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Supporting Information

Synergistic purification of chromium-containing wastewater by adsorption-photocatalysis induced by multi-defective CuS/Cv-CNNs

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Preparation of Cv-CNNs and CuS:

1 Preparation of Cv-CNNs

Typically, CNNs are obtained by thoroughly mixing 10 g of NH_4Cl with 2 g of melamine and then heating to 550 °C at a rate of 5 °C/min for 4 hours. Then, 2 g of CNNs were again mixed with 10 g of NH_4Cl and heated for 2 hours to 500 °C at a rate of 5 °C min^{-1} to produce Cv-CNNs.

2 Preparation of CuS

Slowly drop 50 mL of aqueous $Na_2S·9H_2O$ (3.5169 g) into 50 mL of aqueous $Cu(NO_3)_2·3H_2O$ (1.1792 g) using a dropper at room temperature with stirring. After vigorous stirring for 15 min, The precipitate was collected, cleaned with ethanol and deionized water, vacuum-dried at 60 °C for 10 hours, and crushed to create CuS powder.

Thermodynamic study of adsorption

Adsorption thermodynamic tests were carried out by placing 30 mg of material in 100 ml of hexavalent chromium solution at different temperatures (298 K, 308 K, 318 K, 328, 338 K) and concentrations (0, 20, 40, 60, 80, 100, 120, 240, 480, 960, and 1920 mg/L) in a water bath. The adsorption process is continued for 24 hours to achieve complete adsorption-desorption equilibrium, and then 2 ml of the solution is tested. Equation S(1) and S(2) is used to calculate the thermodynamic parameters:

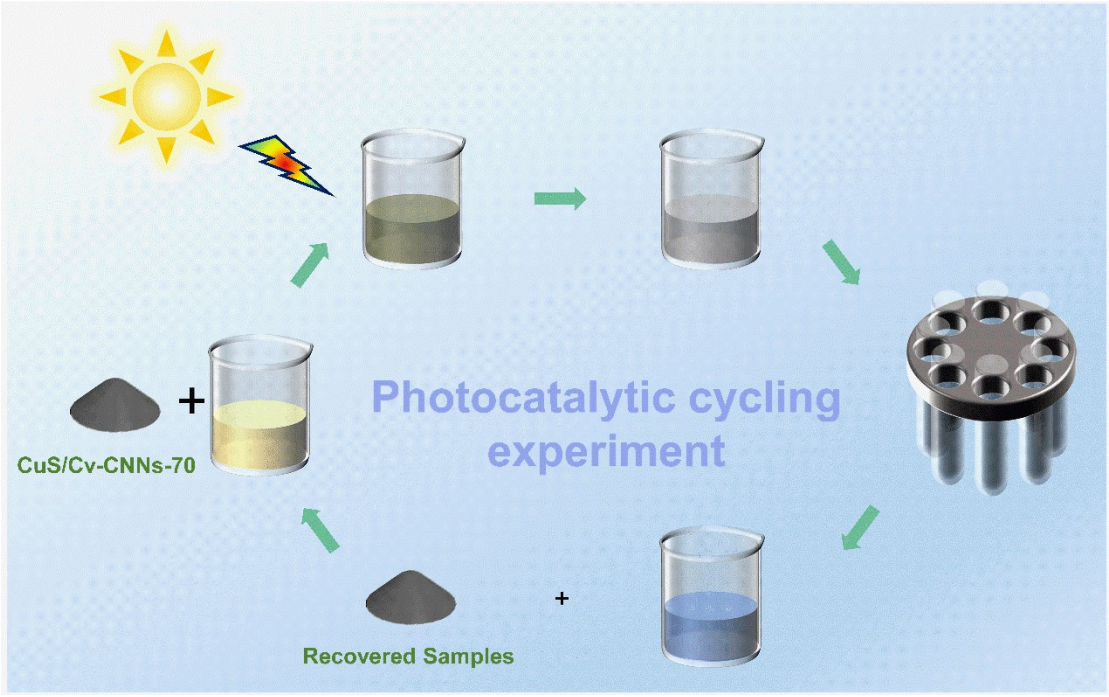
$$\Delta G° = -RT\ln K_F \quad \text{S(1)}$$

$$\ln K_F = \Delta S°/R - \Delta H°/R * 1/T \quad \text{S(2)}$$

where R (8.314 J/(mol K) is the universal gas constant, T (K) is the absolute temperature, and K_F (L/mol) is the Freundlich constant. The values of $\Delta G°$ at different temperatures (298, 308, 318, 328 and 338 K) were calculated according to Equation S(1). In addition, $\Delta H°$ and $\Delta S°$ can be calculated from the slope and intercept of $\ln K_F$ vs. $1/T$.

