

Photocatalytic degradation of dyes over graphene-gold nanocomposites under visible light irradiation

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Experimental Details:

Preparation of graphene oxide (GO)

Graphene oxide was synthesized from natural graphite by a modified Hummers method. Graphite (5 g) and NaNO₃ (2.5 g) were mixed with 120 mL of H₂SO₄ (95%) in a 500 mL flask. The mixture was stirred for 30 min within an ice bath. Under vigorous stirring, potassium permanganate (15 g) was added to the suspension. The rate of addition was carefully controlled to keep the reaction temperature below 20 °C. The mixture was stirred at room temperature overnight. Then, 150 mL of H₂O was slowly added still under vigorous stirring. The reaction temperature was rapidly increased to 98 °C with effervescence, and the color changed into yellow. The diluted suspension was stirred at 98 °C for one day. Then, 50 mL of 30% H₂O₂ was added to the mixture. For purification, the mixture was washed by rinsing and centrifugation with 5% HCl then deionized (DI) water for several times. After filtration and drying under vacuum, solid graphene oxide (GO) was obtained.

Preparation of reduced graphene oxide (GOR)

Reduced graphene oxide (GOR) was prepared by chemical reduction of GO with sodium borohydride. 0.3 g of GO was dispersed in 50 mL of DI water. Then, 0.5 g of sodium borohydride was added and the mixture was heated at 100 °C for 24 h. After the reaction was

completed, the solid GOR was centrifuged, repeatedly washed with DI water, and the final product was dried in a vacuum oven at 80 °C overnight.

The structural and chemical properties of the GO and GOR samples were characterized using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Fourier-transform infrared spectroscopy (FT-IR). The XRD pattern (Fig. S1) of sample GO exhibited a strong peak at $2\theta = 11.6^\circ$, which corresponded to an interlayer spacing of about 0.76 nm, indicating the presence of oxygen functionalities, which facilitated the hydration and exfoliation of GO sheets in aqueous media. After chemical reduction, the hydrophilicity of the water-dispersed GO sheets gradually decreased, leading to an irreversible agglomeration of GOR sheets. The broad peak centered at $2\theta = 25.8^\circ$ in the XRD pattern of the GOR sample confirmed a random packing of graphene sheets in the GOR. The C1s XPS spectrum (Fig. S2) also confirmed the restoration of the C=C bonds in GOR. The two XPS peaks observed on the GO sample indicate the presence of functional groups. After reduction, the C=C bond dominated as revealed by the single peak at 284.5 eV. The noticeable but small peak at around 288.5 eV is due to a small portion of carboxyl carbon in GOR. Consistent with the XPS data, the FT-IR spectra (Fig. S3) clearly showed that GOR has significantly less functional groups than GO. The BET surface area of GOR was about 16.6 m²/g.

Preparation of gold nanoparticles dispersed on GOR (GOR-Au)

0.1 g of GOR was dispersed in 35 ml of DI water. Then, 0.4 ml of chloroauric acid (0.02 M) was added to the GOR suspension under stirring. The mixture was kept at room temperature for 3 h with constant stirring. After repeated washing with DI water, the product was dried at 60 °C for 24 h. The sample thus obtained is denoted as GOR-Au. The BET surface area of GOR-Au was about 1.0 m²/g.

Photocatalytic reactions

Photocatalytic measurements were carried out in an open thermostatic photoreactor. Before irradiation, a suspension containing 100 mL of 5.3×10^{-3} mM RhB solution and 6.3 mg of solid catalyst was sonicated for 5 min and stirred for 30 min in the dark to allow sorption equilibrium. Then, the mixture was irradiated with a 350 W Xenon lamp equipped with a 420 nm cut-off filter. At a given time interval of irradiation, 5 mL aliquots were withdrawn. The residual concentration of RhB in the aliquots was analyzed using a Shimadzu 1601 PC UV-Vis spectrophotometer.

Characterizations

X-ray diffraction (XRD) patterns were collected on a Shimadzu XRD-6000 X-ray diffractometer using Cu K α irradiation operated at 40 kV and 30 mA. Adsorption-desorption isotherms of N₂ were measured on a Micromeritics ASAP2020 system at 77 K. The Brunauer-Emmett-Teller surface area (S_{BET}) was calculated in the relative pressure range of $P/P_0 = 0.05-0.2$. High-resolution transmission electron microscope (HRTEM) images were obtained on a Perkin-Elmer JEM-2010F operated at 200 kV. X-ray photoelectron spectroscopy (XPS) spectra were collected on an AXIS HIS (Kratos Analytical Ltd., UK) with an Al K α irradiation source (1486.7 eV) operated at 15 kV and 10 mA. Fourier-transform infrared spectra were measured on a Shimadzu IRprestige-21 FTIR spectrometer. Fluorescence lifetimes were measured on a Perkin-Elmer LS 50B spectrofluorimeter by the time-correlated single-photon counting method. The exciting and receiving wavelengths were set at 483 nm and 590 nm, respectively. Total organic carbon was analyzed by a Shimadzu TOC-VCSH analyzer.

