Introduction of an Enhanced Binding of Reduced Graphene Oxide to Polyurethane Sponge for Oil Absorption

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ABSTRACT: Reduced graphene oxide (rGO) was covalently bound onto the surface of polyurethane (PU) sponge using two different coupling agents: (3-aminopropyl)triethoxysilane and titanium(IV)(triethanolaminato)isopropoxide. The coupling agents were introduced before and after reduction of graphene oxide to compare the impact of the sequence on the absorbance capacities. The sponges were evaluated based on hydrophobicity and pump oil absorbance capacities. The structure and properties of the sponges were evaluated using scanning electron microscopy and Fourier transform infrared spectroscopy. Results revealed that reacting the graphene oxide PU sponge with the coupling agent titanium(IV)(triethanolaminato)isopropoxide prior to reduction significantly improved oil absorbance. This was due to the improved binding of reduced graphene oxide to the polyurethane framework. The resulting improved rGO-coated PU sponge is a highly efficient and reusable sorbent material and is a promising alternative for oil−water separation applications.

1. INTRODUCTION

Within the last half-century, significant international attention has been focused on oil spill remediation due to a series of major accidental releases of oil into the marine ecosystem.1 Such releases can come from different sources such as tankers,2,3 oil rigs, and underwater pipelines.3 Although the rate of accidental release is steadily decreasing,3 there is still a significant hazard whenever oil is released into the environment. The recent Deepwater Horizon spill of April 2010 released 4.1 million barrels of crude oil containing 1.7 × 10−5 tons of various hydrocarbons into deep water.4 The depth at which the spill occurred prevented the evaporation of many volatile water-soluble compounds, causing a much higher concentration than normal to dissolve into the sea.4 Both deep water and surface spills are a danger to the environment and require optimal remediation strategies and oil−water separation methods.

For this reason, the ability to effectively separate oil and water holds great importance in environmental safety and marine life.2,5 The negative consequences of oil spills also affect human health6 and, as a result, require the development of safe cleanup methods. As there are many possible sources of water contamination,5 the development of a product with the capacity to remove both oil and solvents from water is necessary. Further applications can be extended to the pharmaceutical industry, where organic solvents are often used as reaction media and may require recycling or removal from the reaction.

Typical strategies to remediate accidental oil release include direct burning of surface oil,7 absorption using synthetic or natural materials,8 and emulsification or dilution using dispersants.9 While each strategy differs in terms of their advantages and disadvantages, absorption of contaminants has recently received a high level of attention as it has the potential for cheap, effective, and fast cleanup of oil spills.1 Furthermore, some methods of absorption allow for recovery of the oil that has been absorbed by the material.

There are a wide variety of absorbent materials that are used for oil remediation. Synthetic polymers, zeolites, clays, or natural materials such as peat moss and saw dust are some commonly used absorbent materials.1 In theory, an ideal sorbent material will have good selectivity (i.e., hydrophobicity and oleophilicity), high absorption capacities, stability in aqueous media, high cyclability, and high oil recoverability.10,11 Recently, there has been a surge of research on super-hydrophobic and oleophilic materials for sorbent materials that can selectively separate oil and other organics from water. Many of these new materials are used in the form of sponges or are coated onto a polymer sponge framework. Examples of these include superhydrophobic polyphenol sponges by Huang et al.,12 polydimethylsiloxane sponges by Choi et al.,13 and polyurethane (PU) sponges coated with TiO2 or polypyrrole by Wu et al.14 and Zhou et al.,15 respectively.

Among the new sorbent materials, carbon materials such as carbon nanotubes (CNTs) and graphene are promising because they are both hydrophobic and oleophilic. These properties make carbon materials ideal for use in applications where liquid−liquid separation is needed.10,16,17 Bi et al.16 developed a superhydrophobic, porous graphene sponge that has a high absorption capacity and ability to be used over multiple cycles. Gui et al.17 used carbon nanotubes to make a similar foam with a high absorption capacity. While both methods are appealing, these purely carbon-based sponges are often expensive and difficult to manufacture as they require time-consuming steps such as freeze-drying.

