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Preparation of Pectin–ZnO Nanocomposite

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Abstract Pectin–ZnO nanocomposite was prepared in the aqueous solution condition at room temperature. The Fourier transform infrared, X-ray diffraction, and transmission electron microscope (TEM) measurements confirmed the nanoscaled structure of pectin–ZnO composite. According to the TEM observation, the average composite granules size was about 150 nm and the embedded ZnO nanoparticles were uniform with an average diameter of 70 nm.

Keywords Nanocomposite · Pection · Zinc oxide · Nanocrystallinity · Preparation

Introduction

Pectin is a natural, non-toxic, and amorphous carbohydrate present in cell walls of all plant tissues, which functions as an intercellular and intracellular cementing material. As a secondary product of fruit juice, sunflower oil, and sugar manufacture industries, pectin is both inexpensive and abundantly available. Therefore, pectin is an excellent candidate for eco-friendly biodegradable applications. Pectin is commonly used in the food industry as a gelling and stabilizing agent. Pectin macromolecules are able to bind with some organic or inorganic substances via molecular interactions. So, pectin can be used to construct matrices to absorb desired materials and deliver them in a controlled manner [1]. Indeed, pectin has been used to fabricate delivery systems for controlled drug release [2], implantable cell carriers [3], and so on.

Zinc (Zn) is an essential micronutrient critical for human health, and its deficiency cause serious and sometimes even disastrous health problems [4, 5]. It has been estimated that more than 50% of poor children and 30% of non-poor children get <70% of the recommended dietary allowance of Zn [6–9]. The main reason may be the presence of phytate in staple foods such as cereals and pulses; phytate has a strong negative effect on Zn absorption from composite meals. If suitable Zn fortificants can be developed to fortify staple foods, it will go a long way in alleviating Zn deficiency. Zinc oxide (ZnO), a safe source for Zn supplementation and fortification, will decompose into Zn ions after consumption [10]. Therefore, ZnO is commonly used to fortify foodstuff in the food industry. Wheat products fortified with ZnO have been shown to possess good Zn absorption [11].

Currently, hybrid inorganic–organic nanocomposite materials are of great interest because of their multifunctionality owing to a combination of different compounds incorporated [12]. We have recently reported preparation of ZnO-whey protein isolate nanocomposite [13]. Nanocomposite of ZnO wrapped in pectin will survive the gastric environment and become available in the intestine and readily absorbed due to their nanoscale size. The incorporation of nanocrystalline ZnO into pectin to form nanocomposite may impart unique functionalities to the nanocomposite prepared.

Herein we report the preparation of pectin-coated nanocrystalline ZnO particles with a facile solution approach at room temperature. This approach may find potential application in the food industry.

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Experimental Methods

All reagents used were of analytical grade and were used without further purification. In a typical procedure, 0.2 g pectin, 1.2 g $Zn(NO_3)_2 \cdot 6H_2O$, and 40 mL distilled water were added into a 100-mL beaker. After full dissolution, 40 mL of 0.125 M NaOH solution was added dropwise under constant stirring. The reaction was allowed to proceed at room temperature (~20 °C) for 24 h. Then, the obtained white precipitate was centrifuged at 10,000 rpm for 10 min and collected and washed with distilled water several times to remove the byproducts. After drying in vacuum at 30 °C for 4 h, the final product was obtained as white powder.

Fourier transform infrared (FTIR) spectra of the sample were obtained with a Shimadzu IR-400 spectrometer with the KBr pressed disks. The overall crystallinity of the product was examined by a powder X-ray diffraction (XRD) unit (Scintag Pad V with a Ge solid-state detector; Cu Kα radiation) with the solid specimens mounted on a low background quartz holder. Detailed microstructure analysis was carried out using a transmission electron microscope (TEM, PhilipsCM120). The UV–Vis spectrum of the product dispersed in distilled water was recorded in a UV–Vis spectrophotometer (UV-1601PC, Shimadzu Corporation). A particle size analyzer (90Plus, Brookhaven Instruments Corporation, New York, USA) was used to determine the granular average size distribution of pectin–ZnO nsnocomposite. Thermogravimetric analysis (TGA), differential thermogravimetric analysis (DGA), and differential thermal analysis (DTA) profiles were performed with a Shimadzu-50 thermoanalyzer apparatus under airflow with a heating rate of 10 °C/min.

