Supporting Information

Tuning the Electronic Structure of Ag_3PO_4-based Composites through Graphene Oxide Mediator for Enhanced Photocatalytic Activity

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Experimental Section

1 Catalyst preparation

1.1 Synthesis of Ag_3PO_4

1 mol·L^{-1} ammonia solution was slowly added into 180mL (5.1 g) $AgNO_3$ solution in a drop-by-drop process under mechanical stirring formed the silver ammonia solution. Subsequently, 100 mL Na_2HPO_4 (4.26 g) was added drop by drop to the above dispersion while mechanical agitation and then sonicated for another 30 min. Finally, the precipitates in the solution were centrifuged and washed with deionized water. The as-obtained samples were dried at 65 °C for 10 h under vacuum condition. The synthesized Ag_3PO_4 sample was denoted as APO.

1.2 Synthesis of $CoFe_2O_4$ nanoparticles

The $CoFe_2O_4$ nanoparticles were successfully prepared by a simple hydrothermal method. Briefly, an aqueous solution (60 mL) containing $Co(NO_3)_2 \cdot 6H_2O$ (2.07 g) and $Fe(NO_3)_3 \cdot 9H_2O$ (5.74 g) was added NaOH solution (2 mol·L^{-1}) with magnetic stirring for 1 h forming a transparent solution. The mixture was then transferred into a Teflon-lined stainless-steel autoclave of 100 mL capacity. The sealed tank was heated to and maintained at 160 ºC for 12 h in an oven and cooled to RT. The resulting brown precipitates were collected by filtration and washed with water and ethanol for more than 3 times, and finally dried in an oven at 60 ºC for 12 h. The obtained nanoparticles were then calcined at 600 °C and allowed to keep for 2 h. The as-synthesized $CoFe_2O_4$ sample was denoted as CFO.

1.3 Synthesis of graphene oxide (GO) and $Ag_3PO_4/CoFe_2O_4$

GO was prepared from the natural flake graphite according to the modified Hummer's method [1]. The $Ag_3PO_4/CoFe_2O_4$ composite was prepared by a simple ion-exchange deposition method. The loading of $CoFe_2O_4$ is 10% for $Ag_3PO_4/CoFe_2O_4$ composite. Typically, 1 $mol \cdot L^{-1}$ ammonia solution was slowly added into 100mL (5.1g) $AgNO_3$ solution in a drop-by drop process under mechanical stirring formed the silver ammonia solution. Then a certain amount of $CoFe_2O_4$ (0.059g) sample was added under vigorous stirring and sonicated for 30 min. 100 mL Na_2HPO_4 (4.26g) was added drop by drop to the above dispersion while mechanical agitation and then sonicated for another 30 min. Finally, the precipitates were centrifuged and washed with deionized water. The as-obtained samples were dried at 60 ºC for 12 h under vacuum condition. The as-synthesized $Ag_3PO_4/CoFe_2O_4$ sample was denoted as APO/CFO.

1.4 Synthesis of $Ag_3PO_4/CoFe_2O_4/GO$ composites

The $Ag_3PO_4/CoFe_2O_4/GO$ composites were carried out by a simple ion-exchange deposition method [2]. The GO loading were x% (x = 2.5, 5.0, 7.5) and denoted as APO/CFO/GO(x%). Typically, taking APO/CFO/GO(5%) catalyst as an example, 1 $mol \cdot L^{-1}$ ammonia solution was slowly added into 100mL (5.1g) $AgNO_3$ solution in a drop-by-drop process under mechanical stirring formed the silver ammonia solution. Subsequently, 0.308g GO and 0.059g $CoFe_2O_4$ samples were added under vigorous stirring and sonicated for 30 min. Then, 100 mL Na_2HPO_4 (4.26g) was added drop by drop to the above dispersion while mechanical agitation and then sonicated for another 30 min. The obtained precipitate was centrifuged, washed with deionized water several times, and dried at 60 °C for 12 h. Finally, the products were collected and ground into powder for further use. For convenience, the composite catalyst APO/CFO/GO(5.0%) is only abbreviated to APO/CFO/GO.

