



Composite Based on Chitosan and Graphene Oxide

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Abstract

Graphene oxide (GO) and composites based on it are promising candidates for the implementation of the process of purification from polluting ions of heavy metals and organic compounds in waste and industrial waters. However, the limitations of the use of GO for water treatment are associated with the difficulties of its regeneration and extraction from aqueous solutions due to high hydrophobicity and dispersibility. We have synthesized graphene oxide by the modified Hammer method, which allows further functionalization. To improve the method of wastewater treatment, we obtained a new GO/chitosan nanocomposite by covalent and non-covalent grafting of chitosan to GO, so in the case of a covalent bond, we used thionyl chloride with further sonification of the mixture. Characterization and study of the morphology of the obtained graphene oxide by IR spectroscopy, X-ray diffraction and TEM analysis, which confirmed the possibility of the crosslinking reaction of GO and chitosan through the carbonyl and epoxy groups of GO located on the surface of the graphene oxide layer, which were obtained in large quantities due to the fact that we modified the method obtaining graphene oxide. The synthesized composites were tested as filters for cleaning the waters of the Caspian Sea, which is prone to oil pollution due to its proximity to the oil sector, and the amount of heavy metals is also increased in these waters.

Keywords: graphene oxide; chitosan; TEM; XRD; FTIR.

I. Introduction

The new materials with good sorption characteristics are attracting more and more attention as novel and cost-effective adsorbents for efficient removal of different contaminants from water [1].

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Chitosan and modified chitosan have received great attention due to its adsorption properties toward various toxic metal ions from aqueous solutions. Recently, chitosan has attracted special attention as a natural material that demonstrates excellent biocompatibility, biodegradability, good adhesion and non-toxic properties. Chitosan contains electron-rich hydroxyl and amine groups, the electron pairs of which form a strong coordination bond with the metal surface [2,3].

This allows them to act as corrosion inhibitors. Some researchers have described the effect of chitosan and its derivatives on metal corrosion in acidic environments [4-6]. The presence of hydroxy and amino groups in the structure of chitosan makes possible its modification and crosslinking via non-covalent interactions and covalent bonding with different compounds of interest.

Another very promising material is graphene oxide (GO), have attracted huge attention due to their remarkable physical and chemical properties. The GO layered structure contains functional groups holding oxygen atoms.

Such groups, like carboxylate, epoxy, hydroxy groups are very important for chelating of contaminant ions and organic species; besides, they allow covalent functionalization with other compounds of interest. Recently there are a lot of reports about of functionalization of GO with various organic molecules to improve the adsorption capacity of pollutants.

To enhance the performance of cost-effective and eco-friendly chitosan its functionalization with GO brings to improved properties offered by purposing introduced functional groups.

We carried out the modification of GO by chitosan by non-covalent interaction by ultrasound treatment [7]. Beside this to ensure the successful grafting under mild conditions of chitosan and GO nanolayers, we carried out the modification of GO with chitosan, by means of covalent bonding of amino groups of chitosan to epoxy and carboxy groups of GO [8], that were preliminary activated by thionyl chloride. The covalent bonding provides the durability of prepared composite and prevent leaching.

Thus, functionalized GO has not only mixed properties but moreover, interesting and co-lucrative behaviour emerges [9].

Characterization of nanomaterials was done by the FT-IR, XRD, and TEM methods

II. Experimental

2.1 Materials

Natural flake graphite (99.0% purity) (average particle diameter of 20 μm , 99.9% purity), Chitosan $[(\text{C}_6\text{H}_{11}\text{NO}_4)_n]$, 95% deacetylation], dichloromethane (DCM), HCl (36.0–38.0%), Sulfuric acid, nitric acid, hydrochloric acid, potassium permanganate, and hydrogen peroxide were of analytical grade and obtained from SemAz Co., Ltd. All the chemicals and reagents were of analytical grade.

2.2 Synthesis of Graphene Oxide (GO)

The GO was prepared by a modified Hummer's method. H₂SO₄ and H₃PO₄ were mixed at a volume ratio of 190:10 mL. Then, 1.5 g of graphite powder was added into the mixture, after that 9 g of potassium permanganate (KMnO₄) was added by small portions and reaction mixture was cooled at ice bath. The mixture was stirred for 48 h at room temperature. After the 48 h, 4 mL of H₂O₂ was poured into the mixture to stop the oxidation reaction. A yellow dispersion was obtained and washed repeatedly with H₂O (200 mL) and 40% aq. HCl (400 mL) to remove the remaining salt.