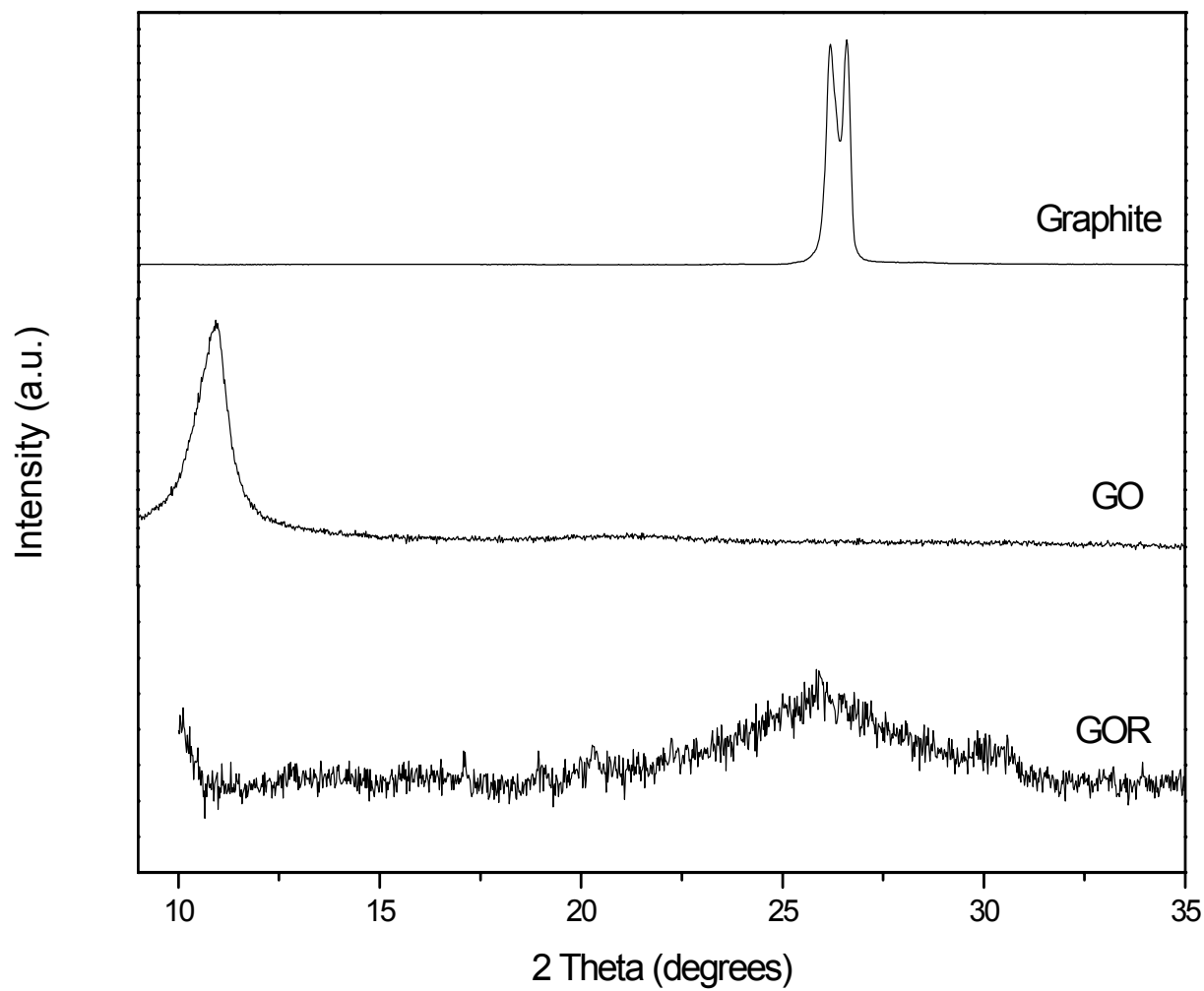


Fig. S1 XRD patterns of graphite, graphene oxide (GO) and reduced graphene oxide (GOR).

