Supplementary Information For

Electrochemical Synthesis of Monodisperse PtCo Nanocrystals

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Doi: 10.1595/205651323X16799975192215

1. Materials and Methods

Cobalt (II) Chloride, anhydrous ($CoCl_2$, 97%), was purchased from Acros Organics. Potassium tetrachloroplatinate (II) (K_2PtCl_4, 98%) and N,N-Dimethylformamide (DMF, 99.8%) were purchased from Sigma-Aldrich. Sulfuric Acid (H_2SO_4, Certified ACS Plus) was purchased from Fisher Chemicals. Hexadecyltrimethylammonium Bromide (CTAB, >98.0%) was purchased from TCI Chemicals. All water used was MilliQ 18 MΩ.

TEM micrographs were collected on either a JEOL JEM-1400 microscope operating at 120 keV or a JEOL JEM-F200 multipurpose electron microscope operating at 200 keV. High-resolution HAADF-STEM and EDS were collected on a JEOL NEOARM operating at 200 kV. The probe current was 150 pA, and the camera length was 4 cm. EDS maps were obtained with Digital Micrograph, software provided by Gatan Inc. XRD patterns were collected in the 2θ range of 20°–90°, with data points collected every 0.02°2θ, and a scan rate of 0.15°/s on a Rigaku Smartlab high-resolution diffractometer with Cu Kα radiation (λ = 0.154 16 nm, 44 mA, and 30 kV). Electrochemical Data were collected on a potentiostat (Epsilon, Bioanalytical Systems Inc.) with a three-electrode system consisting of either a Pt wire or Indium Tin Oxide coated glass slide (Sigma Aldrich) working electrode. An Ag/AgCl reference electrode in 3 M KCl, and a Pt Coil auxiliary electrode were used. All potentials collected during the testing were converted in reference to a reversible hydrogen electrode (RHE).

A detailed methodology for the synthetic approach developed here is presented in detail in Figure 1 of the main text and described in the methods section of the main text.

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2. Additional Electrochemical Data

The currents obtained during the electrochemical synthetic process for each case described in the main text are seen in Figure S1.

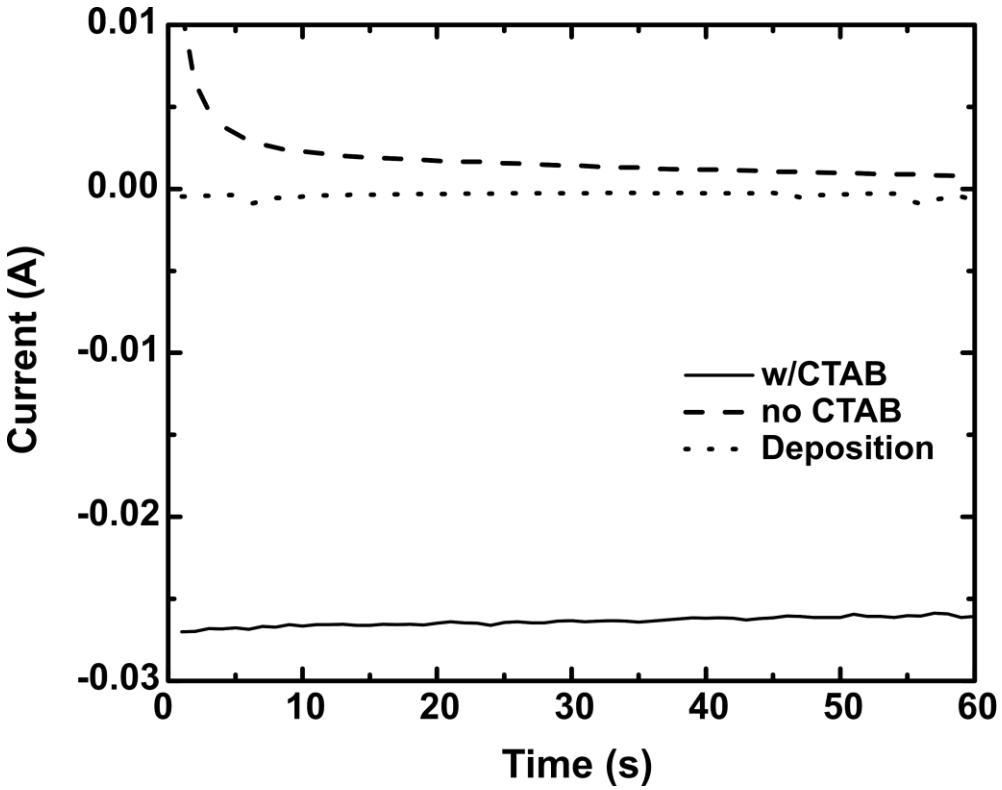

Figure S1. Obtained electrochemical currents during the synthetic process.

