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Electronic Supporting Information

Porous BMTTPA-CS-GO nanocomposite for efficient removal of heavy metal ions from aqueous solutions

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Characterization of the BMTTPA-CS-GO nanocomposite

Fourier transform infrared (FT-IR) spectra were carried out on a Thermo Nicolet 5700 spectrometer using the exhaustively dried KBr pellet method and scanning the range between 500 and 4000 cm^{-1}. Morphological measurements were recorded by field-emission scanning electron microscopy (FE-SEM, SU-8010, Hitachi). TGA curves were measured by using a PerkinElmer TGA-4000 thermogravimetric analyzer from room temperature to 800 °C with heating rate of 10 °C/min and a nitrogen flow rate of 19.8 mL/min. The chemical state and surface composition of BMTTPA-CS-GO were analyzed using X-ray photoelectron spectroscopy (XPS, VG Multilab 2000X instrument, Thermal Electron, USA). Heavy metal ions concentrations were determined using an iCAP Q inductively coupled plasma mass spectrometry (ICP-MS, Thermo Fisher Scientific, USA).

Synthetic Procedures

2,5-Bis(methylthio)terephthalaldehyde was synthesized according to the literature.[1,2]

2,5-Dibromobenzene-1,4-dicarbaldehyde

Sulfuric acid (7 mL) was added dropwise to a suspension containing (2 g), acetic acid (10 mL) and acetic anhydride (20 mL) at 0 °C. CrO_3 (4.19 g) was then added to the mixture in portions. The resulting mixture was stirred vigorously at this temperature for a further 5 h until the reaction was completed. The greenish slurry was poured into ice-water and filtered. The white solid was washed with water and cold methanol. The diacetate was then hydrolyzed by refluxing with a mixture of water (10 mL), ethanol (10 mL) and sulfuric acid (1 mL) for 5 h. After the mixture was cooled, the pale yellow product was separated by filtration. The crude product was purified by recrystallization from chloroform (yield 35%), m.p. 194 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 10.31 (s, 2H), 8.15 (s, 2H).

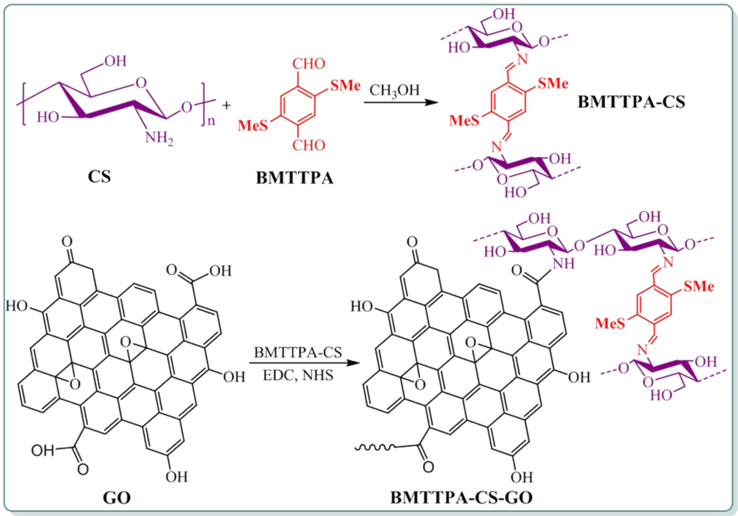
2,5-Bis(methylthio)terephthalaldehyde (BMTTPA)

To a solution of 2,5-dibromoterephthalaldehyde (500 mg) in DMF (30 mL) was added sodium methanethiolate (280 mg), and the resulting mixture was stirred at room temperature for 10 min. The mixture was poured into diluted hydrochloride solution (60 mL), and extracted with chloroform (100 mL) for three times. The combined organic layer was washed with water (50 mL), dried over anhydrous Na_2SO_4, and concentrated under vacuum. The residual solid was purified by column chromatography on silica gel eluted with dichloromethane ($R_f = 0.4$) to yield the product as pale orange solid (335 mg, 87%).

