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Supporting Information

A general route to enhance the fluorescence of graphene quantum dots by Ag nanoparticles

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Experimental Section

1 Materials

Graphene oxide (GO) was prepared from natural graphite (Wodetai Ltd. Co., Beijing, China, 99.9%) by a classical Hummers method with some modification. Silver nitrate (A.R. ≥99.8 %) was purchased from Xi'an chemical reagent factory. Other solvents were used directly as received without further purification.

2 Synthesis of GO

In a typical synthesis, 3 g graphite powder was put into an 80 °C solution of 12 mL concentrated H_2SO_4, 2.5 g $K_2S_2O_8$, and 2.5 g P_2O_5. Then the mixture was kept at 80 °C for 5 h in a water bath. Successively, the mixture was cooled to room temperature and diluted with 500 mL H_2O and left overnight. After that, the mixture was filtered and washed with H_2O using a 0.45 μm Millipore filter to remove the residual acid. Then the product was dried in a vacuum oven at room temperature. This pre-oxidized graphite was then subjected to oxidation by Hummers' method described as follows. Pre-oxidized graphite powder was put into cold (0 °C) 120 mL concentrated H_2SO_4. Then, 15 g $KMnO_4$ was added 1 g at a time under stirring and the temperature of the mixture was kept to be below 20 °C by cooling in ice. Successively, the mixture was stirred at 35 °C for 2 h, and then carefully diluted with 250 mL of H_2O. After that, the mixture was stirred for another 2 h, and then additional 700 mL of H_2O was added under stirring followed by 20 mL of 30% H_2O_2. The resulting brilliant-yellow mixture was filtered and washed with 10 wt% HCl aqueous solution (1000 mL) to remove metal ions and washed repeatedly with H_2O to remove the acid until the pH of the filtrate was neutral. The resulting GO slurry was dried in a vacuum oven at 60 °C.

3 Synthesis of Graphene Quantum Dots (GQDs)

GO was dissolved in DMF with the concentrations of 10 mg/mL, and the GO/DMF solutions were under ultrasonication for 30 minutes. Then, the solutions were transferred to a poly(tetrafluoroethylene) (Teflon)-lined autoclave (50 mL)

and heated at 200℃ for 8 h. After this reaction, the reactors were cooled to room temperature naturally. The supernatant brown transparent suspension was collected after continuous dispersing black precipitates in DMF and centrifuging until the supernatant suspension became colorless transparent. The solid samples can be obtained by evaporating the solvents, and the yield was about 1%.

4 Synthesis of Ag/GQDs composite

In a typical synthesis, 20 mL DI water was added into 20 mL GQDs dispersion (0.1 mg/mL) in DMF under magnetic stirring. Meanwhile, 4 mL $AgNO_3$ aqueous solution (1 mg/mL) was added dropwise into the above solution and stirred for 10 min to ensure complete mixing. After that, the reaction was allowed to proceed under magnetic stirring at 150 °C in oil bath for 3 h. The solid samples can be obtained by evaporating the solvents.

5 Characterization

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were obtained with a JEM-2100 transmission electron microscope (Japan Electron Optics Labortary Co., Ltd., JEOL) with an accelerating voltage of 200 kV. The sample for TEM characterization was prepared by placing a drop of colloidal solution on carbon-coated copper grid and dried at room temperature. UV-vis spectra were recorded on a Jasco V-570 UV/VIS/NIR spectrophotometer at room temperature. PL studies were done using a Gilden Photonics photoluminescence spectrophotometer, the slit widths at the excitation and the emission of the spectrofluorimeter are 5 and 2 nm, respectively.

6 Quantum Yield (QY) Measurements

Rhodamine B in water (literature[S1] quantum yield 0.31) was chosen as a standard. The quantum yield of GQDs and Ag/GQDs in DMF was calculated according to:

$$\Phi = \Phi_r \times (A_r / I_r) \times (I / A) \times (n^2 / n_r^2)$$

Where Φ is the quantum yield, I is the measured integrated emission intensity, n is the refractive index (1.33 for water, 1.43 for DMF), and A is the optical density. The subscript "r" refers to the reference fluorophore of known quantum yield. In order to minimize re-absorption effects, absorbencies in the 1 cm fluorescence cuvette were kept under 0.1 at the excitation wavelength of 360 nm.

