

IMMOBILIZATION AND STABILIZATION OF TiO₂ NANOPARTICLES IN ALKALINE-SOLIDIFICATED CHITOSAN SPHERES WITHOUT CROSS-LINKING AGENT

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Abstract- TiO₂ nanoparticles have been shown to have wide applications in multiple fields. The combining of polymer and TiO₂ nanoparticles to form films or hydrogel materials has further advantages such as reusable, non-aggregated, recyclable and good dispersible. Although the chitosan particles can be easily obtained by crosslinking method, the cytotoxicity of some commonly used crosslinking agents has made it limited in biological applications. In this article, a facile approach to synthesis of TiO₂ nanoparticles-chitosan composite spheres without crosslinking agents was presented. The proposed approach can stabilize and disperse TiO₂ nanoparticles in chitosan matrix, and form chitosan spheres by an alkaline solidification process. The diameter of the synthesized spheres is ranging from 1.5 μm to 2.5 μm. With UV-Visible spectroscopy, EDS, XRD and FTIR, TiO₂ nanoparticles were shown to be embedded in the synthesized spheres. The fabricated spheres are potential for multi-filed applications, such as bactericide, wastewater pollutant treatment, and the others.

Keywords - TiO₂ nanoparticles, chitosan spheres, solidification

I. INTRODUCTION

In the past two decades, titanium dioxide (TiO₂) has wide applications on multidisciplinary areas due to its excellent properties such as nontoxic [1], ultraviolet (UV) blocking and protection [2-5], antibacterial [6, 7], photocatalytic [8-10], self-cleaning [11], *etc.* In spite of the excellent photo catalyst and antibacterial properties, the problems of recycling and agglomeration of the nano-scaled particles have casted limitations of the applications of TiO₂ nanoparticles [12]. In recent years, researches on the immobilization of nano-crystalline TiO₂ on various substrates were presented with different techniques, such as sputtering, chemical vapor deposition, pulsed laser deposition, sol-gel, hydrothermal and the others [13-18]. Recently, the combining polymer such as chitosan or its derivatives with Ag and TiO₂ to form films or hydrogels materials was shown to have improved properties such as antimicrobial activity and tensile strength [19].

Chitosan itself is a hydrolyzed derivative of chitin, containing high amount of amino (-NH₂) and hydroxyl (-OH) functional groups, and possesses very high adsorption ability of dyes [20], metal ions [21-23], organic acids [24, 25], and pesticide [26]. There are several useful features of chitosan, such as non-toxicity, hydrophilicity, biocompatibility, biodegradability, and anti-bacterial property, which make it as a versatile material in many biomedical

applications [27]. The TiO₂ nanoparticles-chitosan composite has several advantages for interdisciplinary applications. For example, polluted waste water usually contains multiple hazardous materials such as pathogenic bacteria, heavy metals, *etc.* The TiO₂ nanoparticles have excellent photocatalytic activity that is quite effective for the elimination of organic pollutants; while chitosan possesses very impressing capability for heavy metal adsorption. Therefore, the integration of TiO₂ and chitosan can complement each other with their own advantages and exert the best effectiveness for wastewater pollutants treatment [28]. By chemical grafting of antioxidant molecules (such as chitosan) directly onto the surface of TiO₂ nanoparticle, it is possible to fabricate UV-blockers that can shield UV radiation with degradation of textiles and skin [29]. In literatures, chitosan composite films with low Ag/TiO₂ nanoparticle have been reported to have anticancer and antibacterial effects [30-32]. In addition, the mechanical properties (Young's modulus, tensile strength and toughness, *etc.*) of the TiO₂ nanoparticles-chitosan composite films can be effectively reinforced [33]. Due to the wide applications, approaches for chitosan composite coatings titanium nanoparticles have been developed. Cordero-Arias *et al.* fabricated TiO₂-chitosan composites for biomedical applications by using electrophoretic deposition (EPD) from ethanol-water suspensions [34]. Zainal *et al.* anchored the

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TiO₂ nanoparticles on chitosan thin film and formed on smooth surface of a glass plate for the photo-degradation and adsorption reaction [35]. The bio-sorption and photo-degradation activity can be combined through immobilization of TiO₂ on chitosan, and sphere is a good structure for these applications.

