Supporting Information

Kinetically Controlled Synthesis of Au-Pt Bi-metallic Aerogels and Their Enhanced Electroanalytic Performances

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EXPERIMENT

**Chemical and Materials.** Sodium borohydride (NaBH₄), Chloroplatinic acid (H₂PtCl₆), were all purchased from Sigma-Aldrich Co. Ltd. Hydrogen tetrachloroaurate(III) hydrate was purchased from STREM Co. Ltd. The water in all experiments was prepared in a three-stage Millipore Milli-Q plus 185 purification system and had a resistivity higher than 18.2 MΩ cm.

**Synthesis of AuPtₓ and Pt metallic hydrogels.** In a typical synthesis of AuPt₅ metallic hydrogels, 0.1 mmol NaBH₄ aqueous solution was rapidly injected to a vial that containing of 33 mL H₂O, 16.7 μmol H₂PtCl₆ and 3.3 μmol HAuCl₄ under stirring at 60 °C for 1 mins. Followed by keeping the vials at 60 °C for 4 hrs without stirring. After washed with water for three times, AuPt₅ metallic aerogels could be obtained from supercritical fluid CO₂ drying technique. AuPtₓ (x=1,3,7) and Pt metallic hydrogels were all obtained via the same method only except changing the feeding ratio of Au and Pt precursors. AuPt₅-DA metallic hydrogels were also obtained with the same method except addition of 2.5 mg DA after rapid injection of NaBH₄ aqueous solution and kept the mixture still.

**Preparation and electrochemical measurements of electrode.** The homogeneous Pt/C catalyst ink (1 mgPt/mL) was prepared via dispersing commercial Pt/C powders into deionized water via ultrasonic agitation.

The electrochemical measurements were conducted on a standard three-electrode electrochemical workstation (CHI 630E) at room temperature. A Pt wire was used as the counter electrode and a Hg/HgCl₂ electrode filled with saturated potassium chloride aqueous solution was reference electrode. The working electrode was prepared by loading 5 μL AuPtₓ metallic hydrogels (1 mgPt/mL) on a glass carbon electrode (GCE) and dried at 60 °C, followed by dropping
5 μL Nafion (0.05%) and dried at 60 °C.

CV measurements with scan rate of 50 mV/s were performed after purging nitrogen into 1 M H₂SO₄ solution without and within 1 M methanol for 30 min. CA measurements were performed in 1 M H₂SO₄ solution within 1 M methanol at 0.55 V.

**Characterization.** Transmission electron microscopy (TEM) images were obtained by Philips CM200 UT (Field Emission Instruments (FEI), USA). FEI sirion field emission scanning electron microscope (FESEM) was used for imaging and energy-dispersive X-ray analysis (EDX). The tube was operated at 40 KV accelerating voltage and 15 mA current. X-ray Diffraction (XRD) characterization was carried out by Rigaku Miniflex 600. X-ray photoelectron spectroscopy (XPS) measurements were performed with a Physical Electronics Quantera Scanning X-ray Microprobe. Supercritical CO₂ drying was conducted using Samdri-PVT-3D instrument (Tousimis research corporation, USA).
Supporting Figures

**Figure S1.** XPS of the Pt 4f and Au 4f of AuPt₅ and Pt metallic aerogels (A) and AuPt₅ metallic aerogels (B) synthesized without any capping agents at 60 °C.

**Figure S2.** TEM images and digital pictures of the as-synthesized Au nanoparticles (A) and Au hydrogels (B).
Figure S3. TEM images of AuPt5-25-DA metallic hydrogels obtained 0.5 min (A), 1 min (B), 5 min (C) and 10 min (D) after addition of NaBH4 and DA.

Figure S4. TEM image and size distribution (inset) of AuPt5 metallic aerogels after CA test.

Figure S5. CV curves (A) and CA curves (B) of GCE modified by AuPt5 and AuPt5-25-DA metallic aerogels measured in 1.0 M H2SO4 solution in the presence of 1.0 M methanol. The scan rate of CV curves are 50 mV/s. CA curves are recorded at 0.55 V.
Figure S6. TEM and digital pictures of as-obtained Pt$_3$Co (A) and Pt$_3$Pb (B) metallic hydrogels.

Table S1. Detailed comparison of self-supported AuPt aerogel with state-of-the-art Pt-based electrocatalysts toward methanol oxidation in acid solutions.

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<td>No carbon supported Pt-based electrocatalysts</td>
<td>Core-shell Au-Pt nanodendrites</td>
<td>35.2 m$^2$/g</td>
<td>0.45 A/mg</td>
<td>0.4 V vs. Ag/AgCl</td>
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<td>Pd@Pt nanocrystals</td>
<td>N/A</td>
<td>0.330 A/mg</td>
<td>0.25 V vs. Ag/AgCl</td>
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<td>Porous PdNi@Pt nanostructures</td>
<td>32.5 m$^2$/g</td>
<td>0.965 A/mg</td>
<td>0.2 V vs. SCE</td>
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<td>Pt-on-Pd nanodendrites</td>
<td>48 m$^2$/g</td>
<td>0.490 A/mg</td>
<td>0.3 V vs. Ag/AgCl</td>
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<td>Mesoporous Pt nanowires</td>
<td>40.5 m$^2$/g</td>
<td>0.398 A/mg</td>
<td>0.55 V vs. NHE</td>
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<td>Dendritic Au@Pt nanoparticles</td>
<td>N/A</td>
<td>0.204 A/mg</td>
<td>0.20 V vs. SCE</td>
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<td>AuPt aerogel</td>
<td>53.9 m$^2$/g</td>
<td>0.510 A/mg</td>
<td>0.2 V vs. SCE</td>
<td>This work</td>
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<td>Carbon Supported electrocatalysts</td>
<td>3D graphene supported PtNi</td>
<td>87.4 m$^2$/g</td>
<td>0.882 A/mg</td>
<td>0.5 V vs. SCE</td>
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<td>PMo/PtRu/MWCNT</td>
<td>103.8 m$^2$/g</td>
<td>0.263 A/mg</td>
<td>0.17 V vs. Ag/AgCl</td>
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<td>PtRu NPs/SNE-CNTs</td>
<td>86.9 m$^2$/g</td>
<td>0.372 A/mg</td>
<td>0.21 V vs. SCE</td>
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<td>Graphene supported AuPt Nanodendrites</td>
<td>100.8 m$^2$/g</td>
<td>0.365 A/mg</td>
<td>0.15 V vs. SCE</td>
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<td>Commercial Pt/C (20% loading)</td>
<td>40.1 m$^2$/g</td>
<td>0.220 A/mg</td>
<td>0.25 V vs. SCE</td>
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References: