Supporting Information for

## Controlled Synthesis of High Metal Loading Pt based Electrocatalysts with Enhanced Activity and Durability toward Oxygen Reduction Reaction

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Figure S1. UV-visible spectrum of 20 mM Pt(II) in aqueous phase before (black) and after 1h of phase transfer process (red line). Insets: Respective photos of the reaction system before (left) and after (right) phase transfer process.



Figure S2. TG diagram of obtained Pt/C electrocatalyst at different metal loadings. The weight loss below 100 °C is due to the release of adsorbed water molecules, and the weight loss in the range of 100-400 °C may come from Pt-catalyzed slow pyrolysis of carbon species, and the sharp weight loss beginning at 400 °C corresponds to the burning of carbon black.



Figure S3. XRD pattern of synthesized Pt/C at varied metal loading: 18.6% (black), 38.1% (red), 59.9% (blue)



Figure S4. XRD pattern of commercial Pt/C at varied metal loading: 20% (black), 40% (red), 60% (blue)



Figure S5. UV-visible spectra and photographs of  $K_2PdCl_4$  (20 mM) (a), NaAuCl\_4 (20 mM) (b),  $K_3FeCl_6$  (19 mM) (c), and  $K_2CoCl_4$  (9 mM) (d) in chloroform before (red) and after (black) phase transfer process.



Figure S6. TEM image (a) and EDX spectrum (b) of PtPd/C electrocatalyst synthesized by using metallic ions-containing reversed micelles. (Inset: elemental analysis based on the EDX spectrum.)



Figure S7. Initial 10 consecutive CV curves for 59.9 wt% Pt/C (red) and commercial 60 wt% Pt/C (black) in N<sub>2</sub>-purged HClO<sub>4</sub> (0.1 M) aqueous solution at 25 °C (0-1.2 V vs RHE, sweep rate 100 mVS<sup>-1</sup>). Reaction conditions: 13 mg EC-600, 10 mL of 20 mM Pt(II) and 10 mL of 40 mM CTAB in chloroform; 10 mL of 300 mM NaBH<sub>4</sub> in water; 90 mL of water; stirring at 1600 rpm.



Figure S8. CV curves for 59.9 wt% Pt/C (a) and commercial 60 wt% Pt/C (c), and ORR polarization curves for 59.9 wt% Pt/C (b) and commercial 60 wt% Pt/C (d) (0.6-1.2 V vs. RHE, 100 mVs<sup>-1</sup>, 0.1 M  $O_2$ -purged HClO<sub>4</sub>). Reaction conditions: 13 mg EC-600, 10 mL of 20 mM Pt(II) and 10 mL of 40 mM CTAB in chloroform; 10 mL of 300 mM NaBH<sub>4</sub> in water; 90 mL of water; stirring at 1600 rpm.



Figure S9 MA value of 18.6 wt% Pt/C (a) and 38.1 wt% Pt/C (b) recorded during the process of potential cycling (0.6-1.2 V vs. RHE, 100 mVs<sup>-1</sup>, 0.1 M O<sub>2</sub>-purged HClO<sub>4</sub>). Reaction conditions: 117 mg (18.6 wt%) and 39 mg (38.1 wt%) VXC-72, 10 mL of 20 mM Pt(II) and 10 mL of 40 mM CTAB in chloroform; 10 mL of 300 mM NaBH<sub>4</sub> in water; 90 mL of water; stirring at 1600 rpm.