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Hydrothermal synthesis, characterization, and bactericidal activities of hybrid from cellulose and TiO_2

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ABSTRACT

The purpose of this study was to explore a new strategy to improve the high value-added applications of biomass. Hybrid from cellulose and titanium dioxide (TiO_2) was successfully prepared by using tetra-n-butyl titanate and cellulose solution via a hydrothermal method at 180 °C for 24 h. The phase, microstructure, morphology, and thermal stability of the hybrid were characterized by X-ray powder diffraction (XRD), Fourier transform infrared spectrometry (FT-IR), thermogravimetric analysis (TGA), differential thermal analysis (DTA), and scanning electron microscopy (SEM). The influences of the tetra-n-butyl titanate concentration and the types of solvent on the products were investigated. The TiO_2 nanoparticles were dispersed on the surface of cellulose and/or in the cellulose matrix. The hybrid possessed an antimicrobial activity against the model microbes *Escherichia coli* (Gram-negative) and *Staphylococcus aureus* (Gram-positive), and were a promising antimicrobial material for the applications in the biomedical field.

1. Introduction

Cellulose is the most abundant renewable material in the world and has been receiving considerable attention due to its biocompatibility, biodegradability, and renewability (Czaja, Young, Kawecki, & Brown, 2007; Klemm, Heublein, Fink, & Bohn, 2005). However, there are numerous intermolecular and intramolecular hydrogen bonds in the structure of cellulose (Nishiyama, Langan, & Chanzy, 2002; Nishiyama, Sugiyama, Chanzy, & Langan, 2003), making the cellulose difficult to dissolve in common solvents and fabricate cellulose-based hybrid. Until now, some solvents including LiCl/DMAc solvent (Butler, O'Driscoll, & Wilkes, 1990), NaOH/urea solvent (Cai & Zhang, 2006), NaOH/thiourea solvent (Weng, Zhang, Ruan, Shi, & Xu, 2004), ionic liquids (Swatloski, Spear, Holbrey, & Rogers, 2002) were employed for the dissolution of cellulose. As a new solvent and "green" approach for the dissolution of cellulose at low temperature, the NaOH/urea solvent system can be used to the preparation of the advanced cellulose-based materials and chemical modifications (Cai et al., 2007). Cellulose-based hybrids have attracted a great amount of attention owing to its unique properties (Eichhorn et al., 2010; Siro & Plackett, 2010). To date, various cellulose-based hybrids have been fabricated in NaOH/urea aqueous solution, such as cellulose/Fe_2O_3 (Liu, Zhang, Zhou, & Wu, 2008), cellulose/CdS (Ruan, Huang, & Zhang, 2005), cellulose/Fe_3O_4 (Zhou et al., 2009), cellulose/carbonated hydroxyapatite (Jia, Li, Ma, Sun, & Zhu, 2010), etc.

TiO_2 has efficient photoactivity, the highest stability, and excellent antimicrobial properties (Hashimoto, Irie, & Fujishima, 2005). Therefore, TiO_2 is attractive to us for the preparation of hybrid from cellulose and TiO_2. Until now, there have been a few reports on the fabrication of hybrids from cellulose and TiO_2 (Daoud, Xin, & Zhang, 2005; Kemell, Pore, Ritala, Leskela, & Linden, 2005; Lei, Lin, Yao, & Zhu, 2004; Marques, Trindade, & Neto, 2006; Nagaoka et al., 2005; Sun, Yang, & Wang, 2010; Uddin et al., 2007; Yu et al., 2008; Zeng, Liu, Cai, & Zhang, 2010; Zhou, Ding, & Li, 2007; Zhou, Liu, Qi, & Zhang, 2006). Some strategies including phase separation method (Nagaoka et al., 2005), surface hydrolysis method (Sun, Yang, & Wang, 2010), and sol–gel method (Uddin et al., 2007; Zeng, Liu, Cai, & Zhang, 2010) were employed for the synthesis of hybrid from cellulose and TiO_2. For example, Zhou et al. (2006) prepared composite films with high tensile strength from cellulose and TiO_2 nanoparticles in a 7.5% NaOH/11% urea aqueous solution by coagulation with H_2SO_4 solution. However, as far as we know, few works have been conducted on the hybrid from cellulose and TiO_2 with antibacterial activity by the hydrothermal method. In previous studies, our research group synthesized the cellulose/Ag hybrid with high antibacterial activity by microwave-assisted method (Li, Jia, Zhu, Ma, & Xu, 2011; Li, Jia, Zhu, Ma, & Zhang, 2011). Moreover,

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Li et al. (2012) also fabricated cellulose/AgCl nanocomposites with high-purity, good thermal stability, and antimicrobial activity.

