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Supporting Information

One-pot synthesis of Pd-Pt@Pd core-shell nanocrystals with enhanced electrocatalytic activity for formic acid oxidation

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Experimental section:

Chemicals: Chloroplatinic acid hydrate (99.9%), Palladium chloride (99.9%), Sodium chloride (99.99%), Sodium bromide (99.9%), Cetyltrimethylammonium bromide (99%), Cetyltrimethylammonium chloride (≥ 95%) and Citric acid monohydrate (99.9%) were purchased from Sigma-Aldrich. Pd black was purchased from Johnson Matthey. Chemicals were used as received without further purification. The super pure water (18 MΩ cm) was used as solvent. 0.1 M of Na_2PdCl_4 aqueous solution was prepared by adding 0.235g (4.0 mmol) of NaCl and 0.354g (2.0 mmol) of $PdCl_2$ into 20 mL of water and stirring for 40 minutes. Then put this solution without stirred for a whole day before it was used.

Synthesis of Pd-Pt@Pd core-shell nanpcrystals:

In a typical synthesis, 0.666 mL of 0.1 M Na_2PdCl_4 and 0.333 mL of 0.1 M H_2PtCl_6 aqueous solution were added into 9.0 mL of aqueous solution containing 0.2916 g cetyltrimethylammonium bromide (CTAB) and 0.210 g citric acid (CA) and stirred for several minutes. Then the resulting emulsion-like solution was transferred to a 15 mL Teflon-lined stainless-steel autoclave. The sealed vessel was then heated at 200°C for 2.5 h before it was cooled to room temperature. The products were separated via centrifugation/washing cycles at 10000 rpm for 15 minutes for three times with water. The collected product was redispersed in water.

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Characterizations: The TEM images of the samples were examined with FEI Tecnai T12 (120 KV). HRTEM, X-Ray energy spectrometer (EDS), High-angle annular dark field scanning TEM (HAADF-STEM) and element mapping were obtained with FEI Titan 80 (300 KV). X-ray diffraction (XRD) patterns of the samples were recorded on a Bruker D8 Advance diffractometer with Cu K_α radiation (λ=1.5418 Å) with graphite monochromator (40 KV, 40 mA).

Characterization of electrocatalytic activity:

Electrochemical experiments were carried out in a standard three-electrode cell at room temperature (about 25 ºC) controlled by PAR 263A potentiostat/galvanostat (EG&G). The super pure water (18 MΩ cm) purified through a Milli-Q Lab system (Nihon Millipore Ltd.) was used as solvent.

The super pure water dispersion of purified nanoparticles was deposited on a glassy carbon electrode (GC, ϕ5 mm; Takai Carbon Co., Ltd., Tokyo, Japan) to get the working electrodes after evaporation of solvent under an IR lamp. A reversible hydrogen electrode (RHE) and a platinum foil were used as the reference and counter electrode, respectively.

The cyclic voltammograms (CVs) were obtained in nitrogen-saturated 0.1 M H_2SO_4 solution, and the potential was scanned from 0.05 to 1.1 V (RHE) at a scan rate 50 mV/s. Voltammogram measurment for formic acid oxidation was carried out in 0.1 M HCOOH + 0.1 M H_2SO_4 solution, and the potential was scanned from 0.05 to 1.1 V (RHE) at a scan rate 50 mV/s.