Results and Discussion

Room temperature FTIR spectra of pectin and the as prepared pectin–ZnO composite are shown in Fig. 1. An obvious absorption peak at about 480 cm^{-1} can be found for the pectin–ZnO composite sample; this is a typical IR absorption peak of ZnO, originating from stretching mode of the Zn–O bond [14]. The remaining peaks in pectin–ZnO composite are induced by pectin, which is confirmed by comparing of the IR spectrum of the composite with that of the pectin [15]. The peak at 1030 cm^{-1} is assigned to C=O or C=C double bond of pectin. The absorption peaks at 1388 and 1633 cm^{-1} are related to stretching bands of COO^- groups of pectin. The peak at about 2358 cm^{-1} arises from the CO_2 atmosphere. It is found that the intensities of two peaks at 1743 and 2944 cm^{-1} (induced by carboxyl and CH_2 groups of pectin, respectively) for pectin–ZnO composite are obviously weaker than that for pectin. This may originate from the participation of COO^- and CH_2 groups in a hydrogen bond system, which stabilizes the pectin conformation in solid state [16]. The above results indicate that the final product is a true composite of pectin and ZnO. The pectin peaks were not removed by washing the sample repeatedly, suggesting that interactions between pectin and ZnO are strong.

A typical XRD pattern of the as-prepared sample is shown in Fig. 2. All the diffraction peaks can be indexed to those of hexagonal ZnO. The lattice constant obtained from the XRD data are $a = 3.249$ Å, $c = 5.212$ Å, which are consistent with the reported values for ZnO ($a = 3.253$ Å, $c = 5.209$ Å, JCPDS card, No. 80-0075). The broadening of the ZnO XRD peaks suggests a nanoscale grain size.

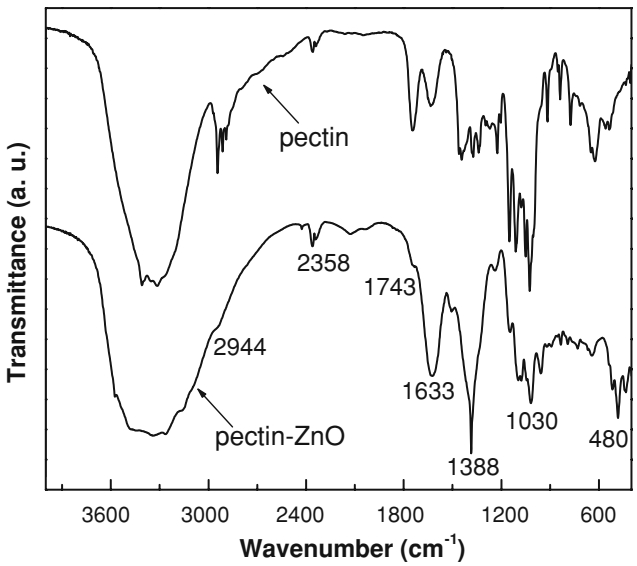

Fig. 1 Room temperature FTIR spectra of pectin and the as prepared pectin–ZnO composite

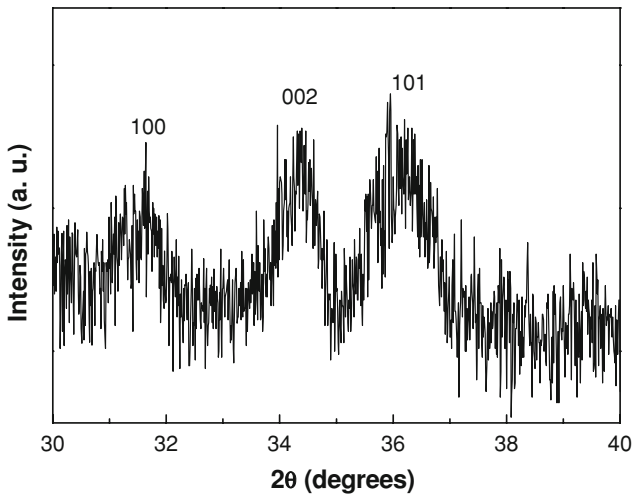

Fig. 2 XRD pattern of the as prepared pectin–ZnO composite sample

The average particles size was calculated to be 60 nm based on the Scherrer equation.

Figure 3 shows the room temperature UV–Vis absorbance spectrum for the as prepared sample. A narrow absorbance peak centered at 371 nm was found. The band gap of the ZnO nanoparticle was calculated to be 3.34 eV under the current measurement condition, consistent with the reported value for bulk ZnO [17], which indicates that crystallinity of ZnO in the composite is as good as (or even better than) that for ZnO prepared with other methods. This may be due to the slow process and long time reactions at room temperature. No blue shift, induced by quantum confinement related effect, was observed in the UV–Vis absorbance spectrum. The asymmetry of the peak was caused by light scattering due to the insolubility of nanoscale pectin–ZnO particles in water [18].

