International Journal of Chemical, Materials and Biomolecular Sciences
ISSN: 2415-6620
Vol:14, No:5, 2020

Graphene/ZnO/Polymer Nanocomposite Thin Film for Separation of Oil-Water Mixture

Suboohi Shervani, Jingjing Ling, Jiabin Liu, Tahir Husain

***Abstract*—**Offshore oil-spill has become the most emerging problem in the world. In the current paper, a graphene/ZnO/polymer nanocomposite thin film is coated on stainless steel mesh via layer by layer deposition method. The structural characterization of materials is determined by Scanning Electron Microscopy (SEM) and X-ray diffraction (XRD). The total petroleum hydrocarbons (TPHs) and separation efficiency have been measured via gas chromatography – flame ionization detector (GC-FID). TPHs are reduced to 2 ppm and separation efficiency of the nanocomposite coated mesh is reached ≥ 99% for the final sample. The nanocomposite coated mesh acts as a promising candidate for the separation of oil- water mixture.

***Keywords*—**Oil-spill, graphene, oil-water separation, nanocomposite.

I. Introduction

THE offshore oil spillover has the cataclysmic effect on our marine and ecological community. Basically, oil spill is liberation of liquid petroleum into the ecosystem [1]. Oil spill normally stands for the marine oil spills, where oil spread into the ocean or coastal areas. Oil spills may be due to drilling rigs, oil from tankers, wells, gasoline, diesel or heavier fuels used by large ships such as bunker fuel. The release of oil harms the sea animals inadequately. It goes inside the plumage of birds and the skin of the sea animals that reduces its protection from the surroundings and makes them more unsafe in harsh temperature conditions and reduces its capacity to float in the water.

The cleaning, recovery, decanting etc. are the important issues occurring in the oil-spill and depend on the type of oil spilled, temperature of the water (affecting evaporation and biodegradation), and also on the nature of shorelines and beaches involved. The separation of oil/water mixture became the most disconcert issue due to the occurrence of several oil-spills such as deep water horizon [2], gulf war oil spill [3], Kuwait oil spill [4] etc.

In recent years, several techniques have been used to separate oil-water mixture such as gravity separation, centrifugation, bioinspired method etc. but they restrain in the application due to poor efficiency and inclusion of chemical contaminants [5]. Apart from them, membrane filtration technique and reverse osmosis process are used for deep purification of water and separation of stable emulsions. As they are immoderate and exhibit membrane fouling complications, these processes restrict their further implementation [6]. Different classes of nanomaterials are being used to overcome this major issue. Due to the high surface area and porosity, these nanomaterials have attracted the enormous attention [7].

Many materials have been used to separate the oil-water mixture according to their wettability properties [8], [9]. Li et al. [8] fabricated the super-hydrophobic carbon soot and silica coated meshes that act as strong repellents for the corrosive liquid and demonstrated the gravity driven separation of oil-water mixtures. The separation efficiency of coated mesh is achieved more than 99.0% while the as-prepared coated mesh showed separation efficiency more than 98.5% [8]. Similarly, Li et al. [10] prepared the ZnO/polyurethane nanocomposite on stainless steel mesh by spray technology. Nanocomposite shows the excellent efficiency i.e. 99.0% oil-water separation. On the other hand, Zhang et al. [11] have fabricated the self-cleaning mesh with sodium silicate and TiO_2 nanocomposite by layer-by-layer deposition method. The coated mesh showed the underwater superoleophobicity with different hydrocarbons [11]. Liu et al. [12] have fabricated the functionalized mesh that shows the underwater oleophobicity. It was synthesized via layer-by-layer deposition of grapheme and silica on stainless steel mesh. The mesh shows excellent stability and reusable separation. The separation efficiency reached more than 99% [12]. Similarly, Wen et al. [13] have prepared a simple way to fabricate zeolite-coated mesh films (ZCMFs) with superhydrophilicity and underwater superoleophobicity [10]. Song et al. [14] synthesized the superhydrophilic cement coated mesh by dipping porous Cu meshes in the cement paste. The separation efficiency reached above 94% and the mesh was tested for 30 cycles. They also showed that the durability of the film remains for 120 hour under water, which makes it cost effective and eco-friendly [14]. Likewise, Liu et al. [15] showed the synthesis of fluorosilane/grapheme oxide (GO) based mesh for the separation of oil-water mixture. They used the Femtosecond laser processing for the fabrication of different laser-induced periodic surface structures (LIPSS) on the mesh [15]. Similarly, Xiong et al. [16] have fabricated the film on different surfaces including stainless steel, glass slide, cotton cloth, nylon membrane by Thiol−acrylate-based hybrid. These in-air superoleophobic/superhydrophilic films deposited onto porous supports showed excellent separation of oil−water emulsions with separation efficiencies of 99.9% with 699 $L \cdot m^{-2}\ h^{-1}$ permeate flux when the superhydrophilic/ superoleophobic films are deposited on 0.45 μm nylon

