

Supporting Information for:

Individually Encapsulated Frame-in-Frame Structure

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METHODS

Chemicals. Chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, $\geq 37.5\%$ Pt basis), nickel(II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\geq 98.5\%$), oleylamine (technical grade, 70%), hexane ($\geq 98.5\%$), hexadecyltrimethylammonium bromide (CTAB, 99%), 2-methylimidazole (99%), zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 98%), and cobalt(II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\geq 98\%$) were purchased from Sigma-Aldrich. Toluene (99.9%) and methanol (99.9%) was purchased from Fisher Scientific. Acetic acid ($\geq 99.7\%$) 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 $K\alpha$ 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 $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and 14.5 mg of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 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 $15^\circ\text{C min}^{-1}$ 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 $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 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 $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was used instead of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

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 1 mL 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 $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 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.

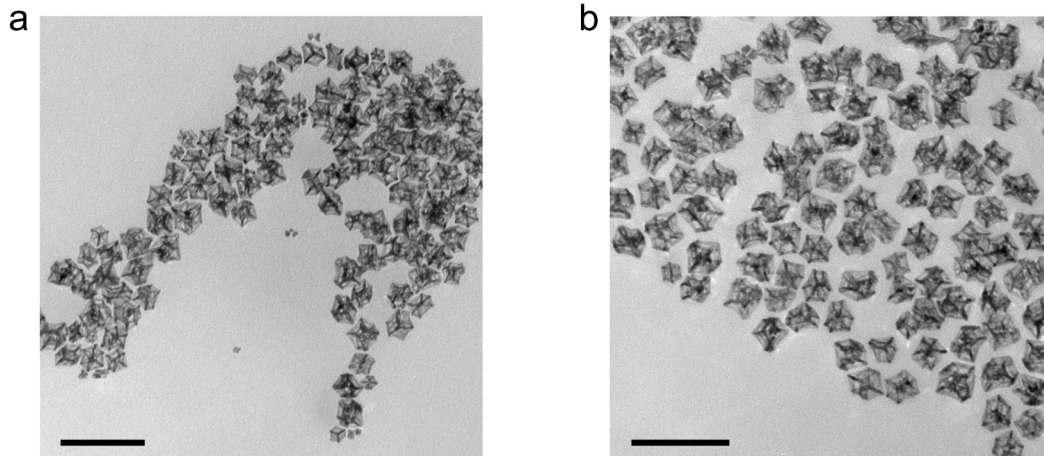


Figure S1. TEM images of Pt–Ni nanoframes (a) with only oleylamine dispersed in hexane and (b) with overlaid CTAB dispersed in water. Scale bar is 100 nm in all images.

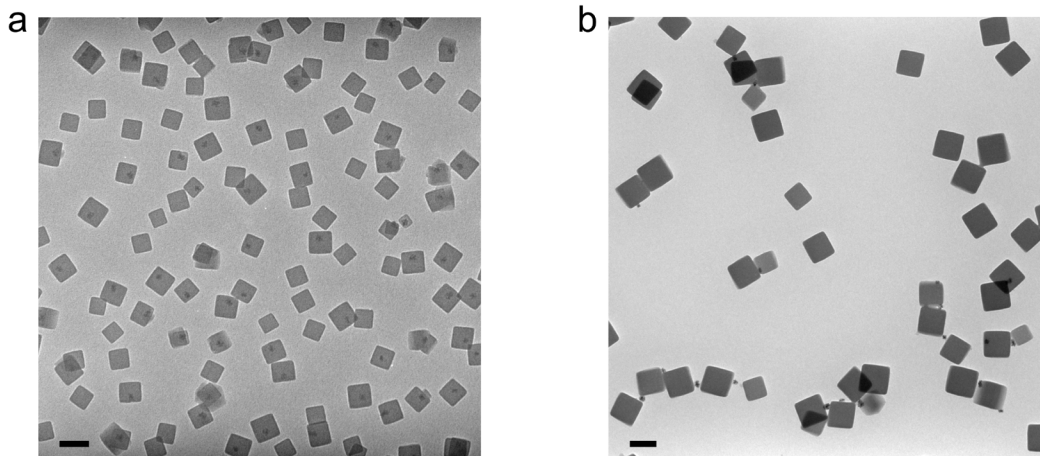


Figure S2. Low-magnification TEM images of (a) Pt–Ni nanoframes encapsulated in ZIF-8 and (b) Pt–Ni nanoframes mixed with ZIF-8. Scale bar is 100 nm in all images.

