Electronic Supplementary Information

Carbon Riveted Pt/C Catalyst with High Stability Prepared by in-situ Carbonized Glucose

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1. Materials preparation

1. 1 Pt/C catalysts prepared by microwave-assisted process

Pt/C catalysts with the Pt loading of 20 wt.% were prepared by microwave-assisted polyol process in ethylene glycol (EG) solution with H_2PtCl_6 as a precursor salt[1]. Briefly, 80 mg Vulcan XC-72 carbon black was dispersed into 60 mL ethylene glycol and isopropyl alcohol (V/V = 4:1) in 100 mL beaker under ultrasonic treatment for 1 h to form uniform carbon ink, then 2.7 mL of 0.038373 mol/L H_2PtCl_6-EG solution with the subsequent mixing process for 3 h. The pH value of the ink was adjusted by adding 1 mol L^{-1} NaOH-EG solution drop by drop to 12.00. Then the beaker was placed in the center of a microwave oven (2450 MHz, 800W) and argon gas was feed into the ink for 15 min to remove oxygen for consecutive microwave heating 50 s to fix platinum nanoparticles on carbon support. The solution was allowed to cool down to room temperature by continuous stirring, and then 0.1 mol/L HNO_3 was added into the cooled mixture to adjust pH value of the solution to about 3 – 4. The mixture was kept stirring for 12 h and then the product was washed repeatedly with ultrapure water (Millipore, 18.25 MΩ·cm) until no Cl^- ions were detected. The homemade Pt/C catalyst was dried for 3 h at 80 °C and then stored in a vacuum vessel.

1.2 Preparation of carbon riveting Pt/XC-72 and annealed Pt/XC-72 catalysts

The carbon riveting process of the Pt/XC-72 catalyst was accomplished as follows. Firstly, 50 mg Pt/XC-72 and 8.26 mg $C_6H_{12}O_6 \cdot H_2O$ was dispersed into 10 mL H_2O (Millipore, 18.25 MΩ·cm) in 50 mL beaker under ultrasonic treatment for 1 hr to form uniform ink. The ink was first dried at 70 °C in a porcelain boat and then heated for 1 hr at 400 °C in the tube furnace under argon. The product was cooled to room temperature in argon and then stored under vacuum. For comparison, standard

Pt/XC-72 catalyst was subjected to the same heat treatment. This product is denoted as annealed Pt/XC-72.

1.3 Preparation of working electrode

The catalyst ink was prepared by ultrasonically dispersing 5.0 mg catalysts in 2.5 mL ethanol and the dispersion was then ultrasonicated for 20 min. The glassy carbon working electrode with 4 mm of diameter and 0.1256 cm^2 of electrode area was polished with 0.05 μm alumina suspensions to a mirror finish before each experiment and served as an underlying substrate of the working electrode. A quantity of 10 μL of the dispersion was pipetted out on the top of the GC and over which 5 μL of a dilute aqueous Nafion® solution (5 wt. % solution in a mixture of lower aliphatic alcohols and DuPont water) was applied. The resulting Nafion® film with a thickness less than 0.2 μm had the sufficient strength to keep carbon particles permanently on the glassy carbon electrode without producing significant film diffusion resistances[2].

2. Electrochemical measurements

Electrochemical measurements were carried out in a conventional sealed three-electrode electrochemical cell at 25 ^{o}C, with the glassy carbon disk electrode made in the above mentioned procedure as the working electrode and a piece of Pt foil (1 cm^2) as the counter electrode. The Hg/Hg_2SO_4 reference electrode was placed in a separate chamber, which is located near the working electrode chamber through a Luggin capillary tube. All solutions were prepared with ultrapure water (Millipore, 18.25 MΩ·cm). The solution of 0.5 mol/L H_2SO_4 was purged with ultrapure argon gas for nearly 30 min before starting the experiment. The cyclic voltammograms (CV) were recorded with CHI650D electrochemical analysis instrument controlled by an IBM PC within a potential range from -0.63 V to 0.52 V. In order to get rid of the possible effects caused by Nafion® film, the working electrode was treated by continuously cycling at 0.05 V/s until a stable response was obtained before the measurement curves were recorded. Fresh electrolyte solution was used for each electrochemical measurement to ensure reproducible results. All the potentials reported herein were with respect to the Hg/Hg_2SO_4.