Suboohi Shervani is with the Faculty of Engineering & Applied Science Memorial University of Newfoundland St. John's, NF, Canada A1B 3X5 (e-mail: sshervani@ mun.ca).

Jingjing Ling, Jiabin Liu, and Tahir Husain are with the Faculty of Engineering & Applied Science Memorial University of Newfoundland St. John's, NF, Canada A1B 3X5

International Journal of Chemical, Materials and Biomolecular Sciences
ISSN: 2415-6620
Vol:14, No:5, 2020

membrane [16]. On the other hand, Qu et al. [17] have developed the process to synthesize the material from kaolin nanoparticles. The fabricated material exhibits the oil repellent property in both air and water and shows excellent property in separation of oil-water mixture i.e. shows efficiency more than 92%. The material also removed the dye contaminants dissolved in the oil-water mixture and purified it [17]. Gao et al. [18] have prepared the superhydrophobic/superoleophilic metal organic framework (MOF) by the reaction of activated MOFs and octadecylamine. The material exhibited the surface superhydrophobic nature of water with contact angle (CA) > 150°. The nanomaterials are also depicting the excessive adsorption capacities toward organic solvents and exhibited excellent oil−water separation efficiency (> 99.5%) without the application of external pressure [18].

The current paper aims to enhance the separation efficiency by using the nanocomposite thin film based mesh. Zinc oxide (ZnO)/graphene oxide (GO)/polyvinyl alcohol (PVA) nanocomposite thin film was deposited on stainless steel mesh via layer-by-layer method. This nanocomposite structure is anticipated to play major part in the separation of oil-water mixture.

II. Experimental

Graphite flakes and sulfuric acid (95-98%) were purchased through the Fisher Scientific. Phosphoric acid (85%), zinc acetate, citric acid, ethylene glycol, PVA and hydrogen peroxide (30%) were purchased from Sigma Aldrich. Stainless steel mesh was purchased from Alfa Aesar.

Graphene was prepared by the improved Hummers method [19]. 3 g graphite flakes were added in 9:1 ratio mixture of H_2SO_4 and H_3PO_4. The material was then placed in an ice bath to maintain the temperature below 10 °C. 18 g potassium permanganate ($KMnO_4$) was added slowly into the abovementioned solution. After an hour, 200 ml water was added in this solution and temperature raised to 90 °C for 30 min. Further, H_2O_2 was added dropwise and kept it for 30 min on stirring. After that, 150 ml HCl was added for the cleaning.

ZnO nanoparticles were prepared by simple solvothermal method [20]. ZnO nanoparticles were prepared by adding 10.975 gm zinc acetate to 100 ml distilled water and stirred at 50 °C. After that, citric acid was incorporated in the solution until the pH of solution reached to 1.5. Further to this, 10 ml ethylene glycol was added. This results in the precipitation of ZnO nanoparticles. After cooling the reaction mixture the precipitate was then centrifuged, and dried at 100 °C. The nanomaterial further was calcined at 320 °C.

The nanocomposite thin film was deposited by layer-by-layer deposition method. 1 ml of PVA was deposited on stainless steel mesh. 1 ml of Go was further incorporated above that layer. Consecutively, 1 ml of ZnO was deposited on top of these layers. At the end of the process, 1 ml of PVA was again deposited on this assembly. This procedure was repeated for 3 times. Finally, the nanocomposite coated mesh was dried at 60 °C.

The emulsion was prepared by mixing 7 gm of NaCl, 200 µl of crude oil and 200 ml of water with the help of high-speed homogenizer (8000 rpm).