A typical TEM image of the pectin–ZnO composite is shown in Fig. 4. The obviously different contrast on every particle indicates its different composition and structure, where the dark part is ZnO and the gray part is pectin. The ZnO particles are all wrapped with pectin and have an average size of about 70 nm. The composite granules are irregular and their average size is about 150 nm according to the TEM observation. The inset in Fig. 4 is a magnified TEM image of a composite particle, which indicates clearly the ZnO parcel (dark area) is wrapped with pectin (gray area).

The granular size distribution of pectin–ZnO composite examined with a particle size analyzer is shown in Fig. 5, which indicates that the composite granular size distributes mainly at about 150 nm. This is consistent with the TEM observation result.

Thermogravimetry is one of the most widely used techniques to monitor the composition and structural

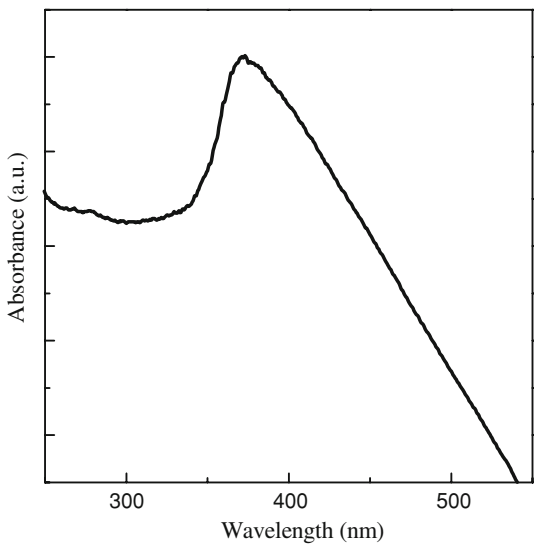

Fig. 3 UV–Vis absorbance spectrum of the pectin–ZnO composite

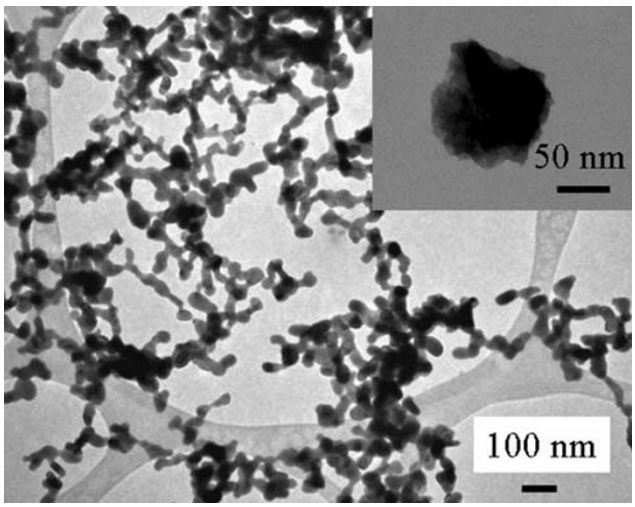

Fig. 4 TEM image of the composite of pectin-wrapped ZnO nanoparticles. The inset is a magnified TEM image of a pectin–ZnO composite particle which indicates clearly the ZnO is wrapped with pectin

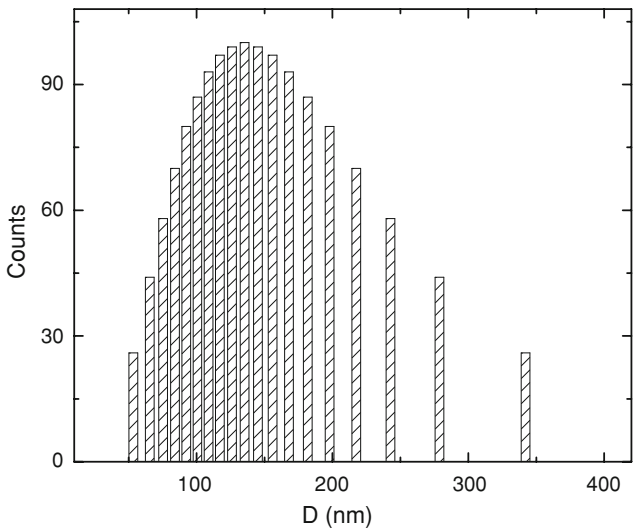

Fig. 5 Histogram of granular size distribution of pectin–ZnO composite sample

dependence on the thermal degradation of a composite. Figure 6 shows the results of thermogravimetric analyses (TGA, DTG, and DTA) of the pectin–ZnO composite. The DTG curve shows an initial peak between 40 and 110 °C with a weight loss of up to 12%, which was related to moisture evaporation. After this peak, DTG shows one sharp peak and two small peaks in the range of 110 to 220 °C, These three peaks may arise from the loss of chemical bonding water. Two obviously endothermic peaks can be observed in the DTA curve between 40 and 200 °C, corresponding to the loss of water in the sample. A strong peak started at 220 °C with the maximum at 258 °C can be found in the DTG curve, it is induced by the thermal

