

Electronic Supplementary Information

Synthesis of Iron(III)-Based Metal–Organic Framework/Graphene Oxide Composites with Increased Photocatalytic Performance for Dye Degradation

Yan Wu^{ab}, Hanjin Luo^{*ab}, Hou Wang^c

a College of Environmental and Energy, South China University of Technology, Guangzhou 510006, P.R. China E-mail: wuyan1101@126.com.

b The Key Laboratory of Pollution Control and Ecosystem Restoration in Industry Clusters of Ministry of Education, Guangzhou 510006, P.R. China E-mail: luohj@scut.edu.cn. Tel.: +86 020 87110517; fax: +86 020 87110517.

c College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China. E-mail: huankewanghou024@163.com.

Materials and Reagents: Solvents and all other chemicals were obtained from commercial sources and were used as received unless otherwise noted. 1,4-benzenedicarboxylic acid (BDC) was purchased from Aladdin China Co., Ltd. (Shanghai, China); Ferric Nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), *N,N*-dimethylformamide (DMF), and ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) were provided by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China); Graphite powder, nitric acid (HNO_3), hydrochloric acid (HCl), sulfuric acid (H_2SO_4), sodium Nitrate (NaNO_3), hydrogen peroxide (30% H_2O_2), and potassium permanganate (KMnO_4) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Methylene blue (MB) solution and rhodamine B (RB) were obtained from Damao Chemical Reagent Co., Ltd. (Tianjin, China). Deionized water was obtained from a Sartorius arium 611DI water purification system. The initial methylene blue (MB) solution and rhodamine B (RB) solution were prepared by dissolving MB and RB in deionized water, respectively.

Preparations:

The synthesis of graphene oxide (GO): GO was synthesized from natural graphite by a modified Hummers method according to our previous reports. Graphite (5.0 g) and NaNO_3 (2.5 g) were mixed with 120 mL of H_2SO_4 (98%) in a 500 mL beaker. The mixture was stirred for 30 min in ice bath. While maintaining vigorous stirring, potassium permanganate (15.0 g) was added to the suspension. The rate of addition was carefully controlled to keep the reaction temperature lower than 288 K. After 90 min, the ice bath was removed and the mixture was stirred at 308 K for 30 min. As the reaction progressed, the mixture gradually became pasty and the color turned into light brownish. At the end, 230 mL of deionized water was slowly added to the paste with vigorous agitation. The reaction temperature rapidly increased, and the color changed to yellow. The diluted suspension was stirred at 371 K for 30 min. Then, 30 mL of 30% H_2O_2 was added to the mixture. For purification, the mixture was centrifuged with 5% HCl then deionized water several times, and finally freeze-dried under vacuum for 24 h.

The synthesis of MOF and MOF@GO: MOF was prepared by mixing 1,4-benzenedicarboxylic acid (BDC) (2 g) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (5 g) in 50 mL of *N,N*-dimethylformamide (DMF), which was stirred and sonicated for 5 min. Then ethanol (50 mL) and deionized water (50 mL) were added to the solution in turn with stirring and sonicating for 5 min and 30 min, respectively. After that, 0.25 g GO was added to the well-dissolved MOF precursor with stirring and sonicating the resulting mixture for 30 min. Finally, the mixture was then transferred to a round-bottom flask and heated at 85°C in an oil bath for 12 h under shaking. After cooling to room temperature, the reaction mixture was filtered and washed several times with sufficient volume of ethanol and deionized water and then dried at 60°C for 24 h before use. Moreover, MOF was also prepared according to the above-mentioned procedure without the adding of GO for comparative analysis.