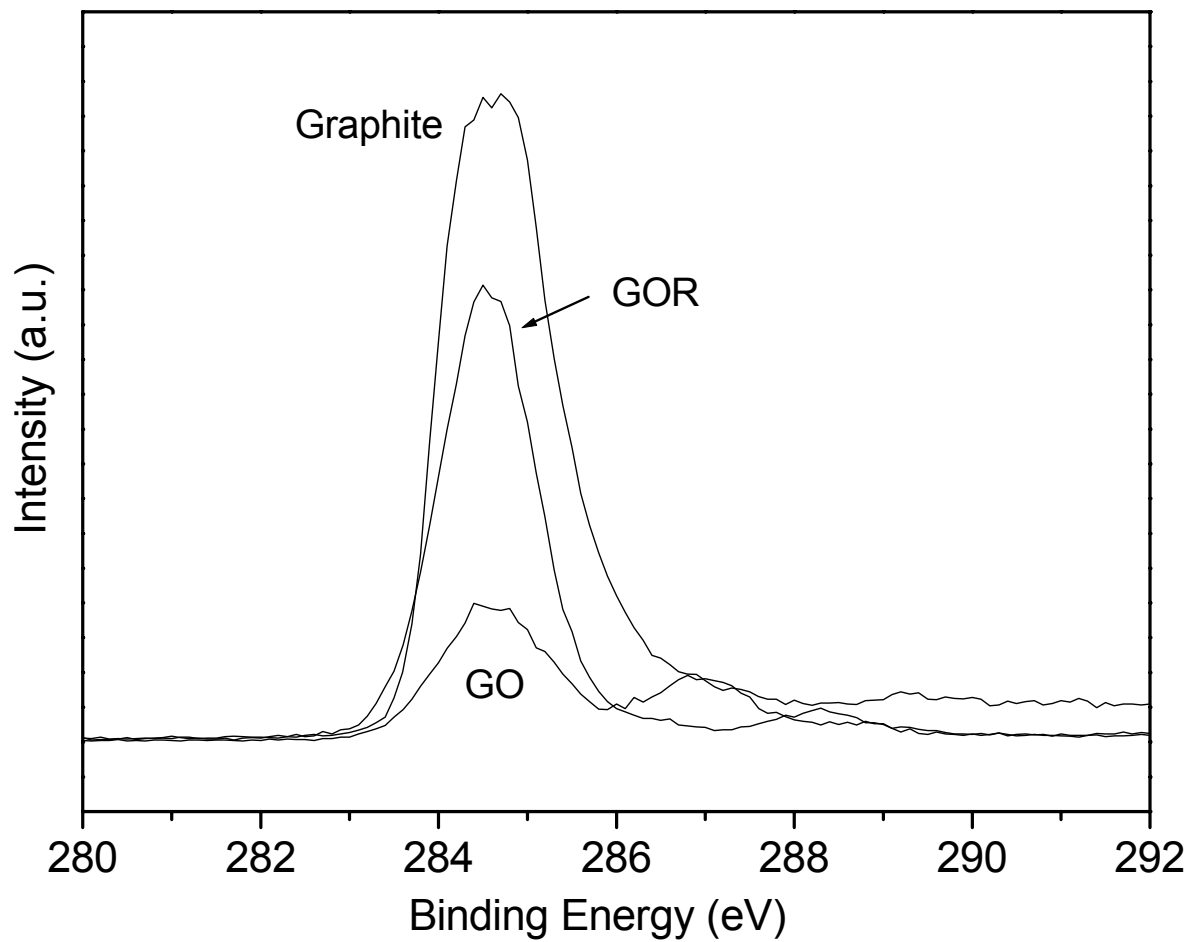


Fig. S2 C1s XPS patterns of graphite, graphene oxide (GO) and reduced graphene oxide (GOR).

