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Supplementary Information

The strong dependence for bi-functionalities of core-shell-like gold-based nanocomposites on the size of gold nanoparticles

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1. Experimental section

1.1. Materials

Chloroauric acid (99%, $HAuCl_4$) was purchased from Shanxi Kaida Chemical Engineering Company. The derivative of glycine (G_6, 99%) was purchased from Shanghai Bioscience & Technology Company. Sodium citrate (99%, $C_6H_5Na_3O_7\cdot H_2O$), sulfuric acid (98%, H_2SO_4), hydrochloric acid (99%, HCl), sodium hydroxide (99%, NaOH), hydrogen peroxide (30%, H_2O_2) and graphite powder (>99.85%) with an average size of 30 μm and other chemicals were purchased from Shanghai Chemical Reagent Company. All the reagents were used without further purification. Deionized water was used throughout the experiments.

1.2. Synthesis of AuNPs

The AuNPs with various sizes were synthesized based on a reported literature.[1] The typical process was as the followed.

Synthesis of Au Seeds: A solution of 2.2 mM sodium citrate in Milli-Q water (150 mL) was added into a 250 mL three-necked round-bottomed flask, and then heated for 15 min with a heating mantle under vigorous stirring. A condenser was utilized to prevent the evaporation of the solvent. After it boiled, 1 mL of $HAuCl_4$ (25.38 mM) was injected. The color of the solution changed from yellow to bluish gray and then to soft pink in 10 min. The resulting particles (~10 nm) were coated with negatively charged citrate ions and hence were well dispersed in H_2O.

Seeded growth of a series of Au NPs: After the synthesis of the Au seeds, it was cooled until the temperature of the solution was nearly 90 °C. Then, 985 μL of a $HAuCl_4$ solution (25.38 mM) was injected into the solution. After 30 min, the process was repeated again. After that, the sample was diluted by extracting 55 mL of sample and adding 53 mL of MQ water. When the temperature of the solution was nearly 90 °C, 2 mL of 60 mM sodium citrate was added into above solution (time delay ~2 min). After 5 min, 985 μL of a $HAuCl_4$ solution (25.38 mM) was injected. After 30 min, 985 μL of a $HAuCl_4$ solution (25.38 mM) was also injected. By repeating this process (sequential addition of 2 mL of 60 mM sodium citrate and 985 μL of 25 mM $HAuCl_4$), up to 15 generations of gold particles of progressively larger sizes were grown. Finally, according to the surface plasmon resonance peaks of various AuNPs, the obtained dimensions of AuNPs were 32 nm, 50 nm, 68 nm, 87 nm and 107 nm, respectively. The excess sodium citrate was removed by centrifugation and then redispersed in H_2O.

1.3. Preparation of GQDs

GO was prepared by a modified Hummers method.[2] GQDs were prepared by using GO as the main reactant.[3] In brief, 250 mg of GO was dissolved in 15 mL of DMF and sonicated for 30 min. Then, the GO/DMF mixture was transferred to a poly (tetrafluoroethylene) (Teflon)-lined autoclave and kept at 200 °C for 5 h. Then, the reactor was cooled down to room temperature. The product contained brown transparent suspension and black precipitate. The black precipitate was removed by suction filtration, and the filtrate was purified by column chromatography on silica gel, using water as the eluent. The eluent was concentrated by the rotary evaporator, and then the GQDs aqueous solution was achieved.

1.4. Preparation of $Au_x/G_6/GQDs$

The preparation procedure for the $Au_x/G_6/GQDs$ composite was as followed. In brief, 3 mL of 4.79×10^{-5} M G_6 solution was added into 100 μL of Au_x (x represents the diameter of AuNPs, it is 32, 50, 68, 87 and 107 nm, respectively) aqueous solution, respectively, and incubated for 30 min, and then washed for three times with deionized water to remove excess G_6. After that, 100 μL of GQDs (0.1 mg mL^{-1}) was added into the Au_x/G_6 aqueous solution and the reaction was incubated for 5 min at room temperature. The excess GQDs were removed by centrifugation and subsequently washed with deionized water for three times. In this way, the Au_x/G_6/GQDs composites with various size of Au_x were achieved. In addition, the Au_x/GQDs were prepared by adding GQDs into Au_x aqueous solution.