Photocatalytic cycling experiment

The experimental procedure is shown in **Scheme S1**. 30 mg of CuS/Cv-CNNs70 was placed into 100 mL of 120 mg/L Cr(VI) solution, the pH was adjusted to 2, and the irradiation was directly irradiated with visible light for 60 min followed by continued irradiation for 3 h to ensure that the Cr(VI) adsorbed on CuS/Cv-CNNs-70 was completely removed. After each round, CuS/Cv-CNNs-70 was collected by centrifugation with anhydrous ethanol and deionized water washing, dried at 60°C for 12 h, and recycled.



Scheme S1 Cycling experiments for the photocatalytic reduction of Cr(VI) by CuS/Cv-CNNs-70

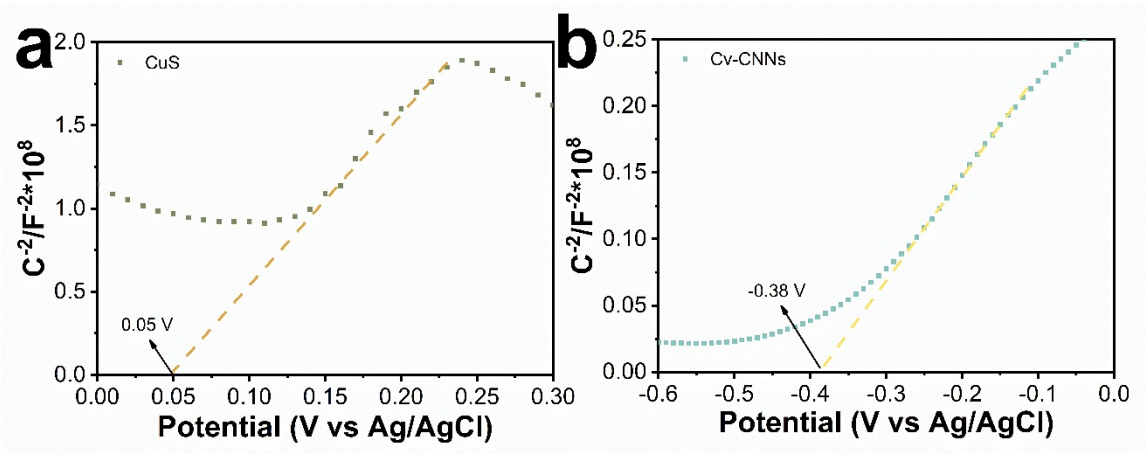


Fig. S1 Mott-Schottky curves of (a) Cv-CNNs, (b) CuS

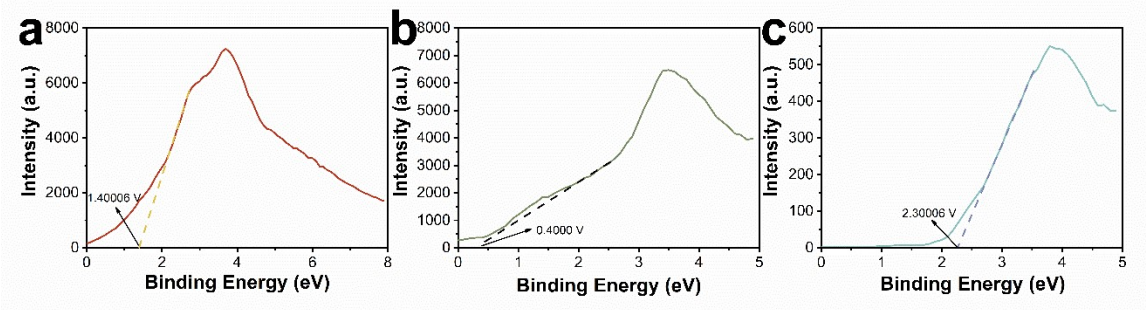


Fig. S2 VB-XPS plot of (a) Cv-CNNs (b) CuS, and (c) CuS/Cv-CNNs-70

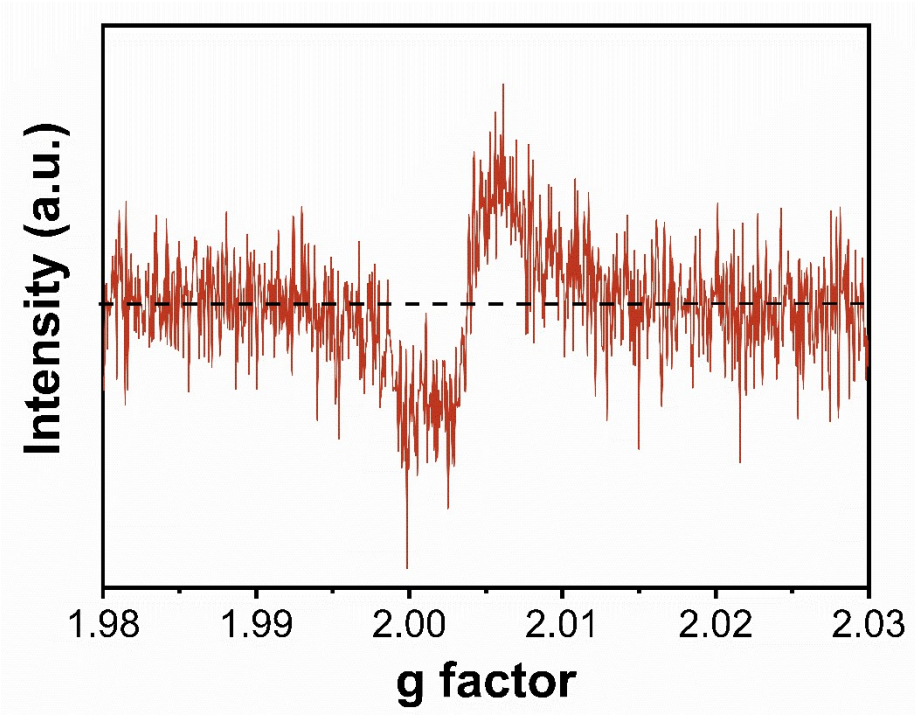


Fig. S3 EPR spectra of CuS/Cv-CNNs-70

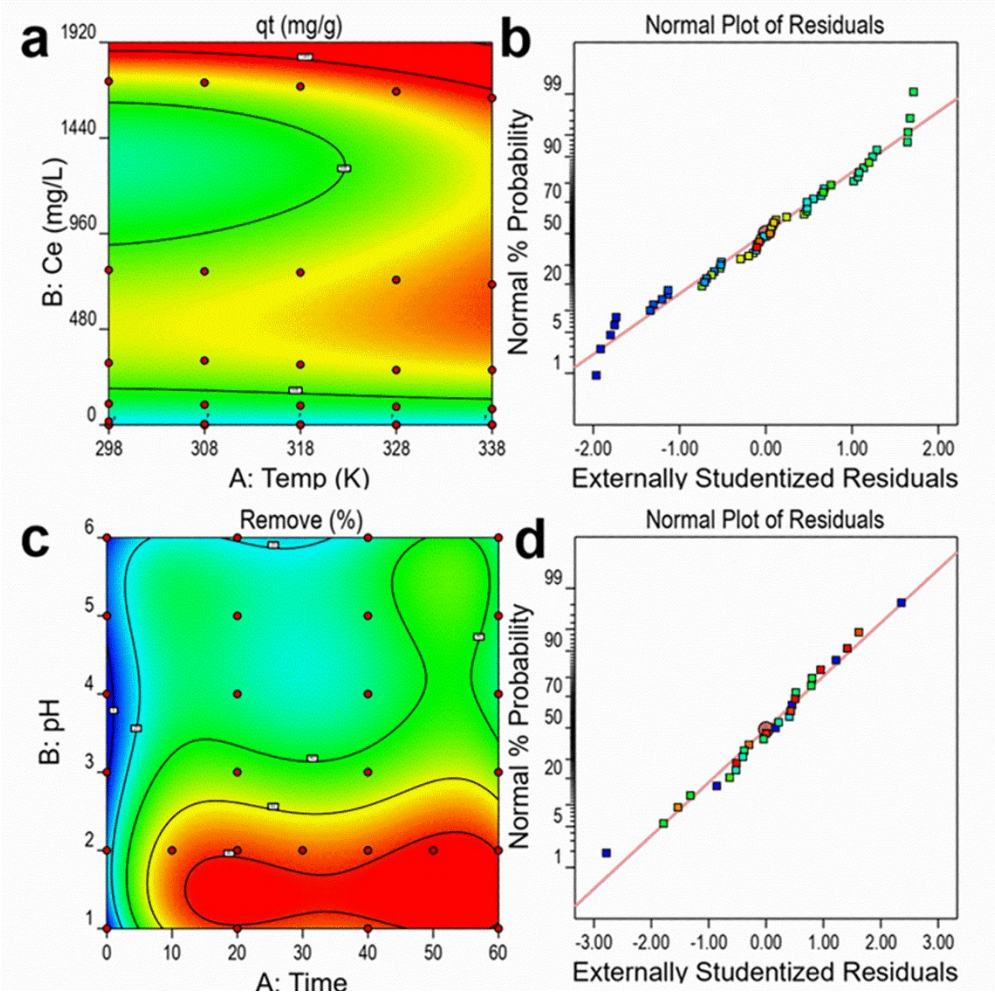


Fig. S4 CuS/Cv-CNNs-70 removal of Cr(VI) (120 mg/L) at different times and pH, (a) a plane