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Authors
Chen, S
Liu, XY
Jin, J
et al.

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Supporting Information for:

Individually Encapsulated Frame-in-Frame Structure

Shouping Chen,[†,§] Xiao-Yuan Liu,[‡] Jianbo Jin,[‡] Mengyu Gao,[†,§] Chubai Chen,[‡] Qiao Kong,[‡] Zhe Ji,[‡,§,∥] Gabor A. Somorjai,[‡,§] Omar M. Yaghi,[‡,§,∥] and Peidong Yang*[,†,‡,§,∥]

[†]Department of Materials Science and Engineering and [‡]Department of Chemistry, University of California, Berkeley, California 94720, United States

[§]Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

[∥]Kavli Energy NanoScience Institute, Berkeley, California 94720, United States

*Corresponding author e-mail: p_yang@berkeley.edu

METHODS

Chemicals. Chloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$, ≥37.5% Pt basis), nickel(II) nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$, ≥98.5%), oleylamine (technical grade, 70%), hexane (≥98.5%), hexadecyltrimethylammonium bromide (CTAB, 99%), 2-methylimidazole (99%), zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, 98%), and cobalt(II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, ≥98%) were purchased from Sigma-Aldrich. Toluene (99.9%) and methanol (99.9%) was purchased from Fisher Scientific. Acetic acid (≥99.7%) was purchased from EMD.

Characterizations. Transmission electron microscopy (TEM) was performed with Hitachi H-7650 and FEI Tecnai T20 S-TWIN. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), energy dispersive X-ray spectroscopy (EDX) mapping and line-scan, and tomography were carried out using FEI TitanX 60-300. X-ray diffraction (XRD) was measured by Bruker AXS D2 Phaser with Cu Kα source. Scanning electron microscopy (SEM) was acquired by Zeiss Gemini Ultra-55.

Synthesis of Pt−Ni nanoframes. In the first step, the Pt−Ni rhombic dodecahedra were prepared as the starting material. To begin with, 20 mg of $H_2PtCl_6 \cdot 6H_2O$ and 14.5 mg of $Ni(NO_3)_2 \cdot 6H_2O$ were pre-dissolved in 0.7 mL of oleylamine by sonication, and 9.3 mL of oleylamine was pre-heated in a 25 mL three-necked flask at 160 °C for 1 h under nitrogen (N_2). Next, the metal precursor solution was injected into the flask and kept under vacuum for 2.5 min. Then, the reaction was heated to 265 °C with a ramping rate of 15 °C min^{-1} in N_2 atmosphere. The reaction was stopped at 4 min after the solution turned black at 265 °C by transferring the flask into a water bath. The products

were washed with hexane/ethanol and collected by centrifugation at 12,000 rpm. In the second step, the Pt−Ni nanoframes were obtained by chemical corrosion. The Pt−Ni rhombic dodecahedra collected by centrifugation were re-dispersed in 2 mL of toluene and 5 mL of acetic acid by sonication. The mixture was heated at 90 °C under stirring for 2 h in air to allow the evolution from rhombic dodecahedra to nanoframes. The products were washed with hexane/ethanol and collected by centrifugation at 12,000 rpm.

Surface functionalization of Pt−Ni nanoframes with CTAB. The as-prepared Pt−Ni nanoframes collected by centrifugation were re-dispersed in 4 mL of 10 mM CTAB aqueous solution through intense sonication. The mixture was then sonicated at room temperature for about a week until all the Pt−Ni nanoframes became well-dispersed in water. The products were washed with water and collected by centrifugation at 14,000 rpm.

Individual encapsulation of Pt−Ni nanoframe in ZIF-8. The CTAB-covered Pt−Ni nanoframes collected by centrifugation were re-dispersed in 0.5 mL of water by sonication. Meanwhile, 1.75 mL of aqueous solution including 0.55 mM CTAB and 790 mM 2-methylimidazole was stirred at 500 rpm for 5 min in a 20 mL vial. Next, 0.25 mL of 97.5 mM $Zn(NO_3)_2 \cdot 6H_2O$ aqueous solution was added into the vial. After stirring for 10 s, the nanoframe solution was added into the mixture and stirred for another 5 min at 500 rpm. Then, the stir bar was taken out and the solution was left undisturbed for 3 h at room temperature. The products were collected by centrifugation at 10,000 rpm.

