

Supporting Information

Pt-Ni Nanodendrites with High Hydrogenation Activity

Weiyang Wang, Dingsheng Wang, Xiangwen Liu, Qing Peng and Yadong Li*

Department of Chemistry, Tsinghua University, Beijing, 100084 (P.R. China). Fax: +86-10-62788765;
Tel: +86-10-62772350; Email: ydli@mail.tsinghua.edu.cn

Experimental Details

Preparation for Pt-Ni nanodendrites:

In a typical synthesis of bimetallic Pt-Ni nanodendrites, 0.025 mmol of Pt(acac)₂ (acac=acetylacetonate), 0.025 mmol of Ni(acac)₂ and 20 mg DDAB were added into the solution with 5 mL of octadecene (ODE), 4 mL oleylamine (OAm) and 2.5 mL oleic acid(OA). After vigorous stirring for 15 minutes, the mixture was transferred to the teflon-lined, stainless autoclave. The reaction lasted for two and a half hours at 200°C. Then the autoclave was taken out to cool down slowly at the ambient temperature. The products were collected and washed with ethanol several times. The as-obtained Pt-Ni nanodendrites were dispersed in 5 mL of cyclohexane.

Preparation for Pt-Ni nanodendrites with a denser structure:

In a typical synthesis of bimetallic Pt-Ni nanodendrites(I), 0.025 mmol of Pt(acac)₂ and 0.025 mmol of Ni(acac)₂ were added into the solution with 7.5 mL of octadecene (ODE) and 4 mL oleylamine (OAm). Then, the mixture was transferred to the teflon-lined, stainless autoclave. The reaction lasted for two and half hours at 200°C. Then the autoclave was taken out to cool down slowly at the ambient temperature. The products were collected and washed with ethanol several times. The as-obtained Pt-Ni nanodendrites were dispersed in 5 mL of cyclohexane.

Preparation for Pt-Ni polyhedra:

In a typical synthesis of bimetallic Pt-Ni polyhedra, 0.025 mmol of H₂PtCl₆·6H₂O and 0.025 mmol of NiCl₂·6H₂O were dissolved in very little water. Then the solutions were added into 4 mL oleylamine (OAm) preheated to 120 °C. And then the whole solution was vacuumized for about 5 minutes to make sure the water was completely moved in the reaction system. Next, the mixture was transferred to a teflon-lined, stainless autoclave and mixed with 5 mL of octadecene (ODE) and 2.5 mL oleic acid(OA). The reaction lasted for two and half hours at 200 °C. Then the autoclave was taken out to cool down slowly at the ambient temperature. The products were collected and washed with ethanol several times. The as-obtained Pt-Ni polyhedra were dispersed in 5 mL of cyclohexane.

Typical procedure for the hydrogenation of nitrobenzene catalyzed by Pt-Ni alloys.

The Pt-Ni nanodendrites (contain 0.0025 mmol Pt, 0.5 mol %) dispersed in cyclohexane and 4.5 mg active carbon were added in a 10 mL round flask. After supersonic for 10 min the cyclohexane was removed by rotary evaporation, and the loaded Pt-Ni nanodendrites were re-dispersed in 5 mL ethyl acetate, then 51 μ L nitrobenzene (0.5 mmol) was added in. The round flask was purged with H_2 . Then, the reaction mixture was stirred at room temperature under a H_2 balloon. When GC monitoring indicated the complete consumption of substrate, the catalyst was separated from the mixture by centrifugation and the liquid phase was concentrated under reduced pressure to remove the solvent. The product was dissolved in $CDCl_3$ and subsequently characterized by 1H NMR.

Characterization of the synthesized nanocrystals. The powder X-ray diffraction (XRD) patterns were recorded with a Bruker D8-advance X-ray powder diffraction -meter with $Cu K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Transmission electron microscopy (TEM) images were obtained with a Hitachi H-7650B transmission electron microscope operating at 100 kV. High-resolution TEM (HR-TEM) and high-angle annular dark-field scanning TEM (HAADF-STEM) characterizations were performed with a FEI Technai G2 F30 Super-Twin transmission electron microscope operating at 200 kV after placing a drop of the synthesized nanocrystals on carbon-coated Cu grids (200 mesh). Energy dispersive spectroscopies (EDS) were recorded to determine the compositions of the obtained products. The contents of highly branched Pt-Ni nanoalloys were determined by inductively coupled plasma mass spectrometry (ICP-MS, X Series).

