Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B

Biopolymer functionalized reduced graphene oxide with enhanced biocompatibility via mussel inspired coatings/anchors

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Supporting Information

Preparation of graphene oxide (GO)

Graphene oxide (GO) was prepared from natural graphite flakes by a modified Hummers method. 2.5 g graphite and 1.875 g $NaNO_3$ were placed in a flask. Then, 75 mL H_2SO_4 was added with stirring in an ice-water bath, and 10 g $KMnO_4$ was slowly added over about 1 h. The mixture was stirred in the ice water bath for 2 h, following by a vigorously stirring for 3 days at room temperature. Then, the mixture was diluted with D.I. water (700 mL) slowly, and the excess $KMnO_4$ was decomposed by H_2O_2 (30 wt. %, 15 mL). The insoluble precipitations were removed by centrifugation. Then, the resulted GO solution was filtered and washed with HCl (10 wt. %, 1 L) and

D.I. water for several times to remove the metal ions. The pristine brown GO solution was dialyzed with deionized water for 1 week before use to remove any residual salts and acids.

Preparation of hydrazine-RGO

In a typical procedure for hydrazine reduced RGO, 25 mg GO was added into 100 mL D.I. water then sonication for 20 min to obtain a homogeneous GO dispersion (0.25 mg/mL). Afterthat, the pH of GO dispersion was adjusted to 12 by ammonia solution, then 100 μL of hydrazine solution (50% w/w) were added to the resulting GO dispersion. After being vigorously stirred for a few minutes, the mixture was then stirred at 90 °C for 1 h. Finally, the black hydrazine-RGO dispersion was centrifuged three times.

Characterization:

AFM images of GO and RGO samples were acquired using a Multimode Nanoscope V scanning probe microscopy (SPM) system (Bruker, USA). The commercially available AFM cantilever tips with a force constant of ~50 N/m and resonance vibration frequency of ~350 kHz (Bruker, USA) were used. TEM images and selected area electron diffraction (SAED) patterns were acquired using a Tecnai G2 F20 S-TWIN transmission electron microscope (FEI Ltd., USA) operated at 200 kV. The specimens of TEM were prepared by placing the aqueous suspension (~0.05 mg/mL) of the supentions on the copper grids and dried under ambient conditions. Absorption spectra were measured by an UV-vis spectrometer (UV-1750, Shimadzu Co., Ltd, Japan). The FTIR spectra were acquired on a FTIR spectrometer (Nicolet

560, USA). The specimens for FTIR measurement were prepared by grinding the dried powder of GO or RGO with KBr together and then compressed into thin pellets. The X-ray powder diffraction patterns were recorded on a BRUKER-AXS diffractometer (Bruker, Germany) using Cu Ka radiation (λ = 0.154 nm). The X-ray photoelectron spectroscopy measurements were performed on X-ray photoelectron spectroscopy (XSAM800, Kratos Analytical, UK) using monochromated Al Kα (1486.6 eV) as radiation source. Dynamic light scattering (DLS) and zeta potential measurements of the aqueous dispersion of the as-prepared RGO were performed using Zetasizer ZS90 (Malvern Instruments Ltd, UK). The as-prepared RGO (~ 0.01 mg/mL) were dispersed in D.I. water and 0.1 M PBS (pH 7.4), respectively. Each measurement was repeated at least three times. Thermo-gravimetric analysis (TGA) spectra of the as-prepared RGO powders were obtained by using TG 209 F1 Iris (NETZSCH, Germany) from 50 °C to 800 °C, heated at 10 °C /min under a dry N_2 atmosphere.

