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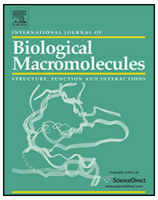

# Entrapment of carbon dioxide with chitosan-based core-shell particles containing changeable cores

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ABSTRACT

Water-soluble chitosan-based core-shell particles that contained changeable cores were successfully applied to anchor carbon dioxide. The entrapment capacity of the particles for carbon dioxide (EC) depended on the cores. It was found that EC of the particles contained aqueous cores was higher than that of the beads with water-soluble chitosan gel cores, which was confirmed with thermogravimetric analysis. In addition, calcium ions and sodium hydroxide were introduced within the particles to examine their effect on the entrapment. EC of the particles was enhanced with sodium hydroxide when the cores were WSC gel. The incorporation of calcium ions was helpful for stabilizing carbon dioxide through the formation of calcium carbonate, which was verified with Fourier transform infrared spectra and scanning electron microscopy/energy-dispersive spectrometry. This phenomenon meant the role of calcium ions for fixating carbon dioxide was significant.

## 1. Introduction

Carbon dioxide is regarded as the major origin for climate issue [1–3]. Meanwhile, it is realized that carbon dioxide is a useful carbon source for preparing chemicals. Several strategies including capture, storage and conversion have been proposed to deal with the excess emission of carbon dioxide [4–6]. Among the reported methods for capturing carbon dioxide, adsorption is well developed and solid sorbents such as metal organic frames (MOFs) and microporous polymer (MOPs) are mostly adopted [7–9]. However, the high costs for preparing solid sorbents as well as other shortcomings make their applications limited. On the other hand, the aqueous solutions that contain potassium carbonate or carbonic anhydrase are considered as benign media for hydration of carbon dioxide, but several practical problems need to be solved [10].

Hydrogel is a three-dimensional hydrophilic network and is capable of imbibing large amounts of water. A variety of hydrogels have been widely applied in pharmaceutical and biomedical fields [11,12]. It is anticipated that the hydrogel is a kind of promising candidate for hydrating carbon dioxide. In order to take the advantages of hydrogel and chitosan, we have prepared chitosan-based hydrogel particles via the physically cross-linking between water-soluble chitosan (WSC) and sodium alginate (SA). The particles are able to bind hydrogen sulfide [13]. It is the basic amino groups on the backbone of WSC make the chitosan-based hydrogel particles acid-philic. Therefore, chtosan-based hydrogel particles may be good reservoirs for entrapping acidic carbon dioxide.

According to what mentioned above, chitosan-based hydrogel particles are potential media to investigate the role of hydration, the $CO_2$-philic property or their combination in anchoring carbon dioxide. Recently, we have obtained core-shell particles with WSC gel or aqueous solution cores by using WSC and SA as starting materials as well [14]. We consider these core-shell particles are suitable platforms for our goal. In order to enhance the fixation capacity of the particles toward carbon dioxide, two means were taken into account and examined. The tunable core-shell particles were pretreated with sodium hydroxide of various concentrations including 0, 1 and 2 M before entrapping. On the other hand, the carbon dioxide entrapped within the particles was mineralized through combining with calcium ions. No similar work has been reported so far. The current experimental results show the particles with tunable cores are good candidates and the mineralization strategy is efficient for capturing carbon dioxide.

## 2. Experimental

### 2.1. Materials

Water-soluble chitosan (WSC, the percentage of $-CO-CH=CH-COOH$ was 19.6%) was prepared in our lab via

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the esterification reaction between chitosan (minimum 90% deacetylation, viscosity average molecular weight was $2.1 \times 10^6$) and maleic anhydride [15]. Sodium alginate (SA, number average molecular weight was ca. $3.3 \times 10^4$), calcium chloride, sodium hydroxide (NaOH), sodium carbonate, hydrochloric acid (HCl), sulfuric acid, and disodium hydrogen phosphate were all analytical grade reagents, purchased domestically and used as received.

