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Manipulation the properties of supramolecular hydrogels of α-cyclodextrin/Tyloxapol/carbon-based nanomaterials

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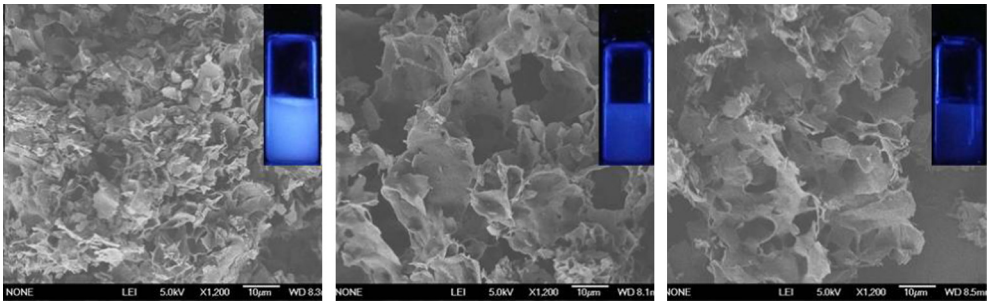
GRAPHICAL ABSTRACT



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ABSTRACT

Supermolecular hydrogels were prepared by α-cyclodeatrin (α-CD) and Tyloxapol, which can be considered as an oligomer of the nonionic surfactant polyoxyethylene tert-octylphenyl ether (TX-100) with a polymerization degree below 7. Two carbon materials, graphene oxide (GO) and graphene, were mixed into the α-CD/Tyloxapol hydrogel to adjust the physicochemical properties of hydrogel. In order to get stable graphene dispersion and then mix it with α-CD/Tyloxapol hydrogel, both TX-100 and Tyloxapol were used to disperse graphene for comparison. Interestingly, it can be found that TX-100 could disperse graphene better than Tyloxapol owing to smaller molecular size of TX-100 compared with Tyloxapol. Then, both the α-CD/Tyloxapol/GO and α-CD/Tyloxapol/graphene hydrogels were characterized by transmission electron microscopy (TEM), field emission scanning electron microscopy (FE-SEM), Fourier transform infrared (FT-IR) spectroscopy, small angle X-ray scattering (SAXS), X-ray diffraction (XRD) and rheological measurements. The results revealed that the addition of carbon materials into α-CD/Tyloxapol hydrogel can change their microstructures and the rheological properties. Furthermore, it can be confirmed that a little amount of carbon materials could induce fluorescence quenching sharply which could be a promising candidate for optical sensor.

1. Introduction

Soft materials constructed through non-covalently cross linking exhibit excellent performances, such as thermo- or pH-sensitive and other stimuli-sensitive properties, and consequently posses

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interesting properties [1–3]. Cyclodextrin-based self-assemblies are a class of promising soft materials which has received widespread attention in recent years [4–7]. Cyclodextrin (CD) are a series of cyclic oligosaccha-rides composed of 6, 7, and 8 D(+)-glucose units linked by α-1,4-linkages and named α-, β-, and γ-CD, respectively. CD could include a variety of guest molecules from polymers (polyethylene glycol, polypropylene glycol) [8,9] to surfactants (SDS, ionic liquid) [10,11] and small molecules (phenylamine, toluene) [12], etc., to establish a complex host–guest chemistry [13].

Among various soft materials, self-assembled supramolecular hydrogels are a new class of important soft materials due to their potential applications in cosmetics, biomaterials, and pharmaceutical formulations [14,15]. Among them, supramolecular CDs hydrogels occupy an important position because of the occurrence of host–guest interaction by the CD cavity in gels for achieving various functions. Recently, a lot of studies have been focusing on optimizing the performance of CD-based hydrogels [16] by using a simple way to adjust the properties of hydrogels with the addition of additives, such as quantum dot [17], salt [18] and carbon materials [19]. Graphene oxide (GO) and graphene, a new kind of carbon materials, has attracted lots of attention owing to its unique mechanical and electrical properties [20–22] and has been used to incorporate into hydrogels. For example, Jiang et al. studied a mild method to synthesize a graphene oxide-formaldehyde (GOP-1) *in situ* polymerization of pyrrole and formaldehyde occurred in the presence of GO, promoting the formation of hydrogel. The composite hydrogel they prepared had a 3D network structure, high nitrogen content, large specific surface area and showed an excellent carbon dioxide uptake capacity [23]. Zo et al. reported GO functionalized cyclodextrin-templated supramolecular hydrogel. The obtained supramolecular gel provides a uniform dispersion with high GO loading and long dispersion stability. Rheological experiments, in comparison to other supramolecular gels, reveal highly elastic characteristics of the hydrogel, exhibiting an increase in the storage modulus at around 35 °C and sturdy stability at an elevated temperature up to 50 °C. Moreover, the results also demonstrates the effect of lithium ions on fine dispersion and complete reduction of GO inside gel matrix which make the hydrogel useful in various applications, including biomedical release systems [24]. In our previous work, the self-assembly behavior of carbon-based star-like copolymer AE73/α-CD hydrogels and GO containing T90R4/α-CD hydrogels have been studied. Phase behaviors, influences factors of gelation, microstructures of hydrogels and the mechanism of the formation of these hydrogels were investigated [25,26]. Moreover, it can be found that GO-contained CD hydrogel had good adsorption of cationic dyes which has potential application of sewage treatment.