2 Characterization techniques

The phase formation in the composites was investigated via powder X-ray diffraction (XRD) technology on a Rigaku D/max 2400/PC diffractometer with Cu K_α (λ=1.5406 Å) at 40 kV and 150 mA. Diffraction patterns in the 10-80° regions were recorded at a rate of 5°/min. The chemical composition and chemical bonding state of the specimen were defined by X-ray photoelectron spectroscopy (XPS, equipped with a standard monochromatic Al *Kα* source (*hv*) 1486.6 eV, ESCALAB 250Xi, ThermoFisher Scientific, UK). Field emission scanning electron microscopy (FE-SEM, HITACHI S-4800) and energy-dispersive X-ray spectroscopy analysis (Thermo Fisher, Noran 7) were employed for detailed discussion of morphology of the specimen. Transmission electron microscopy (TEM) and HRTEM images were taken with a Tecnai-G2-F30 field emission transmission electron microscope operating at accelerating voltage of 300 kV. The absorbance spectra of the samples were recorded by a UV-Vis spectrometer (UV-765 UV-Vis spectrometer, Shanghai Jingke) in the range of 200-800 nm. The UV-Vis diffuse reflectance spectra (DRS) of the samples were recorded using a UV/Vis/NIR PerkinElmer Lambda 950 double beam spectrophotometer equipped with a standard 150 mm integrating sphere, and the total reflectance was measured relative to a $BaSO_4$ reference. TOC was determined using a TOC analyzer (Elementar vario TOC cube, Hanau, Germany). Magnetic hysteresis loops at room temperature were obtained using a VSM (LAKESHORE-7304, USA) at room temperature. The photoluminescence (PL) spectra for samples were investigated on an Edinburgh FL/FS900 spectrophotometer with an excitation wavelength of 380 nm. The fluorescence decay times were measured using the Horiba Jobin Yvon Data Station HUB operating in time-correlated single-photon counting mode (TCSPC) with the time resolution of 200 ps. Light scattering Ludox solution was used to obtain the instrument response function (prompt). The time ranges are 0.055 ns/channel, in 4096 effective channels. Horiba Jobin Yvon DAS6 fluorescence decay analysis software was used to fit the model functions to the experimental data.

3 Photocatalytic activities measurement

3.1 RhB degradation

The photocatalytic activities of all the samples were measured by photocatalytic degradation of aqueous RhB (10 mg/L) solutions, where the photocatalytic reaction was carried out in a specially designed glass reactor with a water-cooling system to maintain the solution at room temperature. The light source was designed for 300 W Xenon short-arc lamps equipped with an ultraviolet cutoff filter (providing visible light ≥400 nm). Typically, a 20 mg sample was added into 100 mL aqueous solution of organic dyes, mingling the reactant quickly. Before irradiation, the suspension was magnetically stirred in the dark for 20 min to establish an adsorption-desorption equilibrium between the photocatalysts and organic dyes. The as-obtained solution was then exposed to light irradiation with a fixed distance of 15 cm under magnetic stirring. At a regular interval of time, 4 mL the suspension was withdrawn and immediately filtrated by filter membrane to remove the photocatalysts, which the initial concentration of RhB (10 mg/L) in the solution is be defined as C_0, and the resulting concentration of solution was named as C. The absorbance of the filtrated solution was measured using UV visible spectrophotometer. The C/C_0 ratio as a function of irradiation time was used to evaluate the degradation efficiency of the photocatalysts. Also, to accomplish the next cycle experiment, the catalyst was recovered from the solution by an external magnet after completion of the reaction. The magnetically recovered-catalyst was washed, dried and weighed for further use.

3.2 Photocatalytic HER

Typically, the prepared sample (10 mg) was suspended in 10 mL aqueous solution of CH_3OH (10%). The suspension was then purged with Ar to drive away from the residual oxygen before sealed in a quartz flask. The photocatalytic hydrogen evolution was carried out by irradiating the suspension with a 300-W Xenon lamp. The amount of hydrogen evolution was measured using gas chromatography (Agilent 7890A, TCD, 13 X columns, Ar carrier).

