

Electronic Supplementary Information for Chemical Communications

Facilely prepared polypyrrole- reduced graphite oxide core-shell microspheres with high dispersibility for electrochemical detection of dopamine

1. Synthesis of PPy-RGO microspheres

GO was synthesized using a modified Hummer's method and dispersed in water with the concentration of 1.0 mg/1.0 g H₂O by ultrasonication. The monodisperse PPy microspheres were prepared according to reported method with a little modification. In a typical synthesis, 0.20 g of ferrous chloride (FeCl₂) to 88.0 mL of deionized water, where 2.0 mL of pyrrole has been pre-dispersed. After the addition of 10.0 mL of H₂O₂ to the pyrrole/FeCl₂/H₂O mixture, pyrrole polymerization was initiated and lasted for 6 h, leading to a deep dark precipitate. The products were concentrated by centrifugating the solution and sequentially washed with water several times to remove unused reactants and reaction byproducts, and then were dispersed in distilled water at a concentration of 0.18 g PPy/ 80.00 g H₂O.

The procedure to prepare PPy-RGO microspheres are the follows: PPy microspheres were dispersed in water with the concentration of 0.18 g PPy/ 80.00 g H₂O; the solution was adjust to pH=2, and heated to 70 °C; 20 mL GO dispersion was dropped into the solution by constant flow pump at the speed of 10.0 mL/h; the resulting PPy-GO microspheres were then reduced by 0.20 mL hydrazine hydrate at 90 °C for 6 h. The PPy-RGO microspheres were obtained.

2. Synthesis of RGO sheets and PS-RGO microspheres

The procedure to prepare RGO sheets are the follows: 100 mL prepared GO dispersion liquid were directly reduced by 1 mL hydrazine hydrate at 90 °C for 6 h.

The monodisperse PS microspheres were prepared by emulsifier-free emulsion polymerization as follows: styrene (10.00 g), polyvinylpyrrolidone (PVP, 0.40 g) and H₂O (80.00 g) was slowly heated to 70 °C in N₂ environment.; AIBA aqueous solution (2, 2'-azobis[2-methylpropionamide] dihydrochloride, 0.06 wt%, 10.00 g) was added; the reaction was carried out at 70 °C for 18 h.

The procedure to prepare PS-GO microspheres are the follows: PS microspheres were dispersed in water with the concentration of 1.00 g PS/ 80.00 g H₂O; the solution was heated to 70 °C; 20 mL GO dispersion was dropped into the solution by constant flow pump at the speed of 2.5 mL/h; the

products were then reduced by 0.20 mL hydrazine hydrate at 90 °C for 6 h, the resulting PS-RGO microspheres were collected by centrifugation, washed with water for three times and dried in a vacuum drier for 24 h.

3. Preparation of the PPy-RGO microspheres modified glassy carbon electrode (GCE)

A GCE was polished to a mirror-like with 0.3 and 0.05 μm alumina slurry on micro-cloth pads, rinsed thoroughly with three distilled water between each polishing step, then washed successively with three distilled water, anhydrous ethanol and three distilled water in an ultrasonic bath and dried in air before use. For the detection of DA, 14 μL of PPy-RGO microspheres aqueous solution was dropped on the surface of GCE and dried at infrared lamp. The sensor was stored under 4 °C when not in use.

4. Characterization

Transmission electron microscopy (TEM) images of PPy, and PPy-RGO microspheres were obtained with a JEM 2100 high-resolution TEM. Scanning electron microscopy (SEM) imaging was performed on a JEOL-JSM-7600F SEM. Raman analysis was performed with a Jobin Yvon HR800. X-ray diffraction (XRD) analysis was performed on a Shimadzu XRD 6000 diffractometer. High-resolution Transmission electron microscopy (HRTEM) images were obtained with a FEI Tecnai F30 operated at 200 kV. UV-Vis spectra were obtained with a Lambda 35 UV-vis spectrometer. Zeta potential was recorded on a Malvern Nano-Z Instrument. Dynamic light scattering (DLS) data were obtained with a BI-200SM DLS spectrometer. Elementary analysis was performed on a CHN-O-Rapid elementary analysis apparatus.

5. Electrochemical analysis

All electrochemical measurements were carried out with a CHI660d (Shanghai CH Instrument Company, China). Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed with a conventional three-electrode system consisting of a bare or modified glassy carbon electrode (GCE; diameter=3mm) as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a platinum wire as the counter electrode.

