

Supporting Information

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Enhancing by Weakening: Electrooxidation of Methanol on Pt₃Co and Pt Nanocubes**

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Part 1. Chemicals, Nanocube Syntheses and Characterization Methods

1.1 Chemicals

Cobalt(II) acetate tetrahydrate ($\text{CoAc}_2 \cdot 4\text{H}_2\text{O}$, 99.999%), tungsten hexacarbonyl ($\text{W}(\text{CO})_6$, 99.9%), oleic acid (90%) and oleylamine (70%) are Sigma-Aldrich products. Platinum(II) acetylacetonate ($\text{Pt}(\text{acac})_2$, 49.3-49.8% Pt), anhydrous ethanol (200 proof) and anhydrous hexane (98.5%) were purchased from Gelest, Alfa Aesar, AAPER and BDH, respectively. Perchloric acid (HClO_4 , 70%, double-distilled) and sulphuric acid (H_2SO_4 , 95.0-98.0%, double-distilled) were obtained from GFS chemicals, and methanol is from Pharmco. All chemicals were used without further purification. Nanocube Synthesis and characterization method are detailed in supporting information.

1.2 Nanocube Syntheses

The general procedure for preparation of Pt_3Co NCbs was reported in our recent work. In a typical experiment, 0.020g of $\text{Pt}(\text{acac})_2$, 0.0125g of $\text{CoAc}_2 \cdot 4\text{H}_2\text{O}$, 8.0 mL of oleylamine and 2.0 mL of oleic acid were loaded into a three-neck flask and heated to 130 °C under an argon stream. 0.05 g of $\text{W}(\text{CO})_6$ was then added into the solution and the temperature was subsequently raised to 240°C and kept for 30-60 min with vigorous stirring. The resultant products were isolated by centrifugation washed with anhydrous hexane for several cycles. The ~9 nm Pt_3Co NCbs were finally re-dispersed in hexane, forming a colloidal suspension. Procedure for synthesis of ~9 nm Pt NCbs is the same as that of ~9 nm Pt_3Co NCbs, except for the absence of $\text{CoAc}_2 \cdot 4\text{H}_2\text{O}$.

