Electronic Supplementary Information

Synergy of Adsorption and Photosensitization of Graphene Oxide for Improved Removal of Organic Pollutants

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Contents

1. Experimental Section

1.1 Chemicals

All the chemical reagents used in this study were at least of analytical grade. All solutions were prepared using 18.2 MΩ cm^{-1} deionized water (DIW) produced by a water purification system (Chengdu Ultrapure Technology Co., Ltd., China). 1 mg mL^{-1} graphene oxide (GO) stable suspension was daily prepared in DIW under sonication using a commercial GO powder purchased from Chengdu Organic Chemicals Co. Ltd. (Chengdu, China). Other reagents were purchased from Kelong Chemical Reagent Co. (Chengdu, China).

1.2 Apparatus

Absorption spectra were recorded on a UV-5200PC UV-vis spectrophotometer (Shanghai Metash Instruments Co., Ltd.). Fluorescence measurements were performed on an Hitachi F-7000 spectrofluorometer equipped with a plotter unit and a quartz cell (1 cm × 1 cm). TEM characterization was performed with a Tecnai G2 F20 S-TWIN transmission electron microscope at an accelerating voltage of 200 kV (FEI Co., USA).

1.3 Adsorption procedures

The HQ solutions for adsorption experiments were prepared via serial dilution of a HQ stock solution (1 mg mL^{-1}) to desired concentrations. And the GO suspension were diluted to the desired concentration with ultrapure water followed by GO stock solution (1 mg mL^{-1}). The adsorption studies were performed with batch equilibration method. Specifically, 1 mL GO (0.2 mg mL^{-1}) suspended was added to 0.1 mL of known concentration of HQ solution and 0.9 mL of phosphate buffered saline solution (PBS, pH, 7.0) in a 2 mL centrifugal tube and adsorption for 1 h at room temperature. Afterwards, centrifugated at 10,000 rpm for 10 min, and the concentrations of HQ in the liquid were analyzed by a UV-visible spectrophotometer at 288 nm. The amount of HQ adsorbed on GO was calculated from the following expression:

$$q_e = \frac{(C_0 - C_e)V}{m}$$

Where q_e was the amount adsorbed at equilibrium (mg g^{-1}) C_0 and C_e were the initial and equilibrium concentration of HQ in solution (mg L^{-1}), respectively. m was the dosage of sorbent (mg), and V was the volume of the solution (mL).

1.4 Study of photosensitization property of GO

The photosensitization experiments was evaluated by photodegradation of hydroquinone (HQ) aqueous solution irradiated by a white LED (3 W). Typically, 0.2 mg mL^{-1} of the GO suspension (1mL) was well dispersed in 0.9 mL PBS solution (pH 7.0) and 0.1 mL HQ with the concentration of 50 mg L^{-1} in the 24 well-plate. Subsequently, the mixed suspension was stirred for several minutes to obtain relatively uniformly dispersed between GO and HQ molecules in the dark. The above solution was irradiated with a white LED (3 W). At given time intervals, the supernatant was separated from the photosensitizer by centrifugation at 10,000 rpm for 10 min. Afterwards, 1.5 mL supernatant was sampled and analyzed the absorbance at 288 nm by a UV-visible spectrophotometer. The HQ was used as a process indicator in all the experiments unless otherwise specified.

2. Study on the adsorption of HQ by GO
2.1 Adsorption mechanism

To investigate the mechanism of the adsorption process, two conventional kinetic models (pseudo-first-order and pseudo-second-order) were applied to analyze the experimental data. The pseudo-first-order model can be expressed as:

$$\ln (q_e - q_t) = ln\, q_e - k_1 t$$

Where q_e and q_t are the adsorbed HQ amounts on GO at equilibrium and at various times t (mg g^{-1}), respectively, and k_1 is the rate constant of the pseudo-first-order model of

adsorption (min⁻¹). The values of q_e and k_1 can be determined from the intercept and slope of the linear plot of ln (q_e-q_t) versus t (Fig. S1).
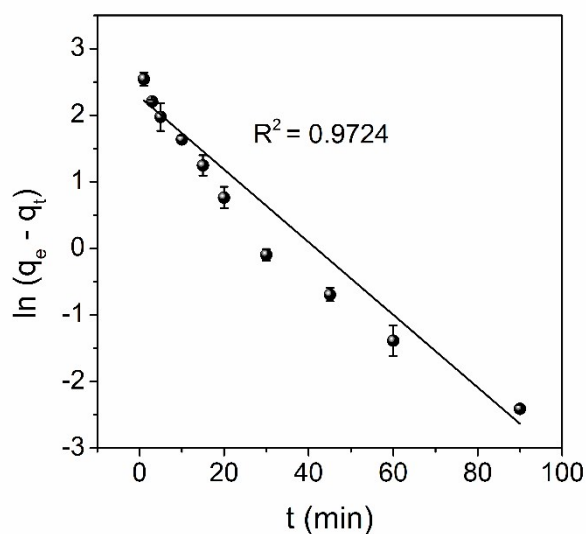

Figure S1. Fitting of the adsorption kinetics (Figure 2A) with pseudo-first-order model.