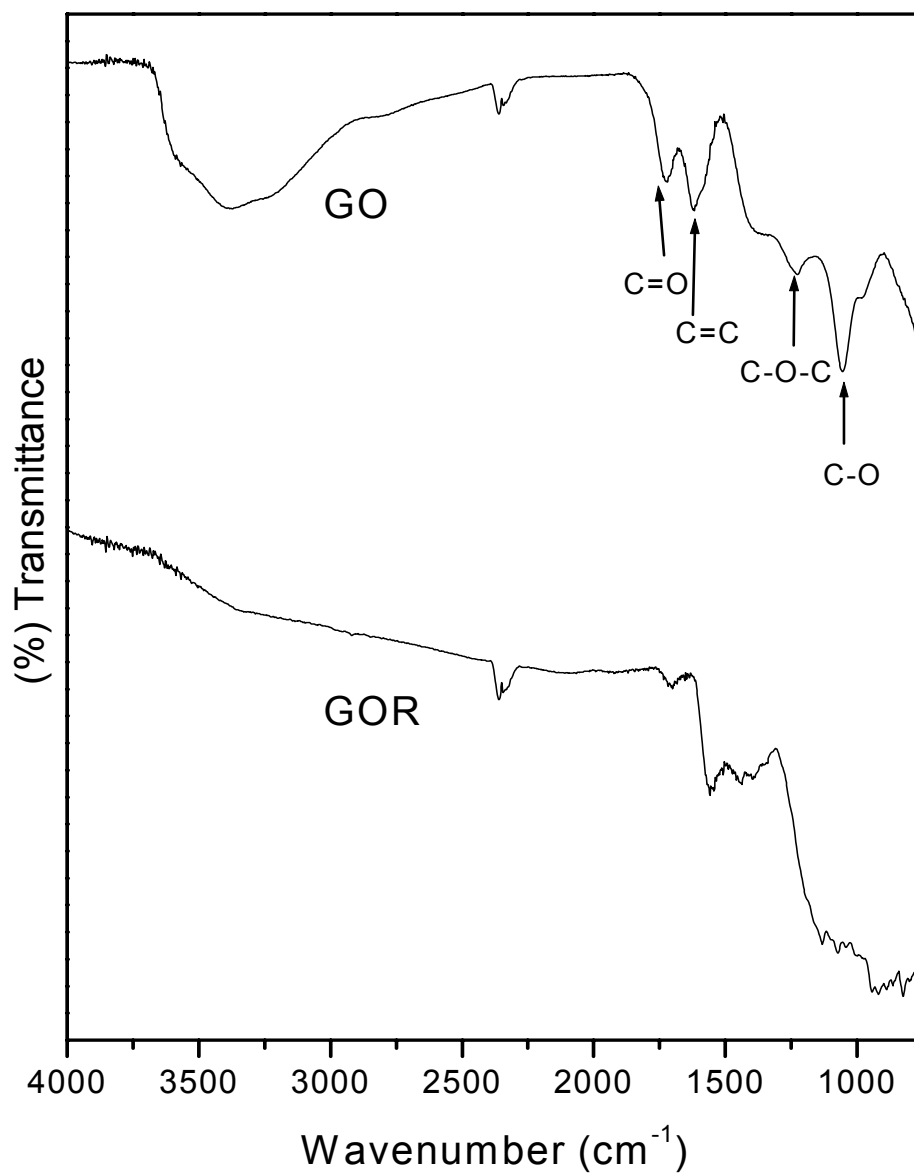


Fig. S3 FT-IR spectra of GO and GOR.

