

Engineered Graphite Oxide Materials for Application in Water Purification

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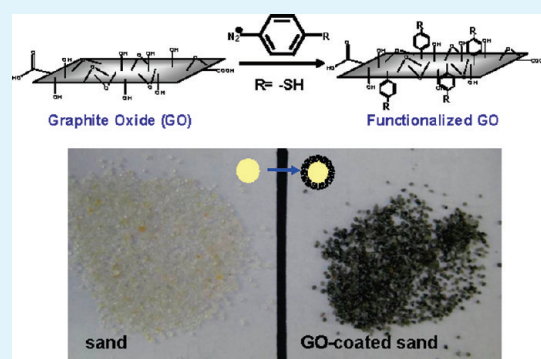
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S Supporting Information

ABSTRACT: Retaining the inherent hydrophilic character of GO (graphite-oxide) nanosheets, sp^2 domains on GO are covalently modified with thiol groups by diazonium chemistry. The surface modified GO adsorbs 6-fold higher concentration of aqueous mercuric ions than the unmodified GO. “Core–shell” adsorbent granules, readily useable in filtration columns, are synthesized by assembling aqueous GO over sand granules. The nanostructured GO-coated sand retains at least 5-fold higher concentration of heavy metal and organic dye than pure sand. The research results could open avenues for developing low-cost water purification materials for the developing economies.

KEYWORDS: water purification, graphite oxide, mercury removal, diazonium chemistry, Rhodamine B, sand coating



1. INTRODUCTION

Graphene—a flat, sp^2 -hybridized, two-dimensional (2D), honeycomb arrangement of carbon atoms with single carbon atom thickness—is expected to have far reaching consequences in not only understanding the fundamental aspects of these materials but also realizing real time applications.¹ Production of graphene through wet chemical oxidation of graphite to graphite oxide (GO) has become a popular method and a primary factor for an overwhelming interest in this new material. The oxygenated functional groups such as carboxylates, and lactols primarily lie at the edge of the nanographene sheets whereas the basal planes contains sp^2 -hybridized graphene-domains along with some epoxy and hydroxyl groups. While the oxygen functional groups impart hydrophilicity,² the graphene domains render hydrophobic character to these amphiphilic GO particles.³ Consequently, GO is soluble in several polar and nonpolar solvents including water but suffer from breakdown of electrical conductivity. The conductivity can be restored to a certain extent by thermal or chemical reduction of the oxygen functionalities, although such treatments also increase the hydrophobicity.⁴ Nevertheless, the intrinsically large surface area of GO have found niche in electrochemical energy storage devices,⁵ hydrogen storage,⁶ and catalysis.⁷

Historically, water purification technologies have utilized high surface area carbon materials in the form of activated carbon for decolorization⁸ and heavy metal ion⁹ retention. Compared to

these materials, GO is produced by room-temperature soft-chemistry principles and is likely to be cost-efficient. Only recently has a report on magnetite-graphene hybrid materials for magnetically controlled speciation of Arsenic¹⁰ from water been published. The possibility of harnessing this readily available and inexpensive material has been relatively unexplored. In this article, we report key surface modification approaches and postsynthesis assembly steps, which will enable exploitation of GO as a novel material for low-cost water purification processes.

Several protocols, including the versatile diazonium grafting chemistry,¹¹ are reported for chemical derivatization of graphene nanosheets; however, these approaches target the electrically conductive and relatively hydrophobic end-product. The low accessibility of water molecules in these hydrophobic materials will reduce the ability of GO to sequester water-soluble contaminants such as heavy metals. We, therefore, covalently modify graphite oxide nanosheets with complexing groups without compromising its inherent hydrophilicity. This is achieved by covalent grafting of aromatic thiol groups on the remaining electron-rich sp^2 carbon domains of graphite-oxide, without using the chemically reduced intermediate.

