Supporting Information

Dimensional Confinement of Graphene in Polypyrrole Microbowl for Sensor Application

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Experimental

Chemicals and Characterization

Lithium perchlorate trihydrate ($LiClO_4 \cdot 3H_2O$, 99%), pyrrole monomer (99%) and 2-naphthalene-sulfonic acid sodium salt (β-NSA, 99%) were purchased from Aladdin (China). GO was synthesized from natural graphite powder according to the Hummers' method.[1] Scanning electron microscope (SEM) images were taken using a JSM-7500F (Japan) electron microscope. Raman spectra were recorded by using a RM 2000 microscopic confocal Raman spectrometer (Renishaw PLC, England) fitted with 633 nm and 532 nm laser. X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALab220i–XL electron spectrometer from VG Scientific using 300W AlKα radiation.

Cyclic voltammetry (CV) and amperometry were performed with a conventional three-electrode system on a CHI 760D electrochemical workstation (CH instruments, China). All of the solutions were de-oxygenated by bubbling nitrogen gas for 15 min before measurements.

Synthesis of PPy bowl-shaped microcontainer

The electropolymerization was carried out on the CHI 760D electrochemical workstation in a 15 mL electrolyte cell using two stainless steel sheets (AISI 321) as the working and counter electrode and a saturated calomel electrode (SCE) working as the reference electrode. The working and counter electrodes were placed 0.5 cm apart, each with a surface area of 0.5 cm^2. The electrolyte was an aqueous solution of 0.25 M pyrrole and 0.2 M β-NSA. Cyclic voltammetric scans were performed to generate H_2 bubbles on the working electrode surface by scanning the potential from -1.05 V to -1.65 V for the first cycle, followed by changing the potential to 1.1 V for 200 s for electrochemical polymerization of pyrrole around the soap bubbles, formed by the surfactants, on the working electrode. The diameter of the PPy microbowl can be simply controlled in the range of 300 μm - 900 μm by changing the diameter of the H_2 bubble. Except for special statement, the potential window was from -1.05 V to -1.65V. Besides, the other excess PPy on the steel electrode is well sealed by nonconductive glue.

Fabrication of PPy/3DG bowl-shaped minisensor

A three electrode system with a SCE and a Pt foil as the reference and counter electrodes was used. A PPy microbowl was used as the working electrode. The PPy/3DG microbowl was prepared by electrochemical reduction of GO suspension (6 mg/mL) under a constant potential of -1.2 V for 2 min in a GO aqueous dispersion consisting of 0.1 M $LiClO_4$ as supporting electrolyte. The 3DG deposited on the working electrode was washed repeatedly with deionized water to remove the remaining GO and then preserved in deionized water.

Live subject statement

The human serum samples were collected from volunteers and were diluted to 100 times with 0.1 M pH 7.0 PBS in advance. The authors state that all experiments were performed in compliance with the relevant laws and institutional guidelines. The institutional committee of the Beijing Institute of Technology approved the experiments. The authors also state that informed consent was obtained for any experimentation with human subjects and the Beijing Institute of Technology is committed to the protection and safety of human subjects involved in research.

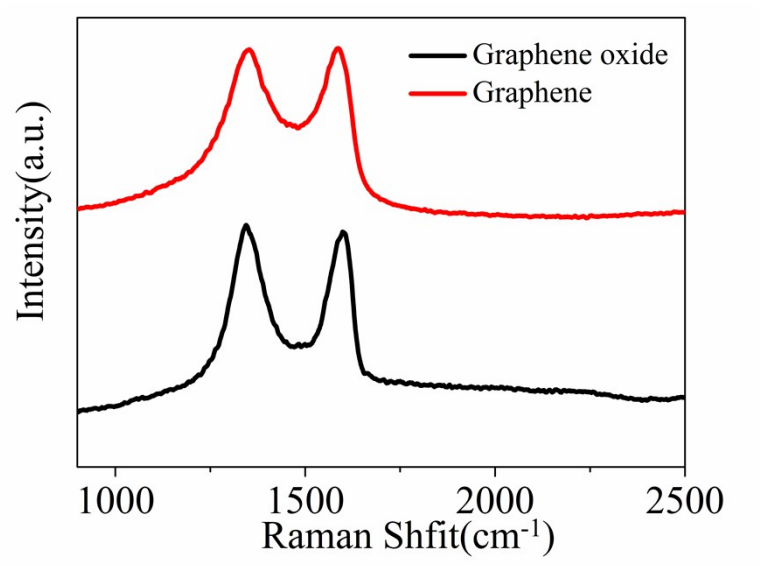

Fig. S1 Raman spectra of GO (black) and RGO (red).