The nanomaterials were characterized through the SEM, X-ray diffractometer (XRD), and GC-FID.

III. Results and Discussions

Fig. 1 (a) shows the SEM micrograph of GO. The image shows the monolayer graphene with flake like structure. Fig. 1 (b) shows the Raman spectrum of GO nanostructure. It shows that both D and G bands present in the nanomaterial. And appeared as broad peaks between 1200 to 1350 cm^{-1} and 1500 to 1650 cm^{-1} ranges respectively [21], [22]. The D-band is due to disordered structure of graphene. G-band occurs due to the stretching of the C-C bond in graphitic materials. This is most common to arise in sp2 carbon materials.

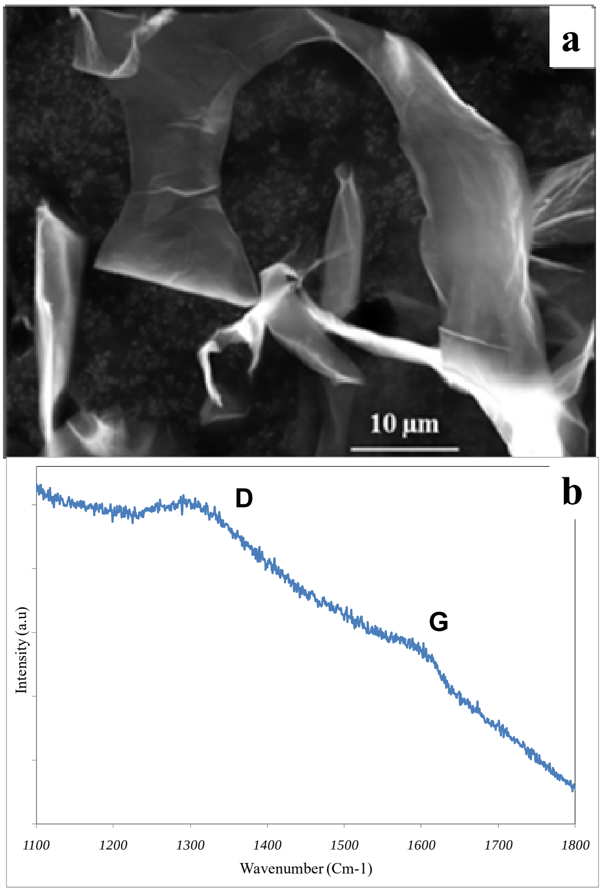

Fig. 1 (a) SEM image of GO, which shows the monolayer grapheme structure, (b) Raman spectrum of GO, showing D and G bands

Fig. 2 (a) shows the XRD pattern of the ZnO nanoparticles. It shows that the polycrystalline wurzite structure with all the peaks exists in the pattern and matches well with the Joint Committee on Powder Diffraction Standards (JCPDS) PDF no 36-1451 [23]. The highest intense peak is observed at angle 36.22° corresponding to the lattice plane (101). Fig. 2 (b) shows the digital image of the nanocomposite based mesh.

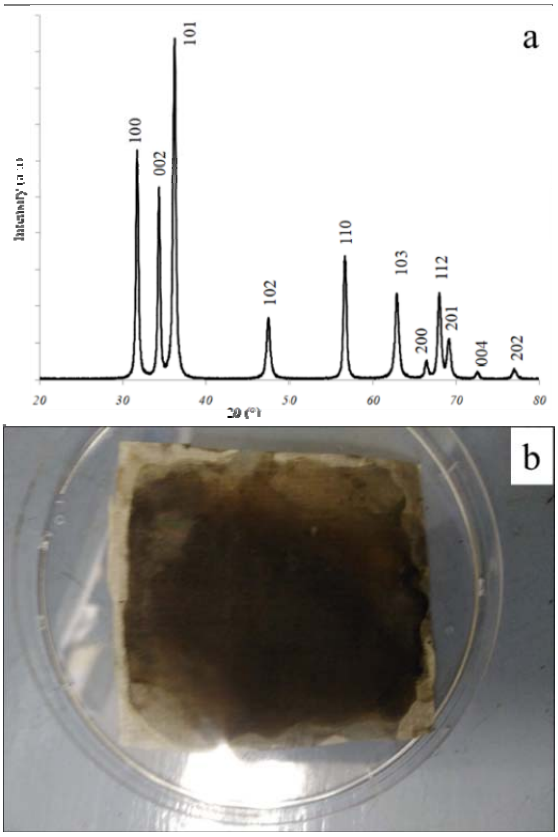

Fig. 2 (a) XRD pattern for the ZnO nanoparticle. This shows the wurzite nature of the ZnO nanoparticles, (b) digital image of nanocomposite coated mesh. This is showing the uniform deposition of the nanocomposite