1.5. Raman spectrum studies

The Raman spectra of all samples were measured by the i-Raman® (USA) with integration time of 2200 ms, multiplier of 2, and time average of 2. An excitation wavelength of 785 nm was used to induce Raman scattering. The SERS substrates were prepared by coating Au_x, Au_x/GQDs or Au_x/G_6/GQDs dispersion on glass substrates, respectively. Then, a certain amount of crystal violet (CV) aqueous solution (1×10^{-5} mol L^{-1}) was dropped onto the treated substrate. After drying and forming a uniform layer, the Raman spectra of the substrates were measured and collected at different spots. For comparison, the Raman spectrum of the glass substrate only dropped with 1×10^{-5} mol L^{-1} CV solution was also measured.

1.6. Characterizations

UV-vis absorption spectra were recorded on a UV-3900 spectrophotometer (Japan). Fluorescence spectra were recorded using a HITACHIF-4600 spectrometer (Japan) at room temperature with an excitation wavelength at 320 nm. Fourier transform infrared (FT-IR) spectroscopic analysis was carried out with Nicolet 6700 FT-IR spectrometer (USA) in the scanning range of 500-4000 cm^{-1} at room temperature. A KBr pellet was utilized for the purpose of calibration. Transmission electron microscope (TEM) images and the high resolution transmission electron microscope (HRTEM) images were taken with a JEOL JEM-2100F microscope device (Japan), and the accelerating voltage was 200 kV. The TEM samples were prepared by dropping the dispersion of the sample on a carbon-coated copper grid and dried at room temperature.

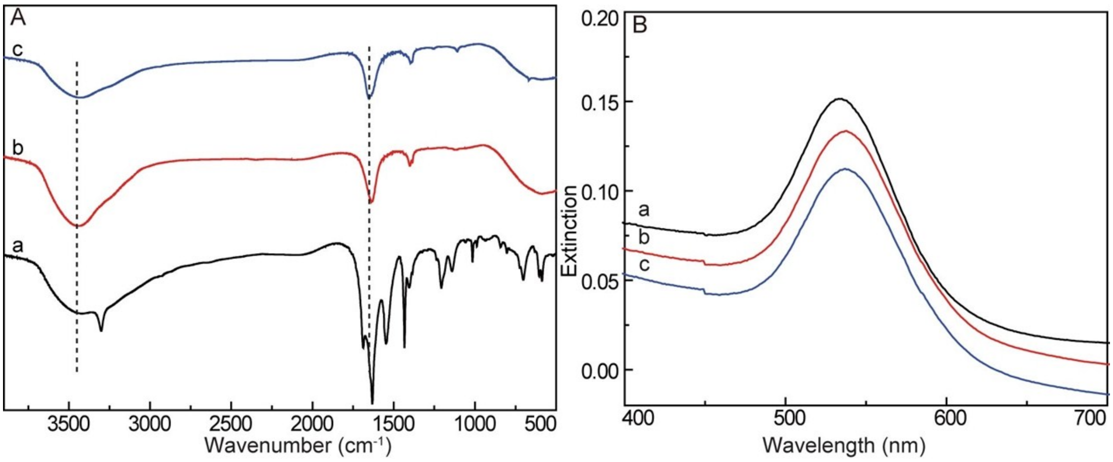

Fig. S1 (A) FT-IR spectra of G_6 (a), Au_{50}/G_6 (b) and Au_{50}/G_6/GQDs (c); (B) UV-vis absorption spectra of Au_{50} (a), Au_{50}/G_6 (b) and Au_{50}/G_6/GQDs (c)

Table S1. Characteristic surface Plasmon peaks (SPR) of Au_x, Au_x/G_6 and Au_x/G_6/GQDs

Samples	SRP peaks (nm)	Red shift (nm)
Au_{32}	525	-
Au_{32}/G_6	538	13
Au_{32}/G_6/GQDs	539	14
Au_{50}	533	-
Au_{50}/G_6	537	5
Au_{50}/G_6/GQDs	538	6
Au_{68}	541	-
Au_{68}/G_6	545	3
Au_{68}/G_6/GQDs	546	4
Au_{87}	552	-
Au_{87}/G_6	556	4
Au_{87}/G_6/GQDs	557	5
Au_{107}	572	-
Au_{107}/G_6	578	6
Au_{107}/G_6/GQDs	579	7

