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## Synthesis and characterization of chitosan:SiO<sub>2</sub> nanocomposite by ultrasonic spray drying

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**Abstract.** Chitosan:SiO<sub>2</sub> nanocomposite (Cs:SiO<sub>2</sub> NCs) is synthesized via aerosol processing. Ultrasonic spray drying apparatus was used to produce smaller sized composite particles with spherical morphology. Composite from shrimp shell and water glass (Na<sub>2</sub>SiO<sub>3</sub>) as silica precursor were used for the preparation. Cs:SiO<sub>2</sub> NCs were characterized by Fourier Transform Infrared (FTIR) spectroscopy and scanning electron microscopy (SEM) to know about the chemical bonding and morphology of the particles, respectively. Based on the FTIR investigation the absorption peak at 1090 cm<sup>-1</sup> represents the reaction of silanol groups of silica with carbonyl groups of polymers leading to the formation of Si-O-C bonds. The morphology of Cs:SiO<sub>2</sub> NCs was more spherical than chitosan particles with relatively narrow size distribution. The smaller particle size of Cs:SiO<sub>2</sub> NCs is potentially applied to engineer the material for drug delivery system.

### 1. Introduction

Nowadays, Matrix formulation has become an essential step in the development of drug delivery systems. Chitosan is a polysaccharide obtained from the deacetylation of chitin, which is widely used as a drug delivery system for gene delivery, implants and nasal, oral, parental and transdermal administration [1]. Chitosan can be prepared by ionic cross-linking between positively charged amino groups of the chitosan chains and negatively charged polymers or ions such as tripolyphosphate (TPP) [2].

The addition of inorganic oxides to chitosan in order to impart resistance to microbial attack, higher mechanical strength, enhanced thermal stability, negligible swelling in organic solvents, and modifiable textural properties, can be an alternative way to increase its chemical and mechanical



stability [3]. Among the inorganic oxides,  $\text{SiO}_2$  is an interesting choice for the formulation of an organic-inorganic composite carrier. Over the past years, the sol-gel process was widely used to create novel hybrid nanoscale materials based on organic and inorganic components [4]. This approach can produce particles at low temperature and pressure.

The advanced utility of chitosan: $\text{SiO}_2$  composite for the development drug carrier can be accomplished by controlling its morphology. The method proposed to obtain particles with a controlled morphology is spray drying, in particular, ultrasonic spray drying is one of the aerosol-assisted spray methods employing ultrasonic nebulizer [5]. By using ultrasonic nebulizer fine droplets in the range of 1-10  $\mu\text{m}$ , particles can be produced which is smaller than particles attained by a nozzle or rotary atomizer [6].

In this work, chitosan: $\text{SiO}_2$  nanocomposite cross-linked with TPP was synthesized by ionotropic-sol gel method using water glass ( $\text{Na}_2\text{SiO}_3$ ) as the silica precursor. The controlled morphology of particles was achieved by ultrasonic spray drying apparatus. The presence of functional groups, the morphology of the particles, and the size distribution of the obtained particles was investigated. In addition, the mechanism of ionotropic-sol gel method was also proposed.

## 2. Materials and methods

### 2.1. Materials

Chitosan was received from commercially available flakes chitosan (>80% deacetylated) in Cirebon, West Java. The raw material of chitosan was pulverized using ball milling to obtain uniform sized powder by sieving with 100 mesh and subjected to further experiments and analysis. Sodium tripolyphosphate (TPP), water glass ( $\text{Na}_2\text{SiO}_3$ ), acetic acid ( $\text{CH}_3\text{COOH}$ ), was purchased from Brataco, Co., Ltd. (Bandung, Indonesia). Distilled water was used for all sample preparation.