Individual encapsulation of Pt−Ni nanoframe in ZIF-67. The procedure was exactly the same as that of ZIF-8 except that $Co(NO_3)_2 \cdot 6H_2O$ was used instead of $Zn(NO_3)_2 \cdot 6H_2O$.

Overgrowth of ZIF-8 on ZIF-67 to form double-shelled structure. The Pt−Ni nanoframe@ZIF-67 core−shell composites collected by centrifugation were first re-dispersed in 1mL of methanol by sonication. Next, 0.2 mL of the mixture was added into 2.5 mL of 30 mM 2-methylimidazole methanol solution in a vial and shaken for 5 s. Then, 2.5 mL of 30 mM $Zn(NO_3)_2 \cdot 6H_2O$ methanol solution was added into the vial and shaken for another 5 s. The solution was left undisturbed for 1 h at room temperature and the products were collected by centrifugation at 6,000 rpm.

Dissolution of ZIF-67 to form yolk−shell structure. The Pt−Ni nanoframe@ZIF-67@ZIF-8 double-shelled composites collected by centrifugation were re-dispersed in 1 mL of methanol in a vial by sonication, followed by the addition 1 mL of water. The solution was left undisturbed for about 3 days at room temperature to allow the complete dissolution of ZIF-67.

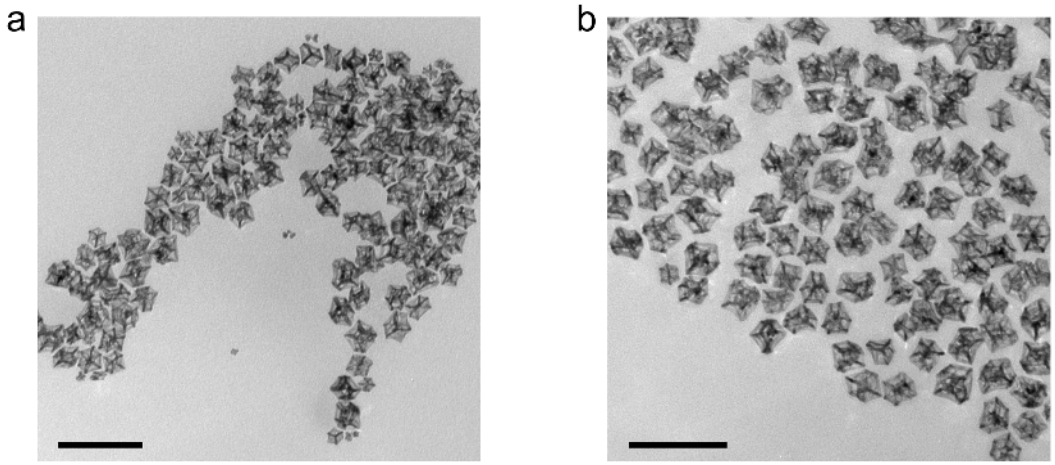

Figure S1. TEM images of Pt−Ni nanoframes (a) with only oleylamine dispersed in hexane and (b) with overlaid CTAB dispersed in water. Scale bar is 100 nm in all images.