figure of 3D response surface plots, (b) Normal probability plot of residuals, adsorption of CuS/Cv-CNNs-70 to different concentrations of Cr(VI) at different temperatures, (c) a plane figure of 3D response surface plots, (d) Normal probability plot of residuals.

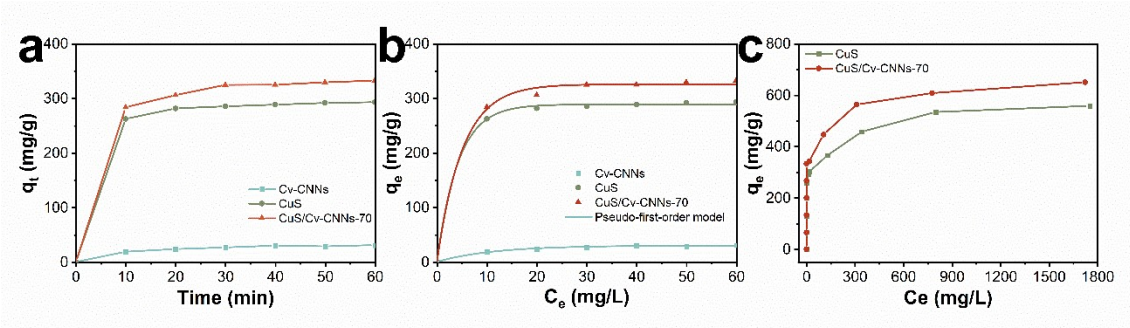


Fig. S5 Cv-CNNs, CuS, and CuS/Cv-CNNs-70 (a) adsorption of Cr(VI) (120 mg/L) at different times, (b) pseudo-first-order kinetic modeling, and (c) adsorption of CuS, CuS/Cv-CNNs-70 at different concentrations of Cr(VI)