The accelerated potential cycling test is a fast way to evaluate the stability of the catalyst. In this work, the stability of the catalyst was also considered by the accelerated potential cycling test which was conducted within the potential range of -0.08 – 0.52 V.

The electrochemical active specific surface area (ESA) of platinum can be calculated with coulombic charges accumulated during hydrogen adsorption and desorption after correcting for the double-layer charging current from the CVs:[3]

$$ESA = \frac{Q_H}{0.21 \times M_{Pt}} \quad (1)$$

Where Q_H (mC) is the charge due to the hydrogen adsorption/desorption in the hydrogen region of the CVs shown in Figure S5, 0.21 mC/cm^2 is the electrical charge associated with monolayer adsorption of hydrogen on Pt, and M_{Pt} is the loading of Pt on the working electrode.

3. Characterization of physical properties

3.1 Transmission electron micrograph (TEM)

TEM for the catalyst samples were taken by a Japan JEOL-2010 transmission electron microscope with a spatial resolution of 0.23 nm. Before taking the electron micrographs, the catalyst samples were finely ground and ultrasonically dispersed in isopropyl alcohol, and a drop of the resultant dispersion was deposited and dried on a standard copper grid coated with a polymer film. The applied voltage was 100 kV.

3.2 X-ray diffraction (XRD)

XRD analysis of nanomaterials was carried out with the D/max-rB diffractometer (made in Japan) using a Cu K*a* X-ray source operating at 45 kV and 100 mA, scanning at a rate of 4 °/min with an angular resolution of 0.05° of the 2θ scan to get the XRD pattern.

3.3 X-ray photoelectron spectrometry (XPS)

X-ray photoelectron spectroscopy (XPS) analysis was carried out to determine the surface properties of the catalysts with a Physical Electronics PHI model 5700 instrument. The Al X-ray source operated at 250 W. The sample to analyzer take-off angle was 45◦. Survey spectra were collected at pass energy (PE) of 187.85 eV over a binding energy range from 0 eV to 1300 eV. High binding energy resolution multiplex data for the individual elements were collected at a PE of 29.55 eV. The C 1s electron binding energy was referenced at 284.6 eV, and a nonlinear least-squares curve-fitting program was employed with a Gaussian-Lorentzian production function[4-5]. During all XPS experiments, the pressure inside the vacuum system was maintained at 1×10^{-9} Pa. Before analysis above, all the samples were dried under vacuum at 80 °C overnight.

