Supporting Information

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

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Experimental:

Synthesis of Co-Ni nanocrystals with hexagon-like caps: 0.750 g $Co(OAc)_2 \cdot 4H_2O$ and 1.250 g stearic acid were mixed into 70 mL propylene glycol and stirred for 30 min. 0.0385 g $Ni(OAc)_2 \cdot 4H_2O$ was added the above solution and stirred for another 30 min. Then the mixture was transferred into a Teflon-lined autoclave (100 mL) and maintained at 160 ^oC for different time. The precipitation was washed with ethanol and water, and finally dried at 60 ^oC for 4 h under vacuum.

Synthesis of Co-Ni nanoparticles: 7.50 g $Co(OAc)_2 \cdot 4H_2O$ and appropriate amount of $Ni(OAc)_2 \cdot 4H_2O$ were mixed into 100 mL deionized water. 3.816 g Na_2CO_3 was added into 100 mL H_2O and then added into the above solution. The mixed solution was aging for 2 h at 40 ^oC and until the violet precipitate was shown. The violet precipitate was filtered and washed several times with deinized water. The sample was dried at 100 ^oC for 10 h in a vacuum oven and calcined at 350 ^oC for 5 h to form Co-based bimetallic oxide. Finally, Co-based bimetallic oxide was reduced into Co-Ni nanoparticles in a tubular oven filled with 10% H_2/N_2 at 300 ^oC for 8 h.

Nitrobenzene hydrogenation: The catalytic hydrogenation of nitrobenzene was carried out in a well-stirred pressure vessel (100 mL). 30 mg catalyst was dispersed in 30 mL ethanol in a pressure vessel. 1 mL nitrobenzene was added. H_2 flow was

applied into the bottle to blow air away for minutes in order to remove any trace of oxygen. The temperature was then increased to 120°C and the vessel was pressurized by 3 MPa H_2. Products were withdrawn at regular intervals, filtered and analyzed by a gas chromatography.

Characterization: The transmission electron microscopy (TEM) including high-resolution transmission electron microscopy (HRTEM), and energy dispersive X-ray spectrum (EDS) were performed on a FEI TECNAI G2 F20 STWIN transmission electron microscope at an operating voltage of 200 kV, equipped with a Gatan Orius CCD camera. The morphology of samples was examined by ZEISS SUPRA^{TM} 55 scanning electron microscope (SEM). X-ray diffraction (XRD) patterns of samples were recorded on a Japanese Rigaku Ultima IV powder diffractometer using Cu Kα radiation with the wavelength of 1.54056 Å at 40 kV and 40 mA. The specific surface areas of the catalysts were calculated from N_2 adsorption isotherms using the BET and BJH methods (ASAP 2010). The X-ray photoelectron spectroscopies (XPS) of the samples were recorded on a Thermo Fisher Scientific K-Alpha X-ray photoelectron spectrometer. The catalytic products were analyzed by a gas chromatograph (Agilent Technologies: GC 7890A/MSD 5975C).