Chemical crosslinking of chitosan is the most straightforward approach to fabricate spherical particles due to the formation of covalent bonds between macromolecular chains. However, the cytotoxicity of some widely used compound, such as glutaraldehyde, has cast limitations on their biological related applications [36, 37]. In this study, we present a facile approach to produce uniform TiO₂ nanoparticles entrapped chitosan composite spheres by solidification process. This approach has the advantage of not using any cross-linking agent. The characteristics of the fabricated spheres were characterized by UV-Visible spectroscopy, Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and energy dispersive spectrum (EDS).

II. MATERIALS AND METHODS

2.1 Materials

Titanium chloride ($\geq 98\%$), chitosan (molecular weight: 150,000, 1.5 % w/v) and sodium hydroxide (NaOH) were purchased from Sigma-Aldrich (Sigma Chemical Co., St. Louis, MO, USA). Ammonium hydroxide (28~30 %) were purchased from J. T. Baker (Avantor Performance Materials, Center Valley, PA 18034, U.S.A.). All chemicals were used as received without further purification.

2.2 Synthesis of TiO₂ nanoparticles

The TiO₂ nanoparticles were prepared by a solution-based processing method by controlling the hydrolysis of TiCl₄ in aqueous solution. As shown in **Fig. 1**, titanium tetrachloride aqueous solution of 10 mL with 1 M concentration was prepared by mixing with distilled water in ice-water bath, and then kept still at a hydrolysis temperature (70 °C) for 1 hour. The mixed solution was treated with 2.5 M diluted NH₄OH solutions until the pH value became 7. The precipitated TiO₂ nanoparticles were then separated from the solution by filtration and repeatedly washed with distilled water to make the TiO₂ free of chloride ions. The synthesized nanoparticles were dried at room temperature until used.

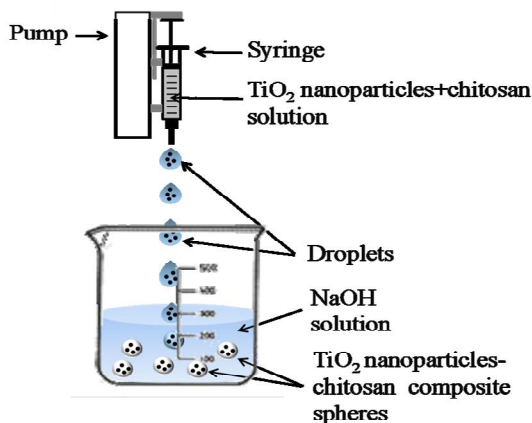


Fig. 1 Schematic graph for the synthesis of TiO₂ nanoparticles-chitosan composite sphere.

2.3 Preparation of TiO₂ nanoparticles-chitosan composite spheres

Chitosan (0.2 g ~ 0.3 g chitosan dissolved in 1 % acetic acid solution, 7 mL) and TiO₂ nanoparticles (0.05 g, dried powder) were mixed through constant stirring for 10 minutes to obtain the TiO₂ nanoparticles-chitosan mixture solution, which was then dropped into NaOH solution (20 wt %) by means of a motor-pumped syringe. After 10 minutes, TiO₂ nanoparticles-chitosan composite spheres having a milk-white color were observed. Spheres were collected by centrifugation and washed twice with dd-H₂O (30 mL) to remove any alkali.

