. The sealed vessel was heated at 210 °C for a 18 h before it was cooled down to room temperature. The products were purified by ethanol, separated via centrifugation three times.

Ni nanoparticles: 0.450 g NiCl₂·6H₂O was dissolved in 90 mL ethylene glycol in a three-necked bottle, and vigorously stirred at room temperature for 30 mins. Then, 1.5 mL ethylene glycol (EG) solution of sodium hydroxide (1 mol) was added to the above solution drop by drop, followed by adding 2.2 mL hydrazine (85%) quickly. The mixture was then transferred into an oil bath kept at 60 °C for 30 mins under vigorously stirring. As the reaction proceeded, the solution gradually changed its color from green to dark, implying the formation of metallic nickel species. The dark precipitate was washed by nanopure water and ethanol for three times.

Catalytic test: Ni nanocrystal catalysts were calcined at 500°C for 4h under H₂ stream in a tubular furnace. Liquid-phase catalytic hydrogenation of toluene was carried out in a 100 mL stainless autoclave containing a catalyst with 25 mg Ni, 2 mL of toluene, 25 mL of cyclohexane., and 5.0 MPa of H₂. After being purged with H₂ three times, the reaction mixture was maintained at 140 °C and stirred vigorously (850 rpm) to eliminate the diffusion effects. During the reaction, samples were withdrawn from the reaction mixture at intervals for product analysis on a gas chromatograph.

Characterization: The surface morphology and the particle size were observed by transmission electron micrography (TEM, JEOL JEM-2100). The crystalline structure was determined by both X-ray diffraction (XRD; Rigaku D/Max-RB with Cu K α radiation) and selective area electronic diffraction (SAED; JEOL JEM-2100). The Brunauer–Emmett–Teller (BET) surface area was determined by nitrogen adsorption-desorption isotherm measurements at 77 K (ASAP 2010). The catalytic products were analyzed by a gas chromatograph (Agilent Technologies: 6890N).

2. Figures

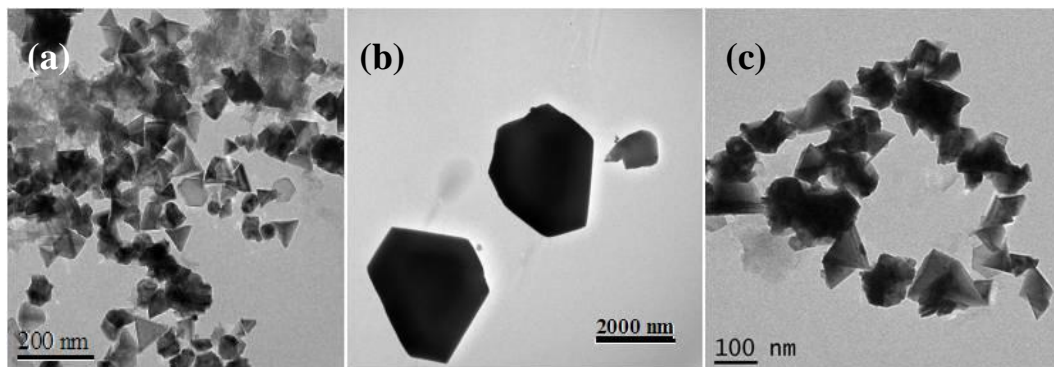


Figure S1. TEM images of nickel morphologies formed (a) in 1 M sodium formate in ethylene glycol at 210 °C, (b) in 2 M sodium formate in ethylene glycol at 190 °C, and (c) in 2 M sodium formate in ethylene glycol at 220 °C.

