Supporting Information

Atom-Scale Interfacial Coordination Strategy to Prepare Hierarchically Porous Fe₃O₄-Graphene Frameworks and their Application in Charge and Size Selective Dye Removal

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Experimental Section

Chemicals

All reagents and solvents were obtained commercially and used without further purification unless otherwise noted. Methylene blue (MB) [$C_{16}H_{18}N_3OS$, MW: 333.6 g mol^{-1}, λ_{max}: 665 nm], rhodamine 6G (Rh6G)[$C_{28}H_{30}N_2O_3$, MW: 442.5494 g mol^{-1}, λ_{max}: 528 nm], Methyl Orange (MO)[$C_{14}H_{14}N_3SO_3Na$, Mw: 327.33 g mol^{-1}, λ_{max}: 467 nm], Rhodamine B (RB) [$C_{28}H_{31}ClN_2O_3$, Mw: 479.01 g mol^{-1}, λmax: 554 nm], Potassium peroxymonosulfate ($2KHSO_5 \cdot 3KHSO_4 \cdot K_2SO_4$ available as Oxone, PMS), 2-Ethoxy-1-ethoxycarbonyl-1,2-dihydrquinoline (EEDQ, 99.9 %) and graphite powder were purchased from Sigma-Aldrich. Dopamine hydrochloride (DPA, 98%) was purchased from J&K Scientific Ltd.. Hydrogen peroxide, sulphuric acid (95–97%), sodium nitrate, dimethyl sulfoxide (DMSO), triethylamine were obtained from Tianjin Med. Water used in this experiment was purified by distillation of deionized water. The dialysis bags (MWCO 8000-14000) were purchased from Shanghai Med.

Instrumentation

The as prepared 3D-MGFs materials was characterized by several techniques. The IR analysis of these graphene oxide materials were conducted on Fourier transform infrared spectroscopy (FT-IR) VERTEX70 with a resolution of 4 cm^{-1} in transmission mode from 4000 to 400 cm^{-1}. X-ray diffraction (XRD) patterns were obtained on a Bruker AXS D8 advance diffractometer with Cu$_{Ka}$ radiation (λ=1.5418 Å). The magnetic measurements were calibrated using a Lakeshore 7404 high-sensitivity vibrating sample magnetometer (VSM) at room temperature. The magnetic hysteresis loop was obtained by using external magnetic fields of 1.5 tesla. The transmission electron microscope (TEM) was operated on a JEM-2100 (200kv) instrument. The specific surface area of the as prepared 3D-MGFs materials was determined by a Beckman Coulter SA3100 surface analyzer. X-ray photoelectron spectroscopy (XPS) measurements were performed using a PHI-5702 multifunctional spectrometer with Al$_{Ka}$ radiation. UV-visible adsorption spectra (UV-vis) were calculated by a UV 1750 spectrometer.

Experimental Procedures

Synthesis of GO-COOH

Hummer's method was used to synthesize GO from graphite powder.[1] Briefly, graphite (1g) was mixed with $NaNO_3$ (1 g) and H_2SO_4 (50 ml) at 0℃, and then the $KMnO_4$ (5 g) was slowly added into the above system within 30 minutes and stirred at 80℃ for 2 hours. Distilled water (80 ml) was slowly added into the system to quench the reaction with the help of ice-bath. The mixture was further added 200 ml distilled water to disperse. After that the mixture was treated with $30\%H_2O_2$ (20 mL) and stirred for 2h. The suspension was centrifuged and washed with distilled water until the pH = 7 and dialyzed in distilled water for 7 days.

