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Featured Letter

Synthesis of konjac glucomannan-silica hybrid materials with honeycomb structure and its application as activated carbon support for Cu(II) adsorption

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ABSTRACT

Hybrid organic-inorganic materials are of interest for a wide range of applications in fields of biotechnology, medical science, and green chemistry. In this study, we illustrated the principles of synthesis, the structure, and the functions of a novel konjac glucomannan (KGM) based biopolymer-silica hybrid materials. Nano-silicon dioxide (SiO_2) was applied as composites, combined with KGM, to form a highly porous structure by using a simple and versatile route – freeze drying. We systematically varied the Nano-SiO_2 concentration and solution pH value, the as-prepared organic-inorganic porous materials are highly ordered and highly strengthened with an average porous diameter of 100 μm, with honeycomb structure, tailored mechanical properties, and excellent support capacity. Activated carbon (AC)-loaded porous materials (CKNSi) exhibited a high Cu(II) adsorption capacity.

1. Introduction

Hybrid organic-inorganic materials have received much attention due to their potential applications in catalysis [1], nanoscale reactors [2], bone tissue engineering [3], and optical science and engineering [4]. To date, Silica is known as the most popular reinforcing agent in polymer blends and also offers very interesting properties such as ability to modification [5]. In this respect, Vecchione et al proposed a synthetic strategy to obtain oil core-multilayered silica-biopolymer shell nanocapsules [6]; Zhao et al designed a new class of pectin–silica hybrid aerogels with low thermal conductivity, tailored mechanical properties, and minimal dust release [7]; and Singh et al reported on the development of a novel activated and hard biointerface of mesoporous silica on the nanofibrous biopolymer scaffolds [8]. Polysaccharide is a new kind of biopolymers extracted from natural lives [9]. So far, there are only a few examples introduced to synthesize hybrid organic-inorganic materials as composites of silica, such as chitin [10], acacia gum [11], and gelatin [12]. Unfortunately, less attention has been paid to the synthesis of hybrid organic-inorganic materials based on other polysaccharides and the challenging also exists that the inherent viscosity of those polysaccharides is much poor [13]. That drives us to explore a viscose biopolymer to form a strength honeycomb structure composite with silica and develop a simple and versatile route for facile production of bio-porous materials.

Herein, we prepare porous konjac glucomannan (KGM)-silica hybrid materials (KNSi) by dissolving KGM with a high purification directly into an aqueous with Nano-silicon dioxide (SiO_2) added, heating with agitating, swelling, quick-frozen with liquid nitrogen, and vacuum freeze drying. KGM is a natural polysaccharide polymer with excellent biocompatibility, biodegradability, and hydrophilicity. It has been used in materials, food, and biomedical fields [14]. We systematically varied the Nano-SiO_2 concentration and solution pH value, and designed a new class of KNSi with honeycomb structure, tailored mechanical properties, and excellent support capacity. Furthermore, we prepared activated carbon (AC)-loaded porous KGM-silica hybrid materials (CKNSi) which exhibited a high Cu(II) adsorption capacity.

2. Experimental

2.1. Chemicals and reagents

Konjac glucomannan (KGM), was obtained from San Ai Konjac Food Co. Ltd. (Yunnan, China). Nano-SiO_2 and activated carbon were purchased from Sinopharm Group Chemical Reagent Co. Ltd. (China). Purified water with a resistance greater than 18 MΩ cm^{-1} was used in all experiments.

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2.2. Synthesis and characterization of porous KNSi

1.0 g KGM was dissolved in 100 mL of 0%–2% w/w Nano-SiO_2 in purified water with agitating (1500 rad min^{-1}) for 4 min at room temperature. The pH value was adjusted from 6.0 to 9.0 and stand for 4 h. After 1 h boiling at 90 °C, the mixture was then poured into a glass petri dish and placed in refrigerator at 4 °C for 24 h to form a hydrogel. The obtained hybrid hydrogel was quick-frozen with liquid nitrogen and vacuum freeze dried for 18 h. Structures were characterized by Fourier Raman spectra (Raman, LabRAM Aramis) and NMR (Bruker AVANCE III HD 400). A nitrogen adsorption-desorption method (ASAP 2460, Micromeritics) was applied for further quantitative analysis of pore structure.

2.3. Preparation of CKNSi and Cu(II) adsorption performance

1.0 g AC powder was introduced during the agitating procedure in 2.2 before pH adjustment. Thermal behaviors were analyzed with a Synchronous thermal analyzer (STA449 F3) at 20 K/min from 28 °C to 600 °C. 0.5 g absorbents (CKNSi, KNSi or AC) in 100 mL Cu_2SO_4 solutions (50 mg/L) with shacking using an Orbital shaker (THZ-C, Taicang) at room temperature for 60 min. The concentrations of the solutions were detected by using an atomic absorption spectrophotometer (AA-6300-C, SHIMADZU) every 5 min. The uptake capacity (q) of adsorbents were calculated as follows [15]:

$$q = (C_0 - C_e)V/1000 \times w$$

where C_0 (mg/L) and C_e (mg/L) are the initial Cu(II) concentration and Cu(II) concentration after adsorption, respectively. V is the volume of the solution in mL and w is the absorbents mass in gram.