2.4 Characterization process

The average diameter of the particles, expressed as mean \pm standard deviation, was obtained from the photographs with a USB digital microscope (UPG621, Upmost, Taipei, Taiwan) by random sampling of about 50 individual particles to minimize selection bias. Fourier transform infrared spectroscopy (FTIR) spectra were recorded with a Spectrum One FTIR spectrometer (Perkin Elmer, Waltham, MA, USA), using KBr pellets, in the range of 400~4000 cm⁻¹, with a resolution of 4 cm⁻¹. The morphology of the TiO₂-chitosan composite spheres was analyzed using a scanning electron microscope equipped with an energy dispersive spectroscopy (EDS) capability (Hitachi S-3400, Kyoto, Japan). Further characterizing the existence of TiO₂ nanoparticles was carried out with an UV-Visible absorbance spectroscopy (Hitachi-U-1800, Kyoto, Japan) and X-ray diffraction (XRD, Bruker AXS GmbH, Germany/ D2 Phaser).

III. RESULTS AND DISCUSSIONS

3.1 Morphology

Figure 2 shows the TiO₂ nanoparticles-chitosan composite spheres obtained from TiO₂ nanoparticles-chitosan mixture solution dripped from a pumped syringe with constant speed and dropped into solidification solution (20 wt % NaOH). Milk white color was observed in chitosan spheres without TiO₂ nanoparticles embedded for 2 % chitosan (**Fig. 2A**) and 3 % chitosan (**Fig. 2C**). The TiO₂ nanoparticles embedded chitosan spheres looked more and more yellowish with increasing concentration of chitosan (**Figs. 2B** and **2D**). The appearances and diameters of spheres have no obvious alterations with various concentrations of chitosan. The relative standard deviation of the sphere diameters under various concentrations of silver nitrate was less than 10 %, suggesting that the manufactured spheres meet the typical criterion for monodispersity [38].

3.2 Characterization

Surface morphology of the TiO₂ nanoparticles-chitosan composite spheres was surveyed through SEM with energy dispersive X-ray Spectrometer (SEM-EDS) analysis. **Figure 3** shows the SEM photographs of the prepared spheres (with 2 % chitosan, 0.05 g dried powder of TiO₂ nanoparticles, and solidified with 20 % NaOH solution). **Figures 3A ~ 3C** show the SEM graphs of an intact TiO₂ nanoparticles-chitosan composite sphere and its zoom in counterparts. It is observed that the outer surface of the prepared sphere was quite smooth (**Figs. 3A ~ 3B**) with small granules (the size of the granules was less than 10 μ m, **Fig. 3C**). **Figures 3D ~ 3F**

show the SEM graphs of a sectioned TiO₂ nanoparticles-chitosan composite sphere. It is observed that the intra surface of the prepared sphere was quite smooth (Figs. 3D ~ 3E) with small granules (the size of the granules was less than 10 μm, Fig. 3C).

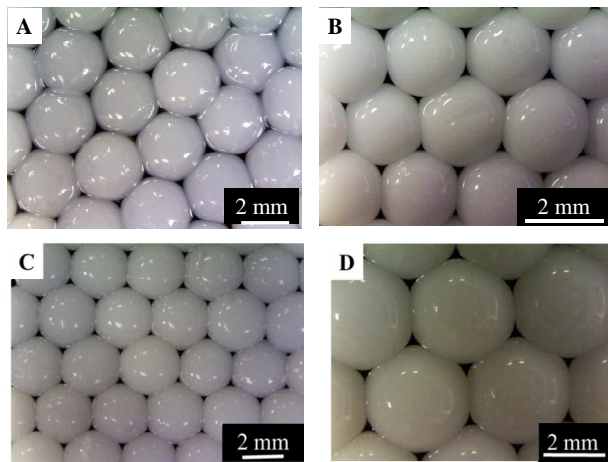


Fig. 2 Photographs of the spheres without / with TiO₂ nanoparticles embedded using various concentrations of chitosan solutions. (A) 2 % chitosan, (B) TiO₂ nanoparticles mixed with 2 % chitosan, (C) 3 % chitosan, (D) TiO₂ nanoparticles mixed with 3 % chitosan. All scale bars are 2 mm.

Compared with the appearance of chitosan spheres with and without TiO₂ nanoparticles [36], we found the former has much smoother structures than the latter including the outer and intra surfaces.

