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Preparation of new GO-based slide ring hydrogel through a convenient one-pot approach as methylene blue absorbent

Khadijeh Soleimani, Abbas Dadkhah Tehrani*, Mohsen Adeli

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

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ABSTRACT

Slide ring hydrogels (SRHG) with supramolecular structures are a new class of hydrogels that contrary to the traditional hydrogels comprise dynamic cross-linking points. Herein, we reported on the fabrication of a new slide ring hydrogel through a very convenient one-pot approach. In this regard, isocyanate functionalized GO was synthesized and used as a stopper as well as cross-linker in the presence of a polypseudorotaxane of cyclodextrin threaded on poly(ethylene glycol) (PR). The surface of the resulting SRHG modified via graft polymerization with polyacrylamide (PAAm) and its application as a new type of absorbent for wastewater treatment was studied. Due to its porous structure and its high content of surface functional groups, the synthesized hydrogel was able to efficiently remove cationic dye methylene blue (MB) from wastewater in a short time. The maximum adsorption capacity of the resulting hydrogel was 92.3 mg/g which exhibited an almost 100% increment as compared to that of untreated GO. The adsorption mechanism of MB was also investigated. The kinetic data, obtained at the optimum pH 7, were fitted well with the pseudo-second-order model. Results from degradation and recycling experiments toward MB showed that the SRHG was stable and reusable.

1. Introduction

Hydrogels, particularly those based on graphene oxide, played a key role in the development of novel functional materials for a wide range of applications. Graphene is a promising material for a wide range of applications and is supposed to be one of the main components of different tools ranging from nanoelectronic devices, to nanocomposites (Brownson & Banks, 2010; Jang, Miura, Koyama, & Takata, 2012; Lim et al., 2012; Liu et al., 2010; Low, Walsh, Chakrabarti, Hashim, & Hussain, 2013; Qi, Tan, Wei, & Zhang, 2013). Graphene oxide (GO) is the oxidized form of graphene which has similar layered structure but with many oxygenated defects and usually utilized as starting material for fabrication of graphene (Guo and Jiao et al., 2015). It also is rather suitable for covalent and non-covalent functionalization because of its good surface activity and solubility (Becerril et al., 2008; Xu et al., 2009; Zhang, Zhai, & He, 2014). Benefiting from its unique 2D structure and physicochemical properties, GO is emerging for many applications ranging from nanocarriers to absorbent for removal of dyes and heavy metals (Wang, Sun, Ang, & Tadé, 2013). For example, Travlou and colleagues reported the functionalization of graphite oxide with magnetic chitosan as a nanocomposite material for the adsorption of a reactive dye (ReactiveBlack5) (Travlou, Kyzas, Lazaridis, & Deliyanni, 2013). Weaver et al. introduced an electrically controlled drug delivery based on GO nanosheets/poly (pyrrole) nanocomposite (Weaver, LaRosa, Luo, & Cui, 2014). They reported safe, efficient and multifunctional 3D blood-contact adsorbents using biopolymers/graphene oxide gels (He et al., 2013). GO is also of high interest as a reinforcing agent and gelator for preparation of hydrogel nanocomposites (Rui-Hong et al., 2016). Hydrogels are three-dimensional networks formed by crosslinking polymer chains by covalent bonds or non-covalent interactions such as hydrogen bonding, physical entanglements and van der Waals interactions (Guo, Duan, Cui, & Zhu, 2015). Bai and colleagues prepared a pH sensitive hydrogel based on GO and poly(vinyl alcohol) (Bai, Li, Wang, & Shi, 2010). They indicated that GO and PVA are a so called "supergelator" with a critical gelation concentration $<$ 1 wt.%. Liu et al. used GO nanosheets as crosslinking agents for preparation of polyacrylamide/graphene oxide nanocomposite hydrogels via *in-situ* free radical polymerization of acrylamide in an aqueous suspension of GO (Liu et al., 2012). Sun and coworkers reported a facile strategy for preparation of a dual responsive hydrogel networks conjugation of PNIPAM-co-AA to GO sheets, covalently (Sun & Wu, 2011). Despite enormous publication regarding graphene or graphite oxide, there is no report on GO based slide ring gels. In fact, there are four types of hydrogels which have been developed: topological gel, nanocomposite gel, double network gel and slide ring gel (Fan, Shi, Lian, Li, & Yin, 2013). In the slide-ring gels, the polymer chains are

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* Corresponding author.
E-mail address: Dadkhah.a@lu.ac.ir (A. Dadkhah Tehrani).

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interconnected neither using covalent cross-links as in chemical gels nor non-covalent interactions as physical gels but are topologically interlocked by slidable cross-linking points (Yu et al., 2015). Therefore, the unfixed cross-link points can pass along the polymer chains freely in order to equalize the tension of the threading polymer chains such as a pulley; this is called the pulley effect (Ito, 2010). The polymer chains in the chemical gel are progressively destroyed because of the heterogeneous polymer length between the fixed cross-links. Besides, the polymer chain in the slide ring gel can pass through the suitable cross-links. As a result, the slide ring gel shows a high stretchability of up to 24 times in length, and a large volume change of up to 24,000 times in weight (Jang et al., 2012). In the present study, a new GO-based 3D structure is prepared through reaction of cyclodextrin polypseudorotaxane with isocyanate functionalized GO. Attachment of PAAm chains to the obtained hydrogel by "grafting from" method promoted its physicochemical properties and its ability to load small molecules. The potential application of this SRHG to remove cationic MB dye from aqueous solution was examined. Taking advantage of the fast and efficient removal of MB from water, this SRHG can be used for the future water cleaning applications.