The GO-COOH was synthesized according to the literature.[2,3] Typically, the dialyzed GO (200 mg) was dispersed in 200 ml distilled water, and then sodium chloroacetate (10 g), sodium hydroxide (10 g) were added to the above system and sonicated for 2.5 h at 30~40 °C, followed by adding concentrated nitric acid (8 ml) to adjust the pH to neutral. The suspension was centrifuged and washed with distilled water until the pH=7 and dialyzed in distilled water for 7 days. The obtained GO-COOH was dried at room temperature under vacuum conditions.
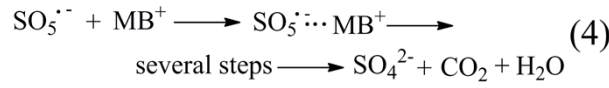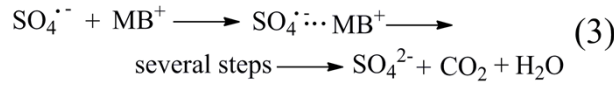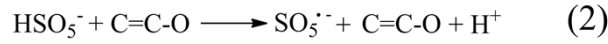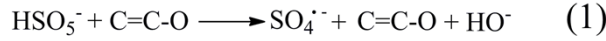
Synthesis of 3D-MGFs

50mg GO-COOH was dispersed in 40ml dried dimethyl sulfoxide and then added 0.555g EEDQ to activate the carboxyl group. 0.585g dopamine (DPA) hydrochloride dissolved in 10 ml dried dimethyl sulfoxide and 120μl triethylamine were added to above system under the protecting of nitrogen and stirred at room temperature for 24h. The products were centrifuged and washed with ethanol and water and then disperse in mixed solution (ethanol : chloform = 2:3). The Fe_3O_4 nanoparticles dispersed in $CHCl_3$ were added to above mixture and stirred for 24 h. the product was collected by centrifugation and dried under vacuum.

Dye adsorption experiments

Four dyes rhodamine 6G (Rh6G), methylene blue (MB) methylene orange (MO), Rhodamine RB were employed to investigate the adsorption behavior of the as prepared 3D-MGFs. In a typical experiment, the as-prepared 3D-MGFs (12 mg) was added into aqueous dye solution (200mL of 20 mg L^{-1}), followed by stirring at room temperature. At predetermined time intervals, 3 mL of the mixture was taken out and centrifugation at 12000 rpm. The dye concentration was measured by UV-Vis spectrometer at the maximum absorbance of each dye (528 nm, 665 nm, 467 nm, 554 nm for Rh6G, MB, MO, and RB respectively).

PMS was chosen as the oxidant catalyst to investigate the desorption and degradation behavior of the loaded dyes on the 3D-MGFs. Wang [4] reported that chemically reduced graphene oxide can effectively activated peroxvmonosulfate (PMS) to produce active sulfate radicals. What's more, the produced sulfate radicals are able to decompose various aqueous contaminants. Because the ketonic (C=O) groups are rich on the surface of the 3D-MGFs, which enable the transport of the electrons. Thus the ketonic (C=O) groups have a great potential to coordinate a redox reaction. The catalysis mechanisms for PMS activation and MB oxidation would be carried out following the equations (1)-(4).

$$HSO_5^- + C=C-O \longrightarrow SO_4^{\cdot-} + C=C-O + HO^- \qquad (1)$$

$$HSO_5^- + C=C-O \longrightarrow SO_5^{\cdot-} + C=C-O + H^+ \qquad (2)$$

$$SO_4^{\cdot-} + MB^+ \longrightarrow SO_4^{\cdot-}\cdots MB^+ \longrightarrow$$
$$\text{several steps} \longrightarrow SO_4^{2-} + CO_2 + H_2O \qquad (3)$$

$$SO_5^{\cdot-} + MB^+ \longrightarrow SO_5^{\cdot-}\cdots MB^+ \longrightarrow$$
$$\text{several steps} \longrightarrow SO_4^{2-} + CO_2 + H_2O \qquad (4)$$

The details were described as follows. 12 mg 3D-MGFs and 0.05g PMS were added into the MB solution stirring for 2 hours. Then with the help of an external magnetic field, the 3D-MGFs were separated from the solution. In case of the residual dye on the surface of the materials, ethanol was used to wash the 3D-MGFs until the solution was colorless. The materials can be subjected to multiple rounds of reuse.