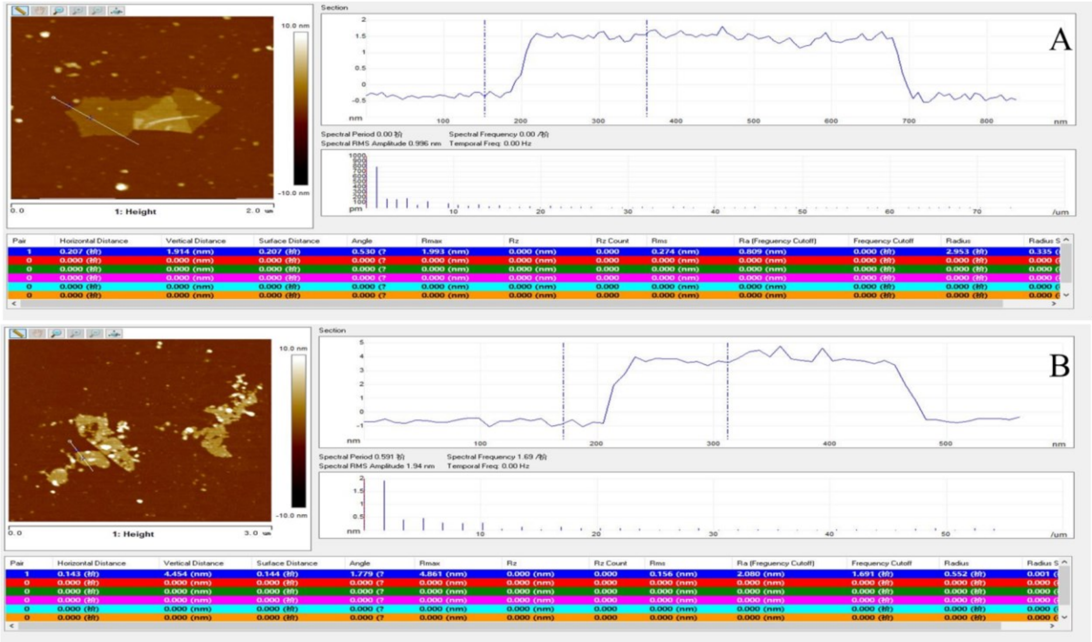
^1H NMR (400 Hz, $CDCl_3$) δ (ppm) = 10.42 (s, 2H, CHO), 7.80 (s, 2H, ArH), 2.58 (s, 6H, SCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 16.5, 130.1, 136.3, 139.8, 190.7.

Preparation of GO

GO was prepared from natural graphite powder by a modified Hummers method.[3] Graphite (3.0 g) was added to concentrated sulfuric acid (70 mL) under stirring at room temperature, then sodium nitrate (1.5 g) was added, and the mixture was cooled to 0 °C. Under vigorous agitation, potassium permanganate (9.0 g) was added slowly to keep the temperature of the suspension lower than 20 °C. Successively, the reaction system was transferred to a 35-40 °C water bath for about 0.5 h, forming a thick paste. Then, 140 mL of water was added, and the solution was stirred for another 15 min. An additional 500 mL of water was added, followed by slow addition of 20 mL of H_2O_2 (30%), turning the color of the solution from brown to yellow. The mixture was filtered and washed with 1:10 HCl aqueous solution (250 mL) to remove metal ions followed by repeated washing with water and centrifugation to remove the acid. The resulting solid was dispersed in water by stirring overnight to make a GO aqueous dispersion. The obtained brown dispersion was purified by dialysis for 2 weeks to remove the remaining acid and salt impurities. Finally, it was subjected to centrifugation at 4000 rpm for 30 min to remove aggregates. The concentration of the suspension was determined by drying the GO dispersion with a certain volume and weighing the residual GO.



Scheme S1. The preparation procedure of 2,5-Bis(methylthio)terephthalaldehyde-chitosan-grafted graphene oxide (BMTTPA-CS-GO).