4 Electrochemical measurements

All the electrochemical measurements were measured on an electrochemical analyzer (CHI660E) in a homemade standard three-electrode quartz cell consisting of an organic glass enclosure with a quartz window and a 1.2 cm diameter opening opposite the window to the work electrode was clamped. Platinum plate was used as the counter electrode and a typical three-electrode system includes Ag/AgCl (in 3 M KCl solution) reference electrode. The working electrode was prepared by drop-coating sample suspensions and Nafion directly onto the pre-cleaned indium tin oxide glass (FTO glass) surface. The surface area of the working electrode exposed to the electrolyte was about 0.95 cm^2. The electrolyte was 0.1 M Na_2SO_4 aqueous solution without any additives. The light irradiation source was a 300-W Xenon lamp (MAX-303, Asahi Spectra, JAPAN) system equipped with a 400 nm cut-off filter. Mott−Schottky plots at a frequency of 1 kHz were measured in 0.1 $mol\cdot L^{-1}$ Na_2SO_4 electrolyte using a standard potentiostat equipped with an impedance spectra analyzer in the same electrochemical configuration and electrolyte under dark condition. The potentials were converted to the reversible hydrogen electrode (RHE) scale *via* the Nernst equation:

$$E_{RHE} = E_{Ag/AgCl} + 0.198 + 0.059pH \quad (1)$$

5 Fluorescence lifetimes measurements

Photoluminescence (PL) intensity decay, as a function of time, is monitored and the PL decay time is obtained by fitting the data in a two-exponential model using the following expression [3]:

$$I(t) = \sum_{i=1,2} B_i \exp(-t/\tau_i) \quad (2)$$

where I is the normalized emission intensity, t is the time after the pulsed laser excitation, B_i and τ_i are the amplitude (pre-exponential factor) and the PL decay time of the individual components, respectively. The average lifetime of two-exponential decay is essential to describe the overall TRPL character [4], which is calculated using equation (3):

$$<\tau> = \sum_{i=1,2} B_i \tau_i^2 / \sum_{i=1,2} B_i \tau_i \quad (3)$$

where $<\tau>$ is the average lifetime, B_i and τ_i are the amplitude (pre-exponential factor) and the PL decay time of the individual components, respectively.

