Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Structural Evolution of Concave Trimetallic Nanocubes with Tunable Ultra-Thin Shells for Oxygen Reduction Reaction

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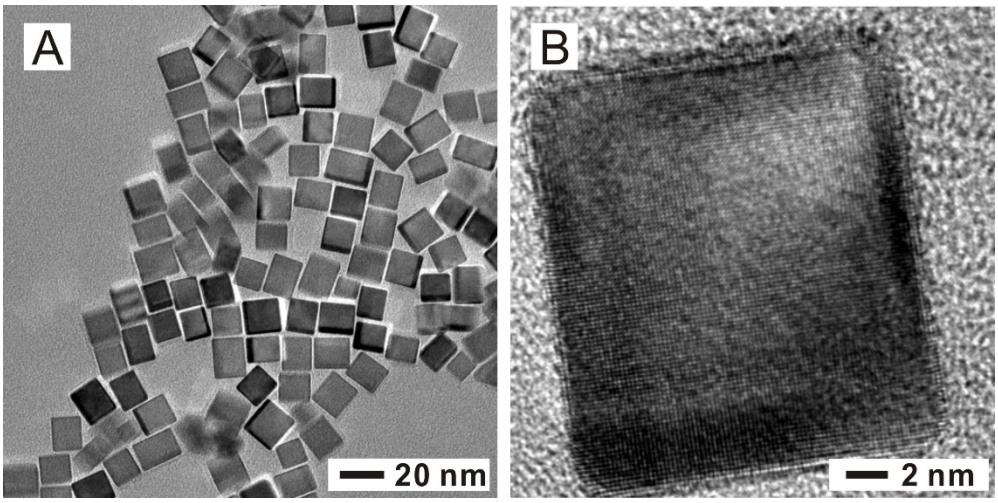

Figure S1. TEM images of the Pd nanocubes used for the deposition of PtNi shells.

Calculation method for the deposition rate and diffusion rate

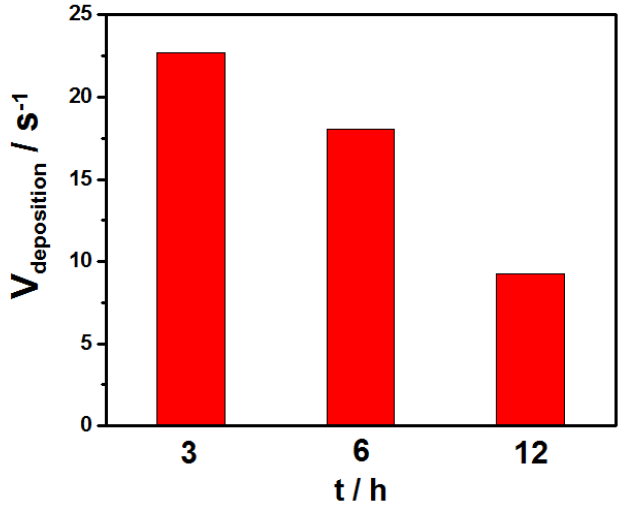

Figure S2. The average deposition rate calculated from the products obtained at 3 h, 6 h and 12 h, respectively.

To illustrate the structure evolution quantitatively, we describe a method to calculate the average deposition and diffusion rate. We choose NCs obtained by the standard procedure as the calculation model. The average length of Pd seeds was measured to be 17.5 nm and the volume was 5359 nm^3. Multiplying volume by the density of Pd, the mass of one individual Pd nanocube can be calculated to be 6.44×10^{-17} g. According to the ICP-MS result (assuming the mass ratio between Pt and Pd is X), we can get the mass of the reduced Pt ($X\times6.44\times10^{-17}$ g). The average deposition rate could be obtained by the following equation:

$$V_{deposition} = \frac{mass_{Pt} \times N_A}{M_{Pt} \times t} = \frac{6.44 \times 10^{-17} \times X \times 6.02 \times 10^{23}}{195 \times t}$$

In the equation, $mass_{pt}$ is the mass of deposited Pt atoms; N_A is the Avogadro's constant; M_{Pt} is the unit molar mass of Pt. The average deposition rate for the products obtained at 3 h, 6 h and 12 h was calculated to be 23, 18 and 9 Pt atoms per second.