1.3 Characterization Methods

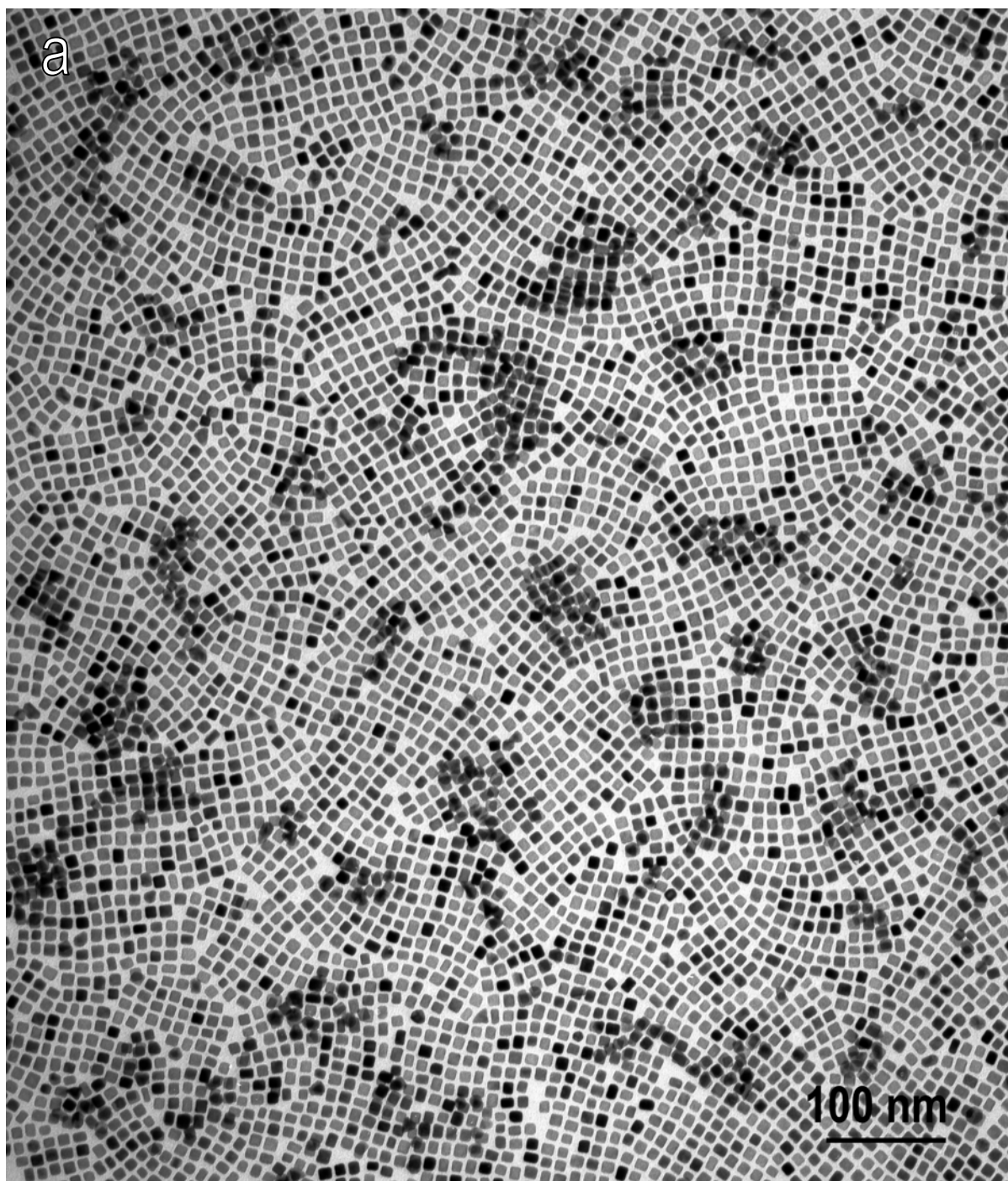
X-ray diffraction patterns were collected using a PANalytical X'Pert X-ray powder diffractometer equipped with a $\text{Cu K}\alpha_1$ radiation source ($\lambda = 0.15406$ nm). A Hitachi 7000 and a Zeiss 10 C transmission electron microscope (TEM) operated at 110 kV were used for TEM imaging. A JEOL-2010 FEG TEM operated at 200 kV was used for high-resolution TEM imaging, selected-area electron diffraction (SAED), and energy dispersive X-ray spectroscopic (EDS) measurements. ICP-MS analysis was conducted at the Department of Geosciences, University of Houston. Scanning electron micrographs were recorded on a field emission scanning electron microscope (Zeiss Supra 35VP).

The electrochemical measurements were conducted by using a CHI 700B electrochemical analyzer in a conventional two-compartment electrochemical cell with a Pt wire as the counter electrode and a Ag/AgCl reference electrode. The potentials in this study, however, are all reported with respect to a reversible hydrogen electrode (RHE). The working electrode is a glassy carbon (GC) disk electrode (Pine Instrument). Before each experiment, the GC electrode was mechanically polished with 1.0, 0.3, and 0.05 μm alumina powder successively till a mirror-finish surface was obtained, and rinsed with ultra-pure water. To form a thin film of catalyst, a given