

Supporting Information for

Self-assembly of natural tripeptide glutathione triggered by graphene oxide

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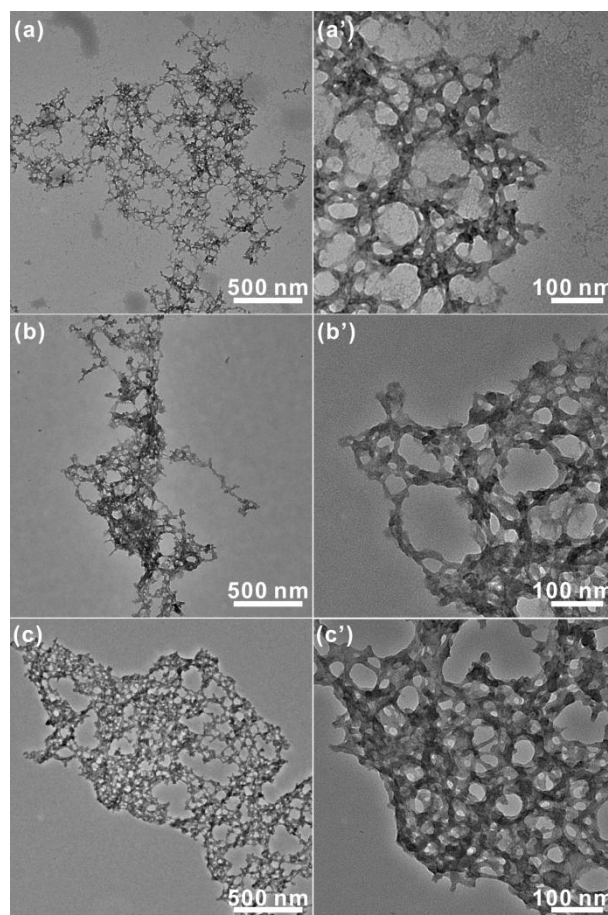


Figure S1. TEM images of GSH gel of 80 mM (a), 53.3 mM (b) and 40 mM (c), respectively. The images on the right were the enlarged view of the left.

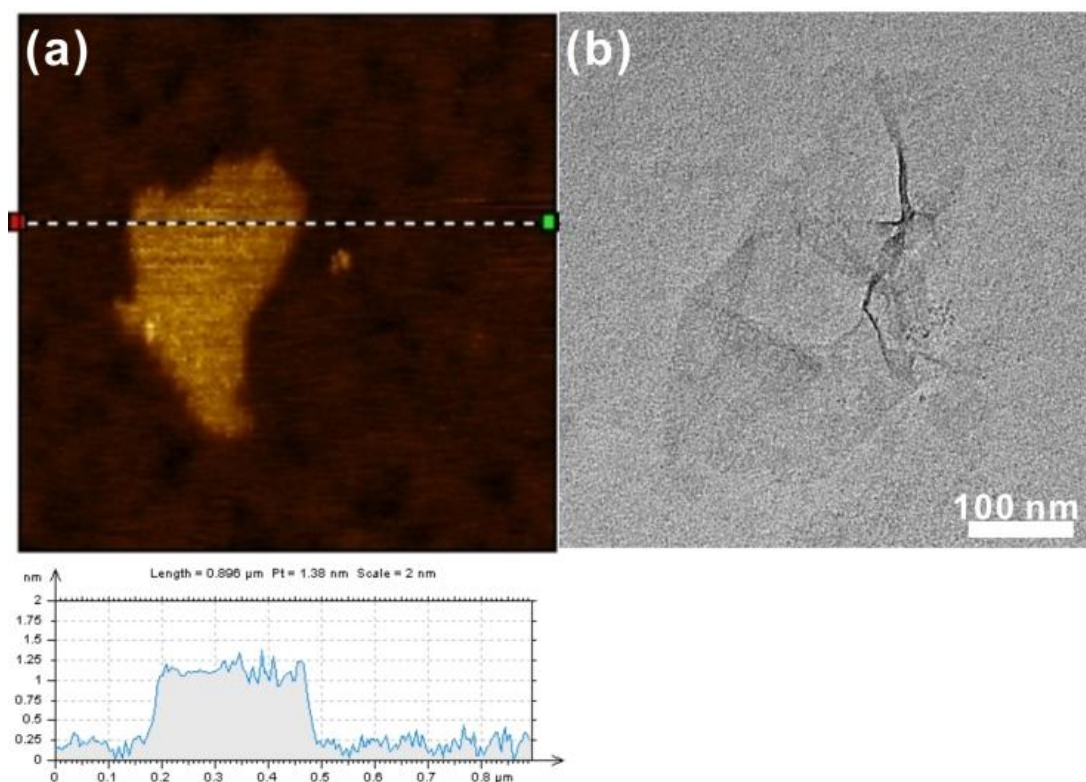


Figure S2. (a) A tapping mode AFM image of exfoliated GO sheet with height profiles. (b) TEM of exfoliated GO sheet.