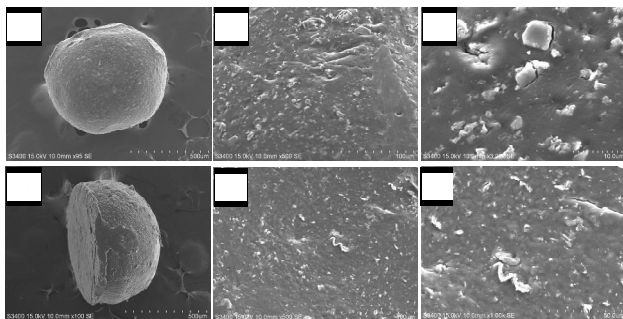
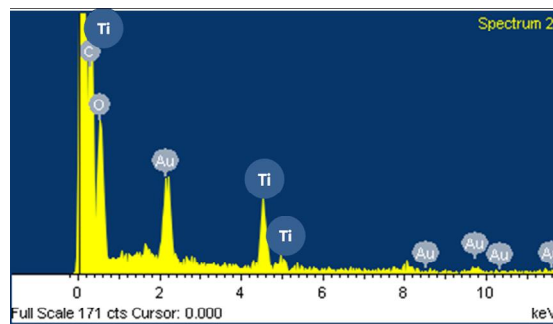


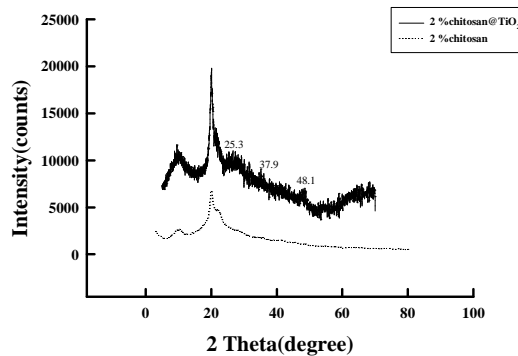
Fig. 3 The SEM photographs and of the synthesized spheres. Panel (A) is the SEM photograph of an intact TiO₂ nanoparticles-chitosan composite sphere. Panel (B) and panel (C) are zoom in counterparts of (A). Panel (D) is the SEM photograph of a sectional TiO₂ nanoparticles-chitosan composite sphere. Panel (E) and panel (F) are zoom in counterparts of (D). The concentration of chitosan was 2 %. The scale bars are: 500 μm for panel (A) and (D), 100 μm for panel (B) and (E), 10 μm for panel (C), and 10 μm for panel (F).

Energy dispersive spectrum (EDS), displayed in Figure 4A, showed peaks confirming titanium and oxygen presence on the outer surface of the synthesized spheres, indicating that TiO₂ nanoparticles were embedded in the synthesized spheres [27]. The small amount of gold shows the sputtered gold film before SEM analysis. The XRD analysis, which was carried out to confirm the TiO₂ polymorphs and crystalline phases, were recorded on a Hitachi X-ray

Diffractometer using Cu Kα radiation. Grated pieces of the prepared spheres were stuck to copper formvar/carbon using double-sided tape. The samples were sputtered with a layer of gold film to prevent the charging effect before analysis. Diffraction patterns were taken over the 2θ ranging from 5° to 60°. The peaks corresponding to the phase of TiO₂ nanoparticles appeared at 2θ = 25.3°, 37.9°, and 48.1°, respectively. The peak at 25.3° got increased, indicating that embedding of TiO₂ nanoparticles has a significant effect on the TiO₂ nanoparticles-chitosan crystallinity [35].



(A)



(B)

Fig. 4 The (A) EDS and (B) XRD spectrum of the synthesized spheres.

Figure 5A shows the UV-Visible absorbance spectra of the synthesized TiO₂ nanoparticles-chitosan composite spheres. The UV-Visible absorbance spectrum of the synthesized spheres has only one main peak at about 356 nm (Fig. 5A). In literature, it has been shown that chitosan only possesses characteristic spectrum at about 265 nm [39]; while TiO₂ nanoparticles also has no obvious absorption band at visible range, but presents characteristic spectrum with the fundamental absorption spectrum in Ti-O bond in ultraviolet range (from 320 nm to 400 nm) [40]. The peak shown in UV-Visible absorption spectrum indicated the existence of TiO₂ nanoparticles embedded in the chitosan spheres.

