

Supporting Information

Material Characterizations

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were performed on a TECNAI G2 20 S-Twin operated at 200kV and TECNAI G2 F30 operated at 300 kV. Elemental mapping and energy dispersive X-ray spectra (EDX) were obtained with a FEI Titan Cubed 60-300 with Chemi-STEM technology and a JEOL ARM200F Cs STEM.

Experimental Section

Structure	Rh(acac) ₃	Zn(OAc) ₂	1,2-hexadecanediol	Stearic acid	Octadecylamine	Gas
Nanotent (Fig. 1,2b)	0.04 mmol	0.01 mmol	0.1 mmol	0.04 mmol	15 mmol	CO
Nanoplate (Fig. 2a)	0.04 mmol	0.01 mmol	-	0.04 mmol	15 mmol	CO
Rolled up nanotent (Fig. 2c)	0.04 mmol	0.01 mmol	0.4 mmol	0.04 mmol	15 mmol	CO
Hierarchically stacked nanoframe (Fig. 3a)	0.04 mmol	0.01 mmol	0.1 mmol	0.60 mmol	15 mmol	CO
Nanoframe (Fig. 4b)	0.04 mmol	0.01 mmol	0.1 mmol	0.12 mmol	15 mmol	CO
Double nanoframe (Fig. 4c)	0.04 mmol	0.01 mmol	0.1 mmol	0.24 mmol	15 mmol	CO
Branched hierarchical nanoframe (Fig. 5)	0.04 mmol	0.01 mmol	0.1 mmol	0.60 mmol	15 mmol	CO → Ar

Preparation of RhZn nanotent structure. (Fig. 1, Fig. 2b)

A slurry of Rh(acac)₃ (0.04 mmol, Strem, 99 %), Zn(OAc)₂ (0.01 mmol, Aldrich, 99.99%), 1,2-hexadecanediol (0.1 mmol, Aldrich, 90%), stearic acid (0.04 mmol, Aldrich, 95%), and octadecylamine (15 mmol, Aldrich, 90%) was prepared in a 100 mL Schlenk tube with a magnetic stirring. The tube, placed in the oil bath, was heated to 78 °C for 20 min and then evacuated for 5 min with a magnetic stirring, and finally purged with CO gas. Resulting reaction mixture was heated up to 260 °C, and kept at that temperature for 15 min under 1 atm CO. Finally, dark black precipitates could be obtained by cooling down the solution to room temperature and then by centrifugation with added methanol/toluene (v/v = 10 mL/15 mL).

Preparation of RhZn nanoplate structure. (Fig. 2a)

A slurry of Rh(acac)₃ (0.04 mmol, Strem, 99 %), Zn(OAc)₂ (0.01 mmol, Aldrich, 99.99%), stearic acid (0.04 mmol, Aldrich, 95%), and octadecylamine (15 mmol, Aldrich, 90%) was prepared in a 100 mL Schlenk tube with a magnetic stirring. The tube, placed in the oil bath, was heated to 78 °C for 20 min and then evacuated for 5 min with a magnetic stirring, and finally purged with CO gas. Resulting reaction mixture was heated up to 260 °C, and kept at that temperature for 15 min under 1 atm CO. Finally, dark black precipitates could be obtained by cooling down the solution to room temperature and then by centrifugation with added methanol/toluene (v/v = 10 mL/15 mL).

Preparation of rolled up RhZn nanotent structure. (Fig. 2c)

A slurry of Rh(acac)₃ (0.04 mmol, Strem, 99 %), Zn(OAc)₂ (0.01 mmol, Aldrich, 99.99%), 1,2-hexadecanediol (0.4 mmol, Aldrich, 90%), stearic acid (0.04 mmol, Aldrich, 95%), and octadecylamine (15 mmol, Aldrich, 90%) was prepared in a 100 mL Schlenk tube with a magnetic stirring. The tube, placed in the oil bath, was heated to 78 °C for 20 min and then evacuated for 5 min with a magnetic stirring, and finally purged with CO gas. Resulting reaction mixture was heated up to 260 °C, and kept at that temperature for 15 min under 1 atm CO. Finally, dark black precipitates could be obtained by cooling down the solution to room temperature and then by centrifugation with added methanol/toluene (v/v = 10 mL/15 mL).

Preparation of hierarchically stacked RhZn nanoframe structure. (Fig. 3a)

A slurry of Rh(acac)₃ (0.04 mmol, Strem, 99 %), Zn(OAc)₂ (0.01 mmol, Aldrich, 99.99%), 1,2-hexadecanediol (0.1 mmol, Aldrich, 90%), stearic acid (0.6 mmol, Aldrich, 95%), and octadecylamine (15 mmol, Aldrich, 90%) was prepared in a 100 mL Schlenk tube with a magnetic stirring. The tube, placed in the oil bath, was heated to 78 °C for 20 min and then evacuated for 5 min with a magnetic stirring, and finally purged with CO gas. Resulting reaction mixture was heated up to 260 °C, and kept at that temperature for 15 min under 1 atm CO. Finally, dark black precipitates could be obtained by cooling down the solution to room temperature and then by centrifugation with added methanol/toluene (v/v = 10 mL/15 mL).