The purification process was performed using HCl and deionized water centrifuged at 4000 rpm for 10 min. The removal of sulphate ions was checked by the disappearance of turbidity when treated with barium chloride. Then obtained black powder was dried in an oven at 70°C for 48 h.

2.3. Preparation of GO/Chitosan Composite (non-covalent grafting)

Different concentrations (25 mg, 50 mg, and 75 mg) of the prepared GO was dispersed into 50 mL of a 0.5% chitosan solution dissolved in 1% (v/v) acetic acid of Chitosan/10% GO, Chitosan /20% GO, and Chitosan /30% GO, respectively, was sonicated for 40 min at power level of 100W to form homogenous mixtures. After that, the homogeneous GO/ Chitosan solutions were poured into glass plates and kept at 100°C for 4 h.

2.4. Preparation of GO/Chitosan Composite (covalent grafting)

GO was first dispersed in DMF via sonication for 10 min at power level of 100W to form homogenous mixtures. Then, SOCl₂ was added into the GO/DMF suspension in the nitrogen atmosphere at 60°C for 24 h to activate the carboxylic and epoxy groups of GO. Triethylamine and chitosan were then added and reaction mixture were stirred at 75°C for 72 h. The resultant suspension was purified thoroughly by several washing cycles and dried under vacuum at room temperature for 72 h to obtain GO/Chitosan composite.

2.5 Characterization Techniques

All prepared samples were characterized using spectroscopic techniques using an IR spectrometer (Vertex 80, Bruker) with spectral range 4000–450 cm⁻¹. Additionally, the prepared GO structure was investigated based on X-ray Diffraction (XRD) and TEM measurement.

There was used 120 kV JEOL JEM-1400 transmitter electron microscope that has equipped with a side camera.

For XRD analysis, there was used Rigaku Mini Flex 600 X-ray diffractometer equipped with a Cu K α radiation source (15 mA and 30 kV).

III. Results and discussion

The synthesis of GO/Chitosan composite was achieved by two methods: 1) ultrasonication and 2) covalent grafting. The optimal synthesis conditions in preparing GO/Chitosan are explored by varying solvent (DMF,

DCM, DMSO), GO and Chitosan ratio, temperature. In case of ultrasonication method (1) the grafting of chitosan to GO occurs by means of non-covalent bonding.

The carboxylic, hydroxylic, carbonyl groups on the surface and edges of GO can form multiple hydrogen, ion-dipole, ion bonds with hydroxyl and amine groups of chitosan molecule.

The covalent grafting (2) occurs by the reaction between GO and chitosan due to the activation of carboxylic and epoxy and some of hydroxyl groups on the GO by using thionyl chloride. Thus, by means of the condensation reaction between acyl-chloride activated GO $-C(O)Cl$ and $-C-Cl$ groups and amino and hydroxyl groups of chitosan is grafting via covalent bonding.

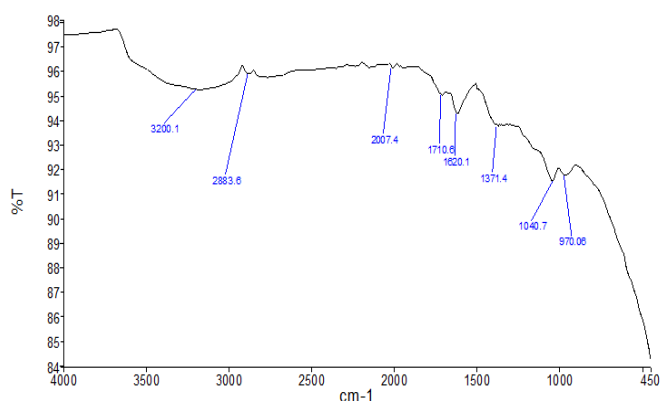


Figure 1: FTIR result of GO.

Table1: FTIR frequencies and functional groups.