The graphite oxide was synthesized by using the modified Hummers' method through oxidation of graphite powder. The graphite oxide solution was then suffered sonication to give solutions of exfoliated GO. GO was reduced to RGO by ammonia solution at 95 °C. AFM data in Figure S2(a) presented that the thickness of single GO sheet was about 1 nm, which was expected to be thicker than a pristine graphene sheet with a well-known Van der Waals thickness of ~0.34 nm. It was due to the presence of oxygen functional groups and the displacement of the sp^3 -hybridized carbon atoms slightly below and above the original graphene plane.^{S1} TEM image in Figure S2(b) showed a shrinking GO sheet with a size about 500 nm, similar to the result from AFM.

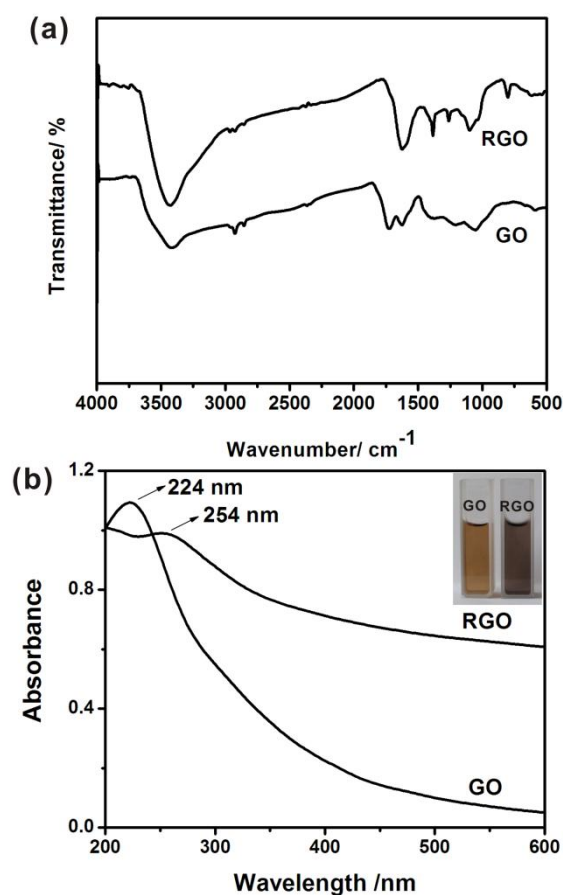


Figure S3. FTIR (a) and UV-vis spectra (b) of GO and RGO. Inset: a photograph of GO and RGO suspensions show the visible color difference.

The FTIR spectrum of GO in Figure S3(a) showed a strong absorption peak at 1725 cm^{-1} , due to the C=O stretching vibration, a peak at 1623 cm^{-1} due to aromatic C=C, as well as peaks due to carboxylic C-O at 1411 cm^{-1} , epoxy C-O at 1224 cm^{-1} , and alkoxy C-O at 1058 cm^{-1} located at the GO nanosheets. The broad band at 3421 cm^{-1} could be assigned to the O-H stretching vibration.^{S2,S3} In comparison to GO, the peaks at 1725 cm^{-1} of RGO almost disappeared, indicating the vibration band for carboxylic acid was significantly reduced after reduction of GO sheets. The peak located at 1621 cm^{-1} could be assigned to the skeletal vibration of graphitic domains.^{S4} UV-vis spectrum (Figure S3(b)) showed the absorption peak of the GO dispersion at 224 nm

red shifted to 254 nm for RGO, suggesting that the electronic conjugation within the graphene sheets was restored upon reduction.^{S2}