Supplementary Figures

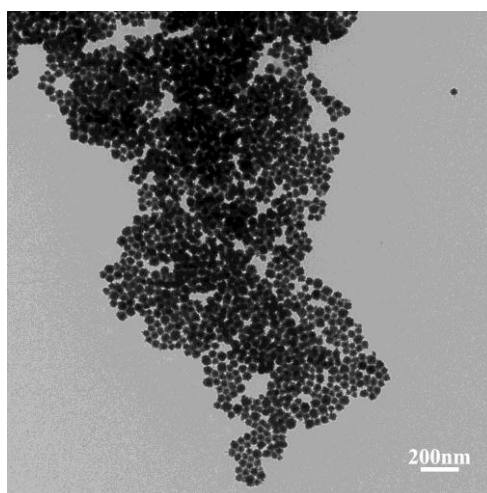


Figure S1. TEM image of Pt-Ni nanodendrites.

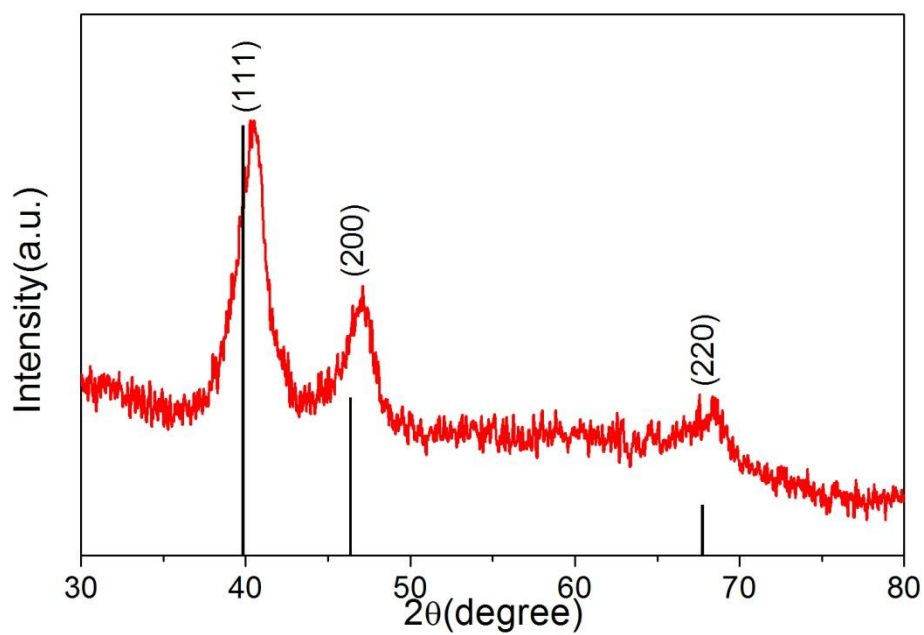


Figure S2. XRD pattern of Pt-Ni nanodendrites.