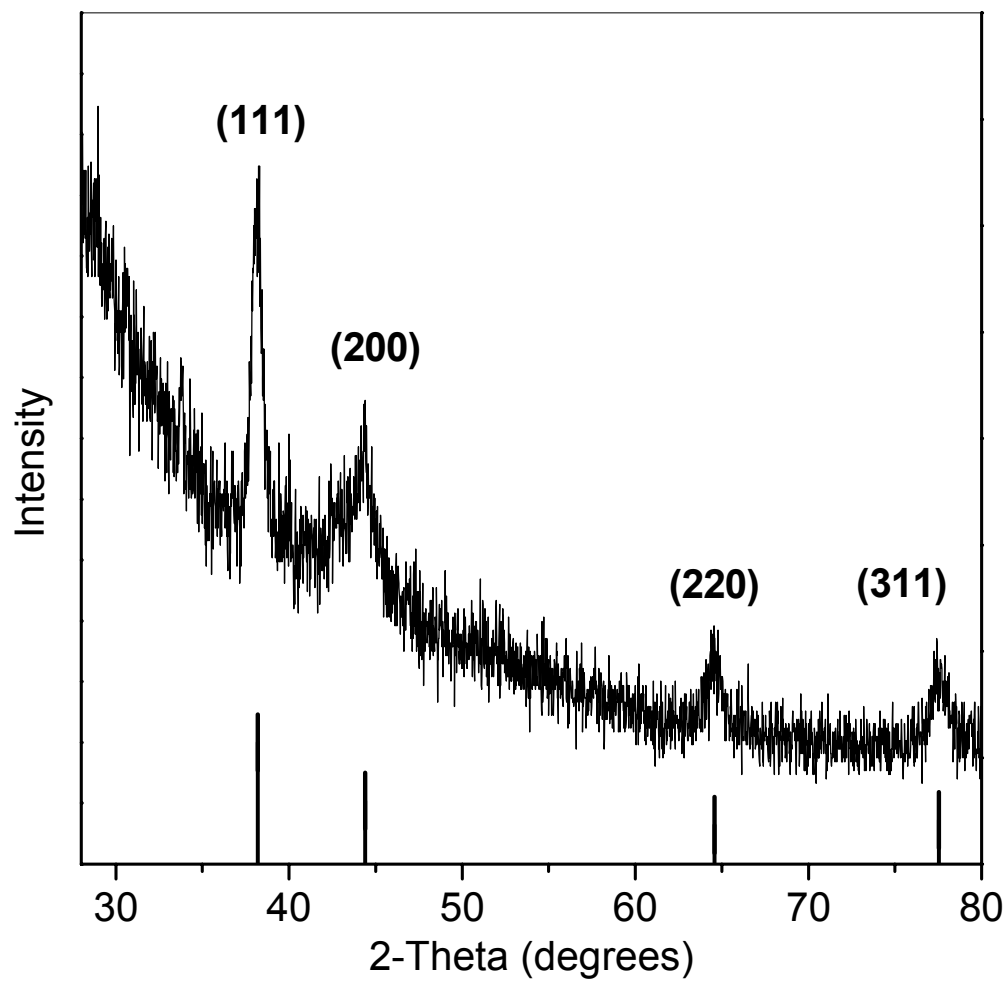


Fig. S4 XRD pattern of GOR-Au and the reference XRD of Au particle.

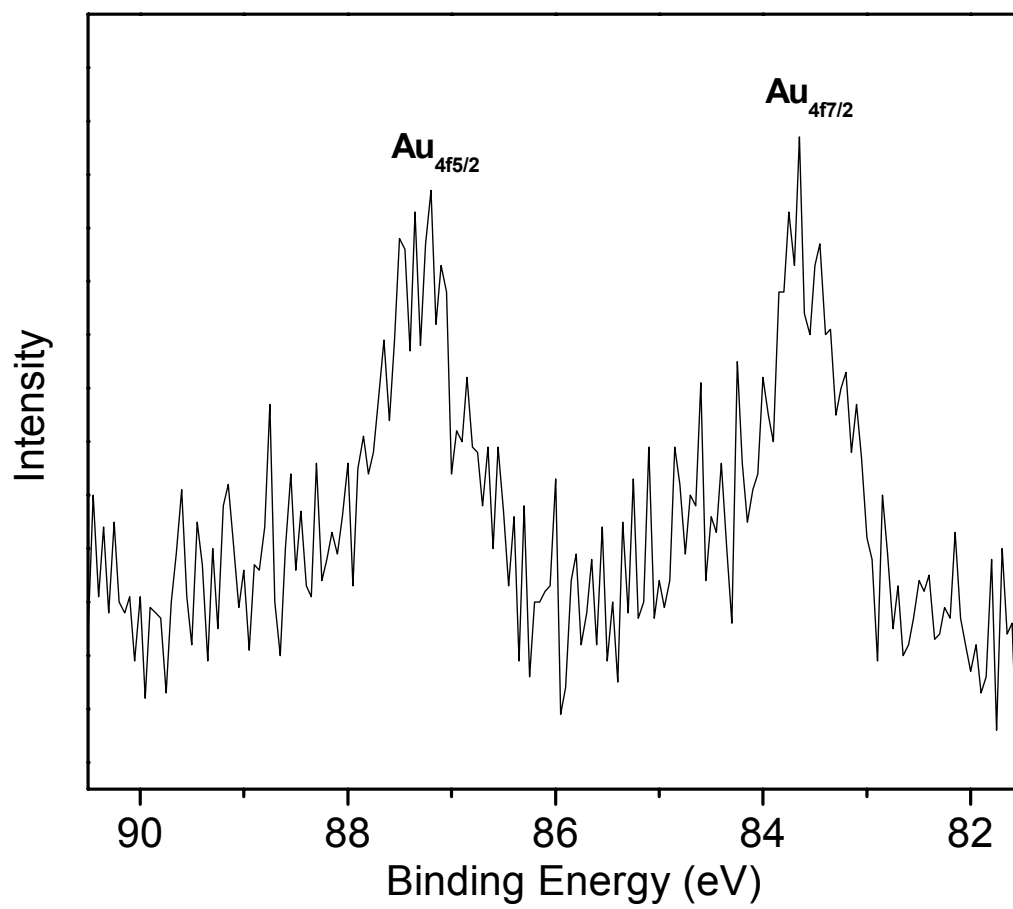


Fig. S5 Au 4f XPS spectrum of GOR-Au.