Supporting Figures

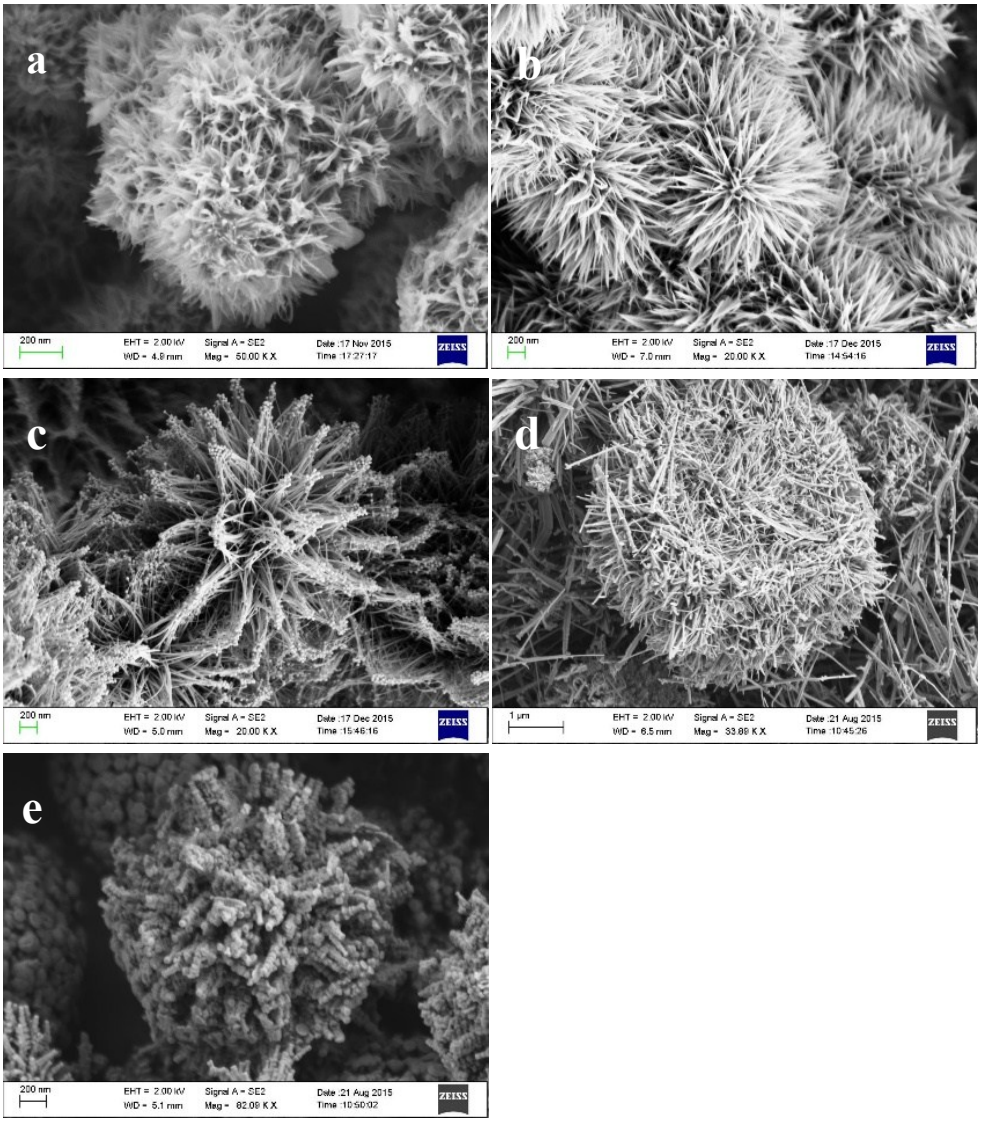

Figure S1. SEM images of Co-Ni nanocrystals synthesized at different reaction temperature: (a) 120^{o}C, (b) 130^{o}C, (c) 140^{o}C, (d) 170^{o}C, and (e) 190^{o}C.

