Electronic Supplementary Material (ESI) for Environmental Science: Water Research & Technology.

Functionalized 3-dimensional (3-d) Graphene Composite for High Efficiency Removal of Mercury

Shervin Kabiri[a], Diana, N.H. Tran[a], Martin A. Cole[a], and Dusan Losic[a]

The University of Adelaide, School of Chemical Engineering, Adelaide, SA 5005, Australia

Synthesis of αFeOOH nanoparticles

Geothite nanorods were synthesised by Zamiri et al.[1] method. Briefly, 11 mmol of iron(III) chloride, 15 mmol of ethylenediamine, and 13 mmol of thiourea were dissolved in 40 ml of distilled water. The mixture was transferred to a 60 ml teflon-lined autoclave and maintained at 130 °C for 8 h. The black percipitate was collected by centrifugation and filtration where the filtrated materials were washed three times with a mixture of water and ethanol (50:50 v/v), and then finally dried in an oven (70 °C) for further use.

Silanization of αFeOOH nanoparticles

To chemically functionalize the αFeOOH nanoparticles they were spread out on a copper mesh, which was placed on top of a beaker containing 500 µl of (3-mercaptopropyl)trimethoxysilane (MPTMS). The beaker was then placed in an autoclave and sealed before incubating in an oven at 135 °C for 1 h. The functionalized material was washed with acetone and dried prior to characterization with FTIR and XRD.

Synthesis of hydrothermally reduced graphene-diatom (GN-DE) composites

In a typical procedure, 20 ml of graphene oxide (GO) solution (20 mg/ml) was sonicated with 5 mg of APTES modified DE for 1 h to obtain a homogenous dispersion. The GO-diatom mixture was then sealed in a 25 ml autoclave and kept at 180 °C for 6 h. The produced hydrogel was removed and freeze dried for 24 h to obtain the aerogel.

Organosilane-modification of hydrothermally reduced GN-DE composites

Hydrothermally reduced GN-DE composites were modified with MPTMS to chemically functionalize the entire surface of the porous structure with thiol functional groups. Organosilane-modified GN-DE composites were prepared according to the following procedure: the freeze dried aerogels were placed on a copper mesh, which was placed on top of a beaker containing 500 ul of MPTMS. The beaker was sealed in a stainless steel autoclave and placed in 135 ºC oven for 1 to 3 h to obtain the thiol modified composite aerogels.

Methylene blue method for specific surface area measurement

Specific surface area (SSA) of the prepared graphene-DE composites was determined using the methylene blue (MB) adsorption method by UV-Vis spectroscopy.[2-4] A known mass of graphene-DE composite was added into a known volume of MB solution of standard solution. The mixed suspension was sonicated for 2-3 h and stirred continuously for 24 h to reach the adsorption-desorption equilibrium. A few millilitres of the mixture was collected and then centrifuged to remove the suspended materials. The MB concentration was determined by analysing the supernatant through UV-vis spectroscopy at a wavelength of 665 nm. The SSA of the composite was then calculated using the following equation:

$$SSA = \frac{N_A A_{MB} (C_0 - C_e) V}{M_{MB} \qquad m_s}$$

where N_A represents Avogadro number (6.02×10^{23}/mol), A_{MB} is the covered area of per MB molecules ($1.35\ nm^2$), C_0 and C_e are the initial and equilibrium concentration of MB, respectively, V is the volume of MB solution, M_{MB} is the relative molecular mass of MB, and m_s is the mass of the sample.