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Liu et al. addressed these issues by using reduced graphene oxide (rGO) to coat commercially available polyurethane foam chosen for its superior mechanical and absorption properties. Coating the surface of this amphiphilic material with rGO results in a water-repelling surface due to the inherent hydrophobicity of rGO. This allows the sponge to selectively absorb oil and other organics with little to no water retention. In addition, rGO can be made from graphite, an abundant and inexpensive material that is easily scalable. However, adhesion between rGO and PU relies only on van der Waals forces. Hence, there is a tendency for the coatings to flake off after repeated use, lowering their absorption capacities. This reduces the recyclability of the sponges and ultimately decreases their overall cost effectiveness.

In this paper, hydrophobic and oleophilic polyurethane sponges were fabricated by covalently binding rGO onto its surface through two different coupling agents: (3-aminopropyl)triethoxysilane (APTES) and titanium(IV)(triethanolaminato)isopropoxide (TTEAI). To determine the best performing samples, the sponges were subjected to an oil absorption capacity test and recycling test using pump oil. Sponges treated with TTEAI prior to reduction demonstrated the best oil absorption performance compared to that of the APTES-treated sample. This is likely due to the higher binding produced through TTEAI. A correlation between water contact angle and oil absorption capacity was found; higher contact angles generally lead to higher oil absorption. The chemical binding also served to significantly decrease the leaching of rGO from the sponge into the liquid after mechanical action. Therefore, the covalently bound rGO-PU sponge makes for a highly selective and reusable solution for separating organics from water.

2. EXPERIMENTAL SECTION

2.1. Materials. Neat PU sponges and gasoline were purchased from a local store. Graphite powder (2–15 μm) was purchased from Alfa Aesar. KMnO4 (ACS Reagent, >99%), NaNO3 (ReagentPlus, >99.0%), H2O2 (ACS Reagent, 30%), H2SO4 (ACS Reagent, 95.0–98.0%), HNO3 (ACS Reagent, 70%), hydrazine hydrate (reagent grade, 50–60%), APTES (>98%), and TTEAI (80% in isopropyl alcohol) were purchased from Sigma-Aldrich. All chemicals were used as received.

2.2. GO Synthesis. GO was prepared using graphite powder via a modified Hummers method that has been previously reported by our group. In brief, flake graphite was reduced using a mixture of H2SO4 and HNO3 in the presence of NaN3 and KMnO4. The prepared GO was then washed to remove excess metal ions and excess reactants.

2.3. Preparation of a GO-Coated Polyurethane Sponge. First, samples of PU sponge were measured and cut down to approximately 1 cm × 1 cm. The sponge samples were then cleaned ultrasonically in acetone for 1 h and dried in a vacuum oven at 80 °C for 1 h. The samples were then submerged in a 2 mg/mL solution of GO at room temperature for 1 h. Finally, the wet GO-coated sponges were dried at 80 °C in a vacuum oven for at least 4 h to remove excess water. Figure 1 illustrates the two main pathways used to further modify the GO-PU sponges.

2.4. Preparation Methods. APTES Functionalization: As-prepared GO-coated PU sponges were submerged in a solution of 2% APTES in ethanol. They were then left to stir for 4 h and dried overnight at 120 °C in a vacuum oven. The prepared sponges were then chemically reduced and dried in a vacuum oven at 80 °C for 4 h.

TTEAI Functionalization: This procedure is similar to APTES functionalization. The as-prepared GO/PU sponges were submerged in a 2% solution of TTEAI in isopropyl alcohol. They were then left to stir for 4 h at 70 °C followed by drying overnight at 80 °C. The as-prepared sponges were then chemically reduced and dried in a vacuum oven at 80 °C until dry.

Reduction of GO-PU Sponge: For all reduction steps, the sponges were submerged in distilled deionized (DDI) water heated to 80 °C and adjusted to pH 9 using sodium bicarbonate. Excess hydrazine 35% (1 mL) was then slowly dropped onto the sponge and left to stir for an hour. Once reduction was complete, the sponges were then washed with copious amounts of DDI water to remove excess graphene debris. Finally, the sponges were dried at 80 °C for 4 h.

Attachment of rGO to the PU Surface: Two major pathways of attaching rGO to the surface of the PU are shown by Figure 1. Route A involves the addition of the coupling agents before the GO reduction, and route B involves the addition of the coupling agents after reduction of GO. The coupling agents used were TTEAI, an organo-titanate, and APTES, a silane. Table 1 shows the different sponges prepared via routes A and B.