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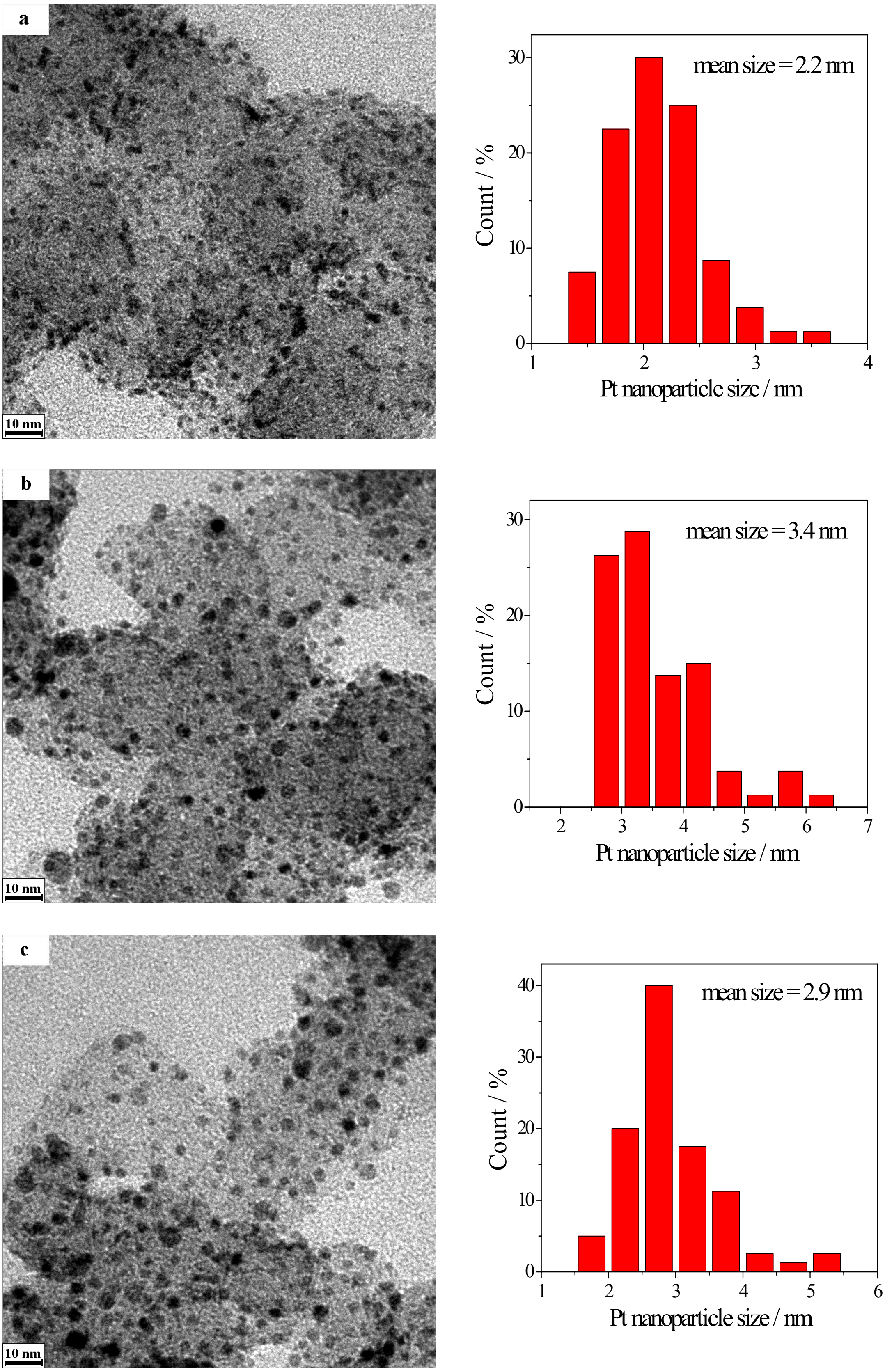

Figure S1 TEM images and the size distributions of as-prepared Pt/XC-72 (a), annealed Pt/XC-72 (b), and carbon riveted Pt/XC-72 (c).

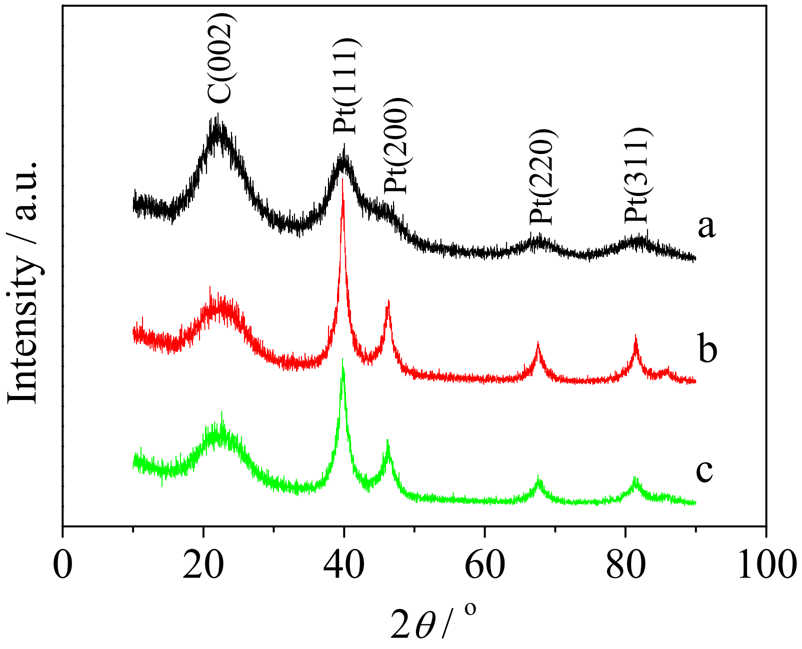

Figure S2 XRD patterns: as-prepared Pt/XC-72 (a), annealed Pt/XC-72 (b), and carbon riveted Pt/XC-72 (c). The results confirm that the Pt nanoparticles have typical face-centered cubic (fcc) crystal structure.