Adsorption isotherm

The amount of dye absorbed on absorbents at time t, q_t(mg g^{-1}), was calculated using the following equation:

$$q_t = \frac{(c_0-c_t)}{m}V \qquad (5)$$

where C_0 and C_t are the concentration of dye in the liquid phase (mg L^{-1}) initially and at time t, respectively, V is the volume of dye solution used (L), and m is the mass of the adsorbent used (g). The adsorption isotherms of these dyes on 3D-MGFs , were analyzed by Langmuir and Freundlich isotherm models. The Langmuir isotherm is mainly due to the monolayer adsorption process (constant heat of adsorption for all sites). The linearized equation was given as :

$$\frac{C_e}{q_e} = \frac{1}{Q_m b} + \frac{1}{Q_m}C_e \qquad (6)$$

where Ce (mg L^{-1}) and qe (mg g^{-1}) are the equilibrium adsorbents concentration in aqueous and solid phases, respectively. Qm is a coefficient represented the maximum monolayer uptake by the adsorbent (mg g^{-1}). Linear regression plot of Ce/q_e versus Ce can get the values of Qm and b. While the Freundlich adsorption isotherm is mainly because of mutilayer adsorption on heterogeneous surface, taken the assumption that the adsorption sites are distributed exponentially with the respect to the heat of adsorption. And can be expressed as:

$$\log q_e = \log K_f + (1/n)\log C_e \qquad (7)$$

K_f is the Freundlich's uptake factor and n denotes Freundlich intensity factor. From the linear regression plot of log q_e versus log Ce we can obtain the value of n which is in the range of 1-10.

Adsorption kinetics

To evaluate the kinetic mechanism for adsorption of these dyes, the adsorption phenomenon has been analyzed with pseudo-first and pseudo-second order kinetic models (eqs 6 and 7).

$$\log (q_e-q_t) = \log q_e - \frac{k_1 t}{2.303} \qquad (8)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (9)$$

Where qe and qt are adsorption capacity at steady state and at time t, respectively; k_1 and k_2 are

pseudo-first and second order kinetic rate constants (g mg^{-1} min^{-1}), respectively. The results indicate that these four dyes uptake on the 3D-MGFs are favorable by the pseudo-second-order kinetic model. The pseudo-second-order model showed a higher correlation coefficient (R) than that of the pseudo-first-order.

Study on adsorption isotherms and kinetics parameters of 3D-MGFs to MB

Furthermore, the adsorption isotherms and kinetics parameters for adsorption of MB were analyzed using eq. 5 to 9 (in supporting information) and the linear plots are shown in Figure S7 to S10. From the correlation coefficients from eq. 6 and 7, the adsorption data could be fitted with both Langmuir and Freundlich isotherms. While the Freundlich model was found to be a better fit for dye adsorption by 3D-MGFs, which suggests that the adsorbent surface was heterogeneous in nature. And the correlation coefficients from eq. 8 and 9 shows that the adsorption process of 3D-MGFs for dyes fits well with the pseudo-second-order kinetic model, which is consistent with these results reported previously.[6,7]

Reference

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[5] M. Feng, W. You, Z.S. Wu, Q.D. Chen, H.B. Zhan, *ACS Appl. Mater. Interfaces* 2013, **5,** 12654−12662.

[6] Sui, Z. Y.; Meng, Q. H.; Zhang, X. T.; Ma, R.; Cao, B. *J. Mater. Chem.* 2012, **22**, 8767−8771.

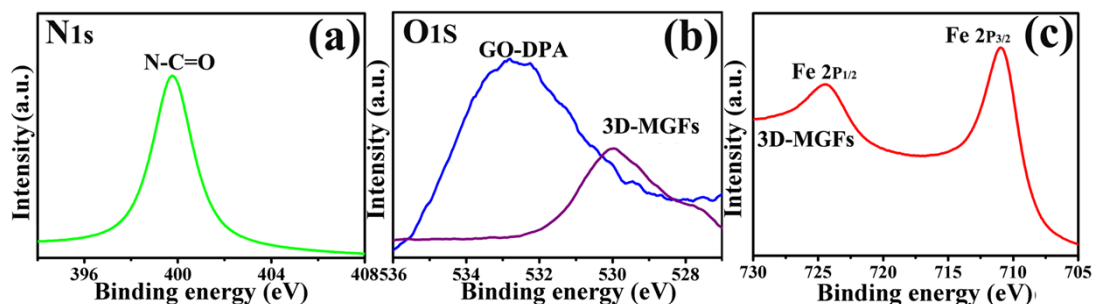[7] Sun, L.; Tian, C.; Wang, L.; Zou, J.; Mu, G.; Fu, H. *J. Mater. Chem.* 2011, **21**, 7232−7239.