Sample	Integrated emission intensity (I)	Abs. at 560 nm (A)	Refractive index of solvent (n)	Quantum Yield (Φ)
Rhodamine B	13013000	0.09817	1.33	0.31
GQDs	83766	0.05991	1.43	0.0038
GQDs/Ag	4717400	0.07816	1.43	0.163

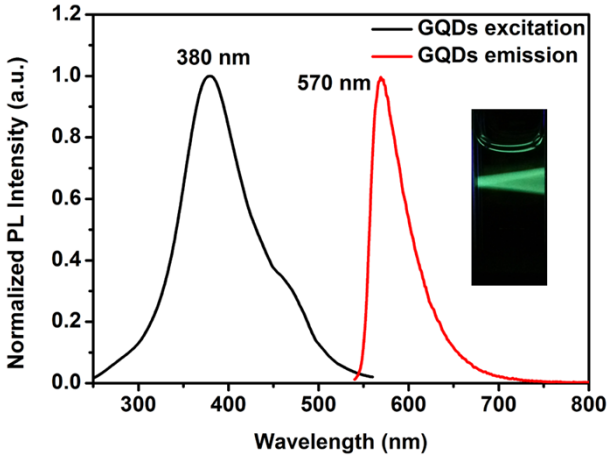

Fig. S1 Normalized optical excitation and emission PL spectra of GQDs, inset: corresponding photograph taken under 380 nm excitation.

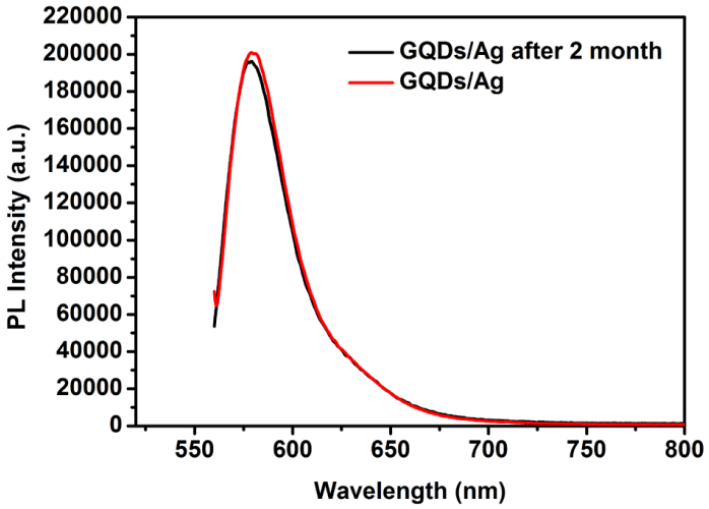

Fig. S2 The long-term stability of GQDs/Ag composite.

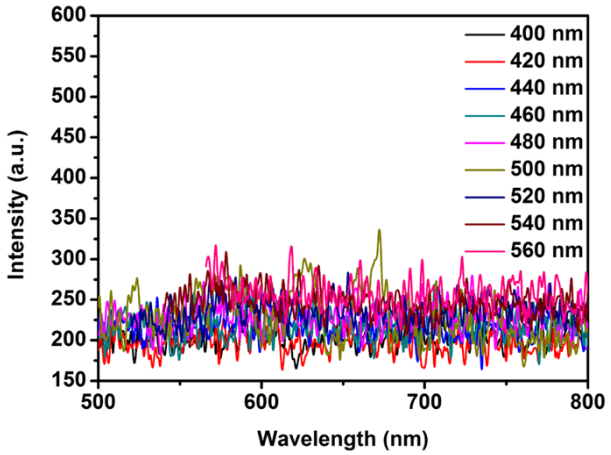

Fig. S3 PL spectra of Ag nanoparticles at different excitation wavelength.

References

(S1) Magde, D.; Rojas G. E.; Seybold, P. G. *Photochem. Photobiol.* **1999**, *70*, 737-744.