

Supporting Information:

Shape-Selective Synthesis and Facet-Dependent Electrocatalytic Activity of CoPt₃ Nanocrystals

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Captions for Table S1 and S2

Experimental Section

Platinum(II) acetylacetonate (48.0% Pt, Pt(acac)₂) and cobalt(II) acetylacetonate (22.5% Co, Co(acac)₂) were purchased from Alfa Aesar. Oleic acid (90%, OA), oleylamine (70%, OLA), 1,2-hexadecanol (90%) and benzyl ether (99%) were obtained from Sigma-Aldrich. Chloroform, ethanol, methanol, perchloric acid, sulfuric acid, and formic acid were all analytical grade, and purchased from Beijing Chemical Reagent Ltd, China. All the reagents were used as received without further purification.

CoPt₃ NCs with different shapes were synthesized via a non-injection method using benzyl ether as the solvent. Typically, 0.033g Pt(acac)₂, 0.039g Co(acac)₂, 1.4mL OLA, 0.6mL OA, 0.260g 1,2-hexadecanol, and 5ml benzyl ether were loaded into a three-neck flask. The mixture was under vacuum to remove O₂ at room temperature, and water at 60°C. Subsequently, the system was heated up to 220°C under nitrogen atmosphere and maintained for 1h to obtain flowerlike CoPt₃ NCs. Following a similar method, except altering the OLA-to-OA ratio, spherical and cubic NCs were synthesized. The as-synthesized CoPt₃ NCs were precipitated with ethanol for two times, and redispersed in chloroform.

For the electrochemistry tests, a three-electrode system was used. The gold disk electrode was used as a supporting substrate for CoPt₃ NCs. Ag/AgCl electrode was employed as the reference electrode. A Pt wire was used as the counter electrode. The potentials were converted to the reversible hydrogen electrode. Before the electrochemical measurements, the gold disk electrodes were carefully polished. A 10uL chloroform solution of CoPt₃ NCs was dropped on electrodes, and followed by chloroform evaporation to form the self-assembly films of CoPt₃. The electrodes were subjected to argon plasma treatment to remove the organic ligands on CoPt₃. The electrocatalytic properties of CoPt₃ NCs were evaluated using cyclic voltammogram (CHI 660C electrochemical analyzer, CH Instruments). The catalytic activity of NCs was normalized to the geometrical area of electrode.

Figure S1. Size distribution of CoPt₃ nanoparticles (a), CoPt₃ nanocubes (b), and flowerlike CoPt₃ (c).

The size distribution was calculated from the TEM images.

