Mussel-inspired polydopamine coating as a versatile platform for in situ synthesis of graphene-based nanocomposites

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Supporting information

Experimental Section.

Materials:

Graphite powder (99.9995%) and tri(hydroxymethyl) aminomethane (Tri) was purchased from Alfa Aesar and Angus chemical company, respectively. Dopamine hydrochloride and titanium(IV) isopropoxide (98%) was obtained from Acros organic. P_2O_5, $FeCl_3$, chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$) and chloroauric acid ($HAuCl_4$) were bought from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). H_2O_2, $KMnO_4$, $K_2S_2O_8$ and concentrated H_2SO_4 were from Beijing Chemical Works (Beijing, China). $FeSO_4 \cdot 7H_2O$ was from Guangdong Xilong chemical Co. Ltd (Guangdong, China). Silver nitrate ($AgNO_3$) was from Shanghai Sangon Biological Engineering Technology & Services Co., Ltd (Shanghai, China). Ultrapure water from a Millipore Milli-Q system (MA, USA) was used throughout. All reagents were of analytical grade unless otherwise noted.

Characterization:

X-ray diffraction (XRD) patterns were collected on a X'Pert PRO MPD X-ray diffractometer using Cu Kα irradiation operated at 40 kV and 40 mA. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Kratos AXIS Ultra DLD（Shimadzu）spectrometer equipped with a monochromatized Al Kα X-ray source (1468.6 eV photons) operated at 150 W. All obtained spectra were calibrated to a C 1s peak at 284.6 eV, and fitted with a mixed Gaussian-Lorentzian function by XPSPEAK (a freeware). TEM images were performed on a Hitachi H-7500 transmission electron microscope operated at 80 kV. Before TEM measurement, samples were prepared by dropping and drying on a copper grid supported carbon film (230 mesh, Beijing Zhongjingkeyi Technology Co., Ltd). Energy-dispersive X-ray (EDX) analysis was obtained with an EDAX detector installed on a HITACHI S-3000N scanning electron microscope operated at 15.0 kV. Before measurements, samples were prepared by dropping and drying on silicon slices. Magnetization curve was measured using a physics property measurement system (VSM, Quantum Design, USA).

Synthesis of graphite oxide:

Graphite oxide was synthesized by a modified hummer’s method [S1-2]. Graphite powder (3 g) was added into an 80 ℃ solution of concentrated H_2SO_4 (12 mL), 2.5 g of $K_2S_2O_8$ and 2.5 g of P_2O_5, and the mixture was kept at 80 ℃ for 4.5 h in a oven. Then, the mixture was diluted with 0.5 L of water and left overnight. After that, the mixture was filtered through a 0.20 μm Millipore nylon membrane and washed with 1 L of water to remove residual acid. The product was dried under ambient condition. This pre-oxidized graphite was added into 120 mL of concentrated H_2SO_4 in an ice-bath, and 15 g of $KMnO_4$ was gradually added into the mixture under stirring and the temperature of the mixture was kept to bellow 20 ℃. Consequently, the mixture was stirred at 35 ℃ for 2 h and then slowly diluted with 250 mL of water in an ice-bath to keep the temperature below 50 ℃. Then, the mixture was stirred for another 2 h and diluted with 0.7 L of water. Shortly after the addition of water, 20 mL of H_2O_2 (30%, v/v) was added and the color of the mixture turned to yellow along with bubbling. The mixture was filtered and washed with 1 L of HCl (1:10, v/v) and 1 L of water. The obtained solid was dialyzed (molecule weight cutoff: 7000) against water for 1 week, and then dried under ambient condition.

Polydopamine modified RGO (PDA/RGO):

PDA/RGO was prepared according to the reference [S3] with a slight modification. 200 mg of graphite oxide was added to 320 mL water and the suspension was dispersed by sonication for 30 min. Subsequently 100 mg of dopamine hydrochloride were added and the mixture was stirred at room temperature for 60 min. After 80 mL of 50 mM Tris-HCl solution (pH=8.5) was added, the reaction mixture was stirred vigorously at 80 ℃ for 24 h. The dark brown suspension turned into a black solution. The solution was cooled down to room temperature and filtered with a 0.45 μm membrane filter. The black solid was washed, redispersed, and dialyzed (molecule weight cutoff: 7000) against water for 3 days to remove unreacted dopamine. The black powders were recovered by filtration and dried under ambient condition. The mass percent of PDA in the prepared PDA/RGO nanocomposites was approximate 12% according to the increase mass of the product.