volume (typically 10 μL) of the catalyst suspension was pipetted onto the GC surface and dried in the air. The catalyst suspension was obtained by washing the as-prepared colloidal solution six times with hexane and ethanol to remove the majority of unbound surfactants and then re-dispersed in hexane. Before electrochemical experiments, the GC electrode supported catalysts were subjected to an argon plasma (100 W, 0.3 Torr) (PX250, March Plasma Systems) treatment for 5 min to remove the residual organic solvent and surfactants on catalysts. The electrode was then immersed in 0.1 M HClO_4 and the potential was cycled between 0.05 and 1.0 V at 100 mV s^{-1} till a stable voltammogram was obtained. For CO stripping experiments, a saturated CO adlayer was formed by bubbling the gas through the electrolyte solution with the electrode potential being held at 0.10 V until complete blockage of the surface. Then CO dissolved in the solution was removed by purging nitrogen through the solution for 15 min. The potential scan started at 0.05 V

towards positive direction. Current is normalized to the Pt area estimated from the hydrogen desorption charge in all of the voltammograms and chronoamperograms. All of the aqueous solutions were prepared with 18.2 M Ω ·cm water purified by a Milli-Q system (Synthesis A10, Millipore). All of the experiments were conducted at room temperature (22 ± 1 °C).