6. Particle size analysis by DLS

DLS was used to analyze the particle size of PPy, PPy-GO, and PPy-RGO. Fig. S6A shows that the particle size of PPy is uniformly distributed in the range between 731-741 nm, which agrees to the SEM results. The data of PPy-GO shows slightly increased particle size comparing to that of

PPy, and additional signals around 200 nm appears, which may correspond to the uncoated GO sheets (Fig. S6B). The particle size distribution of PPy-RGO is similar to that of PPy-GO (Fig. S6C).

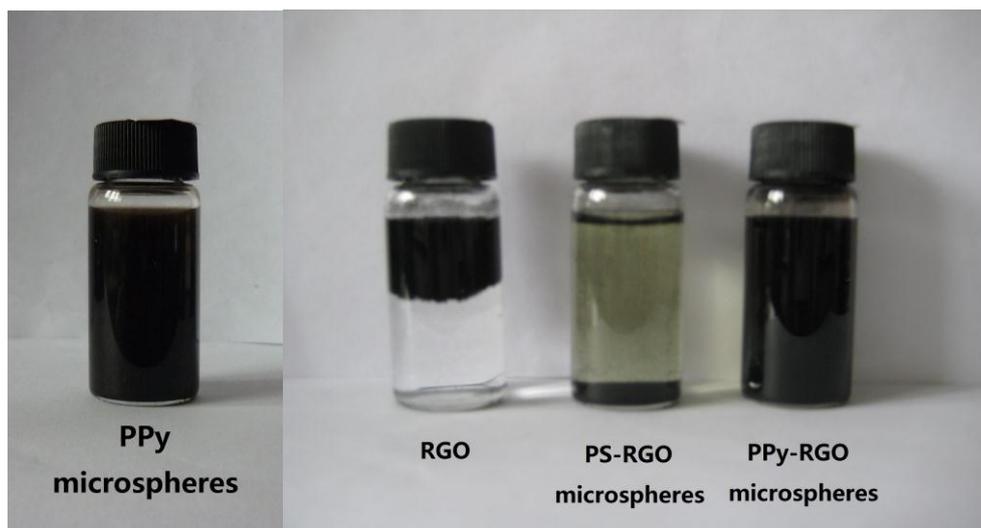


Fig. S1 Photographs of PPy, RGO sheets, PS-RGO, and PPy-RGO microspheres dispersed in water (2 mg/mL) after ultrasonication 1 h and stand for 3 h.

