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Supporting Information

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

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EXPERIMENT

Chemical and Materials. Sodium borohydride ($NaBH_4$), Chloroplatinic acid (H_2PtCl_6), 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 $AuPt_x$ and Pt metallic hydrogels. In a typical synthesis of $AuPt_5$ metallic hydrogels, 0.1 mmol $NaBH_4$ aqueous solution was rapidly injected to a vial that containing of 33 mL H_2O, 16.7 μmol H_2PtCl_6 and 3.3 μmol $HAuCl_4$ 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, $AuPt_5$ metallic aerogels could be obtained from supercritical fluid CO_2 drying technique. $AuPt_x$ (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. $AuPt_5$-DA metallic hydrogels were also obtained with the same method except addition of 2.5 mg DA after rapid injection of $NaBH_4$ aqueous solution and kept the mixture still.

Preparation and electrochemical measurements of electrode. The homogeneous Pt/C catalyst ink (1 mg_{Pt}/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 $Hg/HgCl_2$ electrode filled with saturated potassium chloride aqueous solution was reference electrode. The working electrode was prepared by loading 5 μL $AuPt_x$ metallic hydrogels (1 mg_{Pt}/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 H_2SO_4 solution without and within 1 M methanol for 30 min. CA measurements were performed in 1 M H_2SO_4 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 CO_2 drying was conducted using Samdri-PVT-3D instrument (Tousimis research corporation, USA).

Supporting Figures

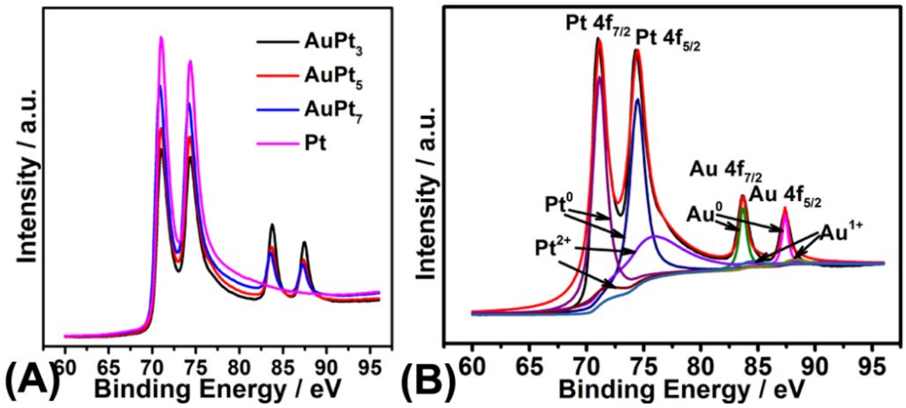

Figure S1. XPS of the Pt 4f and Au 4f of $AuPt_x$ and Pt metallic aerogels (A) and $AuPt_5$ metallic aerogels (B) synthesized without any capping agents at 60 °C.

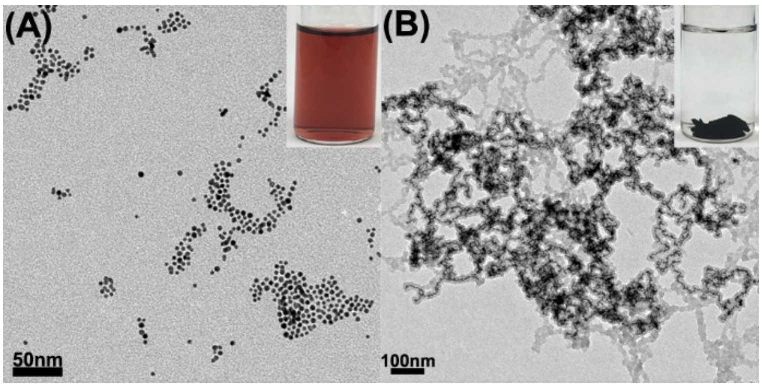

Figure S2. TEM images and digital pictures of the as-synthesized Au nanoparticles (A) and Au hydrogels (B).

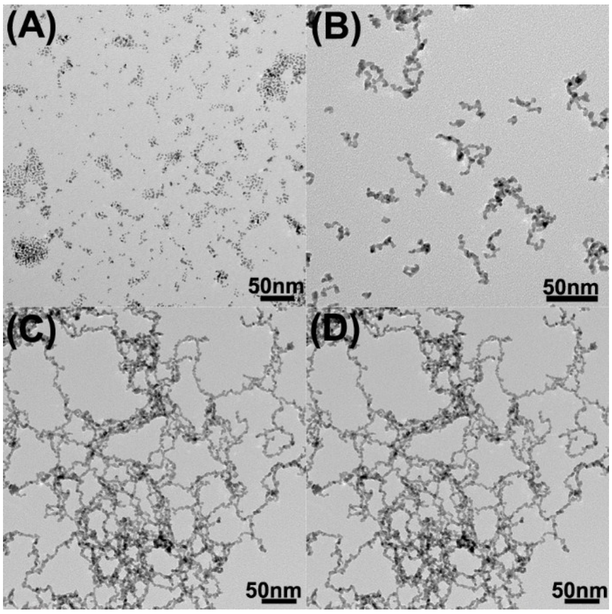

Figure S3. TEM images of AuPt$_5$-25-DA metallic hydrogels obtained 0.5 min (A), 1 min (B), 5 min (C) and 10 min (D) after addition of NaBH$_4$ and DA.

