Supporting Information

Highly active and durable platinum-lead bimetallic alloy nanoflowers for formic

acid electrooxidation

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Experimental section

Reagents and Chemicals

Potassium tetrachloroplatinate(II) (K_2PtCl_4), lead nitrate ($Pb(NO_3)_2$), formic acid (HCOOH), sulfuric acid (H_2SO_4) and formaldehyde (HCHO) solution (40%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Polyallylamine hydrochloride (PAH, Scheme S1, M_w=15 0000) was supplied from Nitto Boseki Co., Ltd. Commercial Pt black was purchased from Johnson Matthey Corporation. All the aqueous solutions were prepared with deionized water.

Preparation of $Pt_{84}Pb_{16}BANFs$

In a typical procedure, 2 mL of 0.5 M PAH, 1.7 mL of 0.05 M K_2PtCl_4, and 3.4 mL of 0.05 M $Pb(NO_3)_2$ aqueous solutions were added into the 3 mL H_2O. After adjusting solution pH to 4.0, 2.0 mL of HCHO solution (40%) was added into themixturesolution. Then, the mixturesolution was heated at 120 ^{o}C for 6 h. After being cooled to room temperature, the obtained $Pt_{84}Pb_{16}BANFs$ were separated by centrifugation, washed with water acetic acid for 12 h, and dried at 60 ^{o}C for 5 h in a vacuum dryer.

Apparatus

X-ray diffraction (XRD) patterns of samples were obtained from Model D/max-rC X-ray diffractometer (Cu Ka radiation source, λ=1.5406 Å, operating at 40 kV and 100 mA). The X-ray (EDX) analysis of samples were carried on a JEOL JSM-7600F SEM instrument. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo VG Scientific ESCALAB 250 spectrometer. The binding energy was calibrated by means of the C 1s peak energy of 284.6 eV. Transmission electron microscopy (TEM), high-resolution TEM (HRTEM), selected area diffraction (SAED), high-angle annular dark-field scanning TEM and EDX mapping imageswere performed on a JEOL JEM-2100 instrument operated at 200 kV.

Electrochemical measurements

Cyclic voltammetry and chronoamperommetry experiments were performed on a CHI 660D electrochemical work station (CH Instruments, Shanghai, Chenghua Co.) at 30 ± 1 °C using conventional three-electrode system. A saturated calomel electrode as the reference electrode, a pure platinum wire as thecounter electrode, and the sample modified glassy carbon (3 mm diameter) electrode as the working electrode.

For the preparation of the working electrodes, 5.0 mg of catalyst was dispersed into 5.0 mL of water to form a homogeneous suspension by ultrasonication for 1 h. Then 4 μL dispersion was covered onto the surface of the glassy carbon electrode. After the drying naturally, 2.0μL of 5.0 wt% Nafion solution was spread on the surface of the catalyst layer. The Pt metal loading on the electrode surface was about 3.2μg. The electrochemically active surface areas (ECSA) of Pt electrocatalysts were calculated from the following equation by measuring the charge collected in the hydrogen adsorption/desorption region after double-layer correction and assuming a value of 210 μC cm^{-2} for the adsorption of a hydrogen monolayer. [1, 2]

$$ECSA = \frac{Q}{m \times C} \qquad (1)$$

Where Q was the charge collected in the hydrogen adsorption/desorption region after double-layer correction,m was the loading amount of Pt metal, C was the charge required for monolayer adsorption of hydrogen on a Pt surface.
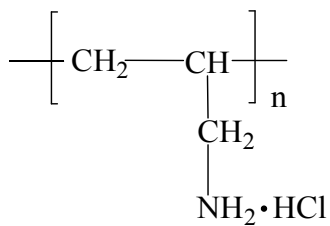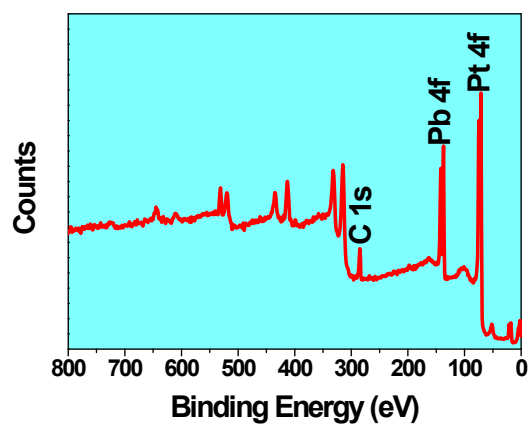
Scheme S1. The molecularstructure of PAH.