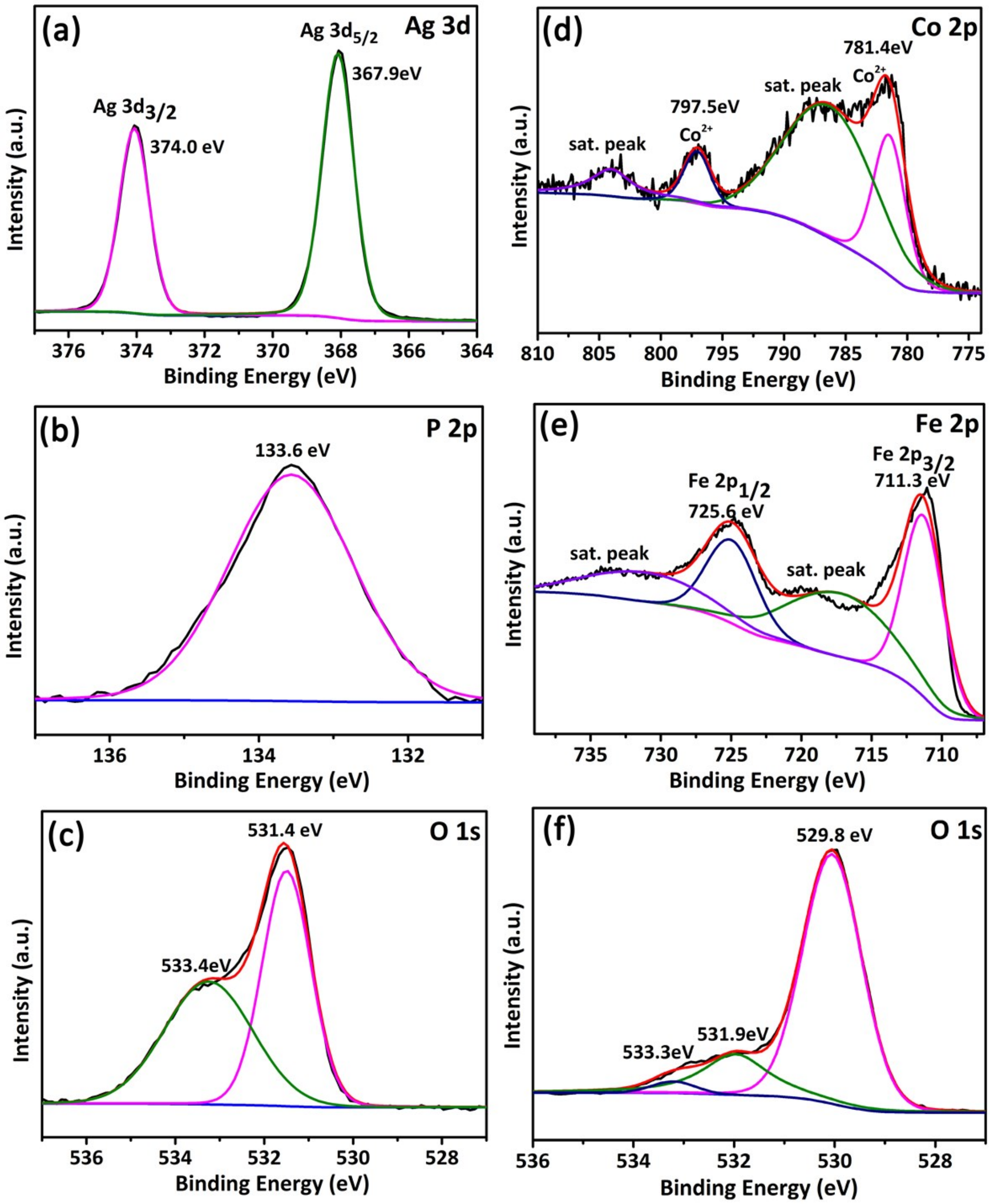

Fig. S1 XPS core level spectra of (a) Ag 3d, (b) P 2p, (c) O 1s Co 2p and (b) O 1s for the APO sample; (d) Co 2p, (e) Fe 2p, and (f) O 1s for the CFO sample.

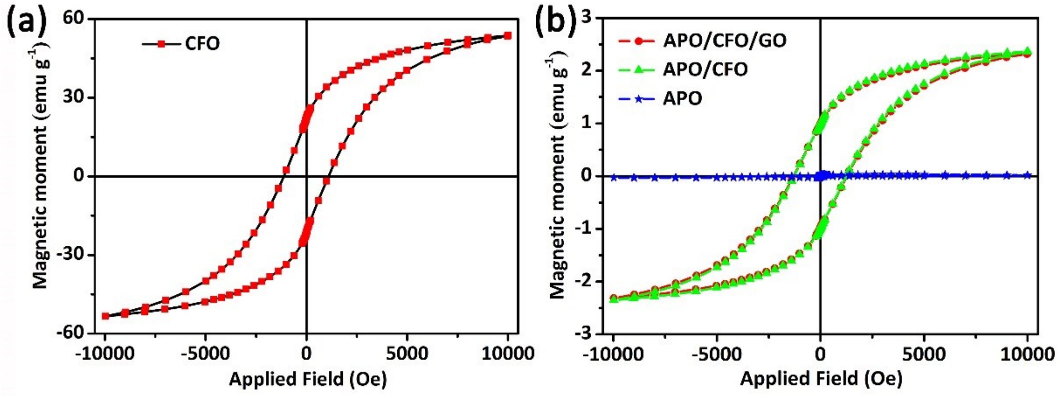

Fig. S2 Magnetic hysteresis (M–H) loops of (a) CFO and (b) APO, APO/CFO, and APO/CFO/GO composites.

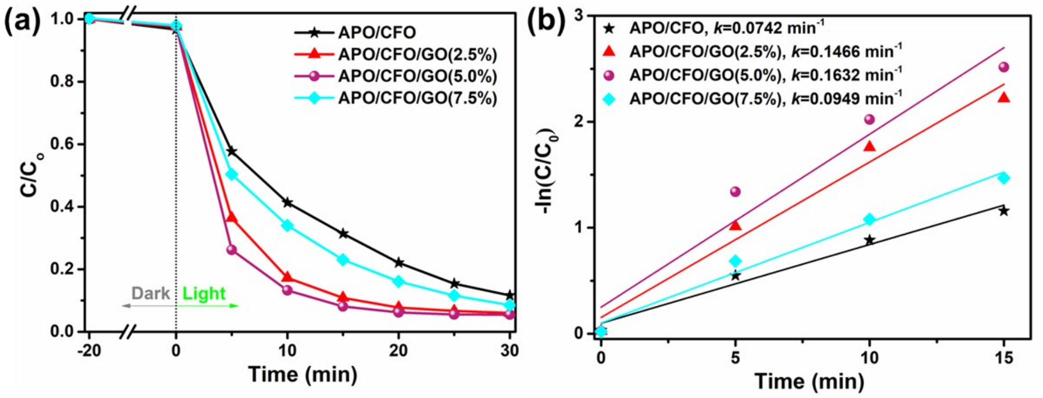

Fig. S3 (a) Photocatalytic activities of APO/CFO/GO(x) (x=0, 2.5, 5.0, and 7.5%) composites for RhB degradation under visible light irradiation and (b) the corresponding first-order kinetics plots.