Preparation of RhZn nanoframe structure. (Fig. 4b)

A slurry of Rh(acac)₃ (0.04 mmol, Strem, 99 %), Zn(OAc)₂ (0.01 mmol, Aldrich, 99.99%), 1,2-hexadecanediol (0.1 mmol, Aldrich, 90%), stearic acid (0.12 mmol, Aldrich, 95%), and octadecylamine (15 mmol, Aldrich, 90%) was prepared in a 100 mL Schlenk tube with a magnetic stirring. The tube, placed in the oil bath, was heated to 78 °C for 20 min and then evacuated for 5 min with a magnetic stirring, and finally purged with CO gas. Resulting reaction mixture was heated up to 260 °C, and kept at that temperature for 15 min under 1 atm CO. Finally, dark black precipitates could be obtained by cooling down the solution to room temperature and then by centrifugation with added methanol/toluene (v/v = 10 mL/15 mL).

Preparation of RhZn double nanoframe structure. (Fig. 4c)

A slurry of Rh(acac)₃ (0.04 mmol, Strem, 99 %), Zn(OAc)₂ (0.01 mmol, Aldrich, 99.99%), 1,2-hexadecanediol (0.1 mmol, Aldrich, 90%), stearic acid (0.24 mmol, Aldrich, 95%), and octadecylamine (15 mmol, Aldrich, 90%) was prepared in a 100 mL Schlenk tube with a magnetic stirring. The tube, placed in the oil bath, was heated to 78 °C for 20 min and then evacuated for 5 min with a magnetic stirring, and finally purged with CO gas. Resulting reaction mixture was heated up to 260 °C, and kept at that temperature for 15 min under 1 atm CO. Finally, dark black precipitates could be obtained by cooling down the solution to room temperature and then by centrifugation with added methanol/toluene (v/v = 10 mL/15 mL).

Preparation of branched hierarchical RhZn nanoframe structure. (Fig. 5)

A slurry of Rh(acac)₃ (0.04 mmol, Strem, 99 %), Zn(OAc)₂ (0.01 mmol, Aldrich, 99.99%), 1,2-hexadecanediol (0.1 mmol, Aldrich, 90%), stearic acid (0.6 mmol, Aldrich, 95%), and octadecylamine (15 mmol, Aldrich, 90%) was prepared in a 100 mL Schlenk tube with a magnetic stirring. The tube, placed in the oil bath, was heated to 78 °C for 20 min and then evacuated for 5 min with a magnetic stirring, and finally purged with CO gas. Resulting reaction mixture was heated up to 260 °C and kept at that temperature for 3 min under 1 atm CO. With the reaction mixture being heated at the same temperature for additional 12 min, the CO gas was continuously purged out from the reaction mixture by Ar flow (100 cc/min). Finally, dark black precipitates could be obtained by cooling down the solution to room temperature and then by centrifugation with added methanol/toluene (v/v = 10 mL/15 mL).

