Ecotoxicology and Environmental Safety 147 (2018) 34–42

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

journal homepage: www.elsevier.com/locate/ecoenv

Bioconjugated graphene oxide hydrogel as an effective adsorbent for cationic dyes removal

Khadijeh Soleimani, Abbas Dadkhah Tehrani*, Mohsen Adeli

Department of Chemistry, Faculty of Science, Lorestan University, Khorramabad, Iran

ARTICLE INFO

Keywords:
Graphene oxide
Hydrogel
Cellulose nanowhisker
Methylene blue
Rhodamine B

ABSTRACT

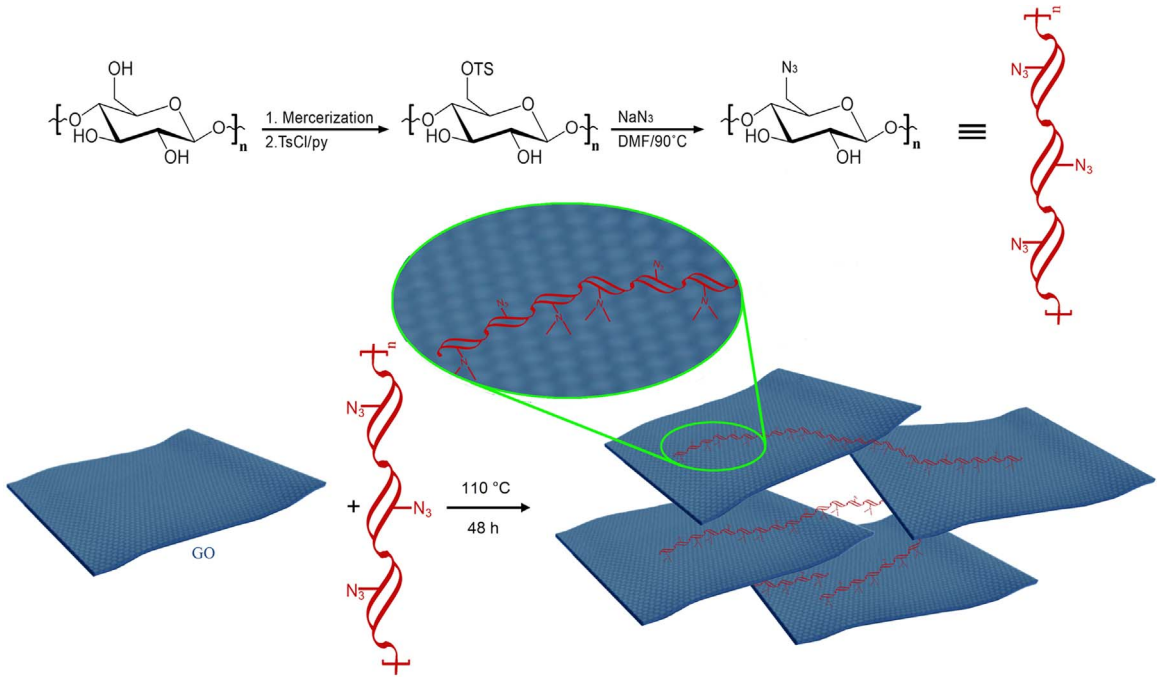
In this study, graphene oxide - cellulose nanowhiskers nanocomposite hydrogel was easily synthesized through covalent functionalization of cellulose nanowhiskers with graphene oxide via a facile approach. The nitrene chemistry applied for covalent functionalization of graphene oxide sheets. The surface morphology and chemical structure of the nanocomposite hydrogel were characterized by FTIR, TGA, Raman, XRD, elemental analysis and SEM. The UV/Visible absorption spectrum revealed that the obtained porous nanocomposite hydrogel can efficiently remove cationic dyes such as methylene blue (MB) and Rhodamine B (RhB) from wastewater with high absorption power. The adsorption process showed that 100% of MB and 90% of RhB have been removed and the equilibrium state has been reached in 15 min for low concentration solutions in accordance with the pseudo-second-order model. Moreover, the sample exhibited stable performance after being used several times. High adsorption capacity and easy recovery are the efficient factors making these materials as good adsorbent for water pollutants and wastewater treatment.

1. Introduction

Nowadays, due to the growing environmental awareness and concerns over the increasing use of dyes in the synthesis, printing, textile and food, it is necessary to resolve environmental problems. Toxicity, low biodegradability and high solubility in water are major problems of cationic dyes (Ma et al., 2016; Meena Sundari and Meenambal, 2015; Mittal et al., 2016). Adsorption process as a physical method is still one of the most effective method for removal of dyes and heavy metal ions from wastewater. Therefore, academic and industrial researchers have been interested to design and produce polymers and composites for the efficient removal of dye of wastewaters. In the design of an economical wastewater disposal system, fast adsorption rate, low cost and easy operation are important parameters for an efficient adsorbent (Batmaz et al., 2014; Mohammed et al., 2016). Polymeric hydrogels are 3D polymer networks with hydrophilic nature that can swell in water without dissolving in it. They maintained their shapes upon swelling because of their cross linked structures and can absorb water even several hundred times of their own weight. Polymeric hydrogels properties, significantly depends on the chemical structure of polymer and the type and amounts of cross-linker (Şolpan et al., 2008). Nowadays, with growing progress in nanoscience and technology, hydrogels based on nanomaterial especially those are based on carbon nanomaterial such as graphene, graphene oxide and carbon nanotubes because of their superior properties have attracted surge of attention among scientists of different fields of researches (Gao et al., 2013; Wang and Chen, 2007). Graphene, a nanocarbon material with layered structure in a hexagonal two-dimensional lattice, has potential applications in many technological areas, such as supercapacitors, fuel cells, field effect transistors, nanoelectronic devices and so on. Also, graphene oxide, the oxidized form of graphene with similar layered structure but with many oxygenated defects can be used for many fields. Up to now, many methods for preparation of GO based hydrogels through covalent and non-covalent interactions using variety of natural and synthetic polymers have been reported (Chabot et al., 2014; Georgakilas et al., 2012). As mentioned above, numerous polymers have been used as polymer matrix for fabrication of GO based hydrogels. However, biopolymers because of their low cost, biocompatibility, renewability and biodegradability, have gained great interest as promising candidates for production of green and ecofriendly materials. For example, Jiao and colleagues (Jiao et al., 2016) used Whelan gum, a microbial carbohydrate polymer, as polymer matrix for preparation of GO based hydrogel. They found that as prepared hydrogel could be used as efficient absorbent for wastewater treatment. Huang et al. (2013) alternatively used silk fibrin as polymer matrix for GO based hydrogels. Preparation of GO based hydrogels using other polymers such as cellulose, chitosan, poly vinyl alcohol and poly acrylamide also have been reported (Chen et al., 2017; Cong et al., 2014). In the most cases, the non-covalent