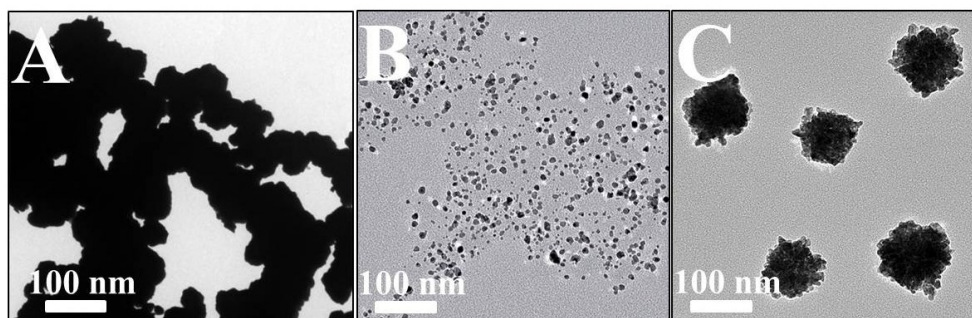**Fig. S1.** XPS spectrum of $Pt_{84}Pb_{16}$ BANFs.

Fig. S2. TEM images of the synthesized products with (A) 0.0 mL, (B) 0.2 mL, and (C) 4.0 mL of 0.5 M PAH.

Fig. S3. Photographs of (a) single-component $Pb(NO_3)_2$ solution at pH 4.0 and (b) white precipitate obtained by adjusting pH value of single-component $Pb(NO_3)_2$ solution to 6.0. (c) Photographs of $PAH/Pb(NO_3)_2$ mixture solution at pH 6.0.

After adjusting pH value of single-component $Pb(NO_3)_2$ solution (Fig. S3a) to 6.0, a lot of white precipitates generate immediately (Fig. S3b). In contrast, no precipitate is observed after adjusting pH value of $PAH/Pb(NO_3)_2$ mixture solution to 6.0 (Fig. S3c). These above experimental phenomena confirm that PAH can interact with $Pb(NO_3)_2$ to generate colorless PAH–Pb^{II} complex via coordination interaction.

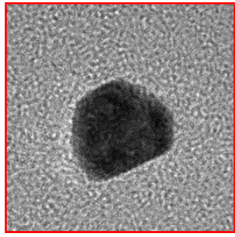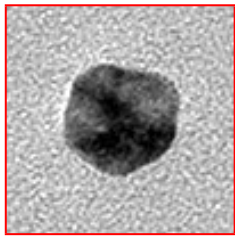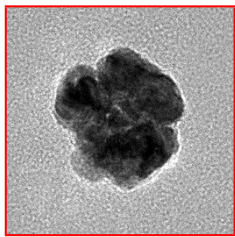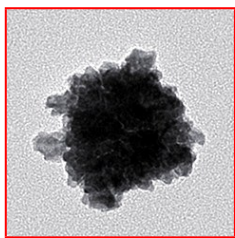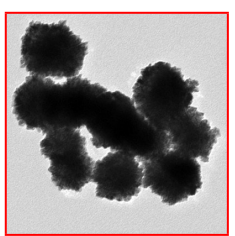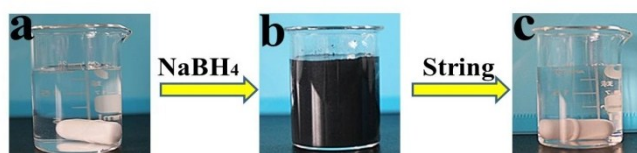**Fig. S4.** (a) Photograph of $PAH/Pb(NO_3)_2$ mixture solution at pH=4.0. (b) Photograph of the black Pb nanocrystals prepared by $NaBH_4$ reduction. (c) Photograph of black Pb nanocrystals solution after the continuous string for 2 h in air.