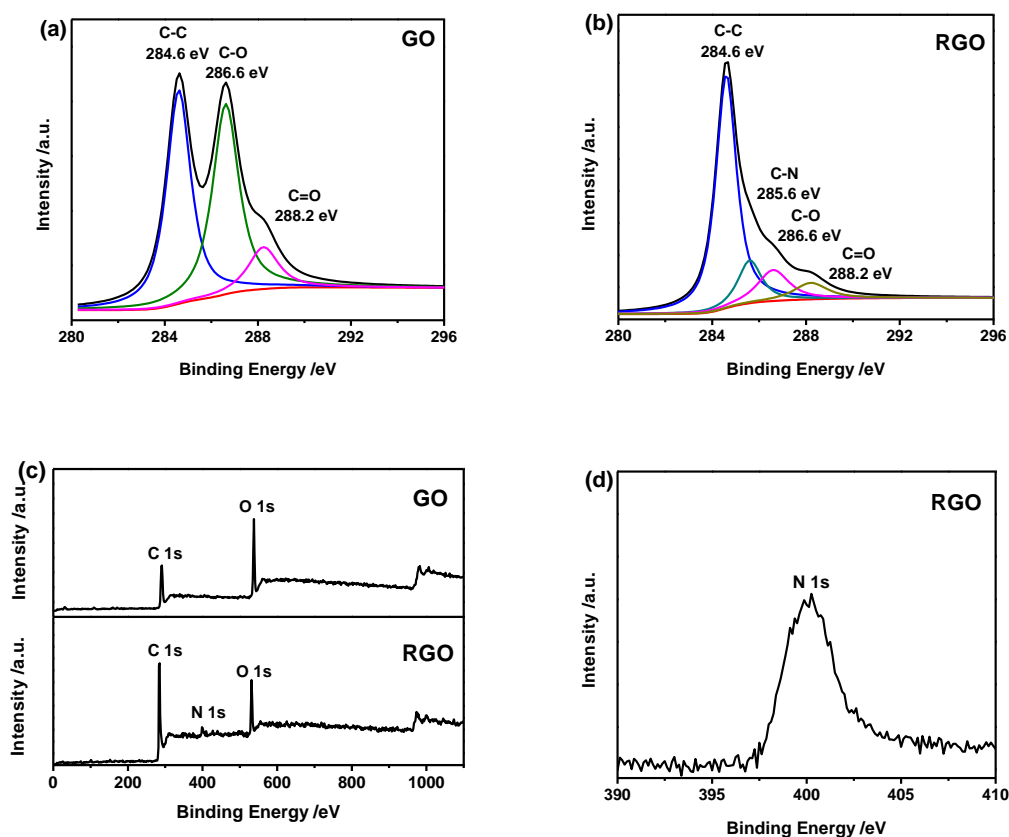


Figure S4. High-resolution C1s XPS spectra of GO (a) and RGO (b) showing significant loss of C-O and C=O groups after reduction, survey scan XPS spectra of GO and RGO (c) showing a small quantity of N doping of RGO, high-resolution N1s spectrum of RGO (d) confirming N incorporation of RGO.

Figure S4 shows the high resolution and survey scan XPS spectra of GO and RGO. It can find that the O/C ratio in the exfoliated GO decreases remarkably after the reduction, and that most of the oxygen functional groups were successfully removed.

Peak fitting of C1s band for GO yields three components located at 284.6 eV, 286.6 eV, and 288.2 eV (Figure S4a). The component at 284.6 eV is assigned to carbons in unoxidized, aromatic sp^2 structures, where as the one at 286.6 eV can be attributed to carbons in hydroxyl and epoxy groups (C-O bonds) and also possibly to C-C bonds in defected structures. The 288.2 eV component can be ascribed to carbons in C=O structures i.e., carbonyl groups. In the case of RGO, the 285.6 eV component can be attributed to C-N bonds (Figure S4b).^{S5} Table S1 presents the information of the area percentages of peaks of C1s XPS spectra of GO and RGO, indicating the significant loss of oxygen groups after reduction.

