

Graphene Oxide and Reduced Graphene Oxide and Their Water Purification Properties

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ABSTRACT

In this work we synthesized graphene oxide (GO) with slight modification of the literature procedure. The graphene oxide was deposited on sand and on a protein modified sand to create GO@sand and GO@protein@sand composites. These composites are further reduced to rGO@sand and rGO@protein@sand composites. Composites thus created were characterized by fourier transformed infrared spectroscopy (FTIR), energy dispersive X-ray (EDX) line analysis and scanning electron microscopy (SEM). We have evaluated these composites for their adsorbabilities of various dye and contaminant molecules by UV-visible spectroscopy.

Keywords: Graphene oxide, composite materials, water purification, contaminants, and SEM

1 INTRODUCTION

In recent years use of nanotechnology in the area of environmental remediation such as purification of air, water and soil is increasingly demanding. Historically carbon based materials have been used for water purification [1; 2]. *Vedic* literature is the earliest account [3] of the use of charcoal for water purification. Activated carbon attained from plants is extensively used as inexpensive adsorption method for various applications including water filtration due to its large surface area [4; 5]. Ion-exchange, reverse osmosis and membrane filtration are modern techniques for water purification [6; 7]. However, these advance techniques are extremely costly in third world countries. In this context, graphene, a one atom thick sheet of carbon is a new member to carbon family and it is considered as the rising star of material science [8]. Like other carbon based materials namely charcoal, activated carbon [9], carbon nanotubes [10], graphene also pose tremendous promises in the area of water filtration [6; 11]. Besides this graphene is also popularly utilized for its ability of DNA sensing, drug delivery, electronic properties and high electrical and thermal conductivity [6]. It is known that graphene and graphene oxide (GO) can be attached [12; 13] to sand to achieve very efficient adsorbent material to get rid of natural dyes [9], pesticides [14], and heavy metals [15]. Previously graphene have been conveniently anchored to sand surfaces with binders such as chitosan [13]. Here we propose to anchor graphene oxide to sand surface with a low cost water insoluble binder protein and also in absence

of the protein. We first attach the binder to the sand surface and then graphene oxide was anchored to the protein binder. Such composite material was tested removing dye molecules, contaminants and carcinogens. The composites were characterized by FTIR, SEM, and EDX line analysis

2 EXPERIMENTAL

2.1 Materials

Graphite flakes, rose bengal (92%), benzidine (>98%), and sodium nitrate (99%) were purchased from Sigma-Aldrich; melamine (98%) and Zein (98%) were purchased from Across Organic; potassium permanganate (98%), sulfuric acid (98%), hydrogen peroxide (30%) and sand were purchased from fisher scientific. All chemicals and solvents were used without further purification. The DI water in all experiments was Milli-Q water (18 M Ω cm, Millipore).

2.2 Synthesis of Graphene oxide (GO)

Graphene oxide (GO) was synthesized with slight modification of Hummers method [16; 17] using graphite flaks. In 23 mL of concentrated sulfuric acid 0.5 g of graphite flakes and 0.5 g of NaNO₃ were stirred in an ice bath. After addition of 3.0 g of KMnO₄ mixture was stirred continuously at 35 °C water bath for 60 minutes. This forms a thick paste. After that 40 mL of water was added and the mixture was stirred for additional 30 minutes at 35 °C. At the end 100 mL of water was added followed by slow addition of 3 mL of 30% H₂O₂. This turns solution color from brown to yellow. The solution was filtered warm and washed with 100 mL of water. The obtained filter cake was redispersed in water by ultra sonication. All the larger visible particles were removed by 3-5 times low speed centrifugation at 1000 rpm for 2 minutes. Finally the supernatant was centrifuged two more times at 8000 rpm for 15 minutes to get rid of small pieces of GO and water soluble impurities. Thus recovered GO was redispersed in water by vortex or mild sonication.

2.3 Sand and GO Composite formation

Pure sand was cleaned with piranha solution and dried in the oven at 80 °C. Cleaned sand was immersed in a 0.5 mM ethanolic solution of Zein for 30 minutes and then dried at 80 °C to form Zein@sand composite. 10 g each of pure sand and Zein@sand composite were treated with GO solution by drop-casting method. Systematically total 20 mL of GO solution were added in 2.0 mL instalments to both sand and Zein@sand and dried in the oven at 80 °C. The final product was heated overnight at 80 °C and finally

rinsed several times with DI water and then dried again before use. This yielded rGO@sand and rGO@Zein@sand composites where rGO represents reduced graphene oxide.

