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An Engineered Membrane Separation System Using Binder-Free Immobilized Heterojunction Photocatalyst for Enhanced Energy-Efficient Organic Dye Separation

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Experimental Section.

Materials.

N, N-dimethylformamide (DMF, 99.8%), sodium hydroxide (NaOH, 98%), and ammonium persulfate ($(NH_4)_2S_2O_8$, 98%) were purchased from Aladdin. 2, 3, 6, 7, 10, 11-hexahydroxytriphenylene (HHTP, 95%), graphitic carbon nitride (g-C_3N_4, 95%), and absolute ethanol were purchased from Shanghai Macklin Biochemical Co. Ltd. Copper foam (thickness: 0.2 cm, 130 ppi) was gained from the local market. Various dyes such as Methylene blue (MB), Congo red (CR), Malachite green (MG), and Crystal violet (CV) were purchased from Sinopharm Chemical Reagent Co. Ltd. All materials and chemicals were used as received without additional purification.

Synthesis of CF-MOF

A copper foam (thickness: 0.2 cm, 130 ppi; CF) was cut into 1 cm^2 pieces, ultrasonically cleaned with absolute ethanol and deionized water. $Cu(OH)_2$ nanowires were then grown on the foam by immersing it in 100 mL of an aqueous solution containing NaOH (10 g) and $(NH_4)_2S_2O_8$ (2.98 g) at room temperature for 20 min, followed by thorough rinsing with Milli-Q water. To grow MOF crystals on the nanowires, the sample was immersed in a mixed solvent of Milli-Q water and DMF (v/v = 10:1) containing 75 mg HHTP in a Petri dish and heated at 70 °C for 20 min in a preheated oven, yielding CF-MOF. After natural cooling to room temperature, the resulting CF-MOF was rinsed sequentially with acetone, absolute ethanol, and deionized water for further use.

Fabrication CF-MOF/g-C_3N_4

First, 100 mg of g-C_3N_4 was dispersed in 25 mL of ethanol and sonicated for 1 h. The resulting suspension was then spray-coated onto CF-MOF at 0.2 MPa using an airbrush. Finally, the CF-

MOF/g-C_3N_4 composite was dried overnight. For comparison, g-C_3N_4 was directly spray-coated onto a 1 cm^2 copper foam sheet (denoted as CF/g- C_3N_4) using the same method.

Characterization

The morphology and microstructure of CF-MOF/g-C_3N_4 were characterized by SEM (TESCAN MIRA LMS). The chemical composition and functional groups were analyzed by X-ray photoelectron spectroscopy (XPS) (AXIS Ultra DLD, Shimadzu Corporation). The dyes were measured by UV-vis spectrophotometer (TU-1801, Persee, China). Solar simulated xenon lamp (CEL-S500L) was used to provide the energy required for photocatalysis.

Photocatalytic degradation experiment

In the photocatalytic degradation experiment, two cationic dyes and two anionic dyes were used for testing. The cationic dyes were methylene blue and crystal violet, and the anionic dyes were Congo red and malachite green. During the experiment, the concentration of all four dye solutions was 10 mg/L. A piece of CF-MOF/g-C_3N_4 sample (1 cm^2) was placed in each of the four dye solutions (25 mL, 10 ppm). Then, the mixture was exposed to a 300 W Xe lamp **(λ = 420-2500 nm, equipped with a 420 nm cut-off filter)** placed at a distance of 10 cm. At predetermined intervals, 25 mL of the solution was sampled for analysis. The absorbance of the dye before and after the test was measured by a UV-vis spectrophotometer, and the concentration of the dye was calculated by substituting the values into the prepared standard curve. The CF-MOF/g-C_3N_4 was then replaced with CF-MOF, g-C_3N_4, and CF/g-C_3N_4 to repeat the above experiment and record the corresponding measurement data. The formula for pseudo-first-order kinetics is as follows:

$$ln(\frac{C_0}{C}) = kt \quad (1)$$

In this equation, C (mg·L^{-1}) represents the concentration of the dye solution after degradation, C_0 (mg L^{-1}) represents the initial concentration of the dye, k (min^{-1} or s^{-1}) is the pseudo-first-order rate constant, and t represents the reaction time.

