



CrossMark
 click for updates

Cite this: *RSC Adv.*, 2016, 6, 62760

Multifunctional reduced graphene oxide coated cloths for oil/water separation and antibacterial application†

Ravi Kant Upadhyay,^a Amrita Dubey,^b Prashant R. Waghmare,^c Richa Priyadarshini^b and Susanta Sinha Roy^{*d}

Multifunctional reduced graphene oxide (RGO) coated cloths were prepared through the thermal treatment of GO coated cloths without using any harmful reducing agent. The effect of heating temperature on the wetting properties of the cloths was also monitored through contact angle measurement. The highest contact angle 141° was observed for the RGO coated dense cloth while the highest contact angle exhibited by the RGO coated sparse cloth was 130°. The as prepared RGO coated cloths were utilized as a filter and an absorbent for oil/water separation. The RGO coated sparse cloth was utilized as a filter for the separation of an oil/water mixture while the dense cloth was utilized as an absorbent for the selective absorption of oil from water. RGO coated cloths were also explored as an antibacterial agent and the effect of the microstructure of coated cloths on their antibacterial properties was also investigated. The cloth with the dense structure exhibited higher antibacterial activity compared to the sparse cloth. A significant loss of percentage viability up to 98% was achieved using the RGO coated cloth, proving it highly efficient as an antibacterial agent, which makes it a suitable bandage material for the dressing of open wounds. Apart from being antibacterial, the RGO coated cloths are also hydrophobic in nature so they can protect wound from water and atmospheric moisture which is not possible with ordinary bandages.

Received 29th March 2016
 Accepted 16th June 2016

DOI: 10.1039/c6ra08079k

www.rsc.org/advances

1 Introduction

Graphene has emerged as a wonder material; its countless intriguing and unprecedented properties have enabled access to it in almost every field.^{1,2} It has been utilized for a diverse range of applications in various fields including electronic, electrical, environment and medicine.³ Out of its wide spectrum of properties, the electrical properties of graphene have been highlighted the most and explored extensively. However, recently a large number of studies have surfaced mentioning the use of graphene for environmental and medicinal applications.^{4,5} Graphene coated substrates have been widely explored for the removal of both organic (dyes, oil and other hydrocarbons) and inorganic (heavy metal ions) waterborne pollutants.⁶ Oil is one of the most common liquid water pollutants, in the

past its spillage in water has caused several harmful effects on living beings.^{7–9} Water pollution either due to the accidental spillage of oil into water or the use of water in different processes in oil industries, is a major concern for both environmental welfare organizations and oil industries. Contamination of water with oil not only makes it unsuitable for human use but also for agricultural and industrial applications. A variety of techniques such as coagulation,¹⁰ electrostatic centrifugation¹¹ and air flotation^{12,13} *etc.*, have been employed for the separation of oil/water mixtures. However, high cost, low separation efficiency and sophisticated instrumentation are the few shortcomings associated with these techniques, which limit their use.¹⁴ In order to overcome the aforementioned shortcomings of traditional approaches, recently several processes involving materials with manipulated wetting properties have been designed for the selective removal of either water from oil or oil from water. Most of these processes are based on the selective absorption or filtration of oil from water or *vice versa*. Recently, graphene functionalized materials have garnered huge attention for oil/water separation. Different types of substrates such as sponge,^{15,16} cotton,¹⁷ paper¹⁸ and stainless steel mesh¹⁹ have been modified with graphene in order to realize the goal of oil/water separation. Graphene consists of carbon arranged in a honeycomb like structure which makes it hydrophobic in nature and endows it with an affinity towards

^aDepartment of Chemistry, School of Natural Sciences, Shiv Nadar University, Gautam Budh Nagar 201314, Uttar Pradesh, India

^bDepartment of Life Sciences, School of Natural Sciences, Shiv Nadar University, Gautam Budh Nagar 201314, Uttar Pradesh, India

^cDepartment of Mechanical Engineering, University of Alberta, Edmonton, Canada T6G 2M9

^dDepartment of Physics, School of Natural Sciences, Shiv Nadar University, Gautam Budh Nagar 201314, Uttar Pradesh, India. E-mail: susanta.roy@snu.edu.in

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c6ra08079k

oil. The excellent water repellent nature of graphene can be exploited in the making of oil selective absorbents and filters. Recently, several studies have appeared establishing graphene as a potential aspirant material for oil/water separation. Qin *et al.*¹⁸ prepared a reduced graphene oxide (RGO) modified filter paper through heat treatment of a graphene oxide (GO) coated filter paper, which showed excellent oil/water separation selectivity. In another report Ge and co-workers¹⁷ utilized RGO coated cotton as an absorbent for the selective absorption of oil from an oil/water mixture. GO coated on cotton was reduced chemically in order to achieve the RGO coating.

Apart from water treatment, recently graphene has garnered attention for its highly anticipated applications in medicine such as for antimicrobial agents, bio-imaging, biosensors and drug carriers.^{20–22} Graphene, its derivatives and its composites have been used as antimicrobial agents and drug carriers, although the status of graphene as an antimicrobial agent is still matter of debate and needs further studies to thoroughly understand its role as an antimicrobial agent.²³ Synthesis wise graphene is a highly flexible material; a large number of preparation approaches are available for its fabrication. In particular, wet chemical synthesis, involving the chemical reduction of GO to RGO, endows RGO with flexibility of use either in solid or in liquid form. Recently a plethora of reports have been documented mentioning the use of graphene and its derivatives for medicinal applications, however most of these reports are focused on the use of graphene and its derivatives in either liquid suspension form or solid form as a drug carrier and antimicrobial agent.^{24,25} Very few reports are available on the application of graphene immobilized surfaces or substrates for medicinal applications and this needs to be explored more. Graphene coated substrates such as cloths and bandages can be useful for making antimicrobial bandages for the dressing of open wounds and also designing odor resistant garments.²⁶ Graphene can be easily coated on any substrate by immersion of it in a GO solution followed by the reduction of the coated GO. In the case of porous materials such as cloths and papers, it is extremely simple to coat with graphene using this approach. Previously, graphene coated flexible materials such as cloths have been used as flexible electrodes for electrochemical applications^{27,28} however the use of these graphene coated flexible substrates for medicinal applications has still not been explored much.