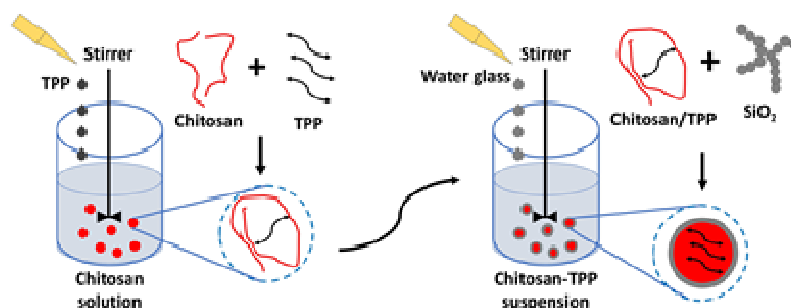


Figure 1. Schematic ionotropic-sol gel process.

### 2.2. Synthesis and characterization

Schematic ionotropic-sol gel process of the chitosan- $\text{SiO}_2$  nanocomposite is shown in figure 1. Briefly, 0.1 g of chitosan dissolved in 200 ml of 1% v/v acetic acid solution at room temperature. The solution was stirred at 600 rpm for 120 min to ensure complete dissolution of the polymer. Chitosan was cross-linked by adding 40 ml of 0.07% (w/v) TPP solution dropwise with a gravitational syringe, and then further stirred at 600 rpm for 60 min. The cross-linked chitosan was coded as Cs NPs. A 6 ml of water glass precursor was added dropwise to the chitosan-TPP solution to prepare nanocomposite. After the addition of water glass, the solution changes from transparent to opalescent. Opalescence occurs due to the hydrolysis of sodium silicate and polycondensation reaction in the chitosan-TPP solution to form an inorganic network in the presence of organic polymer, and the composite particles is coded as Cs: $\text{SiO}_2$  NCs.

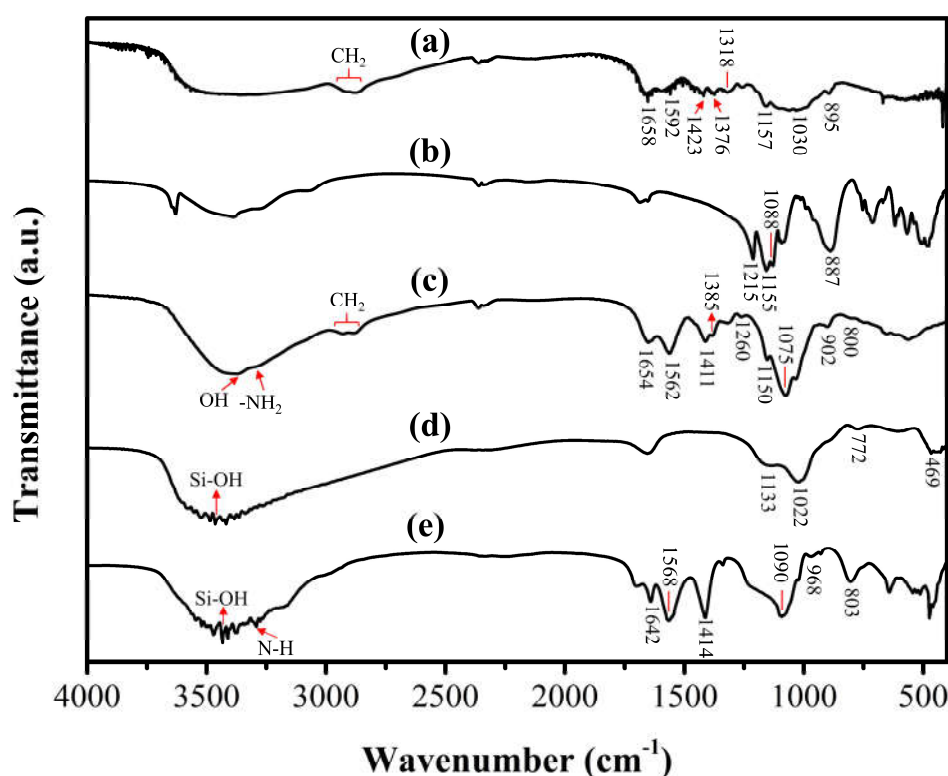
To form structured Cs NPs and Cs: $\text{SiO}_2$  NCs, the colloidal suspension was spray-dried using ultrasonic nebulizer [7]. The temperature of the reaction tube was set at 80°C based on the drying temperature of the suspension, and also related to the residence time of the droplets inside the reactor. Air compressor was used as carrier gas with a flow rate of 5 L/min and the dry powder was collected