Spectral Period 0.00 桁 Spectral Frequency 0.00 /桁
Spectral RMS Amplitude 0.996 nm Temporal Freq: 0.00 Hz

Pair	Horizontal Distance	Vertical Distance	Surface Distance	Angle	Rmax	Rz	Rz Count	Rms	Ra (Frequency Cutoff)	Frequency Cutoff	Radius	Radius S
1	0.207 (桁)	1.914 (nm)	0.207 (桁)	0.530 (?	1.993 (nm)	0.000 (nm)	0.000	0.274 (nm)	0.809 (nm)	0.000 (桁)	2.953 (桁)	0.335 (
0	0.000 (桁)	0.000 (nm)	0.000 (桁)	0.000 (?	0.000 (nm)	0.000 (nm)	0.000	0.000 (nm)	0.000 (nm)	0.000 (桁)	0.000 (桁)	0.000 (
0	0.000 (桁)	0.000 (nm)	0.000 (桁)	0.000 (?	0.000 (nm)	0.000 (nm)	0.000	0.000 (nm)	0.000 (nm)	0.000 (桁)	0.000 (桁)	0.000 (
0	0.000 (桁)	0.000 (nm)	0.000 (桁)	0.000 (?	0.000 (nm)	0.000 (nm)	0.000	0.000 (nm)	0.000 (nm)	0.000 (桁)	0.000 (桁)	0.000 (
0	0.000 (桁)	0.000 (nm)	0.000 (桁)	0.000 (?	0.000 (nm)	0.000 (nm)	0.000	0.000 (nm)	0.000 (nm)	0.000 (桁)	0.000 (桁)	0.000 (
0	0.000 (桁)	0.000 (nm)	0.000 (桁)	0.000 (?	0.000 (nm)	0.000 (nm)	0.000	0.000 (nm)	0.000 (nm)	0.000 (桁)	0.000 (桁)	0.000 (

Spectral Period 0.591 桁 Spectral Frequency 1.69 /桁
Spectral RMS Amplitude 1.94 nm Temporal Freq: 0.00 Hz

Pair	Horizontal Distance	Vertical Distance	Surface Distance	Angle	Rmax	Rz	Rz Count	Rms	Ra (Frequency Cutoff)	Frequency Cutoff	Radius	Radius S
1	0.143 (桁)	4.454 (nm)	0.144 (桁)	1.779 (?	4.861 (nm)	0.000 (nm)	0.000	0.156 (nm)	2.080 (nm)	1.691 (桁)	0.552 (桁)	0.001 (
0	0.000 (桁)	0.000 (nm)	0.000 (桁)	0.000 (?	0.000 (nm)	0.000 (nm)	0.000	0.000 (nm)	0.000 (nm)	0.000 (桁)	0.000 (桁)	0.000 (
0	0.000 (桁)	0.000 (nm)	0.000 (桁)	0.000 (?	0.000 (nm)	0.000 (nm)	0.000	0.000 (nm)	0.000 (nm)	0.000 (桁)	0.000 (桁)	0.000 (
0	0.000 (桁)	0.000 (nm)	0.000 (桁)	0.000 (?	0.000 (nm)	0.000 (nm)	0.000	0.000 (nm)	0.000 (nm)	0.000 (桁)	0.000 (桁)	0.000 (
0	0.000 (桁)	0.000 (nm)	0.000 (桁)	0.000 (?	0.000 (nm)	0.000 (nm)	0.000	0.000 (nm)	0.000 (nm)	0.000 (桁)	0.000 (桁)	0.000 (
0	0.000 (桁)	0.000 (nm)	0.000 (桁)	0.000 (?	0.000 (nm)	0.000 (nm)	0.000	0.000 (nm)	0.000 (nm)	0.000 (桁)	0.000 (桁)	0.000 (

Fig. S1. AFM images of GO (A) and BMTTPA-CS-GO (B).

