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Facile preparation of conductive composite hydrogels based on sodium alginate and graphite

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ABSTRACT

Conductive composite hydrogels based on sodium alginate (SA) and graphite were obtained by a facile method of dispersing homogeneously conductive graphite into SA hydrogel matrix formed by in situ release of Ca^{2+} from Ca-EDTA, which avoids the multistep reactions and tedious purification compared to the previous work. The SA/graphite composite hydrogels exhibit reticulate and layer-type structure. The equilibrium swelling ratio of the composite hydrogels decreased with higher graphite content, although the swelling kinetics with various graphite contents was similar. The conductivity of the composite hydrogels could be tuned by adjusting f ($[Ca^{2+}]/[COO^-$ in alginate]) and the content of graphite, which reaches up to 10^{-3} S/cm.

1. Introduction

Conductive hydrogel is one kind of intelligent hydrogels in response to the electrical stimuli that combines the properties of hydrogels with the conductive components, which have significant applications in biosensor and bioelectronic devices. Conductive hybrid polymer hydrogels based on polyaniline [1–2] and polypyrrole [3] have been attracting the interest of many researchers, however, the most obvious and intractable problems for polymeric conductive hydrogels are probably the complicated synthesis procedures and poor mechanical toughness [4]. In order to improve the strength properties, carbon conducting materials such as graphite, carbon black and carbon nanotubes were added into hydrogels formed by polyacrylamide [5] and chitosan [6] to obtain the carbon conductive composite hydrogels. These composite hydrogels can be strength-enhanced, however, the preparation process is complicated via the methods of free radical polymerization and electrodepositing. Therefore, it is significant to develop a facile method via blending carbon conducting substances with polymeric hydrogels directly to obtain the conductive composite hydrogels.

Sodium alginate (SA), an anionic polyelectrolyte extracted from seaweeds [7], is the commonly used natural macromolecule as promising material for its excellent biocompatibility, biodegradation and nontoxicity. SA is a linear polysaccharide consisting of (1→4) linked β-D-mannuronate (M) and α-L-guluronate (G) residues arranged in a non-regular block pattern [8]. It is easy to form hydrogels by chelating with calcium and other divalent metal ions owing to the numerous hydroxyl groups and the large free volume between the molecular chains [9,10]. In this work, SA/graphite conductive composite hydrogels were fabricated by a facile method of dispersing homogeneously conductive graphite into SA hydrogel matrix formed by in situ release of Ca^{2+} from calcium chelate.

2. Experimental

SA (viscosity: 250–300 cps; $G/M=0.5$) and glucolactone (GDL) were received from Sigma-Aldrich. Ethylene diamine tetraacetic acid (EDTA) and graphite micropowders were purchased from Jiangsu Chemical Regent Co. Ltd., China. Sodium hydroxide was obtained from Tianjin Science and Technology Ltd. Calcium chloride and hydrochloric acid were purchased from Guangzhou Industrial Company. All the reagents were of analytical grade and used as received.

A structure parameter, f, is defined as $[Ca^{2+}]/[COO^-$ in alginate] which controls the gelation process. SA/graphite conductive composite hydrogels were prepared as followed. Firstly, 0.15 g of SA was dissolved in 5 ml deionized water by continuously stirring at room temperature till a homogeneous solution was obtained. Ca-EDTA solution was prepared by adding EDTA and $CaCl_2$ (1:1 in mole) into deionized water, pH was then adjusted to 7 with 0.1 M NaOH solution. 0.015 g of graphite micropowder was added into the 5 ml of Ca-EDTA solution and the mixture was poured into the SA solution. Finally, 3 ml of freshly prepared GDL solution which was

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determined by the calibration curve of pH versus the dosage was added to make the final pH of the solution reduce to 4. In order to disperse the graphite homogeneously, the mixture was magnetic stirred and ultrasonicated for 30 min respectively, then incubated at room temperature for 24 h. The obtained composite hydrogel was rinsed with distilled water. Raman spectra (HJY, France) and scanning electron microscope (Hitachi S-3700, Japan) were applied to characterize the structures of the freeze-dried hydrogels. The conductivities of the composite hydrogels were measured via the four-probe tester (KDY-1, Kunde Science Co., China).

Swelling ratios (SR, *g*/*g*) of the composite hydrogels were measured in distilled water at 30 °C. SR was calculated at intervals according to the following equation: $SR=(W_2-W_1)/W_1$, where W_1 is the weight of the freeze-dried hydrogel and W_2 is the weight of the swollen hydrogel.