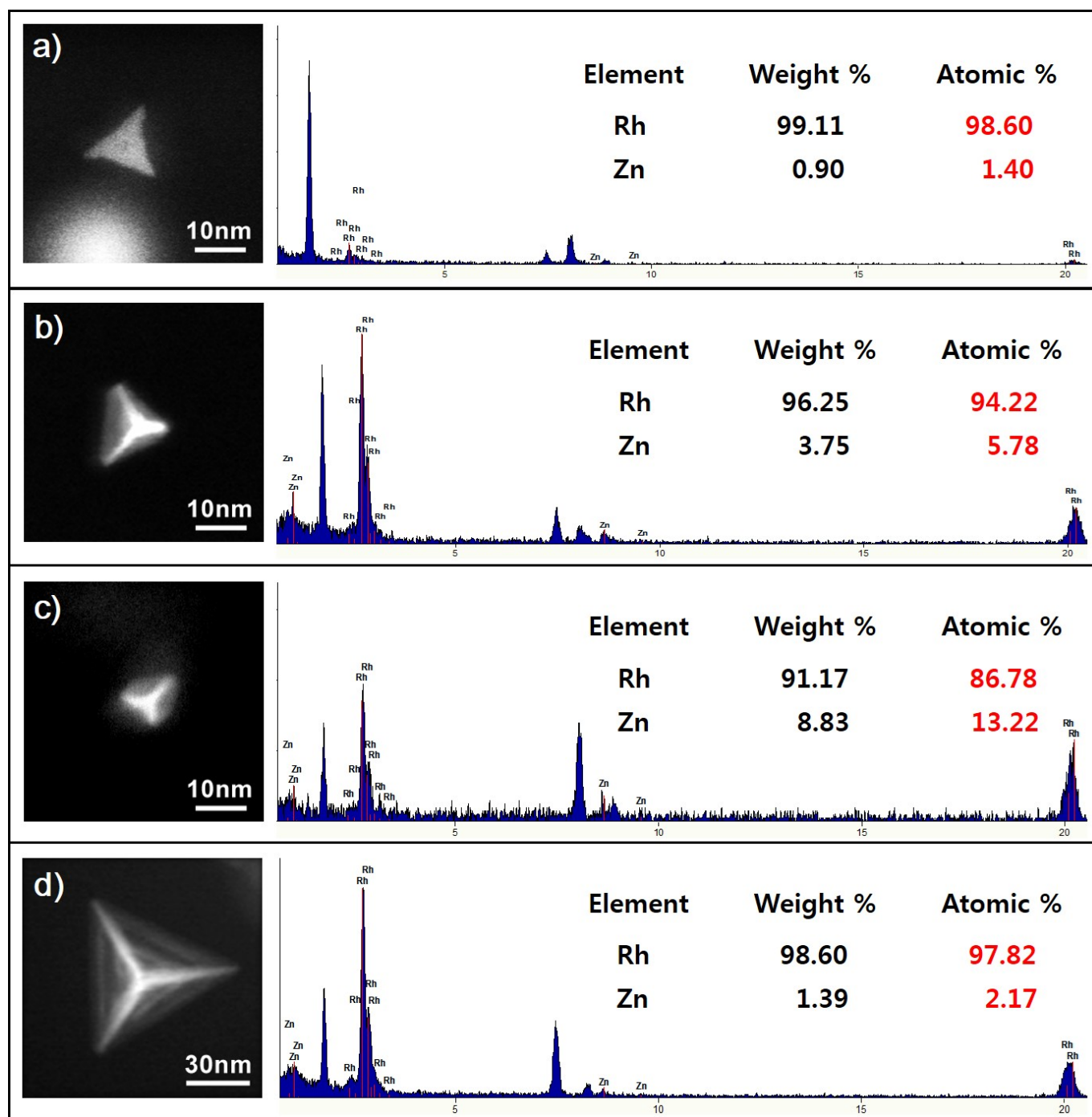


Fig. S1. Energy dispersive X-ray spectrum of a) RhZn alloy nanoplate structure (Fig. 2a), b) RhZn nanotent structure (Fig. 2b), c) rolled-up RhZn nanotent structure (Fig. 2c), and d) hierarchically stacked RhZn nanoframe structure (Fig. 3a).

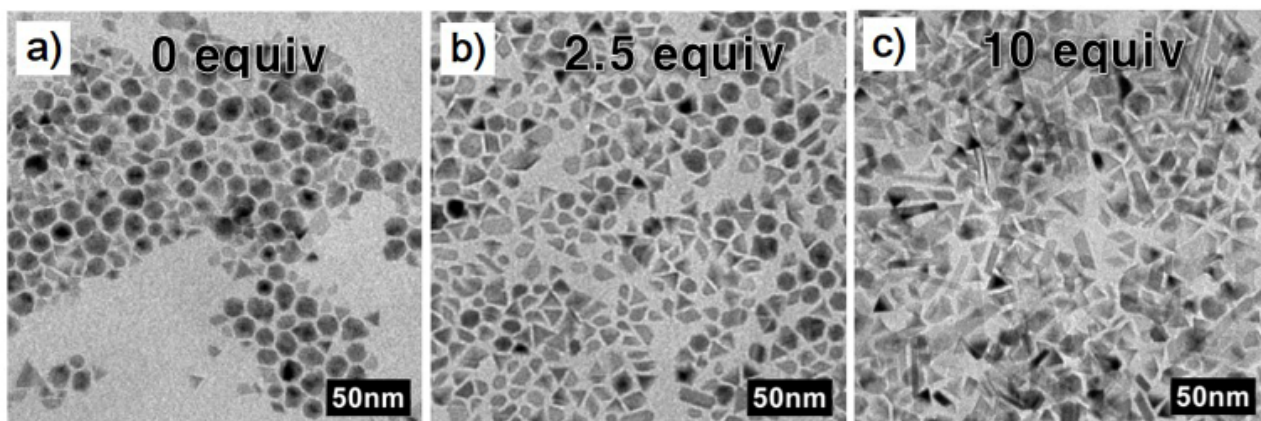


Fig. S2. TEM images of products prepared at the same reaction condition, but without using $\text{Zn}(\text{OAc})_2$, as for the products shown on Fig. 2a-c. It is obvious that Zn doping is crucial in the formation of nanoplate morphology.