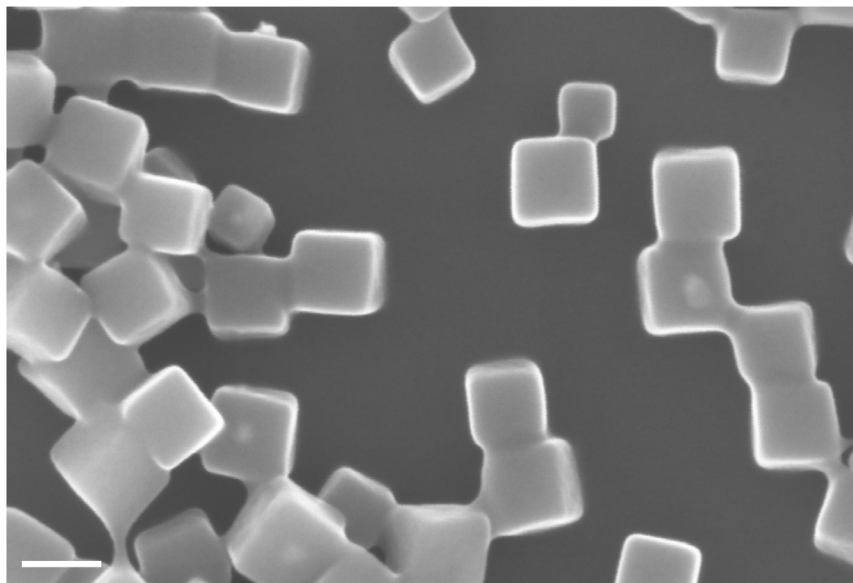


Figure S3. SEM image of single core-shell frame-in-frame structure. The MOF shell is ZIF-8.

Scale bar is 100 nm.

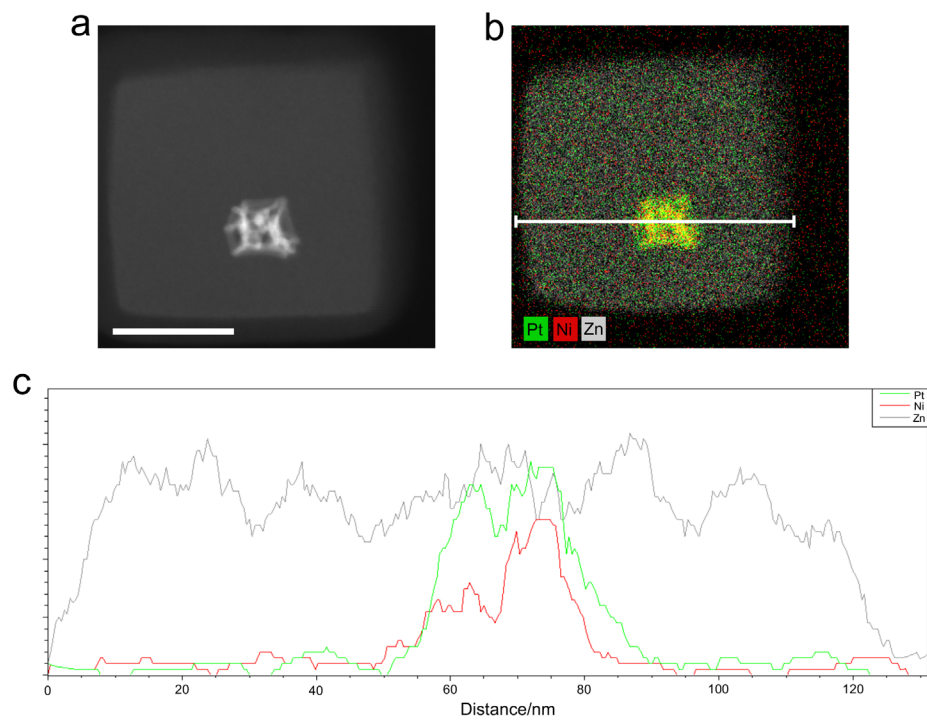


Figure S4. (a) HAADF-STEM image, (b) EDX map, and (c) line-scan profile of single core-shell structure. The MOF shell is ZIF-8. Scale bar is 50 nm.