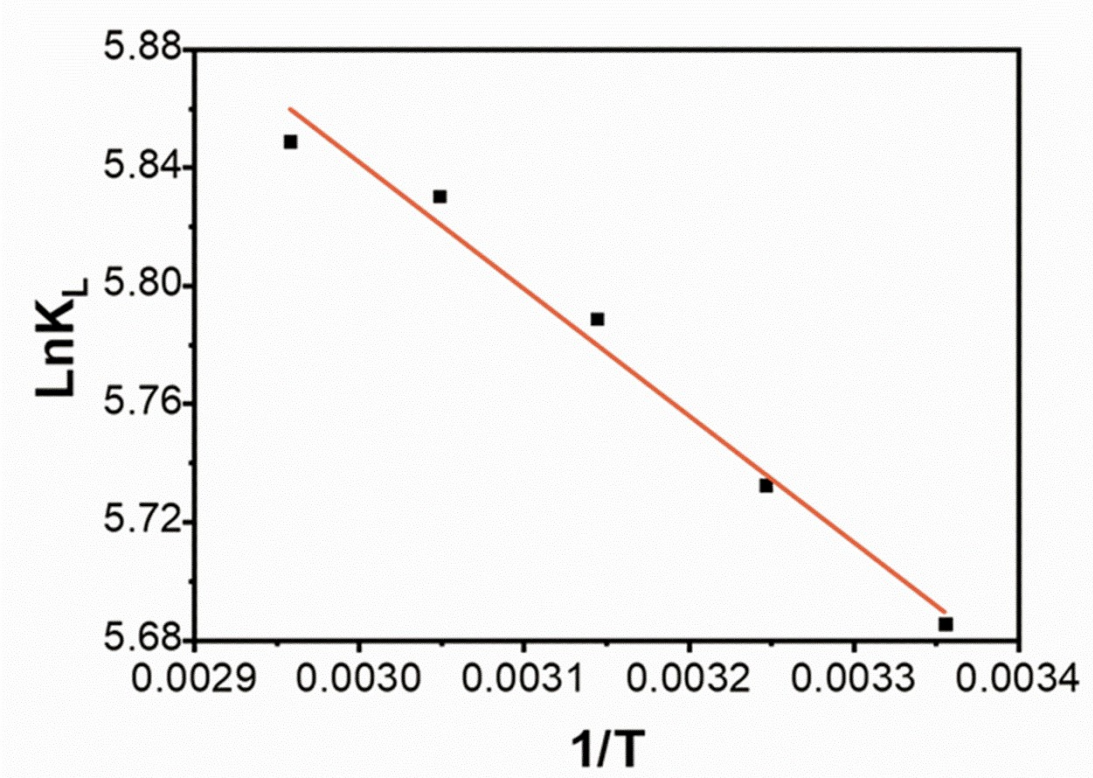


Fig. S6 Thermodynamic curve of adsorption of Cr(VI) by CuS/Cv-CNNs-70.