The pseudo-second-order model includes all the steps of adsorption including external film diffusion, adsorption, and internal particle diffusion, which is described as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

Where q_e and q_t are the the adsorption capacity (mg g⁻¹) at equilibrium and at any time t (min), respectively, K_2 is the rate constant of the pseudo-second-order model of adsorption (g mg⁻¹ min⁻¹). The values of q_e and K_2 were determined from the slope and intercept of the plots of t/q_t against t. And the kinetic parameters and correlation coefficients for HQ adsorbed by GO are summarized in Table S1.

Table S1. Comparison of the pseudo-first and second-order kinetics models on removal of HQ by GO.

Pseudo-first-order model	q_{1e} (mg g⁻¹)	k_1 (min⁻¹)	R^2
	9.757	0.054	0.9724

Pseudo-second-order model	q_{2e} (mg g^{-1})	k_2 (g mg^{-1} min^{-1})	R^2
	20.83	0.017	0.9998

2.2 Adsorption thermodynamics

Temperature effect on adsorption of HQ on GO was carried out at four different temperatures, i.e., 288, 298, 308 and 318 K and shown in Fig. S2. The thermodynamic parameters such as standard free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) were determined based on the following equations:

$$K = \frac{C_s}{C_e}$$

$$\Delta G^0 = -RT \ln K$$

$$\Delta S^0 = -\frac{\Delta G^0 - \Delta H^0}{T}$$

Where K is the adsorption equilibrium constant, C_s is the amount of HQ adsorbed per mass of GO (mg g^{-1}), C_e is the HQ concentration in solution at equilibrium (mg L^{-1}), R is the universal gas constant (8.314 J mol^{-1}·K^{-1}), and T is the absolute temperature (K). The thermodynamic parameters calculated from the above eqs were listed in Table S2.
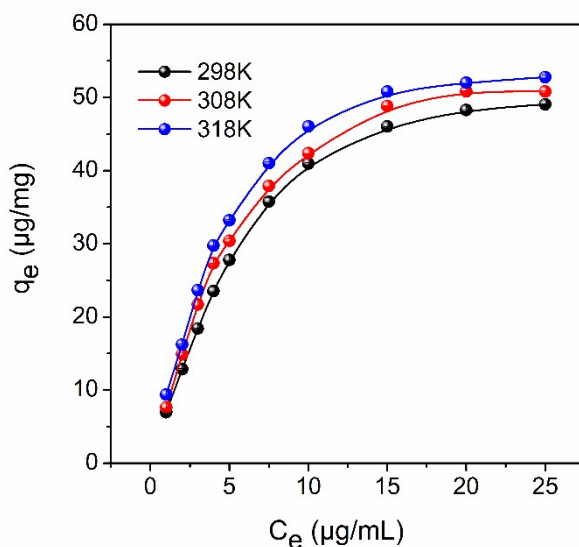

Figure S2. Temperature effect on HQ adsorbed by GO.

Table S2. Thermodynamic parameters for HQ adsorbed by GO.

Thermodynamic constant	Temperature (K)		
	298K	308K	318K
K	18.42	17.47	28.56
ΔG^o (kJ mol^{-1})	-7.23	-7.32	-8.86
ΔH^o (kJ mol^{-1})	12.54		
ΔS^o (kJ mol^{-1} K^{-1})	0.07		

2.3 Adsorption isotherms

To further investigate the mechanism of equilibrium adsorption, the results were subjected to Langmuir and Freundlich isothermal models for simulation. The Langmuir model assumes that adsorption occurs on a homogeneous surface by monolayer coverage and no subsequent interaction between adsorbed species. The equation is as follows:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{q_{max}K_L}$$

where q_e is the adsorbed HQ amount per gram of GO (mg g^{-1}), C_e represents the equilibrium concentration of HQ in solution (mg L^{-1}), K_L is the Langmuir constant (L mg^{-1}), which is related to the affinity of the binding sites, and q_{max} represents the maximum adsorption capacity of the adsorbent (mg g^{-1}).The values of q_{max} and K_L are calculated from the slope and intercept of the linear plot of C_e/q_e against C_e.