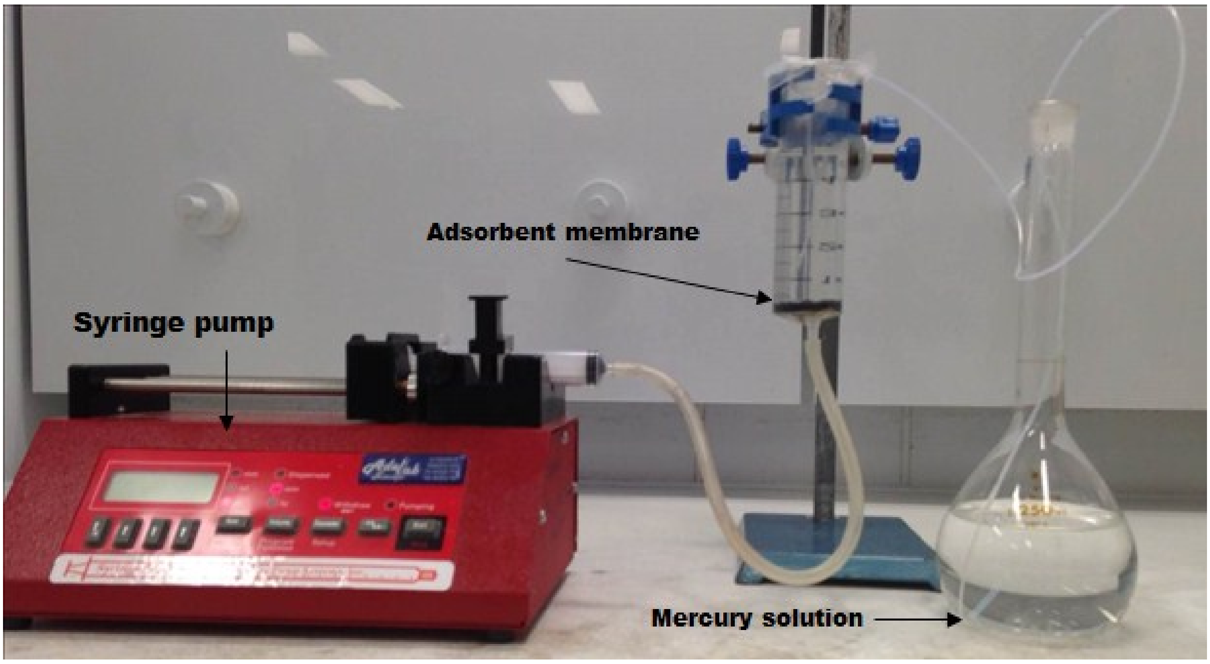


Fig. S1 Set up of a fixed-bed column with composite membrane for Hg removal experiments

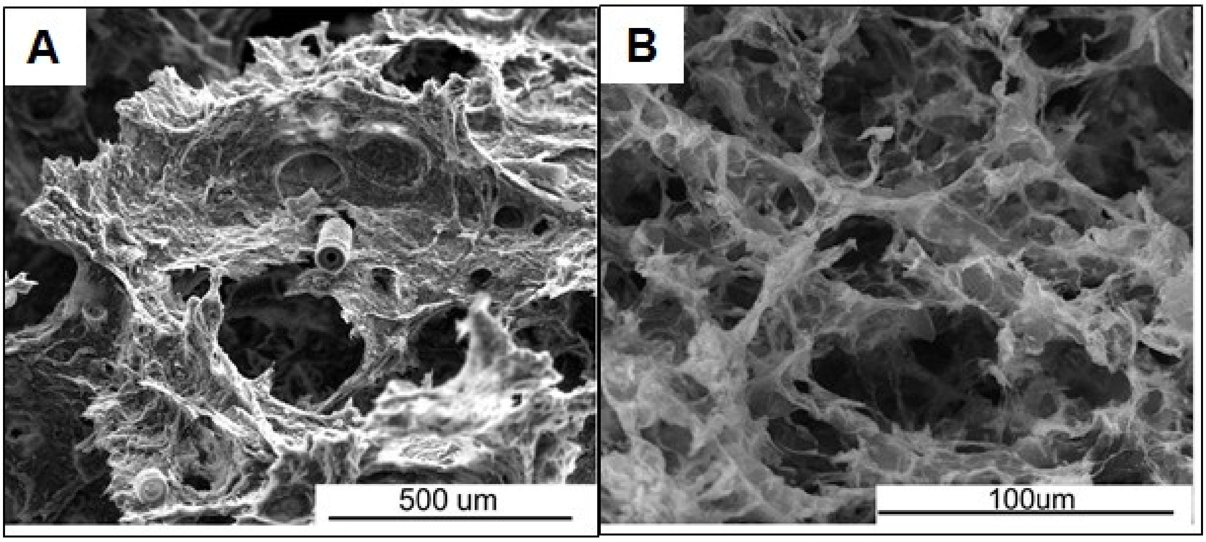


Fig. S2 SEM images of GN-DE-SH composite treated for (a) 3 h and (b) 1 h in an autoclave with MPTMS.