Photocatalytic dye filtration and adsorption experiment

Four dye solutions (CR, MB, CV, and MG; 10 mg/L each) were prepared for filtration experiments. Flux and separation efficiency were evaluated using a filtration setup with a total effective area of 94.2 cm^2 (3.14 cm^2 × 30). In the photocatalytic filtration–adsorption tests, CF-MOF/g-C_3N_4 was first immobilized in the filtration device. Each dye solution (100 mL) was treated separately, and the filtrate was collected for analysis by UV-vis spectrophotometry. For large-volume adsorption experiments, CF-MOF/g-C_3N_4 was fixed in a glass filter funnel, and 500 mL of dye solution was gravity-fed dropwise into the funnel, with the filtrate collected in a beaker. The separation efficiency (R, %) and water flux (F, L m^{-2} h^{-1}) were calculated as follows:

$$R = (1 - \frac{C_0}{C_1}) \times 100\% \quad (2)$$

$$Flux = \frac{V}{A \times T} \quad (3)$$

where C_0 (mg L^{-1}) and C_1 (mg L^{-1}) are the concentration of dye in the solutions before and after adsorption, respectively. V (mL) is the volume of the dye solution, T (h^{-1}) is the filtration time and A (m^{-2}) is the effective adsorption area of the membrane.