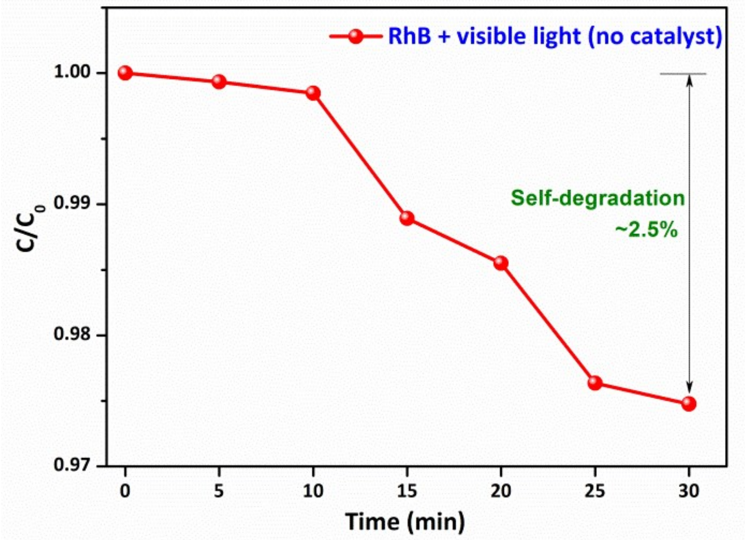

Fig. S4 Photocatalytic degradations of RhB in the absence of catalyst under visible light irradiation.

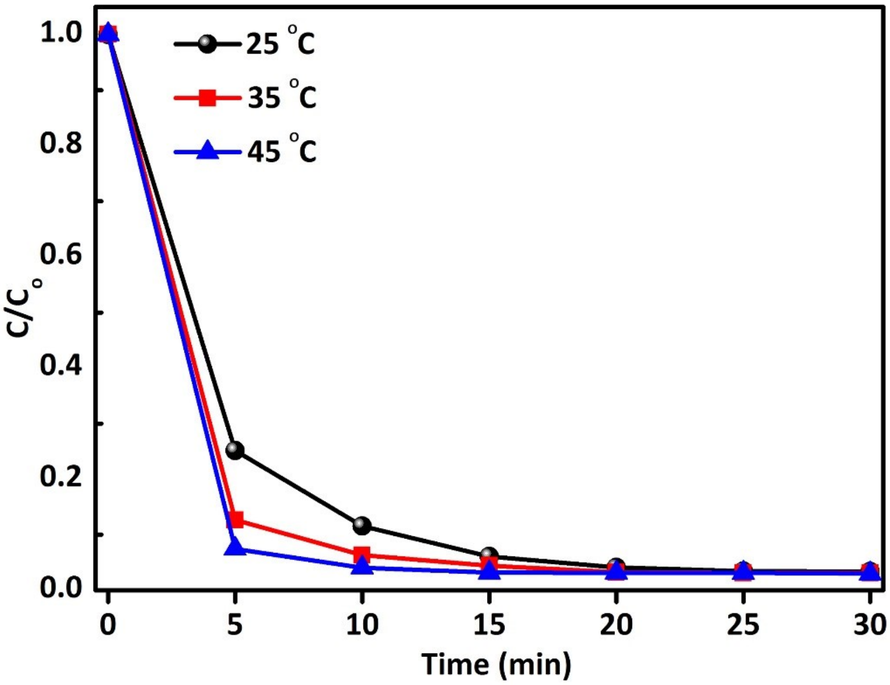

Fig. S5 Effect of the reaction temperature on the degradation of RhB in APO/CFO/GO system.