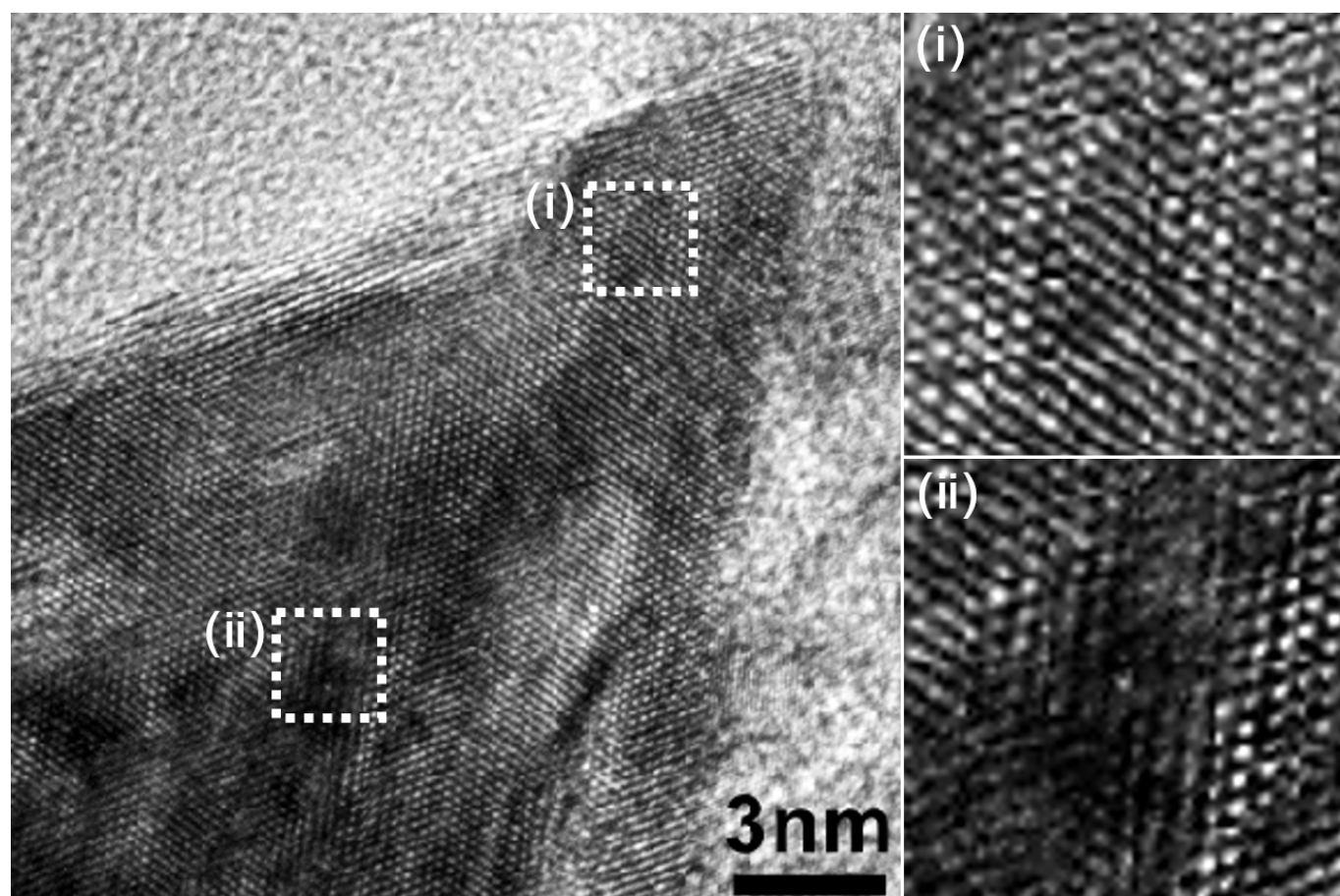


Fig. S3. HRTEM image of a hierarchically stacked RhZn nanostructure. Defect sites, likely due to incorporation of Zn impurities, are observed at the corners of stacked nanoframes and are enclosed by white dotted boxes.