Figure 5B shows the FTIR spectra and the XRD patterns of the TiO₂ nanoparticles-chitosan composite spheres. The bands around 3462 cm⁻¹ to 3460 cm⁻¹ were related to the stretching vibrations of NH- amine amino groups. The bands around 2925 cm⁻¹ to 2891 cm⁻¹ were corresponding to alkane C-H stretching- lipids, and were also a characteristic of surface TiO₂ nanoparticles-OH functional group [35]. The bands around 1632 cm⁻¹ to 1597 cm⁻¹ corresponds to amide amino groups. The band around 1077 cm⁻¹ to 1075 cm⁻¹ is related to carbonyl stretch in proteins. The band at 1632 cm⁻¹

to 1075 cm^{-1} corresponds to the primary amide groups of chitosan and C–O stretching of chitosan respectively [41]. Occurrence of band at 656 cm^{-1} also affirms the existence of TiO_2 nanoparticles compound [35]. These results consist with the works of Jayakumar *et al.* [27].

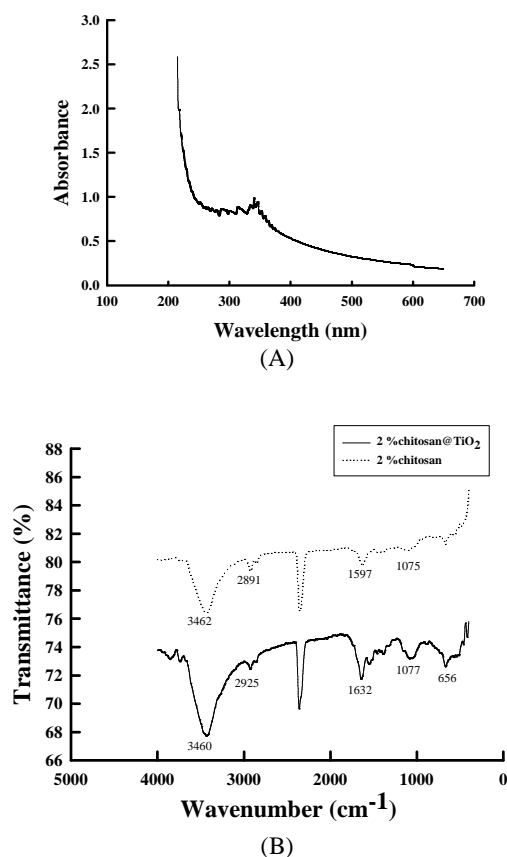


Fig. 5 The UV-Vis (A) and FTIR spectrum (B) of the fabricated TiO_2 nanoparticles-chitosan composite spheres.

IV. CONCLUSION

We propose a facile approach for the manufacture of TiO_2 nanoparticles-chitosan composite spheres that can stabilize and disperse TiO_2 nanoparticles without using cytotoxic crosslinking agents. The residue solidification solution can be easily washed out by using dd-water. Currently the diameters of the fabricated spheres were about 1.5 μm to 2.5 μm , but it is possible to significantly reduce the particle size by employing electrostatic or microfluidic droplets technology in the future. The successful formation of chitosan coating TiO_2 nanoparticles was evaluated with FTIR, XRD and EDS mapping. UV-Visible spectroscopy shows a peak around 356 nm, corresponding to TiO_2 characteristics. Due to the photocatalytic activity in nature, the prepared TiO_2 nanoparticles-chitosan composite spheres are potential for use in biological applications, such as bactericides. Compared with other approaches, the main advantages of this approach are: (i) uniform-sized spheres can be continuously fabricated, (ii) TiO_2 nanoparticles could be stabilized and uniformly dispersed in chitosan matrix, and (iii) spherical shapes can have wider-range applications compared with film structures.

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