Supporting Information

Materials and Measurement

- GO, RGO, G-PSS (poly (sodium 4-styrenesulfonate) modified GO), and G-PAH (poly 5 (allylamine hydrochloride) modified GO) were prepared as previous reports.^[1] The details are described as follows. Graphite (1.0 g) was added to concentrated sulfuric acid (23.3 mL) under stirring at room temperature, then sodium nitrate (0.5 g) was added, and the mixture was cooled to 0 °C. Under vigorous agitation, potassium permanganate (3.0 g) was added slowly to keep the temperature of the suspension lower than 20 °C. Successively, the 10 reaction system was transferred to a 35°C water bath and stirred for about 0.5 h. Then, 50 mL of water was added, and the solution was stirred for 15 min at 90 °C. Additional 170 mL of water was added and followed by a slow addition of 5 mL of H₂O₂ (30%), turning the color of the solution from dark brown to yellow. The mixture was filtered and washed with 1:10 HCl aqueous solution (100 mL) to remove metal ions followed by washing with
- 15 150 mL of water to remove the acid. The resulting solid was diluted to make a GO aqueous dispersion. Finally, it was purified by dialysis to remove the remaining metal species. In a typical procedure for chemical conversion of GO to RGO, 10 mL GO dispersion (0.25 mg/mL) was mixed 5µl of hydrazine solution (35 wt%) and 35.0µl of ammonia solution (28 wt%). After being vigorously shaken or stirred for a few minutes, the vial was put in a
- 20 water bath (95°C) for 1 h. Finally, it was purified by dialysis to remove the remaining hydrazine. The G-PAH was prepared by vigorously stirring a solution of 20 mg of the GO, 100 mg of PAH, and 100 mg of KOH in 50 mL of H₂O at 70 °C for 24 h. Then 10 mL of 1M NaBH₄ solution was added, and the reaction was kept on at 70 °C for 2 h. After that, the G-PAH was collected and purified by centrifugation and adequately washed with water
- 25 several times to remove the impurities and the excess of PAH by physical absorption. G-PSS was prepared by vigorously stirring a solution of GO (1mg/mL) with poly(sodium 4-styrenesulfonate) (PSS) (Mw = 70000, 10 mg/mL) in the present of hydrazine hydrate at 100 °C for 24 h. G-PSS was collected and purified by centrifugation and washed with water several times to remove the excess of PSS.

Cytochrome c was purchased from Sigma-Aldrich Company. Other chemicals were of analytical reagent grade and used without further purification. All water used to prepare buffer solution was obtained by using a Milli-Q water system. The Time-course experiments were carried out on a JASCO V-550 UV/Visible spectrophotometer. The 5 circular dichroism (CD) spectra were carried out on a JASCO J-810 spectropolarimeter. Samples for AFM images were prepared by depositing a dispersed GO (RGO)/cyt c

solution onto a freshly cleaved mica surface and allowing them to dry in air.





Fig. S1 UV/Vis spectra of GO and RGO. The insert is photo of GO and RGO.

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Fig. S2 FTIR of GO and RGO.



Fig. S3 AFM images of GO and RGO (a,b) and the height of GO and RGO (c,d). $10\,$



Fig. S4 The peroxidase activity of cyt c, GO, RGO, G-PSS and G-PAH. The concentrations of cyt c, ABTS and H_2O_2 used are 0.2µM, 0.5mM and 6mM. The concentrations of graphene materials are 0.6 µg/mL, respectively.

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Fig. S5 the peroxidase activity of cyt c in the presence of 0.6 μ g/mL GO, G-PSS and G-PAH. The concentrations of cyt c, ABTS and H₂O₂ used are 0.2 μ M, 0.5mM and 6mM.



Fig. S6 CD spectra of cyt c in the presence of G-PSS and G-PAH. The concentrations of cyt c, GO and RGO used are $2\mu M$, $8\mu g/mL$ and $8\mu g/mL$.

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