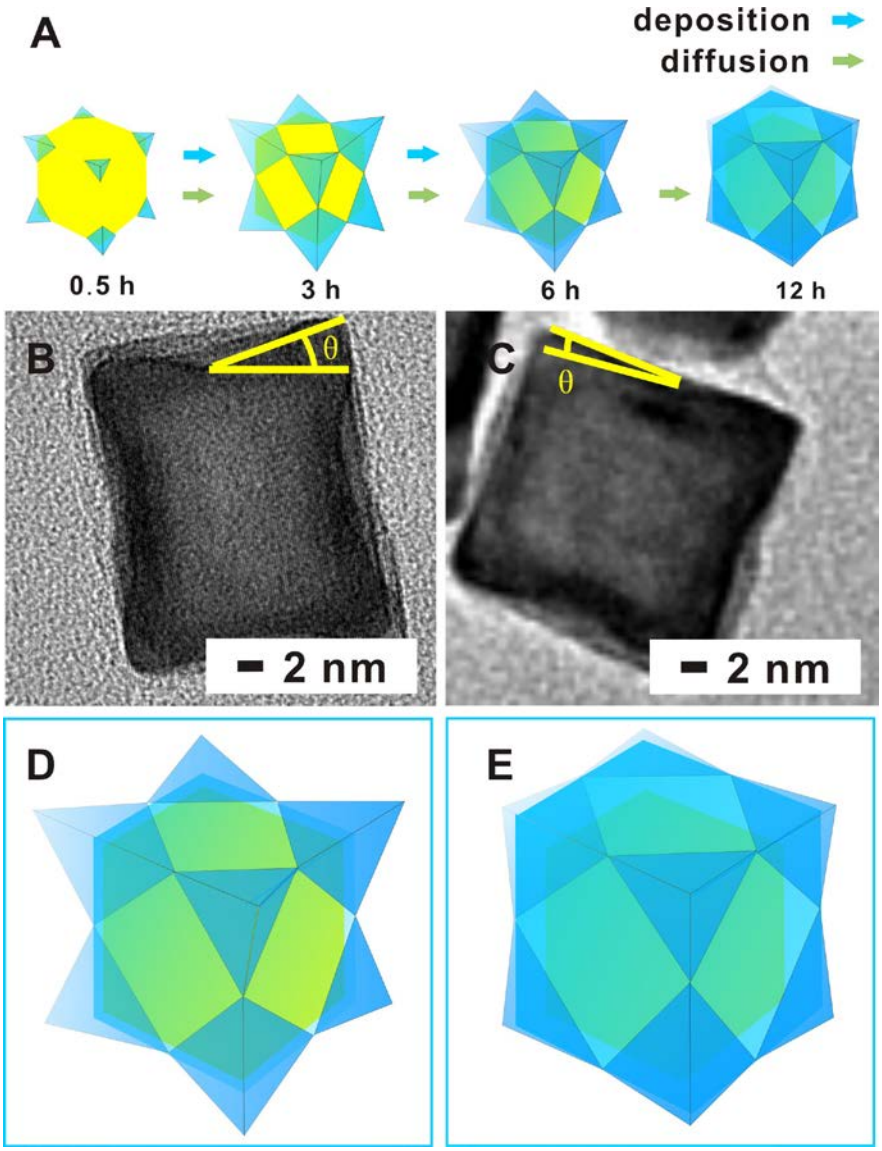

Figure S3. (A) The models of Pd@PtNi NCs at different reaction stages. (B, C) The concave Pd@Pt nanocubes obtained at 6 h and 12 h, respectively, showing a distinct concavity. (D, E) The calculation models for the two typical samples.

The diffusion rate could be determined by the products obtained at 6 h and 12 h, the different concavity of the NCs obtained at 6 h and 12 h (Figure S3) was only attributed to the surface

diffusion during the reaction period between 6 h and 12 h. The concave NCs were assumed to be the specific structure as shown in Figure S3D and S3E. By measuring the concavity of the NCs (the angel (θ) as shown in Figure S3B and S3C) and calculating the volume change of the deposition atoms (volume changes of tetrahedrons from the products of 6 h and 12 h), we can calculate the average diffusion rate of Pt atoms. First, the volume of the yellow tetrahedron (V_1) could be obtained by the following equation:

$$V_1 = \frac{1}{3} \times \frac{1}{2} \times \frac{\sqrt{2}L}{2} \times \sqrt{3} \times \frac{\sqrt{2}L}{4} \times h_1 = \frac{1}{3} \times \frac{1}{2} \times \frac{\sqrt{2}L}{2} \times \sqrt{3} \times \frac{\sqrt{2}L}{4} \times C \times \tan 36^\circ = \frac{\sqrt{2} \times L^3}{48} \times \tan 36^\circ$$