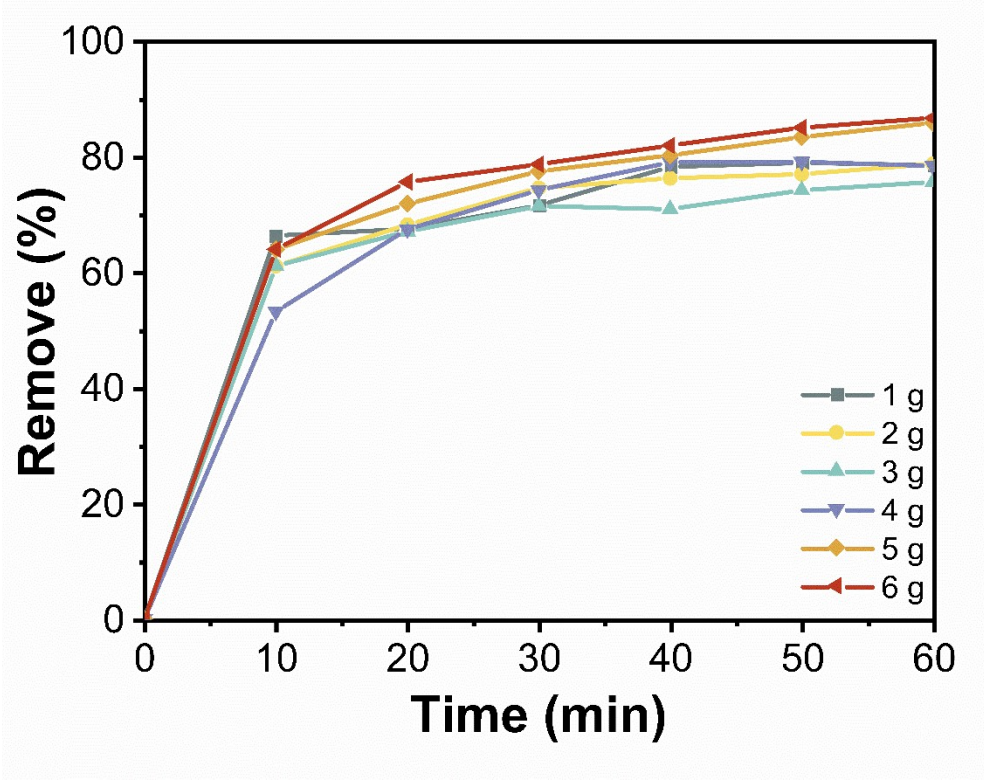


Fig. S7 Effect of different amounts of $CuSO_4 \cdot 5H_2O$ on the adsorption and removal performance of Cr(VI)

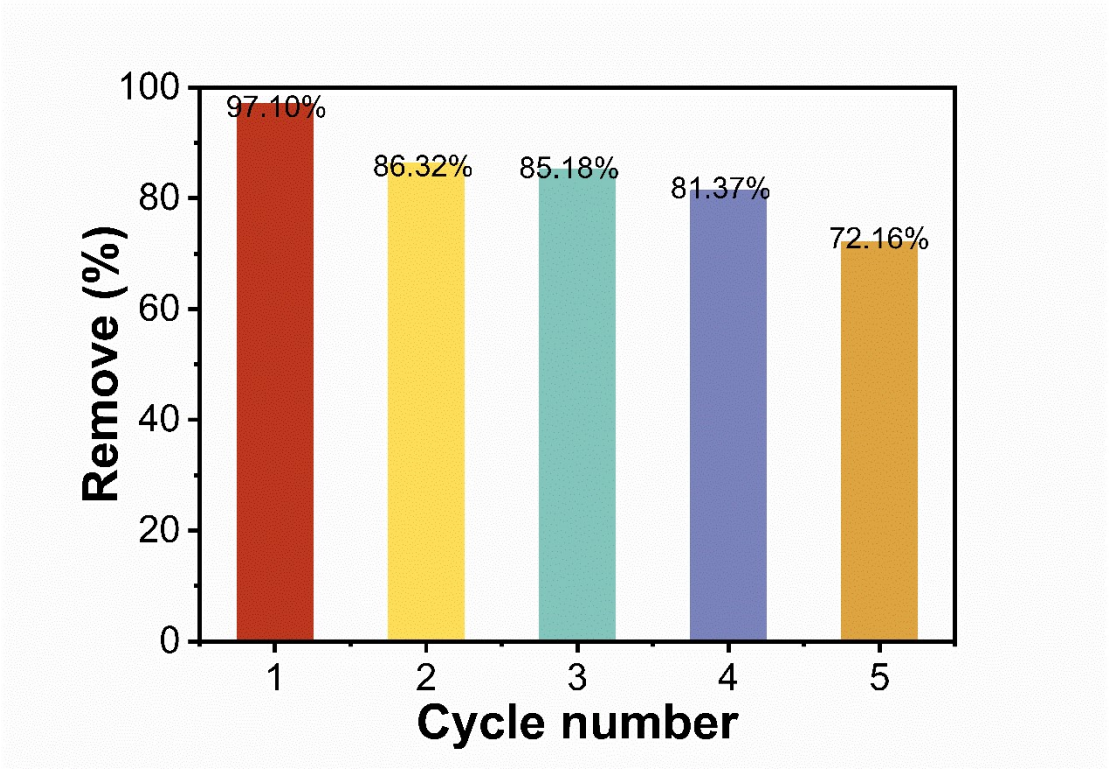


Fig. S8 Photocatalytic cycling experiment of CuS/Cv-CNNs-70 under 50 W LE D lamp irradiation.