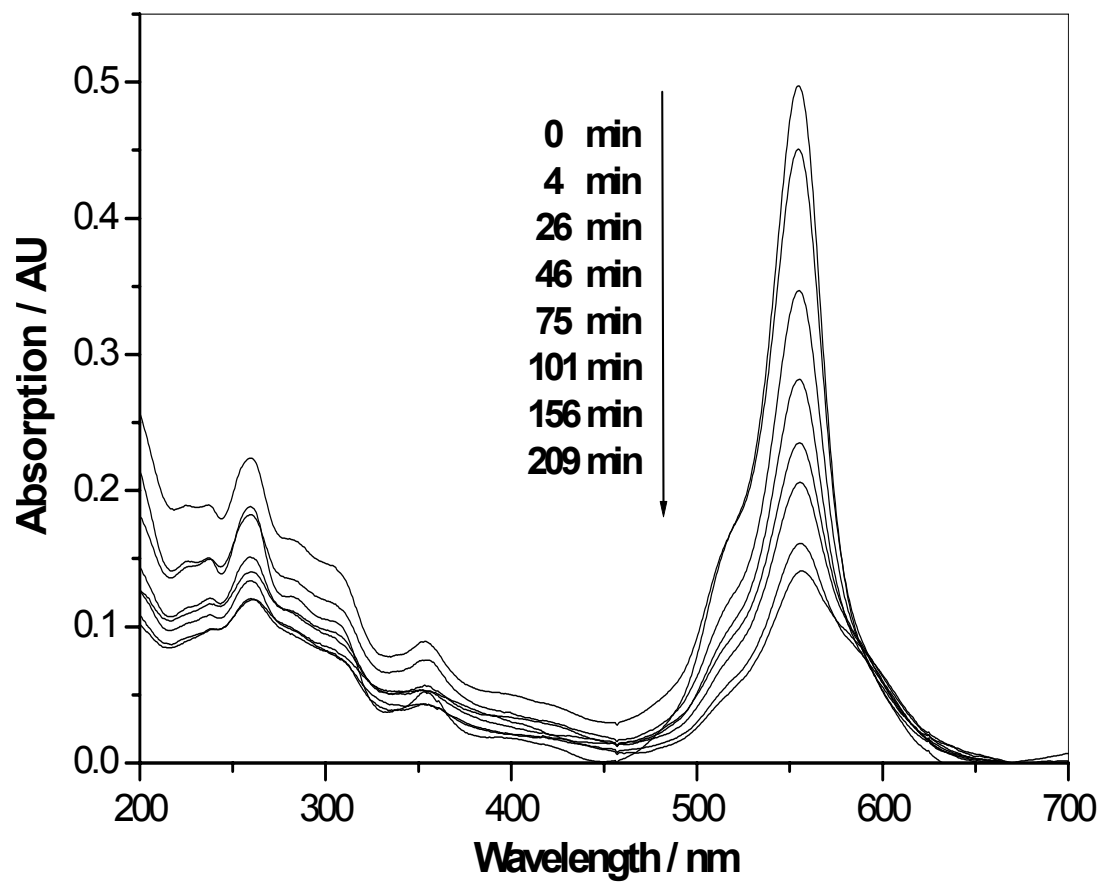


Fig. S6 Absorption profiles of RhB against irradiation time in the presence of GOR-Au.