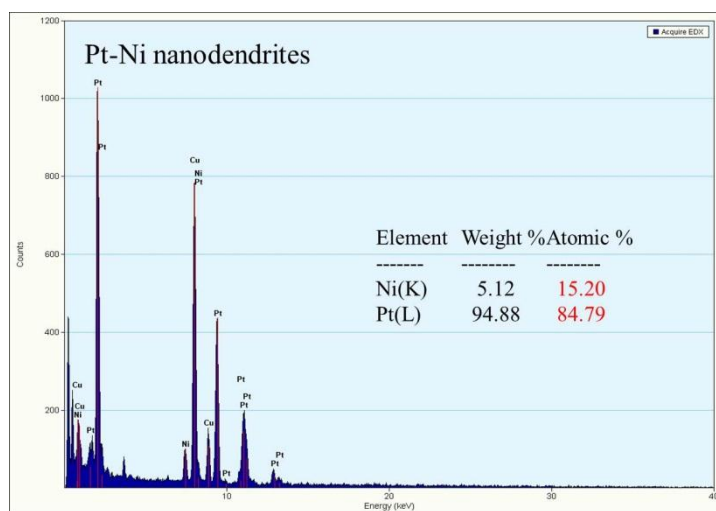


Figure S3. EDS patterns of Pt-Ni nanodendrites

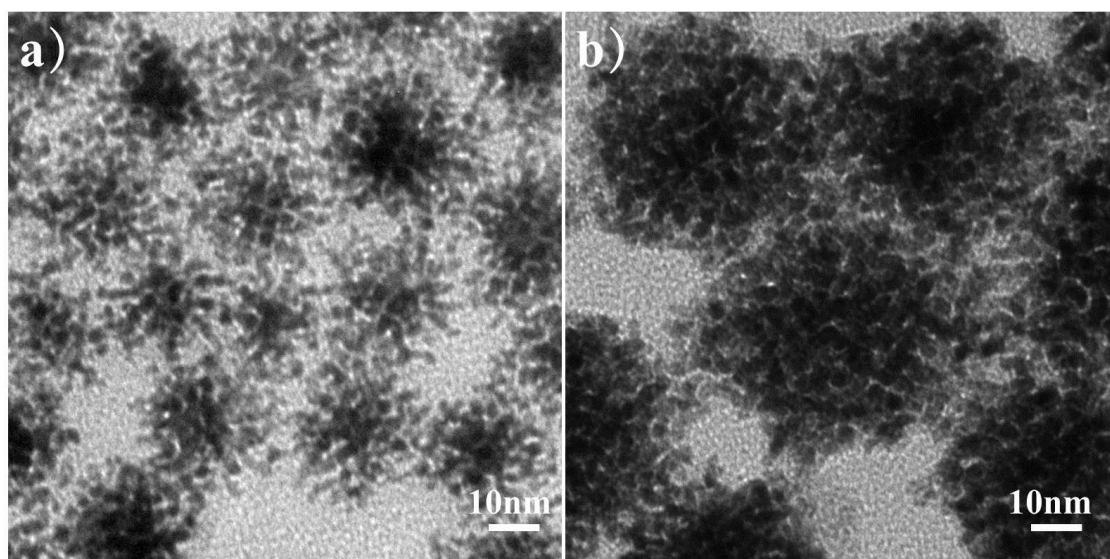


Figure S4. TEM images of Pt-Ni nanodendrites collected at a) 120 min, b) 180 min

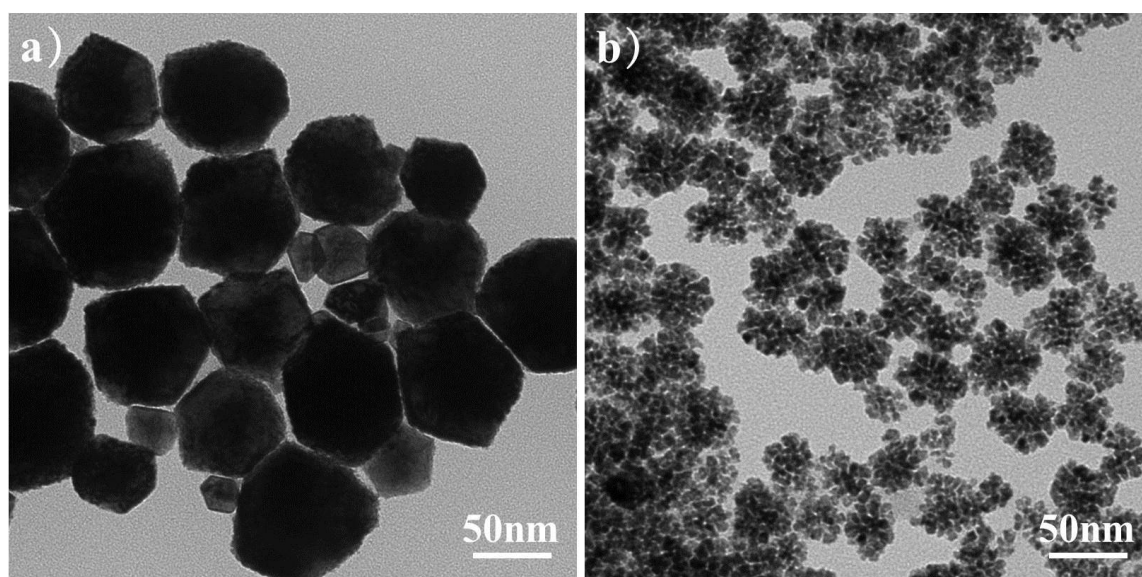


Figure S5 a) TEM image of Pt-Ni polyhedra prepared with phase transferred $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ b) TEM image of Pt-Ni nanodendrites prepared without OA.