Part 2. Experimental Results

Figure S1. (a), TEM image of 9 nm Pt₃Co nanocubes; (b), SEM image of 9nm Pt₃Co nanocubes; (c) TEM image of 9 nm Pt nanocubes.



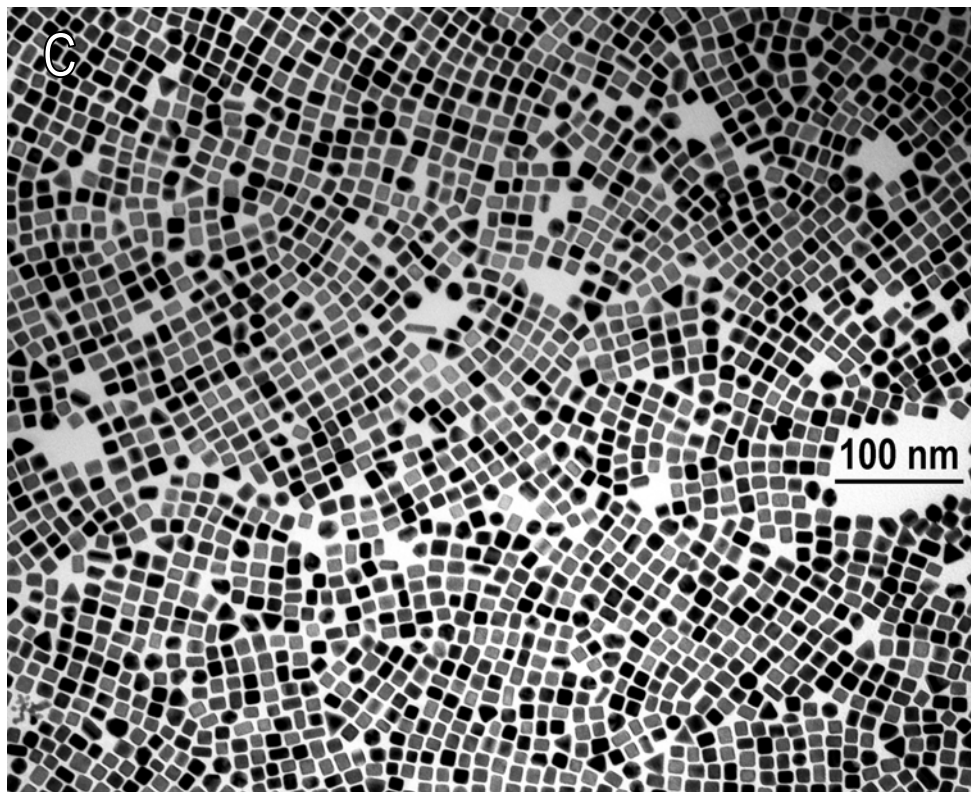
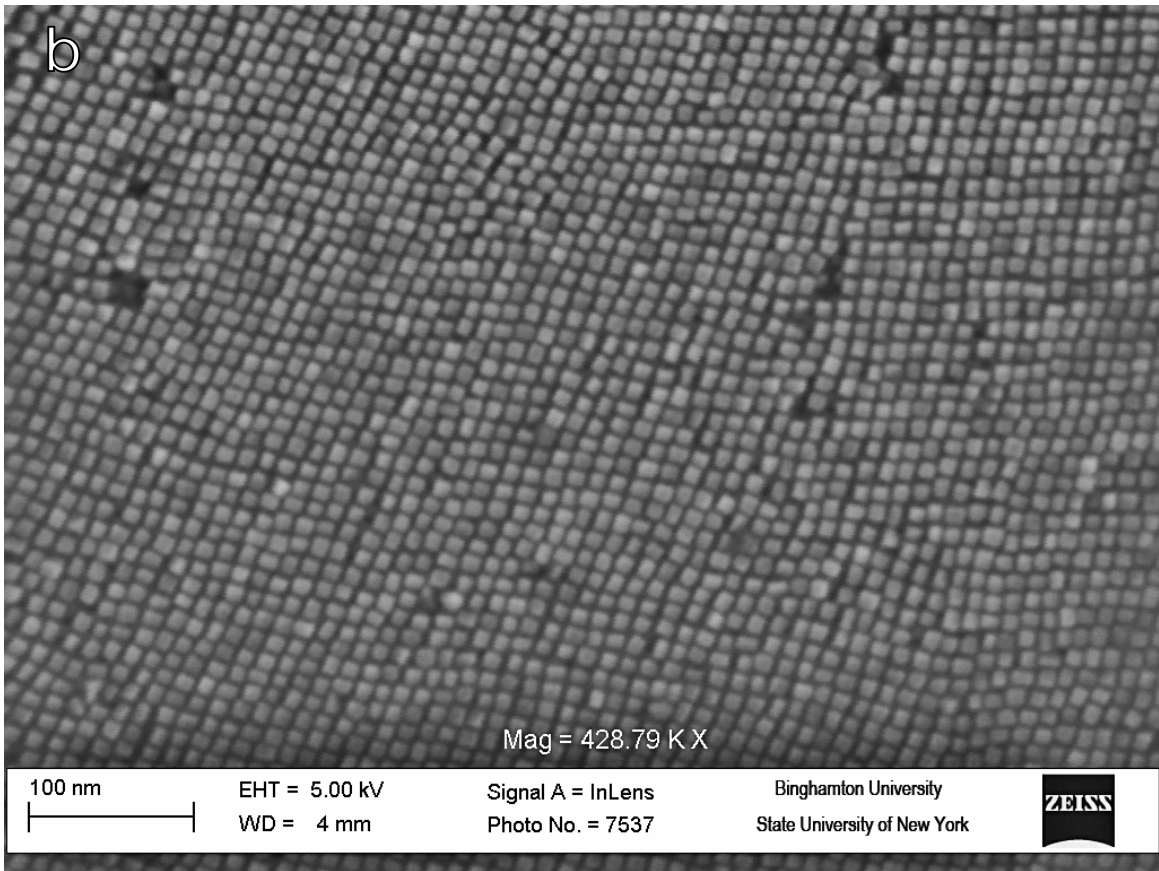


