Colloids and Surfaces A: Physicochem. Eng. Aspects 483 (2015) 112–120

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

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

Effects of graphene oxide and salinity on sodium deoxycholate hydrogels and their applications in dye absorption

Lin Wang[a], Xia Xin[a,b,*], Mengzhou Yang[a], Xin Ma[a], Jinglin Shen[a], Zhaohua Song[b], Shiling Yuan[a,**]

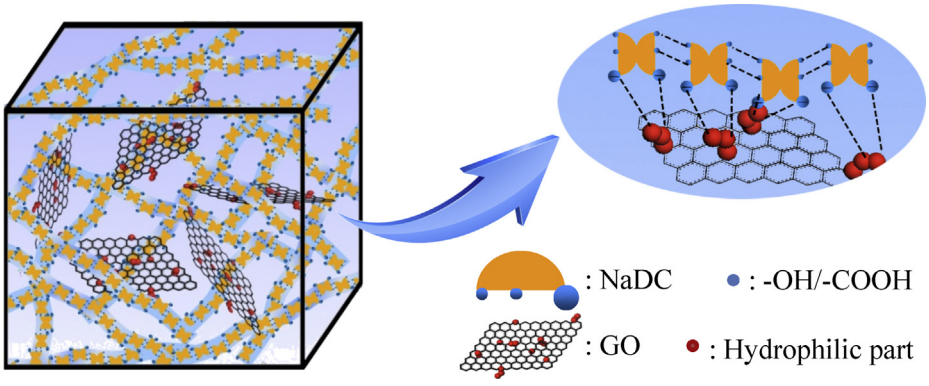
[a] Key Laboratory of Colloid and Interface Chemistry, Shandong University, Ministry of Education, Shanda Nanlu No. 27, Jinan 250100, PR China
[b] National Engineering Technology Research Center for Colloidal Materials, Shandong University, Shanda Nanlu No. 27, Jinan 250100, PR China

HIGHLIGHTS

- We used sodium deoxycholate and graphene oxide to prepare hydrogels.
- The introduction of GO to NaDC hydrogel enhances the mechanical strength of the composite hydrogel.
- The incorporation of GO exhibits good dye absorption property for hydrogels.

GRAPHICAL ABSTRACT

Schematic representation of the structure of NaDC/GO hydrogel.



ARTICLE INFO

Article history:
Received 21 May 2015
Received in revised form 16 July 2015
Accepted 21 July 2015
Available online 26 July 2015

Keywords:
Biological surfactant
Hydrogels
Graphene oxide
Dye absorption
Composite

ABSTRACT

Sodium deoxycholate/graphene oxide (NaDC/GO) composite hydrogels were prepared in varying salinity. The hydrogels were characterized in detail by phase behavior study, transmission electron microscopy (TEM) observations, scanning electron microscopy (SEM) observations, X-ray powder diffraction (XRD) mesurements, Fourier transform infrared (FT-IR) spectra and rheological measurements. It was found that the introduction of GO to NaDC hydrogel enhances the mechanical strength of the composite hydrogel. When contacted with methylene blue solution, methylene blue can be absorbed inside the gel accompanied with a swelling of the gel. On the contrary, the hydrogel forms by NaDC only dissolves in methylene blue solution, forming a homegeous solution. Further study reveals that the gelation of NaDC/GO composite gel can be accelerated by an increase in salinity. This work may open the door for a variety of applications of NaDC/GO composite hydrogels such as in biotechnology, drug delivery and sewage treatment.

1. Introduction

Supramolecular gels constructed from low-molecular-weight molecules by reversible noncovalent interactions have received considerable attention due to their unique structures and wide applications [1]. Hydrogels, which contain a large number of

* Corresponding author at: Key Laboratory of Colloid and Interface Chemistry, Shandong University, Ministry of Education, Shanda nanlu No. 27, Jinan 250100, PR China.
** Corresponding author.
E-mail addresses: xinx@sdu.edu.cn (X. Xin), shilingyuan@sdu.edu.cn (S. Yuan).

http://dx.doi.org/10.1016/j.colsurfa.2015.07.044
0927-7757/

water molecules, are biocompatible and have shown wide applications in biomaterials [2–4], drug delivery [5], biocatalysis [6], stimuli-responsive materials [7,8] and bioanalysis [9]. Specifically, interests on hydrogels formed by amphiphilic molecules have rapidly increased for their responsive properties and functions [10,11]. Sodium deoxycholate (NaDC) is an important biological surfactant and widely exists in the body of vertebrate [12]. Its molecular structure contains a hydrophobic cholesteric ring on the concave α-face and a hydrophilic carboxyl and hydroxyl on the convex β-face [13,14]. The interesting structure leads to novel and abundant self-assembly behavior in solution. For example, NaDC can spontaneously self-assemble into gels in water through van der Waals, H-bonding and hydrophobic effect [15].