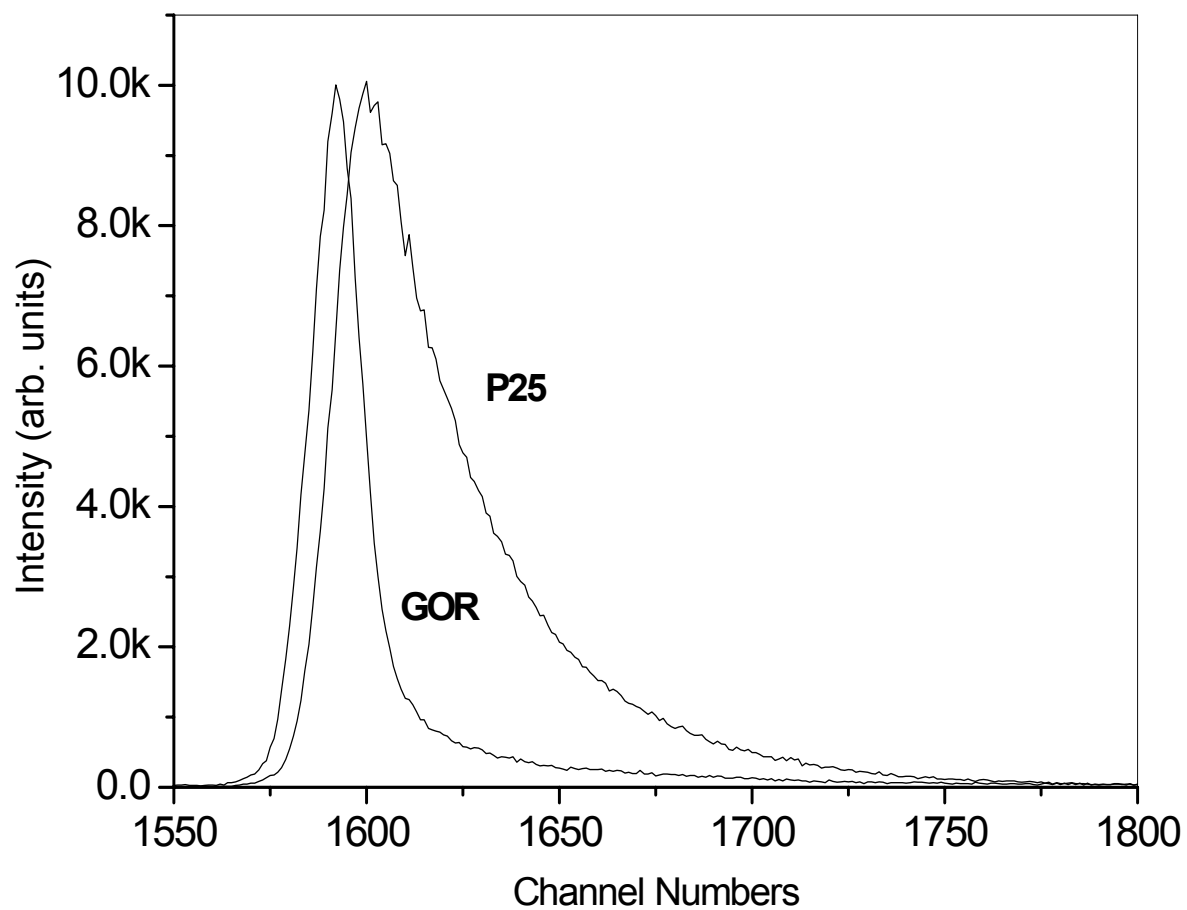


Fig. S7 Fluorescence decays of RhB in P25 and GOR suspensions. The exciting and receiving wavelengths were set at 483 and 590 nm, respectively.