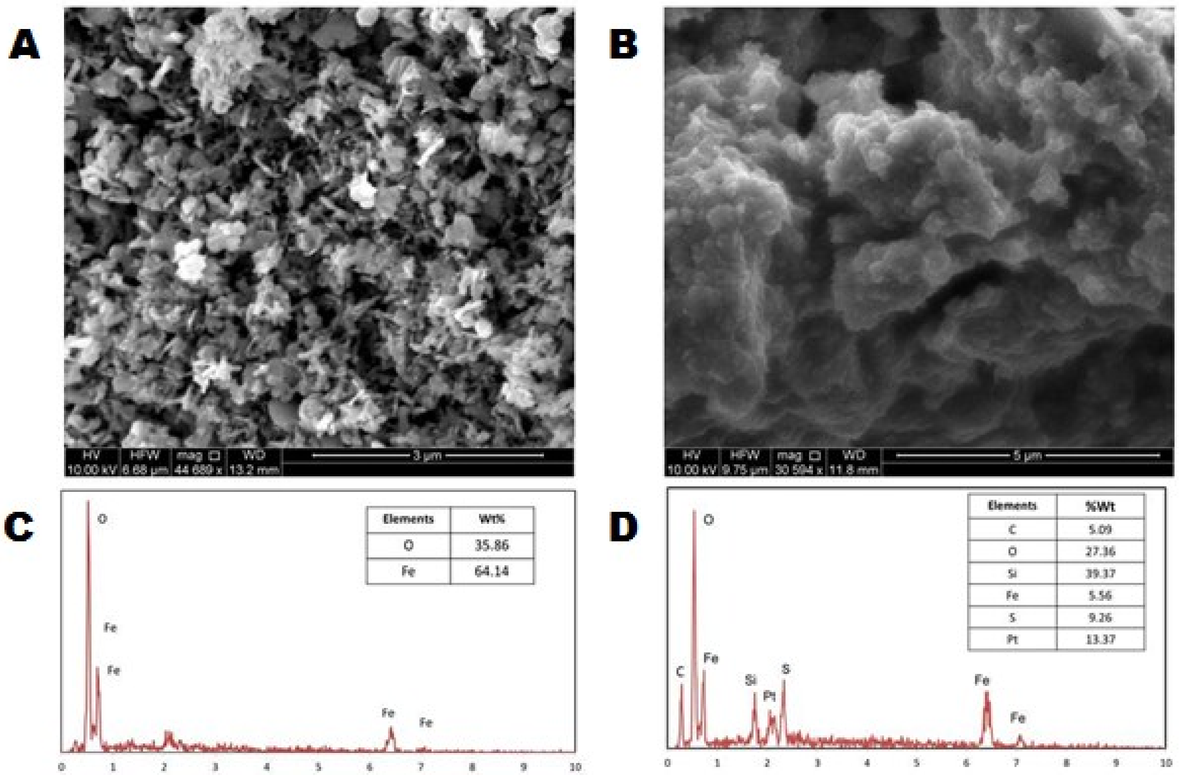


Fig. S3 SEM images of αFeOOH nanoparticles modified (a) with and, (b) without MPTMS, and (c-d) EDX results of (a) and (b), respectively.