In the present report, a facile preparation method has been described for obtaining RGO coated cloths. The as prepared RGO coated cloths have been utilized as an absorbent and filtration medium, based on their porosity and structure, for oil/water separation. The effect of heat treatment on the wetting properties of the GO coated cloths has also been investigated. Apart from oil/water separation, RGO coated cloths have also been explored as antibacterial agents against *E. coli*. The effect of the structure of the RGO coated cloth on its antibacterial activity has also been investigated. The RGO coated cloths exhibited excellent antibacterial activity which makes these highly useful for different medicinal applications such as the dressing of open wounds to avoid microbial infection. Most of the previously published reports deal with the use of GO coated

fabrics as antibacterial bandage materials whereas this study shows that akin to GO, RGO coated cloth can also be utilized as an antibacterial agent. The current study also highlights the effect of the microstructure of the RGO coated cloth upon its wetting properties and antibacterial activity.

2 Experimental

2.1. Materials

Graphite LR was procured from Acros organics. Potassium permanganate (KMnO_4) LR, sulfuric acid (H_2SO_4) LR, hydrogen chloride (HCl) LR and hydrogen peroxide (H_2O_2) LR were purchased from Sigma Aldrich. Both types of cloths; cloth-A (dense structure) and cloth-B (sparse structure), were purchased from a local market. For making solutions and washing de-ionized water was utilized.

2.2. Methods

Graphene oxide was prepared using our previously reported modified Hummer's method.²⁹ In short, 1 g of graphite and 23 ml of concentrated H_2SO_4 were mixed in a conical flask. The as prepared reaction mixture was transferred into an ice bath and about 3 g of KMnO_4 was slowly added to it and stirred for 30 minutes, thereafter the reaction mixture was transferred onto a hot plate with a preset temperature of 35 °C and heated for 1 hour. After heating, ~46 ml de-ionized water was added to the reaction mixture and it was placed in a boiling water bath and further heated for 30 minutes. 10 ml of 30% H_2O_2 was added to the reaction mixture after the completion of heating and the reaction mixture was further diluted by adding 140 ml of de-ionized water. Brown colour graphene oxide was obtained through centrifugation and washed repeatedly with 10% HCl followed by de-ionized water and ethanol.

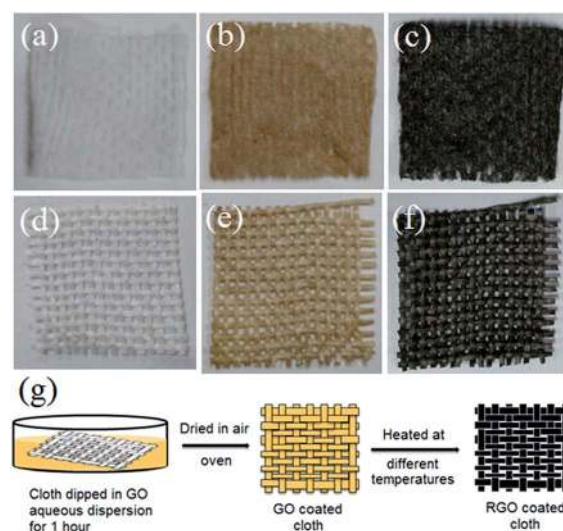


Fig. 1 Real pictures of (a) pristine cloth-A, (b) GO coated cloth-A, (c) RGO coated cloth-A, (d) pristine cloth-B, (e) GO coated cloth-B, (f) RGO coated cloth-B and (g) schematic showing preparation of RGO coated cloth.

Both cloth samples (Fig. 1a and d) were cleaned by sonication in water for 15 minutes. After washing the cloths were dried in air in an oven. The dried cloths were immersed in GO solution (1 mg ml^{-1}) for 1 hour after which the GO solution soaked wet cloths were dried in air in an oven at 70°C . To make cloths coated with GO 20 times, the whole procedure was repeated 20 times with the same cloth sample. The as obtained light brown colour cloths (Fig. 1b and e) were heated in air in an oven at different temperatures ($80, 120, 160$ and 200°C) for 1 hour. Heating of the GO coated cloths at 160 and 200°C changed the colour of the cloths from brown to black (Fig. 1c and f) while samples heated at 80 and 120°C remained brown in colour.

2.3. Characterization details

FTIR measurements of the coated and uncoated cloth samples, were carried out using ATR FTIR spectroscopy (Thermo Scientific Nicolet™ iSTM5 FTIR) with a diamond ATR accessory. Spectra were collected in transmission mode from 4000 to 550 cm^{-1} . The morphology and microstructure of the coated and uncoated cloths were studied using FESEM (Zeiss Sigma 300 VP-FESEM with EDX & EBSD). Contact angle measurements were carried out using a contact angle analyzer DSA-100, the volume of the water droplet used was $10 \mu\text{l}$. The change in the C : O atomic ratio upon heating GO at 200° was investigated using an X-ray photoelectron microscopy (XPS) imaging spectrometer (Kratos AXIS Ultra).