Figure S2. Typical spectra of EDS@TEM on Pt₃Co nanocubes and analytical results of their chemical compositions. In all spectra, no trace of W was detected.

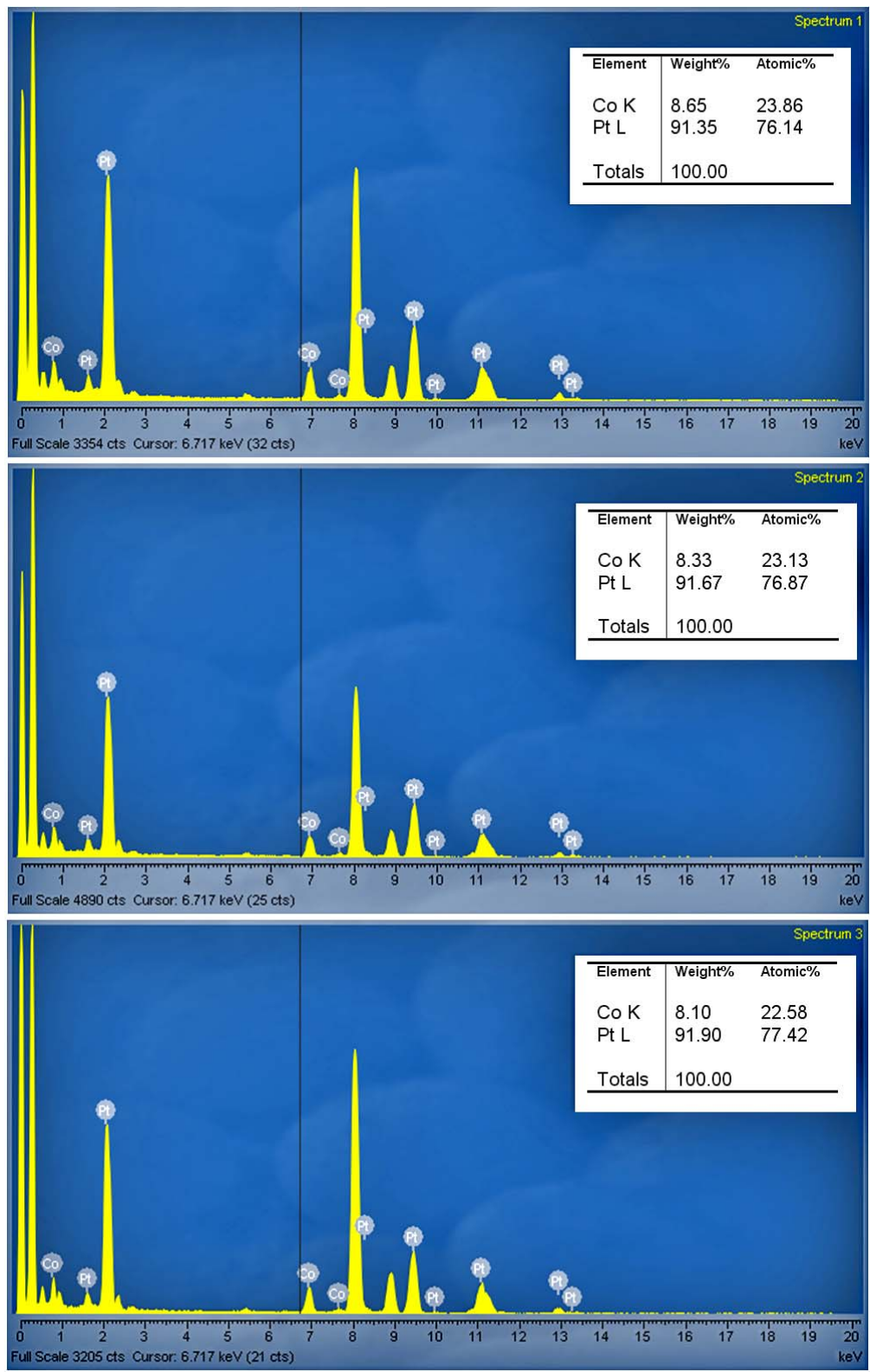


Figure S3. XRD patterns of nanocubes: (a, b) Pt₃Co, and (c, d) Pt. (a, c) Samples were assembled on a surface-polished 25 mm Si <100> wafer. (b, d) Samples were randomly deposited on a PANalytical zero-background Si sample holder.