3. Results and discussion

The construction of KNSi is based on an organic-inorganic hybrids formation, and the hydrogel can be further freeze dried to form a porous materials (KNSi) shown in Fig. 1. The success of this gel formation depends on controlling and matching the gelation kinetics of both phases (silica and polysaccharide) which depend on the pH value. The mechanism of gel formation in KGM solutions results from the acetyl group in KGM was removed under alkaline conditions. However, intermolecular crystallization leads to a hard and crisp texture of the hydrogel with more alkaline added (at higher pH), which further affects the micro structure of the porous materials (Fig. 2a–c). In comparison with the reference KGM porous materials, the presence of silica sources increases the porous orderliness, slightly decreases the bulk density, and increases the specific surface area. The hybrids gelled with no silica sources do not show evidence of "porous" at all pH solutions (Fig. 2a, d, g). KNSi prepared with 1 wt% of Nano-SiO_2 shows a slightly ordered microstructure than those made of organic materials only (Fig. 2b, e, h). At the highest Nano-SiO_2 concentration (2 wt%), a clear ordered porous microstructure exists in all pH conditions (Fig. 2c, f, i). At pH of 7.5, The as-prepared organic-inorganic porous materials are highly ordered and highly strengthened with an average porous diameter of 100 μm (Fig. 2f).

We characterize the structure of the porous materials to compare the differences between KGM and KNSi. Fig. 3a shows Raman spectra for KGM and KNSi in the wavenumber of 4000–400 cm^{-1}. There is an obvious decrease of the peak in KNSi at 3400 cm^{-1}, which indicates the mass loss of the O-H in KGM after silica source added. Meanwhile, the peak around 890 cm^{-1} in KGM is from β-1,4-linkage in polysaccharide [14], but is disappeared in KNSi. Those phenomenon results from the interaction between molecules from KGM and Nano-SiO_2. The new present peaks near 520 cm^{-1} and 1440 cm^{-1} in spectra of KNSi is likely the silicon Raman peak in SiO_2 and the typical third-order Raman peak from silicon source [16]. The specified C-O-C vibration around 1100 cm^{-1} of KGM is absent in the spectrum of KNSi, demonstrating that CH_2OH at C-6 of KGM might crosslink with silicon. Three typical peak areas present in ^{13}C NMR spectrum of KGM (Fig. 3b), which are pyranose ring (70–80 ppm), C1 of both G and M units (100 ppm),

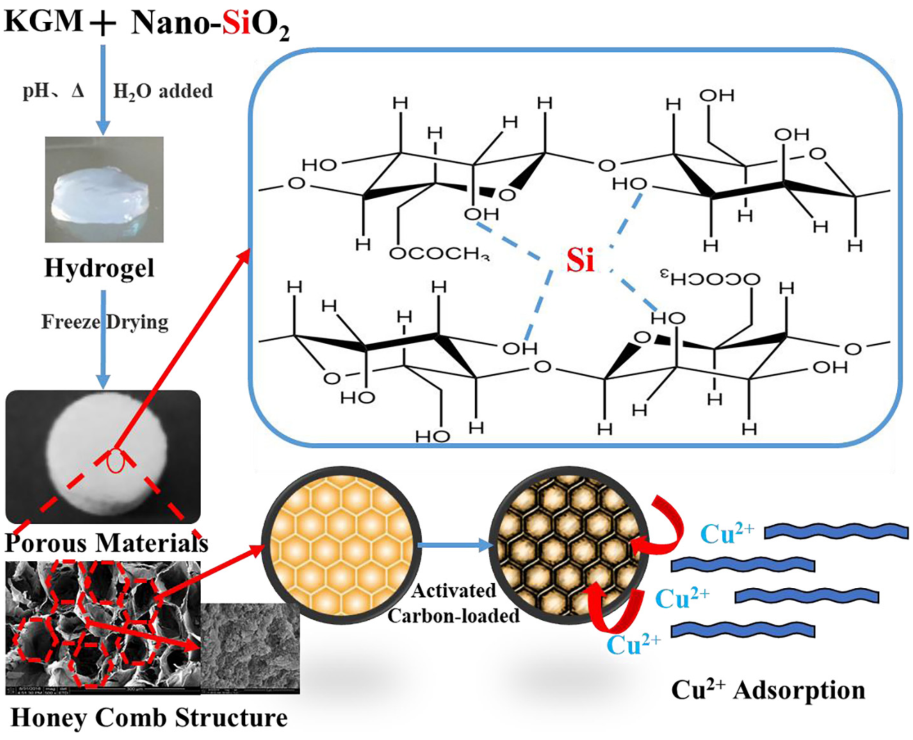

Fig. 1. Schematic representation of KNSi and CKNSi formation and SEM of honeycomb structures in KNSi.