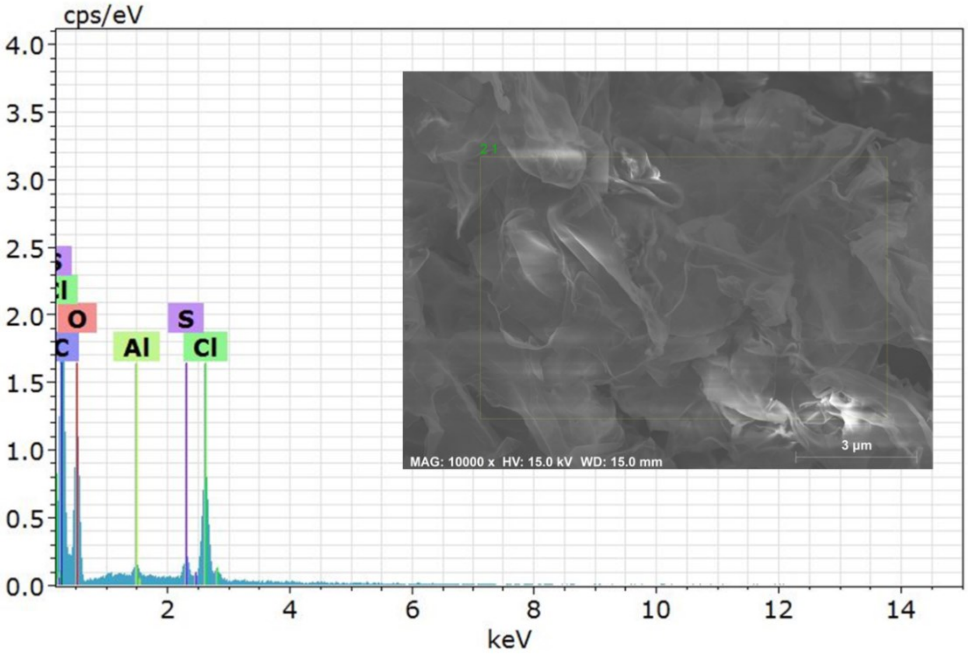


Fig. S2. EDX spectrum of BMTTPA-CS-GO.

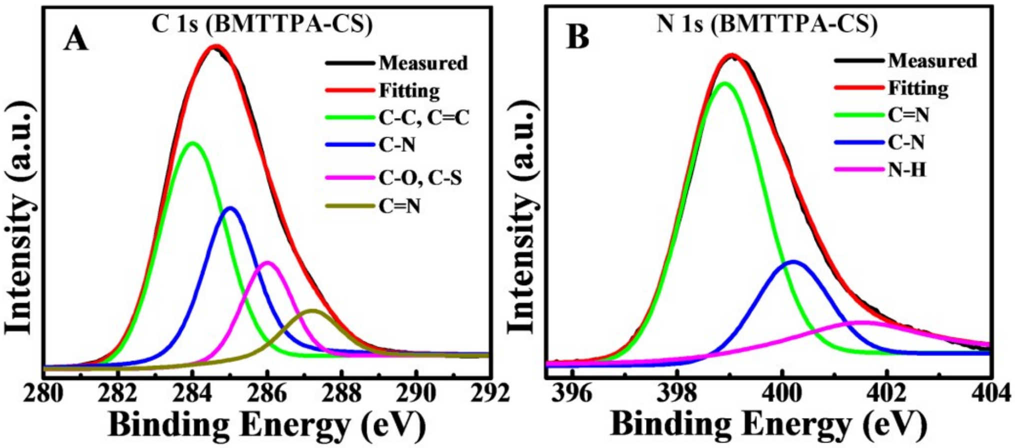


Fig. S3. XPS high-resolution spectra of C 1s in BMTTPA-CS (A), N 1s in BMTTPA-CS (B).

