Solar reduced graphene oxide coated sponge for oil and organic solvent adsorption studies

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Abstract: In this work, we have synthesized solar reduced graphene oxide (SRGO) by facile, fast and cost effective technique. The as-prepared SRGO was coated on polyurethane sponge and used for oil adsorption from the oil-water interface. The material was characterized by x-ray diffraction spectroscopy and scanning electron microscopy for structural, surface and morphological analysis. Further the hydrophobicity of the graphene coated sponge was investigated by measuring the contact angle of water droplet with the graphene coated sponge. The graphene coated sponge demonstrates strong hydrophobicity along with oleophilic property. SRGO coated sponge shows high adsorption and achieves equilibrium in few seconds. Highest adsorption capacity has been obtained for tetrahydrofuran, which is 65.67 g/g. SRGO coated sponge prepared could be a desirable material for cleanup of oil spills in sea.

1. INTRODUCTION

Severe environmental issues arise due to oil spills which can take place either by human error or accidents, taking place in deep sea and ocean. It not only affects human and aquatic life but also birds. Hence, there is a growing demand for the oil-adsorbing materials[1]. A large number of oil absorbents has been developed in past, which includes clay, activated carbon, zeolites, carbon nanotubes, polymers, rubber materials, wool fibers and straw[2-7]. However, these materials possess several issues such as a high cost, low absorption capacity and poor reusability. So, new materials needs to be developed with low prices, excellent absorption capacity and outstanding stability. In recent years, three-dimensional (3D) porous materials have been considered as a promising high capacity absorbents because of their large surface area and porous structure. Nevertheless, these materials absorb water and oil simultaneously.

Since graphene was discovered in 2004, it had attracted scientists across the globe for many applications such as field-effect transistors, memory devices, photovoltaic devices, sensors and many more [8]. Graphene is a two dimensional sheet of sp²-hybridised carbon atoms. There are many techniques for the synthesis of graphene, such as chemical vapor deposition [9], high temperature annealing [10], electrochemical [11], photochemical [12] and thermal reduction [13]. Simple and cost effective method to synthesize graphene had been major challenge for the scientists. Due to higher theoretical surface area, graphene had been reported as better adsorbent [14]. Many publications reported the usage of graphene and graphene oxide coated sponge as an adsorbent for the removal of oil and organic solvents due to high porosity, low density and hydrophobic nature [15-17]. It showed significantly higher adsorption capacity of oil and organic solvent.
In this work, we report simple and cost effective technique to synthesize graphene by the reduction of GO using solar irradiation. The as-prepared graphene was coated on sponge and employed for the removal of oil and organic solvents from water.

2. EXPERIMENTAL DETAILS

2.1. Materials
Graphite flakes, concentrated sulfuric acid (98%), hydrogen peroxide, hydrochloric acid, ethyl alcohol, acetone, nafion were procured from SD fine chemicals Ltd. Castor oil, kerosene, nitrobenzene, n-dodecane, chloroform, n, n-dimethylformamide, polyethylene glycol, acetone, ethanol, paraffin oil, thermanol-6,6-hexane, tert-butanol, tetrahydrofurun, toluene, methanol, carbon tetrachloride were procured from Sigma Aldrich.

2.2. Synthesis of Graphene Oxide (GO)
Graphene oxide (GO) was prepared through simplified Hummers method. Graphite flakes (2 g) was mixed with 100 mL of concentrated \( \text{H}_2\text{SO}_4 \) and 10.6 mL of \( \text{H}_3\text{PO}_4 \). The mixture was stirred for 5 to 10 min. Potassium permanganate (10 g) was added slowly in the mixture to avoid the increase in temperature. The mixture was stirred for 72huntil highly viscous mixture was formed. Then the mixture of hydrogen peroxide and deionized water (1:25) was mixed with the viscous graphite oxide till it became yellowish in colour. The mixture was washed successively with 1M HCl and deionized water till the neutral pH obtained. The obtained GO was dried at room temperature to obtain graphene oxide sheet.

2.3. Synthesis of Solar Reduced Graphene Oxide (SRGO)
As-prepared GO was reduced using focused sunlight with the help of convex lens, as reported earlier by our group [18]. The reduction and exfoliation processes of GO were achieved simultaneously under focused solar radiation. The as prepared GO paper was spread in petridish and kept under solar light. A convex lens of 90 mm diameter was used to focus the solar radiation on it. The rapid reduction of graphene oxide begins due to sudden rise in temperature under focused solar irradiation, which imparts the energy required for the exfoliation. This process was accompanied by color change and volume expansion and this took less than two minutes to complete the reduction and exfoliation process. DynalabAN 2104 radiation indicator was used to measure the intensity of sun light and K1 type thermocouple based digital thermometer (DTM-100) was used to measure the temperature of focused sun light. The power of the focused radiation was approximately 5.4 W and the temperature reached to 204°C. This solar reduced GO (SRGO) was used as it is for coating sponge and doing oil adsorption studies.