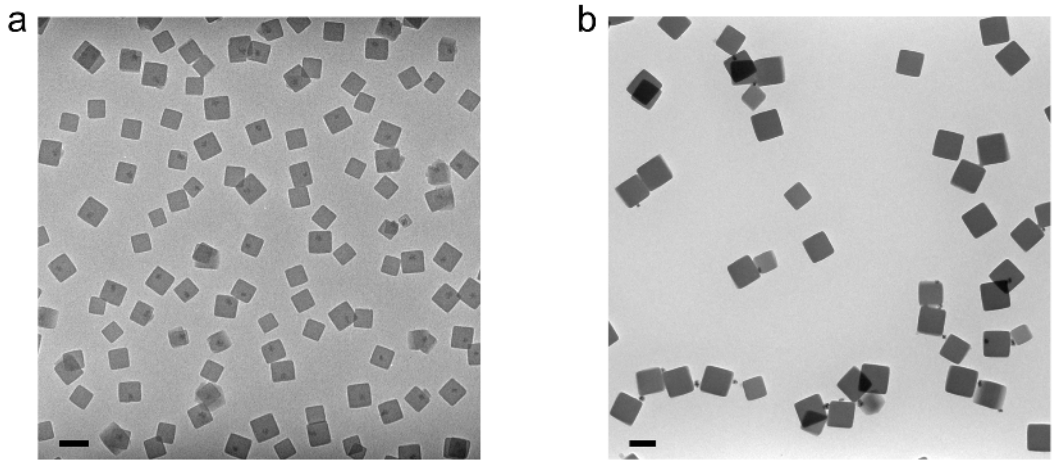

Figure S2. Low-magnification TEM images of (a) Pt−Ni nanoframes encapsulated in ZIF-8 and (b) Pt−Ni nanoframes mixed with ZIF-8. Scale bar is 100 nm in all images.

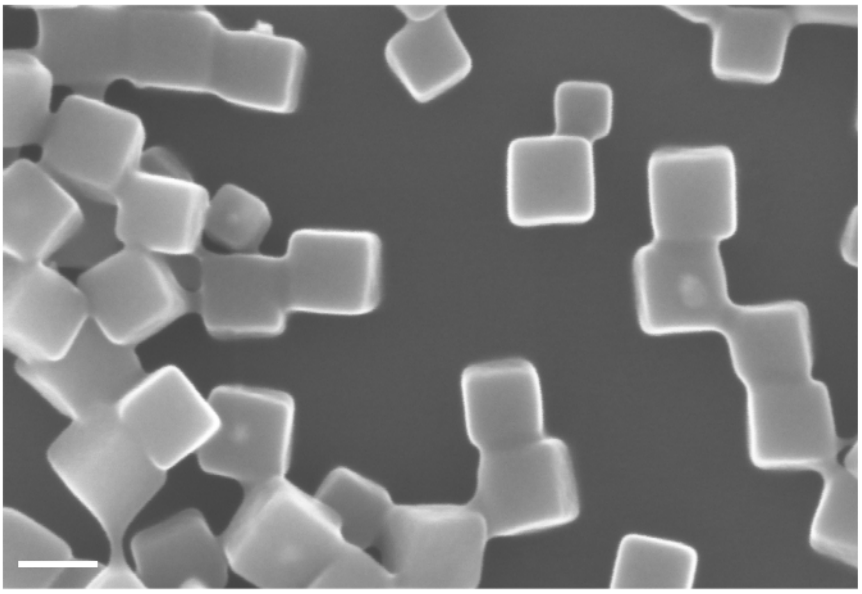

Figure S3. SEM image of single core−shell frame-in-frame structure. The MOF shell is ZIF-8. Scale bar is 100 nm.