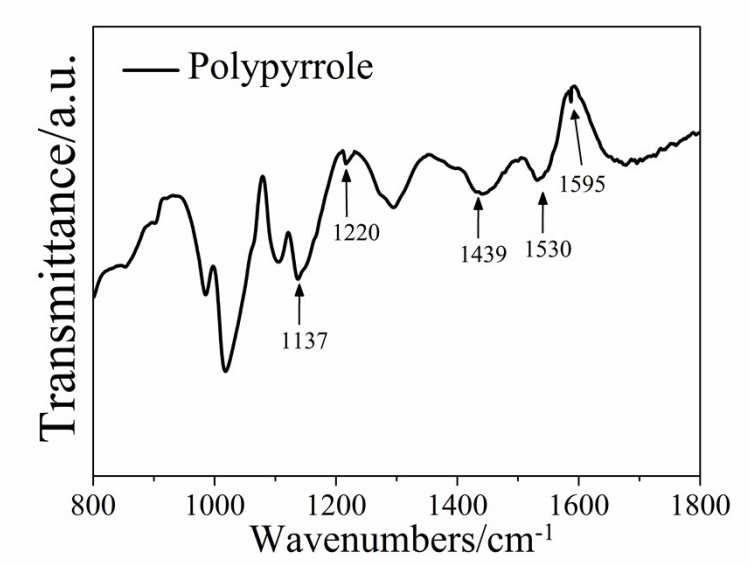

Fig. S2 FTIR spectra of a PPy microcontainer electropolymerized in an aqueous solution of beta-NSA.

As can be seen in Fig. S2, the infrared bands at 1439 and 1137 cm^{-1} are attributed to the N-H /C=C bending vibration and C-N stretching modes of the pyrrole ring.[2] Also, the C=C/C-C stretching vibration absorption peak of PPy-NSA appear at 1530 cm^{-1}. The absorption peaks at 1595 and 1220 cm^{-1} can be assigned to the naphthalene ring and $-SO^{3-}$ group of the dopants, respectively.[3,4] This result indicates that the microbowl was made of slightly doped polypyrrole.

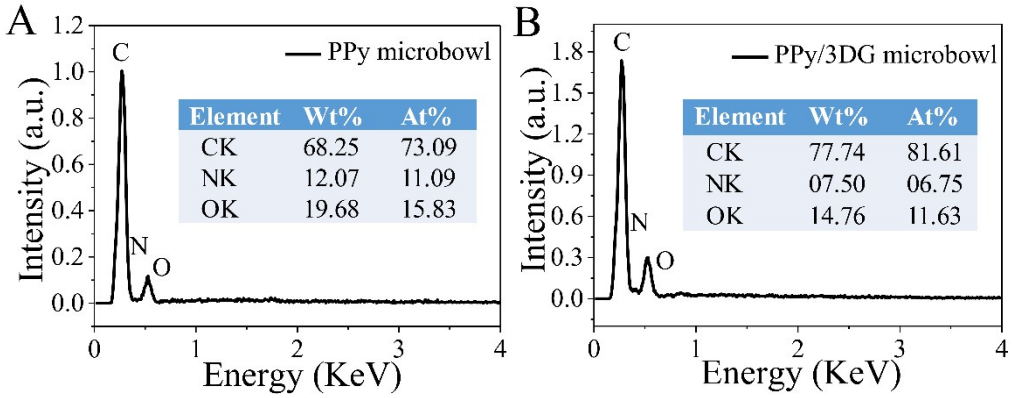

Fig. S3 Energy dispersive spectroscopy (EDS) of a PPy microbowl (A) and PPy/3DG microbowl (B).