L is the average length for the Pd@PtNi nanocrystals. By measuring the angel of concavity (as shown in Figure S3 and Figure S4), we cauculated the volume of the bule tetrahedron (V_2):

$$V_2 = \frac{\sqrt{2} \times L^3}{48} \times \tan(36^\circ + \theta)$$

The volume change (ΔV) between V_1 and V_2 was caused by the diffusion of Pt atoms on the surface. Therefore, the different volume between $\Delta V_{6\,h}$ and $\Delta V_{12\,h}$ could be assumed as the amount of the diffused Pt atoms to the surface or edge sites. The diffusion rate could be derived from this equation:

$$V_{diffusion} = \frac{(\Delta V_{6\,h} - \Delta V_{12\,h}) \times \rho_{Pt} \times N_A}{M_{Pt} \times t} \times 8$$

In the equation, ρ_{Pt} is the density of Pt; N_A is the Avogadro's constant; M_{Pt} is the unit molar mass of Pt. The diffusion rate was calculated to be 2.88 Pt atoms per second.

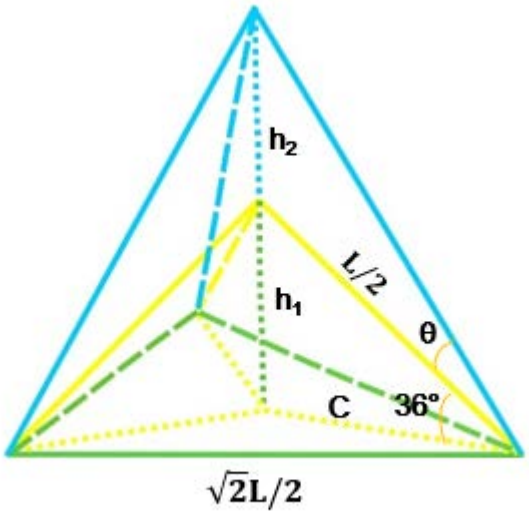

Figure S4. Perspective model of the tetrahedron structures on one corner of the concave Pd@PtNi NC in Figure S3D.