Deposition of Au NPs on the Surfaces of PDA/RGO

0.5 mL of PDA/RGO (1.4 mg/mL) solution and 1.25 mL of $HAuCl_4$ (100 μg/mL) solution were mixed and the mixture was diluted to 25 mL with water. The mixture was stirred at room temperature for 0.5 h. After reaction, the resulting Au NPs-deposited PDA/RGO was separated from the suspension by centrifugation (3500g, 10 min) and washed with water for 3 times.

Deposition of Ag NPs on the Surfaces of PDA/RGO

0.5 mL of PDA/RGO (1.4 mg/mL) solution and 1.25 mL of $AgNO_3$ (10 mg/mL) solution were mixed and the mixture was diluted to 25 mL with water. The mixture was stirred at room temperature for 4 h. After reaction, the resulting Ag NPs-deposited PDA/RGO was separated from the suspension by centrifugation (3500g, 10 min) and washed with water for 3 times.

Deposition of Pt NPs on the Surfaces of PDA/RGO

0.5 mL of PDA/RGO (1.4 mg/mL) solution and 2 mL of H_2PtCl_6 (10 mg/mL) solution were mixed and the mixture was diluted to 25 mL with water. The mixture was stirred at room temperature for 0.5 h. After reaction, the resulting Pt NPs-deposited PDA/RGO was separated from the suspension by centrifugation (3500g, 10 min) and washed with water for 3 times.

Deposition of Fe_3O_4 on the Surfaces of PDA/RGO

0.5 mL PDA/RGO (1.4 mg/mL) was diluted with 20 mL water, 2.5 mL $FeCl_3$ (20.0 mM) and 1.36 mL $FeSO_4$ (25 mM) was added dropwisely to the solution and the mixture was stirred at room temperature for 30 min. 0.5 mL ammonia was added to adjust the pH of the solution about 10. Subsequently, the mixture was heated to 90 ℃ and stirred for 30 min. After the mixture was cooled down to room temperature, the resulting Fe_3O_4-deposited PDA/RGO was separated from the suspension by centrifugation (3500g, 10 min) and washed with water for 3 times.

Deposition of TiO_2 on the Surfaces of PDA/RGO

20 μL of titanium(IV) isopropoxide was added to 5 mL of PDA/RGO (0.2 mg/mL) ethanol solution and the mixture was stirred for 1 h. 0.5 mL water was added to facilitate the hydrolysis and further stirred for another 1h. The black solution was changed to a grey color. After reaction, the resulting TiO_2-deposited PDA/RGO was separated from the suspension by centrifugation (1500g, 3 min) and washed with water for 3 times.

References:

S1.Sung Ho Yang, Sung Min Kang, Kyung-Bok Lee, Taek Dong Chung, Haeshin Lee, Insung S. Choi; Mussel-inspired encapsulation and functionalization of individual yeast cells; J. Am. Chem. Soc.; 2011, 133 (9), 2795-2797

S2. Qian Liu, Jianbo Shi, Lixi Zeng, Thanh Wang, Yaqi Cai, Guibin Jiang; Evaluation of graphene as an advantageous adsorbent for solid-phase extraction with chlorophenols as model analytes; J. Chromatogr. A; 2011, 1218, 197-204

S3. Li Qun Xu, Wen Jing Yang, Koon-Gee Neoh, En-Tang Kang, Guo Dong Fu; Dopamine-induced reduction and functionalization of graphene oxide nanosheets; Macromolecules; 2010, 43, 8336-8339