The Freundlich model is an empirical model based on multilayer adsorption on heterogeneous surfaces. The equation is commonly described as:

$$\ln q_e = lnK_F + \frac{1}{n}lnC_e$$

where q_e and C_e are defined as in the Langmuir isotherm and K_F and n are the Freundlich constants that represent the adsorption capacity and adsorption strength, respectively. K_F and n can be obtained from the intercept and slope of the linear plot of ln q_e versus ln C_e. Moreover, the magnitude of 1/n quantifies the favorability of adsorption and the degree of heterogeneity of the surface. If n > 1, suggesting favorable adsorption. The relative parameters calculated from the Langmuir and Freundlich models at three different temperatures were listed inTable S3.

Table S3. Parameters of the Freundlich and Langmuir adsorption isotherm models for HQ adsorbed by GO.

T (K)	Freundlich			Langmuir		
	n	K_F	R^2	q_{max}	K_L	R^2
298	2.210	18.02	0.9138	54.82	0.4645	0.9996
308	2.550	19.81	0.8849	54.90	0.6945	0.9992
318	3.243	25.14	0.9440	55.55	1.1450	0.9987

3. Study on the photosensitized oxidation of HQ by GO

3.1 Fluorescence lifetime of GO

The effect of irradiation time on fluorescence lifetime of GO was studied under different conditions and shown in Fig. S3. It can be seen that the fluorescence lifetime of GO decreases with the increase in illumination time from 0 to 60min. It validates that GO have the ultralow radiativetransition, confrming that GO plays a key role forgenerating both suffcient singlet oxygen quantum yield, accompanying with minimized fluorescence.
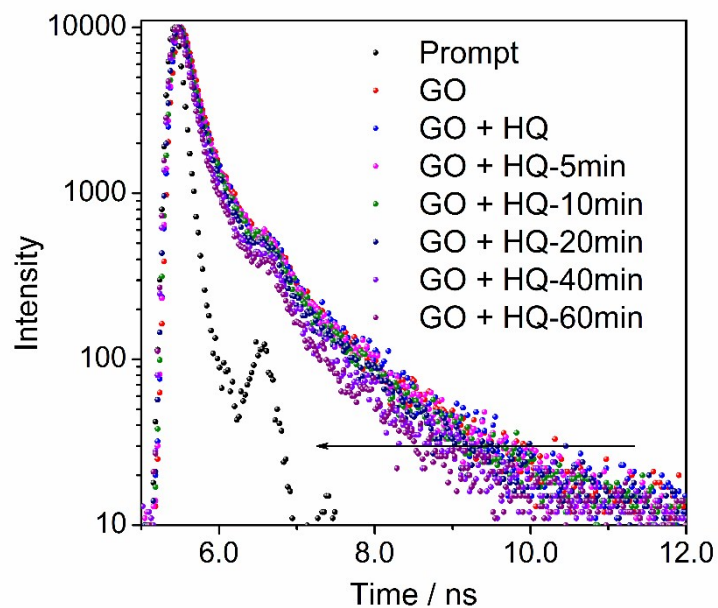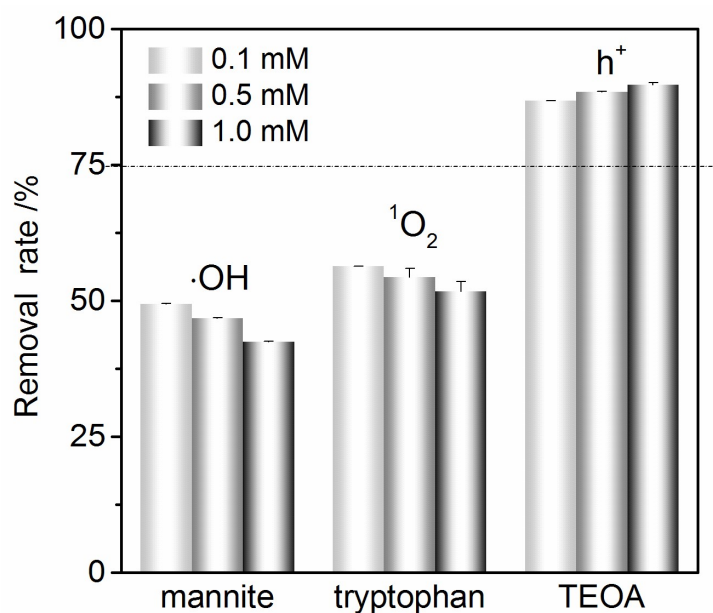
Figure S3. Time-dependent fluorescence lifetime quenching of GO (λex = 350 nm) in the presence of HQ (2.5 mg L^{-1}).Experimental conditions: GO concentration, 0.1 mg mL^{-1}, sample pH 7.0, irradiating with white LED for 0-60 min.