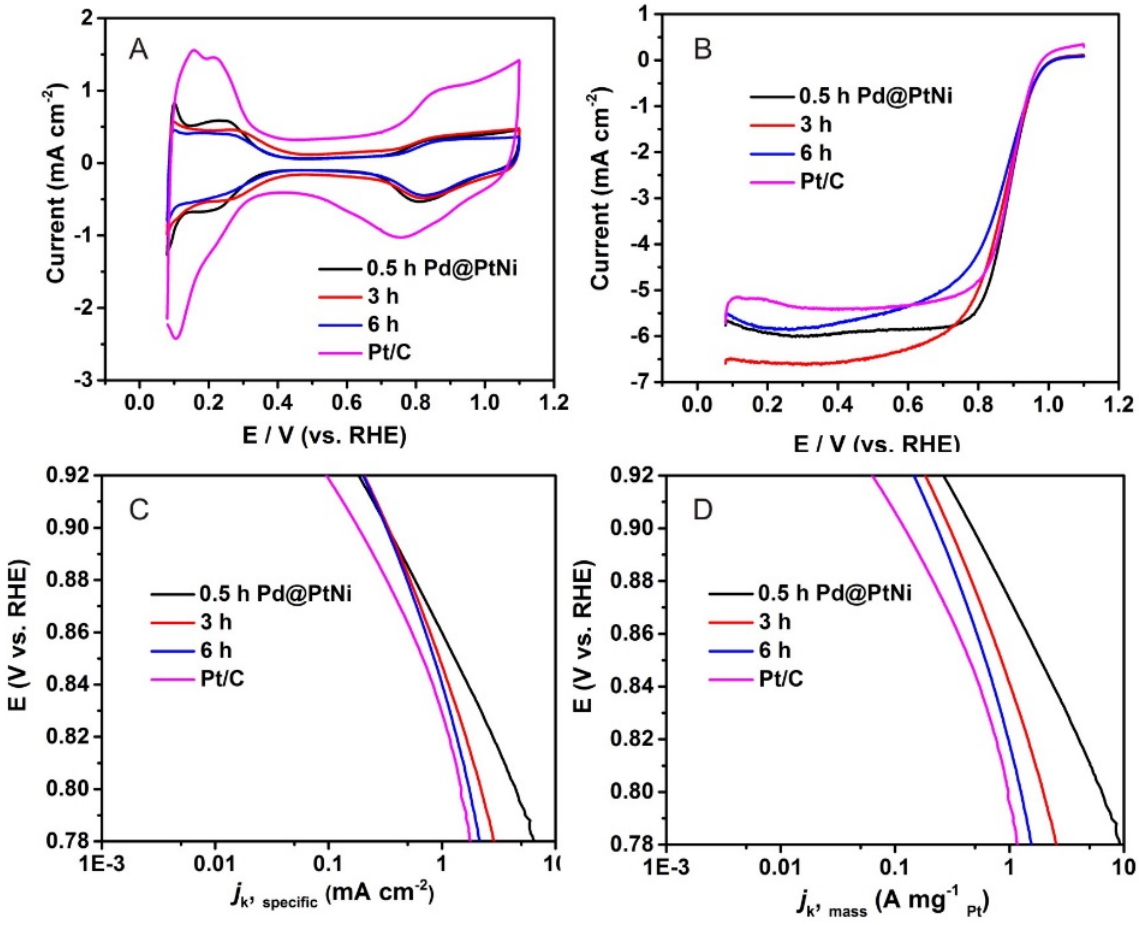

Figure S5. (A) Cyclic voltammograms curves for catalysts at room temperature in a N_2-purged 0.1 M $HClO_4$ solution with a sweep rate of 50 mV/s. (B) ORR polarization curves for the catalysts at room temperature in an O_2-purged 0.1 M $HClO_4$ solution with a sweep rate of 10 mV/s. The currents were all normalized to the geometric area (0.196 cm^2) of the rotating disk electrode. (C) Specific and (D) Pt mass ORR activities given as kinetic current densities (j_k) normalized to ECSA and Pt mass of the catalysts, respectively. The ECSA derived from the charges responsible for the H_{upd} desorption between 0.08 and 0.48 V.

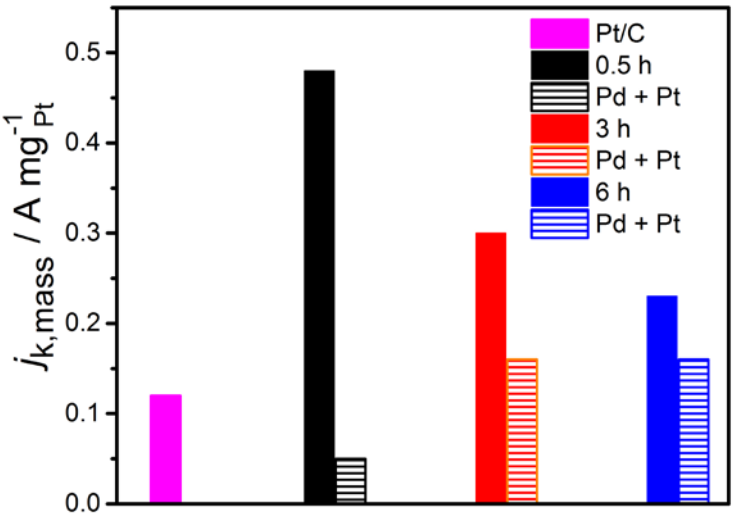

Figure S6. Mass activities given as kinetic current densities (j_k) normalized to the mass of Pt and Pd+Pt.