Fig. S1 The color of GO and PDA/RGO suspension

Fig. S2 XRD patterns of GO and PDA/RGO

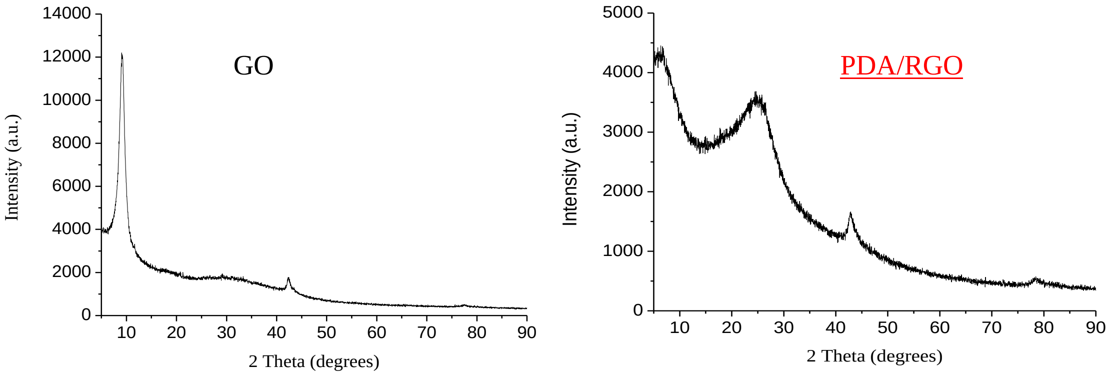
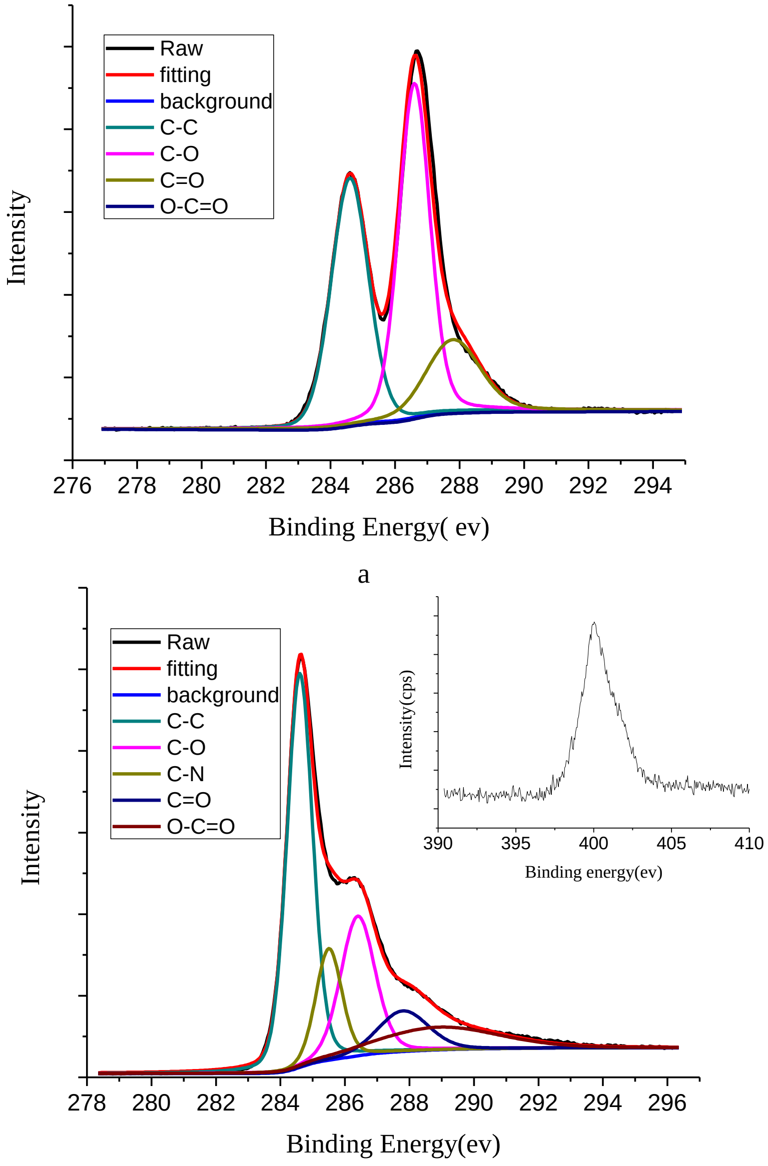


Fig. S3. X-ray photoelectron spectroscopy (XPS) C1s core-level spectra of GO (a) and PDA/RGO (b). Inset of (b) is the N1s core-level spectrum of PDA/RGO. The XPS C1s core-level spectrum of GO (Fig. S3a) can be curve-fitted into four peak components with binding energies (BEs) at about 284.6, 286.6, 287.8, and 288.9 eV, attributable to C-C, C-O, C=O, and O-C=O species, respectively. The XPS C1s core-level spectrum of the PDA/RGO (Fig.S3b) can be curve-fitted into five peak components with BEs at about 284.6, 285.5, 286.4, 287.8, and 288.9 ev, attributable to the C-C, C-N, C-O, C=O, O-C=O species, respectively. The appearance of the C-N peak component at the BE of 285.5 eV in the C 1s core-level spectrum and an N1s core-level spectrum at the BE of ~400 eV (inset of Fig.S3b) are consistent with the presence of a surface modified PDA layer.



a

b

Fig S4 EDX patterns of Au/PDA/RGO (a), Ag/PDA/RGO (b), Pt/PDA/RGO (c), Fe_3O_4/PDA/RGO (d) and TiO_2/PDA/RGO nanocomposites (e)