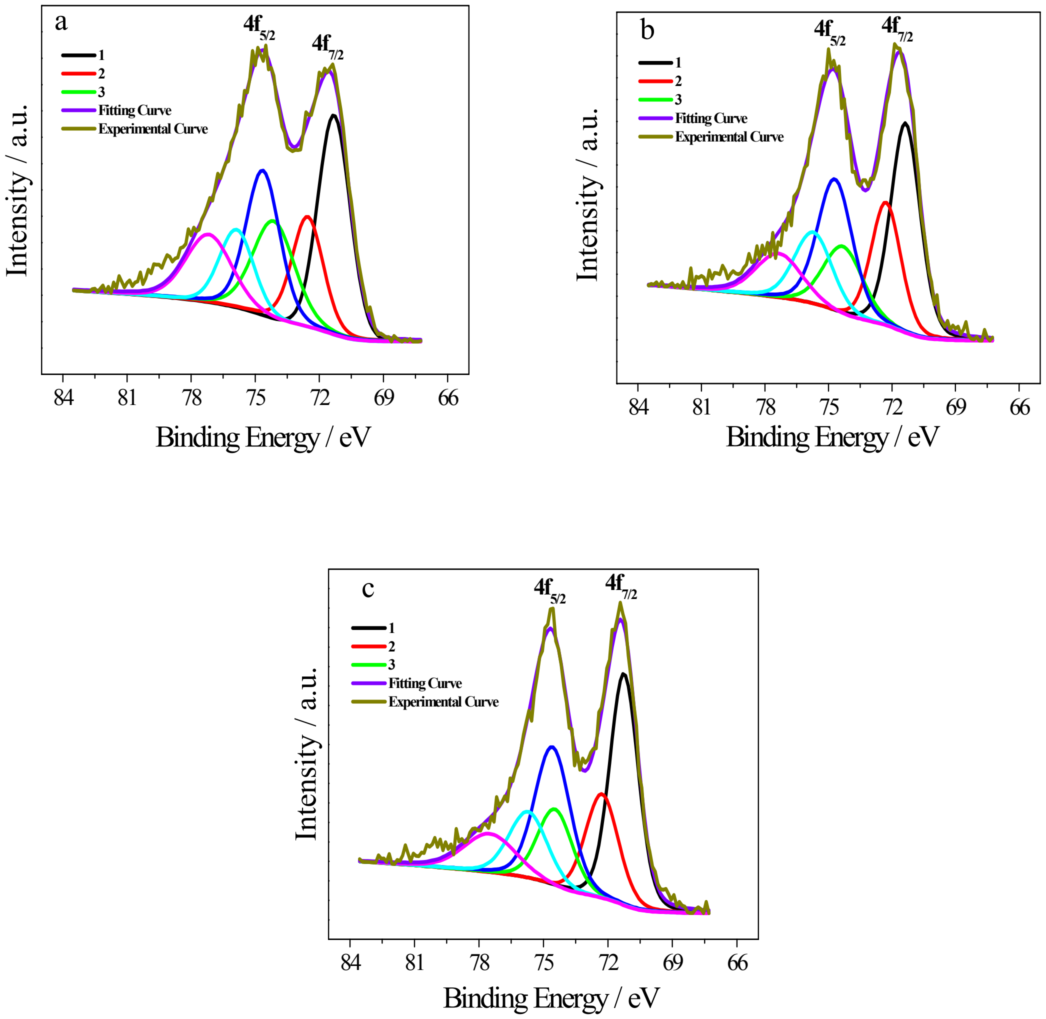

Figure S3 Pt(4f) XPS spectra of various nanomaterials. (a) as-prepared Pt/XC-72, (b) annealed Pt/XC-72, and (c) carbon riveted Pt/XC-72.

