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Design of folic acid based supramolecular hybrid gel with improved mechanical properties in NMP/H_2O for dye adsorption

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ABSTRACT

Folic acid (FA) supramolecular gel was prepared in a mixture solvent of *N*-methylpyrrolidone (NMP)/H_2O at a 1/1 volume ratio by using FA as gelator with a concentration of 0.4% (w/v). In the mixture solvent, NMP was first of time used as a good solvent to tune the solvent properties in order to be able to induce formation of FA supramolecular gel. The folic acid-gelatin (FA-GA) hybrid gels were synthesized by adding different amount of gelatin (GA) into FA gelator. The gelation temperature (T_{Gel}) of the FA-GA hybrid gel is 30 °C which is much higher than that of FA gel (10 °C). The gel to sol transition temperature (T_{GS}) is about 58 °C, which demonstrates that the hybrid gel has good stability at room temperature. The FT-IR and UV–vis spectra of FA-GA hybrid gel indicate that GA involves in the self-assembly process of FA via hydrogen bonding and π-π interactions with FA molecules. Owing to the π-π interaction happened between FA and GA molecules the fluorescence intensity of FA-GA gel is four times as high as that of FA gel. SEM images shows that the hybrid gel has a helical-fiber network structure which would enhance the gel strength to a great extent. Good stability, large specific surface and porosity in three-dimensional network structure of the FA-GA hybrid gel make it a highly promising adsorbent for dye adsorption. The FA-GA hybrid gel is able to absorb 63.5% of Congo red (CR), 68% of methyl blue (MB) and 44% of methyl orange (MO) respectively from their solutions.

1. Introduction

Supramolecular gel is made of low molecular weight gelators. Gelators refer to some small molecular weight organic compounds that can spontaneously gathered and assembled into a three-dimensional network structure of the aggregates in suitable solvents at low concentration (less than 2 wt%) [1–3].The self-assemble driving forces are non-covalent interactions between molecules, such as van der Waals forces, hydrogen bonds, π-π stacking, and hydrophilic/hydrophobic effects [4,5], etc. The solvent molecules, trapped in the three-dimensional networks, cannot flow under gravity because of the surface tension between supramolecular aggregates and the solvents [6,7].The formation process of network structure involves primary nucleation, and subsequent self-assembly of the gelator molecules to forming 1D nanofibers, elongating of the linear fibers and entanglement of the fibers into a 3D network structure [6,8,9]. Such supramolecular gels have their own unique features: (1) they are generally composed of fiber-like structures that can crosslink to three-dimensional networks; (2) they have the respective critical gelation temperatures (T_{Gel}), at which the sol-gel transitions occur [10,11], and the respective critical gelation concentrations (CGC), above which the gels form in certain solvents [12]; (3) they are thermoreversibility, namely, the gels can undergo a gel to sol transition after heating and can be recovered after cooling; (4) the self-assembly process of supramolecular gels is generally controlled by kinetically rather than thermodynamically, so the gelation process is complicated and often compete with other aggregations such as crystal, precipitate [13,14]. These supramolecular gels have been widely investigated for applications in biomaterials [15,16], sensing [17], drug release [18,19], and engineering applications [20,21], etc.

The volume ratio of solvents in the gel system is generally above 90%, therefore, the solvent properties have important effects on the CGC and gel stability except for the gelator types and gelator concentrations. Whether a gelator can self-assemble to form a gel in one solvent, the key point is the interactions among gelators and the interactions between gelator and solvent can reach an equilibrium state, so that gelators are in an equilibrium state of dissolution and precipitation [22]. Although the effect of solvent on the gel has no definite conclusion [22], the influence of the single solvent properties, such as Hansen solubility parameters (HSPs), polarity, dipole-dipole interactions and hydrogen bonds between the solvent molecules on the

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gelators self-assembly has been studied [23–27]. Supramolecular gel is usually prepared by tuning good/poor solvent strategy, which the gelator can be well dissolved in the good solvent and is insoluble in the poor solvent.

In this article, we choose folic acid (FA), a vitamin B [28], as gelator to form FA supramolecular gel. FA supramolecular gel is usually fabricated in a mixed solvent of water-dimethyl sulfoxide (DMSO) at a 1:1 volume ratio. In this work, FA supramolecular gel was prepared in a mixture solvent of *N*-methylpyrrolidone (NMP)/H_2O at a 1:1 volume ratio by using FA as gelator at a concentration of 0.4% (w/v). Owing to the driving force of the self-assemble is weak and reversible non-covalent bonds, the FA supramolecular gel is often brittle with inferior stability. For some applications, such as drug release, pollutant adsorption, gels with higher mechanical properties are required. The mechanical properties could be improved by adding additives such as polymers, inorganic materials [29]. Generally, the external additives can increase the gel strength and stability by enhancing the branching of the fiber networks. This work has the following novelty: (1) Using mixture solvent, NMP is first of time used as a solvent to tune the mixture solvent properties in order to be able to induce formation of FA supramolecular gel. (2) Using gelatin (GA), a polypeptide with a large number of hydroxyl, carboxyl and amino groups on the macromolecules, as an additive to form a FA-GA hybrid gel. The T_{Gel} and mechanical strength of the FA-GA hybrid gel have been greatly improved through adding a small amount of GA. The T_{Gel} and mechanical strength of the FA-GA hybrid gel have been greatly improved through adding a small amount of GA, and the fibers in the network structures of the hybrid gel are spiral which can strengthen the mechanical strength of the hybrid gel. At the same time, the large specific surface and porosity of the hybrid gel make it to be a highly promising adsorbent for the dye adsorption. Therefore, three kinds of dyes, Congo red (CR), methyl blue (MB) and methyl orange (MO), were utilized to study the adsorption capacity of the FA-GA hybrid gel.