2. Materials and methods

2.1. Materials

α-Cyclodextrin, poly(ethylene glycol) with $M_w = 6000$, toluene-2,4-di-isocyanate (TDI), acrylamide (AM), methylene blue (MB), graphite powder, dimethyl sulfoxide (DMSO) (99%), ethanol (99.9%), dichloromethane (DCM, 99.8%), dimethylformamide (DMF, 99%), diethyl ether (99.5%), toluene (99%), HCl (37%), sulfuric acid (95%), hydrogen peroxide (30%), *N, N*'- methylenebis(acrylamide) (99%) and ammonium persulfate (APS) (98%) were purchased from Merck and used directly without further purification. All solutions used in the experiments were prepared using deionized water.

2.2. Instruments

2.2.1. FT-IR

The FT-IR spectra were recorded using a FT-IR Bruker-Tensor 320 spectrometer. The samples were mixed with KBr at a weight ratio of 5/200 mg.

2.2.2. Scanning electron microscopy (SEM)

Morphology and structure of materials were investigated using a LEO 440i scanning electron microscope under vacuum at an operating voltage of 10 kV. Dried samples used for SEM observations were coated with a thin layer of gold by sputtering for 15 s.

2.2.3. Thermogravimetric analysis (TGA)

TGA thermograms were recorded by an STA 409 apparatus (Linsei) at temperature range from 25 to 800 °C with a 10 °C/min heating rate under argon gas.

2.2.4. UV–vis spectroscopy

A Shimadzu UV–vis 1650 PC spectrophotometer with a cell of 1.0 cm path length was used for recording absorption spectra of aqueous solutions of MB.

2.2.5. X-ray diffraction (XRD)

The XRD spectra of GO and hydrogel were obtained by a Siemens diffractometer with Cu-k radiation at 35 kV in the scan range of 2 from 2° to 80°.

2.2.6. Raman spectroscopy

Raman spectra were recorded on a dispersive Raman Microscope with $\Lambda_{exc} = 785$ nm and high spatial & spectral resolution (Spectral Resolution: $< 3\,\text{cm}^{-1}$).

2.2.7. NMR spectroscopy

^{1}H NMR spectra were recorded on a Bruker 300 MHz. The sample was dissolved in DMSO-d_6 with the solution concentration of 15% (w/v) at room temperature.

2.3. Methods

2.3.1. Preparation of PR

PEG (Mw = 6000) (0.025 g, 0.004 mmol) and α-cyclodextrin (α-CD) (0.1 g, 0.1 mmol) were respectively dissolved in water and the solutions were mixed at room temperature. Then the solution was sonicated for 20 min and gradually became turbid (Wang, Li, Zhu, Liu, & Guo, 2009). The mixture was stirred at room temperature overnight to yield the white paste of the inclusion complex. Then, the precipitate was washed with water to separate extra α-CD and PEG. The washed precipitate was dried in vacuum for 24 h to give the polypseudorotaxane as a white powder (0.085 g, 68%). The average number of PEG repeat units per α-CD molecule was calculated from the ^{1}H NMR of PR (Fig. S1), comparing the integrations of the signal at 4.78 ppm related to the anomeric protons of α-CD (H_1) with that of ethylene protons of PEG at 3.49 ppm. The number of ethylene glycol repeat units per α-CD molecule was evaluated to be about 7. The peak assignments were based on literature values (Ooya & Yui, 1997).

2.3.2. Synthesis of GO

GO was synthesized according to improved Hummers' method (Marcano et al., 2010). At first, graphite powder (1.5 g) was added to a mixture of phosphoric acid (33 mL) and sulfuric acid (200 mL) and stirred for 30 min in an ice bath. Then $KMnO_4$ (9 g, 0.06 mol) was slowly added to the mixture and the temperature was kept below 20 °C. The temperature was raised gradually to 40 °C, maintained at this temperature for 30 min, and the excess potassium permanganate was removed by hydrogen peroxide and washed with distilled water. The mixture was filtered and washed with 250 mL of 30% HCl solution to remove metal ions, followed with centrifugation to remove the acid. Then, the reaction mixture was ultrasonicated for 1 h. The resulting brown dispersion was centrifuged for 30 min at 5000 rpm in order to remove any aggregate. Finally, water was removed by freeze-drying to give GO (0.34 g, 23%). The yield was calculated according to the method described by Jasim et al. based on starting graphite (Jasim, Lozano & Kostarelos, 2016).

2.3.3. Synthesis of isocyanate functionalized graphene oxide (TDI-rGO)

The as-prepared GO (100 mg) was suspended in dimethylformamide (4 mL) and sonicated for 20 min in an ultrasonic bath. Subsequently, the suspension was transferred into a round-bottom flask, and toluene-2,4-diisocyanate (3 g) was added to suspension upon stirring. The mixture was stirred in a nitrogen atmosphere at room temperature for 24 h. The slurry was poured into dichloromethane (15 mL) to coagulate the product. The mixture was filtered and washed with additional dichloromethane (10 mL) and dried under vacuum to give TDI-rGO (90 mg). The yield based on starting GO was 90%.

2.3.4. Synthesis of GO hydrogel

A mixture of polypseudorotaxane (0.020 g), TDI-rGO (0.008 g) and DMF (3 mL) were introduced into a reaction flask. The reaction started at room temperature under a nitrogen atmosphere, followed by stirring for 12 h. Then, the mixture was heated at 80 °C for 3 h. The mixture was cooled to room temperature and the product obtained as a precipitate that was filtered and washed with diethyl ether (20 mL) and 0.1% sodium chloride aqueous (20 mL). Then, the resulting paste was dispersed in DMSO (2 mL). After 3 h at room temperature, a viscous compound was obtained. The product was allowed to swell in DMSO until equilibrium swelling was achieved. DMSO was renewed several times in