2.4. Antimicrobial test

E. coli MG1665 has been used in the reported experiments. Cells were grown in Luria–Bertani (LB) broth (Hi-Media, Mumbai). *E. coli* MG1665 were grown overnight in LB at 37°C . Cells from the overnight culture were centrifuged at 6000 rpm for 10 minutes and washed three times with sterile isotonic saline. Cells with an OD_{600} of 0.1 were then re-suspended in saline and used for further experiments. Four swatches of both cloth-A and B samples having dimensions of $1 \text{ cm} \times 1 \text{ cm}$ were used in the experiments. To determine the antimicrobial activity of the cloths both RGO coated and uncoated cloth-A and B were dipped in the cell samples and kept at 37°C for 24 h at 200 rpm . Uncoated cloth-A and B samples were used as a control. Briefly, after every 8 h a series of 10 fold serial dilutions were made and $100 \mu\text{l}$ was plated onto a LB agar plate. Subsequently cultures of *E. coli* MG1665 treated with both RGO coated cloth samples were serially diluted and spotted on the LB agar plate. The plates were incubated at 37°C and photographed.

The antimicrobial activity of both RGO coated cloth samples was expressed in terms of percentage loss of bacterial cell viability L (%) which was calculated using following equation:

$$L(\%) = \frac{A - B}{A} \times 100$$

where, A and B are the number of colonies present for the uncoated and coated cloth samples, respectively.

3 Results and discussion

Out of several available methods for the graphene preparation, chemical or thermal reduction of GO are some of the most frequently practised methods because of the simplicity and cost effectiveness of these approaches. However in the case of the chemical reduction of GO, the most commonly used chemical reducing agents such as hydrazine and sodium borohydride (NaBH_4) are highly toxic and not environmentally friendly. Recently, these hazardous chemicals have been replaced with a few environmentally benign reducing agents^{29–31} however most of these are comparatively less effective and can't achieve the percentage reduction which can be achieved using NaBH_4 and hydrazine. In a few cases green reducing agents required prolonged reaction time in order to achieve satisfactory reduction.²⁹ The thermal reduction of GO is an attractive alternative which is quick and can produce RGO with a higher C : O ratio. Unlike the chemical synthesis of RGO, thermal reduction mediated synthesis doesn't require any post treatment, such as washing in order to remove chemical impurities from the RGO sample, which gives an edge to the thermal reduction mediated synthesis over chemical reduction. Apart from this, thermal reduction is also suitable for the *in situ* reduction of GO on any substrates which are not inert to the abovementioned chemical reducing agents. In the literature a plethora of reports are available mentioning the heating of freestanding or coated GO at various temperatures in order to obtain RGO.^{32–35} Acik *et al.*³² carried out a detailed investigation using a FTIR technique in order to probe the heating based reduction of GO to RGO and it was observed that the removal of hydroxyl groups starts at 75°C while decomposition of epoxides and carboxyls starts at 175°C . It has been previously reported that the thermal reduction of GO to RGO follows a free radical mechanism which involves the reaction of hydroxyl and hydronium radicals, generated from the trapped water molecules, with the oxygen containing functional groups of GO.³²

The pristine cloths are white (Fig. 1a and d) and coating with GO changes their appearance from white to brown (Fig. 1b and e). Heat treatment of the GO coated cloth samples reduced GO to RGO which also changed the colour of GO coated cloth samples from brown to black (Fig. 1c and f). The pristine cloth samples readily absorb water while the RGO coated cloth samples float on it. Water droplets placed on the RGO coated cloth-A sample appeared to be spherical in shape (Fig. 2a and b) suggesting the strong hydrophobic nature of the sample, on the other hand for the RGO coated cloth-B the contact area of the

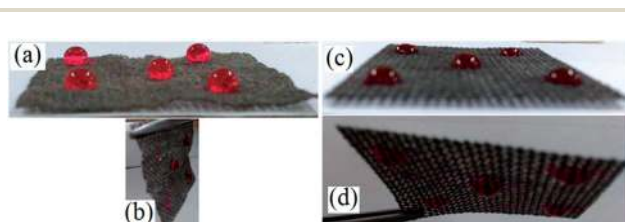


Fig. 2 Real pictures of water droplets on (a, b) RGO coated cloth-A and (c, d) RGO coated cloth-B.

water droplet with the surface is high (Fig. 2c and d) suggesting comparatively lower hydrophobicity.

The pristine cloths are hydrophilic in nature however a coating of RGO makes these materials hydrophobic; the fibrous structure of cloth surface endows these materials with roughness which further improves the water repelling ability of the RGO coated cloths. It is well reported that the surface roughness plays a crucial role in deciding the wetting properties of materials. For instance the surface of rose petals is composed of a periodic array of micropapillae which also has several nanostructures on it. The presence of these hierarchical nano- and microstructures impart a roughness to the surface which makes it superhydrophobic but at the same time these structures also have adhesion forces, therefore in spite of being superhydrophobic in nature, a drop on surface of rose petals doesn't roll off even on flipping it upside down. The RGO coated cloth samples also exhibited a "petal effect" and water droplets placed on the cloths didn't fall off on turning it upside down (Fig. 2b and d). Similar to a rose petal, the surface of the cloth samples also consists of fibrous microstructures which are clearly visible in the FESEM images (Fig. 3); these microstructures not only improve the hydrophobicity but also enable an adhesion force to the cloth surface when it comes in contact with water.

FESEM images of the pristine and RGO coated cloth samples are shown in Fig. 3. It can be easily noticed that both cloths are composed of micron-sized fibres however in case of cloth-B, the fibres are arranged in a more systematic manner (Fig. 3e and f) compared to cloth-A where the fibres are aggregated in a random fashion (Fig. 3a and b). Both cloth samples exhibit

large pores having micrometer size. The coating of RGO on the cloth samples maintained the microstructure of the fibres and didn't cause any significant change in the thickness of fibres suggesting a very thin coating of RGO on them. Moreover the RGO coated cloths retained their air-breathing properties since RGO didn't fill the pores, which is crucial for wound dressing applications.²⁶ The coating of RGO also improved the contrast of the fibres of both cloth samples. In the high magnification images of the RGO coated cloth samples (Fig. 3d and h), wavy and wrinkled graphene sheets elongating from the cloth surface are clearly visible, confirming the coating of graphene on the cloths.