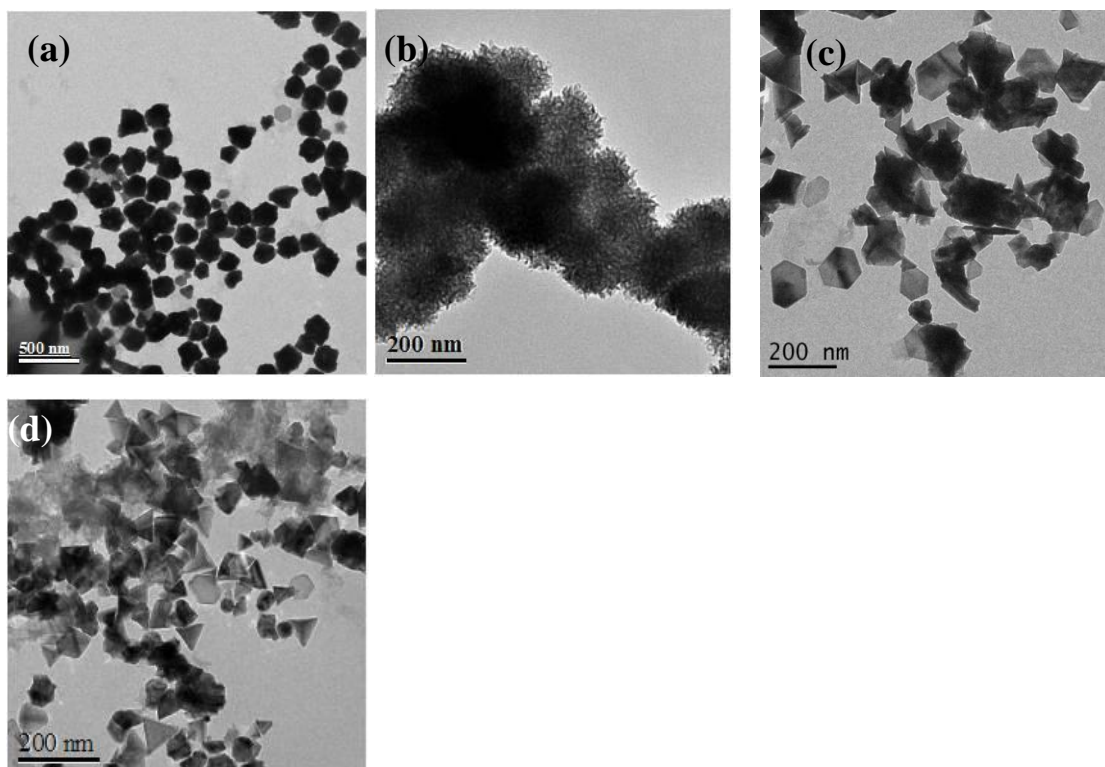


Figure S2. TEM images of nickel morphologies (a) using PVP as a capping agent, (b) in 0.5 M sodium citrate in ethylene glycol, (c) 0.75 M sodium citrate in ethylene glycol, and (d) 1.5 M sodium citrate in ethylene glycol, respectively.

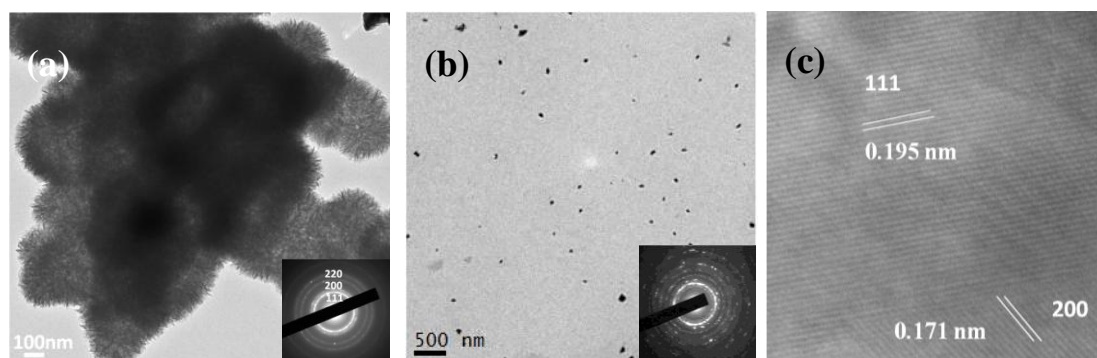


Figure S3. (a) TEM image of Ni nanoflowers and inset is the corresponding SAED pattern. (b) TEM image of Ni nanoparticles and inset is the corresponding SAED pattern of Ni nanoparticles. (c) HRTEM image of Ni nanoparticles.