Sand—an abundant natural resource of earth—is widely used for processes of the magnitude of municipal water supplies to

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small domestic water filters, particularly as packed bed filters. History, affordability and the granular nature of sand that forms filter beds have popularized sand-filtration (SF). Indeed, early Indian and Greek writings dating back 6000 years refer to sand- and gravel-filtration as means to securing clean water¹² and currently is a water purification process endorsed by the World Health Organization.¹³ Of the two broad classifications of SF, fine-SF has higher retention of pathogens, organic matter, and heavy metal ions but has low throughput. Although the production rates are higher for the more popular coarse-SF, the absence of functionality and nanostructures limit pathogen, organics and heavy metal ions retention.¹³ We demonstrate a simple technique for conversion of regular filtration sand into “core–shell” graphene-oxide coated sand (GO_{sand}) granules by assembling water dispersible graphite-oxide on sand grains. Two model contaminants namely mercuric ions and a bulky dye molecule (Rhodamine B) are utilized to quantify the effects of the nanostructured GO coating for improvements to the well-established coarse sand-filtration process.

2. EXPERIMENTAL SECTION

2.1. Preparation of Graphite Oxide Dispersion. The GO is prepared according to the modified Hummers method that has been reported previously and utilizes graphite powder purchased from Bay Carbon, Inc. (SP-1 grade 325 mesh). In detail, concentrated H₂SO₄ (50 mL), K₂S₂O₈ (10 g), and P₂O₅ (10 g) are mixed in a 2 L Erlenmeyer flask and heated to 80 °C with a hot plate. Twelve g of graphite powder (purchased from Bay Carbon, Inc. SP-1 grade 325 mesh) is added to the mixture under strong magnetic stirring for 4.5 h. After that, 2 L of deionized (DI) water is added to the suspension (initially, water is added very slowly to avoid large amount of heat from the dilution of H₂SO₄). After dilution, the mixture is left overnight and then filtered through a 0.1 μm Teflon Millipore membrane; the filter cake is allowed to dry in air overnight. On the second day, the filter cake is slowly dispersed into 0.46 L concentrated H₂SO₄ in a 4 L Erlenmeyer flask in an ice bath with stirring. The temperature of the mixture is carefully controlled not exceeding 10 °C. The dispersion is kept at 35 °C for 2 h and then diluted with 900 mL of DI water. (Water should initially be added slowly to avoid rapid heating. During the whole process, the temperature is controlled below 50 °C.) Subsequently 2.8 L of DI water is added over 2 h with continuous stirring, giving a brownish dispersion. Immediately after finishing dilution, 50 mL of 30% H₂O₂ is slowly added to the dispersion, leading to tremendous bubbling as well as an obvious color change from brown to bright yellow. The mixture is left untouched for at least 2 days and then filtered through a 0.1 μm Millipore Teflon membrane, and washed with 10% HCl and 5 L DI water sequentially. The final filter cake is left to dry in air and then kept in desiccators with P₂O₅. The graphite oxide product can be easily dispersed in water by mild sonication.

2.2. Preparation and Characterization of GO_{SAND}. Filpro-sand was a gift from US Silica Company. It was washed with 10% HCl before use. Ten gram of clean sand was put in a Petri dish, with 10 mL 0.35 wt % of GO/DI water dispersion, and heated up to 150 °C in a vacuum oven for two hours. The process could be repeated to increase the GO-coating thickness on sand. SEM and EDAX data were obtained on Hitachi SEM S-5500, with 4,000-fold magnification and 7100 nA emission current. TGA experiments were executed on the Q-600 Simultaneous TGA/DSC from TA Instruments under 100 mL/min Ar. Raman spectra were characterized with the Renishaw Raman instrument (514.5 nm Laser beam, 50% power, room temperature, solid samples on glass).

2.3. Batch Adsorption Tests on GO and Column Test on GO_{SAND}. For the batch tests, about 20 mg GO is added to 20 mL of

200 ppm Hg²⁺ solution while the pH of the solution was adjusted to 2.0. To facilitate thorough mixing, we mildly sonicated the solution for 20 min, then allowed it to cool to room temperature and finally equilibrated it for 24 h at room temperature. The solution is separated from the solid by syringe filtration. The adsorption isotherm was obtained by changing the concentration of Hg²⁺ solution in the range of 4 ppb to 4000 ppm and repeating the experiment under similar conditions.

For the column tests, a filtration column (6.6 mm diameter x 400 mm long) was filled with GO_{SAND}, and the feed solution was flowed through the column at controlled flow rate, the eluted solution was collected at specific time intervals, and concentrations of all the eluates were determined by ICP-MS analysis for mercury ion or by UV–vis spectrometer for Rhodamine B. For mercury, the feed solution was 400 ppb mercury solution in 1% nitric acid, and flow rate was 1.000 mL/min. For Rhodamine B, the feed solution was 10 ppm Rhodamine B in DI water, and flow rate was 1.000 mL/min.