The FTIR spectra of the pristine cloths (Fig. 4a and b) exhibit major bands at 1714, 1241, 1089, 1071 and 721 cm^{-1} which correspond to C=O stretching, OH in plane bending, asymmetric in plane ring stretching and CH_2 rocking, respectively.^{36–38} A broad band in the region 3000–3500 cm^{-1} was also observed which can be assigned to the O–H stretching vibrations of the physically adsorbed water. The presence of different oxygen containing moieties in the pristine cloth samples has also been confirmed by the XPS analysis (Fig. S1†). The presence of these oxygen containing functional groups makes the cloths hydrophilic in nature. In the case of the RGO coated cloth-A this broad band in the region 3000–3500 cm^{-1} completely disappeared and a slight decrease in the percentage transmittance around 4000 cm^{-1} has been observed (Fig. 4a). The FTIR spectrum of the pristine cloth-A exhibited a band at 2918 cm^{-1} corresponding to $-\text{CH}_2$ vibrations, and in the case of the RGO coated cloth-A, the intensity of this band reduced significantly suggesting that the $-\text{CH}_2$ groups facilitate the adsorption of GO on to the cloth. In order to highlight the change in the FTIR spectrum of cloth due to the RGO coating, the spectrum of the RGO coated cloth prepared by coating the cloth 20 times with

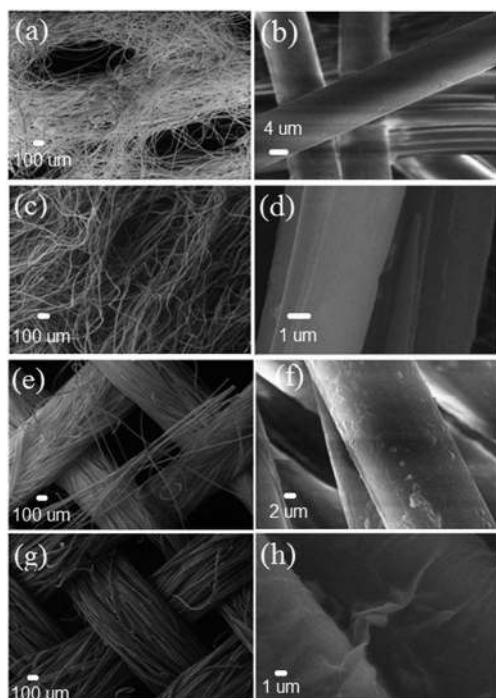


Fig. 3 FESEM images of (a, b) pristine cloth-A, (c, d) RGO coated cloth-A, (e, f) pristine cloth-B and (g, h) RGO coated cloth-B.

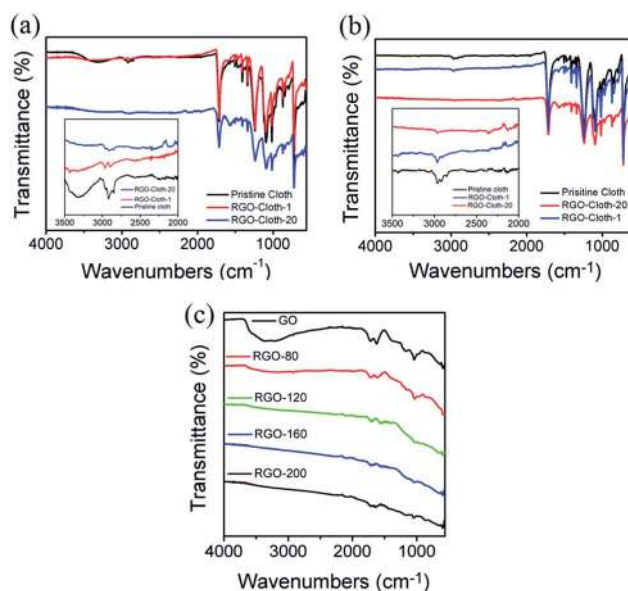


Fig. 4 FTIR spectra of (a) pristine and RGO coated cloth-A, (b) pristine and RGO coated cloth-B and (c) comparison of GO with RGO samples prepared by heating GO at different temperatures.

RGO was also recorded. In this case a significant decrease in the intensity of the band corresponding to $-\text{CH}_2$ has been observed further confirming the fact that the coated GO interacts with the CH_2 groups of the cloth. A substantial decrease in the percentage transmittance in the case of the 20 times coated cloth-A sample has also been observed. Similar to the RGO coated cloth-A, a decrease in the intensity of band at 2918 cm^{-1} has been observed in the case of the RGO coated cloth-B also and this band almost disappeared in the case of the 20 times coated RGO coated cloth-B sample; a concomitant reduction in the percentage transmittance was also observed (Fig. 4b). In order to probe the change in the chemical structure of GO upon heating, the FTIR spectrum of the RGO sample, prepared by heating GO at $200\text{ }^\circ\text{C}$, was compared with the spectrum of GO which is shown in Fig. 4c. The FTIR spectrum of GO is rich in bands corresponding to various oxygen containing functional groups such as bands at 1718 and 1041 cm^{-1} , bands which can be assigned to the $\text{C}=\text{O}$ and $\text{C}-\text{O}$ stretching vibrations, respectively.³⁹ A broad band centred at 3313 cm^{-1} is also present which corresponds to $\text{O}-\text{H}$ stretching vibrations. Another prominent band at 1619 cm^{-1} can be assigned to the $\text{C}=\text{C}$ stretching of un-oxidized sp^2 bonds.⁴⁰ Heat treatment of GO at $200\text{ }^\circ\text{C}$ results in a significant decrease in the intensity of the bands which have been assigned to the oxygen containing functional groups, indicating the reduction of GO to RGO. However the presence of lower intensity peaks suggests that the GO has not been completely reduced and still some oxygen is present.

