

Electronic Supplementary Information for Chemical Communications

A facile, controllable fabrication of polystyrene/graphene microspheres and its application in high-performance electrocatalysis

1. Preparation of graphene oxide (GO)

Graphite (CP, ignition residue $\leq 0.15\%$, granularity $\leq 30 \mu\text{m}$) was purchased from Sinopharm Chemical Reagent Co. (China). GO was prepared by the modified Hummers method. Graphite was preliminary oxidized (2.50 g) with potassium peroxydisulfate (KPS, 2.50 g) and phosphorus pentoxide (P_2O_5 , 2.50 g) in concentrated sulfuric acid (H_2SO_4 , 98%, 150 mL) at first. The product was neutralized with potassium hydroxide solution (KOH), and then dried at $80 \text{ }^\circ\text{C}$. The dried product was stirred with potassium permanganate (KMnO_4 , 25.00 g) in H_2SO_4 (98%, 150 mL) at the temperature of $0 \text{ }^\circ\text{C}$, $5 \text{ }^\circ\text{C}$, $10 \text{ }^\circ\text{C}$, $15 \text{ }^\circ\text{C}$ and $20 \text{ }^\circ\text{C}$ for each 2 h, then the system was heated to $35 \text{ }^\circ\text{C}$ to keep another 2 h, at last 100 mL water was added in the system to keep the temperature in the range of $80 \text{ }^\circ\text{C}$ to $100 \text{ }^\circ\text{C}$ for 30 min. The oxidation product was treated with hydrogen peroxide (H_2O_2) to consume the remained KMnO_4 , and the solution emerged luminous yellow. After washing and centrifugalization, GO was dispersed in water with the concentration of 1.0 mg/1.0 g H_2O by ultrasonication.

2. Preparation of polystyrene (PS) template

The monodisperse PS microspheres in the size of 280 nm were prepared by emulsifier-free emulsion polymerization as follows: styrene (10.00 g), polyvinylpyrrolidone (PVP, 0.40 g) and H_2O (80.00 g) were charged into a 250 mL fourneck flask equipped with a heating mantle, a mechanical stirrer, a thermometer with a temperature controller, a N_2 inlet and a condenser. The mixture was slowly heated to $70 \text{ }^\circ\text{C}$, followed by addition of AIBA aqueous solution (2, 2'-azobis[2-methylpropionamide] dihydrochloride, 0.06 wt%, 10.00 g), and the reaction was carried out at $70 \text{ }^\circ\text{C}$ for 18 h.

3. Preparation of polystyrene/graphene (PS/GP) microspheres

The typical procedure to prepare PS/GP microspheres was below: PS microspheres were dispersed in water with the concentration of 1.00 g PS/ 90.00 g H₂O, and the solution was heated to 70 °C with slow stirring, and then 10 mL GO dispersion was dropped into the solution by constant flow pump at the speed of 2.5 mL/h. At last, the system was heated to 90 °C, and then 5 mL hydrazine hydrate was added and stirred for 6 h, the PS/GP microspheres were obtained.

4. Preparation of the PS/GP microspheres modified glassy carbon electrode (GCE)

PS/GP microspheres were dispersed in deionized water with the concentration of 5.0 mg/1.0 g H₂O. To obtain the modified GCE, the sample solution of 60 μL was dropped on the surface of GCE and it was dried naturally in the air after several hours.

5. Characterization

Transmission electron microscopy (TEM) images of PS, PS/GO and PS/GP microspheres were obtained with a FEI Tecnai F30 operated at 200 kV. Scanning electron microscopy (SEM) imaging was performed on a Hitachi S-4800 SEM. Raman analysis was performed with a Jobin Yvon HR800. Thermo-gravimetric analysis (TGA) was performed by using a Perkin-Elmer Pyris 1 instrument. X-ray photoelectron spectroscopy (XPS) analysis was performed with a PHI 5000 versaprobe instrument with a monochromatic Mg K α X-ray source.

6. Electrochemical analysis

Electrochemical measurements were carried on a CHI 660D potentiostat. The DA solution (0.1 mM, 0.01 mol/L PBS with pH=6.5 as the supporting electrolyte) was placed in electrolytic cell, including PS/GP microsphere-modified GCE, a saturated calomel electrode (SCE) and a platinum electrode. CV tests were performed at a scan rate of 0.1 V/s and over a potential range of -0.2~0.7 V (VS. SCE). Before or after differential pulse voltammetry (DPV) tests, the electrochemical active surface area of PS/GP microsphere-modified GCE was estimated by cyclic voltammetry (CV) using a dopamine (DA) solution for 20 times. For DPV tests, the DA solution of different concentration was placed in electrolytic cell, which containing a PS/GP microsphere-modified GCE, a SCE and a platinum electrode. DPV tests were carried

out at accumulation time of 120 s, accumulation potential of 0.1 V, pulse amplitude of 50 mV and pulse period of 200 ms.