Figure S1. XPS spectra of (a) N $_{1s}$ spectra GO-DPA; (b) O $_{1s}$ spectra of GO-DPA and 3D-MGFs; (c) Fe 2p spectra of the 3D-MGFs.
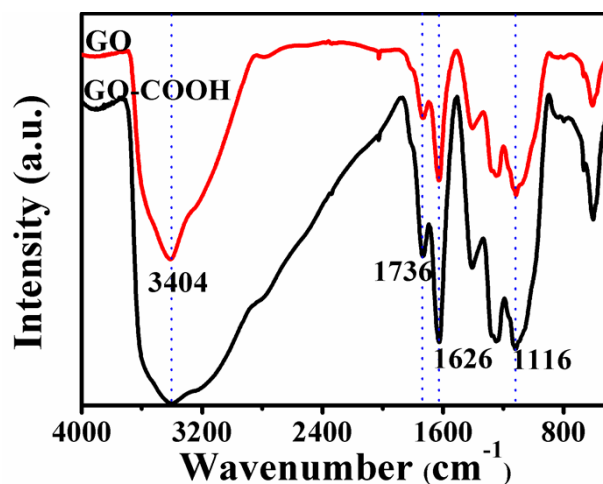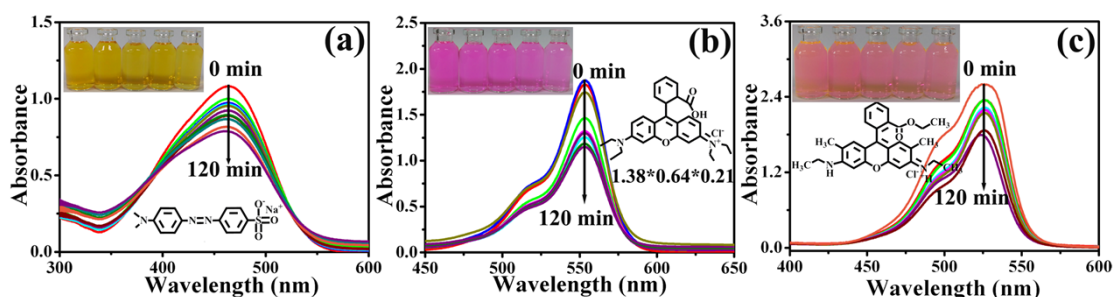
Figure S2. FTIR of GO and GO-COOH.

Figure S3. UV-vis spectra and photographs of aqueous solution of (a) MO, (b) RB and (c) Rh6G dyes with 3D-MGFs after magnetic separation in different time intervals, the inset shows the molecule structure of the corresponding dyes, respectively.
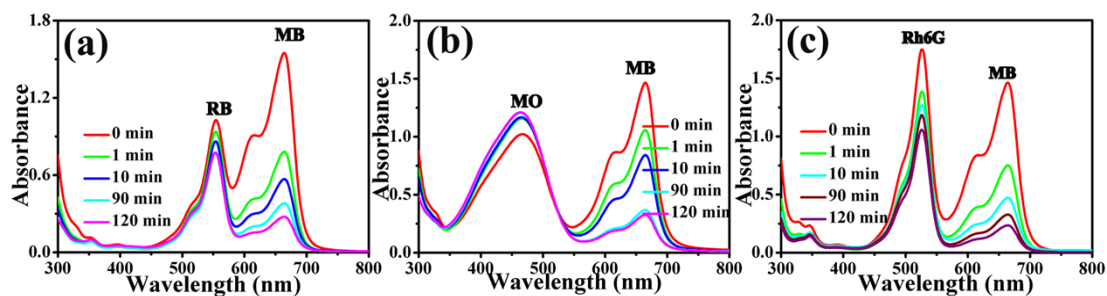