In order to probe the change in the chemical composition of GO after heating, the XPS spectrum of GO was compared with the RGO sample prepared by heating GO at $200\text{ }^\circ\text{C}$ (Fig. 5). The XPS survey scans for both GO and RGO- $200\text{ }^\circ\text{C}$ are shown in Fig. 5a. The C : O atomic ratios calculated from the XPS spectra of the GO and RGO samples were found to be 2.65 and 5.46, respectively. Heating of the GO at $200\text{ }^\circ\text{C}$ produced RGO with a C : O ratio more than twice that of the GO indicating the loss

of oxygen containing functional groups during the heating.^{41,42} The origin of the hydrophobicity in RGO coated cloth samples can be attributed to the loss of oxygen containing functional groups present in GO, during heating. The reduction of GO to RGO increases the carbon content and lowers the surface energy of the RGO coated cloth which make it hydrophobic.^{43,44}

The change in the hydrophobicity of the GO coated cloth samples with temperature was monitored by recording the contact angle (Fig. 6). Both types of pristine cloth samples were found to be hydrophilic in nature and readily absorbed water. Similarly the GO coated cloth samples heated at $80\text{ }^\circ\text{C}$ also exhibited a hydrophilic nature and within 1 minute both samples absorbed water droplets. Heating of the GO coated cloth-A at $120\text{ }^\circ\text{C}$ resulted in a hydrophobic cloth and the contact angle was found to be 139° however the RGO-cloth-B-120 sample was still found to be hydrophilic in nature. Heat treatment of the GO coated cloth-A and B samples at $160\text{ }^\circ\text{C}$ produced hydrophobic cloths with contact angles ~ 140 and 130° , respectively. A further increase in the temperature up to $200\text{ }^\circ\text{C}$ caused a slight change in the hydrophobicity and the contact angles were found to be 141 and 130° for the RGO-cloth-A-200 and RGO-cloth-B-200 samples, respectively. In order to investigate the durability of the hydrophobic RGO coated cloth samples prepared at 160 and $200\text{ }^\circ\text{C}$, a change in the contact angle up to 11 minutes was monitored and no significant change in the contact angle was observed for all four samples, suggesting excellent durability of the RGO coated cloths as hydrophobic surfaces. The RGO coated cloth-A samples prepared at temperatures of 120 , 160 and $200\text{ }^\circ\text{C}$ exhibited almost the same contact angle however the RGO-cloth-A-120 sample was found to be less hydrophobic since on dipping in water it absorbed some water suggesting the presence of a hydrophilic region in the sample. In contrast no water absorption was observed for the RGO coated cloth-A and B samples prepared at 160 and $200\text{ }^\circ\text{C}$.

Cloth is one of the most frequently used materials for cleaning and almost every household and industrial cleaning process involves it. Owing to their good fluid absorption capacity, cloths have been used widely for mopping and therefore in the present report cloths have been selected as substrates for the deposition of RGO and oil/water separation. The RGO coated cloth-A has been used for the selective absorption of oil from an oil/water mixture and on the other hand the RGO coated cloth-B has been utilized for the selective

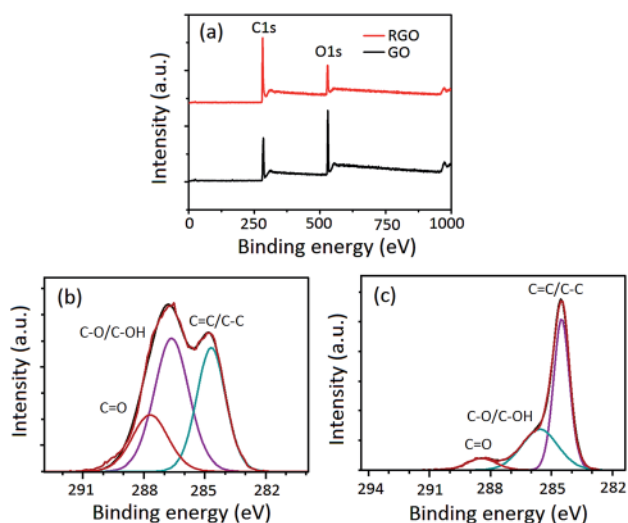


Fig. 5 XPS analysis of the GO and RGO (a) survey scan of GO and RGO, de-convoluted spectrum of (b) GO and (c) RGO.

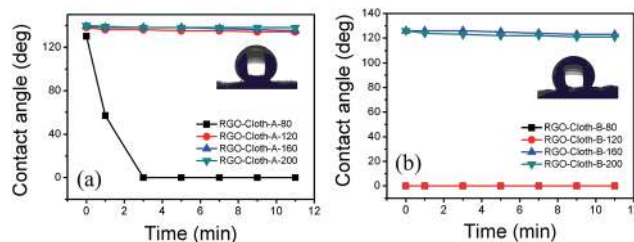


Fig. 6 Change in hydrophobicity with time for the RGO coated cloth samples prepared at different temperatures (a) RGO coated cloth-A and (b) RGO coated cloth-B.

filtration of oil from an oil/water mixture. Cloth-B has a mesh like structure with large pore size, which facilitates the easy flow of oil through it and even in the case of dense oil such as paraffin oil it exhibits minimum resistance to the oil flow, so it has been used as a filtration medium for oil/water separation. On the other hand cloth-A has a dense structure thus it resists the flow of oil through it and has more tendency to absorb oil because of which it has been utilized as an absorbent for the selective absorption of oil from an oil/water mixture.

Fig. 7a shows the selective absorption of the oil from an oil/water mixture by the RGO-cloth-A-200 sample. The oil/water mixture shown in Fig. 7a contains canola oil (red) and a CuSO_4 aqueous solution (blue). Owing to the hydrophobic nature of the RGO coated cloth, it absorbs oil selectively from the oil/water mixture leaving behind the aqueous solution (Fig. 7a). The absorption of oil by the RGO coated cloth was quantified and explained in terms of absorption capacity which was calculated using following formula.

$$\text{Absorption capacity} = (W_a - W_b)/W_b$$

where W_a = weight of cloth with absorbed oil and W_b = weight of the RGO coated cloth.