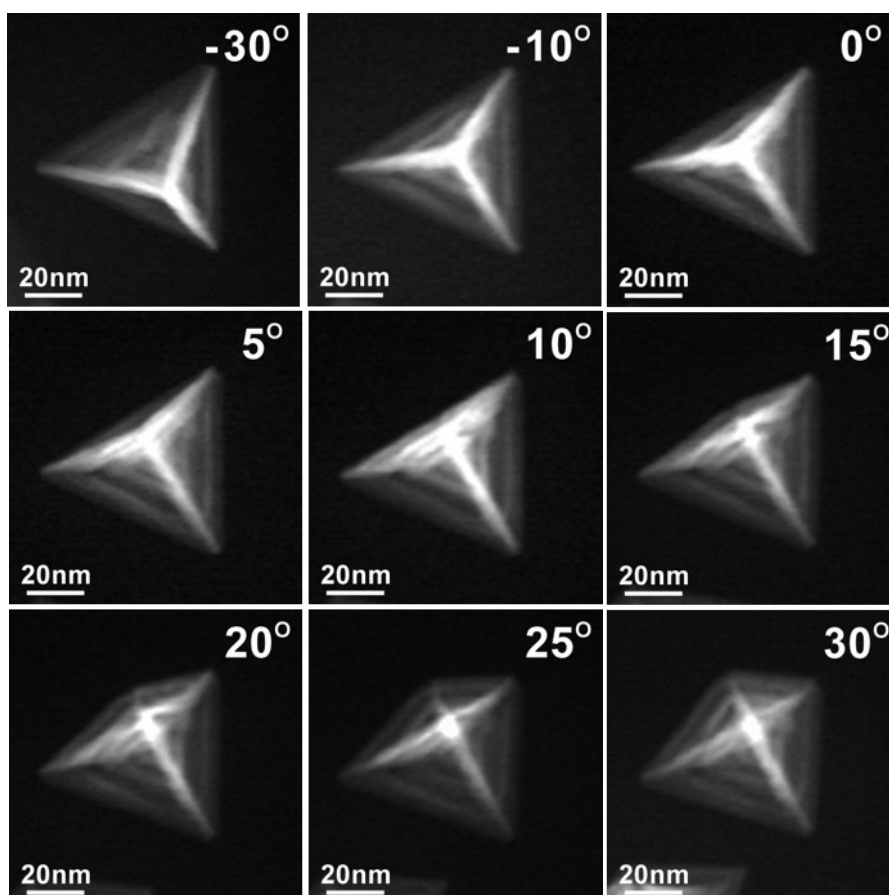


Fig. S4. STEM images of hierarchically stacked RhZn nanostructures in Fig. 3a recorded at different tilting angles.

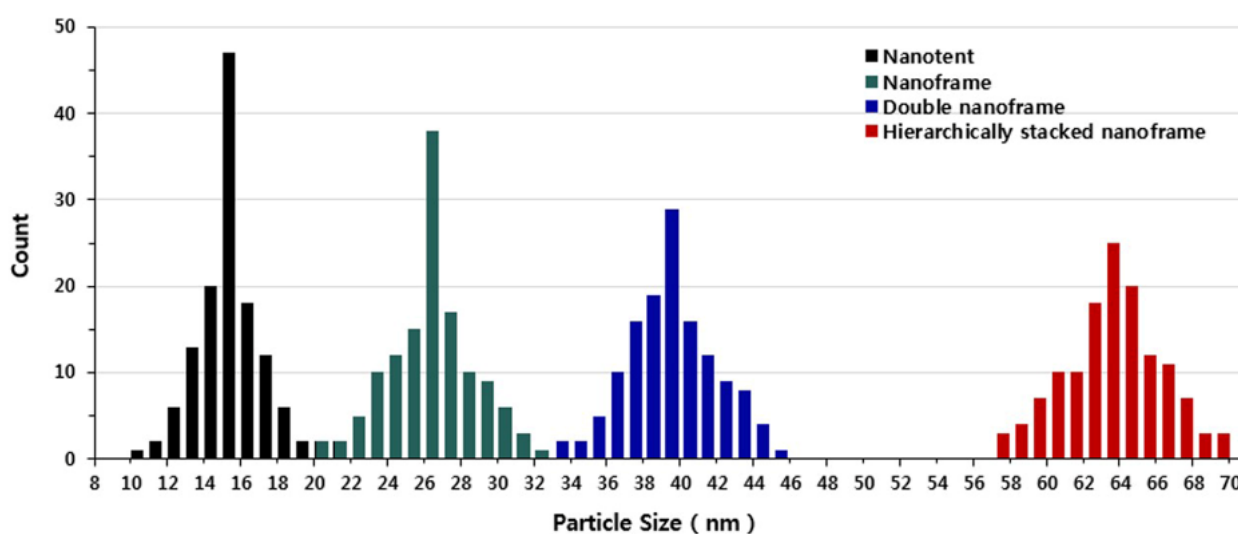


Fig. S5. Size distribution of the RhZn nanotent structures (Fig. 4a), nanoframe structures (Fig. 4b), small double nanoframe structures (Fig. 4c), and hierarchically stacked nanoframe structures (Fig. 4d).