Figure S4. The UV−vis absorption spectra of mixed aqueous dye solution (20mg/L) in the presence of 3D-MGFs :(a) RB and MB, (b) MO and MB, (c) Rh6G and MB.
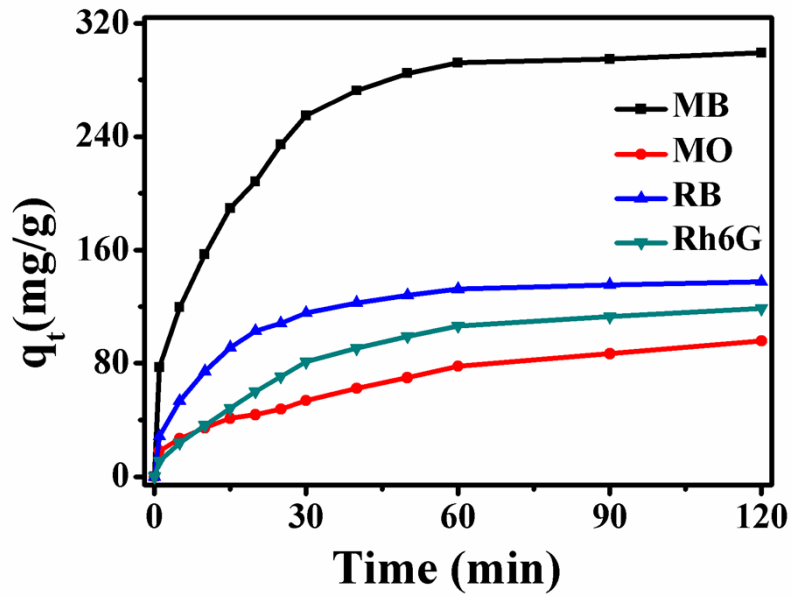
Figure S5. The adsorption capacity of the 3D-GMFs towards the MB, MO, RB and Rh6G.
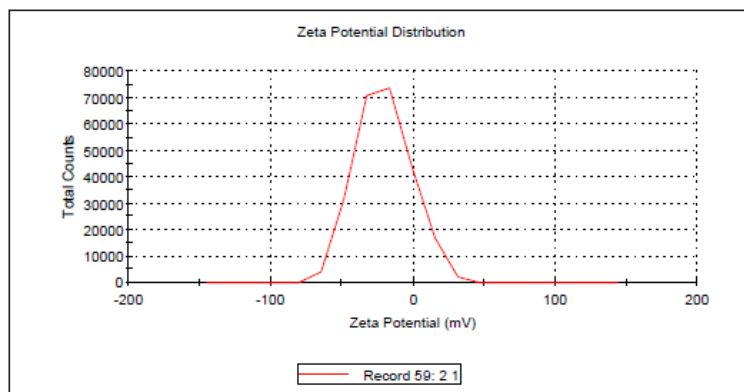
Figure S6. The Zeta potential distribution of the 3D-GMFs.
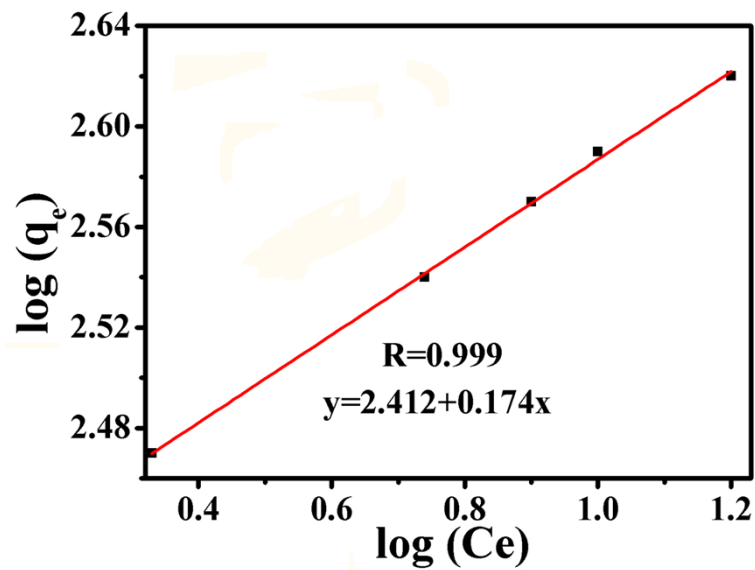
Figure S7 Analysis of Freundlich isotherm model for the adsorption of MB.
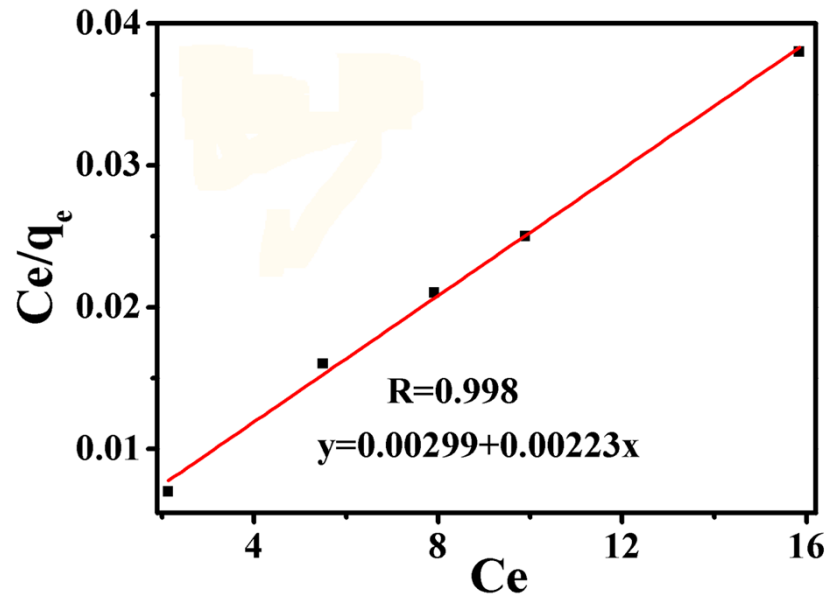
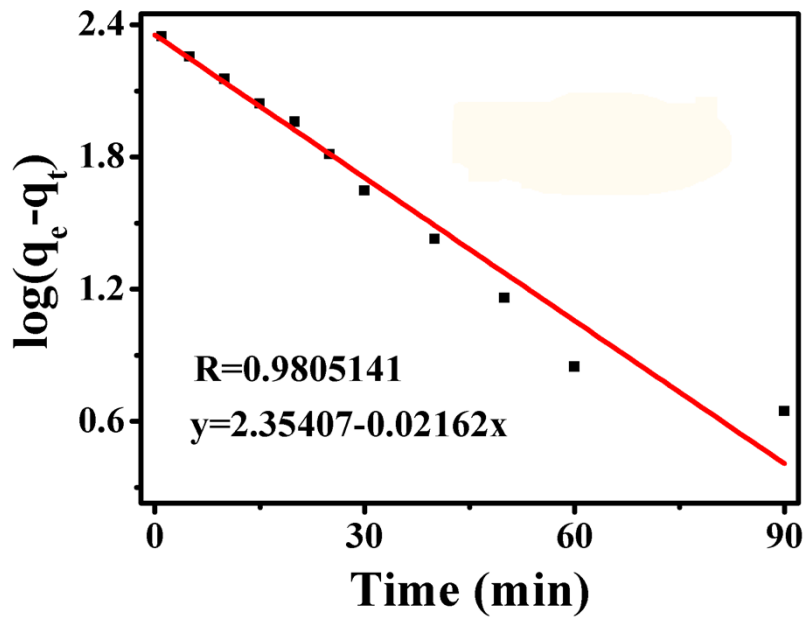**Figure S8** Analysis of Langmuir isotherm model for the adsorption of MB.