The absorption capacities of the RGO coated cloth-A for different oils and organic solvents are shown in Fig. 7b. The RGO coated cloth-A was found to be highly efficient as an absorbent and absorbed oil more than 10 times of its weight (Fig. 7b). The absorption capacity depends upon the viscosity, density and surface tension of the oil.^{45–47} Usually absorbents show high absorption capacity for oils with low viscosity but high density and surface tension.⁴⁷ High surface tension and viscosity of oils resist the molecular disruption and diffusion of oil towards the absorbent which leads to a slow absorption rate for oils.⁴⁸ In the present case the absorption capacity of the RGO coated cloth was found to be higher for oils compared to the organic solvents due to the higher density of the oils. In case of organic solvents the absorbed volume can be similar to the viscous oils but because of the low density of the organic solvents, weight gain by the absorbent remains less compared to the oil which is reflected in the lower absorption capacity in the case of organic solvents compared to the viscous oils for the same absorbent.⁴⁸

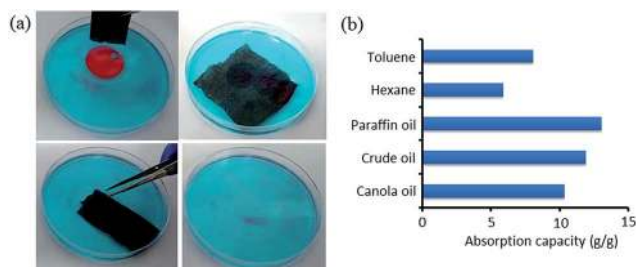


Fig. 7 (a) Removal of oil (red color) from water (blue color) using RGO coated cloth-A and (b) absorption capacity of the RGO coated cloth-A for different oils.

The RGO coated cloth-B was used as a filtration medium for the oil/water separation. Cloth-B exhibits larger pores compared to cloth-A which facilitate the flow of oil through it however the hydrophobic nature of the RGO coated cloth-B doesn't allow the water to pass through which leads to the oil/water separation. Apart from hydrophobicity, the coating of RGO endows mechanical strength to cloth-B also and makes it stiff therefore it doesn't bend under the flow of the oil/water mixture. Fig. 8a–c shows the separation of the oil/water mixture using the RGO-cloth-B-200 sample. An oil/water mixture containing canola oil (red) and aqueous CuSO_4 solution (blue) was passed through the RGO coated cloth-B. The cloth allowed oil to pass through while water remained on the surface of the cloth (Fig. 8b), oil was collected in the beaker and water was removed from the top of the filter (Fig. 8c).

The antimicrobial activity of graphene and its derivatives has been widely investigated, however in most cases graphene derivatives in suspension form have been utilized and studies have been focused more on GO compared to RGO. Very few studies have been reported on the antimicrobial activity of immobilized graphene and its derivatives. In these reports mostly the antimicrobial activity of GO coated substrates has been discussed. GO exhibits a high affinity towards water therefore it can be leached out from the substrate into a culture medium so identifying the antimicrobial activity due to the detached GO and surface attached GO can be difficult. RGO exhibits a low affinity towards water so the chances of its leaching are less compared to GO. Therefore in the present study RGO coated cloth substrates have been used as antibacterial surfaces. The antibacterial activities of both RGO coated cloth samples (RGO-cloth-A-200 and RGO-cloth-B-200) against a Gram negative bacterium *E. coli* (MG1665) have been investigated and are shown in Fig. 9. The results revealed that the RGO coated cloth-A sample has a higher antibacterial efficacy in comparison to the RGO coated cloth-B sample (Fig. 9b and d). In order to examine time dependent antibacterial activity, the RGO coated cloth samples were incubated with *E. coli* (MG1665) and the percentage reduction in bacterial cell viability was recorded after 8, 16 and 24 h. As shown in Fig. 9e, an increase in the exposure time also enhanced the loss of percentage viability of bacterial cells for both RGO coated cloth samples and it was always higher for the RGO coated cloth-A compared to cloth-B at all exposure time intervals. Moreover, in the case of the RGO

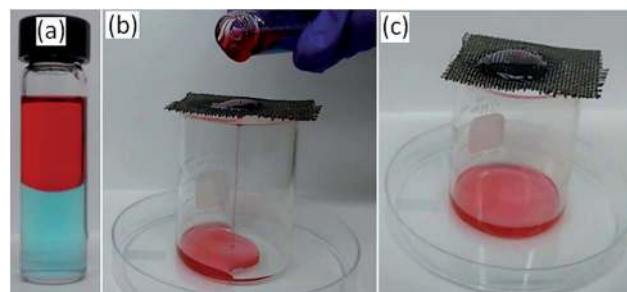


Fig. 8 (a–c) Separation of an oil/water mixture using RGO coated cloth-B as a filter.

