Supporting Information Available

Water-based synthesis and sensing application of polyallylamine

functionalized platinum nanodendrite assemblies

Xiaoyu Qiu,[‡] Gengtao Fu,[‡] Yue Zhao, Yawen Tang, Yu Chen,* and Tianhong Lu

Jiangsu Key Laboratory of New Power Batteries, Jiangsu Collaborative Innovation Center of Biomedical Functional Materials, College of Chemistry and Materials Science, Nanjing Normal University, Nanjing 210023, PR China.

‡Equal contribution to this work.

*Corresponding author. Tel: +86-25-85891651; fax: +86-25-83243286.

E-mail: ndchenyu@gmail.com (Y. Chen)

Experimental section

Reagents and chemicals

PAH (Scheme 1, weight-average molecular weight 15 0000) was supplied from Nitto Boseki Co., Ltd. (Tokyo, Japan). Potassium hexachloroplatinum(II) (K₂PtCl₄), hydrazine hydrate (N₂H₄·H₂O, 85%) and Sodium nitrite (NaNO₂) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Glassy carbon (GC) electrode (3 mm diameter) was purchased from Shanghai Chenghua Co (Shanghai, China). Other reagents were of analytical reagent grade and used without further purification. The solution pH was adjusted by the addition of H₃PO₄ solution. All the aqueous solutions were prepared with Millipore water having a resistivity of 18.2 MΩ.

Preparation of the Pt-NDAs

In a typical synthesis, 1.0 mL of 0.05 M K₂PtCl₄ aqueous solutions and 1.0 mL of 0.50 M PAH (molarity of PAH given with respect to the repeating unit) were added to 8 mL water with continued stirring. After adjusting solution pH to 1.0 by H_3PO_4 solution, 0.1 mL of N₂H₄·H₂O (85%) was rapidly added to the mixture solution and mechanically stirred for 15 min at 35 °C. After reaction, the obtained black Pt-NDAs were separated by centrifugation at 15000 rpm for 10 min, washed several times with water, and then dried at 60 °C for 5 h in a vacuum dryer. Finally, the Pt-NDAs were treated with UV/Ozone (wavelength at 185 and 254 nm in air for 4 h) to remove the most PAH capping agent (noting: PAH could not be completely removed due to the excellent chemical stability of PAH, which was confirmed by FT-IR and XPS in our pervious works¹⁻³).

Instruments

Transmission electron microscopy (TEM) measurements were made on a JEOL 2000 transmission electron microscopy operated at an accelerating voltage of 200 kV. Scanning transmission electron microscopy (STEM) and elemental maps were carried out under the high-angle annular bright field mode. Scanning electron microscopy

(SEM) images were taken on a JSM-2010 microscopy at an accelerating voltage of 20 kV. Energy dispersive X-ray (EDX) analysis of particles was carried out on a JEOL JSM-7600F SEM or JEOL 2000 TEM. X–ray diffraction (XRD) patterns were obtained with Model D/max–rC X–ray diffractometer using Cu K_a radiation source (λ = 1.5406 Å) and operating at 40 kV and 100 mA. X–ray photoelectron spectroscopy (XPS) measurements were performed with a Thermo VG Scientific ESCALAB 250 spectrometer with a monochromatic Al Ka X–ray source (1486.6 eV photons), and the vacuum in the analysis chamber was maintained at about 10⁻⁹ mbar. The binding energy was calibrated by means of the C 1s peak energy of 284.6 eV. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 520 SXFTIR spectrometer.

Self-assembly of the Pt-NDAs on GC electrode

The GC electrode was polished first with emery paper and then with aqueous slurries of fine alumina powders (0.3 and 0.05 mm) on a polishing cloth, and was finally cleaned with ethanol and Milli-Q water under an ultrasonic bath, each for 5 min. The Pt-NDAs/GC electrode was obtained by immersing the glassy carbon (GC) electrode into the aqueous solution of Pt-NDAs (0.1 mg mL⁻¹) for 12 h.

Electrochemical measurements

All electrochemical experiments were carried out on a CHI 660 C electrochemical workstation (CH Instruments, Shanghai, Chenghua Co.). A standard three-electrode system was used for all electrochemical experiments assembled with a platinum wire as the auxiliary electrode, a saturated calomel electrode (SCE) as the reference electrode, and a bare or modified GC electrode as the working electrode. All potentials in this study were reported with respect to the SCE. Prior to the electrochemical measurements, N₂ was bubbled through the solution for 10 min to remove dissolved O₂. During experiments, a continuous N₂ flow was maintained over the solution. All of the electrochemical measurements were carried out at 30 ± 1 °C.



Fig. S1 EDX spectrum of the Pt-NDAs.



Fig. S2 XPS spectrum of the Pt-NDAs in the Pt4f region.



Fig. S3 XRD pattern of the Pt-NDAs.



Fig. S4 The photographs of color evolution of the reaction solution.



Fig. S5 TEM image of the products synthesized under the same condition as in Fig. 1, except the use of HCHO instead of N_2H_4 · H_2O and reaction temperature at 120 °C for 6 h.



Fig. S6 Cyclic voltammograms of the obtained Pt-NDAs in N₂-saturated 0.5 M H₂SO₄ solution at a scan rate of 50 mV s⁻¹. Electrode preparation: an evenly distributed suspension of the Pt-NDAs was prepared by ultrasonicating a mixture of 5 mg of Pt-NDAs and 2.5 mL of H₂O for 30 min. 6 μ L of the resulting suspension was laid on the surface of the pre-cleaned glassy carbon electrode (3 mm diameter). After drying at room temperature, 2.5 μ L of Nafion (5 wt.%) solution was covered on the Pt-NDAs modified electrode surface and allow to dry. The Pt metal loading on the electrode surface was about 12 μ g.

References

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