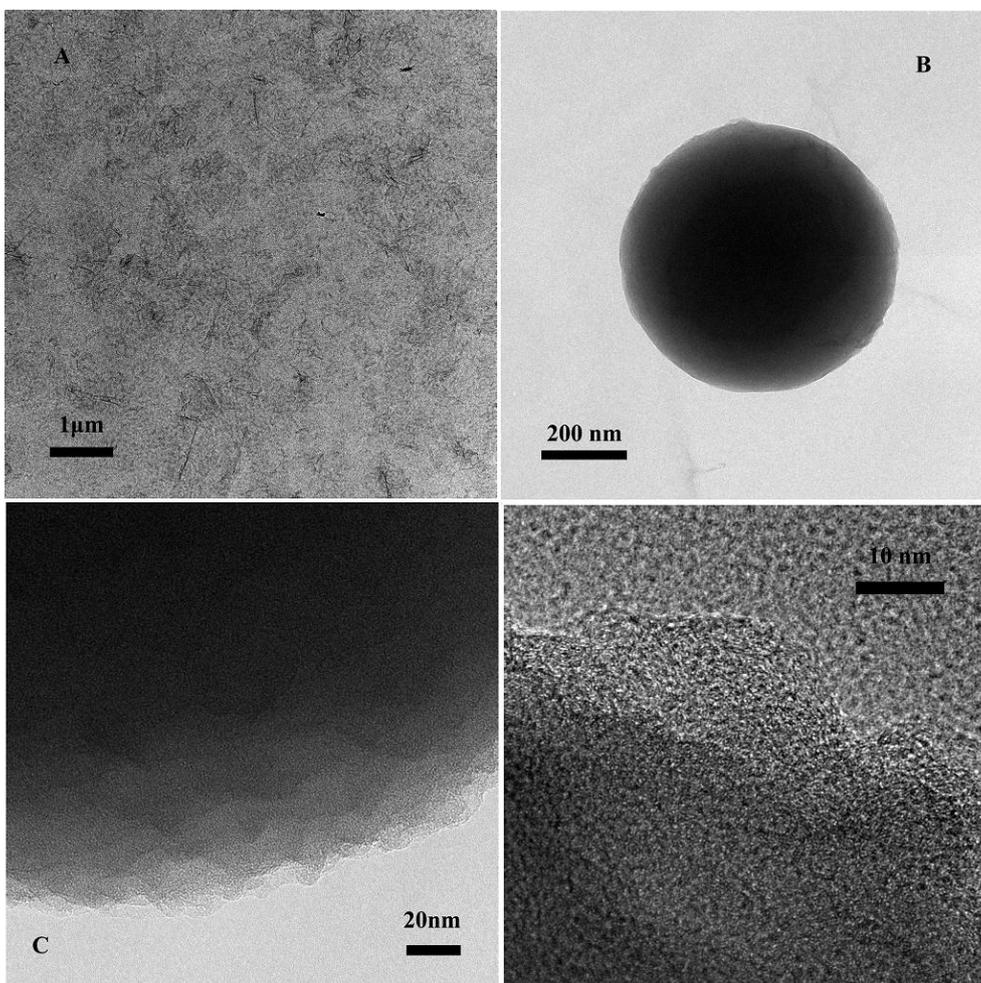


Fig. S2 HRTEM images of (A) RGO sheet, (B) PPy-RGO microsphere, (C, D) PPy-RGO microsphere with partial enlarged.

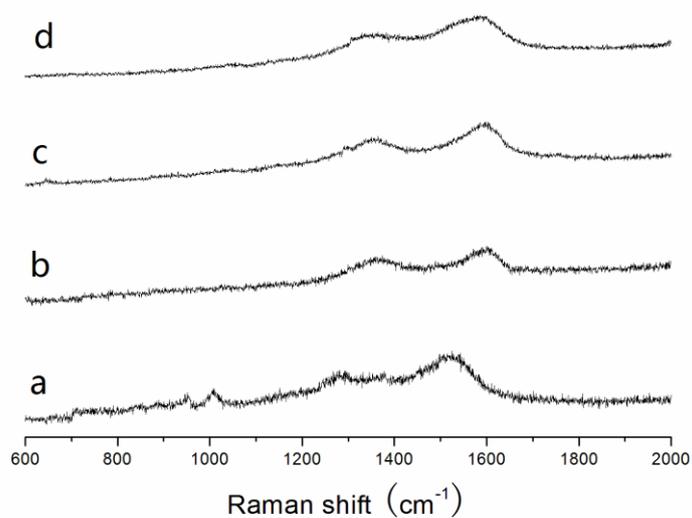


Fig. S3 Raman spectra of (a) PPy microspheres (b) GO sheets (c) PPy-GO (d) PPy-RGO core-shell microspheres.

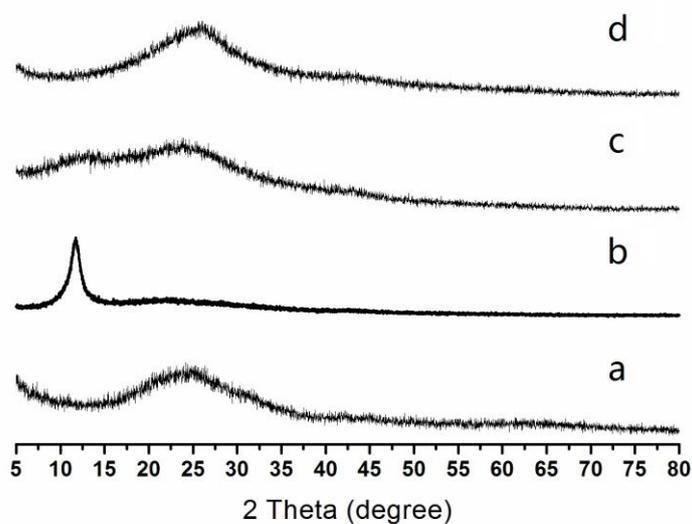


Fig. S4 XRD patterns of (a) PPy (b) GO (c) PPy-GO (d) PPy-RGO core-shell microspheres.