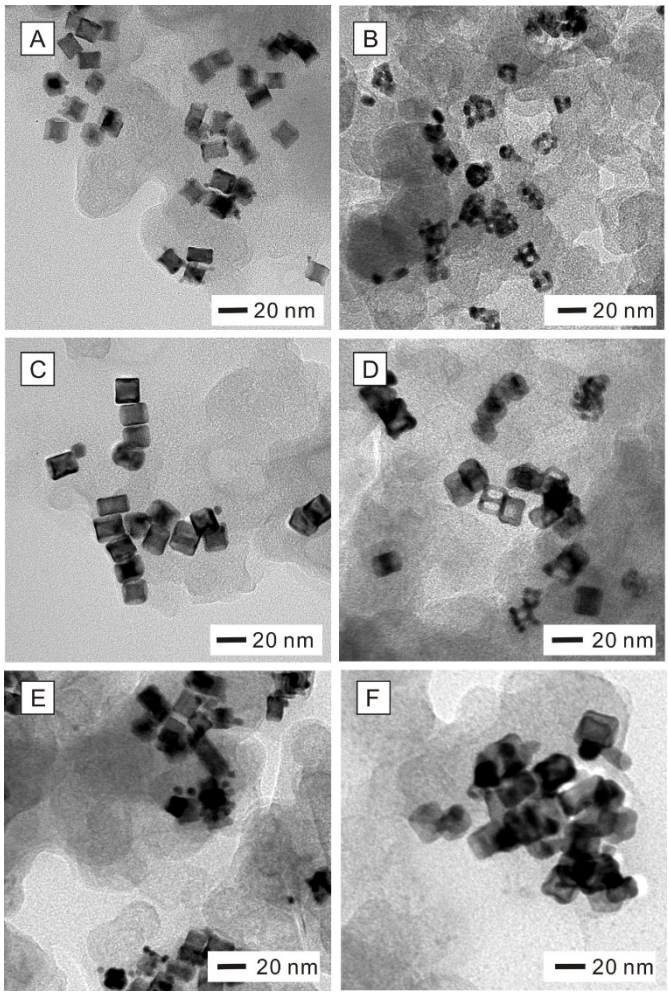

Figure S7. Comparison of the concave Pd@PtNi core-shell nanocubes before and after the durability test. (A, C, E) TEM images of catalysts before durability test. (B, D, F) TEM images of catalysts after test. The Pd@PtNi catalysts were obtained by a standard procedure with the reaction time of (A, B) 0.5 h. (C, D) 3 h and (E, F) 6 h, respectively.

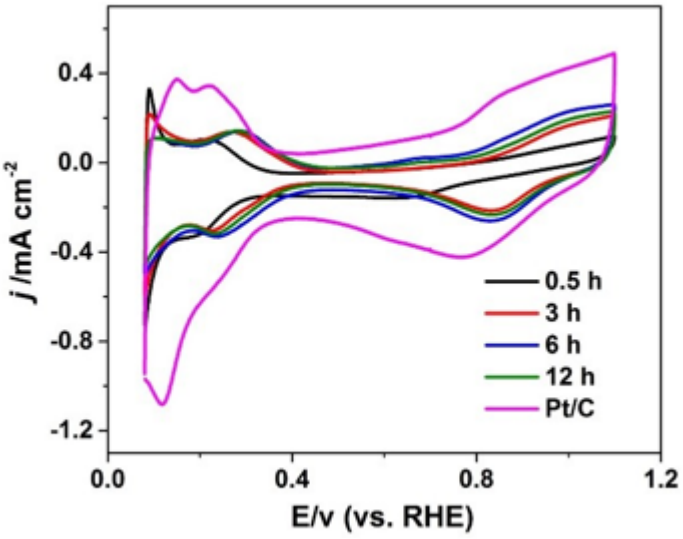

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Figure S8. Cyclic voltammograms curves for a series of Pd@PtNi NCs obtained using the standard procedure at different reaction times, together with that of commercial Pt/C. All the curves are recorded at room temperature in a N_2-purged 0.1 M $HClO_4$ solution with a sweep rate of 50 mV/s. The current densities were normalized to the geometric area of the RDE (0.196 cm^2).

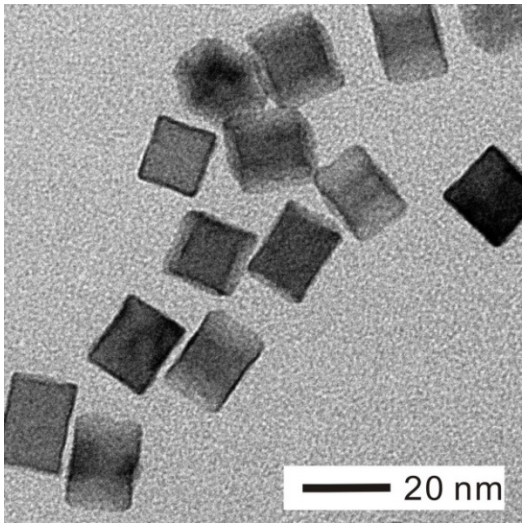

Figure S9. TEM images showing the concave Pd@Pt nanocubes, which obtained at 0.5 h when only Pt precursor was introduced.