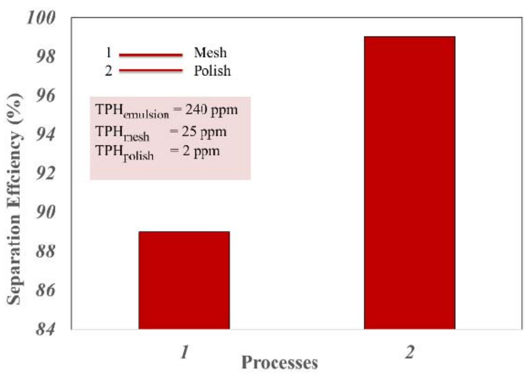

Fig. 3 Separation efficiency of the nanocomposite based mesh for the two processes mesh and polish

Fig. 3 shows the separation efficiency of the nanocomposite based mesh for the two processes i.e. mesh and polish. After passing the emulsion through mesh, the separation efficiency reaches up to 89%. Then, 1 ml GO/ZnO mixture was mixed in the 20 ml as received water from the mesh. It removes the nanosize oil droplets from the water. Go/ZnO mixture removed from the water by filter paper. This process is mentioned as polish and the separation efficiency is achieved up to 99%. The TPHs reduced to 25 ppm and 2 ppm from 240 ppm for the two processes i.e. mesh and polish respectively.

Fig. 4 shows the schematic representation of the mechanism for oil/water separation. Inset shows the digital images of emulsion, water received from the mesh and water received from the polish. It shows that water received from the polish is clearer than other two.

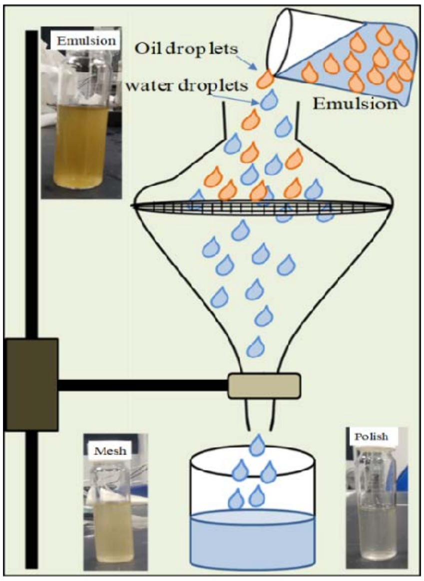

Fig. 4 Schematic depicting the mechanisms for oil/water separation along with the real images of the three stages of oil-water mixture

In summary, the nanocomposite based mesh shows the significant reduction in the TPHs in the final samples for the two processes. Separation efficiencies are also improved considerably for these samples.

IV. Conclusion

ZnO/GO/polymer nanocomposite based mesh is successfully synthesized via layer-by-layer deposition method. The TPH has been reduced to 25 ppm and 2 ppm for mesh and polishing processes respectively. For the two processes i.e. mesh and polish, the separation efficiency reached up to $\geq$ 89% and $\geq$ 99% respectively. Considering the above-mentioned results, the nanocomposite coated mesh acts as promising candidate for the separation of oil-water mixture.

Acknowledgment

The authors would like to acknowledge Department of Fisheries and Oceans Canada for supporting this work. They also acknowledge Dr. Erika Merschrod and Silvana Rodrigues Pereira for their help in Raman Spectroscopy measurements.

References

[1] Carpenter A. "Oil pollution in the north sea: The impact of governance measures on oil pollution over several decades. Hydrobiologia, 845, 109-127, 2019.
[2] C. Safina, A Sea in Flames: The Deepwater Horizon Oil Blowout, US: Broadway paperbacks, Crown publishing group, 2011.