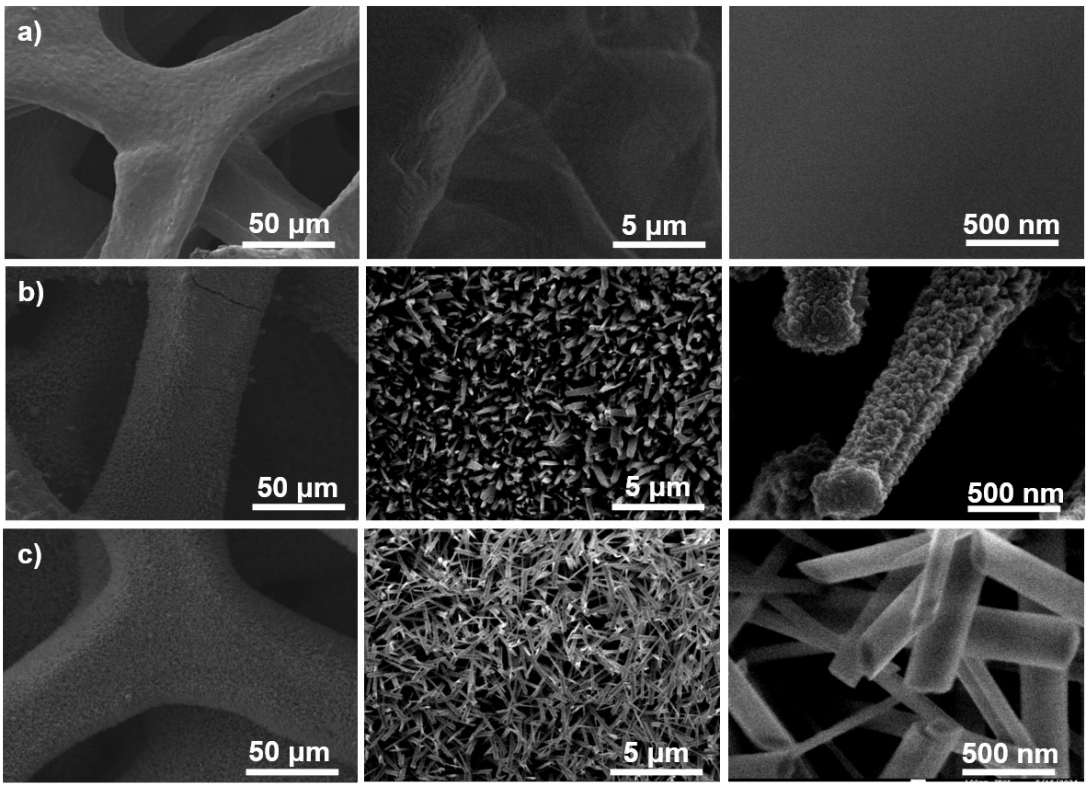

Figure S1. SEM images of pristine CF (a), CF-Cu $(OH)_2$ (b) and Cu-MOF (c).

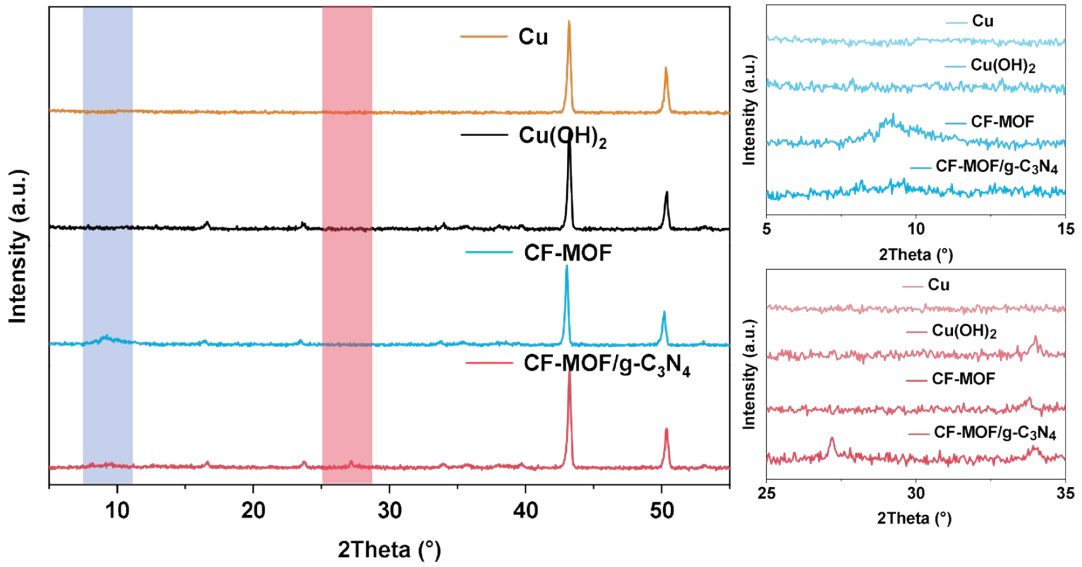

Figure S2. XRD patterns of CF,$Cu(OH)_2$ NWs,CF-MOF and CF-MOF/g-C_3N_4.