by an electrostatic precipitator. The functional groups of chitosan and chitosan-SiO<sub>2</sub> nanocomposite were characterized by Fourier-transform infrared (FTIR) analysis (Shimadzu prestige 21) operating in the wavenumber range of 400–4000 cm<sup>-1</sup> with KBr as a beam splitter. The morphology of the particle was characterized by SEM Hitachi SU 3500 measurements.

### 3. Results and discussion

#### 3.1. FTIR analysis

The functional groups present in the spray-dried Cs NPs and Cs:SiO<sub>2</sub> NCs are compared with raw Cs, TPP, and water glass by FTIR analysis. The FTIR spectrum of raw Cs (Figure 2 (a)), shows broadband at range 3200–3400 cm<sup>-1</sup> which is contributed to different vibrations, namely hydrogen bonded O–H stretching at around 3400 cm<sup>-1</sup> and NH stretching involved in hydrogen bonding at 3200 cm<sup>-1</sup> [8]. The absorption band at 2873 cm<sup>-1</sup> is related to the C–H stretching vibrations. The absorption peak at about 1658 cm<sup>-1</sup> represents C=O stretching of the amide I band. The band at 1592 cm<sup>-1</sup> corresponds to the vibrations of -NH (N-acetylated residues, amide II bands) and peaks at 1423 cm<sup>-1</sup> and 1376 cm<sup>-1</sup> are attributed to -CH<sub>2</sub> wagging coupled with -OH in plane deformation [8]. The smaller peak at 1318 cm<sup>-1</sup> is ascribed C–N stretching of amide III.



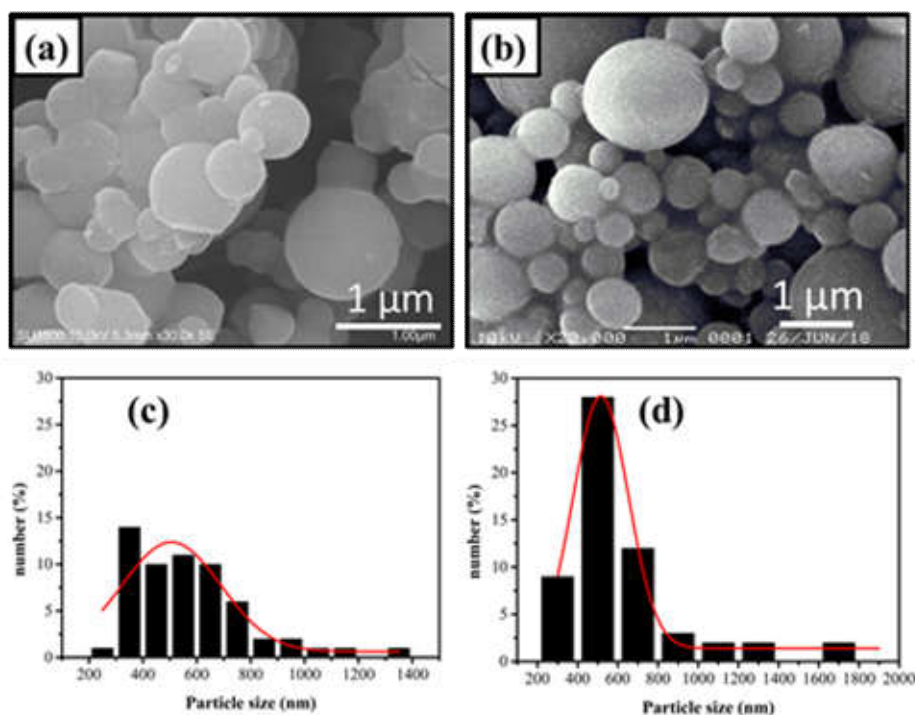
**Figure 2.** FTIR Spectra of (a) raw chitosan, (b) TPP, (c, e) Cs NPs and Cs:SiO<sub>2</sub> prepared by ultrasonic spray drying, (d) pure water glass.