2.4. Fabrication of Graphene Coated Sponge
The SRGO was mixed in ethanol in the ratio 4 mg/mL and sonicated for 30 min to obtain uniform suspension. Nafion(500µL) was then added to the mixture and sonicated for 10 min to increase the binding strength of the solution. Several pieces of polymeric sponge were washed with acetone and deionized water to remove any impurities. The sponge pieces were then dipped in SRGO suspension for 24 h for proper binding. The graphene coated wet sponge was dried in furnace at 75°C for 2 h to obtain graphene coated hydrophobic sponge (GS). Optical image of SRGO coated sponge is shown in Figure 1.
Figure 1. Graphene coated hydrophobic sponge.

2.5. Characterization of Synthesized Materials
GO and SRGO were characterized by X-ray diffractionspectroscopy to study the structural and phase studies. Powder XRD (Bruker D8 Advance) with Copper K-alpha (Cu Kα) radiation (λ =1.54 Å) was used for the confirmation of the diffraction patterns. The material was further characterized by scanning electron microscopy(SEM, Zeiss Supra 40) for surface structure and morphology.

2.6. Investigation of Hydrophobicity of Graphene Coated Sponge
The graphene coated sponge was investigated to study the hydrophobic/hydrophilic nature using contact angle measurement system. In order to get hydrophobicity, a drop of water was allowed to adsorb onto the surface of graphene coated sponge and the contact angle of the drop with the surface of graphene coated sponge was measured.

2.7. Adsorption Capacity of Graphene Coated Sponge
The graphene coated sponge was immersed in various oils and organic solvents until saturation. The adsorption capacity was calculated by equation (1) [15].

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\text{Adsorption capacity} = \frac{W_s - W_i}{W_i}
\]  

Where, \(W_i\) and \(W_s\) are the initial and final weights of the graphene coated sponge respectively.

3. RESULTS AND DISCUSSION

3.1. Characterization of GO and SRGO
GO and SRGO were synthesized by simplified Hummers method and solar irradiation respectively. As-prepared GO and SRGO were characterized by X-ray diffraction technique. Figure 2a shows XRD spectra of both the materials. There is a sharp peak obtained at 10.5° which is attributed to the reflection from plane (002). This depicts that GO was successfully synthesized from graphite flakes. The obtained d-spacings for GO is 0.93 nm. The interlayer spacing for materials is directly proportional to the degree of oxidation. So, it confirms high degree of oxidation for GO. In case of SRGO, twobroader peaks at 23.7° and 42.7° have been observed, which correspond to reflection from plane (002) and (100). Further, both the materials were characterized by scanning electron microscope. Figure 2b and c show the SEM images for GO and SRGO respectively. There is more exfoliation in case of SRGO than GO indicates better reduction of GO happened by solar irradiation.
3.2. Investigation of Hydrophobicity of Graphene Coated Sponge

In order to investigate hydrophobicity of the graphene coated sponge, water droplet was allowed to adsorb onto the surface of the sponge without graphene coating and the graphene coated sponge. The contact angle of the drop with the surface of both the sponges was measured. As shown in Figure 3a, the sponge without graphene coating showed the contact angle of 34°. On the other hand, the graphene coated sponge showed the contact angle of 123° as shown in Figure 3b. The increase in the contact angle confirms that the sponge after loading of graphene possesses highly hydrophobic nature which is in agreement with the finding from Li et al. (2014) [19]. The actual photographs of both the sponge with water droplet are shown in Figure 3c and d.

3.3. Adsorption Capacity of GS for Oil and Organic Solvent

The graphene coated sponge (GS) was immersed in the water containing oil or organic solvents for several experiments with different type of organic oil. The GS was allowed to adsorb different oils or organic solvents present in the water as shown in Figure 4a. The oil or organic solvent was adsorbed within a few seconds of time indicating efficient adsorption as shown in Figure 4b. The GS kept floating on the surface of water without penetrating the water within the structure or releasing oil or organic solvent. The adsorption capacity was calculated for each experiment from eq. (1). The adsorption capacities for different oil and organic solvents are shown in Figure 5. There are better adsorption capacities up to 50-65 times of its own weight for organic solvents such as toluene (58.07 g/g), tertiary butanol (47.57 g/g) and n-dodecane (42.92 g/g). Highest adsorption capacity was obtained for tetrahydrofuran (65.667 g/g).
Figure 3. Water droplet on (a) GO; (b) SRGO; (c) sponge without graphene coating, (d) graphene coated sponge (GS).

Figure 4. (a) Solution before adsorption, (b) Solution after 2s of adsorption.

Figure 5. Adsorption capacities of GS for different solvents.

4. CONCLUSION

In the present work, we have synthesized solar reduced graphene oxide (SRGO) by facile, fast and cost-effective method. The as-prepared SRGO was loaded on sponge that was used for oil adsorption study. The X-ray diffraction spectra and scanning electron microscope images confirmed that GO is successfully reduced to SRGO. The graphene loaded sponge (GS) showed excellent hydrophobic nature when investigated by measuring the critical angle of water droplet with the surface of GS. Highest adsorption capacity obtained for tetrahydrofuran was 65.67 g/g of adsorbent. The GS should
be considered as a promising candidate for oil and organic solvent adsorption during oil spills and for separation of oils and organic solvents from water.

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