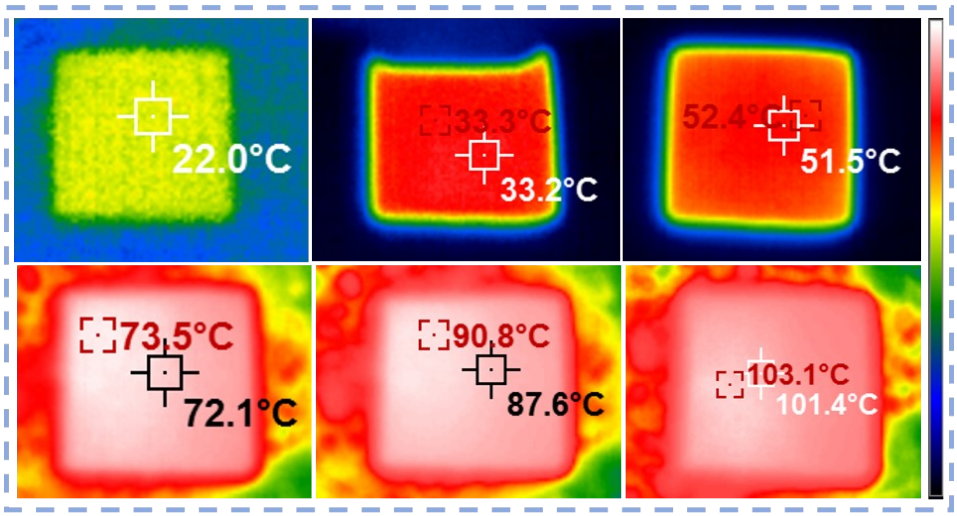

Figure S3. Thermal images of Cu-MOF/g-C_3N_4 under the simulated sunlight irradiation.

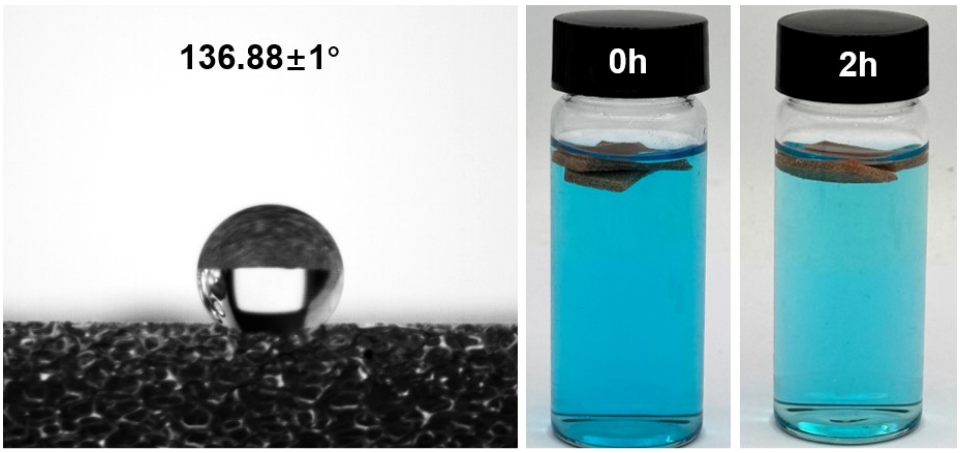

Figure S4. (a) WCA of the Cu/g-C_3N_4. (b) Cu/g-C_3N_4 dyes remove digital images under light.