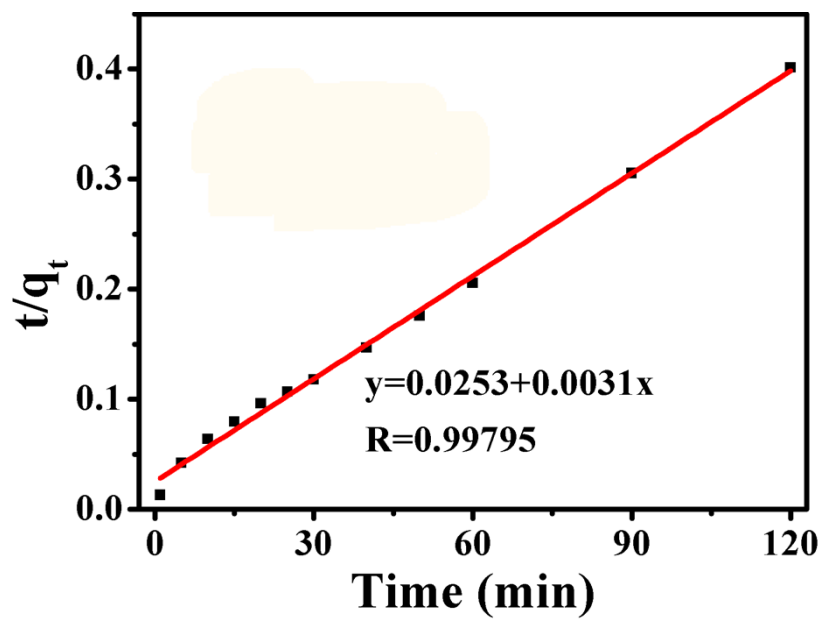**Figure S9.**Pseudo-first order kinetic models of analysis of adsorption of MB on 3D-GMFs.