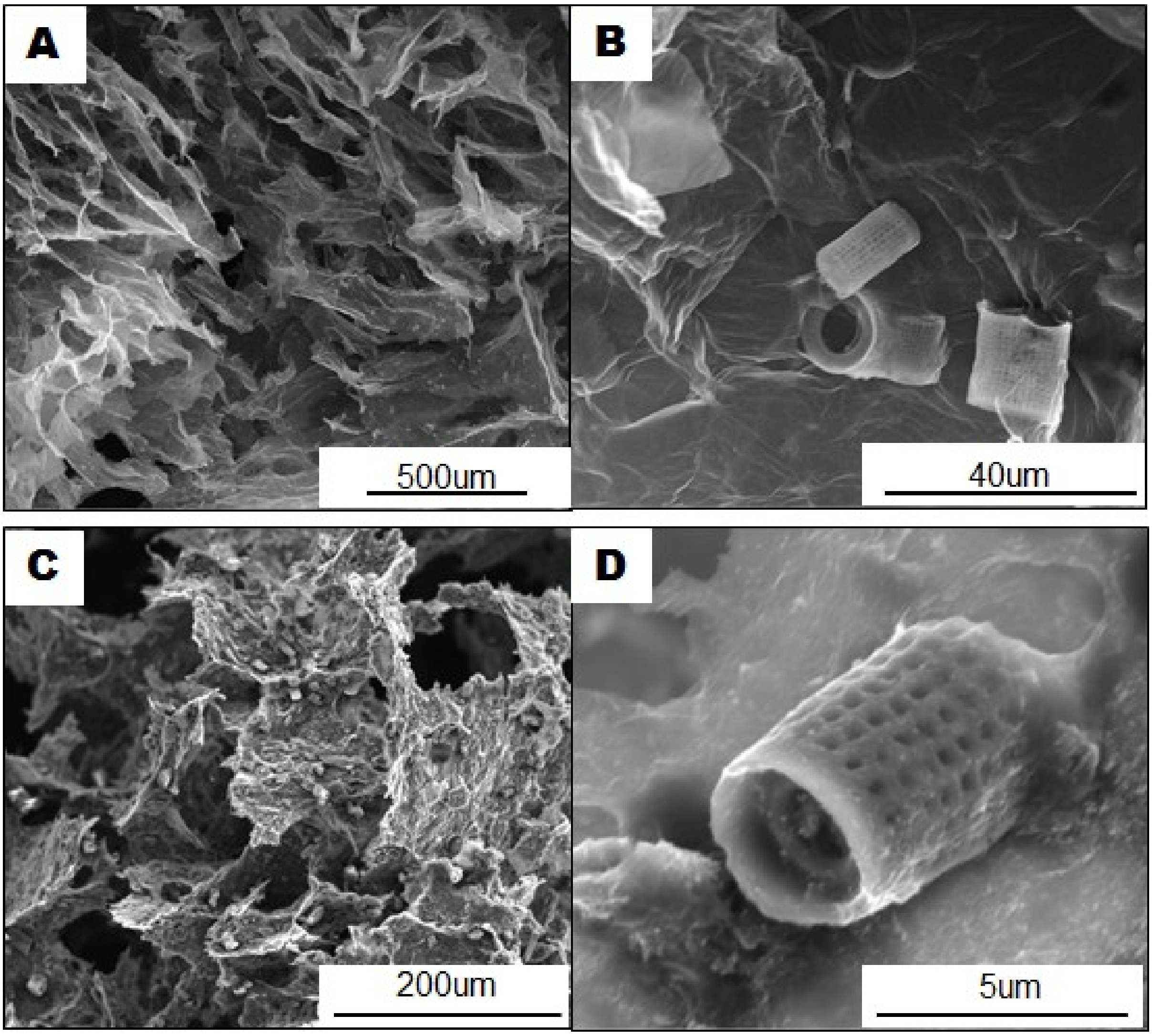
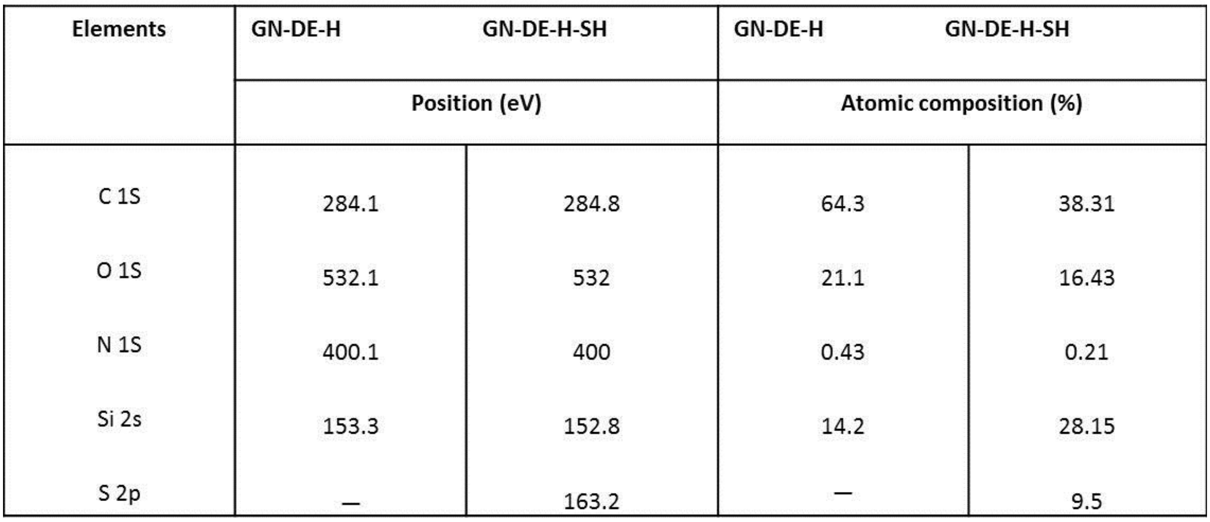