[3] R.Gramling and W. Freudenburg, Blowout in the Gulf: The BP Oil Spill Disaster and the Future of Energy in America. USA: MIT Press, 2011.
[4] T. Husain, Kuwaiti Oil Fires: Regional Environmental Perspectives. US:Pergamon press, Elsevier, 1995.
[5] P. Kajitvichyanukul, Y.-T. Hung and L. Wang, Handbook of Environmental Engineering, 4, 521, 2006.
[6] M. Cheryan and N. Rajagopalan, J. Membr. Sci., 151,13, 1998.
[7] J. Yang, Z. Zhang, X. Xu, X. Zhu, X. Men and X. Zhou. "Superhydrophilic–superoleophobic coatings". Journal of Materials Chemistry,22, 2834–37, 2012.
[8] J. Li, L. Yan, W. Li, J. Li, F. Zha and Z. Lei, "Superhydrophilic underwater superoleophobic ZnO-based coated mesh for highly efficient oil and water separation". Materials Letters, 153, 62–65, 2015.
[9] J. Li et al., "Superhydrophobic meshes that can repel hot water and strong corrosive liquids used for efficient gravity-driven oil/water separation", Nanoscale, vol. 8, pp. 7638-7645, 2016.
[10] S. Li et al., "A review on special wettability textiles: theoretical models, fabrication technologies and multifunctional applications", J. Mater. Chem. A, vol. 5, pp. 31–55, 2017.
[11] L. Zhang et al. "A self-cleaning underwater superoleophobic mesh for oil-water separation", Sci. Rep., vol. 3, pp. 2326, 2013.
[12] J. Liu et al., "Synthesis of graphene oxide–SiO2 coated mesh film and its properties on oil–water separation and antibacterial activity", Water Sci. Technol., vol. 73 no. 5, pp. 1098-103, 2016.
[13] Q. Wen et al., "Zeolite-coated mesh film for efficient oil–water separation". Chem. Sci., vol. 4, pp. 591-595, 2013.
[14] J. Song et al. "Superhydrophilic cement coated mesh: An acid, alkali and organic reagent-free material for oil/water separation", J Nanoscale, vol. 00, pp. 1-3, 2017.
[15] Y. Q. Liu et al. "Laser-structured Janus wire mesh for efficient oil-water separation", Nanoscale, vol. 9, pp. 17933-17938, 2017.
[16] L. Xiong, W. Guo, B. M. Alameda, R. K. Sloan, W. D. Walker and D. L. Patton. Rational Design of Superhydrophilic/Superoleophobic Surfaces for Oil−Water Separation via Thiol−Acrylate Photopolymerization. ACS Omega, 3,10278−10285,2018.
[17] Qu M, Ma L., Zhou Y., Zhao Y,, Wang J., Zhang Y., Zhu X., Liu X. and He J., "Durable and Recyclable Superhydrophilic− Superoleophobic Materials for Efficient Oil/Water Separation and Water-Soluble Dyes Removal". ACS Applied.Nano Materials, 1, 5197– 5209,2018
[18] Gao M. L., Zhao S. Y., Chen Z. Y., Liu L. and Han Z. B., "Superhydrophobic/Superoleophilic MOF Composites for Oil−Water Separation". Inorganic Chemistry,.58,2261–2264,2019.
[19] Chen, J. et al. "An improved Hummers method for eco-friendly synthesis of graphene oxide". Carbon, vol. 64, pp. 225-229, 2013.
[20] S. Shervani, et al. "Synthesis and structural evolution of ZnO/TiO2 nanocomposites". AIP Conference Proceedings, vol. 277, pp. 1447, 2012.
[21] J-B Wu et al., "Raman spectroscopy of graphene-based materials and its applications in related devices", Chem. Soc. Rev., vol. 47, pp. 1822, 2018
[22] Y Guo et al., "Intercalation Polymerization Approach for Preparing Graphene/Polymer Composites", Polymers, vol. 10 no. 61, pp 1-28, 2018.
[23] K. A. Alim, et al. "Micro-Raman investigation of optical phonons in ZnO nanocrystals", J. Appl. Phys., vol. 97, pp. 124313, 2005.