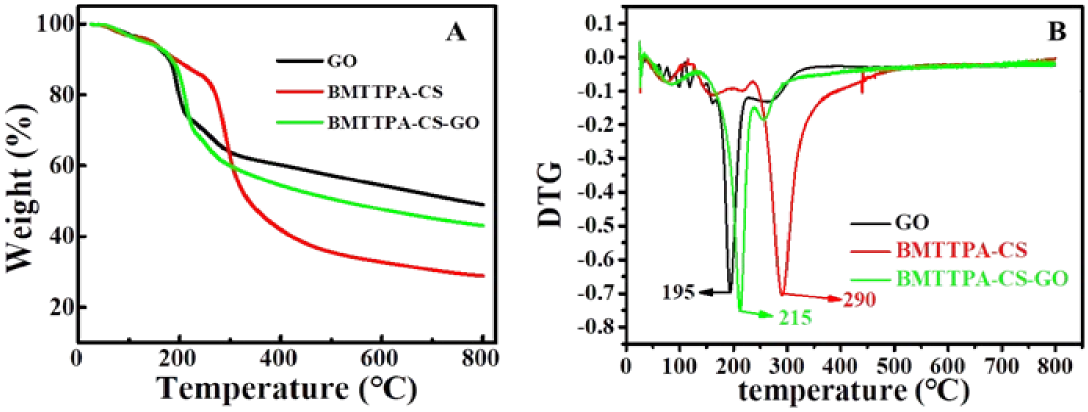


Fig. S4. TGA (A) and DTG (B) thermograms of BMTTPA-CS, GO and BMTTPA-CS-GO.

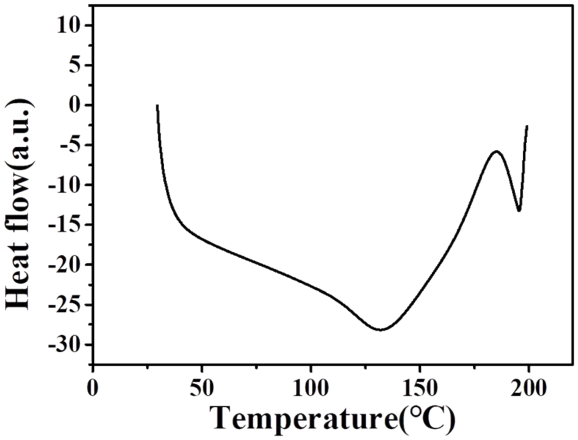


Fig. S5. Differential scanning calorimetry (DSC) of BMTTPA-CS-GO.