In Figure S1, currents can be observed for the synthesis with a stabilizing agent (solid line), without a stabilizing agent (large dash), and through electrodeposition (small dash). The largest observed current is observed for the stabilized particles, indicating they are the most adept to form NCs. To further analyze the NCs that formed, we performed EDS as shown in the main text in Figure 4. In order to better quantify the ratio of Pt and Co, we collected an EDS spectrum, as shown in Figure S2.

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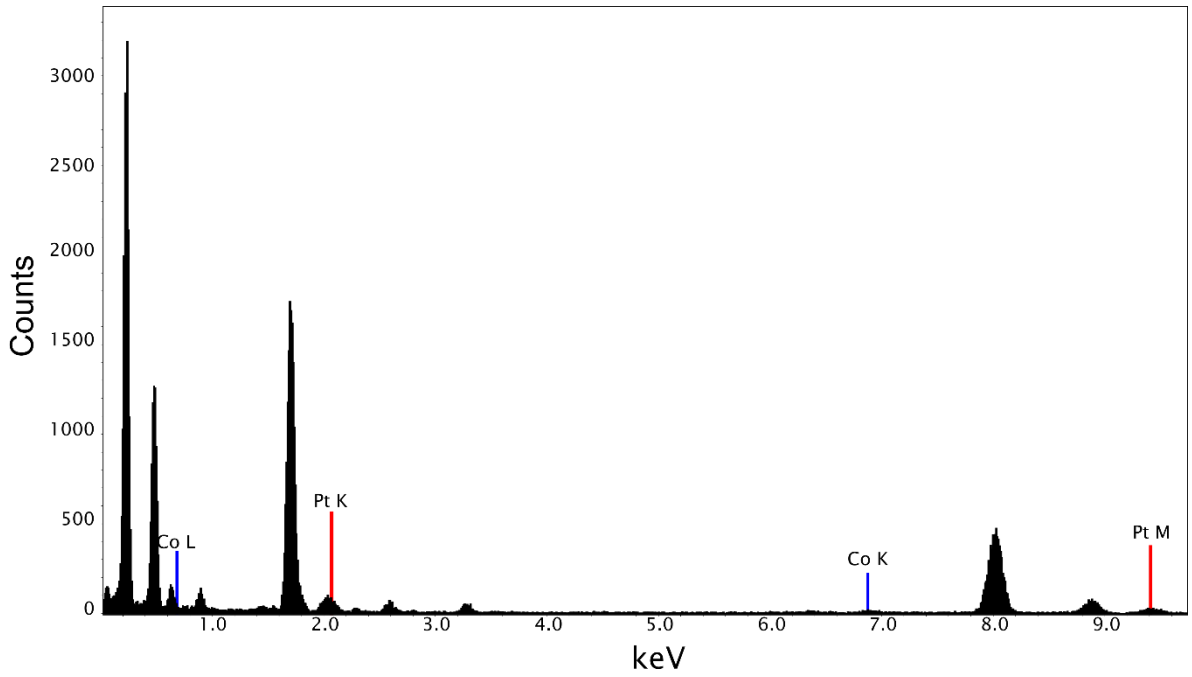

Figure S2. EDS Spectrum for stabilized electrochemically synthesized PtCo NCs, with Pt peaks labeled in red and Co peaks labeled in Blue. Additional peaks correspond mainly to the carbon background, Cu TEM grid, and Si contamination of the system.

As seen in Figure S2, relative intensities of the Co L and Pt K peaks show a near 1-1 ratio of Pt to Co in the system. This is consistent with the XRD shown in Figure 4A, as well as the visual interpretation of the EDS maps shown in Figures 4C and D.

3. Solution Imaging

The pre-synthesized starting solution shown in Figure 1C is without CTAB as a stabilizing agent. Figure S3 is the initial starting solution with the addition of 100 mM CTAB.

Figure S3. Electrochemical starting solution with CTAB.