However, the viscoelastic and mechanical properties of NaDC hydrogels are not strong enough. Thus, we need to add some novel additives to construct composite hydrogels to regulate their function. For example, with the addition of reinforcing organic/inorganic fillers, the viscoelastic and mechanical properties of hydrogels can be improved greatly [16,17]. Previous study has been demonstrated that graphene oxide (GO), which is a novel carbon material, can be successfully incorporated into the hydrogels to form graphene-based hydrogels [18,19]. Until now, a lot of researches have been devoted to improving the strength of hydrogels with incorporating GO [20–22]. Liu et al. synthesized a polyacrylamide (PAM)/graphene oxide (GO) nanocomposite hydrogels with GO nanosheets as cross-linkers [23]. Compared with conventional PAM hydrogels, the nanocomposite hydrogel exhibits higher tensile strength, better toughness and a larger elongation at break. Fan et al. prepared a GO/sodium alginate (SA)/PAM ternary nanocomposite hydrogel through free radical polymerization of acrylamide and SA in the presence of GO in an aqueous system followed by ionically crosslinking of calcium ions [24]. The ternary nanocomposite hydrogel possessed excellent mechanical performance. In our previous work, we incorporated CNTs [25,26], GO and graphene [27] into a nonionic polyoxy-ethylene surfactant ($C_{12}E_4$ or $C_{12}E_6$) lyotropic liquid crystal (LLC) matrix and our results also indicated that the viscoelastic properties of the LLC materials were increased due to the addition of carbon materials.

In this paper, we gave a detailed study of the incorporation of GO into NaDC hydrogels in different concentrations of phosphate buffered saline (PBS) and explored their capabilities in dye adsorption. The properties of NaDC/GO hydrogels have been investigated deeply and systematically by transmission electron microscopy (TEM) and scanning electron microscopy (SEM) observations, X-ray powder diffraction (XRD), Fourier transform infrared (FT-IR) spectra, and rheological measurements. It can be seen that the viscoelasticity of the NaDC/GO hydrogels increase with increasing concentration of GO. Moreover, the NaDC/GO composite hydrogels were excellent adsorbents to remove the dye (methylene blue) from aqueous solutions, during which a swelling of the volume of the gels was noticed. For NaDC hydrogels (i.e., without GO), however, the gels dissolved into the dye solution and no absorption was observed. The effects of GO and salinity on the gelation of NaDC hydrogels were also demonstrated.

2. Experimental

2.1. Chemicals and materials

Sodium deoxycholate (NaDC, A.R.), NaH_2PO_4 and Na_2HPO_4 (A.R.) were purchased from Sinopharm Chemical Reagent Co. Graphene oxide (GO) with an averaged size of 0.5–5 μm and an averaged thickness of 0.8–1.2 nm was obtained from Nanjing XFNANO Materials Tech Co., Ltd. All the reagents were used without further purification. Water used was triply distilled using a quartz water purification system.

2.2. Sample preparation

NaDC stock solution was prepared by dissolving an appropriate amount of NaDC in water. Stock solutions of phosphate buffer salines (PBS) with varying salinity were prepared by dissolving different amount of NaH_2PO_4 and Na_2HPO_4 in water. GO dispersions were prepared by sonicating the solid GO for 3 h in water. The hydrogels were obtained by mixing different amounts of stock solutions mentioned above.

2.3. Adsorption study of dye methylene blue

To a bottle containing 1 mL hydrogel, 3 mL methylene blue solution (0.1 mmol L^{-1}) was added followed by gentle stirring. At last, the efficiency of methylene blue absorption by the hydrogel was monitored by measuring the absorbance of the by UV–vis–NIR measurements.

2.4. Methods and characterization

For transmission electron microscopy (TEM) observations, ~5 μL of solution was placed on a copper grid and the excess solution was wicked away by a piece of filter paper. After drying, the copper grid was checked by a JEOL JEM-100 CXII (Japan) at an accelerating voltage of 80 kV. For field-emission scanning electron microscopy (FE-SEM) observations, a drop of hydrogel was placed on a silica wafer to form a thin film, which was then freeze-dried in vacuum at −55 °C. The wafer was checked by a JSM-6700F. Fourier transform infrared (FTIR) spectrum was recorded on a VERTEX-70/70v spectrometer (Bruker Optics, Germany). XRD patterns were obtained on a Rigaku D/Max 2200-PC diffractometer with Cu Ka radiation (λ = 0.15418 nm) and a graphite monochromator. Data were collected at $1^\circ < 2\theta < 70^\circ$. UV–vis–NIR measurements were performed on a Hitachi U-4100 spectrophotometer (Japan).

Rheological measurements were carried out on an Anton Paar Physica MCR302 rheometer with a cone-plate system (diameter, 25 mm; cone angle, 2°). For the shear-dependent behavior, the viscosity measurements were carried out at shear rates ranging from 1 to 1000 s^{-1}. In oscillatory measurements, an amplitude sweep at a fixed frequency of 1 Hz was performed prior to the following frequency sweep in order to ensure that the selected stress was in the linear viscoelastic region. The viscoelastic properties of the samples were determined by oscillatory measurements in the frequency range of 0.01–10 Hz. The samples were measured at 20.0 ± 0.1 °C with the help of a cyclic water bath.

3. Results and discussion

3.1. Dispersion states of graphene oxide

Because of the presence of the oxygen-containing functional groups (—COOH and —OH), GO can be dispersed in water directly by ultrasonication and the dispersion can be stable for months. GO dispersions at different concentrations were prepared by diluting the stock solution. A typical TEM image of 5 mg mL^{-1} GO in water is shown in Fig. S1. We can clearly see that GO nanosheets are wrinkled with low contrast. The transparent and plicated GO nanosheets contain mono- or few layer planar sheets [28]. Hence, the result of TEM indicated that GO has been well-dispersed in water.