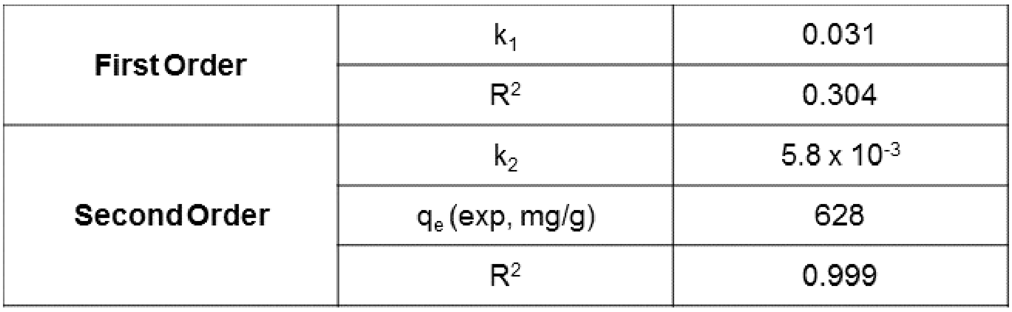
Fig. S4 Low and high magnification SEM images of the hydrothermally reduced graphene oxide and diatom mixture (a-b) without and (c-d) with MPTMS modification.

Table S1. Peak area and atomic composition of hydrothermally reduced GN-DE (GN-DE-H) and functionalized GN-DE-H with MPTMS (GN-DE-H-SH) from XPS survey scans.



Elements	GN-DE-H	GN-DE-H-SH	GN-DE-H	GN-DE-H-SH
	Position (eV)		Atomic composition (%)	
C 1S	284.1	284.8	64.3	38.31
O 1S	532.1	532	21.1	16.43
N 1S	400.1	400	0.43	0.21
Si 2s	153.3	152.8	14.2	28.15
S 2p	—	163.2	—	9.5

Table S2. Adsorption parameters of pseudo-first-order and pseudo-second-order kinetic models of GN-DE-SH composite for mercury removal from water.



First Order	k_1	0.031
	R^2	0.304
Second Order	k_2	5.8×10^{-3}
	q_e (exp, mg/g)	628
	R^2	0.999

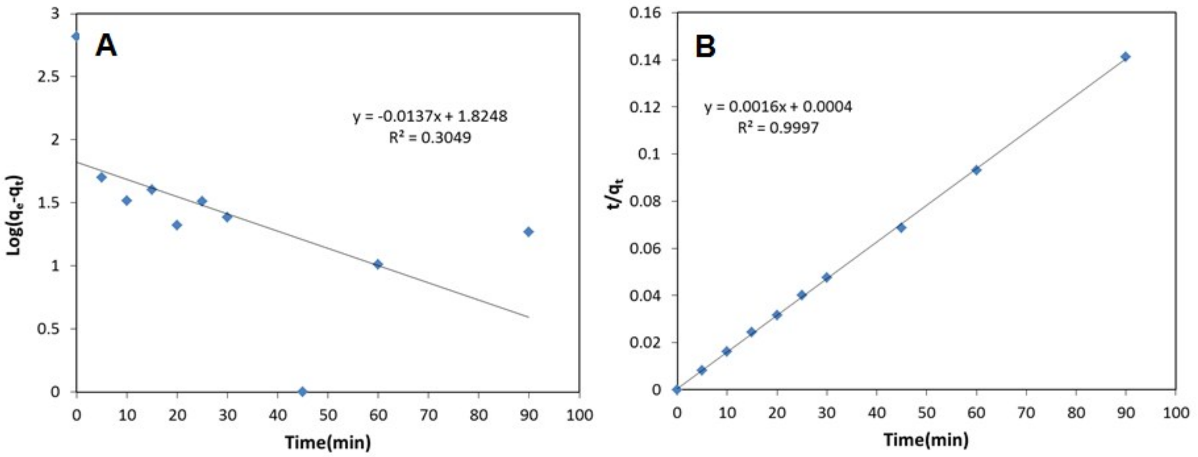


Fig. S5 Hg^{+2} adsorption kinetic of (a) pseudo-first-order and (b) pseudo-second-order kinetic for GN-DE-SH composite