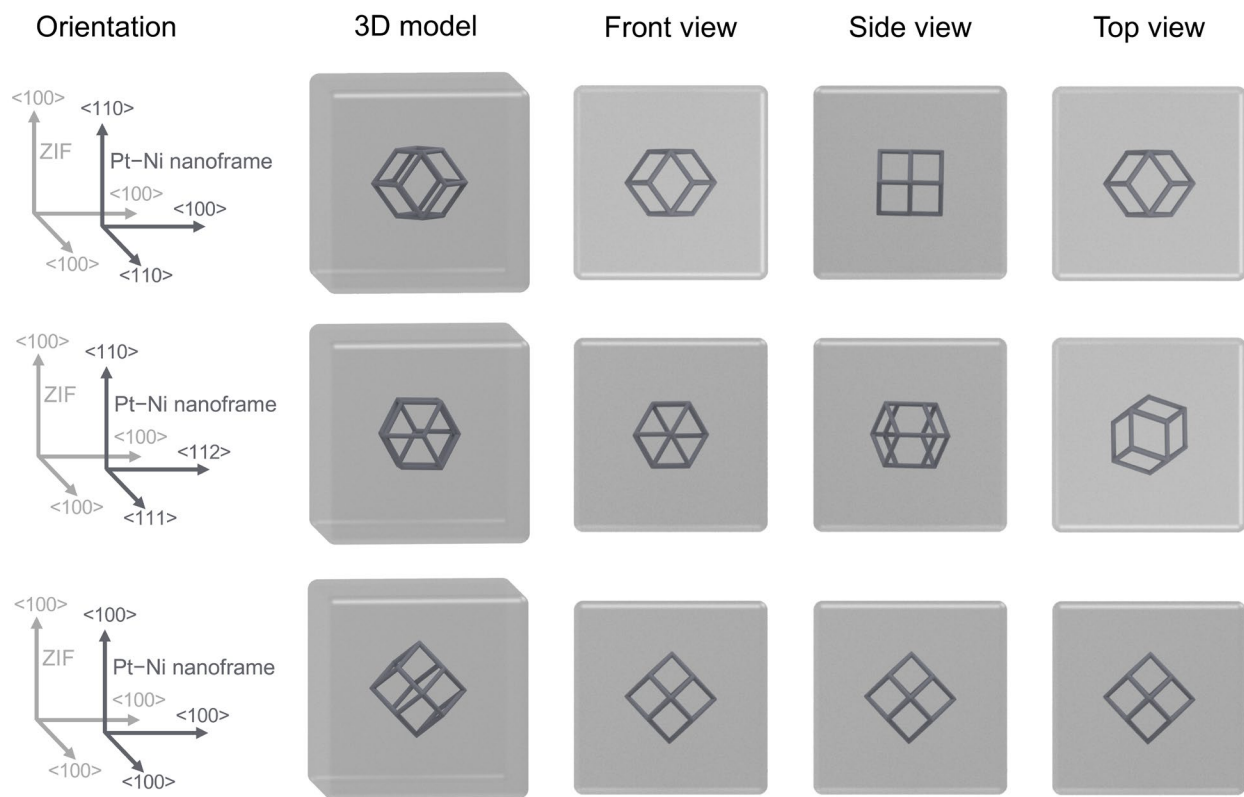


Figure S5. Models of alignments between Pt–Ni nanoframe and ZIF in single core–shell structure.