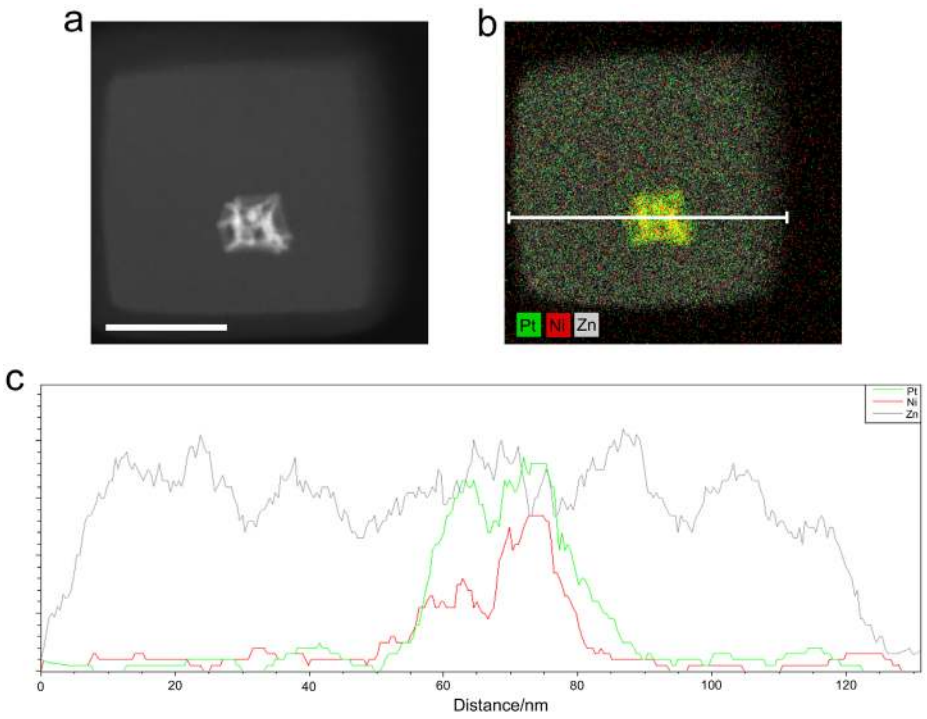

Figure S4. (a) HAADF-STEM image, (b) EDX map, and (c) line-scan profile of single core−shell frame-in-frame structure. The MOF shell is ZIF-8. Scale bar is 50 nm.