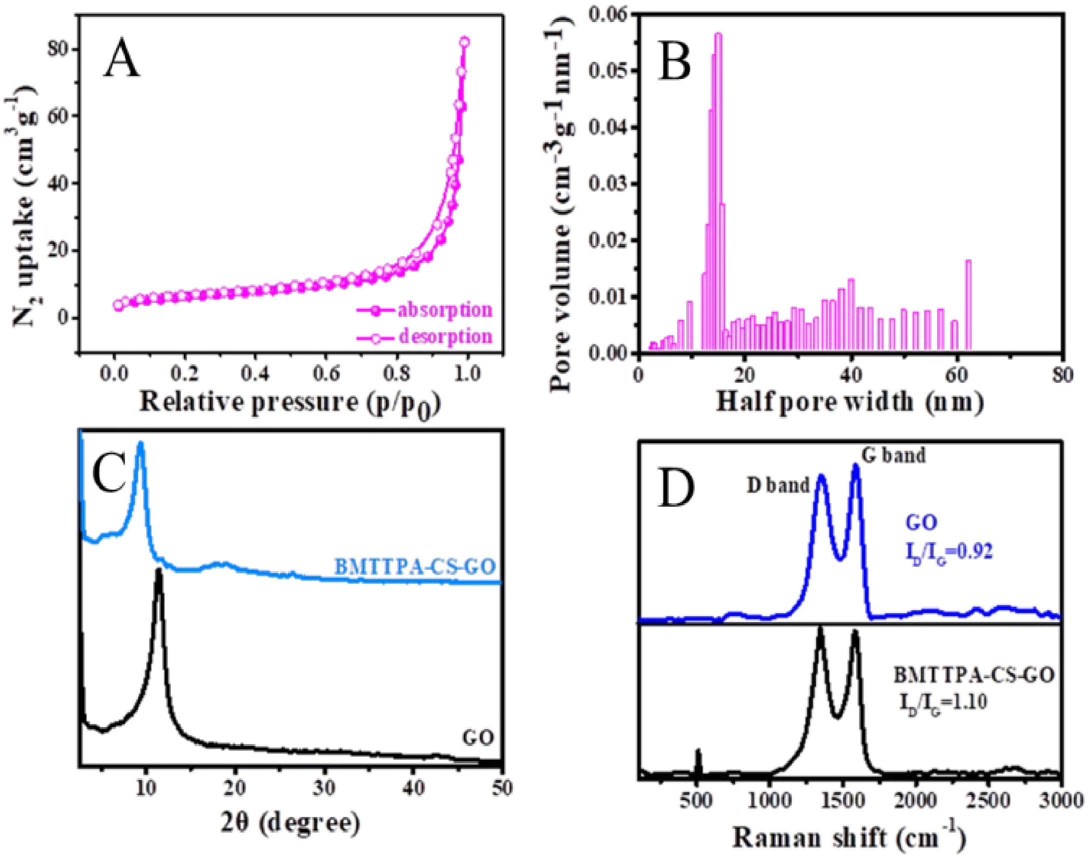


Fig. S6. Nitrogen adsorption-desorption isotherms (A) and Barrett-Joyner-Halenda (BJH) pore distribution curve (B) of BMTTPA-CS-GO. XRD patterns (C) and Raman spectra (D) of GO and BMTTPA-CS-GO.

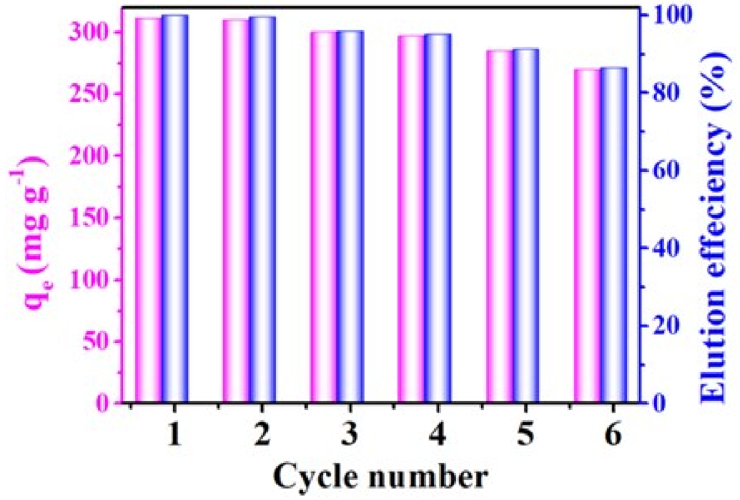


Fig. S7. Reusability and elution efficiency of the BMTTPA-CS-GO for extracting Hg^{2+}.