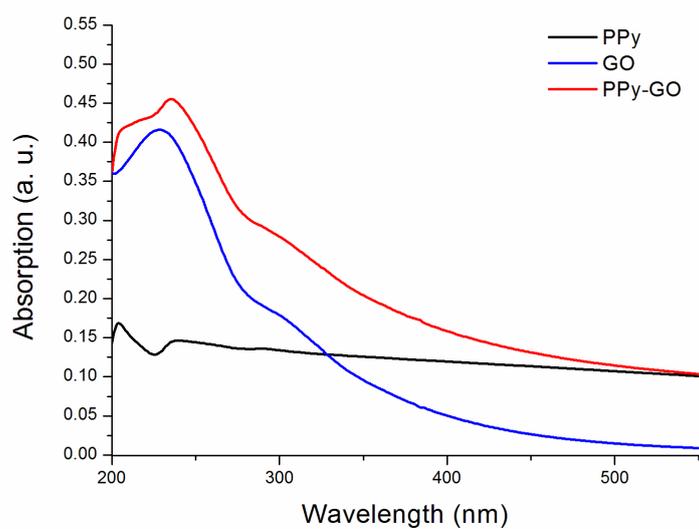


Fig. S5 UV-Vis spectra of PPy (72 mg L^{-1}), GO (8 mg L^{-1}), and PPy-GO (80 mg L^{-1}).

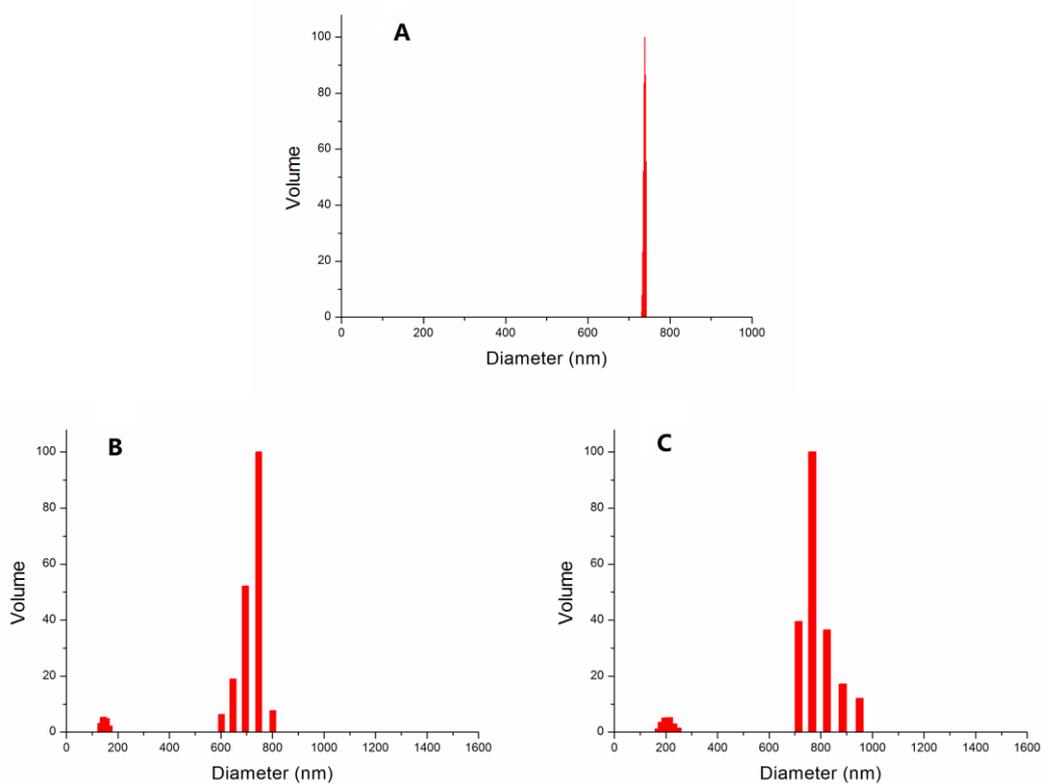


Fig. S6 DLS data of (A) PPy, (B) PPy-GO, and (C) PPy-RGO microspheres.