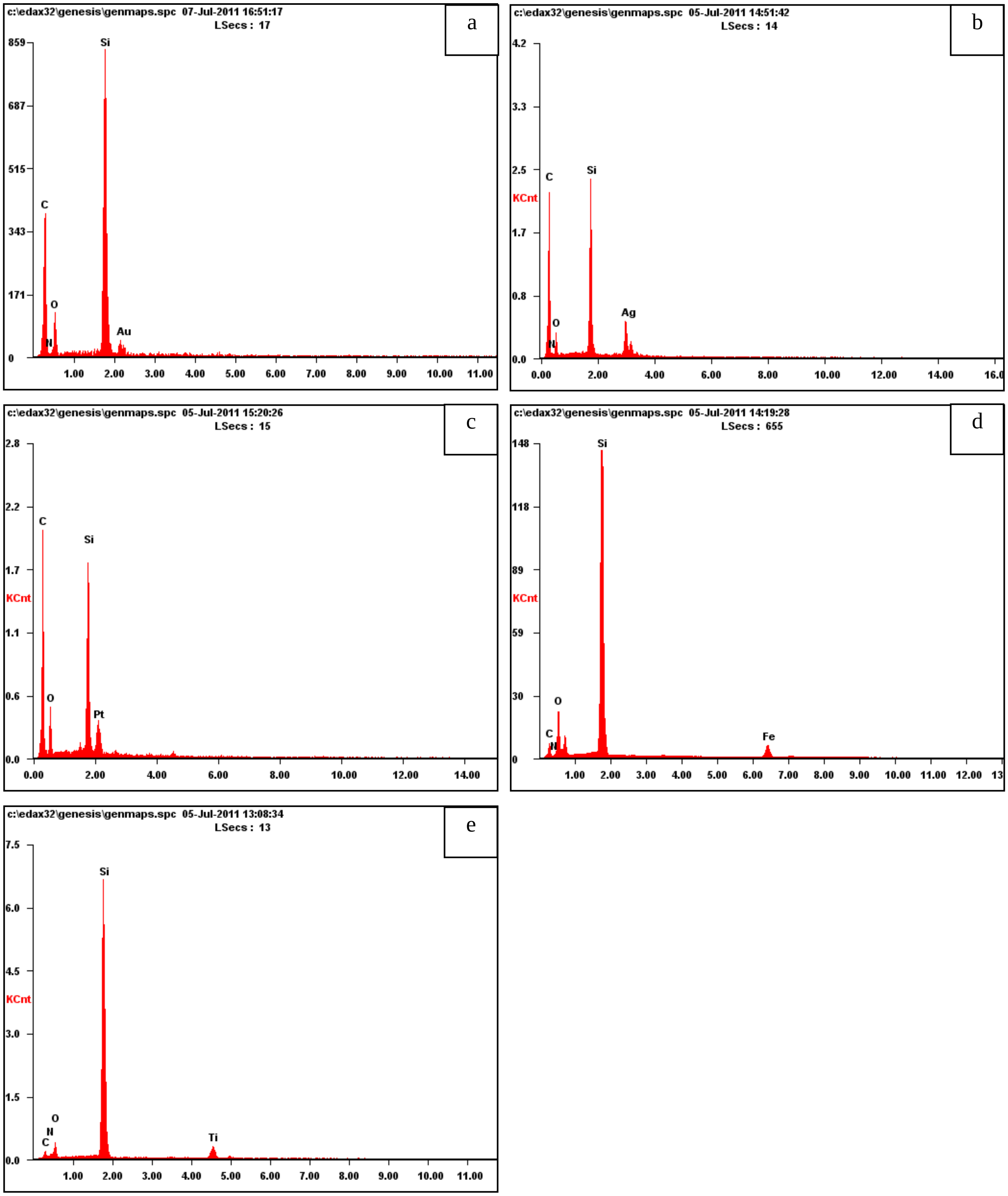


Fig S5 XRD pattern of Au/PDA/RGO nanocomposites

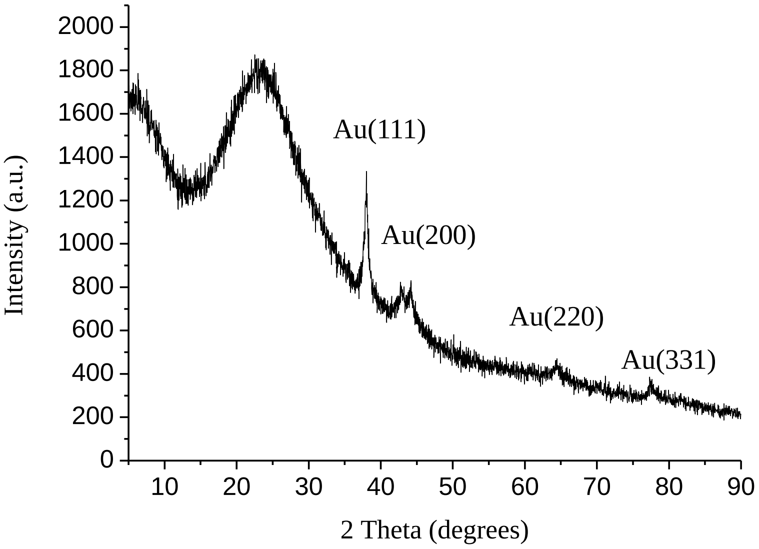


Fig. S6 Typical TEM images of Au/GO nanocomposites

The preparation method of Au/GO nanocomposites was the same with that of Au/PDA/RGO nanocomposites except PDA/RGO was substituted by GO. The concentration of chloroauric acid was 1 μg/mL (sample a), 5 μg/mL (sample b) and 20 μg/mL (sample c) during the preparation of Au/GO nanocomposites