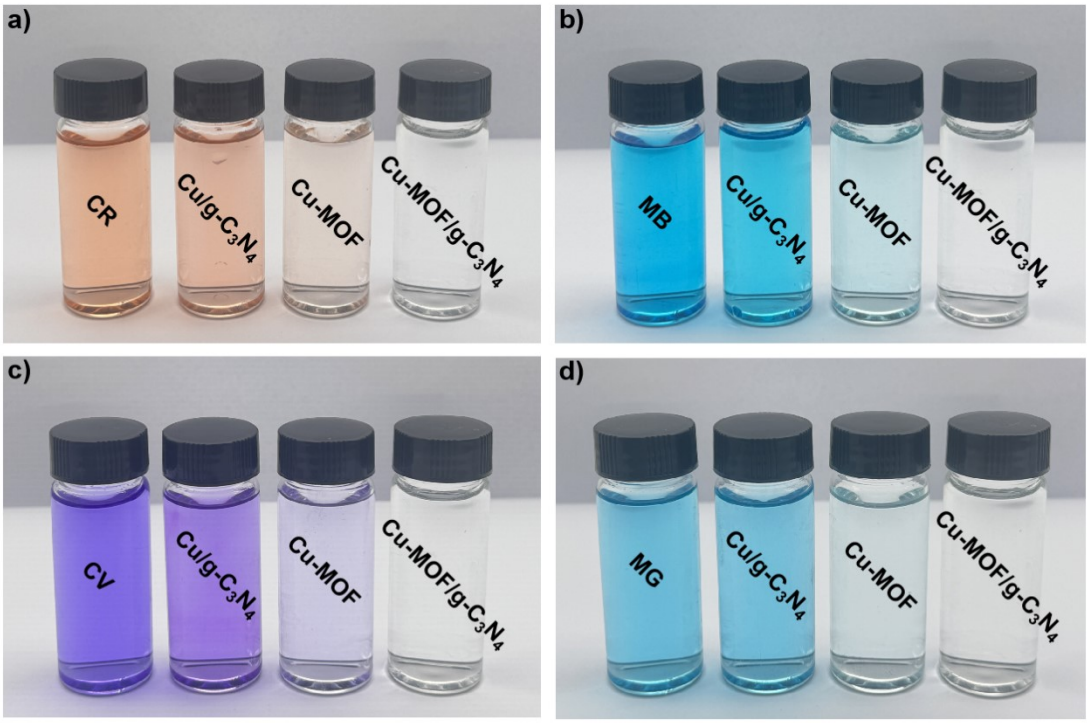

Figure S5. Digital images of Cu/g-C_3N_4, Cu-MOF and Cu-MOF/g-C_3N_4 photocatalytic processes were recorded (a: Light 30min, CR; b: Light 42min, MB; c: Light 50min, CV; d: Light 35min, MG).