2.5. Characterization. The physical characteristics of the sponge samples and precursors were characterized using...
scanning electron microscopy (SEM), powder X-ray diffraction (XRD), Raman spectroscopy, and Fourier transform infrared (FTIR) spectroscopy. SEM images of the samples were taken using a Zeiss Leo 1530 and Ultra Plus FESEM. A thin layer of gold was sputtered on each sponge sample to increase conductivity and facilitate imaging. XRD was performed using a Bruker AXS D8 diffractometer using a Cu radiation source with a wavelength of 0.154 nm. Raman spectroscopy was done using a Bruker SENTERRA with a 532 nm laser source. Transmission electron microscopy (TEM) was performed using a JEOL 2010F.

2.6. Absorption Testing. In a typical experiment, an excess amount of oil or solvent was placed in a beaker. The preweighed sponge samples were then submerged in the substance and fully compressed to allow for saturated absorption. Once removed from the substance, the saturated sponge mass was obtained. Finally, the sponge was squeezed thoroughly to remove most of the absorbed liquid, and the process was repeated for the required number of cycles. All of the sponges were tested for at least five cycles using pump oil. The sample with highest absorption after five cycles was then subjected to additional absorption testing with acetone, gasoline, and chloroform using the aforementioned procedure.

3. RESULTS AND DISCUSSION

The GO used in this work was synthesized from small-flake graphite using a modified Hummers method. The GO was then dispersed in DDI water and ultrasonicated, forming a highly stable dispersion that was used for all further experiments. The GO used in this work has been characterized using SEM, TEM, Raman spectroscopy, and XRD, and the results are shown in Figure 2. Both the SEM and TEM show the highly wrinkly nature of the GO, which is preserved even after reduction to rGO.

A representative Raman spectrum of GO is shown in Figure 2c. The ratio of the D and G peaks (i.e., \( I_D/I_G \)) expresses information on the degree of disorder in the graphite structure. A higher \( I_D/I_G \) shows that there is more disorder in the carbon aromatic structure, which can be related to the attachment of different oxygen functionality to the carbon.

The oxygen functionality that is present in GO can form hydrogen bonds, which facilitates the dispersion of GO in aqueous solvents. When the GO is reduced to rGO, the oxygen functional groups are removed and part of the aromatic structure of the carbon is restored, making it more hydrophobic. The \( I_D/I_G \) ratios of the GO and rGO shown on Figure 2c are 1.25 and 0.74, respectively. The decreased ratio from GO to rGO confirms that the reduction, while not fully complete, is successful, and some of the carbon structure is restored. This is also confirmed by the XRD patterns of both GO and rGO, which are shown in Figure 2d. The GO diffractogram shows a characteristic peak around 11.9° that corresponds to the (002) plane. This peak provides information concerning the interlayer spacing of the GO sheets and is proportional to the degree of oxidation of the starting graphite. As the GO is reduced to rGO, the XRD peak shifts and broadens, corresponding to the short-range order from the restacking of graphene sheets.

The roughness and hydrophobicity of rGO makes it a perfect candidate for oil/water separation applications. Furthermore, the fact that its precursor (GO) is highly stable in aqueous solutions makes it even more attractive because simple and low-cost methods such as dip-coating can be utilized.

Figure 3 gives a qualitative illustration of the hydrophobicity of the sponges by showing water droplets on the sponge samples. As seen in Figure 3a, the neat PU sponge is slightly hydrophobic even before any treatments. However, we can see that the contact angles of most of the treated sponges have increased when compared to the neat PU sponge (Figure 3b–e).

The neat PU sponge was both slightly oleophilic and hydrophilic, which makes it unable to selectively absorb organics from water. Upon treatment with rGO and the binding agents, the sponge became both hydrophobic and oleophilic, able to preferentially remove organics from water. The hydrophobicity can be explained by the rGO coating on the surface of the sponge matrix.

The surface morphology of the neat and modified sponges was observed under SEM and is shown in Figure 4. The sponges possess macro pores with sizes that range from tens to hundreds of micrometers in diameter. The surface of neat PU is smooth and flat, while the surface of the modified sponges are wrinkled and textured. This confirms the presence of rGO in all samples.
of the modified samples. The average GO loading for all of the samples was calculated to be approximately 7 wt %.