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4. Additional Microscopy

The images shown in Figure 4 C-F were taken from the micrograph shown in Figure S4A and filtered as shown in Figure S4B. The filter was applied using DeconvGUI software.

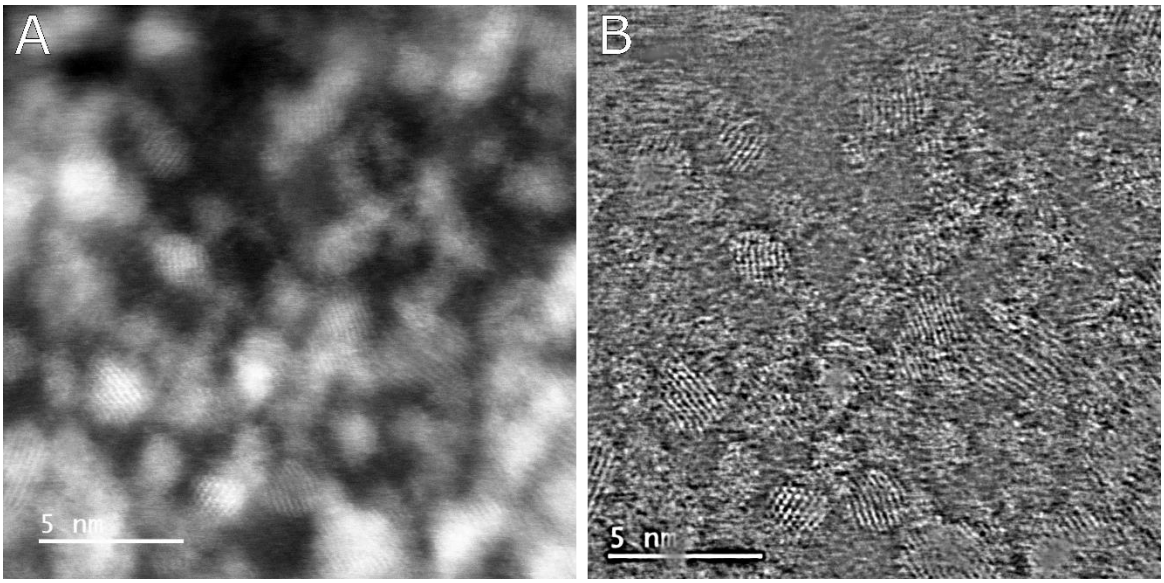

Figure S4. A) Unfiltered STEM image containing components of Figure 4 C-F. B) Identical micrograph filtered with DeconvGUI software.

The EDS scan shown in Figure 4G was taken from the area shown in Figure S5.

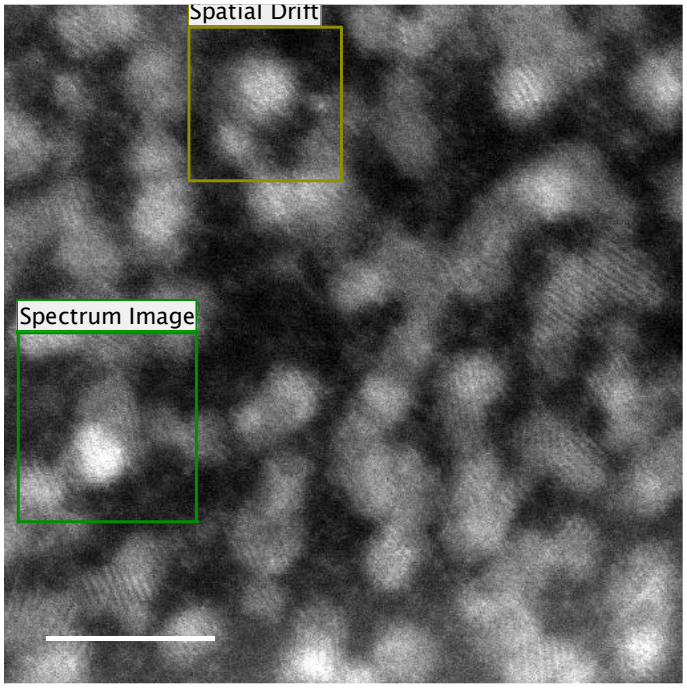

Figure S5. STEM micrograph indicating the location of EDS scan as spectrum image, and indicating the area used to correct for drift during the measurement. Drift was corrected after every two scan lines of data.

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