3.2. Effect of different scavenger concentrations

Figure S4. The removal rate of HQ by GO with the different scavenger concentrations. Experimental conditions: GO concentration, 0.1 mg mL^{-1}, HQ concentration, 2.5 mg L^{-1}, sample pH 7.0, irradiating with white LED time for 10 min.

3.3. Optimization of removal conditions
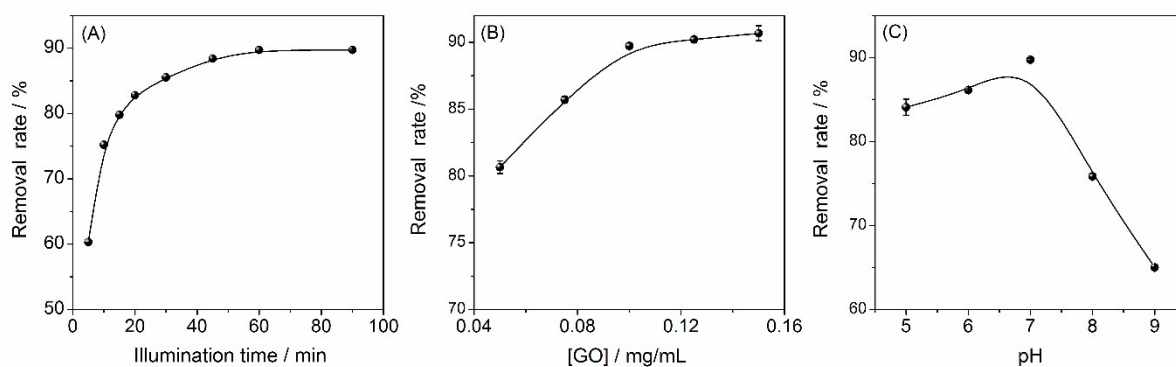
Figure S5. Factors that influence the removal rate of HQ by synergic adsorption and photosensitization of GO: (A) white LED illumination time; (B) the concentration of GO; and (C) sample pH. Experiments were carried out using 0.1 mg mL^{-1} GO and 2.5 mg L^{-1} HQ in PBS buffer (pH, 7.0) with a white LED illumination for 60 min unless otherwise stated.