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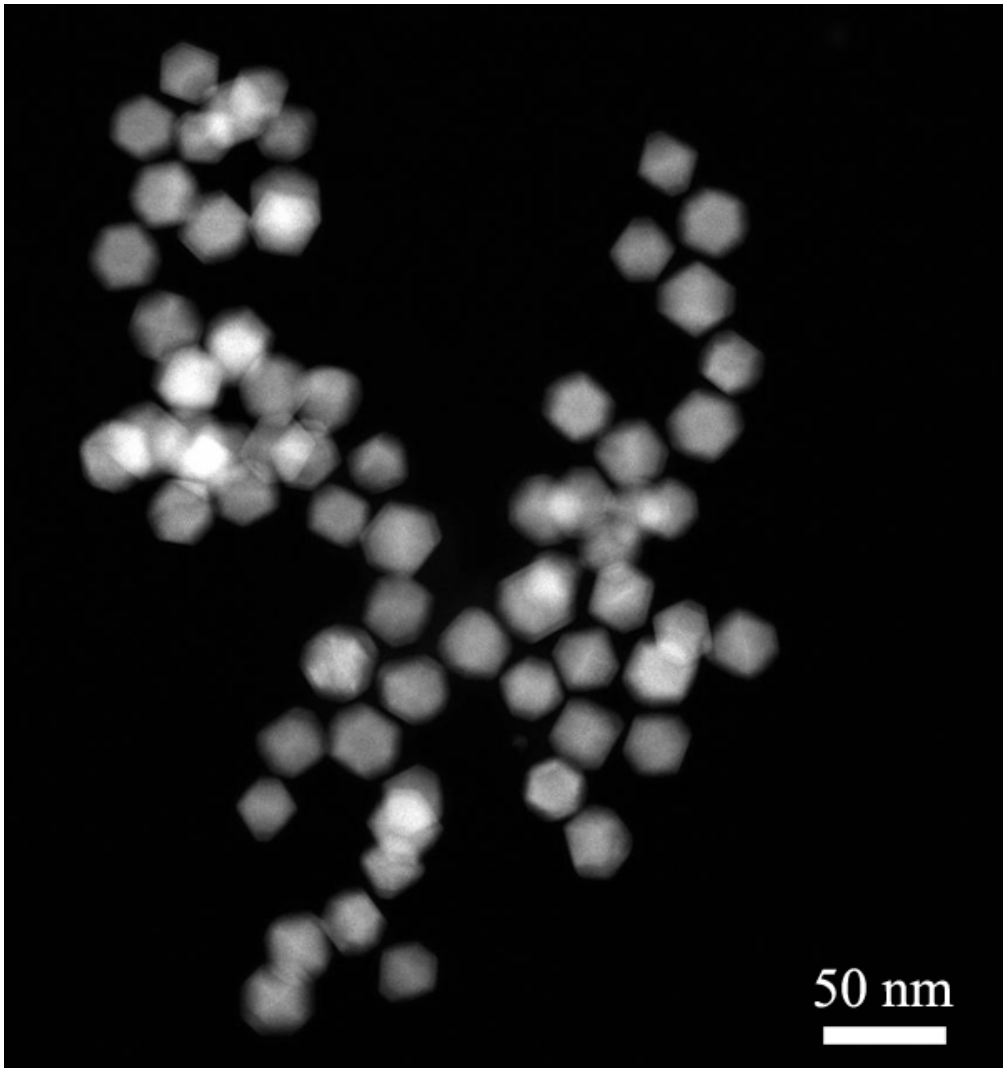

Figure S1. HADDF-STEM image of as-synthesized Pd-Pt@Pd core-shell nanocrystals.

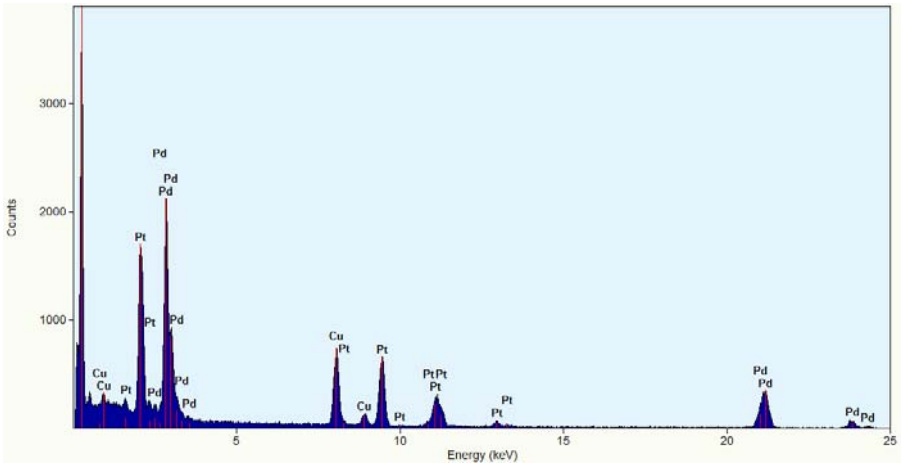

Figure S2. EDX profiles of as-synthesized Pd-Pt@Pd core-shell nanocrystals.

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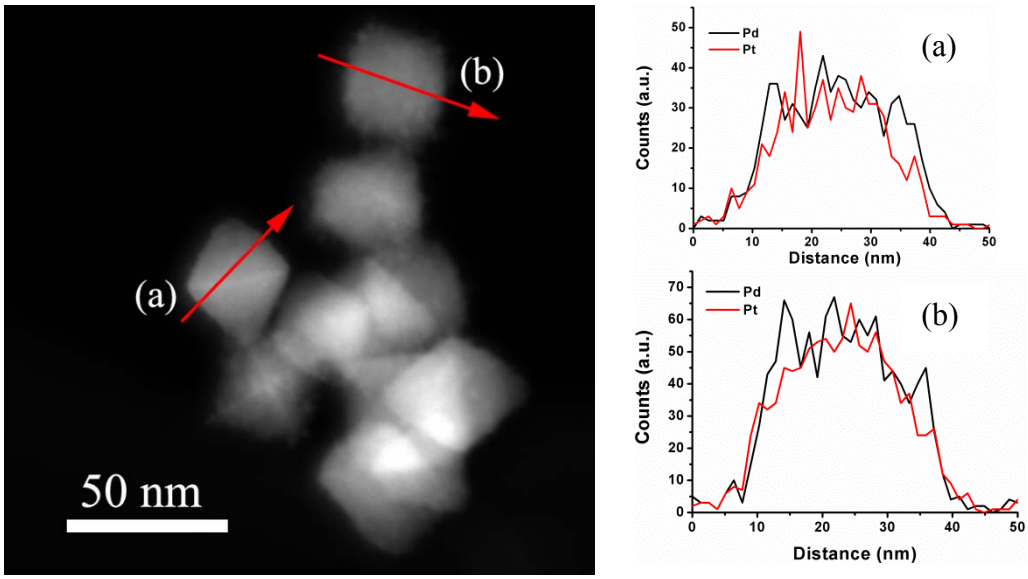

Figure S3. HADDF-STEM image and EDX line scanning profiles of nanocrystals synthesized with equal mole CTAC replaced CTAB.