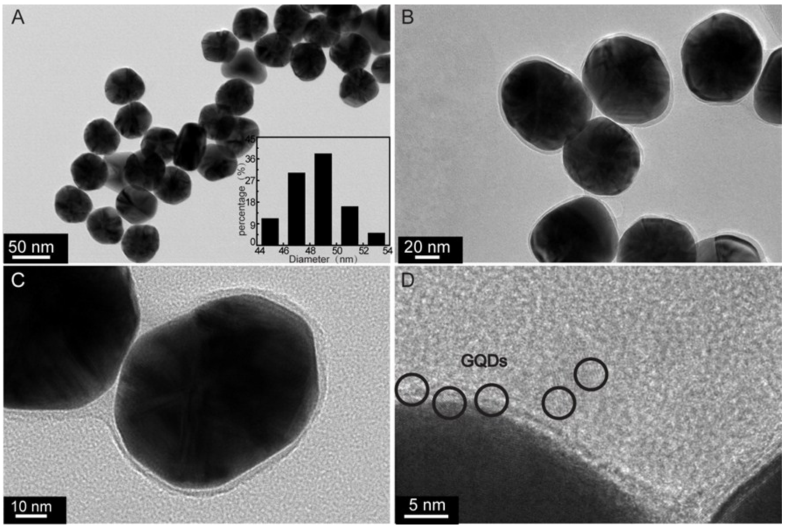

Fig. S2 TEM images of Au_{50} (A), Au_{50}/G_6 (B), and high-resolution TEM images of Au_{50}/G_6 (C) and Au_{50}/G_6/GQDs (D). The inset in A: size distribution histogram for AuNPs.

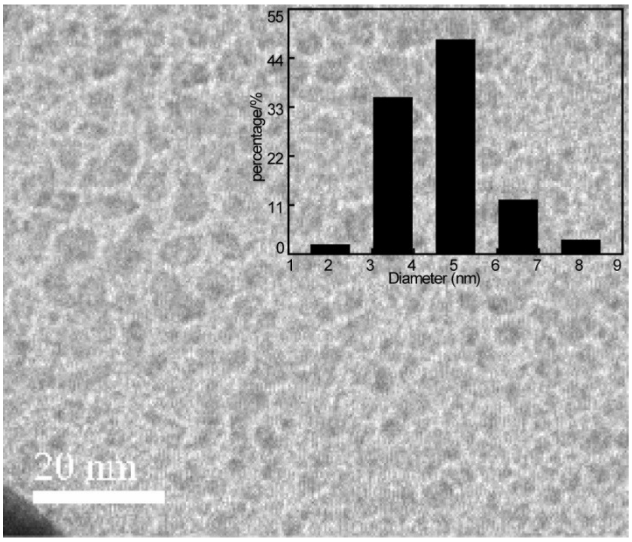

Fig. S3 TEM images of GQDs, the inset: the size distribution histogram for GQDs

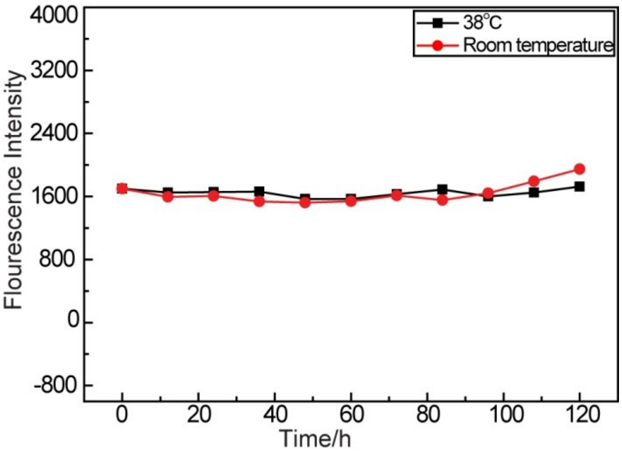

Fig. S4 The time-dependent fluorescence behaviors of the Au_{50}/G_6/GQDs composite at room temperature and physiological temperature.

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