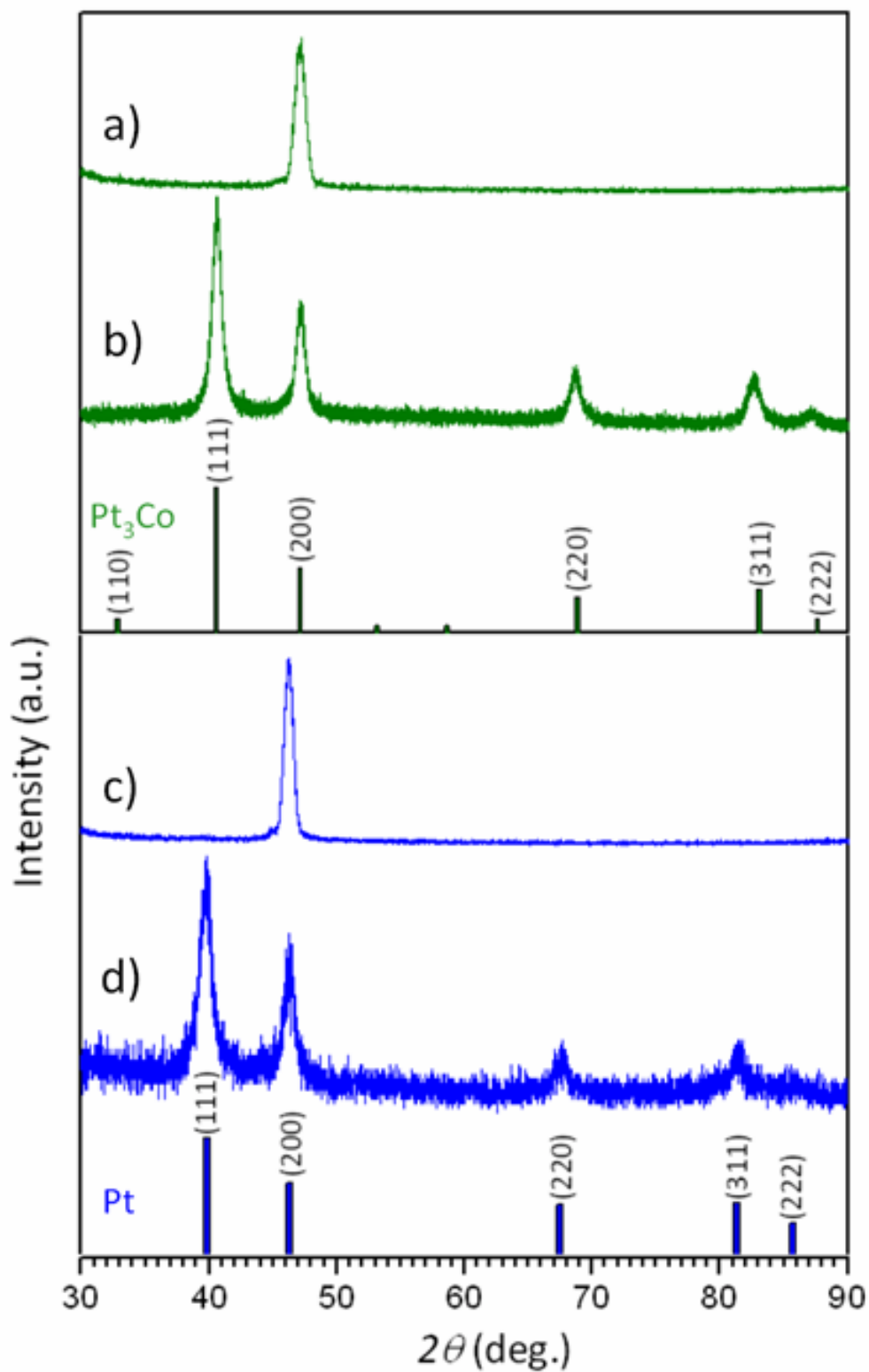


Figure S4. TEM images of (a) Pt₃Co NCs and (b) Pt NCs after plasma and electrochemical treatments.

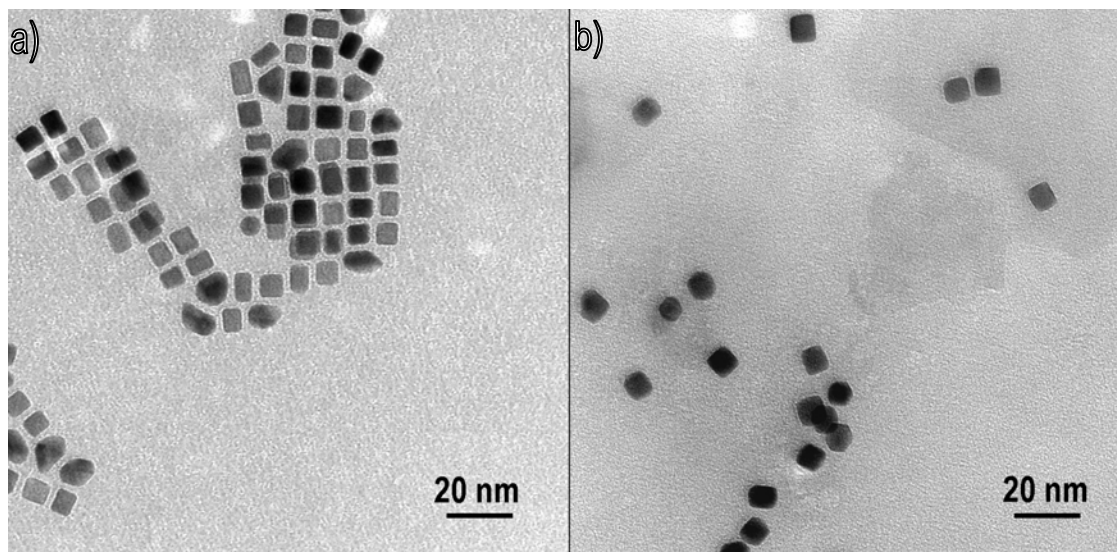


Figure S5. SEM image of the Pt₃Co nanocubes after an electrochemical experiment.