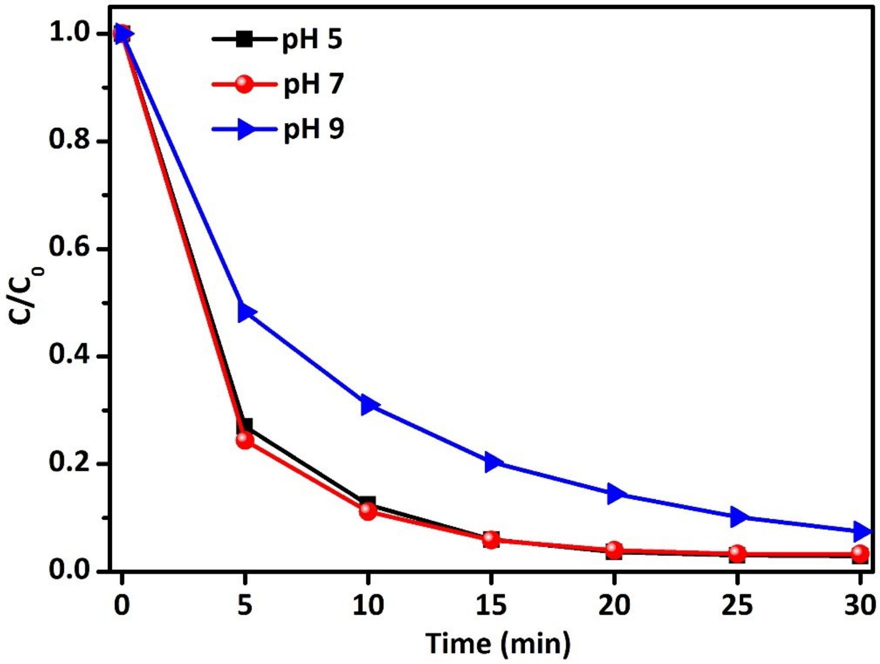

Fig. S6 Effect of the initial pH on the degradation of RhB in APO/CFO/GO system.

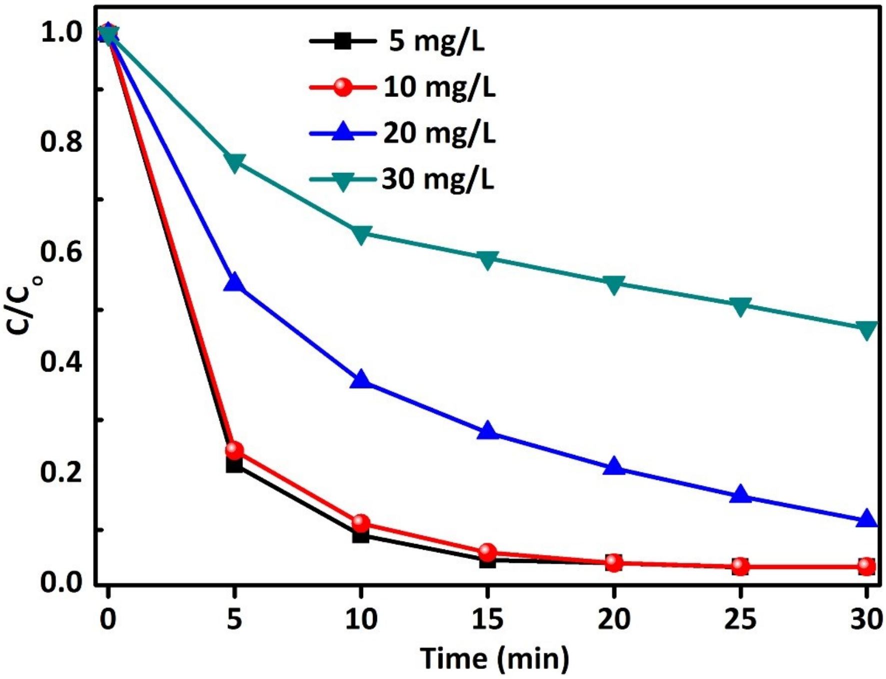

Fig. S7 Effect of the concentration of RhB on the degradation of RhB in APO/CFO/GO system.