2883.6 cm^{-1}	vibration of stretching C-H
1710.6 cm^{-1}	vibration of deformation for C=O
1620.1 cm^{-1}	deformation for a double bond C=C
1040.7 cm^{-1}	deformation of C-O
970.06 cm^{-1}	deformation of vinyl group

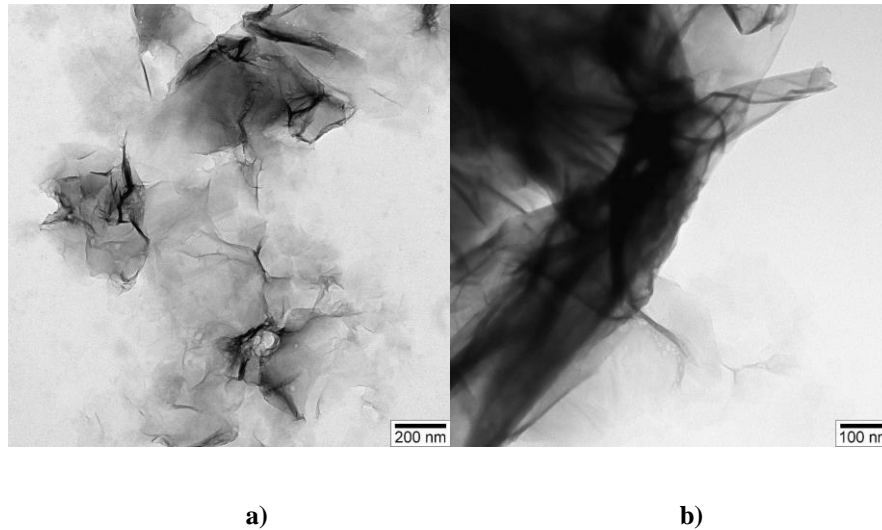


Figure 2: TEM spectra of.

a) pure GO, b) GO/Chitosan

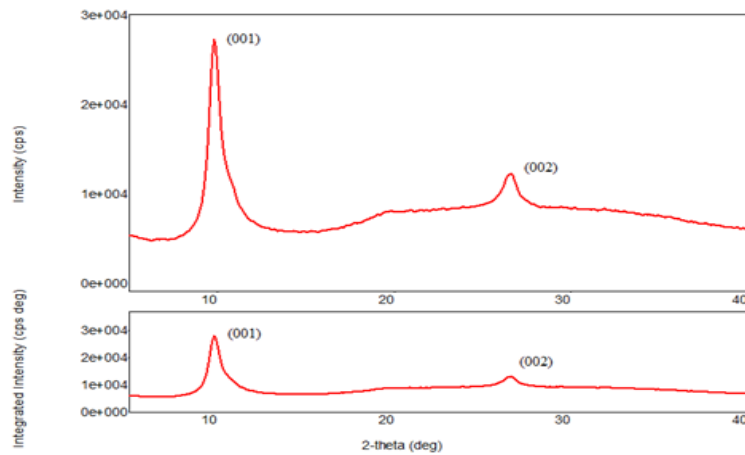


Figure 3: X-ray diffraction of GO by modified Hummer’s method. The large increment in the separation of the graphene layers due to the oxidation of graphite can be clearly observed.

Figure 3 clearly shows the X-ray diffraction peak for GO which is clearly marked at 9.8° , so you can calculate the interlayer distance which will be (d) equal to 0.905 nm, this peak is indicated by the index (001).

Also, in addition to peak 001, one more peak can be marked in the figure, which is located at 27° , the interlayer ratio for this peak is 0.334 nm, this peak is indicated by the index (002).

Table2: The result of the initial and final value after cleaning the test water (Caspian Sea Boulevard - 92 Neftchilar Avenue, Baku) from heavy metals.

Metals	Amount of metal	Amount of metal
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	Before cleaning ($\mu\text{g/l}$)	After cleaning ($\mu\text{g/l}$)
Fe	35.7	23.8
Mn	3.8	1.2
Zn	7.2	5.4
Ni	2.6	2.2
Pb	3.1	0.7

IV. Conclusion

We obtained graphene oxide by the modified Hummer's method, where the output of graphene oxide was more than the product of the original method. By increasing the oxidizing agents in conducted reaction, amount of graphene oxide in the product has increased correspondingly. As shown from the XRD results, comparing with original modified Hummer's method, the output of graphene oxide in product has increased.

It is shown that the concentration of the pollutant after cleaning with composite materials based on graphene oxide with chitosan decreased, which indicates the possibility of using this composite in the wastewater treatment process. An analysis of the water sample of the Caspian Sea was carried out and it was determined that the composite obtained by us gives a good result for wastewater treatment.

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