2.4. Functionalization of GO by Diazonium Chemistry. The involved diazonium precursor here is 4-aminothiophenol. In detail, 12 mmol 4-aminothiophenol was added to 15 mL of 1N HCl, gently heated to 53 °C while stirring (solution 1). Twelve mmol NaNO₂ was dissolved in 20 mL DI water, cooled down in an ice bath, and then added dropwise to the solution under constant stirring. The resulting solution was separated equally into two batches, and to each batch, a certain amount of GO (500 mg in 100 mL DI water) and reduced GO (RGO) (240 mg in 1 wt % aqueous sodium dodecylsulfate (SDS)) was added, and the reaction was kept in an ice bath with gentle stirring overnight. The product was separated by filtration, washed with acetone, ethanol, and copious amount of DI water. The resulting filter cake was redispersed in DI water and dialyzed in Cellu Sep membrane (H1 high grade regenerated cellulose tubular membrane, pore size 5000) against DI water for more than a week.

3. RESULTS AND DISCUSSIONS

3.1. Adsorption on GO and GO-f: NMR Characterization and Batch Tests. GO is synthesized by exfoliation and chemical oxidization of graphite.¹⁴ Recent solid-state ¹³C NMR⁴ has shown that about 60% of the carbon atoms in GO are sp³-hybridized and oxidized, mostly in the form of alcohols and epoxides but also as lactols, whereas the remaining 40% of the carbon atoms remain sp²-hybridized, mostly as unfunctionalized alkene or aromatic carbons but also as carbonyl groups in lactols, esters, acids, and ketones. The oxygen-containing functional groups while imparting hydrophilicity can also exhibit limited complexing capacity with mercuric ions.¹⁵ Figure S1a shows magic angle spinning (MAS) ¹³C NMR spectra of GO before and after Hg²⁺ adsorption. Small spectral changes occur upon complexation of Hg²⁺, presumably because Hg²⁺ is not directly bound to carbon in carboxylates and alkoxides and thus has only a modest influence on the ¹³C chemical shifts, as shown by the similarity of the carbonyl carbon chemical shifts in phenylmercuric benzoate¹⁶ and phenyl benzoate¹⁷ and by the similarity of the carbonyl and methyl carbon chemical shifts in mercuric acetate,¹⁸ cyclohexylmercuric acetate,¹⁹ phenylmercuric acetate,¹⁶ and acetic acid.²⁰ Limited experiments performed so far indicate that the adsorption behavior of Hg²⁺ ions on the native GO nanosheets can be represented by Langmuir type adsorption models (see Figure S1b,c in the Supporting Information).

Covalent modification of porous materials with complexing groups such as thiol (SH)²¹ can significantly increase the adsorption efficiency. The Tour group has investigated the grafting of aromatic diazonium compounds for covalent modification of reduced-graphene oxide (RGO).^{22,23} But reduced-graphene