2.4 UV-visible and FTIR Spectroscopic Studies

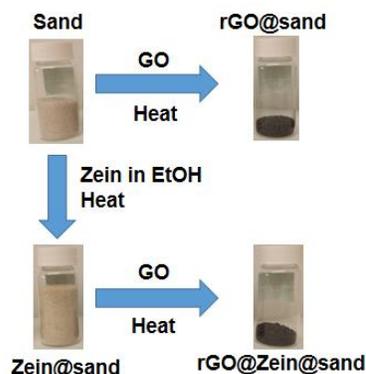
The absorption spectra of GO and all other samples were recorded using a Cary 4000 UV-visible spectrophotometer. FTIR spectroscopy was performed using Perkin-Elmer FTIR Spectra 100 spectrometer fitted with diamond ATR. The spectra were further processed and plotted with Origin 8.0 software.

2.5 SEM and EDX analysis

SEM images were collected using JOEL JSM-5800LV Scanning electron microscope equipped with Bruker Esprit 1.9 microanalysis software. This is also connected to a EDX detector and EDX line analysis data were obtained by using the back-scattered detector at a working distance of 10-12 mm at 15.0 kV of accelerating voltage. A few particles of sand, Zein@sand, rGO@sand, and rGO@Zein@sand composites were fixed on an aluminum stage with copper tape and affixed into the chamber.

3 RESULTS AND DISCUSSION

In this study we demonstrated fabrication of sand with graphene oxide. In a typical route the pretreated sand was modified with Zein protein by dip-coating and then dried in the oven to obtain Zein@sand. Later pretreated sand and Zein@sand were treated with GO solution by drop-casting method in small aliquotes and then dried in the oven. This was repeated several times until a satisfactory coverage of the sand by GO was achieved. The color of the sand and Zein@sand were turned black indicating formation of rGO@sand and rGO@Zein@sand as illustrated in Scheme 1.



Scheme 1: Schematic representation of fabrication of sand and Zein@sand into rGO@sand and rGO@Zein@sand composites.

3.1 Characterization of GO by FTIR Spectroscopy

FTIR spectroscopic data suggests the formation of GO from graphite. The FTIR spectrum of GO is depicted in Figure 1. The signals at 3202, 1735, and 1621 cm^{-1} are assigned to O-H stretch, C=O stretch, and C=C stretch, respectively. Few

more additional signals in the fingerprint region 1392, 1222, and 1039 cm^{-1} correspond to O-H deformation, C-O stretch (epoxy), and C-O stretch (alkoxy), respectively.

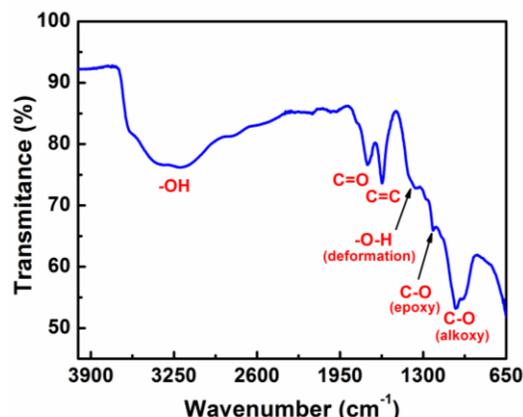


Figure 1: FTIR spectrum of graphene oxide (GO) solution in DI water.

3.2 Characterization of GO by UV-visible Spectroscopy

Figure 2 illustrates the UV-visible absorption spectrum of GO solution in DI water. The absorption of GO depicts two characteristic features. The signal at 230 nm corresponds to the π - π^* transition of C=C and the shoulder at 304 nm due to n - π^* transition corresponding to the C=O bond [18].

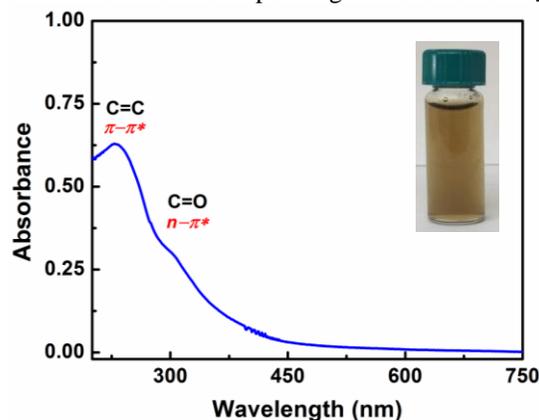


Figure 2: UV-visible spectrum of graphene oxide (GO) solution in DI water.

