Colloids and Surfaces A 529 (2017) 668–676

Contents lists available at ScienceDirect

Colloids and Surfaces A

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

Preparation of graphene oxide-polymer composite hydrogels via thiol-ene photopolymerization as efficient dye adsorbents for wastewater treatment

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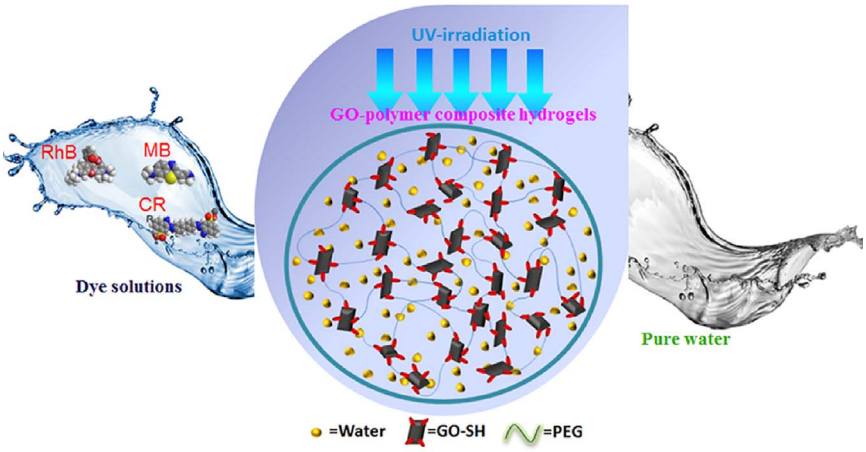
HIGHLIGHTS

- GO composite hydrogels via thiol-ene photopolymerization.
- Hydrogels prepared in an eco-friendly and effective manner.
- Hydrogels exhibit good removal rates for model dyes.
- Significant potentials towards wastewater treatment.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Composite hydrogel
Self-assembly
Thiol-ene photopolymerization
Adsorbent

ABSTRACT

The design and self-assembly of graphene oxide (GO)-based hierarchical composite gels have attracting numerous attentions due to wide applications in nanomaterial and environmental fields. In this research work, a facile strategy is demonstrated to prepare chemically modified graphene oxide-poly(ethylene glycol) diacrylate (GO-PEG) composite hydrogels by thiol-ene photopolymerization. The photopolymerization process between thiol groups on GO surface and ene segments in soluble PEG derivatives is critically predominant for the formation of composite hydrogels. The obtained composite hydrogels show good removal capacities and fit in pseudo-second-order model for used three model dyes. Thus, the present obtained GO-PEG composite hydrogels constructed by thiol-ene photopolymerization via eco-friendly prepared manner demonstrate new clues for preparing GO-based composite hydrogels and soft matter towards wastewater treatment applications.

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http://dx.doi.org/10.1016/j.colsurfa.2017.06.050
Received 12 April 2017; Received in revised form 15 June 2017; Accepted 16 June 2017
Available online 21 June 2017
0927-7757/

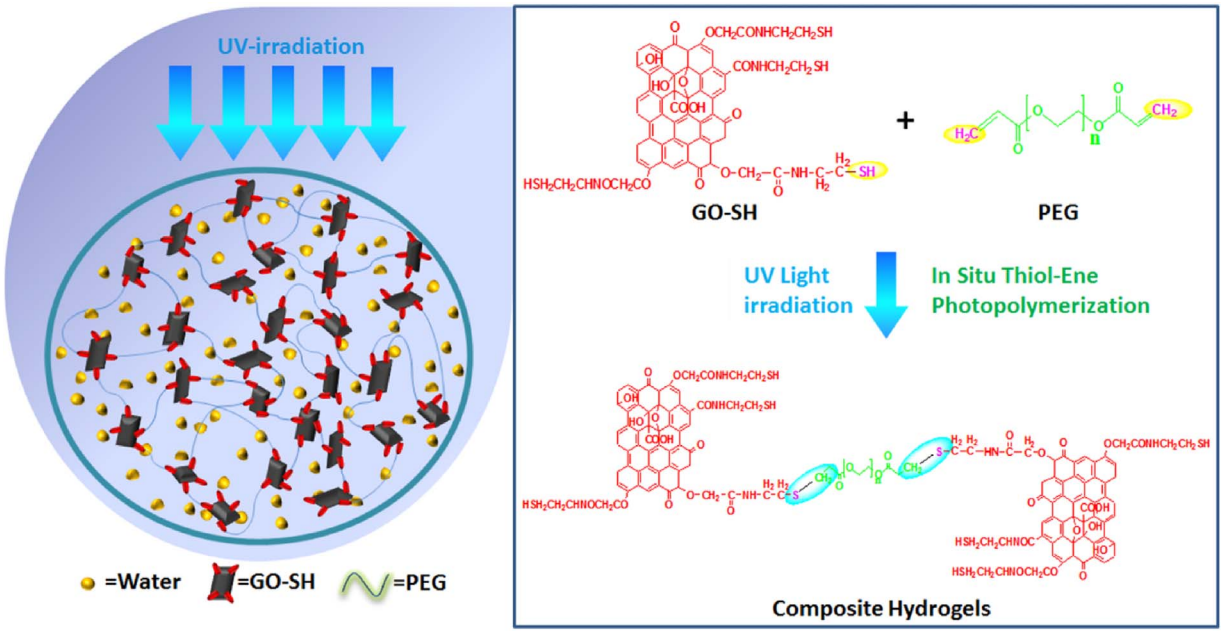

Fig. 1. Scheme illustration of GO/PEG composite hydrogels constructed by thiol-ene photopolymerization.