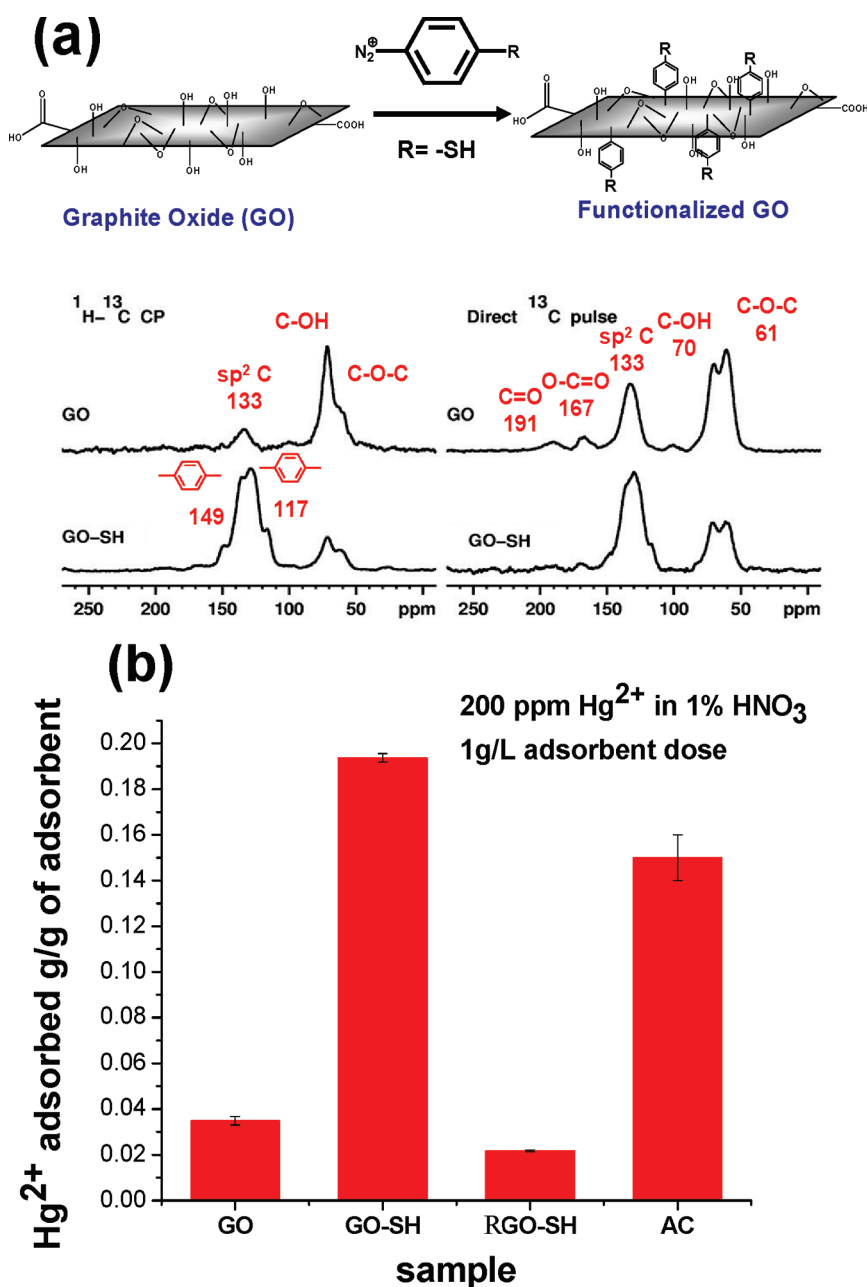


Figure 1. (a) Schematic of functionalization chemistry on GO, and corresponding NMR analysis of the functionalized product. (b) Batch tests of functionalized material for mercuric ion adsorption. The NMR spectra support the functionalization chemistry by the increased intensity in the aromatic region (around 130 ppm).

oxide (RGO) is hydrophobic and has limited access to water molecules. The diazonium grafting chemistry, nevertheless, provides a means to modify electron rich graphene domains by carbon attachment to the nanosheets. We performed a direct diazonium grafting without the intermediate reduction step in order to retain the available hydrophilic groups (see Figure 1a) and to modify the remaining sp^2 carbon domains. The strong increase in the intensity of the aromatic/alkene carbon region (~ 110 – 150 ppm) in the 1H – ^{13}C CP and direct ^{13}C pulse spectra of the product (GO-SH) in Figure 1a shows that covalent modification of GO occurred. Additional support for this conclusion is provided by dipolar dephasing experiments (Figure S2 in the Supporting Information), which show a significant decrease

in signal intensity in the aromatic/alkene region attributed to the elimination of the aromatic C–H signals. In contrast, the signal intensity from the quaternary aliphatic carbon atoms in the alcohol/epoxy region is, as expected, essentially unchanged.