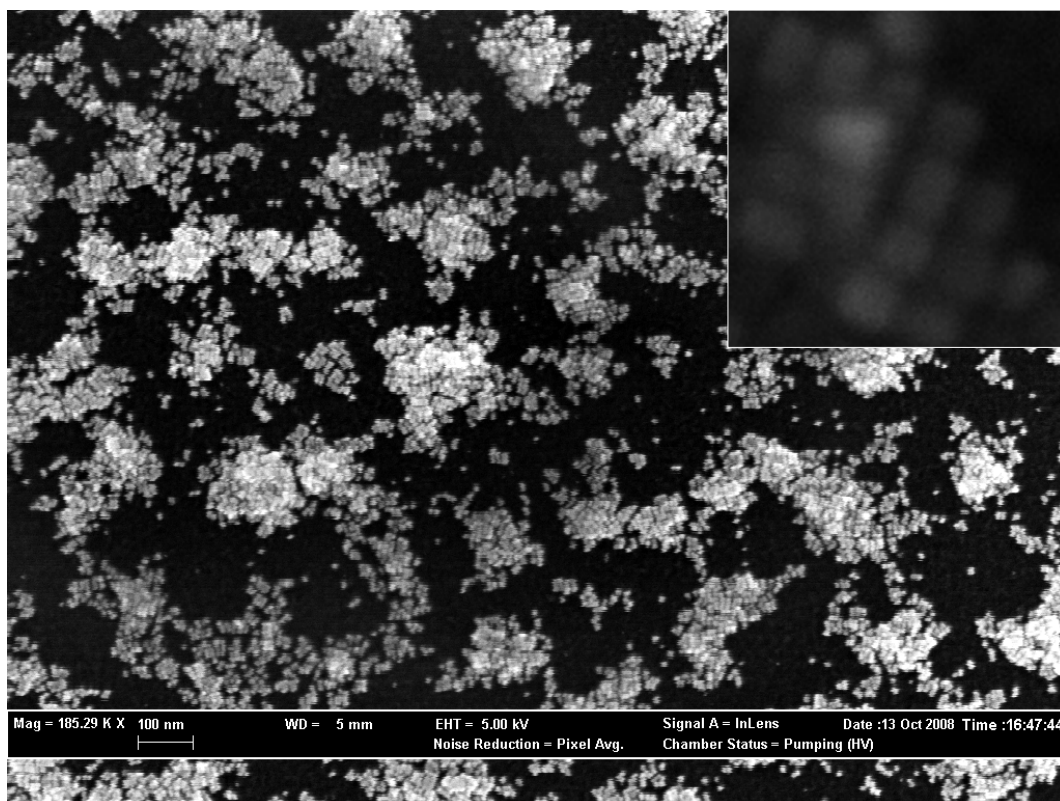


Figure S6. Cyclic voltammograms of cubic Pt₃Co and Pt NCs in 0.5 M H₂SO₄, scan rate: 0.1 V s⁻¹.

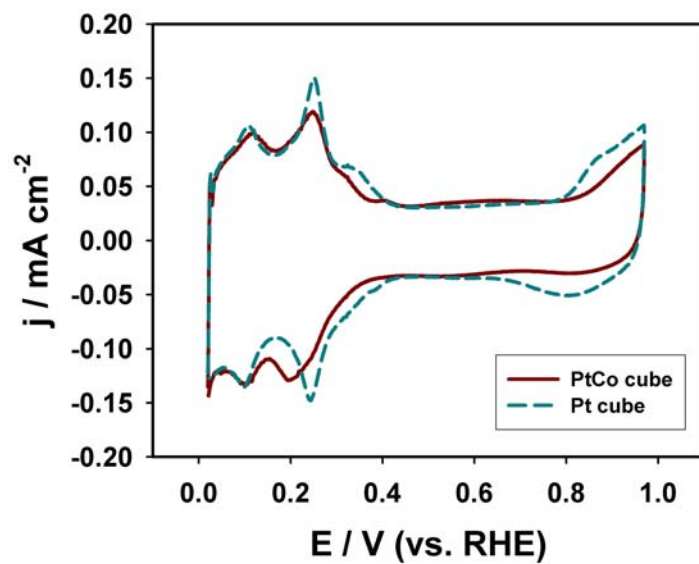


Figure S7. Cyclic voltammograms of CO stripping on cubic Pt₃Co and Pt NCs in 0.1 M HClO₄, scan rate: 0.1 V s⁻¹. The arrow indicates the potential scan direction.