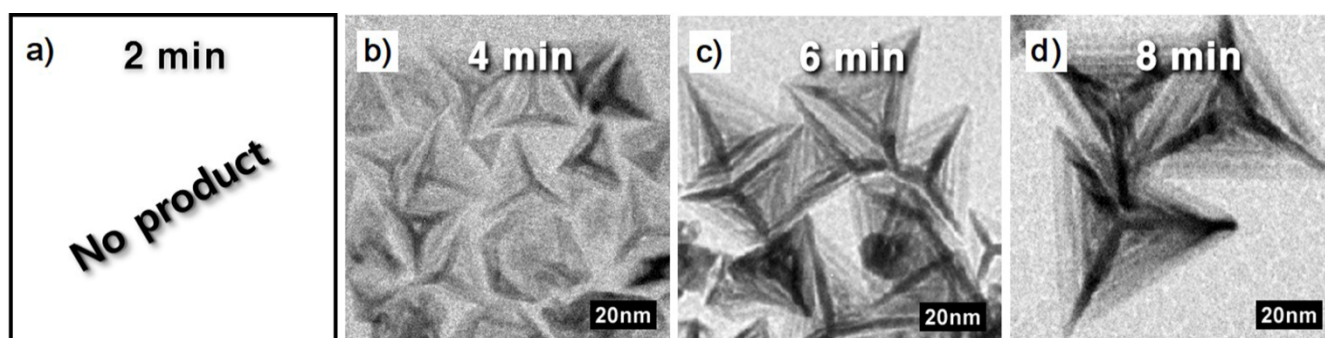


Fig. S6. TEM images of intermediates at different reaction times of a) 2 min, b) 4 min, c) 6 min, and d) 8 min. At initial stage, we could not find any nanostructures. At 4 min, RhZn nanoframe could be seen. The size of hierarchically stacked nanoframe structure and the number of stacks increase gradually with time.

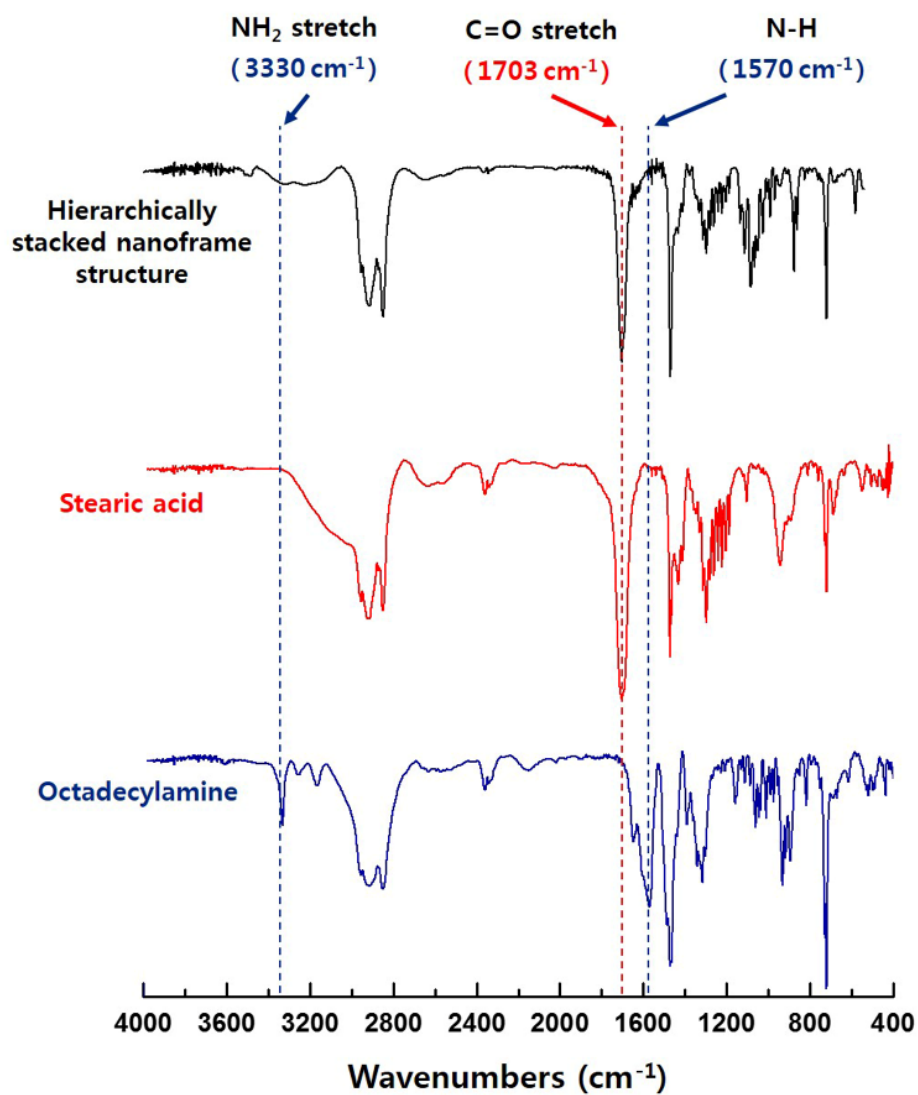


Fig. S7. IR spectra of hierarchically stacked nanoframe structure, octadecylamine, and stearic acid.