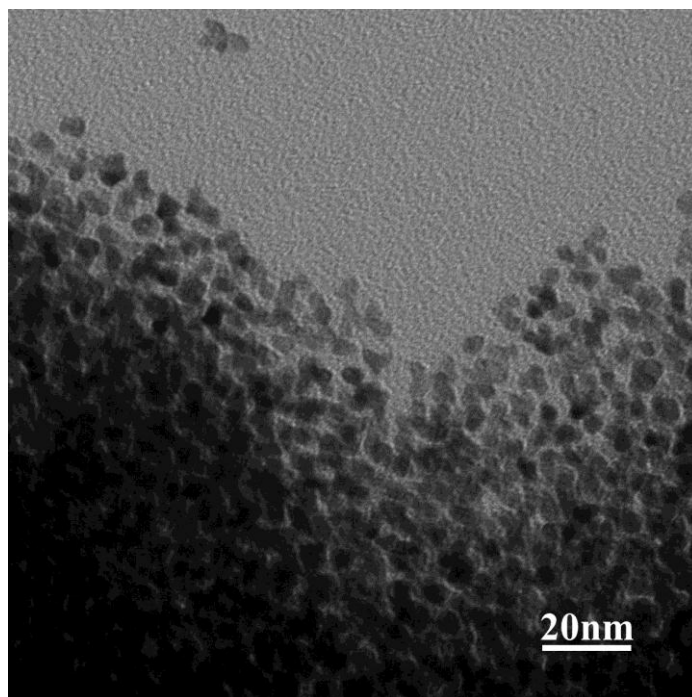


Figure S6. TEM image of Pt-Ni samples prepared with little OAm.

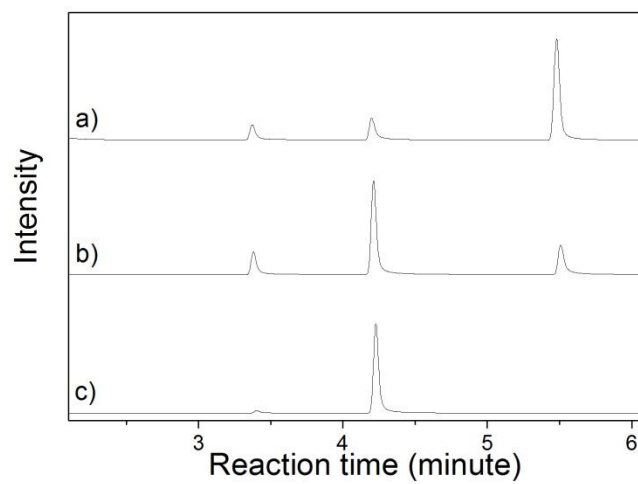


Figure S7. GC data for nitrobenzene hydrogenation after a) 10 min, b) 30 min, and c) 60 min catalyzed by Pt-Ni nanodendrites.

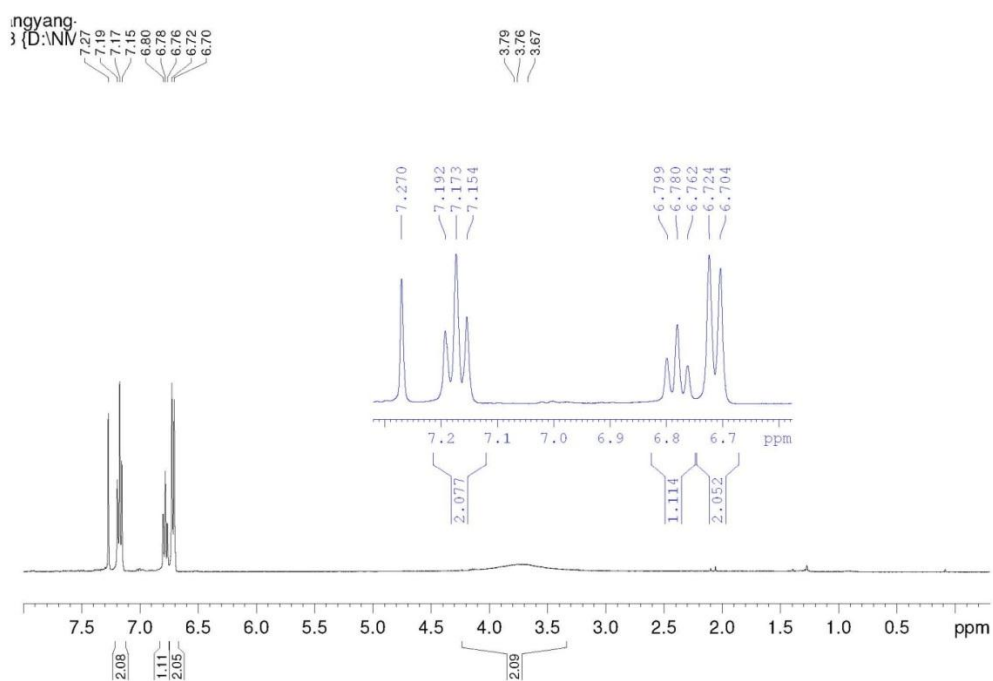


Figure S8. ^1H NMR (400 MHz, CDCl_3) of prepared aniline after hydrogenation of nitrobenzene using Pt-Ni nanodendrites as catalyst. δ 3.76 (s, NH, 2 H), 6.78 (m, *Ph*, 1 H), 6.70-6.72 (m, *Ph*, 2 H), 7.15-7.19 (m, *Ph*, 2 H).