at the presence of 0.028 mg/mL GO. The particle size distribution of Au NPs on pure GO was much broader than that on PDA/GO in the same reaction condition, and some Au NPs even come to aggregation.

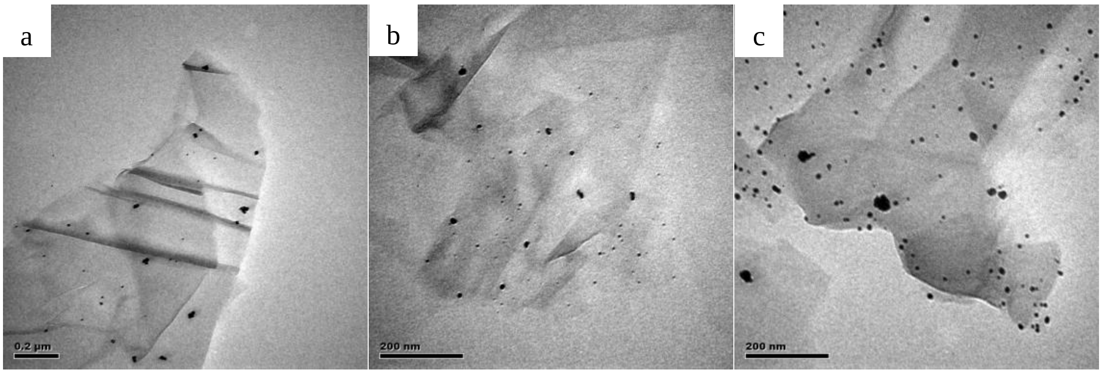


Fig. S7 XRD pattern of Fe_3O_4/PDA/RGO nanocomposites

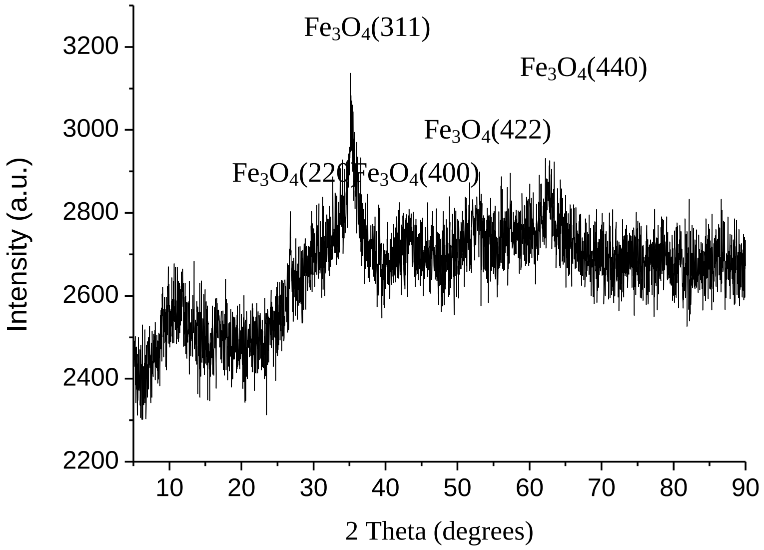


Fig. S8 Photographs of PDA/RGO ethanol solution before (a) and after (b) hydrolysis of titanium(IV) isopropoxide with water.