### *2.2. Entrapment of carbon dioxide onto core-shell particles with tunable cores*

Chitosan-based hydrogel core-shell particles with tunable cores were prepared according to our previous report [14]. Briefly, SA-WSC layer was formed around WSC gel cores through static-electric self-assembly to obtain core-shell particles SA-WSC@WSC. Subsequently, Ca-SA-WSC@WSC beads were formed by treating SA-WSC@WSC spheres with saturated calcium chloride. The core-shell particles Ca-SA-WSC@O were generated by maintaining Ca-SA-WSC@WSC beads in 1 M HCl.

A predetermined amount (ca 1 g) of Ca-SA-WSC@WSC or Ca-SA-WSC@O particles were added into a bottle that contained 100 mL distilled water, 1 M or 2 M NaOH solution respectively, and purged with carbon dioxide produced from sodium carbonate and diluted sulfuric acid for 5 h. Then, the particles were contacted with 50 mL saturated calcium chloride for 20 min, filtered and rinsed with water to remove the Ca(II) ions remained on the surfaces. The obtained particles, represented as Ca-SA-WSC@WSC-$CaCO_3$ and Ca-SA-WSC@$CaCO_3$, was stored in sealed bottles for analyzing.

In order to verify the combination between calcium ions and carbonate, calcium phosphate (CP) was formed within the particles with tunable cores. A predetermined amount (ca 1 g) of Ca-SA-WSC@WSC or Ca-SA-WSC@O particles were immersed in 200 mL saturated calcium chloride for 1.5 h, filtered and rinsed with water to remove the Ca(II) ions remained on the surfaces. The obtained Ca-SA-WSC@WSC-Ca(II) or Ca-SA-WSC@Ca(II) particles were immersed in 120 mL solution that contained disodium dihydrogen phosphate for 20 min to obtain Ca-SA-WSC@WSC-CP or Ca-SA-WSC@CP particles.

### *2.3. Measurements*

Fourier transform infrared (FTIR) spectra of Ca-SA-WSC@O, Ca-SA-WSC@$CaCO_3$ and Ca-SA-WSC@CP particles were recorded using a Shimadzu DTG-60H spectrometer. Thermogravimetric analysis (TGA) of dried Ca-SA-WSC@O, Ca-SA-WSC@WSC, Ca-SA-WSC@$CaCO_3$, Ca-SA-WSC@CP and Ca-SA-WSC@WSC-CP particles were performed with a TA V2.4F thermoanalyzer, which was conducted over the temperature range from 25 to 800 °C with a programmed temperature increment of 10 °C/min under $N_2$ atmosphere. The air-dried Ca-SA-WSC@$CaCO_3$ and Ca-SA-WSC@CP particles were examined with a Hitachi SU8010 scanning electron microscopy/energy-dispersive spectrometry (SEM/EDS).

### *2.4. Results and discussion*

Ca-SA-WSC@WSC and Ca-SA-WSC@O represent core-shell particles with water-soluble chitosan hydrogel and aqueous cores respectively. Several inherent characteristics make them suitable for entrapping carbon dioxide. Firstly, the outer shell Ca-SA-WSC is a hydrophilic and porous interpenetrated network, which is composed of calcium alginate hydrogel and the polyelectrolyte complex of SA and WSC. Thus, it is anticipated that water-soluble substances are easily to exchange through this shell. Secondly, there are $CO_2$-philic groups and a certain amount of water within the cores of Ca-SA-WSC@WSC, whereas much greater amount of water existed in the cores of Ca-SA-WSC@O. Obviously, the role of hydration and selective adsorption for Ca-SA-WSC@WSC and Ca-SA-WSC@O toward carbon dioxide are different.