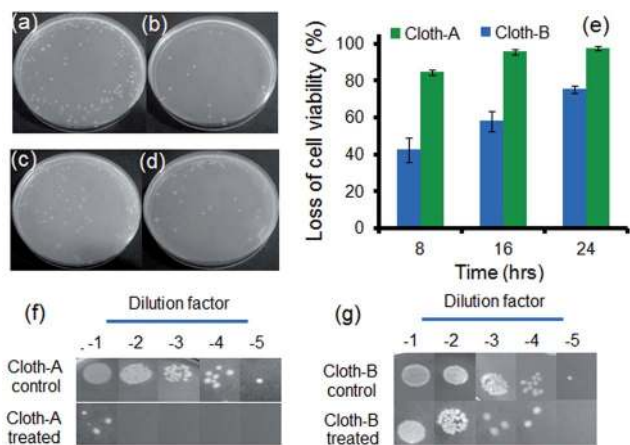


Fig. 9 Antibacterial activity of RGO coated cloth-A and B against *E. coli*. Typical photographs of LB agar plates showing the effects of (a) uncoated cloth-A, (b) RGO coated cloth-A, (c) uncoated cloth-B and (d) RGO coated cloth-B; (e) graphical representation of the loss of percentage viability of the bacterial cells treated with RGO coated sparse and dense fabrics after 8, 16 and 24 h of contact; cultures of strain MG1665 (WT) serially diluted and spotted on LB agar plate (f) after treatment with coated cloth-A and (g) after treatment with coated cloth-B.

coated cloth-A the loss of percentage viability reached almost 98% while for cloth-B it was found to be around 75% which indicates that the RGO coated cloth-A has a higher deleterious effect on the viability of bacterial cells. The results suggest that the RGO coated cloth-A is better antibacterial material than cloth-B, the reason for the lower antibacterial activity of the RGO coated cloth-B might be its bigger pore size and the lower density of the fabric. The pore size of cloth-B is higher than cloth-A and its structure is also comparatively less dense so for similar size of cloths, the amount of deposited RGO per centimeter is less for cloth-B compared to cloth-A. Based on several experimental studies, mainly three mechanisms including the piercing of bacterial cell membranes by the sharp edges of graphene, oxidative stress mediated reactive oxygen species (ROS) generation and the wrapping of bacteria by the graphene sheets, have been accepted for explaining the antimicrobial activity of graphene derivatives.^{6,23} In the present case we believe that the first mechanism, disruption of the cell membrane of the bacteria by the sharp edges of the deposited graphene could be the prime mode of action for the RGO coated cloth samples. As shown in the FESEM images, the coated graphene sheets are elongating from the surface making it rough which might damage the cell membrane. Zhao *et al.* also suggested that the same mechanism was responsible for the antibacterial activity of GO coated cotton fabrics.²⁶ Oxidative stress mediated reactive oxygen species (ROS) generation, might also contribute to the antibacterial activity of the cloths. Besides being antibacterial, these RGO coated cloths are also hydrophobic in nature and thus can also protect the surface from water which gives these an additional advantage over ordinary bandages for wound dressing applications. Usually ordinary bandages can easily absorb water so after dressing a wound it needs to be protected

from water since its exposure may cause infection in the wound, while owing to the hydrophobic nature this additional precaution is not required in the case of the RGO coated cloths.

4 Conclusions

The reduction of GO to RGO coated cloths was carried out by thermal treatment, an increase in the contact angle was observed on raising the heating temperature from 80 to 200 °C suggesting an increase in the hydrophobicity of the cloths on increasing temperature. The as prepared RGO coated cloths were explored as an absorbent and a filter for oil/water separation. The cloth with a dense structure was used as an absorbent and the cloth with large pores and a mesh kind of structure was used as a filter. The RGO coated cloths were found to be highly efficient for oil/water separation. The RGO coated cloths have also shown excellent antibacterial activity against *E. coli*, the cloth with a dense structure was found to be a better antibacterial material compared to the other cloth with a sparse structure. The RGO coated cloths appear to be promising for medicinal applications such as for antibacterial agents and the dressing of open wounds.

Acknowledgements

Ravi Kant Upadhyay is indebted to Shiv Nadar University (SNU) for providing a scholarship. He is also thankful to IC-IMPACTS for supporting his visit to the University of Alberta. The authors would like to thank Prof. S. C. Ray, University of South Africa, for his help with the XPS analysis.

References

- 1 P. Avouris and C. Dimitrakopoulos, *Mater. Today*, 2012, **15**, 86–97.
- 2 X. Zhang, B. R. S. Rajaraman, H. Liu and S. Ramakrishna, *RSC Adv.*, 2014, **4**, 28987–29011.
- 3 S. Bai and X. Shen, *RSC Adv.*, 2012, **2**, 64–98.
- 4 M. Yusuf, F. M. Elfgi, S. A. Zaidi, E. C. Abdullah and M. A. Khan, *RSC Adv.*, 2015, **5**, 50392–50420.
- 5 C. Wang, X. Wang, T. Lu, F. Liu, B. Guo, N. Wen, Y. Du, H. Lin, J. Tang and L. Zhang, *RSC Adv.*, 2016, **6**, 22461–22468.
- 6 R. K. Upadhyay, N. Sooin and S. S. Roy, *RSC Adv.*, 2014, **4**, 3823–3851.
- 7 S. M. Mudge, *Spill Sci. Technol. Bull.*, 1995, **2**, 187–191.
- 8 T. Caramés-Alfaya, M. P. Gómez-Carracedo and J. M. Andrade, *Microchem. J.*, 2013, **110**, 379–385.
- 9 M. A. Cohen, in *Encyclopedia of Energy, Natural Resource, and Environmental Economics*, Elsevier, Waltham, 2013, pp. 121–126.
- 10 C.-L. Yang, *Sep. Purif. Technol.*, 2007, **54**, 388–395.
- 11 J. S. Eow and M. Ghadiri, *Chem. Eng. J.*, 2002, **85**, 357–368.
- 12 A. Al-Shamrani, A. James and H. Xiao, *Water Res.*, 2002, **36**, 1503–1512.
- 13 A. Zouboulis and A. Avranas, *Colloids Surf., A*, 2000, **172**, 153–161.