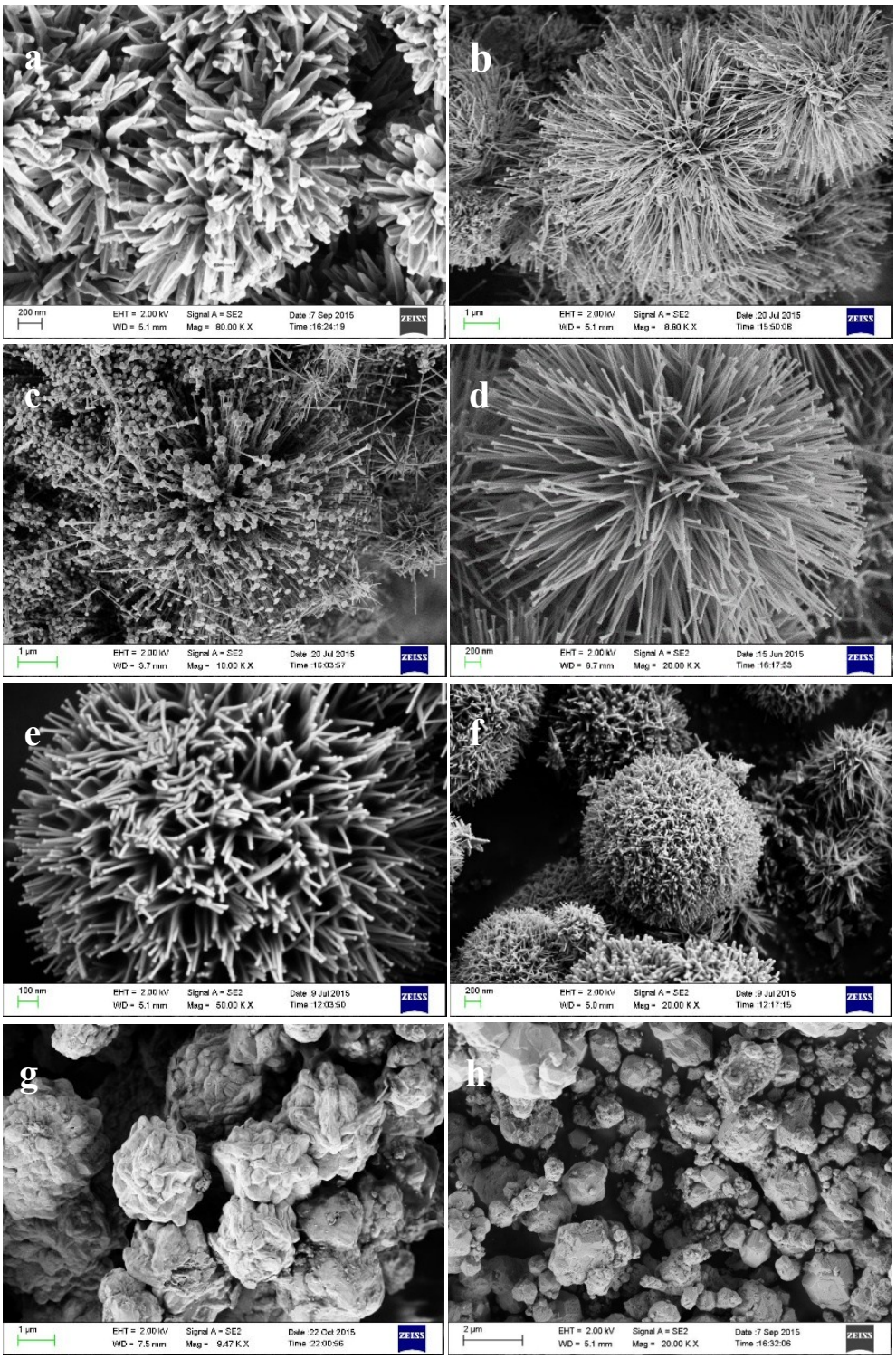

Figure S2. SEM images of Co-Ni with different content of Ni: (a) pure Co without Ni, (b) 1 wt% Ni, (c) 5 wt% Ni, (d) 10 wt% Ni, (e) 20 wt% Ni, (f) 30 wt% Ni, (g) 50 wt% Ni, and (h) pure Ni without Co.

In the absence of Ni in the synthesic system, the microspheres of Co were formed in the final product (Figure S2a). When the content of Ni was limited to 10 wt

%, the screw-like structure was created in Figure S2b-d. While the amount of Ni was added in the 20 wt% or 30 wt%, the nanorods without caps could be produced, shown in Figure S2e-f. As the Ni content was up to 50 wt% and more, microspheres of Co-Ni were obtained (Figure S2g-h).