TABLE S1. The Area Percentages of Peaks of C1s XPS Spectra of GO and RGO

	C-C	C-O	C=O	C-N
GO	45.44%	43.62%	10.94%	—
RGO	65.70%	13.20%	7.50%	13.60%

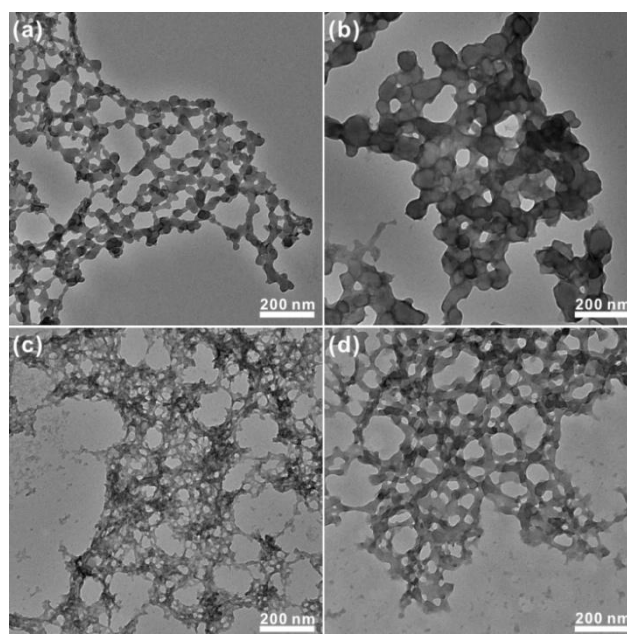


Figure S5. TEM images of GSH/GO gel with different contents of GO (a) 0.5 wt%, (b) 4.0 wt%, (c) 9.0 wt%, and (d) 17.0 wt%, respectively.

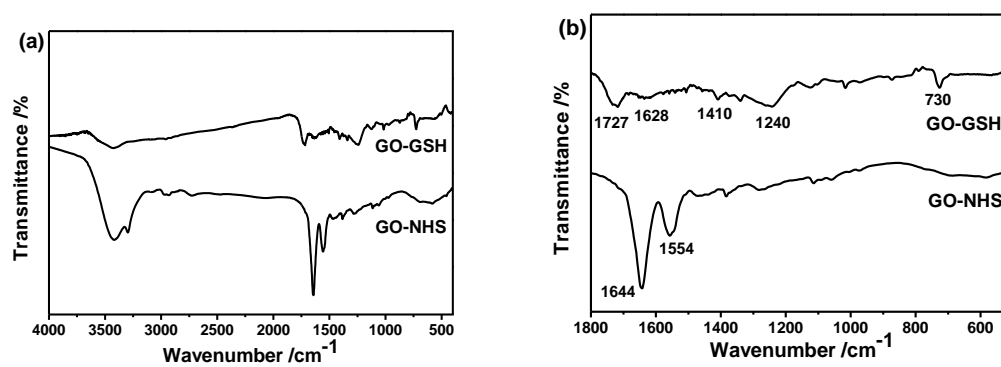


Figure S6. (a) FTIR spectra of GO-NHS and GO-GSH. (b) is the narrow spectra in 1800-500 cm^{-1} .

FTIR spectrum of GO-NHS has two prominent and sharp peaks at about 1644 cm^{-1} and 1554 cm^{-1} which are the amide I and II bands, respectively. The broad band at 3421 cm^{-1} could be assigned to the O-H stretching vibration. The band at 3301 cm^{-1}

was attributed to N-H stretching vibration. This result indicates that NHS was binding to GO after the reaction. The FTIR spectrum of GO-GSH in Figure S6 is similar to that of GO in Figure S3a, except for red shifts at 1727 cm^{-1} (C=O stretching vibration), 1628 cm^{-1} (aromatic C=C stretching vibration) and 1240 cm^{-1} (epoxy C-O stretching vibration), respectively. It is probably due to the binding of GO with small amount of GSH.