Characterization: Scanning electron microscope (SEM) images were obtained using a JEOL (Japan) S-3700N SEM at different magnifications with an accelerating voltage of 15 kV. Fourier transform infrared spectrum (FTIR) patterns were determined using a Bruker Tensor 27 FTIR spectrophotometer. Typically, 100 scans were collected at a resolution of 4 cm^{-1} in the range of $4000\text{--}400 \text{ cm}^{-1}$. The X-ray diffraction (XRD) patterns were recorded using a Bruker D8-advance X-ray diffractometer at 40 kV and 40 mA. A Cu $K\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$) source was used in the X-ray tests. All patterns were collected at a scanning rate of $0.020^\circ/\text{step}$ and 17.7 s/step , 2θ ranging from 5° to 90° . The X-ray photoelectron spectroscopy (XPS) measurements were conducted with an Axis Ultra DLD spectrometer (Kratos Analytical Ltd., England) with a monochromatized Al $K\alpha$ X-ray source ($h\nu=1486.6 \text{ eV}$). Raman spectra were recorded with Renishaw R-3000QE system in the backscattering configuration using an Argon ion laser with wavelength 785 nm. Thermogravimetric analysis (TGA) curves were measured by using a SDT Q600 thermogravimetric analyzer from room temperature to 800°C with heating rate of $10^\circ\text{C}/\text{min}$ and an air flow rate of 100 mL/min under air flow. UV-vis diffuse reflectance spectra (DRS) were measured over the spectral range 200–800 nm on a Cary 300 UV/Vis spectrophotometer (Agilent, USA).

Photocatalytic reaction experiment: The catalytic activity of MOF@GO catalyst has been explored through degradation of two important dyes, methylene blue (MB) and rhodamine B (RB) under exposure to natural sunlight. The average intensity of sunlight was measured using Light Meter (LX1010B), which was found to be 760–840 W/m². The photocatalytic experiment was performed in natural atmosphere, without any external source of aeration. In each experiment, 50 mg catalyst was added into 100 mL aqueous solution of RB (100 mg L⁻¹) or MB (100 mg L⁻¹). The suspension was then exposed to natural sunlight under constant stirring at room temperature. At a given interval of time, 5 mL of suspension was taken out, and then filtered through 0.45 μm filter membrane. The filtrate was analyzed to determine the concentration of RB or MB remaining in the solution, using a UV–vis spectrophotometer (UV-1750, SHIMADZU, Japan) at an absorbance wavelength of 554 or 665 nm, respectively. The normalized concentration of RB or MB after exposing to sunlight was calculated as C_t/C_0 , where C_0 is the initial concentration of RB or MB and C_t is the concentration of RB or MB measured after exposure at a particular interval of time. All the experiments were performed under direct sunlight during June between 1 p.m. and 3 p.m..

UV-vis diffusion spectra: Fig. S1 displays the UV-vis diffuse reflectance spectra (DRS) of the as-prepared samples. The UV-vis spectrum of GO displays an absorption band from 230 nm to around 260 nm, which could be assigned to π - π^* transitions of aromatic C-C bonds and n - π^* transitions of C=O bonds.¹⁻³ The UV-vis spectrum of the MIL-88(Fe) shows a distinct absorption band from 250 to 350 nm and the absorption edge is around ~700 nm. After the introduction of GO into the MIL-88(Fe), a broad background absorption in the visible-light region (400–700 nm) for the MIL-88(Fe)@GO can be observed. In addition, the UV-vis spectrum of MIL-88(Fe)@GO displays both the characteristic absorption bands corresponding to GO and MIL-88(Fe).

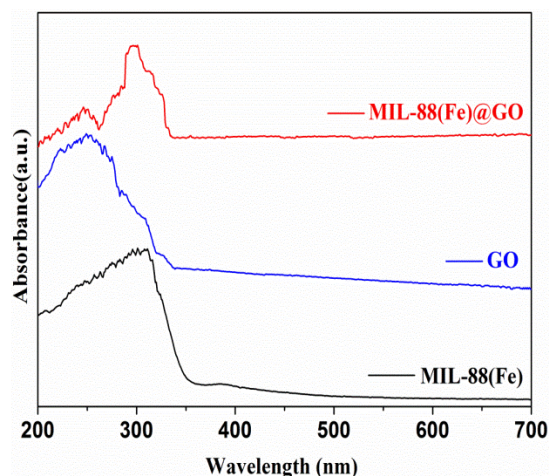


Fig. S1 UV-vis diffuse reflectance spectra of the GO, MIL-88(Fe) and MIL-88(Fe)@GO composites.

References:

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