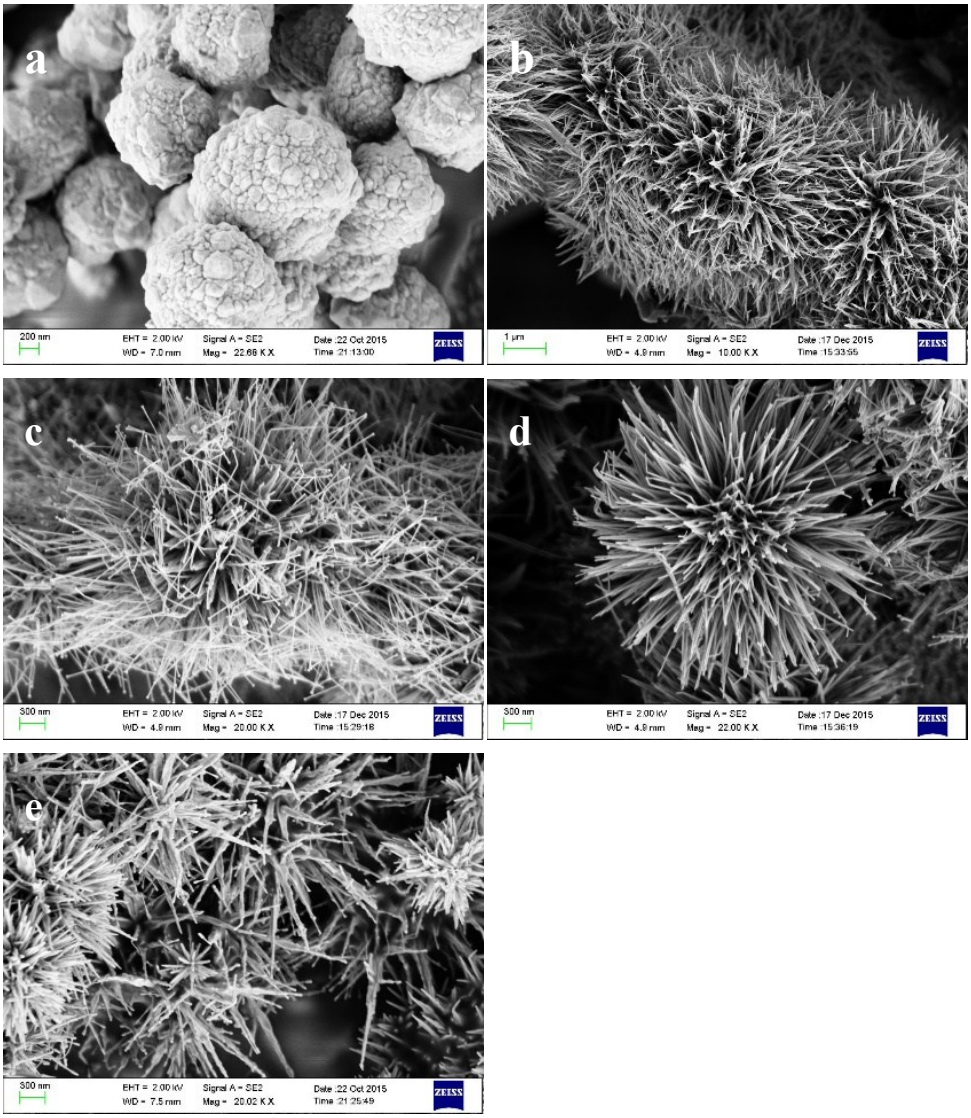

Figure S3. SEM images of Co-Ni nanocrystals synthesized using different surfactants: (a) citric acid, (b) salicylic acid, (c) lauric acid, (d) trans-cinnamic acid, and (e) myristic acid.

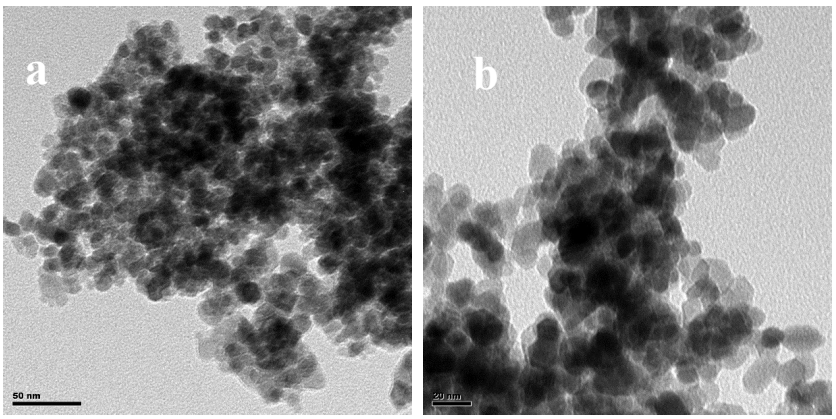

Figure S4. TEM images of (a) Co-Ni (5 wt% Ni) nanoparticles and (b) Co-Ni (1 wt% Ni) nanoparticles.

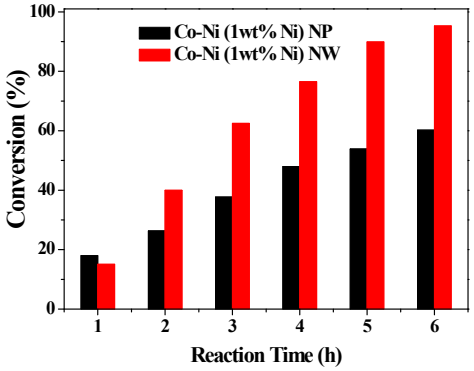

Figure S5. Catalytic performance of Co-Ni (1 wt% Ni) catalysts for nitrobenzene hydrogenation.

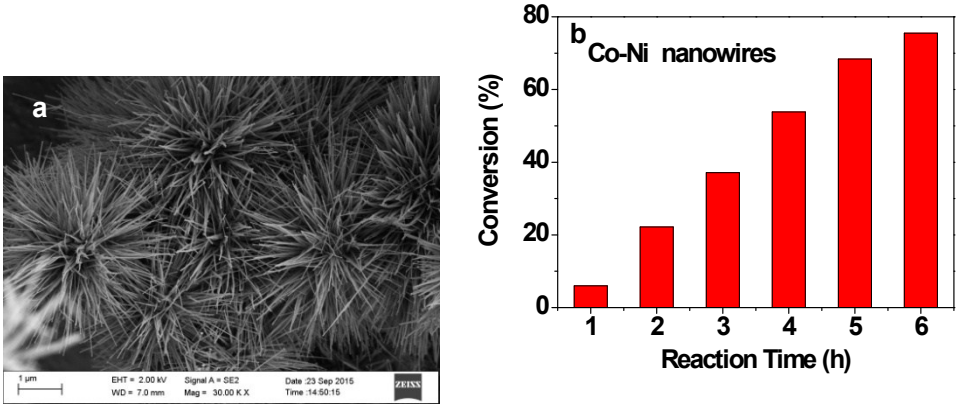

Figure S6. (a) SEM image of Co-Ni nanowires without caps. (b) Catalytic activity of Co-Ni nanowires without caps for Hydrogenation of nitrobenzene. (Note: the content of Ni is 5 wt%.)