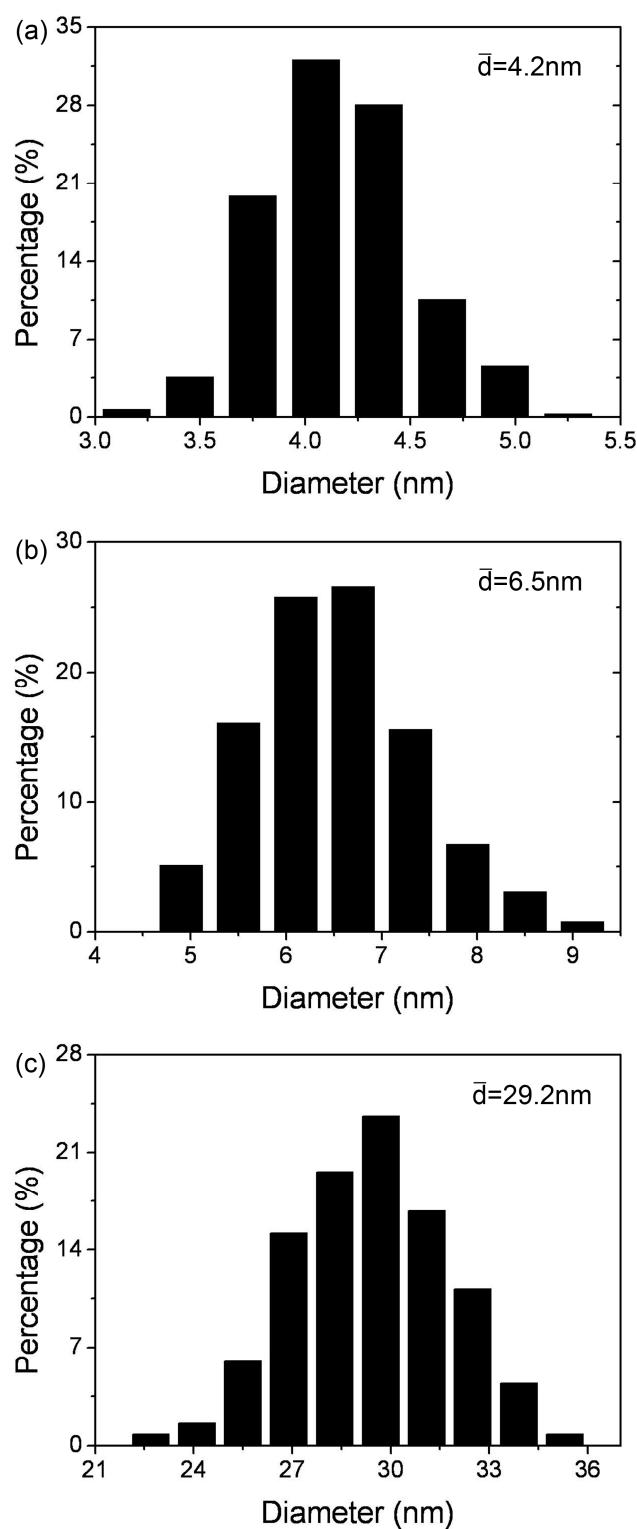


Table S1. The correlation of OLA-to-OA ratio, shapes of the as-synthesized CoPt₃ NCs, and Co-to-Pt ratio of NCs.

OLA-to-OA ratio	Shapes of CoPt ₃ NCs	Co-to-Pt ratio
1:9	nanoparticle	1 : 3.01
4:6	nanocube	1 : 3.02
7:3	nanoflower	1 : 2.98

Figure S2. TEM observation of the formation of flowerlike CoPt₃ NCs from preformed octapods.

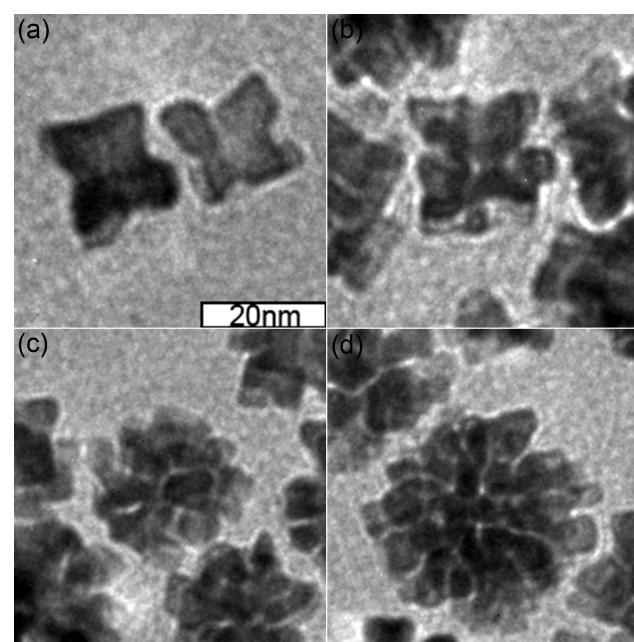


Table S2. Comparison of the XRD peak intensities of CoPt₃ NCs in different shapes, among which the (220) peaks was normalized.

CoPt ₃ shapes	Relative intensities of XRD peaks			
	(111)	(200)	(220)	(311)
nanoparticle	2.52	1.12	1.00	1.25
nanocube	2.60	1.20	1.00	1.13
nanoflower	3.42	1.34	1.00	1.02

Figure S3. Cyclic voltammograms of spherical (black), cubic (red), and flowerlike (green) CoPt₃ NCs in a mixture of 0.1M HClO₄ and 0.5M HCOOH. The sweep rate is 0.05V/s.

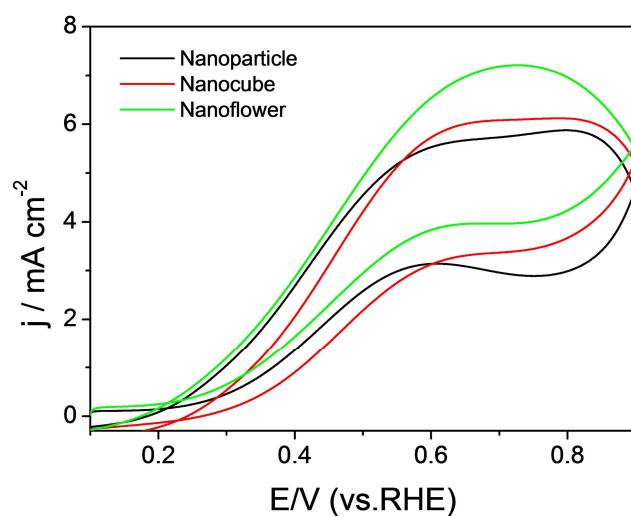


Figure S4. An enlarged picture of Figure 1e.