2. Experimental

2.1. Materials

Both folic acid and gelatin were purchased from Aladdin-reagent Co. Ltd., Shanghai, China. Congo red, methyl blue, methyl orange were purchased from Aladdin Chemical Reagent. The organic solvents and all other chemicals were purchased from Tianjin Chemical Reagent Co. Ltd.

2.2. Preparation of FA gel in different mixture solvents

It was reported that FA can form supramolecular gel in the mixed solvent of DMSO/water at a 1/1 volume ratio. Here other good-poor mixed solvents were chosen to investigate whether FA can form supramolecular gel in these solvents. The good solvents include NMP, *N*,*N*-dimethyl formamide (DMF), *N*,*N*-dimethylacetamide (DMA), formamide, acetone (the molecular structures of the good solvents were shown in Fig. 1); and the poor solvents include methanol, ethanol, propyl alcohol, propylene glycol, glycerol. The concentration of FA gelator changed from 0.1%–0.5% (w/v) and the volume ratio of the mixture solvent was adjusted in order to select the final optimal gelation condition. For instance, a certain amount of FA power was dissolved in 5 mL NMP in glass vial and stirred at 70 °C to get a transparent solution, and then 5 mL H_2O was added and continued to stir to obtain a homogeneous solution. The FA solution stayed at 70 °C for 20 min and then it was gradually cooled down to T_{Gel} (the temperature at which a solution transferred into gel) without any disturbance to form FA gel. The formation of the gel was recognized by inverting the glass vial.

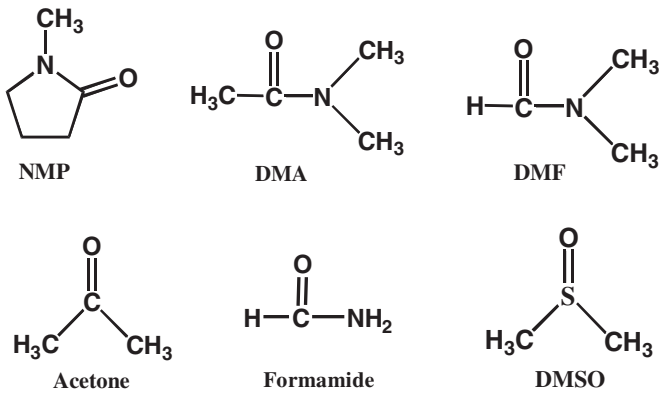

Fig. 1. Structures of the good solvents.

2.3. Preparation of FA-GA hybrid gel

The FA-GA hybrid gel was prepared by adding different amount of gelatin in the FA solution at 70 °C in a screw cap vial under stirring. After complete dissolution, the mixture was cooled to get FA-GA hybrid gel. Briefly, 0.03 g GA was added into 10 mL 0.4% (w/v) FA solution (the volume ratio of NMP/water was still 1:1) and stirred to obtain a transparent solution at 70 °C, and then the solution was cooled to T_{Gel} to obtain the FA-GA hybrid gel.

The xerogels (dried gels) were prepared by freezing the gels in liquid nitrogen and then lyophilizing in a freeze dryer system under vacuum for at least 24 h.

2.4. Properties of the FA and FA-GA hybrid gels

T_{Gel} was measured by cooling the hot solution. 10 mL FA (or FA-GA solution) prepared at 70 °C was cooled gradually with a rate of 0.5 °C. During the cooling process, the glass vial was inverted to observe whether the gel was formed. The temperature at which the gel was formed was designed as T_{Gel}.

The phase transition of gel to sol temperature (T_{GS}) was obtained usually by "falling steel ball method". 10 mL FA solution with a certain GA concentration was added into a screw cap vial and then kept at room temperature for about 1 day to ensure that the hybrid gel was stable. The vial was heated in a thermostat water bath slowly (heating rate: 1 °C min^{-1}) and a steel ball (diameter: 0.84 cm, weight: 1.45 g) was put on the top of the FA-GA hybrid gel. T_{GS} was defined as the temperature at which the steel ball can arrive at the bottom of the vial. The average value of three measurements represents T_{GS}.

The gel resistance to external pressure was measured by putting a glass rod with a diameter of 0.442 cm on the surface of the gel and applying pressure on the top of glass rod to measure the maximum pressure that the gel can endure, as shown in Fig. 2.

2.5. Dye adsorption test

In this paper, we chose CR, MB, and MO to investigate the adsorption properties of the gels. A certain amount of CR, MB and MO were dissolved in distilled water respectively to get solutions with

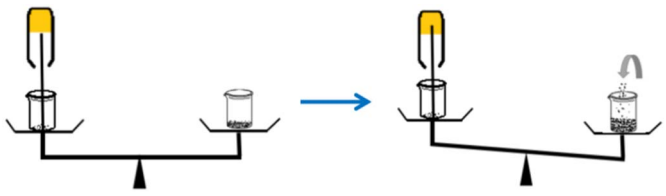

Fig. 2. Schematic drawings of the resistance to external pressure test.