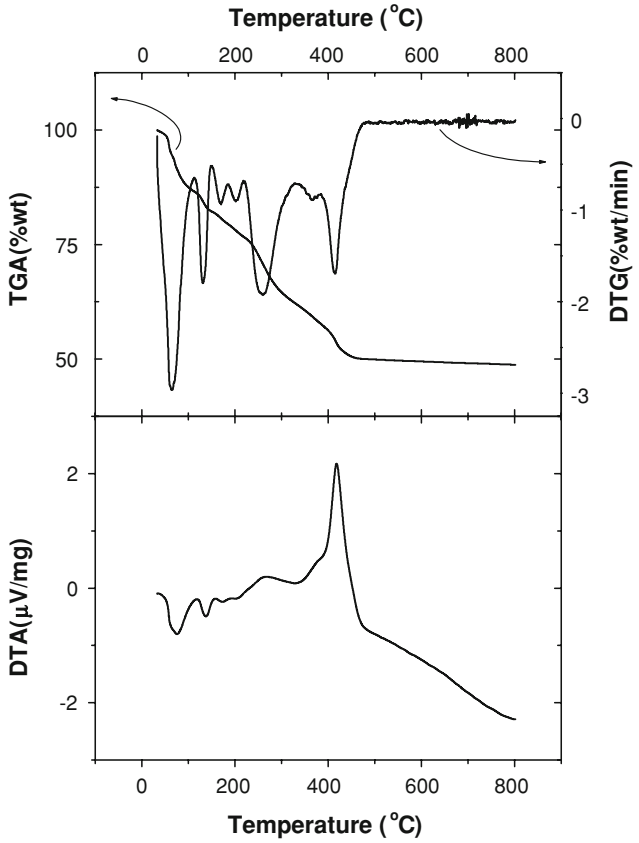

Fig. 6 TGA, DTG, and DTA curves for pectin–ZnO composite sample

depolymerization of pectin chains. Accordingly, this thermal event also caused a broad exothermic peak in the range of 220 to 330 °C in the DTA curve. The temperature for thermal depolymerization of pectin chains in pectin–ZnO composite is about 20 °C higher than that of pectin alone [19], revealing the depolymerization has been hindered to some degree. This may be due to the existence of strong interactions between pectin molecules and ZnO. The similar influence of ZnO on the degradation of polymer has been reported [20]. The last sharp DTG peak centered at 415 °C accompanied by a strong exothermic peak in the DTA curve should arise from the oxidation decomposition of pectin in the air [21].

It is well known that the ZnO can precipitate from alkaline aqueous environment via the hydroxide. The main Zn species in hydrothermal alkaline solution are $ZnOOH^-$, $Zn(OH)_4^{2-}$, ZnO_2^{2-}, the transport, and growth processes can be described as:

$$Zn(OH)_4^{2-} \rightarrow Zn(OH)_2 + 2OH^-,$$

$$Zn(OH)_2 \rightarrow 2H^+ + ZnO_2^{2-}.$$

The two oxygen atoms of zinc hydroxide are highly repulsive since they all have lone pair of electrons. This makes the dehydration of zinc hydroxide quite quickly at low temperature and facilitates the production of ZnO nanoparticles. Due to the high polarity of water, ZnO nanoparticles usually agglomerate immediately and form larger particles. In our approach, pectin is added into the solution and bind with ZnO molecules with COO^- and CH_2 groups in a hydrogen bond system to restrain the formed ZnO nanoparticles from further agglomeration by the action of steric hindrance. After a long time reaction, the pectin-wrapped ZnO nanocomposites are formed.

Summary

We developed a novel yet simple approach to prepare pectin–ZnO nanocomposite in aqueous solution at room temperature. The structural properties, morphology, thermal decomposition process, and optical absorption of the nanocomposite were studied. The experimental results confirm the true pectin–ZnO composite structure and the existence of strong interaction between pectin molecules and ZnO. This method may be extended to prepare other hybrid inorganic–organic nanocomposite materials.

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