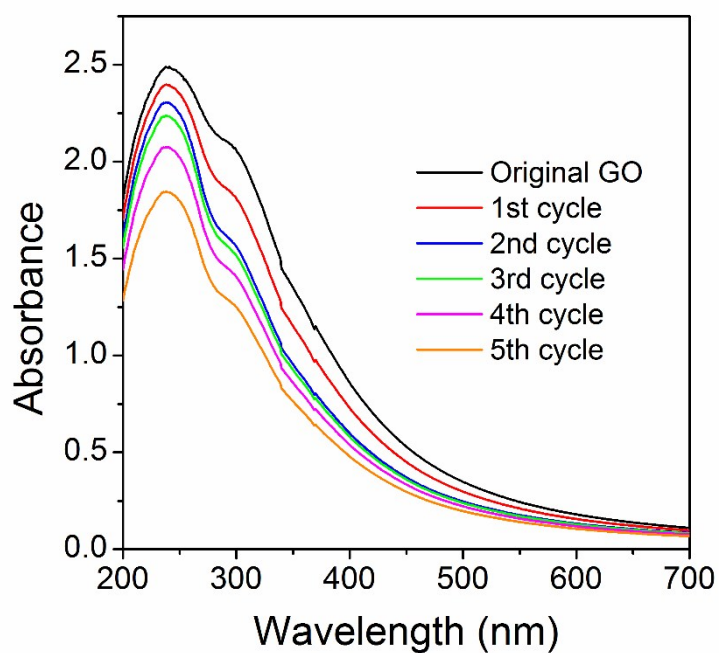## 4. Stability and Reusability of GO
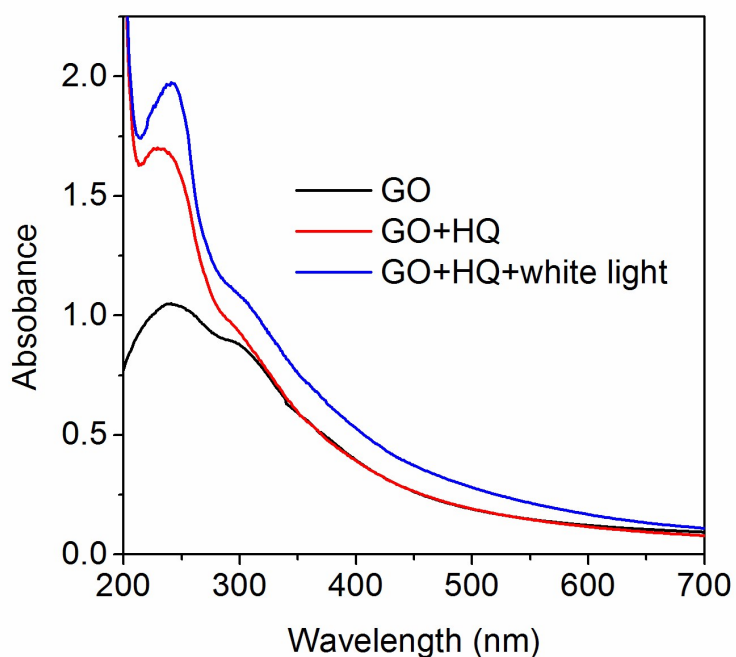
Figure S6. UV-Vis absorption spectra of GO before and after interaction with HQ.
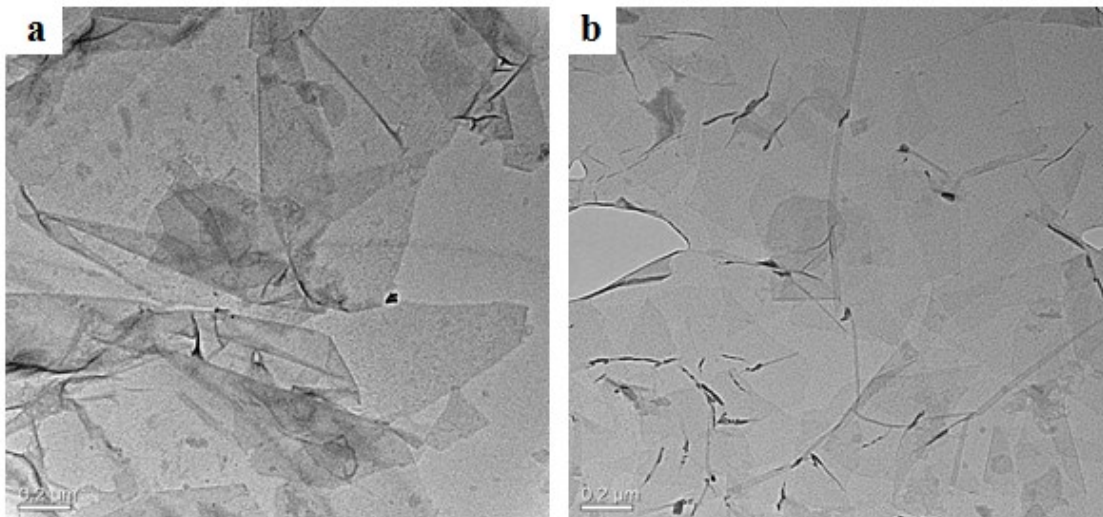
Figure S7. TEM images of GO nanosheets before (a) and after HQ adsorption (b).

Figure S8. The amount of GO suspension after several cycling. Experimental conditions: GO concentration, 0.1 mg mL^{-1}; HQ concentration, 2.5 mg L^{-1}; sample pH 7.0; irradiating with white LED for 60 min; elution was carried out with 2 mL deionized water.

5. Performance of polluant removal in real samples

Table S4. Pollutant (0.5 mg/L) removal performance of GO via synergic adsorption and photosensitization in real-world samples.

Sample matrix	Pollutants	Removal rate (%)
Tap water	PE	100.0 ± 0.2
	HQ	100.0 ± 0.2
	PCP	100.0 ± 0.2
Lake water	PE	98.2 ± 0.1
	HQ	98.6 ± 0.1
	PCP	97.4 ± 0.4
River water	PE	95.8 ± 0.2
	HQ	96.2 ± 0.1
	PCP	96.1 ± 0.2