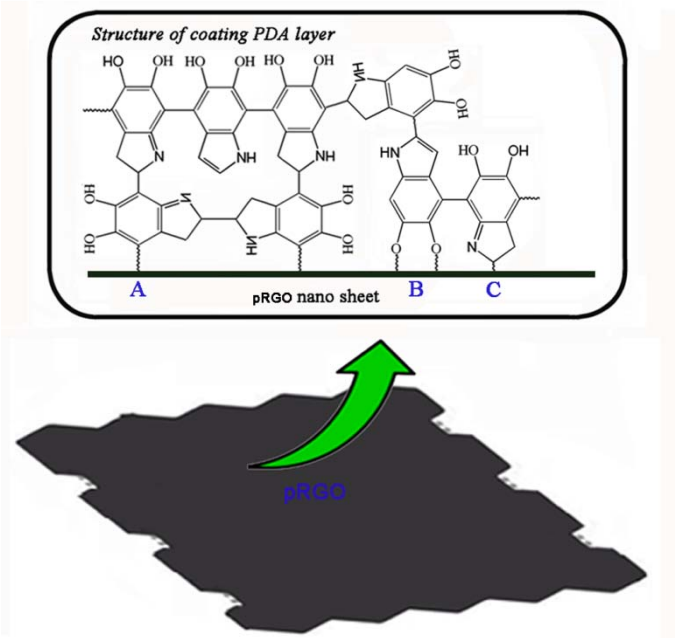

Figure S1. The suggested chemical form of the adhered polydopamine based on earlier reports [1, 2], the DA can generate a lot free radicals during the pH induced oxidization and polymerization, which can directly attached to the sp^2 hybridized or double bonds of RGO.

1. Chemical functionalization of graphene sheets by solvothermal reduction of a graphene oxide suspension in N-methyl-2-pyrrolidone, J. Mater. Chem., 2011, 21, 3371.

2. General Avenue to Individually Dispersed Graphene Oxide-Based Two-Dimensional Molecular Brushes by Free Radical Polymerization, Macromolecules, 2011, 44, 444.

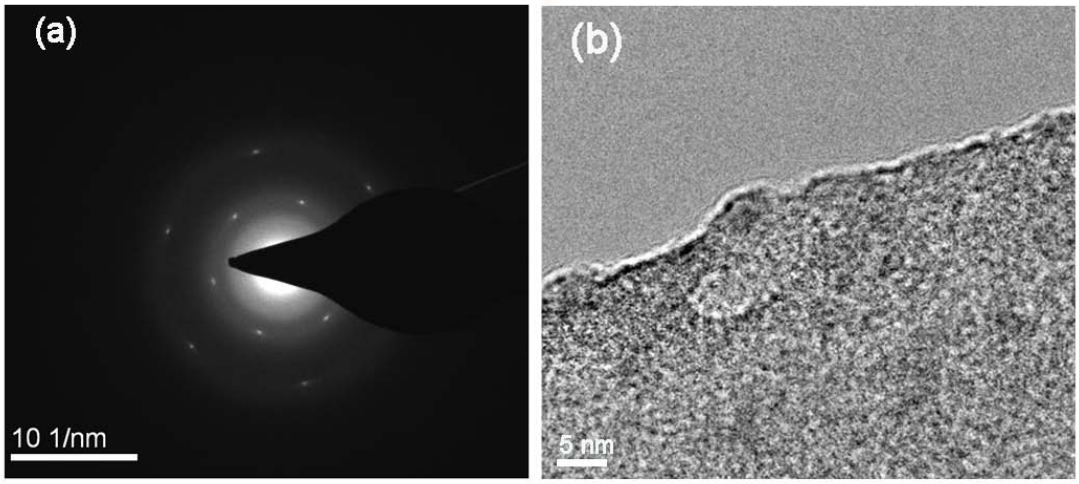

Figure S2. Corresponding SAED pattern (a) and HRTEM image (b) of pRGO, and the well-defined six-fold-symmetry diffraction pattern, which is expected for the chemical reduced RGO nanosheets, is observed. The folded edge structure of the HRTEM image indicates that the pRGO is assembled by PDA coated single-layer RGO; meanwhile, the pRGO exhibits a single-sheet structure with no aggregation.

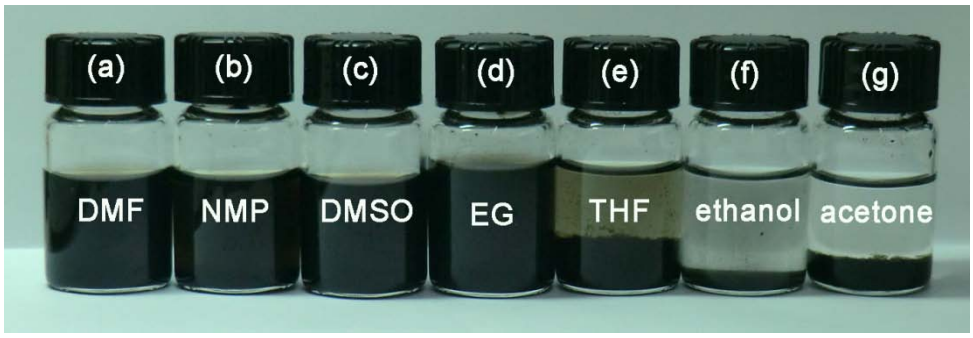

Figure S3. Photographs of the dispersions (0.2 mg/mL) for pRGO in various organic solvents after storage for 3 days; (a) N,N-dimethylformamide (DMF) ,(b) N-methyl pyrrolidone (NMP) , (c) dimethyl sulfoxide (DMSO), (d) ethylene glycol (EG), (e) tetrahydrofuran (THF), (f) ethanol, and (g) acetone.