Table S1 Binding energy [BE($4f_{7/2}$), eV] and atomic percentages (%) of different Pt [Pt(0), Pt^{2+} and Pt^{4+}] obtained from Pt(4f) XPS spectra.

Sample	Pt(0) BE=71.3	Pt(□) BE=72.5	Pt(□) BE=74.3
As-prepared Pt/XC-72	46.35	24.53	29.11
Annealed Pt/XC-72	49.22	29.19	21.59
Carbon riveted Pt/XC-72	51.75	27.09	21.15

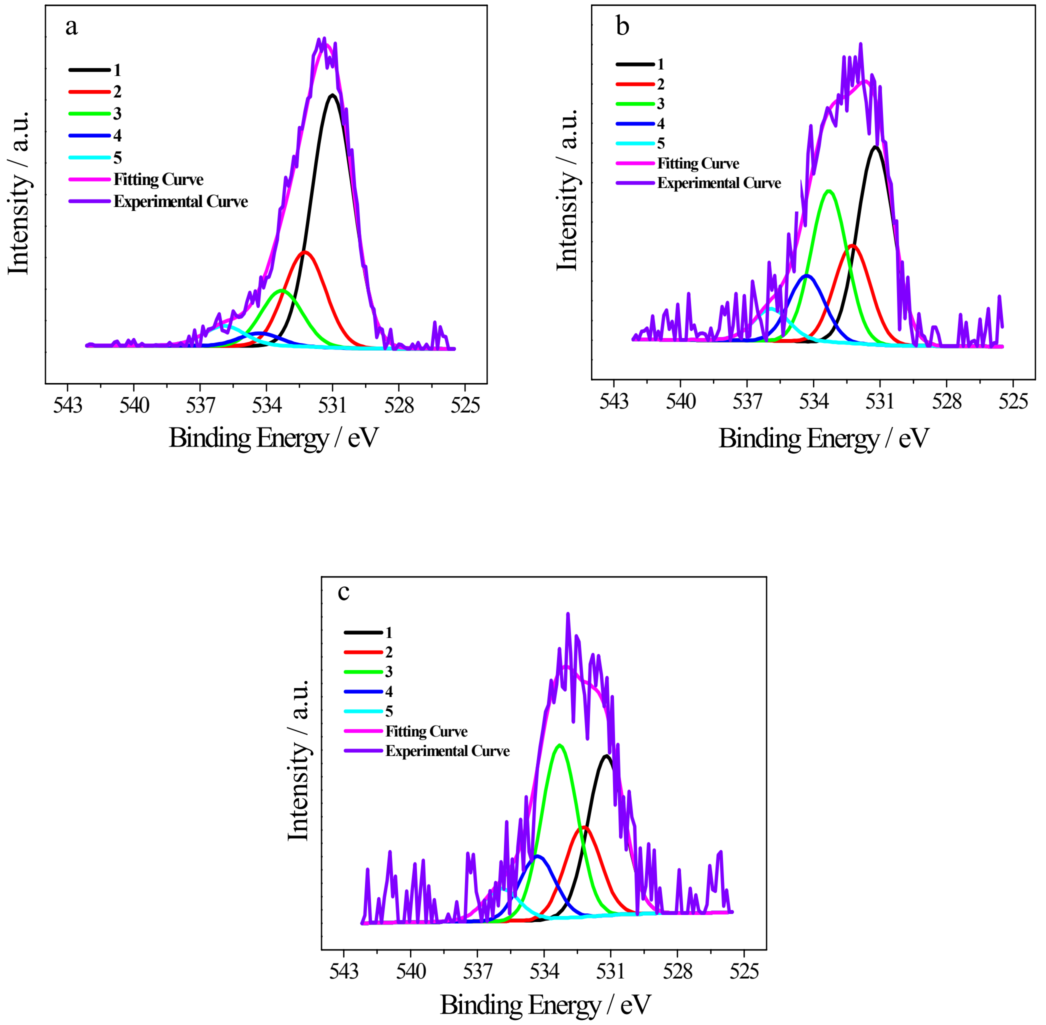

Figure S4 Deconvoluted O1s peaks from XPS analysis of various nanomaterials. (a) as-prepared Pt/XC-72, (b) annealed Pt/XC-72, and (c) carbon riveted Pt/XC-72.