As observed in Figure 4b−d, rGO is coated onto the skeleton of the PU sponge and also present between the pores, effectively blocking them. This is mainly due to the difficulty of producing rGO with a monodispersed size distribution in the current stage. While the starting graphite has a size distribution of 2−15 μm, the size of resulting rGO will be a few hundred nanometers to a few micrometers after the intercalation, oxidation, and reduction processes. Although the blocked pores may impact the absorbance capacities of the modified sponges, we have not observed significant change of the amount of oil absorbed by the modified sponges. This is the case because the pores inside the PU skeleton are also connected to each other. Increasing the coating uniformity of rGO on the PU sponge fibers as opposed to its pores will increase the hydrophobicity, resulting in an improvement of organic absorption. Therefore, further optimization of the rGO coating on the PU sponge fibers while reducing the presence in the pores may lead to improved performance.

Figure 5 illustrates the selectivity and the absorption process of a-TTEAI-rGO. A 1 × 0.5 cm³ sponge was tested by using it to separate a film of pump oil (approximately 0.5 mL, dyed with Sudan Blue II) from water. In this test, the sponge was simply placed over the separation and left to absorb the oil. The sponge was able to remove the pump oil from the water, leaving no visible trace of the contaminant, as illustrated in Figure 5d.

In practical scenarios, such as environmental spills, oil and other solvents will emulsify in the water, thus complicating removal of the spilled products. To test the separation capabilities of a-TTEAI-rGO in such scenarios, an oil-in-water emulsion was formed using a vortex. Figure 6 shows the absorption process of a-TTEAI-rGO in the prepared oil−water emulsion. The sponge was used to remove the emulsified oil both above and in the water. In the absence of a surfactant, most of the pump oil remained on the surface of the water, as shown by Figure 6. However, the water’s transition from clear to cloudy (Figure 6a,b) clearly demonstrates that some of the oil has formed microdroplets in the water phase. The sponge removed the oil from the surface of the water phase; it was also able to remove the emulsified oil present in the water phase (Figure 6f).

In order to quantitatively evaluate the performance of each sponge, a standard test was conducted to compare the absorbance of each sample. The absorbance capacity of each sample was tested using pump oil as the reference substance to be absorbed. Each sponge was submerged under 30 mL of pump oil and pressed in the liquid to maximize oil absorption. The sponges were then taken out and compressed manually using a quick-grip clamp. The summary of the pump oil absorbance capacities of all the modified sponges is shown in Figure 7a.

**Figure 4.** SEM photos of (a) neat PU, (b) rGO, (c) a-APTES-rGO, and (d) a-TTEAI-rGO with higher magnifications in the insets.

**Figure 5.** (a−d) Separation of pump oil dyed with Sudan Blue II from the surface of DI water by a-TTEAI-rGO.

**Figure 6.** (a−f) Separation of emulsified (via vortex) pump oil dyed with Sudan Blue II from DI water by a-TTEAI-rGO.

**Figure 7.** (a) Normalized absorbance capacities for pump oil over five cycles for (left to right) rGO, a-APTES-rGO, a-TTEAI-rGO, b-APTES-rGO, and b-TTEAI-rGO. (b) Absorbance of a-TTEAI-rGO in various organic media.
The absorbance capacity is largely determined by the porosity of the sponge. More porous structures will offer a higher liquid absorbance. All the prepared sponges have similar initial porosity, leading to similar initial absorbance of around 30 g/g. However, sponges with higher hydrophobicity will absorb organic liquids more readily and separate oil from water more effectively. Although initial absorbance of oil was almost the same, the sponge with higher hydrophobicity absorbed oil much faster than the others. As the sponges were reused, their absorbance capacities slightly decreased due to the loss of absorption capability as a result of the small amount of oil remaining on the sponge even after compression. Of the five samples prepared, a-TTEAI-rGO shows the best performance over the five cycles. Samples with higher contact angles demonstrated, on average, a higher absorbance of the pump oil.

In general, samples prepared using route A showed an absorbance capacity higher than that prepared with route B. The best performing sample, a-TTEAI-rGO, was used for further absorption testing using other organic liquids. Figure 7b shows a summary of the absorption capacities of a-TTEAI-rGO in different media. Significant swelling of the sponge was observed when absorbing organic solvents such as acetone and chloroform. This is most likely due to the diffusion of the solvent into the material.17 The sponge returned to its original size once dry.

APTES was chosen because it has previously been shown to have functionalizing capabilities with graphene.22 When the APTES is added to the GO-coated PU sponge, the silane groups can undergo a condensation reaction with the hydroxyl and carboxylic acid groups on the surface and edges of GO, forming covalent Si–O bridges. Similarly, the amine group in...
APTES can react with the terminal isocyanate groups on PU, covalently attaching the GO to the PU sponge surface. Similar reasoning was used to choose TTEAI as an alternative coupling agent. The proposed functionalization reaction for both APTES and TTEAI is illustrated in Figure 8a,b.