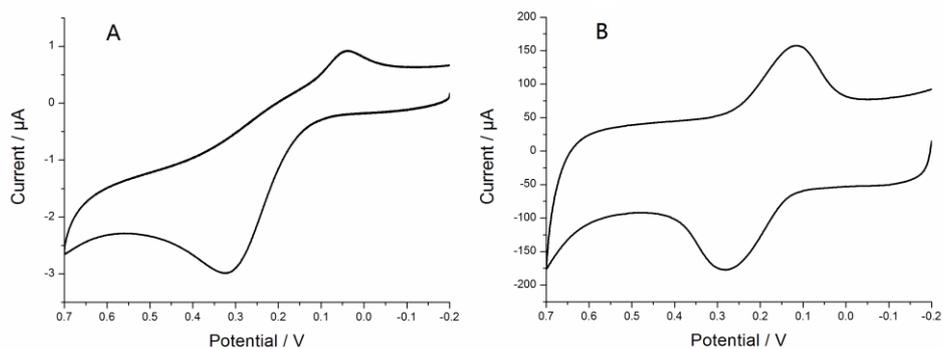


Fig. S7 CVs of the (A) bare GCE, and (B) PPy-RGO microspheres doped GCE in 0.1 M PBS (pH 6.5) in the presence of DA (0.1 mM) at a scan rate of 100 mV s^{-1} .

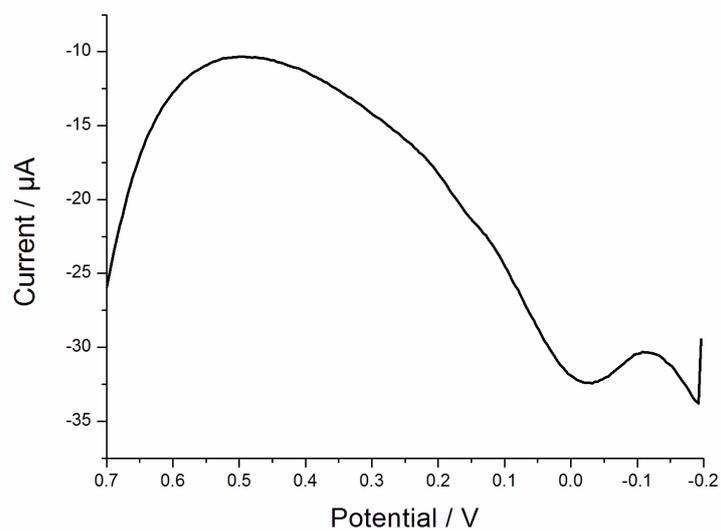


Fig. S8 DPV respond curve of 1 nM DA (detection limit) in 0.1M PBS (pH=6.5).

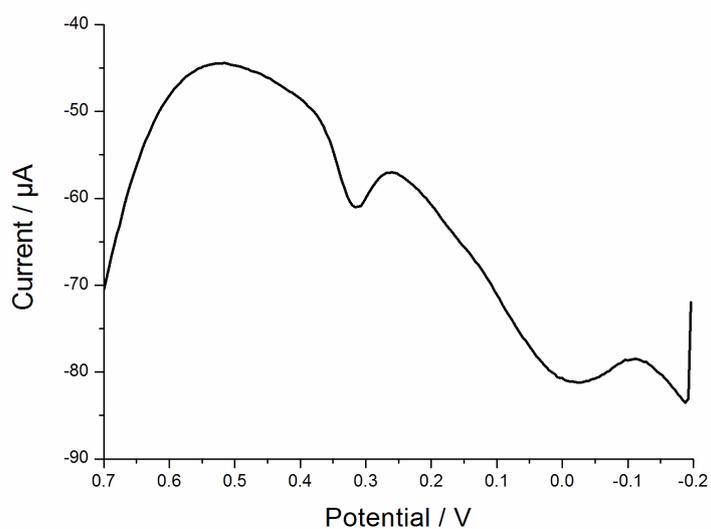


Fig. S9 DPV respond curve of 6 nM DA (detection limit) in the present of 100 μM AA and 5 μM UA.