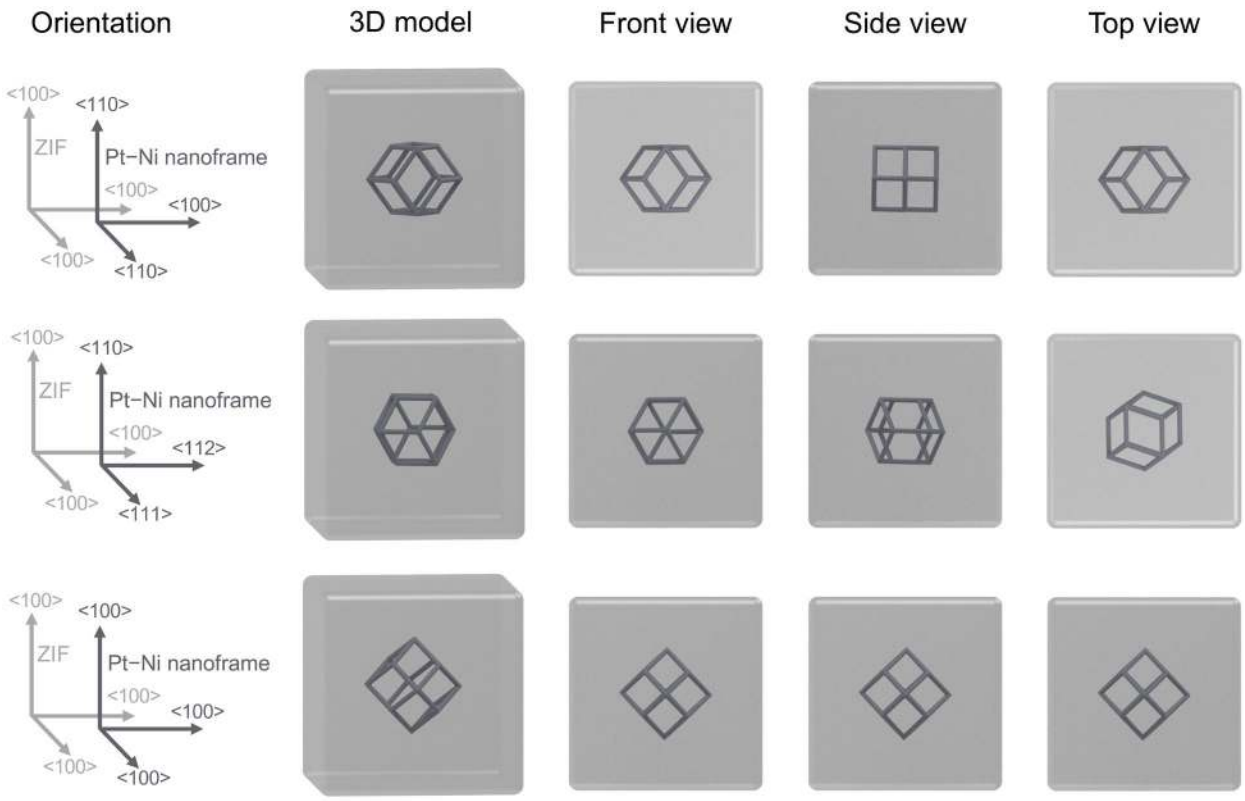

Figure S5. Models of alignments between Pt−Ni nanoframe and ZIF in single core−shell structure.

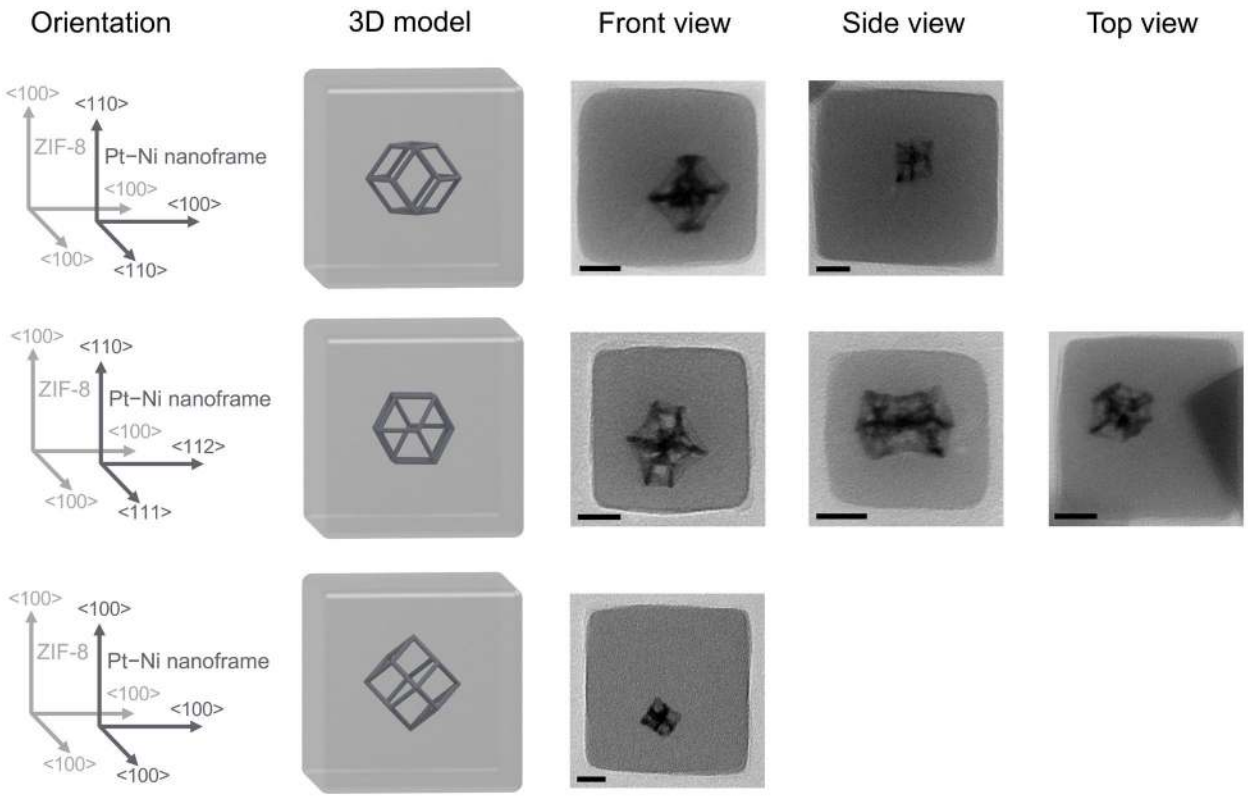

Figure S6. TEM images of alignments between Pt−Ni nanoframe and ZIF-8 in single core−shell structure. Scale bar is 20 nm in all images.