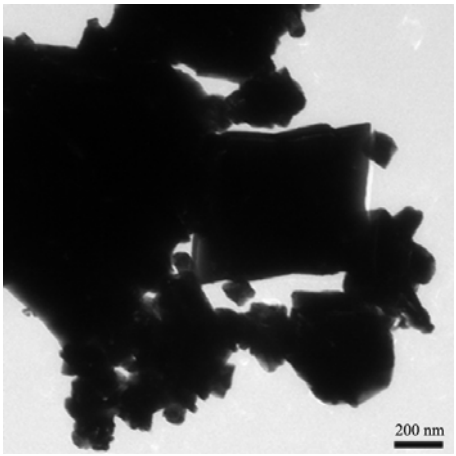

Figure S4. TEM image of nanocrystals synthesized with equal mole NaBr replaced CTAB.

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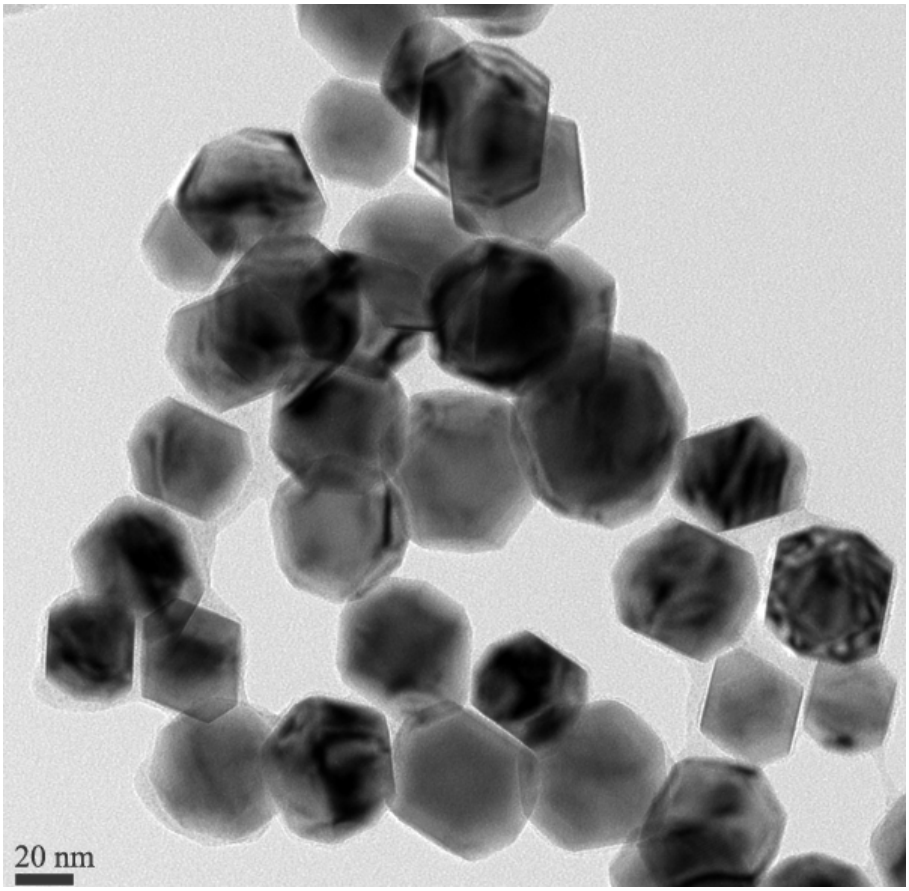

Figure S5. TEM image of as-synthesized nanocrystals with the ratio of Na_2PdCl_4 to H_2PtCl_6 of 4:1.

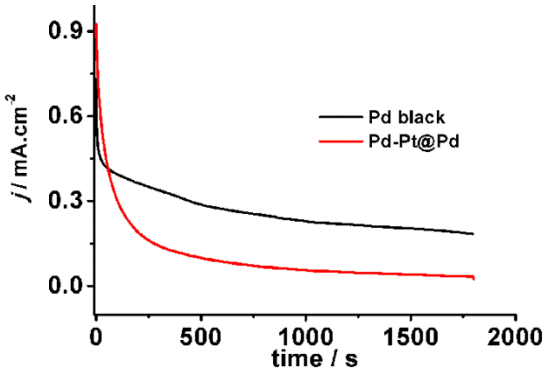

Figure S6. Chronoamperometric curves of as-synthesized Pd-Pt@Pd core-shell nanocrystals in a 0.1 M formic acid + 0.1 M H_2SO_4 solution at 0.25 V for 1800 seconds.