The peak at 1157 cm<sup>-1</sup> is assigned to asymmetric stretching vibrations of glycosidic linkage (C–O–C). The absorption band in the region of 1030 cm<sup>-1</sup> is associated with the C–O stretching vibration and peak at 895 cm<sup>-1</sup> corresponds to the saccharide structure. Figure 2 (b) represent the FTIR spectra of sodium tripolyphosphate (TPP) as a cross-linking agent that shows the absorption band at 1215 cm<sup>-1</sup> corresponding to P=O stretching vibration. The peak at 1155 cm<sup>-1</sup> is related to the symmetrical and asymmetric stretching vibration of the PO<sub>2</sub> groups. Two bands at 1088 cm<sup>-1</sup> and 887 cm<sup>-1</sup> are due to

the symmetric and asymmetric stretching vibration of the  $\text{PO}_3$  groups and Stretching vibration of P–O–P bridge, respectively [9].

FTIR spectrum of spray-dried Cs NPs is shown in Figure 2 (c). The peak between  $3372\text{ cm}^{-1}$  and  $3290\text{ cm}^{-1}$  become sharper which is indicative of the enhanced O–H and N–H groups. The weak absorption band in the region of  $2931\text{--}2882\text{ cm}^{-1}$  is due to the presence of C–H stretching vibration. The amide I band at  $1658\text{ cm}^{-1}$  was shifted to  $1654\text{ cm}^{-1}$  in the Cs NPs. The absorption peak at  $1592\text{ cm}^{-1}$  was reduced and a new peak appeared at  $1562\text{ cm}^{-1}$  confirming that amino groups were cross-linked by phosphate anion (N–O–P) [10]. The band at  $1260\text{ cm}^{-1}$  which indicates P=O stretching and P–O bending, occurs at  $800\text{ cm}^{-1}$  [11].

Figure 2 (d) and (e) shows the FTIR peaks for water glass ( $\text{Na}_2\text{SiO}_3$ ) and spray-dried Cs: $\text{SiO}_2$  NCs, respectively. The broadband of water glass at  $3420\text{ cm}^{-1}$  is attributed to Si–OH stretching vibration bounded with water molecules [12]. The two characteristic peaks at  $1022\text{ cm}^{-1}$  and  $772\text{ cm}^{-1}$  are assigned to Si–O bending vibration and asymmetric stretching vibration of the siloxane bonds (Si–O–Si). The absorption peak at  $469\text{ cm}^{-1}$  corresponds to Na–O bond structure. After addition of water glass, the presence of amino groups in the Cs surface facilitates the hydrolysis of water glass and condensation of the created silanol groups (Si–OH) [13] as seen at  $3372\text{ cm}^{-1}$  and  $968\text{ cm}^{-1}$  (figure 2 (d)). Specific bands in the region of  $1000\text{--}1250\text{ cm}^{-1}$  reveals the characteristic absorption for Si–O–Si bond after the complete condensation of water glass [14]. On the other hand, the silanol groups of silica can interact with carbonyl groups of polymer to form of Si–O–C bonds as assigned by a peak at  $803\text{ cm}^{-1}$ .