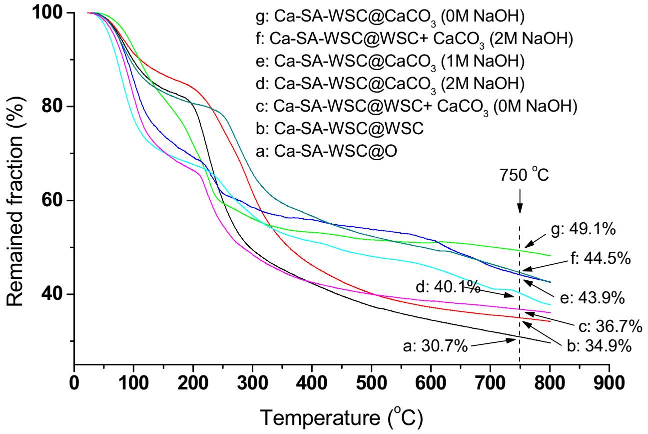

**Fig. 1.** Thermogravimetric analysis curves of Ca-SA-WSC@O, Ca-SA-WSC@WSC and Ca-SA-WSC@$CaCO_3$ particles.

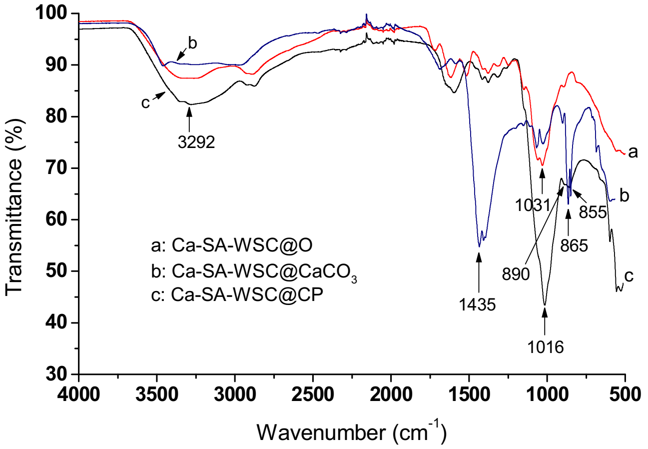

**Fig. 2.** Fourier transform infrared spectra of Ca-SA-WSC@O, Ca-SA-WSC@$CaCO_3$ and Ca-SA-WSC@ CP particles.

Owing to the fact that the core-shell particles are hydrophilic, there is water in the samples. In fact, the compositions of the samples are variable. Thus, the amount and state, i.e. bound or free [11], of water in the samples are different. As shown in Fig. 1, all the profiles of samples exhibit an initial stage to remove water and the removal rate is various accordingly. Subsequently, the decomposition of the samples can be regarded as one stage, which is attributed to the degradation of polymeric components. Though the degradation processes of the samples are varied with changing their compositions, the residues at the temperature higher than 700 °C represent those difficult to decompose further. It is found that the remained fractions (RFs) of Ca-SA-WSC@O, Ca-SA-WSC@WSC, Ca-SA-WSC@$CaCO_3$ and Ca-SA-WSC@WSC-$CaCO_3$ at 750 °C are 30.7, 34.9, 49.1 and 36.7% respectively. RF of Ca-SA-WSC@$CaCO_3$ or Ca-SA-WSC@WSC-$CaCO_3$ particle obtained without pretreatment is higher than that of the particles that contain aqueous cores or WSC gel respectively, which indicates that something has been produced within the core-shell particles. FTIR analysis results have verified that the formed substances within the cores are $CaCO_3$ (Fig. 2). Compared to the FTIR spectra of Ca-SA-WSC@O, two extra characteristic peaks appear at 865 and 1435 $cm^{-1}$ on that of Ca-SA-WSC@$CaCO_3$. The absorption peaks are assigned to those of $CaCO_3$ [16]. In other words, carbon dioxide has been bound or hydrated within the cores of Ca-SA-WSC@WSC or Ca-SA-WSC@O particles. The difference of