Table S2 Results of the fits of the O1s spectra, values given in % of total intensity.

Sample	531.20 eV	532.25 eV	533.30 eV	534.30 eV	535.9 eV
As-prepared Pt/XC-72	58.12	21.40	12.62	2.93	4.94
Annealed Pt/XC-72	36.53	17.71	27.46	11.95	6.36
Carbon riveted Pt/XC-7	30.92	17.17	33.03	12.15	6.73

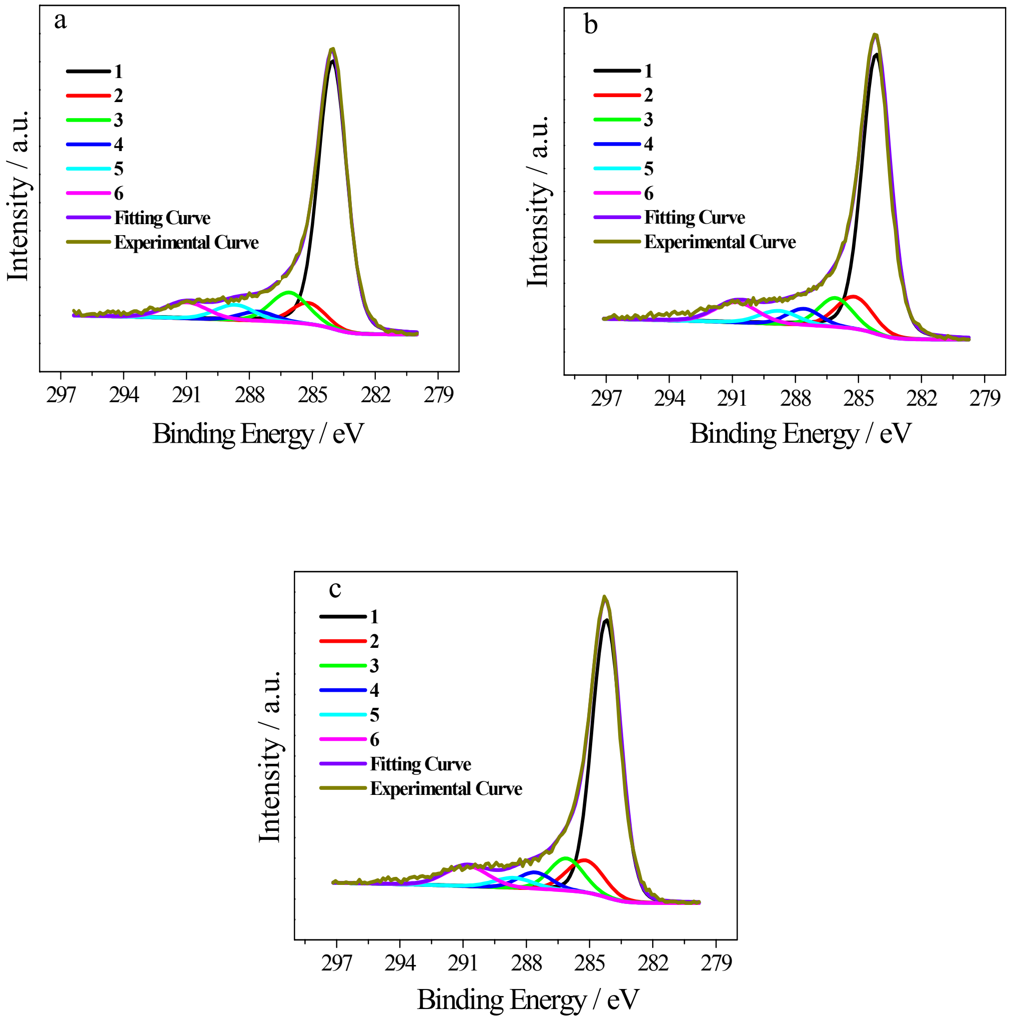

Figure S5 Deconvoluted C1s peaks from XPS analysis of various nanomaterials: as-prepared Pt/XC-72 (a), annealed Pt/XC-72 (b), and carbon riveted Pt/XC-72 (c).

