Supporting Information

Synthesis of N-GQDs/CuS/Cv-CNNs hydrogels and their performance in hexavalent chromium wastewater treatment

Jianrong Wang[a,b], Luhua Wang[a], Yi Ren[a], Hongfang Zhao[a], Hongxia Li[a], Xiaohui Niu[a], Deyi Zhang[a], Yi Wang[a], Kunjie Wang*[a]

* Kunjie Wang (corresponding author), wangkj80@163.com
a School of Petrochemical Technology, Lanzhou University of Technology, Lanzhou, 730050, China
b GanSu Maternity and Child-care Hospital, China, Lanzhou 730070, China

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Materials

Melamine ($C_3H_6N_6$) is produced in the Tianjin Damao Chemical Reagent Factory. Ammonium chloride (NH_4Cl), Potassium bromate ($KBrO_3$) and p-benzoquinone (p-BQ) were produced from Shanghai Aladdin Biochemical Technology Co. Sodium sulfide ($Na_2S·9H_2O$) from Tianjin Best Co. Copper nitrate ($Cu(NO_3)_2·3H_2O$) was produced from Shanghai Merry Co. Citric acid ($C_6H_8O_7$) produced by Tianjin Jindong Tianzheng Fine Chemical Co. Anhydrous calcium chloride ($CaCl_2$) produced by Tianjin Zhiyuan Chemical Reagent Co. Sodium alginate ($C_6H_7NaO_6$) is produced by Tianjin Guangfu Fine Chemical Research Institute. Isopropyl alcohol (IPA), phosphoric acid (H_3PO_4), sulfuric acid (H_2SO_4) were produced from Sinopharm Chemical Reagent Co. Anhydrous methanol (CH_3OH) and anhydrous ethanol (C_2H_5OH) were produced by Lianlong Bohua (Tianjin) Pharmaceutical Chemical Co. Potassium dichromate ($K_2Cr_2O_7$) was produced from Chengdu Cologne Chemical Co. 1,5-Diphenylcarbazide ($C_{13}H_{14}N_4O$) was produced in Shanghai Zhan Yun Chemical Co.

Preparation of N-GQDs/CuS/Cv-CNNs:

Preparation of CuS/Cv-CNNs:

CNNs are obtained by thoroughly mixing 10.000 g of NH_4Cl with 2.000 g of melamine and then heating to 550 °C at a rate of 5 °C/min for 4 hours. Then, 2.000 g of CNNs were again mixed with 10.000 g of NH_4Cl and heated for 2 hours to 500 °C at a rate of 5 °C min^{-1} to produce Cv-CNNs.

0.200 g of Cv-CNNs was 30 min of sonication in 50 mL of water, then 1.1792 g of Cu(NO3)2·3H2O was added and sonication was continued for 15 min. The suspension was annealed at 60 °C for 60 min with vigorous stirring. Meanwhile, 50 mL of water was used to dissolve 3.5169 g of Na2S·9H2O and slowly added dropwise into the suspension with vigorous stirring for 15 min. The precipitates were washed with anhydrous ethanol and deionized water and collected, then dried under vacuum at 60 °C for 10 h. CuS/Cv-CNNs powders were obtained after grinding. Depending on the amount of complexation, CuS/Cv-CNNs were labeled as CuS/Cv-CNNs-X (X=30, 40, 50, 60, 70, 80).

Preparation of N-GQDs:

CA (1.000 g) and melamine (0.400 g) were mixed with deionized water (15 mL) by sonication. The mixture was then transferred to a 50 mL Teflon-lined autoclave and heated at 180 °C for 12 h. At the end of the reaction, the reactor was naturally cooled to room temperature. The brown-colored supernatant was collected by centrifugation at 8,000 rpm for 5 min to remove large particles. The resulting solution was dialyzed in a dialysis bag for 24 h (retaining a molecular weight of 1000 Da) and freeze-dried for 48 h.

Preparation of N-GQDs/CuS/Cv-CNNs:

First, 0.098 g of CuS/Cv-CNNs-70 was dispersed in 15 mL of ethanol and sonicated for 30 min to obtain a homogeneous suspension. Then a certain amount of 0.002 g of N-GQDs was dispersed in the above solution, stirred for 12 h. After the ethanol was vaporized, the powder was dried at 80 ℃.

Thermodynamic study of adsorption

The adsorption kinetics of the N-GCC hydrogel were tested by adding 30 mg of sample to 100 mL of a Cr(VI) solution at 100 mg/L under magnetic stirring. The color development reaction was monitored by sampling 2 mL of the solution at 10 min intervals using a 1,5-Diphenylcarbazide colorimetric method, on a UV-visible spectrophotometer (UV-1800, λ = 540 nm). Eqs. S(1) and (2) were used to fit pseudo-first-order and pseudo-second-order kinetic models for adsorption, respectively.

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad \text{(S1)}$$

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad \text{(S2)}$$

Where, q_e - saturated adsorption, q_t - adsorption of t time, k_1, k_2 - rate constants for different kinetic models.

Photocatalytic cycling experiment

30 mg of N-GCC hydrogel was placed into 100 mL of 100 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 N-GCC hydrogel was completely removed. After each round, N-GCC hydrogel was collected by centrifugation with anhydrous ethanol and deionized water washing, dried at 60°C for 12 h, and recycled.

Table S1 Adsorption-photocatalytic removal capacity of hexavalent chromium by different materials

Materials	Catalyst dosage (mg)	Cr(VI) concentration (mg/L)	Adsorption capacity (mg/g)	Adsorption-photocatalytic efficiency (%)	reference
leonardite	75	20	33.333	100	1
MoS_2-PVP	20	30	-	99.5	2
GSPC-20	100	200	149.525	99.92	3
N-GCC-10 hydroel	30	100	251.32	95.76	This work

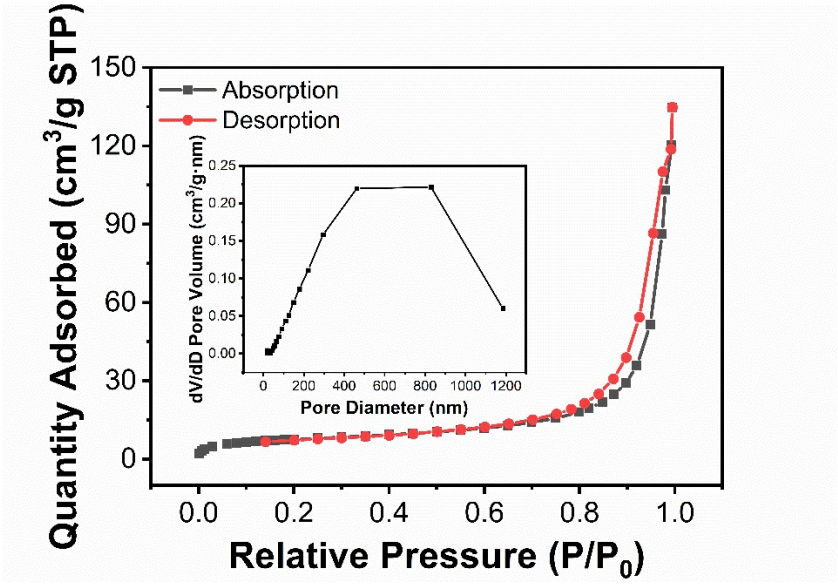

Fig. S1 N_2 adsorption–desorption isotherms for N-GCC hydrogel

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