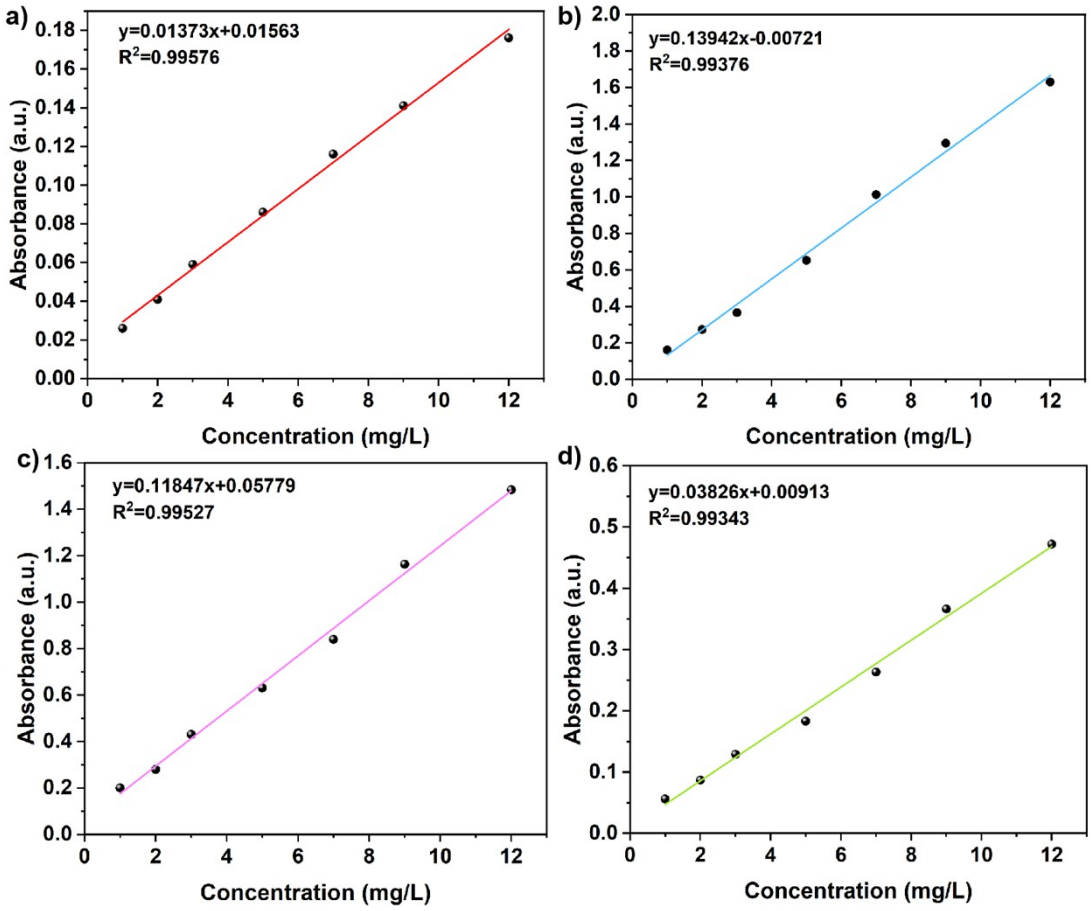

Figure S6. Standard curve of absorbance concentration of CR (a), MB (b), CV (c) and MG (e).

Figure S7. Photodegradation of MB without any catalyst under light irradiation.

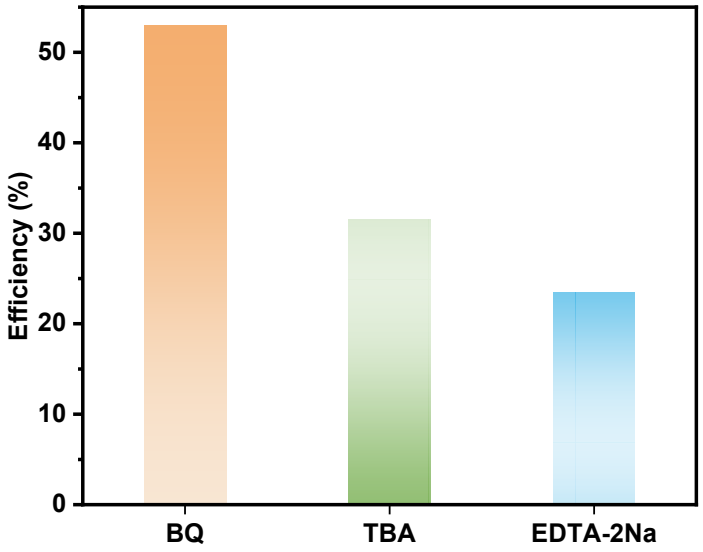

Figure S8. Degradation efficiency of MB by CF-MOF/g-C_3N_4 after adding different radical scavengers.

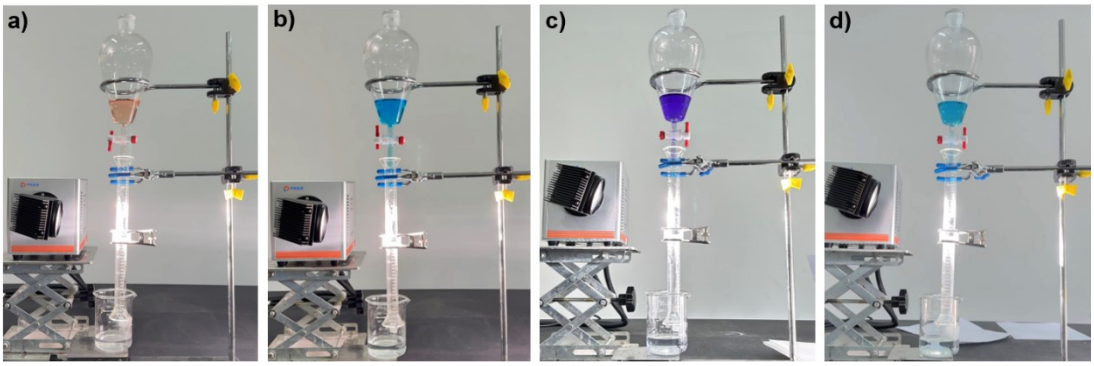

Figure S9. Diagram of the separation process of various dyes (a: CR, b: MB, c: CV, d: MG) under light conditions.