Table S1 Comparison of the PPy/3DG microsensor with other graphene-based materials in the determination of DA.

Materials	Detection limit (nM)	Linear range (μM)	Sensitivity (μA/μM)	References
Graphene/GCE	2.64	4-100	0.0659	[5]
Chitosan/Vacuum stripped graphene/PPy scaffold	19.4	0.1-200	0.3493	[6]
3D-reduced graphene oxide/GCE	170	0.5-60	0.482	[7]
PPy-eRGO composites/GCE	23	0.1-150	0.031	[8]
RGO microelectrode array	260	/	0.00191	[9]
Graphene-coated carbon fiber microelectrode	500	1-100	0.81×10^{-3}	[10]
Nitrogen doped graphene fiber microelectrode	30	0.1-80	0.00415	[11]
PPy/3DG microbowl	200	1-900	0.072	This work

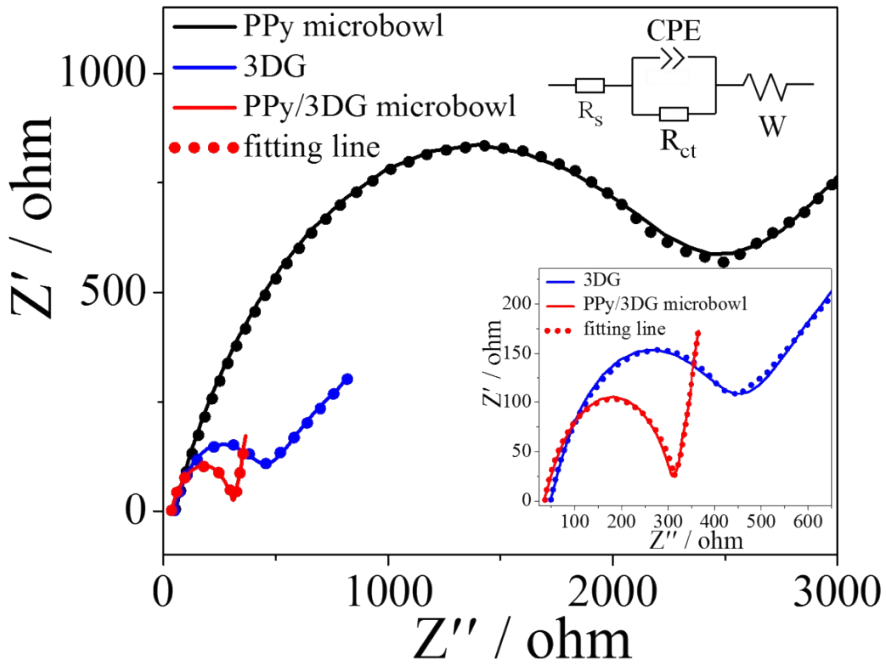

Fig. S4 Impedance spectrum of a PPy microbowl (black line), 3DG (blue line) and the PPy/3DG microbowl (red line) in PBS solution containing 100 μM dopamine. Inset: The enlarged view of Nyquist plots of the 3DG and the PPy/3DG

microbowl.

The electrochemical impedance spectroscopy (EIS) measurements were performed in the presence of 100 μM dopamine PBS solution in the frequency range from 0.1 Hz to 1000 kHz using signal amplitude of 10 mV. The Nyquist plot of the EIS commonly contains two parts: a semicircle portion at higher frequency attributing to the charge-transfer limited process and a linear portion at lower frequency related to the diffusion process. The modified equivalent circuit (inset of Fig. S4) was chosen to fit the impedance data. Here, R_s is the serial resistance of the whole electrolytic cell system and R_{ct} is the charge transfer resistance, which can be used to describe the interface properties of the electrode.[12,13] As shown in Fig. S4, the R_s of the PPy microbowl is the lowest among all the value of the samples, indicating the good conductivity of it. Besides comparing with the R_{ct} value of the PPy microbowl (2726 ± 60Ω) and 3DG (460 ± 10 Ω), the lowest Rct of PPy/3DG microbowl (289 ± 6 Ω) indicating the good electron transfer nature at the surface of PPy/3DG microbowl.

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