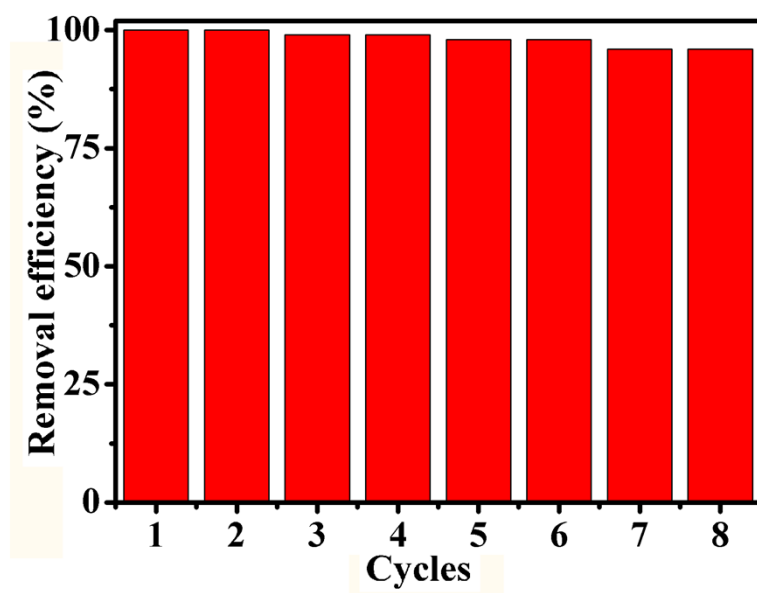**Figure S10.** Analysis of pseudo-second order kinetic models adsorption of MB on 3D-GMFs.