In this paper, a new CD-surfactant hydrogel system was developed which is composed by α-cyclodeatrin (α-CD) and Tyloxapol. Tyloxapol is considered as an oligomer of the nonionic surfactant polyoxyethylene tert-octylphenyl ether (TX-100) with a polymerization degree below 7. Then, GO and graphene were successfully incorporated into α-CD/Tyloxapol hydrogel. The native hydrogel, as well as hybrid hydrogels, have been thoroughly characterized by using various microscopic techniques, including transmission electron microscopy (TEM), field emission scanning electron microscopy (FE-SEM), Fourier transform infrared (FT-IR) spectroscopy, small angle X-ray scattering (SAXS), X-ray diffraction (XRD) and rheological measurements. Moreover, it is interesting to find that the hydrogel containing carbon materials could quench fluorescence of Tyloxapol significantly through Forster resonance energy-transfer (FRET).

2. Experimental section

2.1. Materials

Tyloxapol and Trion X-100 (polyoxyethylene tert-octylphenyl ether, TX-100) were purchased from Sigma. Their chemical structures are shown in Fig. S1. Graphene and GO were obtained from Nanjing XFNANO Materials Tech Co., Ltd. α-CD was bought from Shandong Binzhou Zhiyuan Bio-Technology Co., Ltd. All the above reagents were used without further purification. Ultra-pure water used in the experiments was triply distilled by a quartz water purification system.

2.2. Preparation of GO and graphene dispersions

For graphene oxide dispersions, a suspension of graphene oxide sheets was obtained upon ultrasonication for 2 h in deionized water. Graphene dispersions can be obtained from sonicating the mixtures of Tyloxapol or TX-100 aqueous solution and graphene at 40 kHz and 250 W using KQ-250DB ultrasonic apparatus (shanghai) for 2 h, from which small amounts of black precipitates was noticed after standing for 2 weeks, then the upper phase was collected for further use.

2.3. Preparation of carbon based α-CD/Tyloxapol composites

Tyloxapol and α-CD were weighed and dissolved in test tube and heated up to 70 °C to obtain stock solution. Carbon-based composited with different concentrations of α-CD, Tyloxapol and carbon materials were prepared by mixing stock solutions with GO/graphene dispersions. The solution were stirred vigorously and then kept at room temperature for at least one week. The formation of hydrogel was verified upon inversion of the vial.

2.4. Characterizations

The structure of graphene and GO was characterized by transmission electron microscopy (TEM) (JEOL JEM-100 CXII, Japan). Atomic force microscopy (AFM) were observed using Dimension Icon (American) with scan asyst. FE-SEM observations were carried out on a JSM-6700F. FT-IR spectrum was recorded on a VERTEX-70/70v spectrometer (Bruker Optics, Germany).

The dispersion of graphene was measured by Hitachi U-4100 UV–Vis absorption spectra. The fluorescence measurements were performed on a LS-55 spectrofluorometer (PerkinElmer, Waltham, MA, USA) with a quartz cell (1 × 1 cm). XRD patterns of the freeze-dried samples were measured between 8° and 90° in the 2θ scan mode (2.5° min^{-1}) using a Rigaku D/Max 2200-PC diffractometer with Cu Ka radiation ($\lambda = 0.15418$ nm) and a graphite monochromator at room temperature. Raman spectra were obtained from an NXR FT-Raman module (Nexus 670, Nicolet Co.) equipped with a Ge detector. The samples were excited by a laser source with a wavelength of 633 nm and a power of 0.103 W. SAXS measurements were performed using an Anton-paar SAX Sess mc^2 system with Ni-filtered Cu Kα radiation (1.54 Å) operating at 50 kV and 40 mA.

The rheological measurements were carried out on an Anton Paar Physica MCR302 rheometer with cone-plate system (diameter, 25 mm; cone angle 2°). Before frequency sweep, an amplitude sweep at a fixed frequency of 1 Hz was operated to ensure the selected stress was in the linear viscoelastic region. The frequency sweep was carried out from 0.01 to 100 Hz at a fixed stress of 1 Pa. The samples were measured at 20.0 ± 0.1 °C with the help of a cyclic water bath.