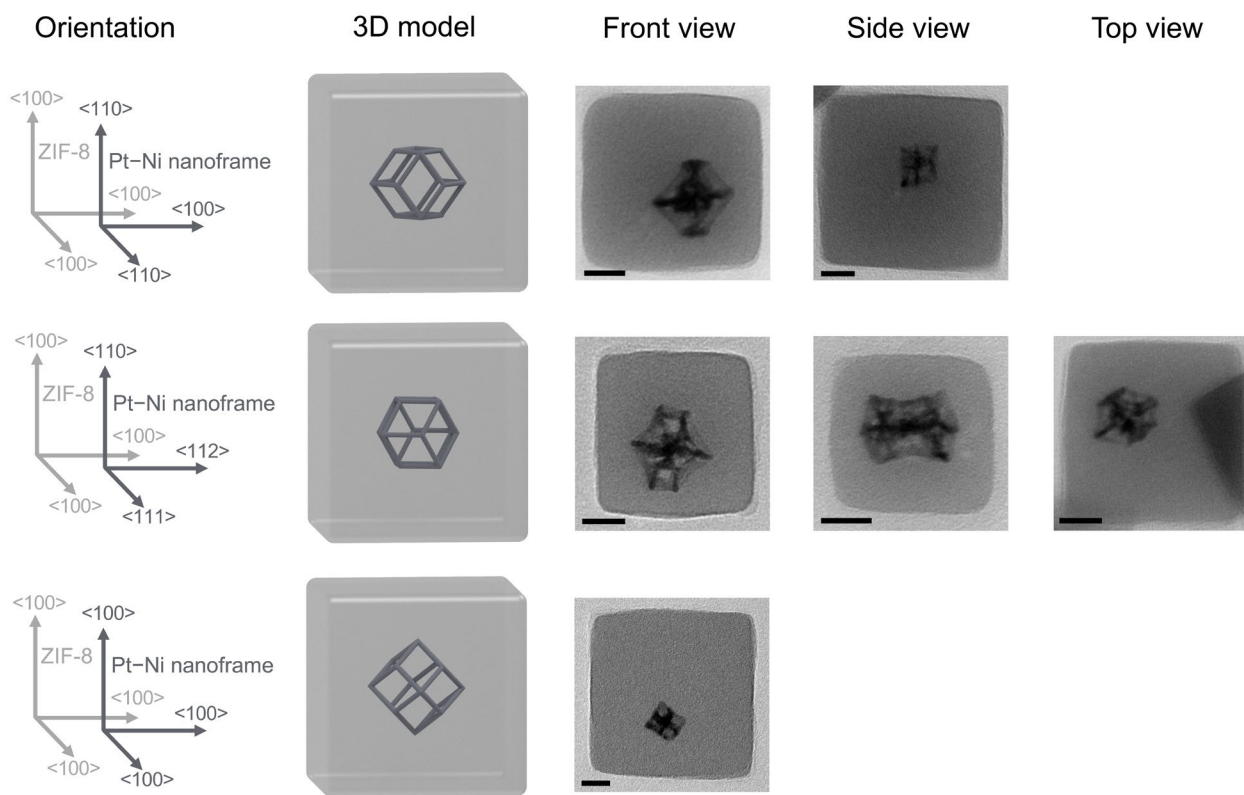


Figure S6. TEM images of alignments between Pt–Ni nanoframe and ZIF-8 in single core–shell structure. Scale bar is 20 nm in all images.

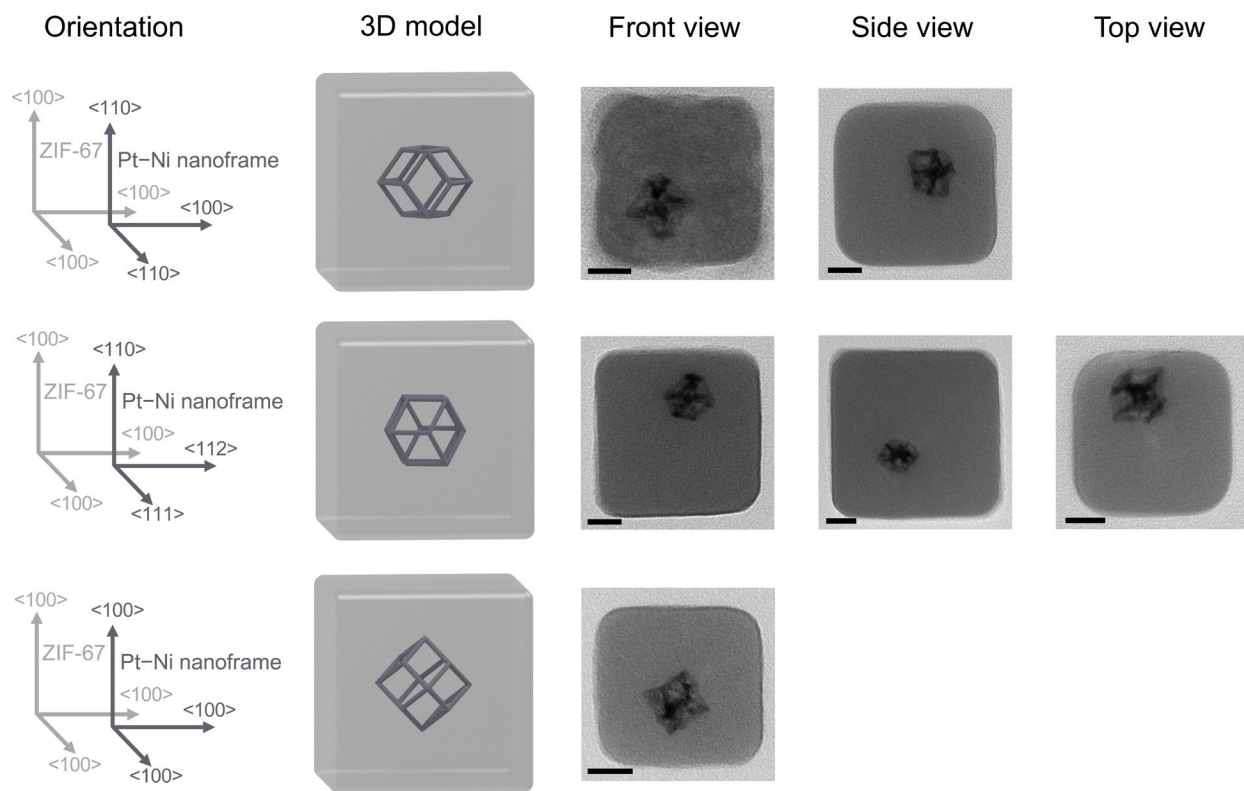


Figure S7. TEM images of alignments between Pt–Ni nanoframe and ZIF-67 in single core–shell structure. Scale bar is 20 nm in all images.