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Synthesis and Characterization of Chitosan/TiO_2 Nanocomposites Using Liquid Phase Deposition Technique

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Abstract

The development of rapid and reliable processes for the synthesis of nano materials is of great importance in the field of nanotechnology. In this paper, the synthesis of Chitosan/TiO_2 nanocomposites was carried out by using LPD technology in aqueous medium. The method was performed by mixing the chitosan with TiO_2 in the presence of polyvinyl alcohol as the capping agent. In this work, Chitosan/TiO_2 encapsulated nanocomposites powder was prepared where chitosan and PVA were used as the solid support and polymeric stabilizer. The optimum concentration of TiO_2 in the synthesis of nanocomposites is 0.40%. The stirring time plays an important role in the process. Hence, the time of five hours has been fixed as stirring process and temperature at 70^{o}C. The developed Chitosan/TiO_2 nanocomposites were characterized by the FTIR spectroscopy, XRD, SEM and TEM analysis. The shape and size of nanocomposites are a distorted octahedron with anatase TiO_2 and mean size is about 12.1 nm respectively.

Keywords: Chitosan; Titanium dioxide; Polyvinyl alcohol; LPD; Nanocomposites.

Introduction

Nanoscale materials are structures ranging from 1 to 100 nm, as defined in the chemistry context, which have contributed to the development of Nanoscience and nanotechnology at the exponential rate in recent years. Nanomaterials often have a significant degree of difference in physico-chemical and biological properties to their macroscale counterpart in spite of the similar chemical composition they possess[1,2]. In the broadest sense this definition can include porous media, colloids, gels and copolymers, but is more usually taken to mean the solid combination of a bulk matrix and nano-dimensional phase(s) differing in properties due to dissimilarities in structure and chemistry. The mechanical, electrical, thermal, optical, electrochemical, catalytic properties of the nanocomposites will differ markedly from that of the component materials[3]. Chitosan is a linear polysaccharide, produced usually by deacetylation of chitin, which is the structural element in the exoskeleton of crustaceans (crabs, shrimp, etc.). Due to its special structure containing many functional groups such as aminyl or hydroxyl, it has a tendency to form complexes with metals [4-6]. Over recent years, hybrid materials based on chitosan have been developed, including conducting polymers, metal nanoparticles, and oxide agents, due to excellent properties of individual components and outstanding synergistic effects simultaneously [7]. Currently, the research on the combination of chitosan and metal oxide has focused on titanium dioxide, as the titanium dioxide has excellent photocatalytic performance and is stable in acidic and alkaline solvents[8-10]. In this communication, we report the synthesis of Chitosan/TiO_2 nanocomposites powder via LPD method and was characterized by FTIR spectroscopy, XRD, SEM and TEM analysis.

Materials and Methods

Chitosan was prepared from the shrimp and crab shell by the chemical method. The synthesis of Chitosan/TiO_2 nanocomposites was carried out by mixing titanium dioxide and chitosan in the ratio 3:2 and the aqueous mixture was kept for 24 hr. The mixture was stirred well with 4g of polyvinyl alcohol at 70^{o}C for five hours. Then the mixture was calcined at 400^{o}C to get Chitosan/TiO_2 nanocomposites[11].

The crystallinity and phase purity of the sample was examined by powder X-ray diffraction (XRD) on a Philips PW 3050/10 model with Cu-K_α radiation. FTIR spectroscopy was measured using FTIR model; Nexus 690. The sample were mixed uniformly with KBr at 1:5 ratio, respectively. The KBr pellets were prepared by compressing the powder at pressure of 5 times for 5 min in a hydraulic pressure. The pellets were scanned in the range of 400-4000 cm^{-1} to obtain FTIR respects. The surface morphology of the sample were analyzed by using SEM, from Japan in the magnification range 35-10,000, resolution 200 Å and acceleration voltage of 19 Kv. The morphologies and micro structure of the as-synthesized samples were investigated by TEM model (JEOL 2010).

Results and Discussion

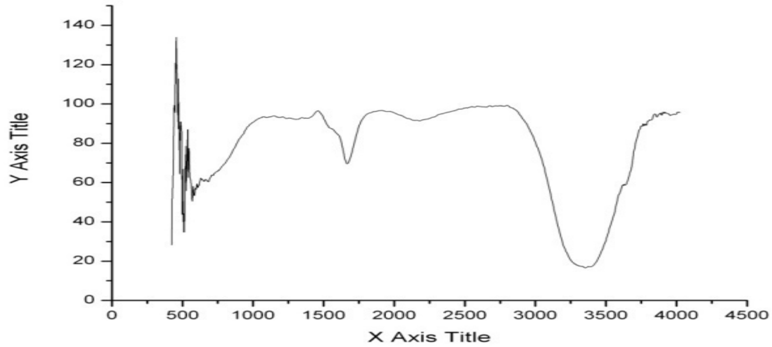

Figure.1.a. FTIR pattern of Chitosan.