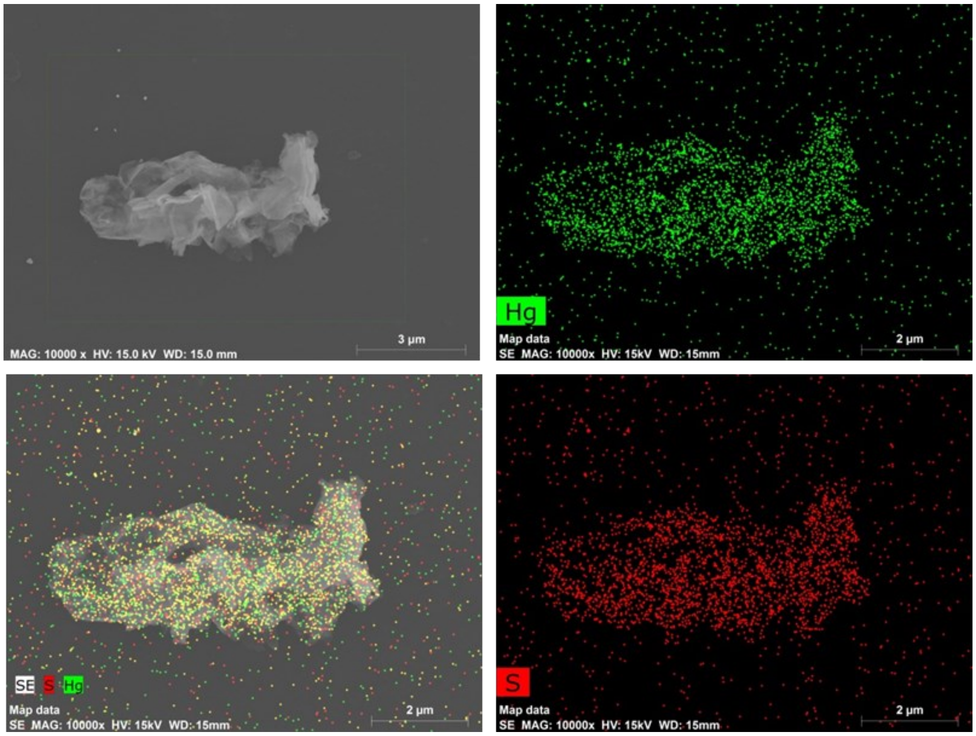


Fig. S8. Element mapping spectra photographs of BMTTPA-CS-GO showing their distribution on the solid surface ather adsorption.

Table S1. CHN analysis of BMTTPA-CS-GO.

element	C(%)	H(%)	N(%)
	7.21	42.870	5.185

Table S2. The Langmuir isotherms parameters for the adsorption of Hg^{2+}, Cu^{2+}, Pb^{2+} and Cd^{2+} on BMTTPA-CS-GO nanocomposite.

metal ion	R^2	b	$q_{m,fitted}$	$q_{e,exp}$
Cd^{2+}	0.995	0.101	67.4	65.1
Cu^{2+}	0.998	0.086	81.4	78.0
Pb^{2+}	0.993	0.078	211.4	206.1
Hg^{2+}	0.992	0.094	312.0	306.8

Table S3. Kinetic parameters for adsorption of Hg^{2+}, Pb^{2+}, Cu^{2+} and Cd^{2+} on the BMTTPA-CS-GO nanocomposite.

metal ion	R^2	$q_{e,calc}$	$q_{t,exp}$	K_2
Cd^{2+}	0.9995	65.9	65.1	0.0062
Cu^{2+}	0.9993	79.2	78.0	0.0041
Pb^{2+}	0.9989	208.7	206.1	0.0019
Hg^{2+}	0.9992	309.6	306.8	0.0017

Table S4. Comparison of Hg^{2+} adsorption on BMTTPA-CS-GO and other adsorbents.

Adsorbent	q_m (mg/g)	Ref
poly(benzoxazine-co-sulfur)	79	[4]
activated carbon cloth	71	[5]
amine-modified activated carbon	118	[6]
SH-SWCNT	130	[7]
Fe_3O_4-xGO	119	[8]
GO-thiol-functionalized magnetite	163	[9]
GO_{sand}	196	[10]
DMSA-Fe_3O_4	201	[11]
TF-MNPs	344	[12]
mercaptosuccinic acid-LDH	161	[13]
IT-PRGO	624	[14]
AMT-OCMK-3	450.5	[15]
SH-MAC	38.1	[16]
SH-CNTs/Fe_3O_4	66.2	[17]
GO-MNPs	17.1	[18]
amino-modified GO/Fe_3O_4	167.8	[8]
MNPC-T700-M3-T	382	[19]
Fe_3O_4/M-COFs	97.7	[20]
BMTTPA-CS-GO	312	This work

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