It was found that the pRGO could be stable in various organic solvents such as DMF, NMP, DMSO, EG; but it could not be stable in THF, ethanol, and acetone. The

readily dispersible ability of pRGO in various solvents should benefit from the presence of a large amount of catechol and imine groups on the surfaces of the pRGO sheets. The high stability and abundant functional groups of the pRGO might make it a better candidate than RGO as a 2D template for polymer grafting or polymerization in organic solvents.

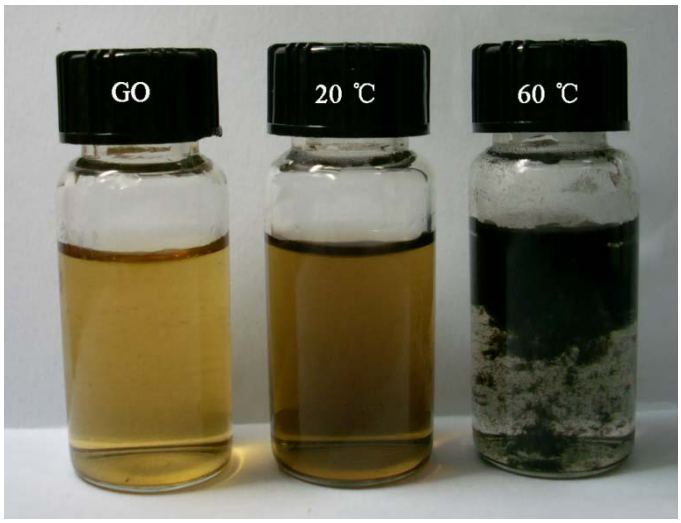

Figure S4. Photographs of GO aqueous solutions after adding dopamine for 4 h at different temperatures (concentration of these three GO suspensions in D.I. water = 0.15 mg/mL, and dopamine = 0.5 mg/mL). At 20 °C, the suspension was still yellow brown after 4 h, which indicated that GO was not reduced significantly. However, when the reaction temperature increased to 60 °C, the GO suspension became black and water insoluble, which indicated that the hydrophobic nature of RGO was restored and the GO was reduced significantly by dopamine with heating.

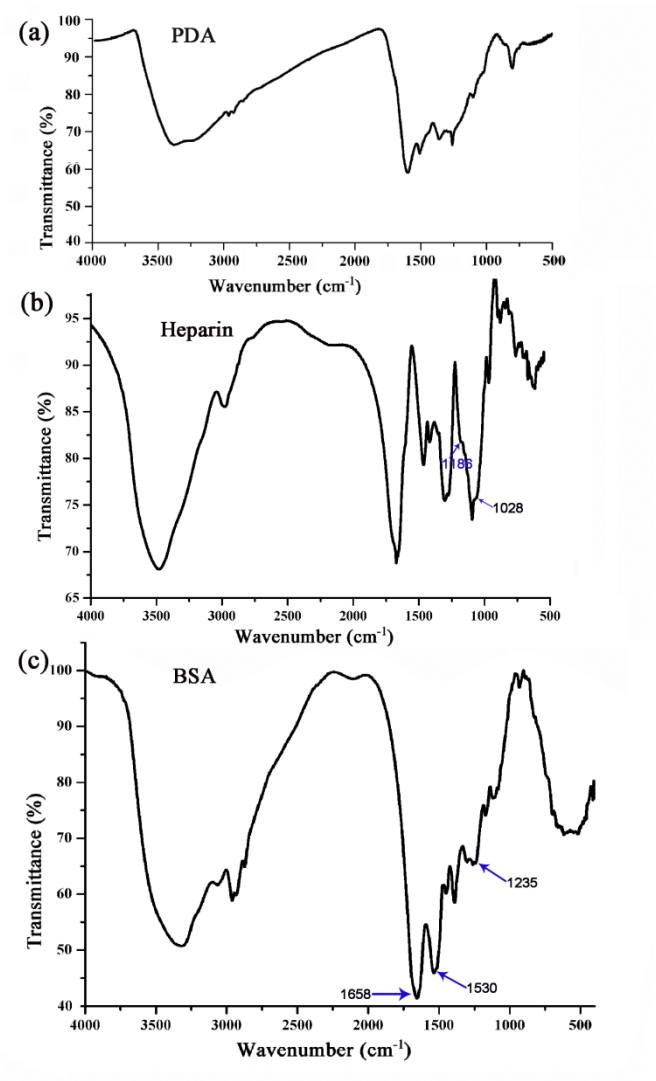

Figure S5. FTIR spectra for pure PDA (a), pristine heparin powder (b), and pristine BSA powder (c).