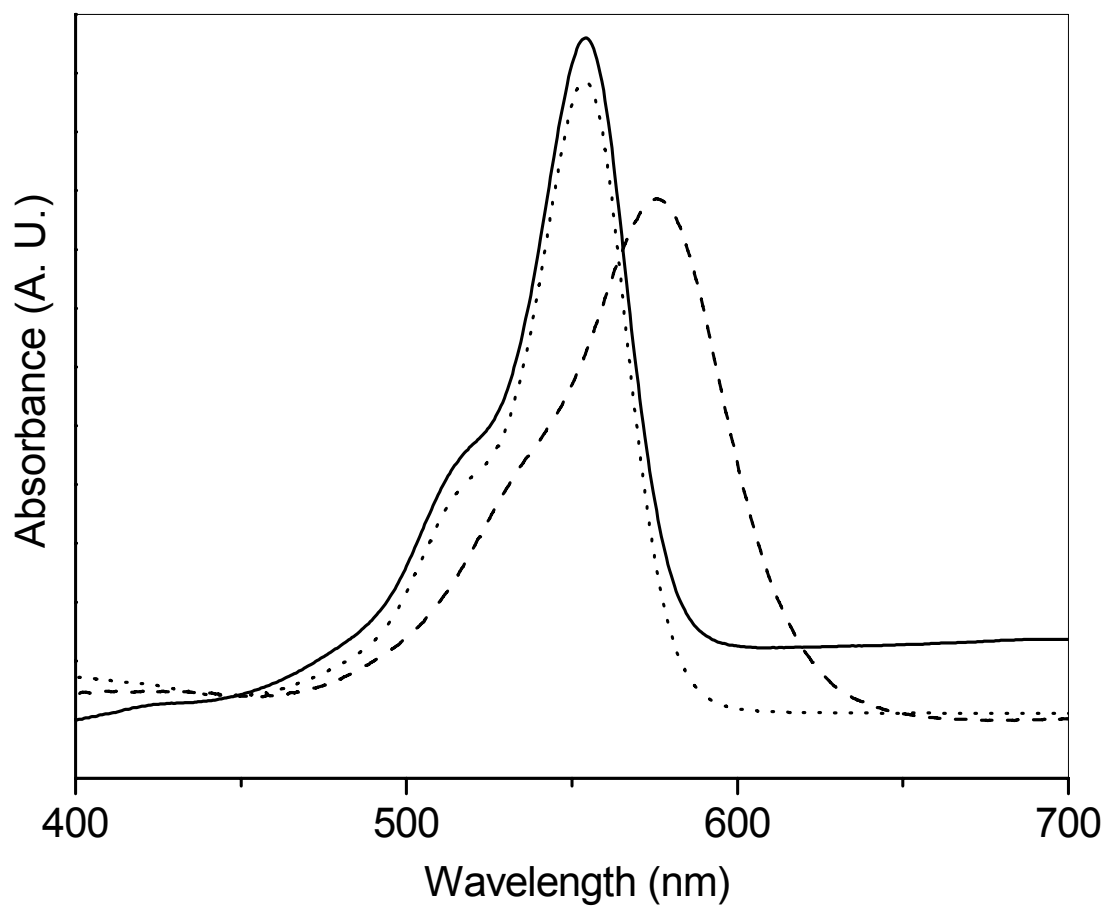


Fig. S8 Absorption spectra of RhB in water (the dot line), TiO₂ (the solid line) and GOR suspensions (the dash line).

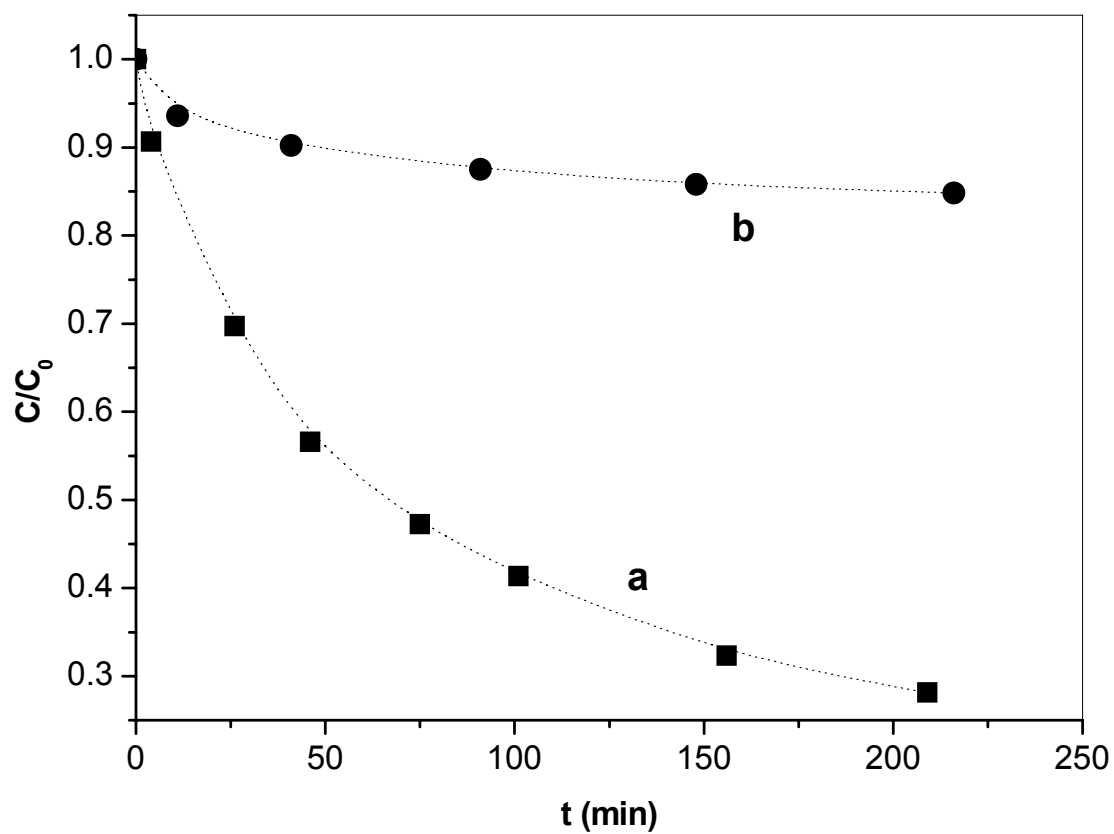


Fig. S9 Degradation of RhB over GOR-Au (a) without EtOH, and (b) with the addition of EtOH.