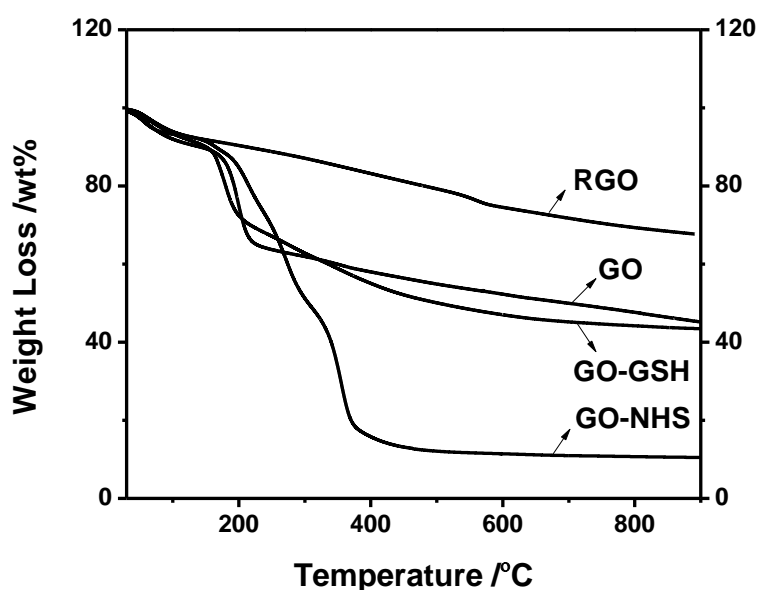


Figure S7. TGA curves of GO, RGO, GO-NHS and GO-GSH, respectively.

GO is thermally unstable and starts to lose mass upon heating below 100 °C (Figure S7), which can be attributed to the loss of adsorbed water. The major mass loss occurs at 200 °C , presumably due to pyrolysis of the labile oxygen-containing functional groups.^{S1} The content of these groups is estimated to be 48 wt%. On the other hand, the removal of the oxygen functional groups by chemical reduction results in much increased thermal stability for the RGO. Apart from a slight mass loss below 100 °C , the mass loss of RGO was much less than that of GO when RGO is heated up

to 900 °C. GSH content in GO-GSH can be estimated to be 3 wt% with two mass loss at about 200 °C and 400 °C attributed to GSH moieties. The two mass loss peaks at about 200 °C and 330 °C of GO-NHS are arising from the pyrolysis of the oxygenated functional groups and NHS moieties respectively.

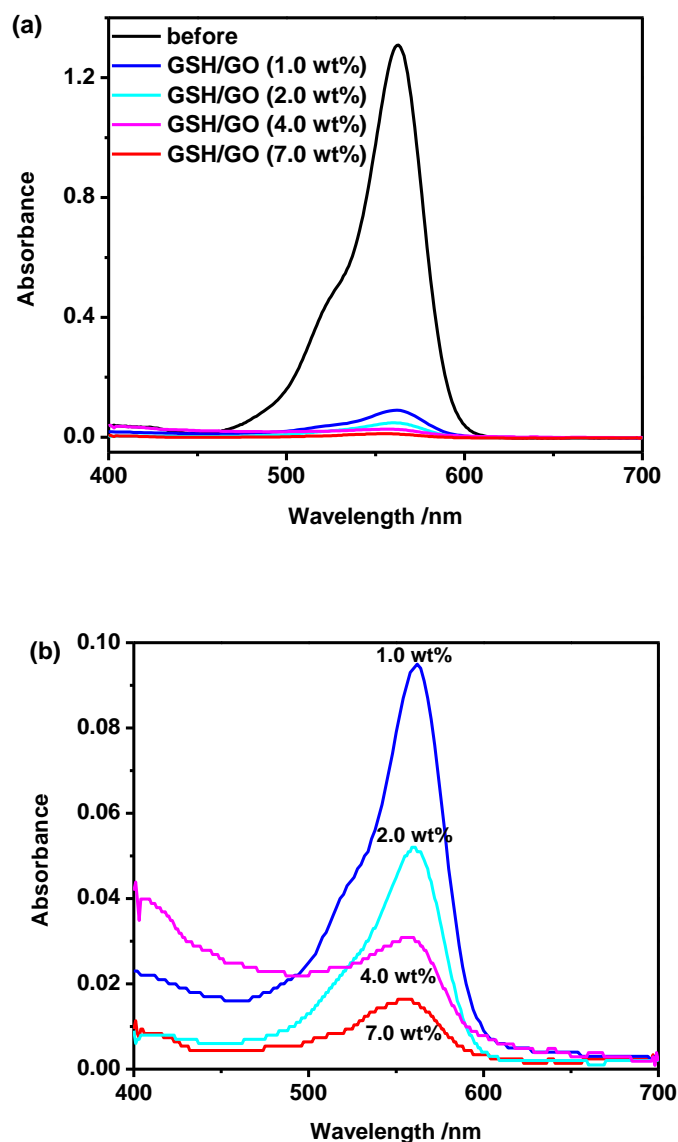


Figure S8. Absorption spectra of Rhodamine B before and after adsorption by GSH/GO gel with different contents of GO (a). (b) is the enlarged view.

Supplementary References

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