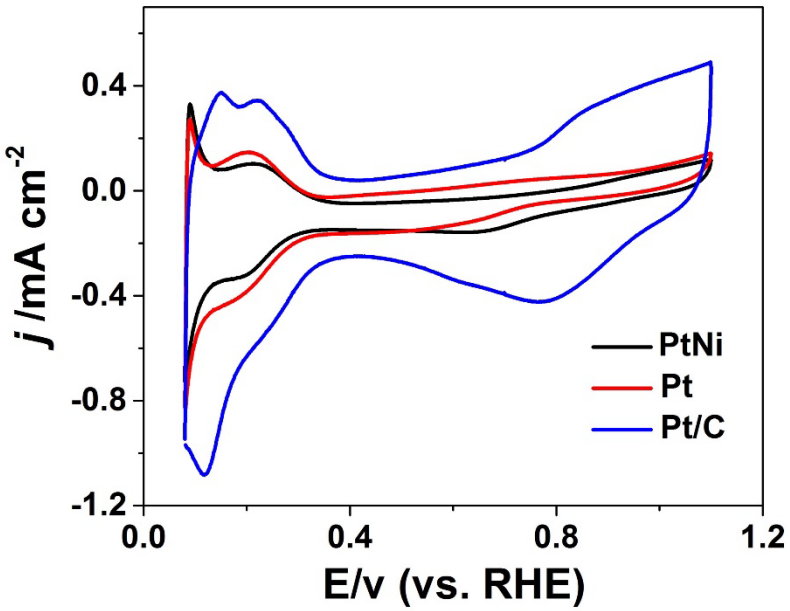

Figure S10. Cyclic voltammograms of the Pd@Pt NCs, Pd@PtNi NCs and Pt/C catalysts. All curves are recorded at room temperature in a N_2-purged 0.1 M $HClO_4$ solution with a sweep rate of 50 mV/s.

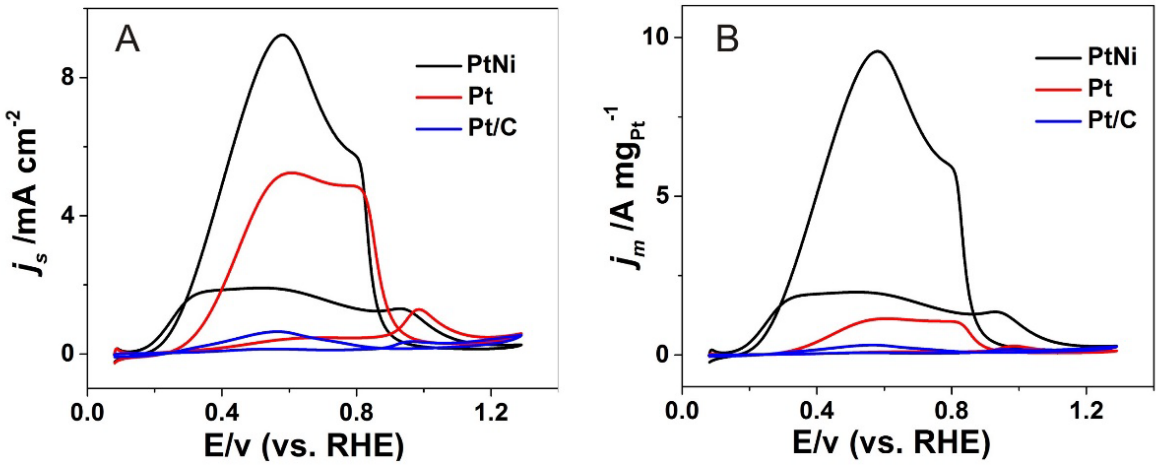

Figure S11. Formic acid electro-oxidation properties of Pd@Pt NCs, Pd@PtNi NCs and Pt/C catalysts. Curves are recorded at room temperature in a solution containing 0.1 M $HClO_4$ and 0.25 M HCOOH at a sweeping rate of 50 mV s^{-1} and normalized to the corresponding (A) ECSA and (B) loading amount of Pt, respectively.