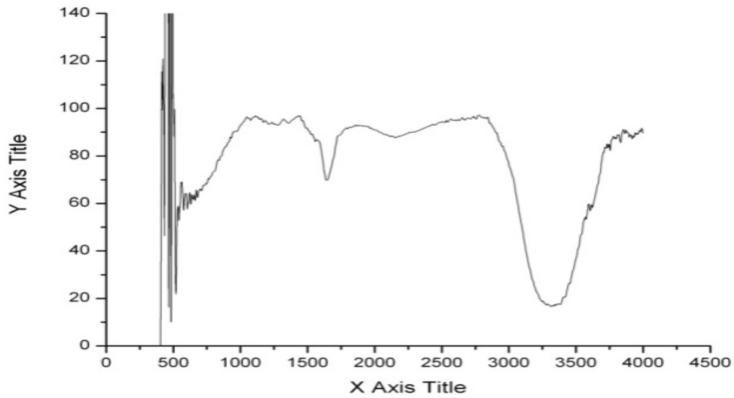

Figure.1.b. FTIR pattern of Chitosan/TiO_2 nanocmposites.

Figure.1.a and 1.b, show the FTIR of chitosan and Chitosan/TiO_2 nanocomposites. The figure.1.a shows the absorption peak at 3350 cm^{-1}, which attributed to the combined peaks of the NH_2 and OH group stretching vibration[12] and figure.1.b has the broader and stronger peak moved noticeably to lower wave number at 3300 cm^{-1} which indicated the strong interaction between these groups and TiO_2[13]. While the absorption peaks at 1647 and 1078 cm^{-1} are ascribed to bending vibration of $-NH_2$ group and C–O stretching group, compared with chitosan, there are new absorption peaks at 671 cm^{-1} and 385 cm^{-1} which are due to the attachment of amide group and stretching mode of TiO_2[14]. In addition to these results, the characteristic peaks of figure.1.b is shifted to lower wavenumber, the wide peak at 3350 cm^{-1}, corresponding to the stretching vibration of hydroxyl, amino and amide groups, moved noticeably to lower wavenumbers 3300 cm^{-1}, and became broader and stronger, which confirm the formation of nanocomposites.

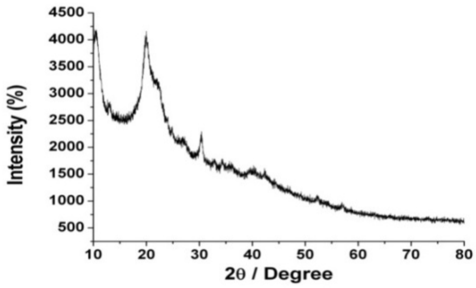

Figure.2.a. XRD pattern of Chitosan**.**

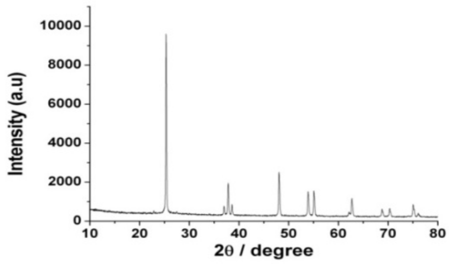

Figure.2.b. XRD pattern of Chitosan/TiO_2 nanocmposites**.**

Figure.2 shows the X-ray diffraction patterns of chitosan and Chitosan/TiO_2 nanocomposites. The typical peaks of chitosan (Figure.2.a) appeared at 10.67° and 21.8°[15], while these peaks become weak in the XRD pattern of Chitosan/TiO_2 nanocomposites (Figure.2.b). Other diffraction peaks in figure.2.b are sharper and stronger at 26.1°, 37.2°, 48.49°, 54.2°, and 68.90° were assigned to the (1 0 0), (1 0 1), (1 1 0), (1 0 3), and (1 1 2) planes of distorted octahedral titanium dioxide can be indexed to the anatase TiO_2 with high crystallinity. All the diffraction peaks are in good agreement with those of octahedral anatase structure of TiO_2 (JCPDS card 36-1451). The hydrogen bond absorption at 3300 cm^{-1} is strengthened after TiO_2 was introduced. These findings reveal that the hydrogen bonding in the chitosan complex became stronger after complexing with TiO_2. The results also suggest that there is strong interaction between the chitosan and nanocrystalline TiO_2[16,17]. This, indeed, revealed that it is successful formation of nanosized Chitosan/TiO_2 complex[14].

Scanning electron microscopy (SEM) was used to investigate the surface morphology of Chitosan/TiO_2 nanocomposites powder with reference to chitosan powder and titanium dioxide nanoparticles. The SEM picture of Chitosan/TiO_2 nanocomposites powder is shown in figure.3.