A comparison of the abilities of various GO and the functionalized GO systems to speciate Hg^{2+} is shown in Figure 1(b). Adsorption experiments were undertaken with ~ 200 ppm Hg^{2+} solution, acidic pH, and 1 g/L of adsorbent dosage. Although RGO-SH (thiol groups attached to GO with the intermediate reduction step) did not improve over the nonfunctionalized GO, a significant increase (~ 6 fold) was observed for the GO-SH material. More specifically, the Hg^{2+} uptake capacity of GO is ~ 0.03 g/g of adsorbent, which can be increased to ~ 0.2 g/g for

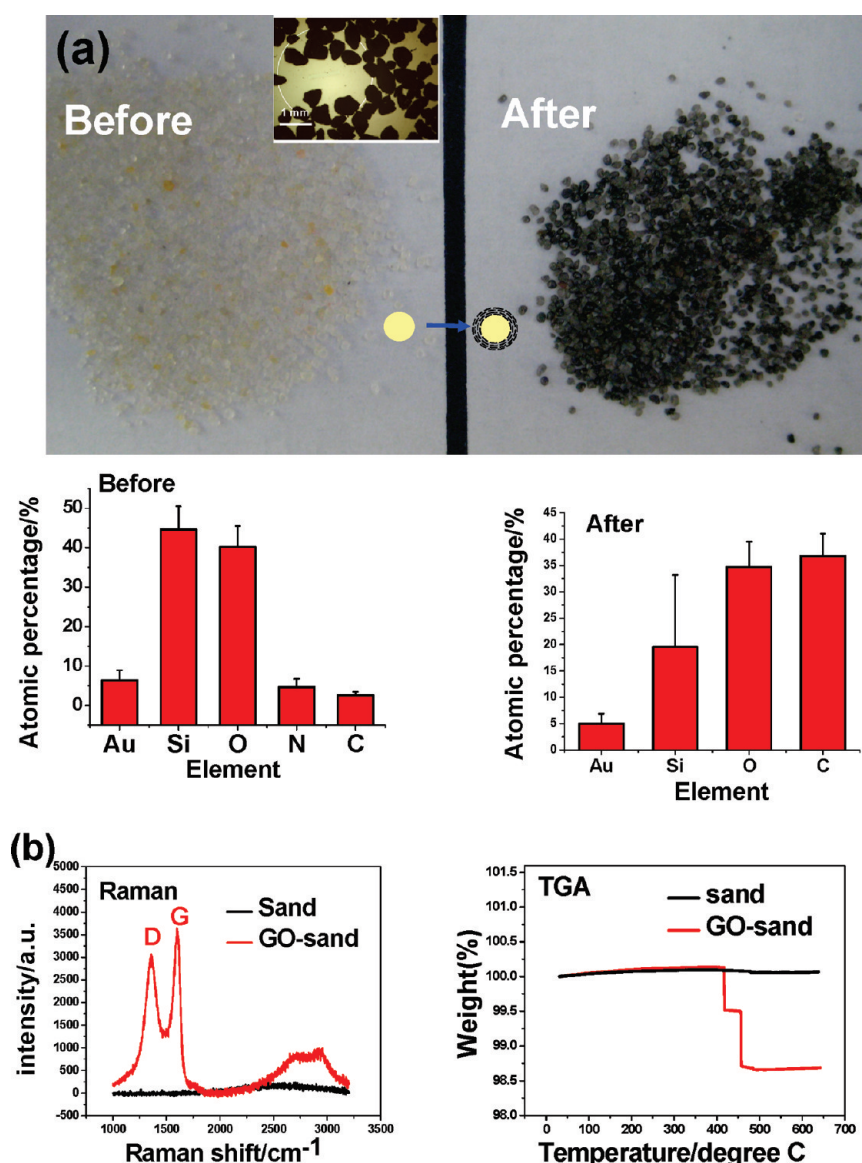


Figure 2. (a) Photographic images and EDAX analysis of sand and GO_{SAND} . EDAX analysis from the surface of the grains clearly showed a significant increase in carbon content. (b) Clearer evidence for coating from Raman spectra, and estimation of the coating thickness from TGA data.

GO-SH. These results conclusively show that this route of derivatization of GO creates a novel hydrophilic material with enhanced heavy metal removal efficiency. Under similar conditions, Mohan et al. reports in Figure 1 of his article, an uptake of 0.15 g of mercury/g (AC in figure 1(b)) of activated carbon formed by high temperature pyrolysis.⁹ Compared to the above cited report, these tailored GO-SH material have better performance, but their capacities are lower than the self-assembled monolayer functionalized mesoporous silica ($\sim 0.05\text{--}0.3$ g/g) discovered in the late 1990s²⁴ and currently being commercialized. We believe that more efficient adsorbent systems can be created using similar derivatization approaches to modify the sp^2 graphene domains of the GO nanosheets.