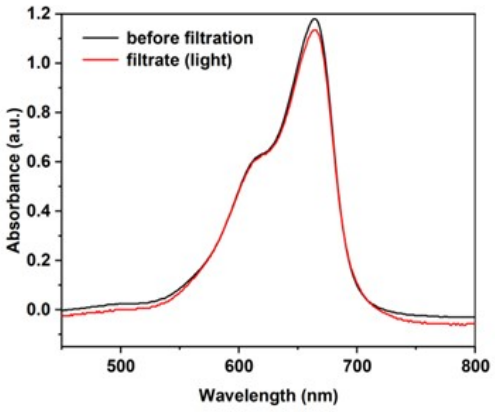

Figure S10. Dye removal efficiency of the CF-MOF/g-C_3N_4-based columnar separation system under dark conditions.

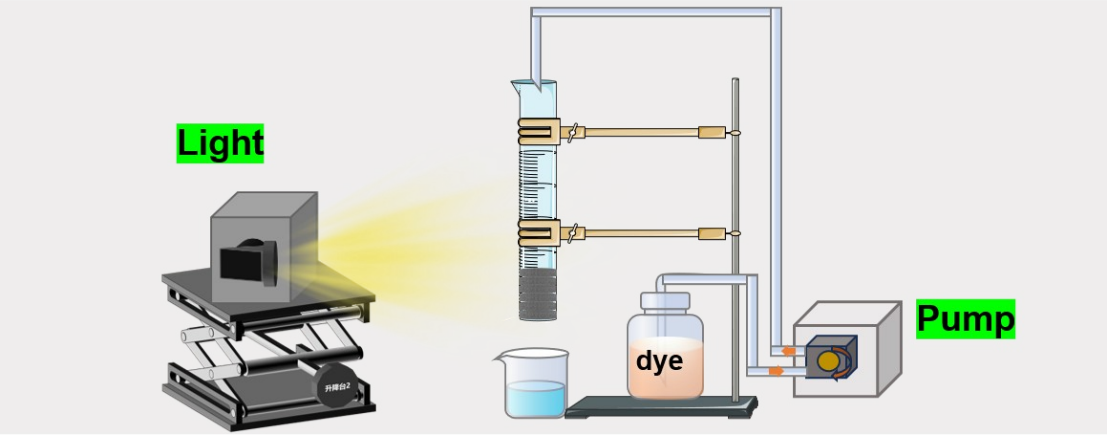

Figure S11. Schematic diagram of the long-term massive dye separation process.

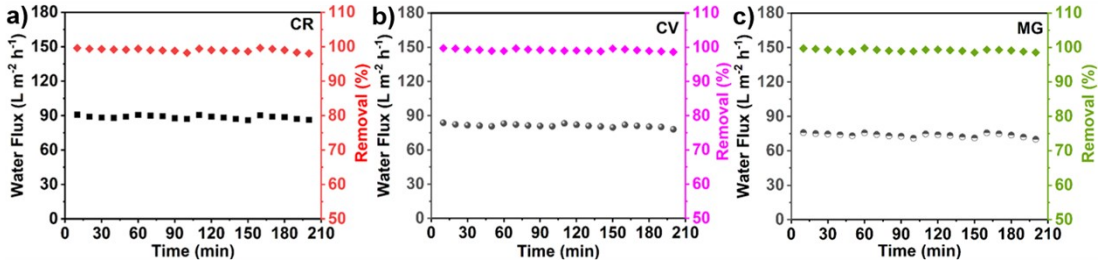

Figure S12. Dynamic changes in permeability and removal rate of dyes.

Sample	E_{fb} (V vs RHE)	E_{CB} (V vs RHE)	E_{VB} (V vs RHE)	E_g (eV)
CF-MOF	+0.115	+0.115	+2.435	2.32
CF-MOF/g-C_3N_4	+0.25	+0.25	+2.11	1.86

Table S1. Band position parameters of CF-MOF and CF-MOF/g-C_3N_4.