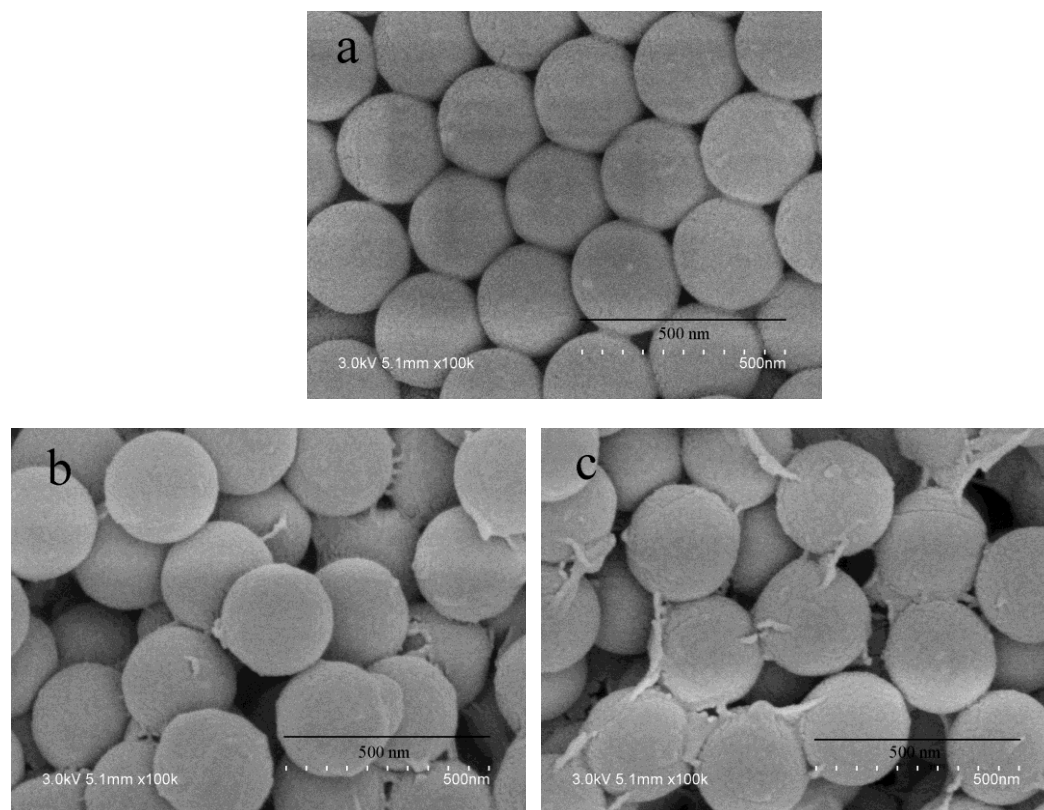
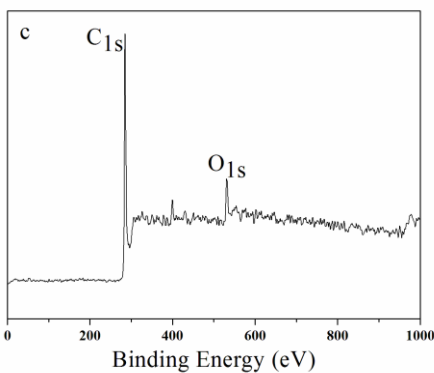
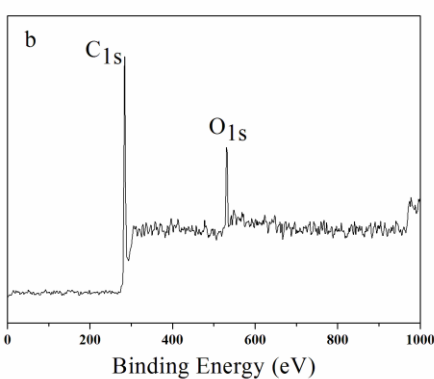
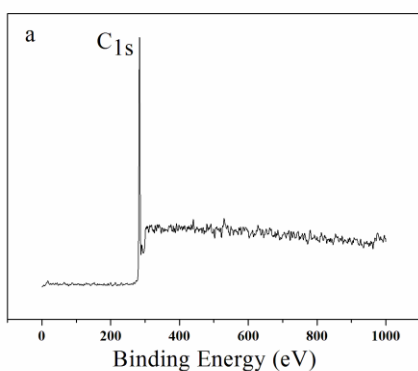