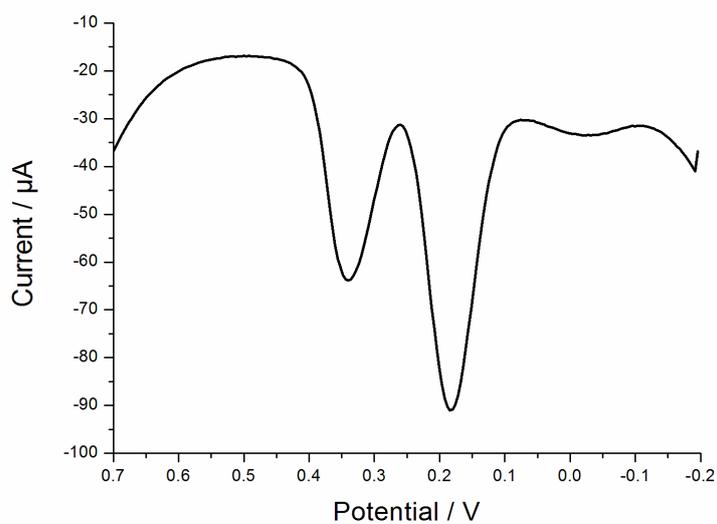


Fig. S10 DPV respond curve of 10 μM DA in the present of 125 μM AA and 330 μM UA (an environment similar to human blood serum).

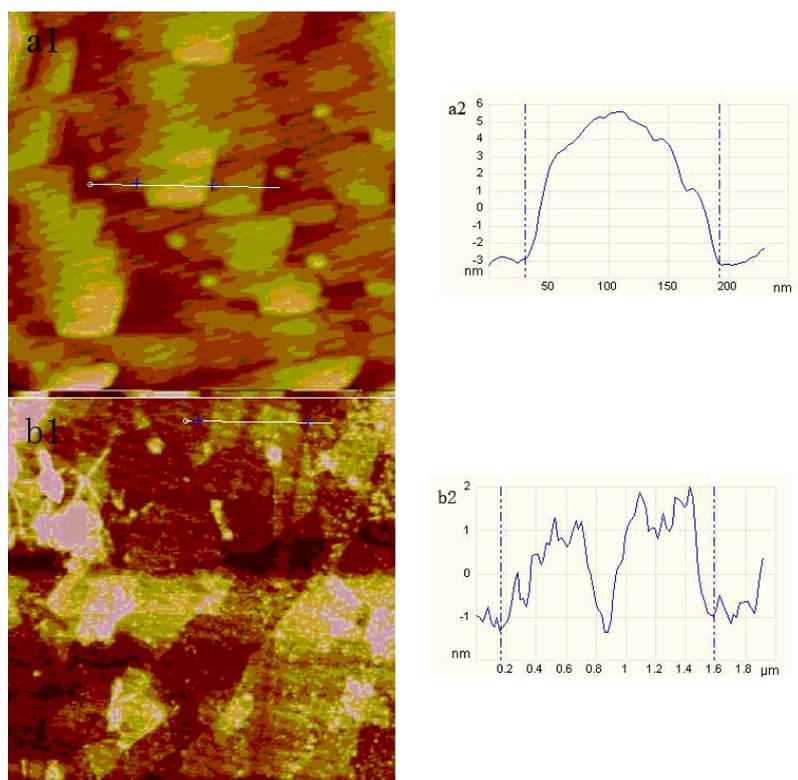


Fig. S11 AFM images and the corresponding height profiles of GO (a1, a2) and RGO (b1, b2).

Table S1 Zeta potential data of RGO, PS-RGO, and PPy-RGO.

	RGO	PS-RGO	PPy-RGO
Zeta potential (mV), pH=7.0	-3.5	-11.2	-36.2

Table S2 Elementary analysis of PPy-GO and PPy-RGO microspheres.

	C %	H %	N %	O % (calculated value)
PPy-GO	76.97	4.13	12.86	6.04
PPy-RGO	78.80	3.72	13.65	3.83

Table S3 Comparison of the proposed PPy-RGO microspheres -GCE with other electrochemistry methods in the determination of DA.

Modified materials	Detection limit (nM)	Linear range (μM)	Sensitivity ($\mu\text{A}/\mu\text{M}$)	References
graphene/Pt ^a	30	0.03-8.13	0.970	[1]
TCCP/CCG ^b	10	0.01-70	1.403	[2]
NG ^c	250	0.5-170	0.032	[3]
Nafion/graphene/Fc-NH ₂ ^d	20	0.05-200	0.042	[4]
PPy-eRGO composites ^e	23	0.1-150	0.031	[5]
PS-GP microspheres ^f	20	0.1-20	2.07	[6]
PPy-RGO microspheres	1	0.01-10	6.33	This work

^a graphene/size-selected Pt nanocomposites.

^b porphyrin-functionalized graphene.

^c nitrogen doped graphene.

^d Nafion/graphene/phenylethynyl ferrocene nanocomposite.

^e composites of polypyrrole and graphene.

^f polystyrene/graphene core-shell microspheres.

References

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