3.2. GO_{SAND} : A Novel “Core–Shell” Adsorbent System and Implications to Sand Filtration. Packed bed columns are the preferred mode of operation in most water-purification systems because of their simplicity and rapid kinetics.²⁵ We show a simple assembly process (see Figure S3 in the Supporting Information)

for conversion of conventional sand granules to a ‘core–shell’ adsorbent granules in which the GO coating imparts nanostructural features on the surface of sand granules. The assembly process essentially consists of physical mixing of the water dispersible GO colloids with sand, followed by a mild heat treatment that causes the nanosheets to adhere to each other over the sand surface, likely through van der Waals interaction. Easily apparent in the photographs of Figure 2a is the change in color from yellowish white to blackish gray after the coating process. In the inset of Figure 2a is shown the idealized schematic of the many-layer GO coating and the resultant GO_{SAND} filtration granules. Because the small field-of-view of the SEM does not allow us to discern the coating on the mm-scale granules, and because there is lack of contrast between the sand and the heavily oxidized carbon particles, we resorted to EDAX analysis (see Figure 2a) at different locations on the surface of the sand granules. A typical elemental composition of the sand granules is compared to GO_{SAND} granules which demonstrates

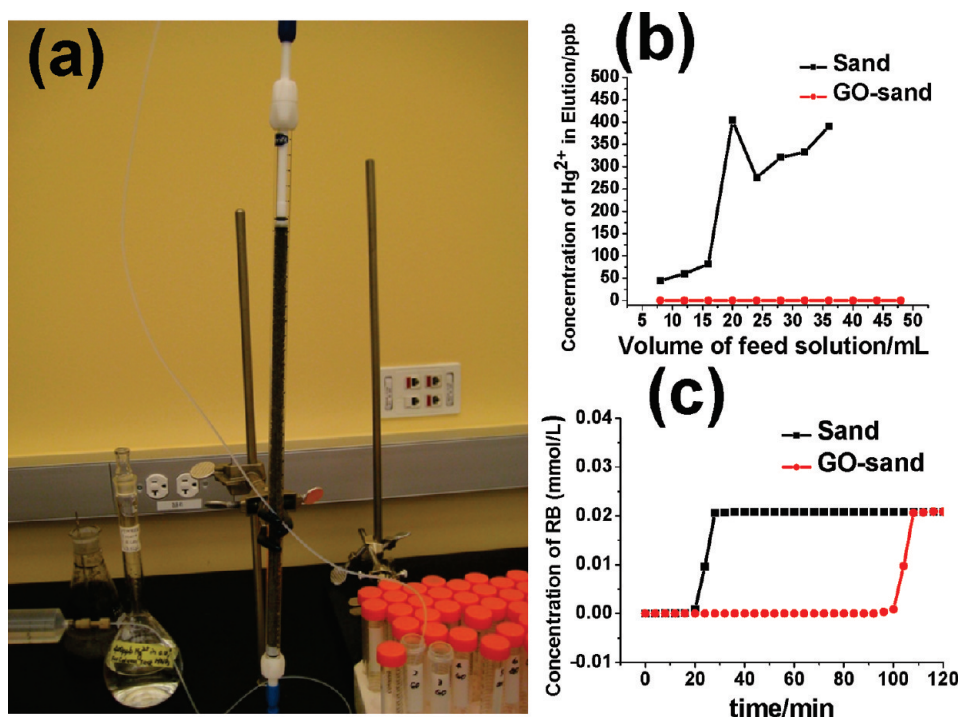


Figure 3. (a) Photographic images of adsorption column using GO_{sand} granules and column test results for removal of (b) Hg^{2+} and (c) Rhodamine dye B. Feed solution: 400 ppb Hg^{2+} in 1% HNO_3 for b and 10 ppm (~ 0.02 mmol/L) Rhodamine B in DI water for c. Flow rate: 1 mL/min. Column height: 400 mm; Column diameter: 6.6 mm.

