



# Tunable core–shell particles generated from smart water-soluble chitosan seeds



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## ABSTRACT

A chain-like route was presented to create various core–shell particles with soft, aqueous or inorganic cores respectively. Water-soluble chitosan (WSC) gel particles were obtained through gelating the aqueous WSC solution of 0.02 g/mL at its isoelectric point. Then, polyelectrolyte complexes were formed and surrounded on the outer surfaces of WSC gel particles by immersing the particles in 2 wt% aqueous sodium alginate. Soft WSC cores in these core–shell particles disappeared after maintaining the particles in 1 M HCl for 6 h. The cores of obtained particles at this step became aqueous, and could be further transformed into inorganic ones via contacting the particles with copper sulfate and sodium sulfide aqueous solutions successively. The composition of the shell was verified with Fourier transform infrared spectroscopy. The formation of various core–shell particles was confirmed with digital photographic observation, thermogravimetric and fluorescence analyses. The whole process was a chain-like one and was able to stop at any stage to harvest a corresponding target.

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## 1. Introduction

Polymer-based core–shell particles are attractive, and they have been applied in a lot of fields recently (Kang, Baginska, White, & Sottos, 2015; Kempe, Noi, Ng, Müller, & Caruso, 2014; Latnikova & Yildirim, 2015; Soppimath, Tan, & Yang, 2005; Xiao, Chu, Chen, Wang, & Li, 2003). Their versatile architectures and characters make them quite charming. The common core–shell particles are various core materials encapsulated with polymer shells. Among these particles, the cores may be active or inert polymers, liquid compounds or inorganic substances (Hellweg, 2013; Sun et al., 2014), and the composition, molecular weight and property of the polymeric shells can be quite different. In addition, the polymers can be stimuli-responsive or possess special structure like macroporous one (Gan & Lyon, 2001; Menzel, Cambón, & Yeates, 2013).

Usually, the core–shell particles are formed through polymerization, self-assembly or solvent removal technique (Haag, 2004; Suthiwangcharoen et al., 2014; van Zyl, Sanderson, de Wet-Roos, & Klumperman, 2003; Zuo, Liu, & Han, 2014). Indeed, a variety of particles with various core–shell structures have been fabricated by using these methods. However, the components, morphology and properties of the formed particles are fixed for each

system. In other words, one synthesis route can produce only one kind of particles. For example, in order to take advantage of the thermo-sensitive property of poly(N-isopropylacrylamide) (PNIPAM), PNIPAM-based core–shell particles are prepared via two ways. One is to prepare core–shell microgels through the emulsion polymerization of N-isopropylacrylamide (NIPAM) and N-isopropylmethacrylamide (NIPMAM) monomers (Berndt, Pederson, & Richtering, 2005), and the other one is to form PNIPAM-based core–shell nanostructure via Michael-addition reaction of PNIPAM-NH<sub>2</sub> and vinyl terminal of a hyperbranched polymer (You, Hong, & Pan, 2009). Obviously, not only the synthesis procedure, but also the composition, morphology and properties of two kinds of PNIPAM-based particles are quite different.

Is there any other facile way to develop new members of core–shell particles? This is an issue for whom pays attention to the core–shell particles. It is well known that nature grows things step by step and provides us a series of relevant but completely different objects. This reminds us to learn something from nature to design an effective way for preparing core–shell particles. Herein, we present a strategy to generate various core–shell particles at different stages. By adding different compounds, one can harvest corresponding particles with core–shell structure from the same procedure. In order to carry out this goal, we need an intelligent seed. A substance which is sensitive to the external stimuli is able to grow or disappear under suitable condition. We have demonstrated that the hydrogels prepared from water-soluble chitosan exhibit

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multi-sensitive behaviors (Xiao & Sun, 2013; You, Xiao, Zhang, & Dong, 2015). Thus, we consider water-soluble chitosan may be a suitable seed for creating core-shell particles in a novel way.

## 2. Experimental

### 2.1. Materials

Water-soluble chitosan (WSC, the content of  $-\text{CO}-\text{CH}=\text{CH}-\text{COOH}$  was 19.6 wt%) was prepared in our lab according to the method reported previously (Xiao & Sun, 2013). Sodium alginate (SA, number average molecular weight was ca.  $3.3 \times 10^4$ ) was dried before use. Calcium chloride, citric acid, sodium carbonate, sodium bicarbonate, sodium dihydrogen phosphate, disodium phosphate, copper sulfate ( $\text{CuSO}_4$ ), and sodium sulfide ( $\text{Na}_2\text{S}$ ), were all analytical grade reagents purchased domestically and used as received.