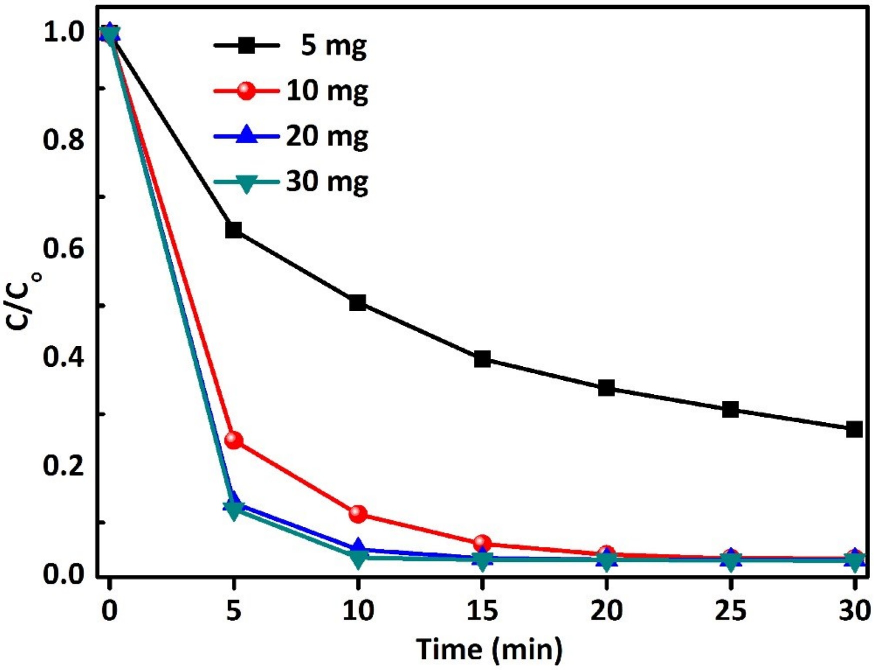

Fig. S8 Effect of the catalyst mass on the degradation of RhB in APO/CFO/GO system.

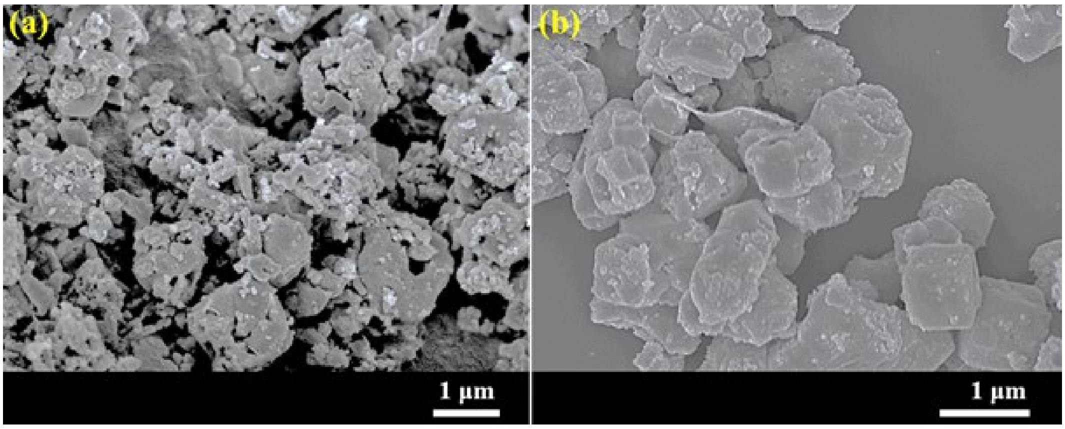

Fig. S9 SEM images of the (a) APO and (b) APO/CFO/GO used photocatalysts.

Table S1. The attribution of the binding energy of the elements for Ag 3d, P 2p, Co 2p, Fe 2p, and O1s XPS over APO and CFO samples.

Samples	**Element**	**Binding Energy (eV)**	**Attribution**
APO	Ag	367.9/374.0	Ag^+
	P	133.6	PO_4^{3-}
	O	531.4	P-O
		533.4	adsorbed H_2O
CFO	Co	781.4/797.5	Co^{2+}
		~786.8/~804.1	satellite peak of Co^{2+}
	Fe	711.3/725.6	Fe^{3+}
		~718.1/~731.8	satellite peak of Fe^{3+}
	O	529.8	lattice oxygen
		531.9	O-H
		533.3	adsorbed H_2O

Table S2. Structural parameters obtained from N_2 adsorption isotherms analysis

Samples	**S_{BET} ($m^2 \cdot g^{-1}$) a)**	**Pore volume ($cm^3 \cdot g^{-1}$) b)**	**Average pore size (nm) b)**
CFO	56.17	0.2279	15.48
APO	0.24	0.0014	8.76
APO/CFO	2.01	0.0108	17.75
APO/CFO/GO	3.59	0.0172	15.50

a) Obtained from BET method;

b) Total pore volume taken from the N_2 adsorption volume at a relative pressure (P/P_0) of 0.99.

Reference

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