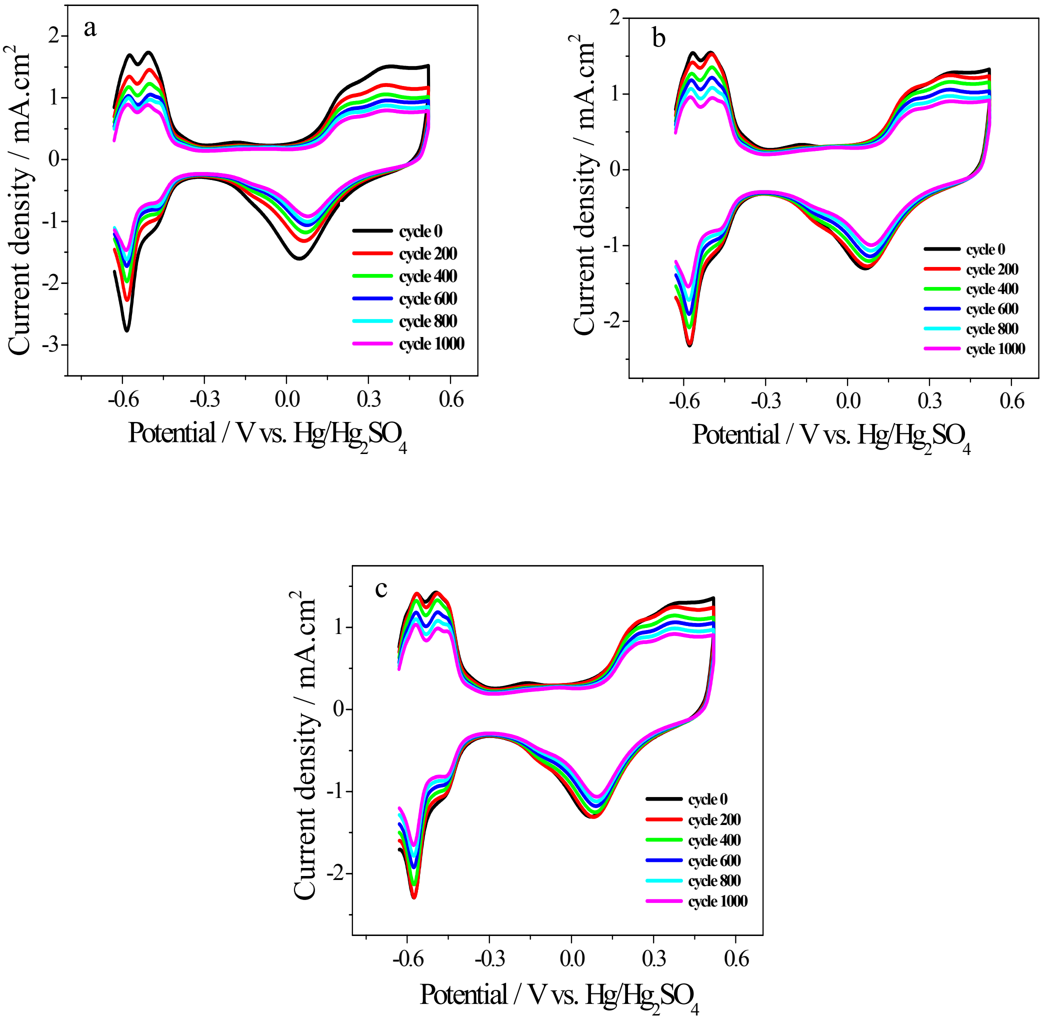

Figure S6 Cyclic voltammograms in 0.5 mol/L H_2SO_4 for all nanomaterials during the accelerated potential cycling test. (a) as-prepared Pt/XC-72, (b) annealed Pt/XC-72, (c) carbon riveted Pt/XC-72. Scanning rate: 50 mV/s; Test temperature: 25°C.

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