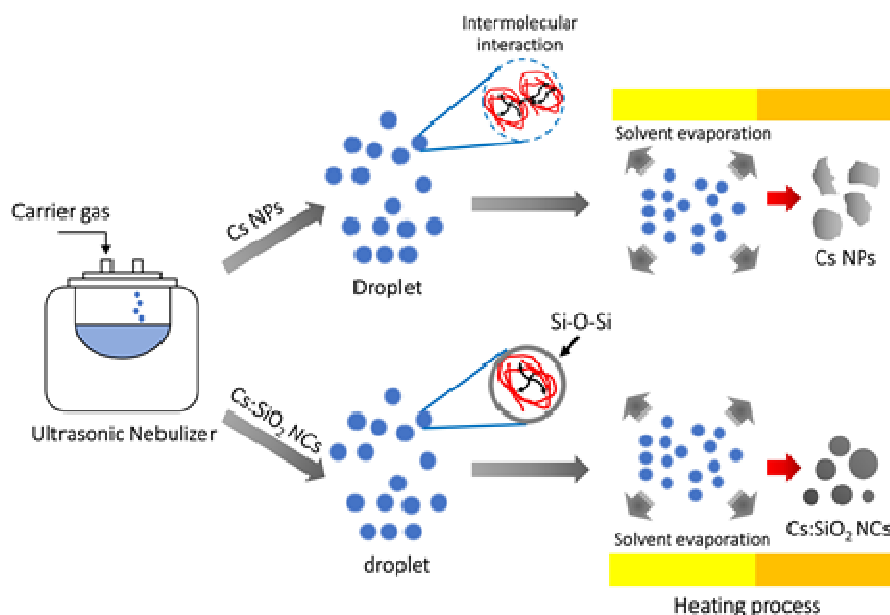


**Figure 3.** (a-b) SEM images of Cs NPs and Cs: $\text{SiO}_2$  (c-d) size distribution of CS NPs and Cs: $\text{SiO}_2$  NCs prepared by ultrasonic spray drying.

### 3.2. Morphology of particles

Scanning electron microscopy (SEM) was used to observe the morphology of the Cs NPs and Cs: $\text{SiO}_2$  NCs prepared by ultrasonic spray drying. Figure 3 (a) shows the Cs NPs have nearly spherical in shape with agglomerated particles indicated with a red arrow, while the Cs: $\text{SiO}_2$  NCs have a compact spherical shape. The agglomerated particles of Cs NPs after spray drying are due to the interaction of polyanions (TPP) and chitosan during the synthesis process. At the end of addition of polyanions,

chitosan molecules are completely cross-linked and excess TPP got involved in intermolecular cross-linking resulting in larger particle size or agglomeration [15]. On the other hand, Cs:SiO<sub>2</sub> particles have a compact shape (figure 3 (b)) due to the hydrolysis and condensation of water glass. Therefore, it is suggested that the SiO<sub>2</sub> on the surface are bound with polymer forms some –Si–O–Si– chains covering the surface of Cs:SiO<sub>2</sub> NCs to prevent the excess intermolecular cross-linking by TPP anions. The particle size distribution calculated from SEM images using the Image-J free software is shown in figure 3 (c-d). Generally, the Cs NPs and Cs:SiO<sub>2</sub> have a mean size distribution at around 500 nm obtained by ultrasonic spray drying. However, the Cs NPs droplet produced by ultrasonic atomizer which have intermolecular interaction between chitosan particles tend to bring them together and generate broader distribution (figure (c)). In contrast, Cs:SiO<sub>2</sub> droplet containing –Si–O–Si– chains covering the surface particles achieved irregular to compact spherical shape with relatively narrow size distribution (figure (d)). Based on FTIR analysis and SEM observation, The possible formation of Cs NPs and Cs:SiO<sub>2</sub> NCs were obtained by ultrasonic spray drying as illustrated in figure 4.



**Figure 4.** Schematic illustration of Cs NPs and Cs:SiO<sub>2</sub> NCs formation prepared by ultrasonic spray drying.

#### 4. Conclusion

Cs:SiO<sub>2</sub> nanocomposite has been successfully prepared by ultrasonic spray drying with a compact spherical shape and relatively narrow distribution of particles. Furthermore, the TPP as anions play a crucial role in Cs NPs synthesis, it can be concluded that the intermolecular interaction between chitosan molecules along with the cross-linking tends to make the particle agglomerated or leads to a formation of large particles. It is established that Cs:SiO<sub>2</sub> NCs prepared by spray drying have greater potential as a drug delivery agent.

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