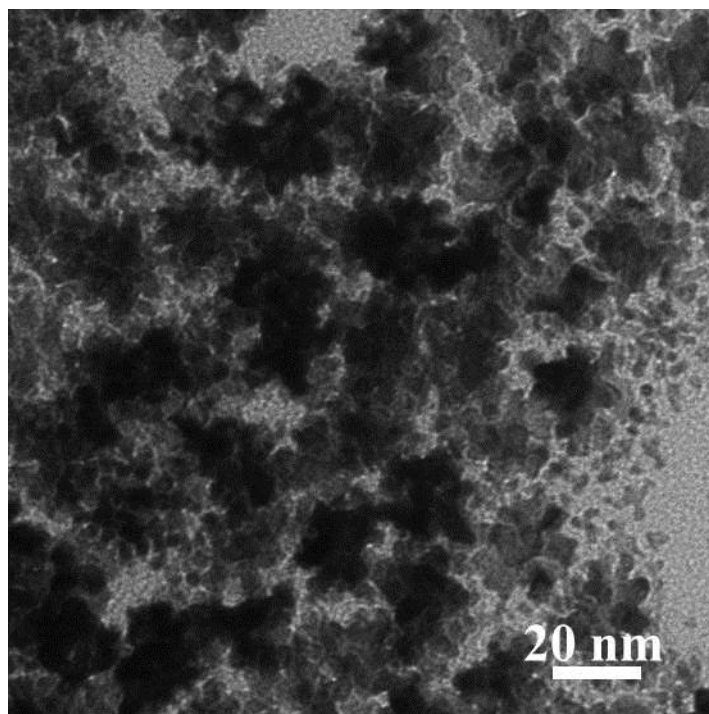


Figure S9. TEM image of irregular Pt-Ni particles

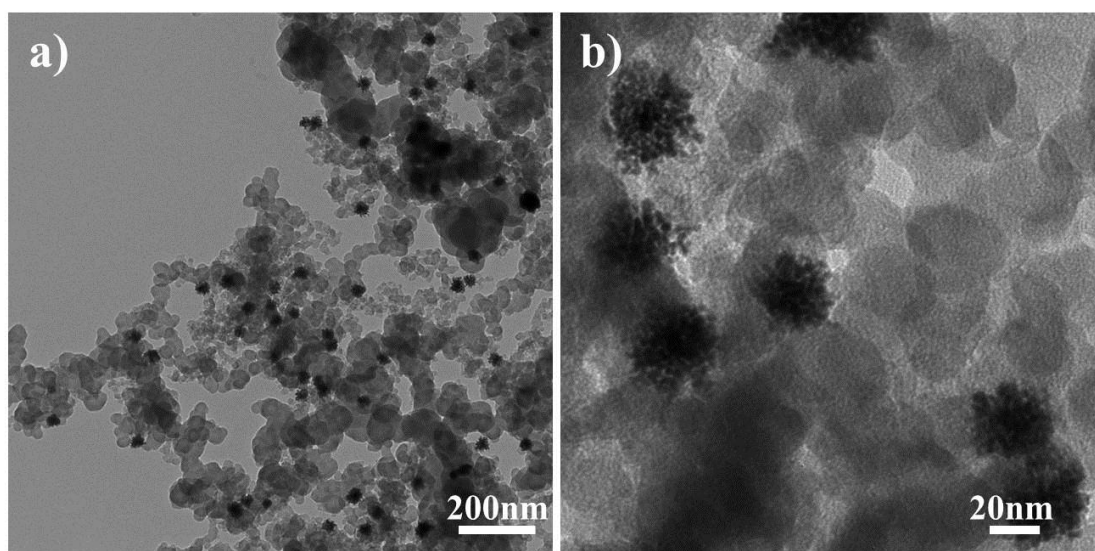


Figure S10. TEM image of Pt-Ni nanodendrites after catalyzing hydrogenation of nitrobenzen.