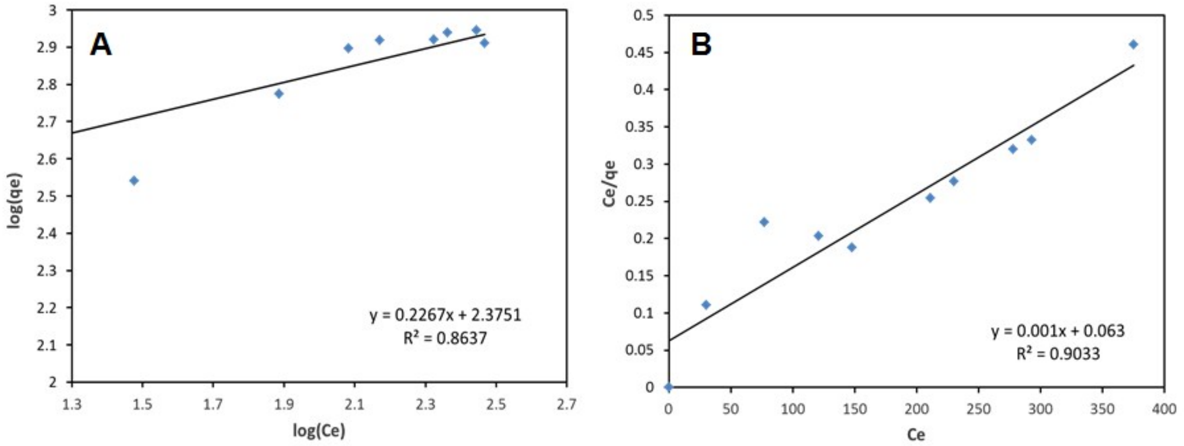


Fig. S6 Hg^{+2} adsorption kinetic of (a) Langmuir and (b) Freundlich isotherm models for GN-DE-SH composite