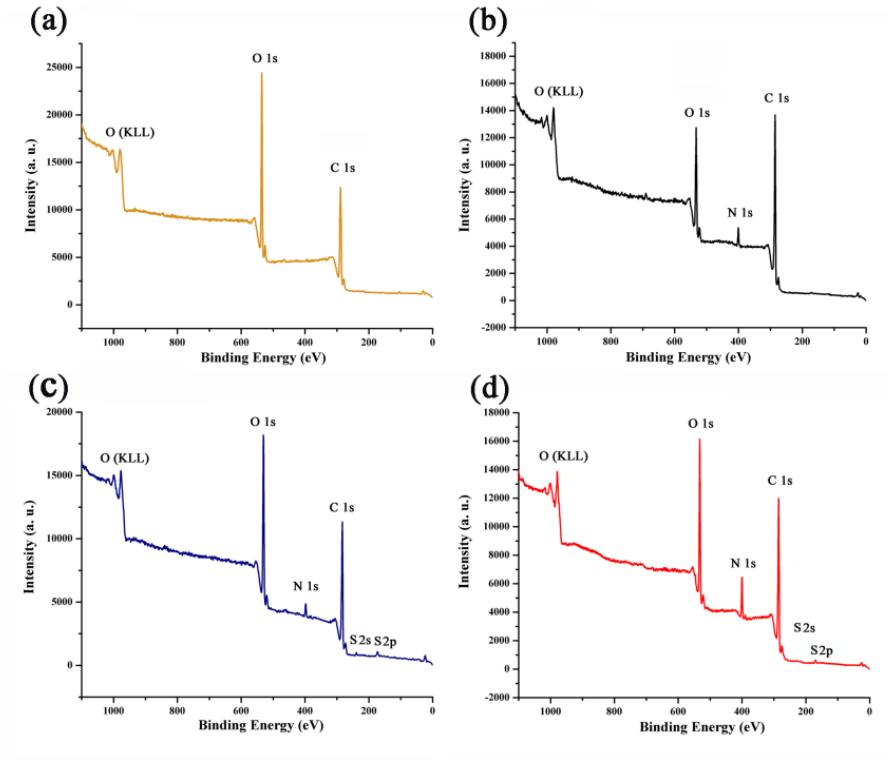

Figure S6. XPS spectra for (a) GO, (b) pRGO, (c) Hep-g-pRGO, and (d) BSA-g-pRGO.

The existence of the S_{2s} and S_{2p} peaks in Hep-g-pRGO confirmed the successful grafting of heparin compared with the XPS spectrum of pRGO. Meanwhile, the increased intensity of the N_{1s} for BSA-g-pRGO indicated that BSA had been immobilized successfully.

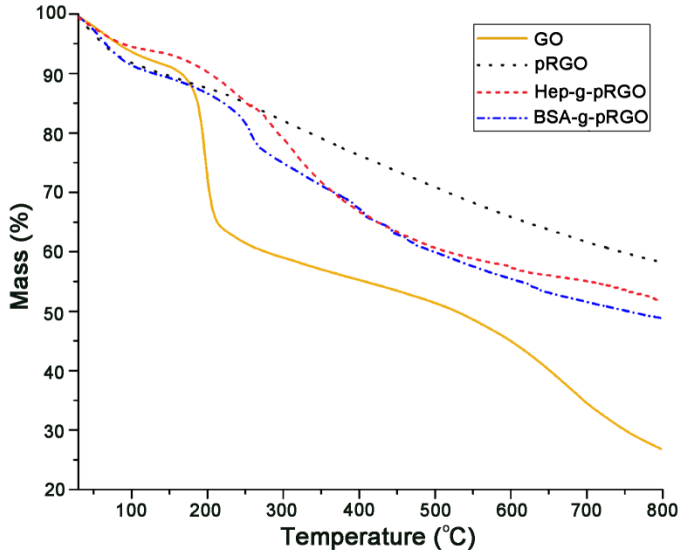

Figure S7. Thermogravimetric (TGA) curves for GO, pRGO, Hep-g-pRGO, and BSA-g-pRGO at a nitrogen atmosphere.