Table S1. The preparation condition, chemical composition, and morphology of various PtPb alloy nanocrystals in Fig. 4

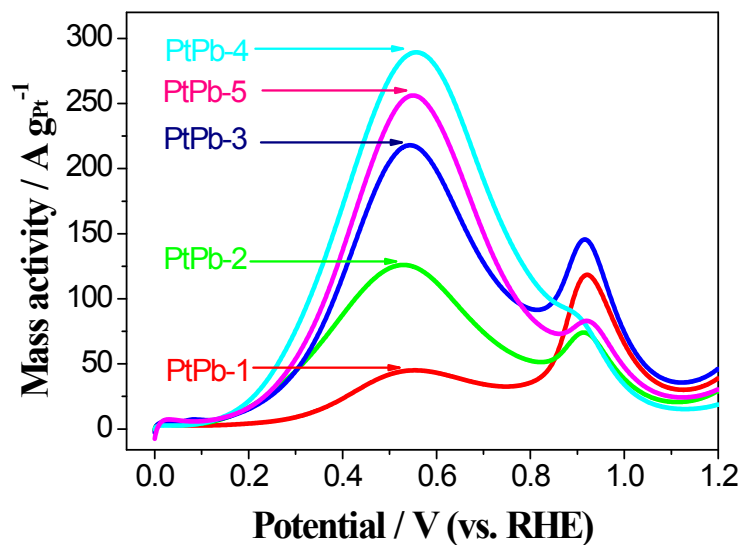| Sample	Pt^{II}/Pb^{II} feeding ratio	Pt/Pb atomic ratio measured by EDX	Pt/Pb atomic ratio measured by XPS	Morphology
PtPb-1	4:1	88.2:11.8	82:18	
PtPb-2	2:1	87.6:12.4	79:21	
PtPb-3	1:1	86.6:13.4	75:25	
PtPb-4 (i.e., Pt$_{84}$Pb$_{16}$ BANFs)	1:2	83.8:16.2	73:27	
PtPb-5	1:4	83.1:16.9	70:30	

Fig. S5. Pt mass-normalized cyclic voltammograms of various PtPb alloy nanocrystals in Tables S1 in the N_2-saturated 0.5 M HCOOH + 0.5 M H_2SO_4 solution at the scan rate of 50 mV s^{-1}.
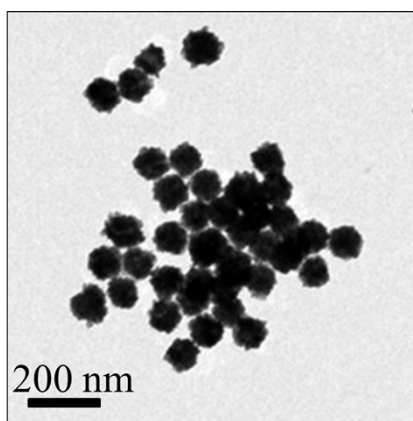

Fig. S6. TEM image of $Pt_{84}Pb_{16}$ BANFs after chronoamperometry run.

1.   B. Lim, M. Jiang, P. H. C. Camargo, E. C. Cho, J. Tao, X. Lu, Y. Zhu and Y. Xia, *Science*, 2009, **324**, 1302-1305.
2.   R. Kou, Y. Shao, D. Mei, Z. Nie, D. Wang, C. Wang, V. V. Viswanathan, S. Park, I. A. Aksay and Y. Lin, *J Am Chem Soc*, 2011, **138**, 2541-2547.