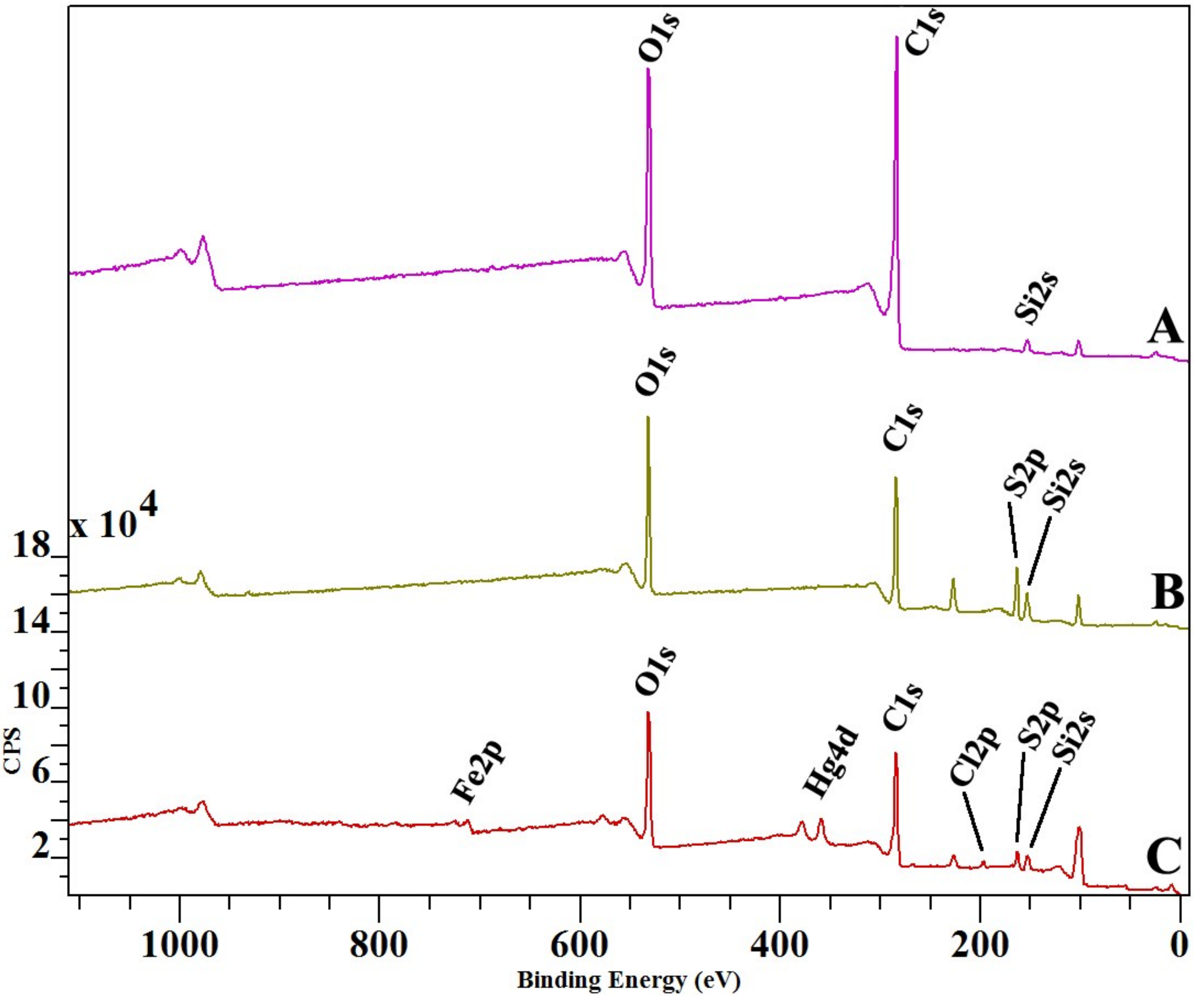


Fig. S7 Wide-scan XPS spectra of GN-DE-SH composite confirming mercury adsorption on material.

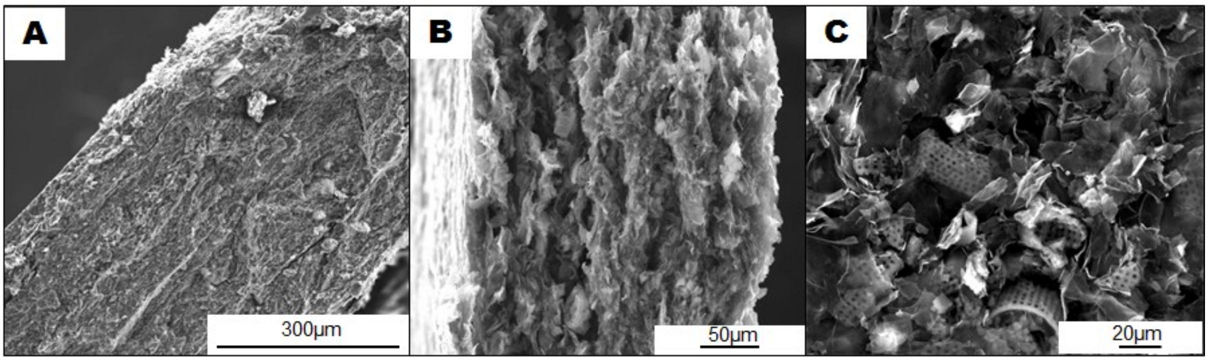


Fig. S8 (a-c) SEM images of GN-DE-SH membrane at different magnifications.

Reference

1. R. Zamiri, H. A. A. , A. Z. , G. Z. , H. R. B. and G. P. C. D. , *Journal of nanoparticle research*, 2014, DOI: DOI 10.1007/s11051-014-2333-2.
2. M. F. El-Kady, V. Strong, S. Dubin and R. B. Kaner, *Science*, 2012, 335, 1326-1330.
3. S. Kabiri, D. N. H. Tran, T. Altalhi and D. Losic, *Carbon*, 2014, 80, 523-533.
4. S. Kabiri, D. N. H. Tran, S. Azari and D. Losic, *ACS Applied Materials & Interfaces*, 2015, 7, 11815-11823.