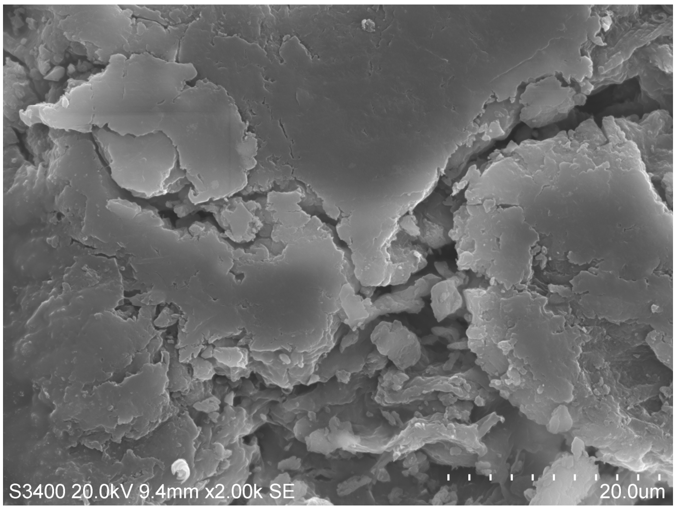

Figure. 3. SEM image of Chitosan/TiO_2 nanocmposites.

The Chitosan/TiO_2 nanocomposites powder has aggregated particle structures, however, the micrographs of chitosan and TiO_2 are uniform. The image reveals the surface structure of nanocomposites with small-flake surface presented separately in the exterior morphology of nanocomposites. This phenomenon shows that, the stirring times of five hours, the nanocomposites with better compatibility were produced [18].

Transmission Electron Microscopy (TEM) images and the particle size distribution for Chitosan/TiO_2 nanocomposites with constant stirring times of reaction was gives in figure.4.

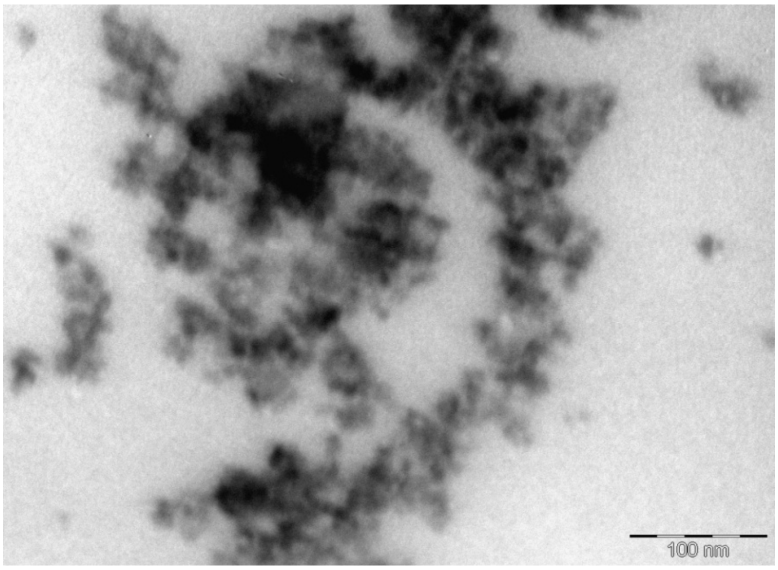

Figure.4. TEM image of Chitosan/TiO_2 nanocmposites.

From the it reveals that the nanocomposites powders are octahedron with anatase TiO_2 in shape and their average size is about 12.1 nm. When the stirring time is increased, the particle aggregation was being promoted to form larger particle. Similar results have already reported by Jiang et.al[19]. These results showed that the diameter of Chitosan/TiO_2 nanocomposites were influenced by the stirring time of reaction. The results also revealed that the stirring time of 5 h was the optimum in order to obtained the smallest particle size of Chitosan/TiO_2 nanocomposites at 70^{o}C.

Conclusion

Synthesis and characterization of Chitosan/TiO_2 nanocomposites were studied by using LPD process. The optimum concentration of TiO_2 for formation of nanocomposites is 0.40%, and the temperature is 70^{o}C. The FTIR results indicated that the formation of nanocomposites. The XRD result confirmed that the resultant nanocomposites possessed a distorted octahedron with anatase TiO_2 crystal structure. This is also noticed the Chitosan/TiO_2 nanocomposites were the main composition present in the nanocomposites without any contamination peaks. This structures and sizes of nanocomposites were characterized by using TEM.. The image of SEM revealed that, the optimum reaction time and smaller particle sizes presented in this Chitosan/TiO_2 nanocomposites. From the above results, this innovation is important because it may allow it’s practical use for industrial application.

Abbreviation

LPD – Liquid Phase Deposition

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