- 14 H. Yoon, S.-H. Na, J.-Y. Choi, S. S. Latthe, M. T. Swihart, S. S. Al-Deyab and S. S. Yoon, *Langmuir*, 2014, **30**, 11761–11769.
- 15 D. D. Nguyen, N.-H. Tai, S.-B. Lee and W.-S. Kuo, *Energy Environ. Sci.*, 2012, **5**, 7908–7912.
- 16 E.-C. Cho, Y.-S. Hsiao, K.-C. Lee and J.-H. Huang, *RSC Adv.*, 2015, **5**, 53741–53748.
- 17 B. Ge, Z. Zhang, X. Zhu, X. Men, X. Zhou and Q. Xue, *Compos. Sci. Technol.*, 2014, **102**, 100–105.
- 18 H. Qin, T. Gong, Y. Cho, C. Shin, C. Lee and T. Kim, *RSC Adv.*, 2015, **5**, 57860–57864.
- 19 Y. Dong, J. Li, L. Shi, X. Wang, Z. Guo and W. Liu, *Chem. Commun.*, 2014, **50**, 5586–5589.
- 20 J. Shen, Y. Zhu, X. Yang and C. Li, *Chem. Commun.*, 2012, **48**, 3686–3699.
- 21 L. Yang, F. Wang, H. Han, L. Yang, G. Zhang and Z. Fan, *Colloids Surf., B*, 2015, **129**, 21–29.
- 22 F. Perreault, A. F. de Faria, S. Nejati and M. Elimelech, *ACS Nano*, 2015, **9**, 7226–7236.
- 23 X. Zou, L. Zhang, Z. Wang and Y. Luo, *J. Am. Chem. Soc.*, 2016, **138**, 2064–2077.
- 24 J. Liu, L. Cui and D. Losic, *Acta Biomater.*, 2013, **9**, 9243–9257.
- 25 J. Chen, H. Peng, X. Wang, F. Shao, Z. Yuan and H. Han, *Nanoscale*, 2014, **6**, 1879–1889.
- 26 J. Zhao, B. Deng, M. Lv, J. Li, Y. Zhang, H. Jiang, C. Peng, J. Li, J. Shi, Q. Huang and C. Fan, *Adv. Healthcare Mater.*, 2013, **2**, 1259–1266.
- 27 L.-L. Xu, M.-X. Guo, S. Liu and S.-W. Bian, *RSC Adv.*, 2015, **5**, 25244–25249.
- 28 L. Liu, Y. Yu, C. Yan, K. Li and Z. Zheng, *Nat. Commun.*, 2015, **6**, 7260.
- 29 R. K. Upadhyay, N. Soin, G. Bhattacharya, S. Saha, A. Barman and S. S. Roy, *Mater. Lett.*, 2015, **160**, 355–358.
- 30 M. T. H. Aunkor, I. M. Mahbubul, R. Saidur and H. S. C. Metselaar, *RSC Adv.*, 2016, **6**, 27807–27828.
- 31 Y. Feng, N. Feng and G. Du, *RSC Adv.*, 2013, **3**, 21466–21474.
- 32 M. Acik, G. Lee, C. Mattevi, A. Pirkle, R. M. Wallace, M. Chhowalla, K. Cho and Y. Chabal, *J. Phys. Chem. C*, 2011, **115**, 19761–19781.
- 33 K. S. Andrikopoulos, G. Bounos, D. Tasis, L. Sygellou, V. Drakopoulos and G. A. Voyiatzis, *Adv. Mater. Interfaces*, 2014, **1**, 1400250, DOI: 10.1002/admi.201400250.
- 34 H. Xingyi, Z. Chunyi, J. Pingkai, G. Dmitri, B. Yoshio and T. Toshikatsu, *Nanotechnology*, 2012, **23**, 455705.
- 35 H. Chen, Z. Song, X. Zhao, X. Li and H. Lin, *RSC Adv.*, 2013, **3**, 2971–2978.
- 36 C. Chung, M. Lee and E. K. Choe, *Carbohydr. Polym.*, 2004, **58**, 417–420.
- 37 P. Zhang, S. Tian, H. Fan, Y. Chen and J. Yan, *Prog. Org. Coat.*, 2015, **89**, 170–180.
- 38 W. Xue, H. He, J. Zhu and P. Yuan, *Spectrochim. Acta, Part A*, 2007, **67**, 1030–1036.
- 39 J. Molina, J. Fernández, J. C. Inés, A. I. del Río, J. Bonastre and F. Cases, *Electrochim. Acta*, 2013, **93**, 44–52.
- 40 E.-Y. Choi, T. H. Han, J. Hong, J. E. Kim, S. H. Lee, H. W. Kim and S. O. Kim, *J. Mater. Chem.*, 2010, **20**, 1907–1912.
- 41 O. C. Compton, B. Jain, D. A. Dikin, A. Abouimrane, K. Amine and S. T. Nguyen, *ACS Nano*, 2011, **5**, 4380–4391.
- 42 A. Ganguly, S. Sharma, P. Papakonstantinou and J. Hamilton, *J. Phys. Chem. C*, 2011, **115**, 17009–17019.
- 43 S. Wang, Y. Zhang, N. Abidi and L. Cabrales, *Langmuir*, 2009, **25**, 11078–11081.
- 44 J.-S. Lee, J.-C. Yoon and J.-H. Jang, *J. Mater. Chem. A*, 2013, **1**, 7312–7315.
- 45 Y. Yang, H. Yi and C. Wang, *ACS Sustainable Chem. Eng.*, 2015, **3**, 3012–3018.
- 46 A. Turco, C. Malitesta, G. Barillaro, A. Greco, A. Maffezzoli and E. Mazzotta, *J. Mater. Chem. A*, 2015, **3**, 17685–17696.
- 47 Y. Gao, Y. S. Zhou, W. Xiong, M. Wang, L. Fan, H. Rabiee-Golgir, L. Jiang, W. Hou, X. Huang, L. Jiang, J.-F. Silvain and Y. F. Lu, *ACS Appl. Mater. Interfaces*, 2014, **6**, 5924–5929.
- 48 D. N. H. Tran, S. Kabiri, T. R. Sim and D. Losic, *Environ. Sci.: Water Res. Technol.*, 2015, **1**, 298–305.