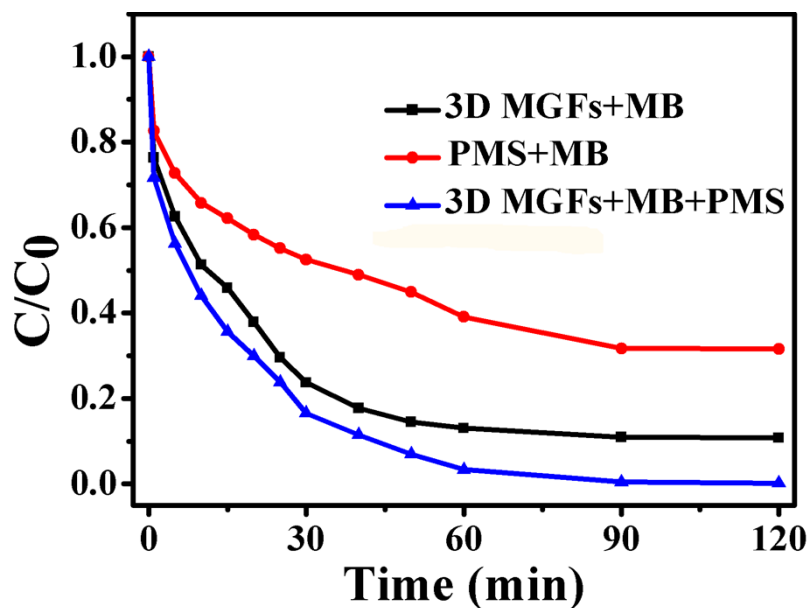**Figure S11.** Recycling of 3D-MGFs in the removal of MB.

Figure S12. MB adsorption and removal with PMS as oxidant and 3D GMFs as adsorbents and catalysts. Firstly, PMS and MB were adsorbed onto the surface of GO to initiate the oxidant reaction. When the reaction was over, the MB was changed into CO_2 and H_2O, as the equation shows in (1)-(4).
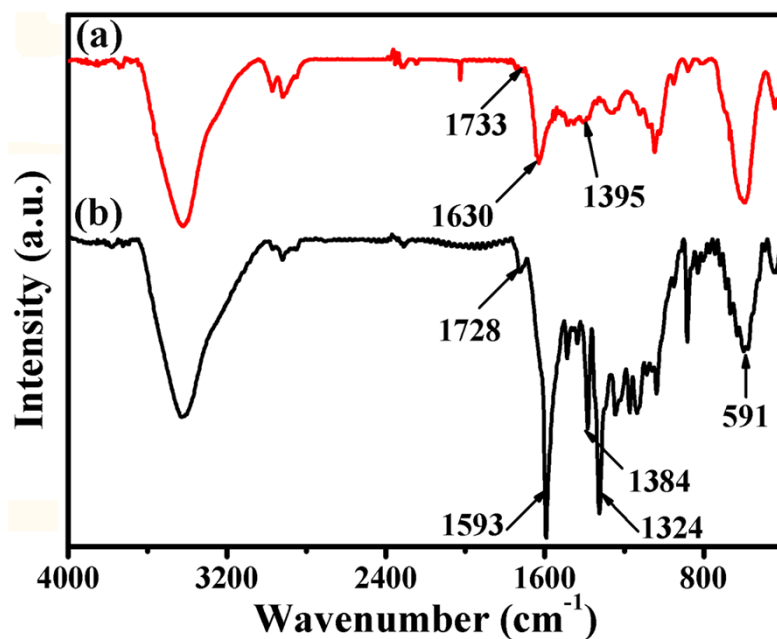

Figure S13. FT-IR spectra of: (a) the 3D-GMFs adsorbed MB with the addition of PMS. (b) the 3D-GMFs adsorbed MB. The characteristic spectrum of MB, such as its ring stretch at 1593cm^{-1}, the symmetric stretch of C−N at 1384 cm^{-1}, and symmetric deformation of −CH$_3$ at 1324 cm^{-1} was recorded in the spectrum of the adsorptive adduct.[5] While, after added PMS in the system, and washed with water and ethanol several times, the characteristic peak of the MB disappeared. Which means that, the MB adsorbed on the 3D-GMFs was removed.