Figure 8c shows the typical FTIR spectrum for the PU, rGO-PU, a-APTES-rGO, and a-TTEAI-rGO sponges. The neat PU sponge spectra agree well with other PU spectra in the literature, containing the defining peaks for PU, namely, the N−H peak at 3280 cm−1 and C=O peak at 1700 cm−1 that are derived from the urethane linkage in PU and the peak at 1533 cm−1 that is typically associated with the C−N−H band.23

Typically, peaks around 3404, 1725, 1402, 1402 cm−1 are associated with the O−H, C=O, OH, epoxy C−O, and alkoxy C−O groups, respectively, that are present in GO.24 We can see that the spectra for all samples but PU lack strong peaks in these regions, which indicates that the oxygen functional groups were removed and the reduction of GO to rGO was successful.

Compared to both the rGO and neat PU sponges, the N−H and C−N−H peaks for a-TTEAI-rGO and a-APTES-rGO have reduced in intensity or have completely disappeared. Additionally, this trend is also present for the C=O peak around 1700−1725 cm−1 that can be attributed to the C=O bond present in polyurethane and rGO. This suggests that there are new bonds being formed as per Figure 8a,b.

From the data, we see that a-TTEAI-rGO has absorbance values higher than those of other modified sponges. Since the porosity of the samples is equivalent, we can assume that the difference in absorbance comes from other factors. It was observed during absorbance testing that some rGO flakes were removed from the PU skeleton into the pump oil. The a-APTES-rGO and a-TTEAI-rGO sponges released almost no rGO compared to the other samples. This might explain the performance difference between the sponges after recycling. When rGO flakes off, it reduces the hydrophobicity of the sponge, reducing its capability to absorb and retain pump oil. rGO flaking has previously been reported, and our experiments with the unmodified rGO sponge show similar results. The treated samples show little to no rGO flaking because of the covalent coupling of rGO to PU by either TTEAI or APTES, which was confirmed via FTIR. This results in sponges that can be reused for many cycles while still retaining their hydrophobicity and retention capabilities.

In route B, the GO was attached covalently to the PU after reduction to rGO. This means that there is a reduced density of oxygen functionalities on the surface of the flakes which reduces the probability that the coupling agents can form a successful bridge between the rGO and the PU sponge. This reduction will translate to less covalent bonding between the rGO and the coupling agents, which will make the rGO more likely to flake off due to reduced adherence. This explains the relatively poorer performance of sponges prepared via route B compared to sponges prepared via route A.

Although both sponges that are modified via route A showed good absorbance capacities for pump oil, a-TTEAI-rGO showed a better average absorbance than a-APTES-rGO. However, since both APTES and TTEAI are added before reduction (route A), their performance difference must stem from some other factors involved. One possibility is that TTEAI has stronger binding capabilities toward GO and PU compared to APTES. This would result in a stronger and more abundant binding of GO to the PU framework, which will enhance both its absorbance capacities and reusability. Further study and more advanced characterization will be applied to investigate the enhanced binding of TTEAI to rGO and PU.

4. CONCLUSIONS

rGO was covalently bound onto PU sponges using two different coupling agents, TTEAI and APTES, and via two different routes: route A (functionalization prior to GO reduction) and route B (functionalization after GO reduction). The modified PU sponges exhibited both hydrophobic and oleophilic properties, making it highly selective toward the absorbance of oil and other organics from water. The sponges that were coupled using TTEAI before the reduction of GO (a-TTEAI-rGO) exhibited the highest average pump oil absorbance compared to all of the other modified sponges. This can be explained by the abundance of oxygen functional groups on GO that are able to interact with TTEAI. It has also shown high absorbance capacities for several different organic media such as gasoline (46 g/g), chloroform (34 g/g), and acetone (32 g/g).

Furthermore, the sponge remained hydrophobic and oleophilic after repeated mechanical action. This can be attributed to the covalent binding of rGO to the PU framework which prevents the rGO from leaching into the liquid and reducing its hydrophobicity and oleophilicity. The highly reusable and selective nature of the covalently bound rGO PU sponge makes it a very attractive solution for oil−water separation applications.

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