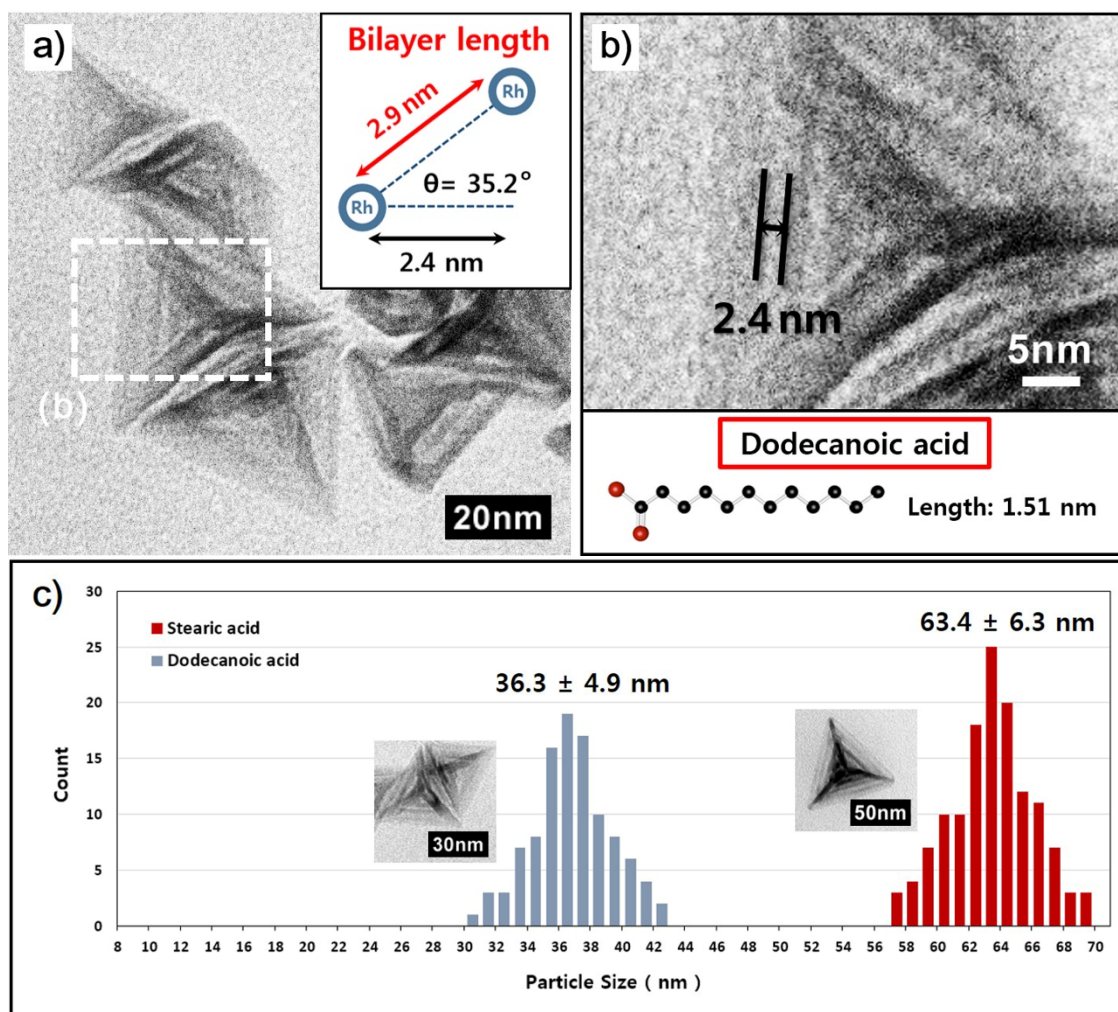


Fig. S8. a) TEM image of hierarchically stacked nanoframes prepared by using 15 equiv dodecanoic acid instead of stearic acid. (Inset: simplified view of the stacked-up nanoframe and its unique geometrical feature exhibiting the frame-to-frame distance of ~ 2.9 nm, which corresponds to the bilayer thickness of dodecanoic acid). b) HRTEM image of hierarchically stacked nanoframe prepared by using dodecanoic acid. c) Size distribution diagram of the hierarchically stacked nanoframe structures using stearic acid (red) and dodecanoic acid (gray). The nanoframe formed by using dodecanoic acid is smaller than that formed by using stearic acid.