Fig. S1 SEM images of PS microspheres (a), PS/GO microspheres (b) and PS/GP microspheres (c)



d XPS Atomic Concentrations (%)

	PS microspheres	PS/GO microspheres	PS/GP microspheres
C	96.50	87.86	91.84
O	3.50	12.14	8.16

Fig. S2 XPS survey for the (a) PS microspheres, (b) PS/GO microspheres, (c) PS/GP microspheres and (d) their compositions determined by XPS.

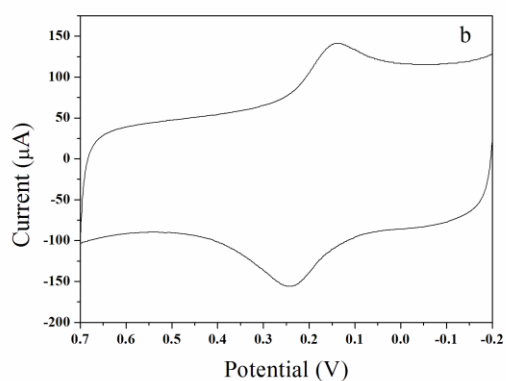
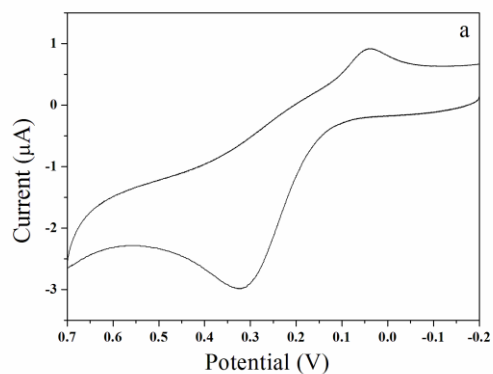


Fig. S3 CVs of 0.1 mmol/L DA in 0.01 mol/L PBS buffer solution (pH=6.5) at bare GCE (a) and PS/GP microsphere-modified GCE (b) with the scan rate of 0.1 V/s in the range of -0.2~0.7 V.

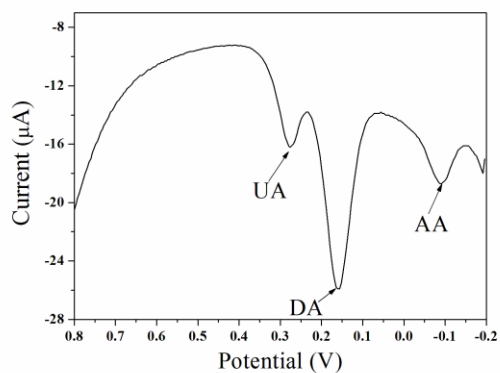


Fig. S4 DPV of 15 μM DA, 6 μM UA and 100 μM AA in 0.01 mol/L PBS buffer solution (pH=6.5) at PS/GP microsphere-modified GCE. Accumulation time: 120 s; Accumulation potential: 0.1 V; pulse amplitude: 50 mV, pulse period: 200 ms.

Table S1 The detection limits and linear ranges of different modified electrodes for the determination of DA

Electrode materials	Detection limit ($\mu\text{mol/L}$)	Linear range ($\mu\text{mol/L}$)	Ref.
MWCNT/CCE ^a	0.31	0.5-100	Habibia and Pournaghi-Azar (2010) [1]
CNF-CPE ^b	0.04	0.04-5.6	Liu et al. (2008b) [2]
PGE ^c	0.11	1-20	da Silva et al. (2008) [3]
OMC/Nafion ^d	0.5	1-90	Zheng et al. (2009) [4]
Graphene	2.64	4-100	Kim et al. (2010) [5]
3D graphene nanoflake	0.17	1-50	Shang et al. (2008) [6]
PS/GP microspheres-GCE	0.02	0.1-0.9, 1.0-20.0	This work

a Multiwalled carbon nanotube modified carbon–ceramic electrode.

b Carbon nanofiber modified carbon paste electrode.

c Pyrolytic graphite activated electrodes.

d Ordered mesoporous carbon/Nafion composite film.

Reference

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