3.3 SEM and EDX Analysis of Composites

Figure 3 shows the typical SEM images of sand, Zein@sand, rGO@sand and rGO@Zein@sand composites. From the digital photographs shown in scheme 1 and SEM images it is clear that rGO has successfully been deposited on the sand and the Zein@sand. The presence of oxygen and silicon in the EDX spectra was attributed to sand. In samples Zein@sand, rGO@sand and rGO@Zein@sand an additional signal for carbon appears indicating presence of carbon based materials. The EDX data is presented in Figure 4.

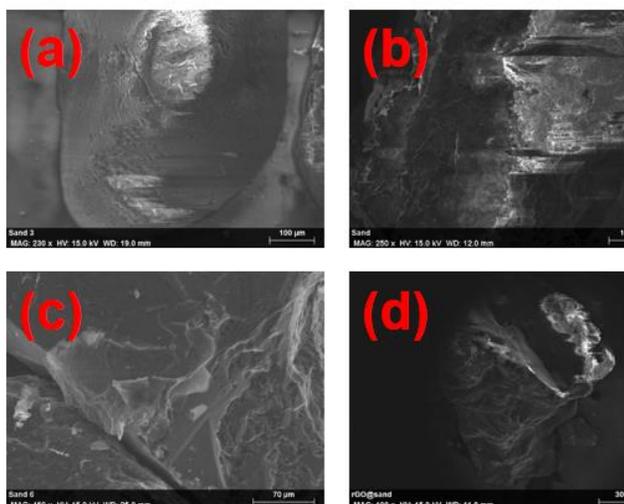


Figure 3: SEM images of (a) sand, (b) Zein@sand, (c) rGO@sand and (d) rGO@Zein@sand composites. Images were taken with JOEL JSM-5800LV scanning electron microscope at an operating voltage of 15 kV in SE mode and analyzed with Bruker Esprit 1.9 microanalysis software.

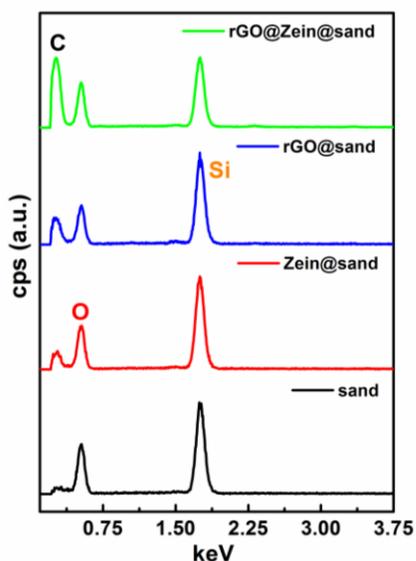


Figure 4: EDX line analysis of (a) sand, (b) Zein@sand, (c) rGO@sand and (d) rGO@Zein@sand composites. Data collected using a JOEL JSM-5800LV scanning electron microscope at an operating voltage of 15 kV in SE mode and analyzed with Bruker Esprit 1.9 microanalysis software.

3.3 Water Filtration Performance of rGO@sand and rGO@Zein@sand composites.

The adsorption capacity of the designed rGO@sand and rGO@Zein@sand composites were tested using three different molecules. A food contaminant, melamine [19]; a negatively charged dye molecule, rose bengal (RB); and benzidine, a carcinogen [20]. The melamine removal capacity of the rGO@sand and rGO@Zein@sand was

tested using 20 μM aqueous solution of melamine at pH 3.24. Four different adsorbent column (glass column of 15 cm length and 8 mm diameter with 20 micron polyethylene bed support) were prepared adding 5 gm each of sand, Zein@sand, rGO@sand, and rGO@Zein@sand. The prepared columns were thoroughly rinsed with DI water before adsorption test. 1.0 mL of 20 μM aqueous solution of melamine was first allowed to go through all four columns. After that another 1.0 mL 20 μM aqueous solution of melamine was allowed to pass through each of the columns and collected for UV-visible absorption measurement. Melamine has 2 prominent absorption signals at 209 and 236 nm in its UV-visible absorption spectrum as illustrated in Figure 5. After passing through sand, and rGO@Zein@sand a very minimum adsorption is observed. Through Zein@sand column no change was observed. However, after passing through rGO@sand column the absorption signal disappears completely and almost matches with the absorption spectrum of DI water (see Figure 5) indicating complete adsorption.