* Corresponding author.
E-mail addresses: Dadkhah.a@lu.ac.ir, A_dadkhahtehrani@yahoo.com (A.D. Tehrani).

http://dx.doi.org/10.1016/j.ecoenv.2017.08.021
Received 24 January 2017; Received in revised form 9 July 2017; Accepted 8 August 2017
Available online 18 August 2017



Scheme 1. Schematic illustration of the synthesis strategy of the GO – CNW nanocomposite hydrogel.

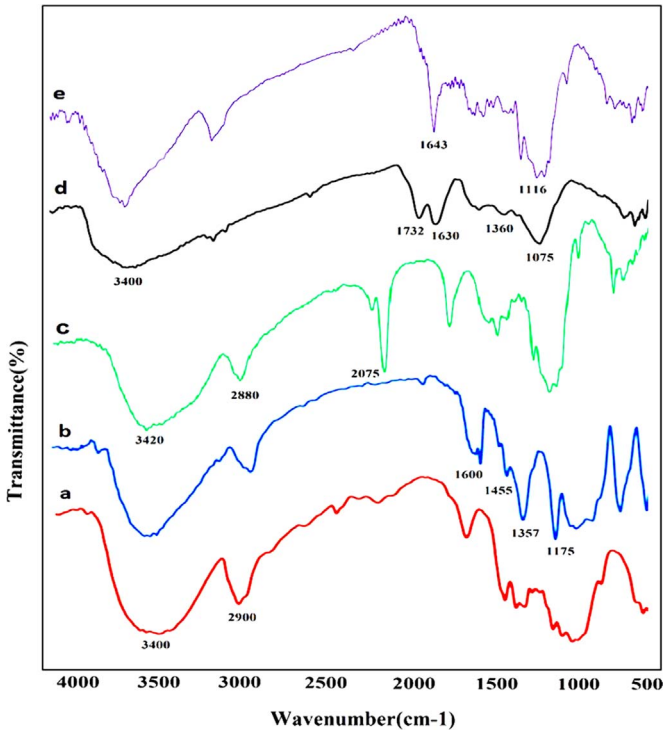


Fig. 1. FTIR spectra of (a) CNW, (b) CNW-OTS, (c) CNW–N3, (d) GO, and (e) nanocomposite hydrogel.

interactions such as H- bonding, hydrophobic interactions because of their versatility have been used as the main driving force of gelation. However, preparation of hydrogels through covalent cross-linking is usually led to more stable structures and stronger interfacial adhesion between hydrogel components. Consequently, much attempt has been targeted on preparation of graphene based hydrogels using covalent cross-linking. The nitrene chemistry approach broadly examined for grafting compounds with azide functional groups onto the graphene oxide surface by a one-step reaction. Nitrenes, as electron deficient species produced by photochemical or thermal decomposition of the organic azides, have been cycloadded to graphene via aziridino-rings with the sp^2 carbon structure.

The present study focuses on the cellulose nanowhiskers as polymer matrix. Cellulose nanowhiskers due to their excellent properties such as high crystallinity, good mechanical performance and their renewability considered as safe, green materials in nanoscale dimensions promising for various fields of applications (Thakur and Thakur, 2014, 2015; Trache et al., 2017).

To the best of our knowledge, up to now, no cellulose nanowhisker GO hydrogel prepared through covalent cross-linking and facile, robust method for fabrication of stable GO /CNW hydrogel with strong interfacial adhesion is still being sought. Therefore, in the present study, the nitrene chemistry addressed for successful bioconjugation and gelation of GO nanosheets. For the first time, polysaccharide azides directly synthesized from tosylated ones and used as aliphatic source of nitrites for cycloaddition reaction between cellulose azide and graphene oxide double bonds. Production of polysaccharide nitrene and their conjugation through this method compared to the other reported methods in literature is more advantageous due to the following features: easy operation, simple workup process and good yields. Furthermore, remaining azide groups can be used for further functionalization of as prepared hydrogels via click reaction.

2. Materials and methods

2.1. Materials

The cellulose material used in this study was commercial cotton linters. Para toluene sulfonyl chloride, sodium azide, methylene blue (MB), Rhodamine B (RhB) and graphite powder were purchased from Merck and used directly without further purification. Sodium hydroxide (NaOH), methanol, sulfuric acid (H_2SO_4) and dimethylformamide (DMF) were purchased from Sigma-Aldrich. All aqueous solutions were prepared with deionized water (DI water).

2.2. Preparation of graphene oxide

GO was synthesized using natural graphite powder by Hummer's