a large ($\sim 30\%$) increase in carbon abundance and hence the presence of a carbon coating. We note that these results do not confirm that the coating is conformal as idealized in inset of Figure 2a, but is likely to coat majority of the surface of individual sand granule. This many-layer GO coating can additionally be confirmed with Raman spectra as well as its thickness estimated by TGA (Figure 2b). Prominent D (1359 cm^{-1}) and G (1598 cm^{-1}) peaks, consistent with the GO Raman data reported previously,⁴ are observed from GO_{SAND} sample, while barely any features are obtained from pristine sand spectrum. Shown in Figure 2(b) right is typical TGA data for GO_{SAND} showing a weight loss of $\sim 1.5\%$ contrasted with that of sand. The thickness can be estimated from this weight loss data, the size of the sand granules (measured) $\sim 597\text{ }\mu\text{m}$ (see Figure S4 in the Supporting Information), density of sand ($\sim 2\text{ g/cm}^3$),²⁶ and the density of GO ($\sim 1.68\text{ g/cm}^3$).²⁷ This thickness can be adjusted by changing the concentration of GO solution or repeating of the vacuum heating process and in our typical experiments vary from ~ 0.15 to $1.5\text{ }\mu\text{m}$. This novel GO-coated sand material easily fills the filtration column (see Figure 3(a)) and can be used in typical packed-bed experiments. We have utilized two model contaminants: Hg^{2+} (400 ppb in 1% HNO_3) and Rhodamine B dye (10 ppm) to experimentally measure the adsorption breakthrough of GO_{SAND} and to compare it with sand. While the adsorption capacity of sand granules toward Hg^{2+} (Figure 3b) was saturated within 10 min of filtration, the GO_{SAND} maintained the adsorption capacity for more than fifty minutes of fluid flow. The treated water had less than 1 ppb of Hg^{2+} . Similar results were also obtained for the dye molecule, where the dye molecule evolves through the GO_{SAND} column after 100 min, whereas it is after 20 min that the dye evolves in the sand column. We have checked the possibility of solubilization of GO by attaching a

piece of filter paper on top of the column. After a series of column filtration experiments running 2–3 h, we did not observe any precipitation on the paper evidencing the stability of the GO sand composites. We were also interested in comparing the performance of GO_{SAND} with activated carbon granules (Darco, 400–800 μm). We note that a large dye molecule will have high diffusion resistance inside the granules and consequently observe that the “core–shell” GO_{SAND} granules with micrometer thick coating on $\sim 600\text{ }\mu\text{m}$ sand granules perform comparably to the commercially available $\sim 600\text{ }\mu\text{m}$ activated carbon granules (see Figure S5 in the Supporting Information). We are investigating the diffusion mechanisms in these “core–shell” filtration granules that is likely to overcome the intragranular diffusion limitations in more conventional adsorbents.¹⁵ Nevertheless, the experimental evidence imply that this novel ‘core–shell’ adsorbent system can sequester heavy metal or organic contaminants at 5-fold higher capacity than regular sand and its performance is comparable to some commercially available activated carbon. We are currently investigating strategies that will enable us to assemble functionalized GO particles on the sand grains to further enhance contaminant removal efficiencies.

5. CONCLUSIONS

We have employed a surface modification technique, originally utilized for functionalization of chemically reduced and hydrophobic graphene nanosheets, to synthesize hydrophilic GO nanosheets containing covalently attached thiol groups. The modification is affected through carbon–carbon attachment of benzene-thiol groups to the sp^2 lattice within the nanosheets, as confirmed by NMR spectroscopy. We therefore demonstrate that the intermediate chemical reduction step is not necessary for

the diazonium chemistry and that the GO nanosheets retain significant electron-rich sp^2 domains that can be utilized for grafting additional complexing groups. This modification results in ~ 6 -fold increase in adsorption capacity of mercuric ions.

Water-soluble GO, prior to chemical modification, can be assembled on sand to create novel “core–shell” granules that find use in filtration columns readily. We conclude that the nanostructured GO coating can significantly increase the retention of heavy metals and organic dye over the parent sand granules.

Thus suitably engineered graphite oxide, particularly derived from natural graphite, can improve existing processes and spawn low-cost water purification technologies suited for the developing economies.

■ ASSOCIATED CONTENT

S Supporting Information. MAS ^{13}C NMR spectra of GO-SH, filpro-sand size distribution analysis, and column test results for Rhodamine B removal with GO_{SAND} and activated carbon are included. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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