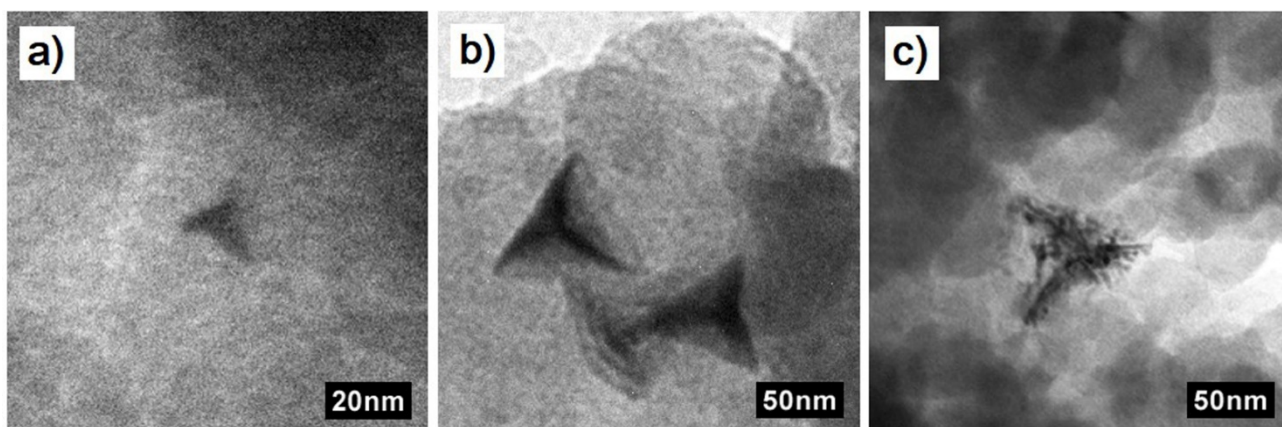


Fig. S9. TEM of a) nanotent, b) hierarchically stacked nanoframe, c) branched hierarchical RhZn nanoframe supported on carbon black after catalytic application for reduction of a phenyl ring of phthalimide. No discernable structural deformations are observed after the catalysis.

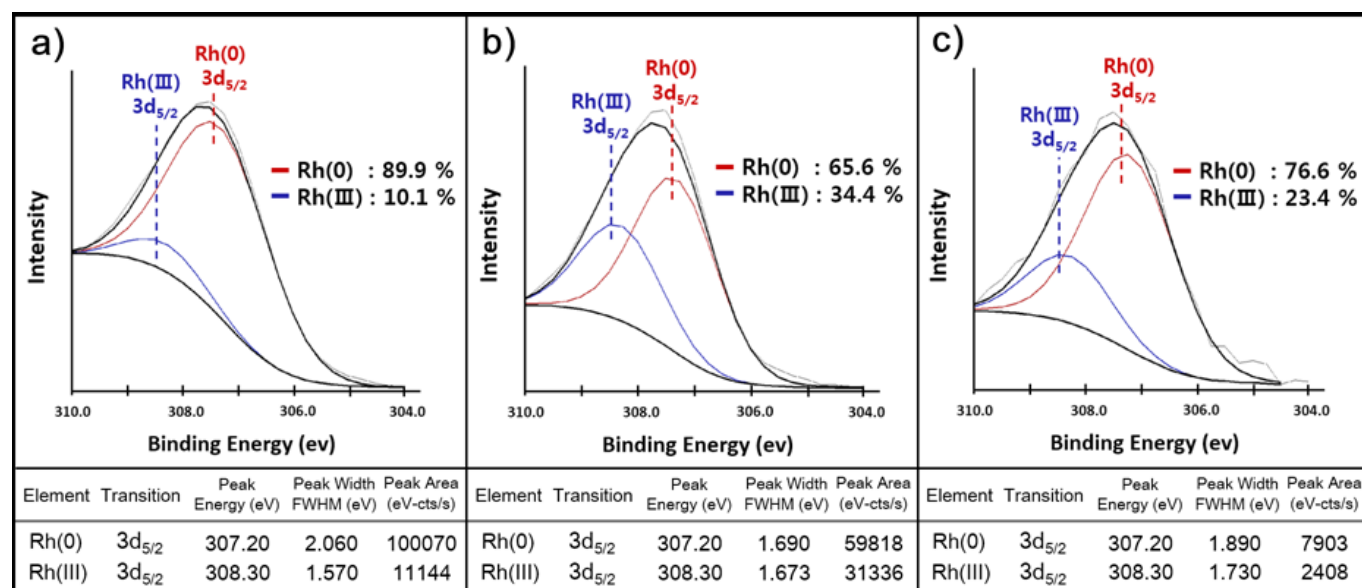


Fig. S10. X-ray Photoelectron Spectroscopy (XPS) data of RhZn a) nanotent, b) hierarchically stacked nanoframe, and c) branched hierarchical nanoframe.