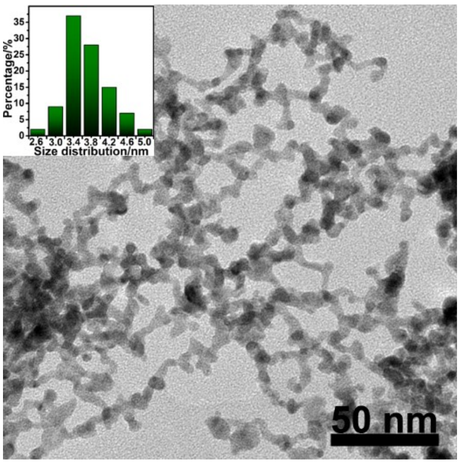

Figure S4. TEM image and size distribution (inset) of AuPt$_5$ metallic aerogels after CA test.

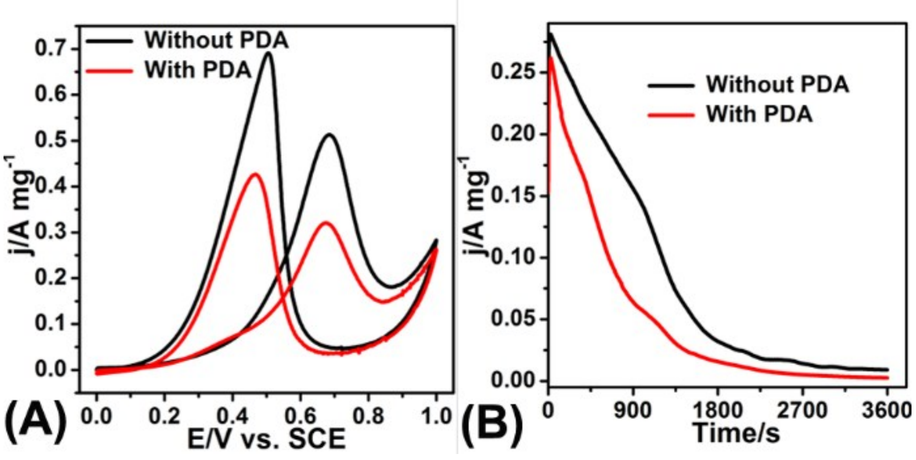

Figure S5. CV curves (A) and CA curves (B) of GCE modified by AuPt$_5$ and AuPt$_5$-25-DA metallic aerogels measured in 1.0 M H_2SO_4 solution in the presence of 1.0 M methanol. The scan rate of CV curves are 50 mV/s. CA curves are recorded at 0.55 V.

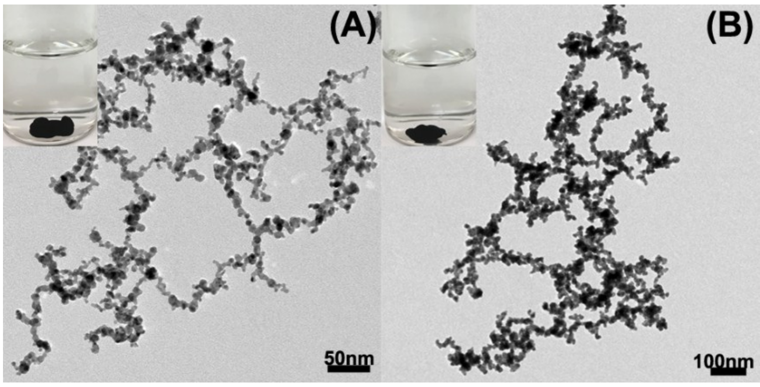

Figure S6. TEM and digital pictures of as-obtained Pt_3Co (A) and Pt_3Pb (B) metallic hydrogels.

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

	Materials	ECSA	Mass Activity	On-set Potential	Ref.
No carbon supported Pt-based electrocatalysts	Core-shell Au-Pt nanodendrites	35.2 m^2/g	0.45 A/mg	0.4 V vs. Ag.AgCl	1
	Pd@Pt nanocrystals	N/A	0.330 A/mg	0.25 V vs. Ag.AgCl	2
	Porous PdNi@Pt nanostructures	32.5 m^2/g	0.965 A/mg	0.2 V vs. SCE	3
	Pt-on-Pd nanodendrites	48 m^2/g	0.490 A/mg	0.3 V vs. Ag/AgCl	4
	Mesoporous Pt nanowires	40.5 m^2/g	0.398 A/mg	0.55 V vs. NHE	5
	Dendritic Au@Pt nanoparticles	N/A	0.204 A/mg	0.20 V vs. SCE	6
	AuPt aerogel	53.9 m^2/g	0.510 A/mg	0.2 V vs. SCE	This work
Carbon Supported electrocatalysts	3D graphene supported PtNi	87.4 m^2/g	0.882 A/mg	0.5 V vs. SCE	7
	PMo/PtRu/MWCNT	103.8 m^2/g	0.263 A/mg	0.17 V vs. Ag/AgCl	8
	PtRu NPs/SNE-CNTs	86.9 m^2/g	0.372 A/mg	0.21 V vs. SCE	9
	Graphene supported AuPt Nanodendrites	100.8 m^2/g	0.365 A/mg	0.15 V vs. SCE	10
	Commercial Pt/C (20% loading)	40.1 m^2/g	0.220 A/mg	0.25 V vs. SCE	This work

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