### 2.2. Formation of WSCA-based core-shell particles

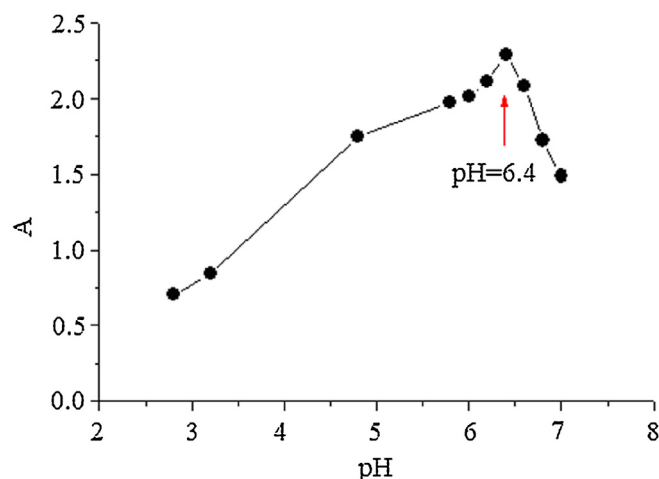
WSC gel spheres were obtained by adding 0.02 g/mL WSC solution into buffer saline of pH 6.4 drop by drop and being kept for 10 min to provide compact beads. WSC spheres were removed by filtering, rinsed with distilled water, and served as initial cores. WSC cores were immersed in 2 wt% SA solution for 1 min, removed and washed to offer the first kind of core-shell particles, which was represented as SA-WSC@WSC. SA-WSC@WSC spheres were placed into saturated calcium chloride for 30 s, filtered, rinsed with distilled water to form the second kind of core-shell particles, which was represented as Ca-SA-WSC@WSC. Subsequently, Ca-SA-WSC@WSC beads were maintained in 1 M HCl for 6 h, filtered, and rinsed with distilled water to generate the third kind of core-shell particles, which was noted as Ca-SA-WSC@O (O represented aqueous solution). Then, Ca-SA-WSC@O capsules were immersed in 0.5 mg/mL copper sulfate for 10 min, filtered and rinsed with water to remove the Cu(II) ions remained on the surfaces. Finally, Ca-SA-WSC@O capsules that contained copper ions (Ca-SA-WSC@Cu(II)) were kept in saturated  $\text{Na}_2\text{S}$  for 30 min, removed and washed to obtain the fourth kind of core-shell particles, which was labeled as Ca-SA-WSC@CuS.

### 2.3. Characterizations

Two milliliter WSC aqueous solution of 0.1 wt% was mixed with 3 mL 0.2 M buffer solution of different pH values respectively, and the absorbencies at 291.0 nm were recorded with a Shimadzu UV-2450 UV-Visible spectrophotometer immediately as the solution was homogeneous. Powdered WSC-SA and WSC-SA gel was mixed with dry KBr and compressed into disk respectively. Then, Fourier transform infrared (FTIR) spectra of the samples were recorded using a Nexus 470 FTIR spectrometer. Thermogravimetric analysis (TGA) of dried Ca-SA-WSC@WSC, Ca-SA-WSC@O and Ca-SA-WSC@CuS samples 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  $\text{N}_2$  atmosphere. The fluorescence spectra of CuS, Ca-SA-WSC@O, Ca-SA-WSC@WSC and Ca-SA-WSC@CuS suspension solutions were recorded at emission wavelength  $\lambda_{\text{em}} = 350$  at 1200 nm/min scan speed using an F-7000 FL fluorescence spectrometer. The visual change of the particles was recorded with a Nikon D3X digital camera directly.

## 3. Results and discussion

In our earlier research, it is found that WSC is soluble in neutral water and can carry out ionically cross-linking with an anionic



**Fig. 1.** pH-triggered sol-gel transition of the WSC aqueous solution (2 mL 0.1% WSC aqueous solution was mixed with 3 mL buffer solution of a certain pH values, and the absorbency at 291 nm were recorded immediately as the solution was homogeneous).

polysaccharide (Xiao & Sun, 2013; You et al., 2015). There are lots of amino and  $-\text{CO}-\text{CH}=\text{CH}-\text{COOH}$  groups on the WSC chains, i.e. it is an ampholyte. As shown in Fig. 1, the isoelectric point of WSC is 6.4. It is anticipated that WSC aqueous solution is pH-sensitive. In fact, WSC aqueous solution is gelatinated when pH value of the solution reaches its isoelectric point. Moreover, this sol-gel transition is reversible when the pH value of the medium is changed. Such a responsive transition can be regarded as a growing up or dying away process. In other words, WSC is a potential smart seed for generating core-shell particles in the way we designed.

The chain-like strategy to construct various core-shell particles is shown in Scheme 1. The procedure includes the formation of cores, the growth and enhancement of shells, the erosion of the original cores and regeneration of new cores. Firstly, we drop WSC aqueous solution (Scheme 1a) into buffer saline to prepare WSC gel beads (Scheme 1b) by taking advantage of the pH-sensitive character of WSC. The obtained WSC gel beads are employed as seeds to produce core-shell particles. Secondly, we conduct the self-growth of shell via anchoring SA onto the cores. There are positively charged groups on the surfaces of WSC gel beads, which enable the molecular recognition and self-assembly of oppositely charged SA toward WSC gel beads occur (Harada & Kataoka, 1999). As a result, a polyelectrolyte complex shell is formed around every bead to produce core-shell spheres (Scheme 1c, SA-WSC@WSC). For avoiding the penetration of SA into the cores, the WSC gel beads should be compact enough and the time of the seeds contacting with SA solution must be well controlled. The shells of the spheres formed in such a way may be weak and labile. Thirdly, we strengthen the particles through further physically cross-linking. Herein, the property of easy combination between calcium ions and SA is adopted to offer enhanced core-shell spheres (Scheme 1d, Ca-SA-WSC@WSC). Fourthly, we form core-shell spheres with aqueous cores. In viewing of WSC is pH-sensitive and soluble in water, once we keep Ca-SA-WSC@WSC spheres in dilute acid solution for a pre-determined time, the WSC gel cores will transform into solution and diffuse into the aqueous medium outside the shell. As a consequence, the spheres become soft capsules with aqueous cores (Scheme 1e, Ca-SA-WSC@O). It is such a kind of core enables us to carry out the fifth step to obtain core-shell particles with new cores. One application of the polymeric capsules, Ca-SA-WSC@O, is to be utilized as templates to form core-shell particles with inorganic cores (Sasidharan & Nakashima, 2014). Being contacted with copper sulfate solution, the aqueous cores of Ca-SA-WSC@O

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