1. Introduction

In recent years, graphene oxide (GO)-based nanocomposites have attracted numerous interests owing to vast functional oxygen-containing groups, regulated dispersibility and nanostructures, and preferred reactive positions/sites for special chemical functionalization [1–3]. Up to now, more research work have been focused on rational preparation of controlled GO-based organic/inorganic nanocomposites, which is expected to display better optical and electronic properties for nanomaterial applications [4–6]. Thus, the chemical functionalization and surface modification for GO composite materials with different organic components are frequently needed to regulate their dispersion and reactive sites for various applications fields [7–12]. Up to now, it have been reported that various organic molecules, such as isocyanate derivatives, long-chain alkylamine, porphyrin, dopamine as well as tetrathiafulvalene, have been investigated to functionalize GO sheet to obtain well dispersed states and enhanced optical/electronic properties [13–17]. On the other hand, polymers have been also displayed to hybridize GO sheet to regulate and change some properties in GO-based composites. For example, two polymer molecules, poly(vinyl alcohol) and poly(2-(dimethylamino) ethyl methacrylate), have been reported to modify GO sheet with different chemical reactions [18,19]. However, this strategy in some content suffers from some experimental limits, such as large aggregation between GO sheets, incomplete adsorption process for dye compounds, and adverse side effects, suggesting poor application fields. Thus, it is interesting to mention that click chemistry has showed more attention due to eco-friendly manner, high selectivity and satisfactory yields [20–23]. In comparison with CuI system in click chemistry [24], additional catalyst is not needed because of the special reaction initiated thermally or photochemically. Now many research groups have investigated the click reactions in some systems and demonstrated to hybridize GO sheet with the special azide-alkyne reactions and thiol–ene/thiol–yne reactions [25–28]. However, it represents a challenging strategy to design and synthesize GO-based nanocomposites and self-assembled nanostructures with eco-friendly manner.

In addition, hydrogels are regarded as effective and sophisticated systems to self-assemble various building blocks in a three-dimensional (3D) space and prepare hierarchical porous nanostructures [29–31]. Some studies present the successful preparation of polymer/GO composite hydrogels, which display enhanced breaking elongation, tensile and compressive strength [32–34]. It seemed that a strategy of GO-based composites with click reaction and organized hydrogel systems should be advantageous due to moderate nanostructures, excellent biocompatibility, and enhanced chemical and mechanical properties. For example, An and coworkers reported the synthesis of triblock-graft copolymers/graphene oxide composite hydrogels via click reaction between tBG-N_3 and alkyne-functioned GO, which exhibited excellent mechanical strength and toughness [35]. Thus, in present work, aqueous soluble poly(ethylene glycol) diacrylate (abbreviated as PEG) has been utilized for the preparation of composite hydrogels. The PEG derivatives include some ethylene glycol as molecular skeleton and ene groups as reactive sites for photopolymerization.

Herein we report the preparation of new GO-PEG composite hydrogels by thiol-ene photopolymerization without addition of other stabilizing or crosslinking compounds by an eco-friendly style. The speculated photopolymerization reaction appeared between thiol groups and ene groups is crucial for the preparation of hierarchical composite nanostructures. In addition, the obtained hydrogels exhibit good removal rates for used three model dyes in accordance with pseudo-second-order model. Thus, the obtained GO-PEG composite hydrogels give perspective clues for soft matter design as well as wastewater treatment applications.

2. Experimental method

2.1. Materials

The experimental materials, cysteamine (CA), poly(ethylene glycol) diacrylate (PEG, 1000 g·mol^{-1},), and chloroacetic acid were obtained from Aladdin Shanghai Chemicals. N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC-HCl) and N-hydroxysuccinimide (NHS) were obtained from Sigma-Aldrich (Shanghai) Chemicals. Graphite powder was obtained from Alfa Aesar Chemicals. Congo red (CR), Rhodamine B (RhB), and methylene blue (MB) were acquired from Tianjin KaiTong Chemical Co., Ltd. Potassium permanganate ($KMnO_4$), potassium nitrate (KNO_3), sulfuric acid (H_2SO_4, 98%), hydrochloric acid (HCl), and hydrogen peroxide (H_2O_2, 30%, w/w) were obtained from Sinopharm Chemical Reagent Co., Ltd. For the materials preparation, graphene oxide (GO) was obtained according to the literature report [36]. After that, the carboxyl groups were modified on GO sheets to obtain GO-COOH material [37]. Finally, thiol modification was finished according to some describing literatures [38,39] and