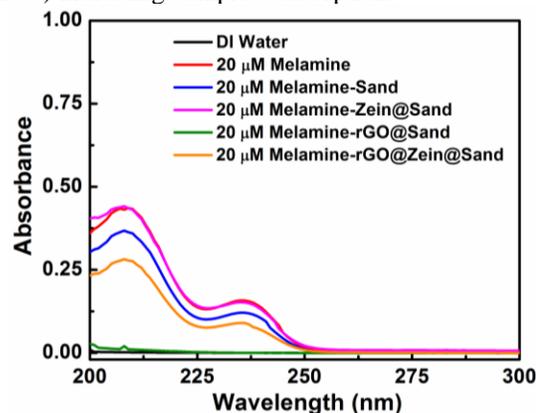


Figure 5: UV-visible spectra of DI water (black line), 20 μM melamine (red line), 20 μM melamine through sand column (blue line), 20 μM melamine through Zein@sand column (pink line), 20 μM melamine through rGO@sand column (green line) and 20 μM melamine through rGO@Zein@sand column (orange line).

Dye molecule RB has several characteristic signals at 212, 263, 316, and 549 nm in the UV-visible spectrum as shown in Figure 6. As above, after passing through sand, a minimum lowering of adsorption is observed. After passing through Zein@sand, rGO@sand and rGO@Zein@sand columns the absorption signals disappear nearly completely and almost match with the absorption spectrum of DI water (See Figure 6). rGO@sand column performs best among these.

Benzidine has one distinct signal at 282 nm in the UV-visible spectrum as shown in Figure 7. As above, after passing through sand, about 50% decrease in the absorption signal is observed. After passing through Zein@sand and rGO@Zein@sand columns the absorption signals decrease about 80%. And finally, after passing through rGO@sand column the absorption signal disappears completely and almost matches with the absorption

spectrum of DI water (See Figure 7). rGO@sand column performs best among all these.

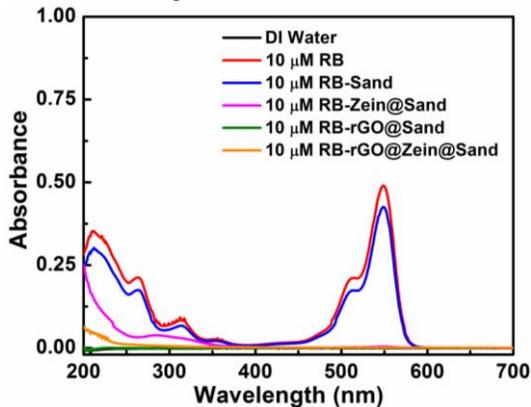


Figure 6: UV-visible spectra of DI water (black line), 10 μM RB (red line), 10 μM RB through sand column (blue line), 10 μM RB through Zein@sand column (pink line), 10 μM RB through rGO@sand column (green line) and 10 μM RB through rGO@Zein@sand column (orange line).

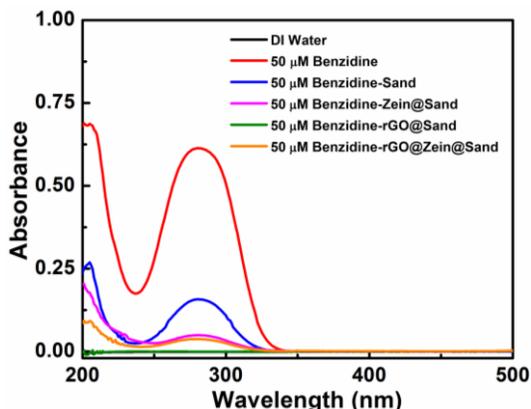


Figure 7: UV-visible spectra of DI water (black line), 50 μM benzidine (red line), 50 μM benzidine through sand column (blue line), 50 μM benzidine through Zein@sand column (pink line), 50 μM benzidine through rGO@sand column (green line) and 50 μM benzidine through rGO@Zein@sand column (orange line).

4 CONCLUSIONS

In this work we have successfully synthesized the GO and successfully coated sand and Zein@sand with rGO to achieve rGO@sand and rGO@Zein@sand composites. Both rGO@sand and rGO@Zein@sand composites were utilized for the water purification tests. We have tested three different molecules to assess the adsorbance capacity of the composite materials. It was observed that rGO@sand performed much better than rGO@Zein@sand composite in most cases. The SEM images indicated that sand was not 100% coated with rGO. Improvement in the surface coverage effort is in progress.

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