3. Results and discussions

Raman spectra of SA hydrogel and SA/graphite composite hydrogel are shown in Fig.1. Peaks at 1324 cm^{-1} and 1584 cm^{-1} could be obviously seen in SA/graphite composite hydrogel (Fig.1b). The peak at 1324 cm^{-1} is usually associated with the vibrations of carbon atoms with dangling bonds for the in-plane terminations of disordered graphite and is labeled as the D-band; the peak at 1584 cm^{-1} (G-band) (corresponding to the E_{2g} mode) is closely related to the vibration in all sp^2 bonded carbon atoms in a 2-dimensional hexagonal lattice [11]. Optical image and SEM micrographs of SA hydrogel and SA/graphite composite hydrogels are shown in Fig.2. SA hydrogel is transparent and colorless, while SA/graphite composite hydrogel is black (Fig.2a). The surface of SA hydrogel (Fig.2b) is coarse and disorderly without any obvious

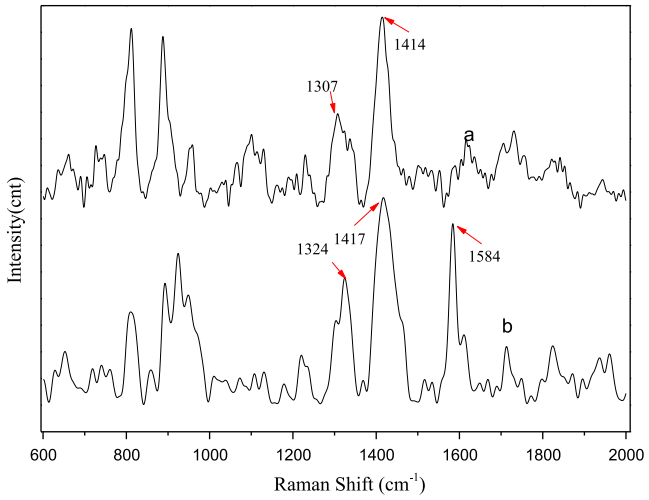

Fig. 1. Raman spectra of SA hydrogel (a) and SA/graphite composite hydrogel (b).

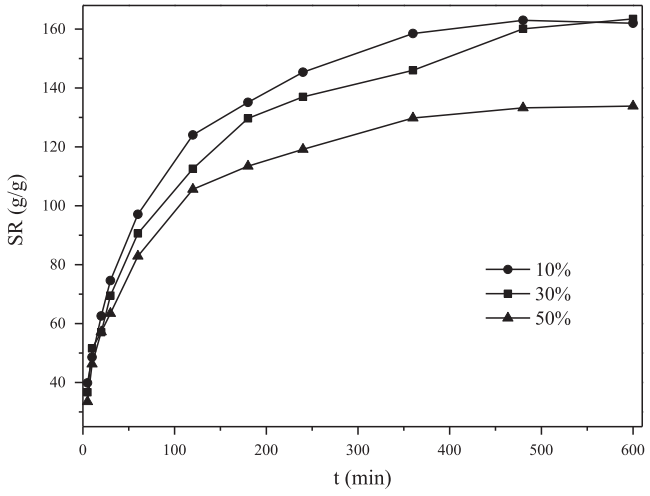

Fig. 3. SR of the SA/graphite composite hydrogels at various graphite contents (f=0.6 and T=30 °C).

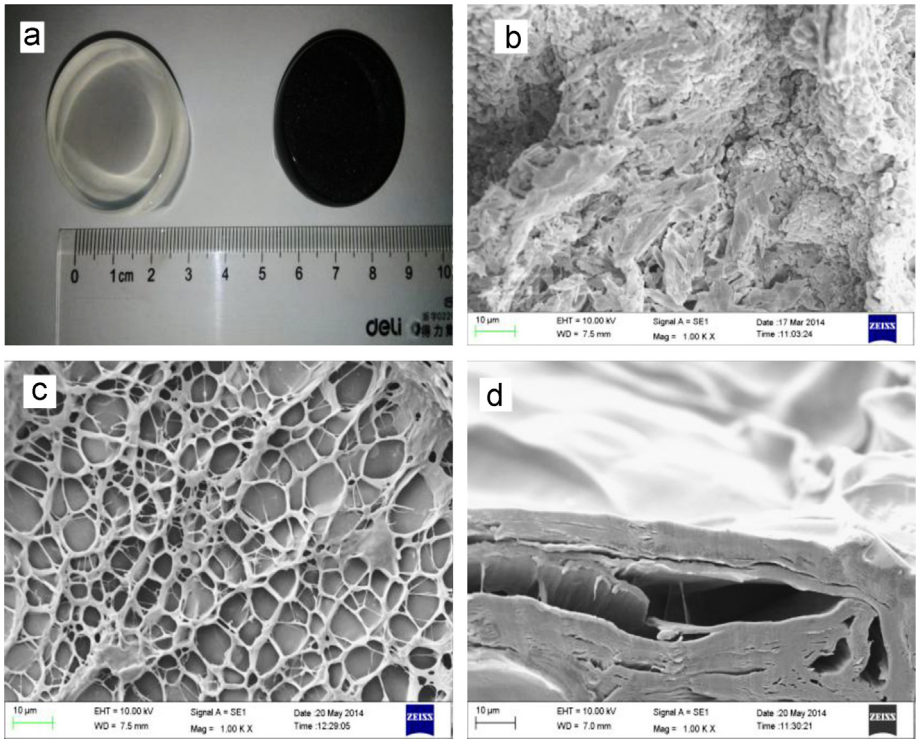

Fig. 2. Optical image (a) and SEM micrographs (b, c, and d) of SA hydrogel and SA/graphite composite hydrogel (b: surface of SA hydrogel; c & d: composite hydrogel; c: surface; and d: cross section).