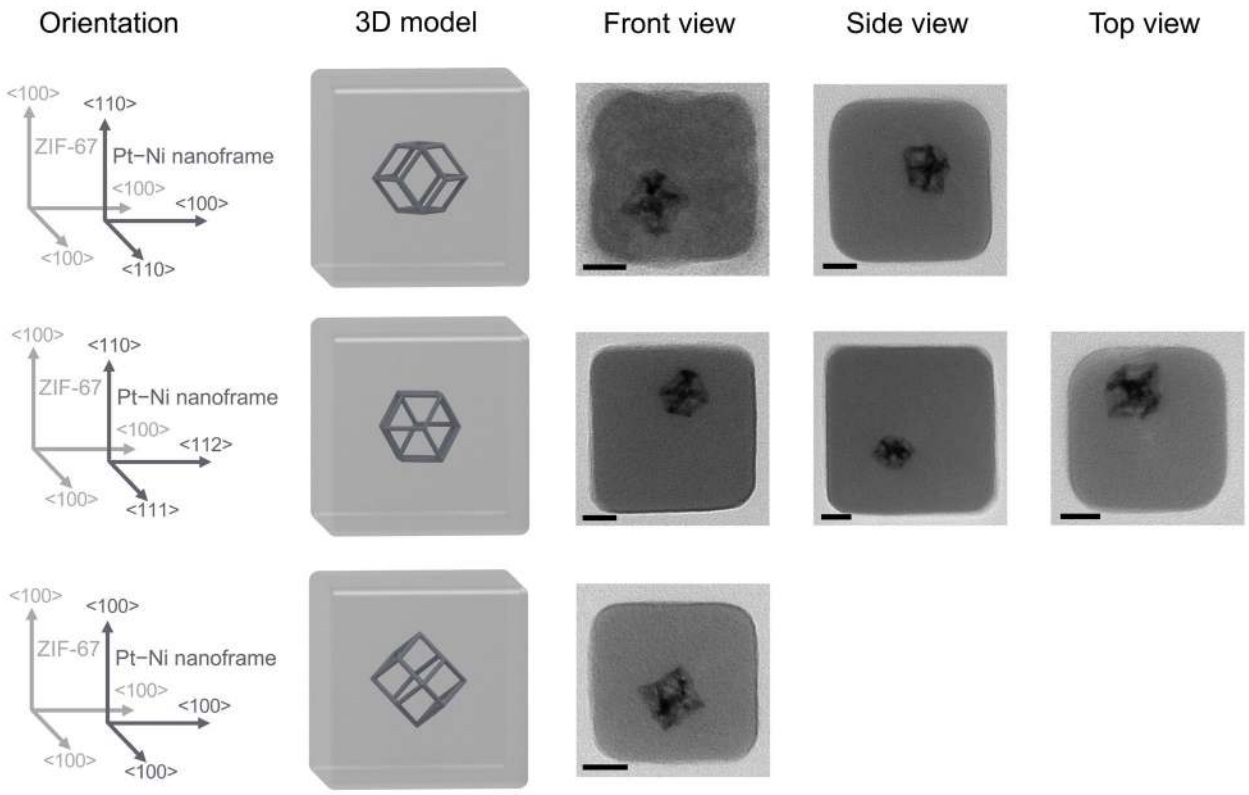

Figure S7. TEM images of alignments between Pt−Ni nanoframe and ZIF-67 in single core−shell structure. Scale bar is 20 nm in all images.