The purpose of this article was to explore a new strategy to improve the high value-added applications of biomass and provide a promising antibacterial candidate for the applications in biomedical field. Herein, a hydrothermal method was applied to the synthesis of hybrid from cellulose and TiO_2 by using tetra-n-butyl titanate and cellulose solution. The phases, microstructure, morphology, thermal stabilities, and antibacterial activity of the hybrid were characterized. TiO_2 crystals were obtained by calcination the hybrid in air.

2. Experimental

2.1. Preparation of hybrid from cellulose and TiO_2

All chemical materials and solvents used in the experiments were analytical grade reagents, and were used without further purification. In a typical synthesis, 1.62 g of microcrystalline cellulose (MCC) was added immediately into the 50.0 g of NaOH/urea aqueous solution (7:12 in wt%) under vigorous stirring at room-temperature, and then the suspension solution was cooled down to −12 °C for 12 h. The obtained cellulose solution was used to fabricate the cellulose-based hybrid.

The mixture of tetra-n-butyl titanate (5 mL) and cellulose solution (10 mL) was poured into a 20-mL Teflon-lined stainless steel autoclave. The autoclave was maintained at 180 °C for 24 h. The product was obtained from the solution by centrifugation, washed by ethanol three times and dried at 60 °C in air for further characterization. For comparison, the sample was also prepared using the mixture of tetra-n-butyl titanate (1 mL) and cellulose solution (14 mL) by hydrothermal treatment at 180 °C for 24 h.

Moreover, the influences of types of cellulose solution on the products were also investigated. 3.04 g of LiCl was added into 40 mL of *N*,*N*-dimethylacetamide (DMAc) under vigorous stirring to form LiCl/DMAc solution. After that, 2.85 g of MCC was dissolved directly into the LiCl/DMAc solution under vigorous stirring at 90 °C for 3 h to form cellulose solution. The samples were prepared using the mixture of tetra-n-butyl titanate (5 mL)/cellulose solution (10 mL) and tetra-n-butyl titanate (1 mL)/cellulose solution (14 mL) by hydrothermal treatment at 180 °C for 24 h, respectively.

2.2. Characterization

X-ray powder diffraction (XRD) patterns were recorded using a Rigaku D/Max 2200-PC diffractometer with Cu Kα radiation (λ = 0.15418 nm) and graphite monochromator at ambient temperature. Fourier transform infrared (FT-IR) spectra of the cellulose-based hybrid were taken on a Fourier transform infrared spectrophotometer (Nicolet 510) in a range of wavenumber from 4000 to 400 cm^{-1}, using the KBr disk method. The morphologies of cellulose-based hybrid were examined using a Hitachi 3400N scanning electron microscopy (SEM) operating at 15 kV. All samples were Au coated prior to examination by SEM. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were taken with a heating rate of 10 °C min^{-1} from room-temperature to 600 °C in flowing air with a simultaneous thermal analyzer (DTG-60, Shimadzu, Japan).

2.3. Antimicrobial activity studies

The antimicrobial activities of hybrid from cellulose and TiO_2 were investigated against *Escherichia coli* as the model Gram-negative bacteria and *Staphylococcus aureus* as the model Gram-positive bacteria by the disc diffusion method. In the inhibition zone experiment, nutrient agar was poured into disposable sterilized Petri dish and solidified. Then 100 μL of *E. coli* or 100 μL of *S. aureus* were streaked over the dish and spread uniform. After that, circular pieces of the control and the test samples were gently placed on Petri dishes. This was done for both the bacterial strains (*E. coli* ATCC 25922 and *S. aureus* ATCC 25923). The hybrid from cellulose and TiO_2 were cut into a disc shape with 1.4 cm diameter, sterilized by autoclaving at 120 °C for 20 min, and placed on *E. coli*-cultured and *S. aureus*-cultured agar plates, which were then incubated at 37 °C for 24 h. Finally, the inhibition zone was monitored.

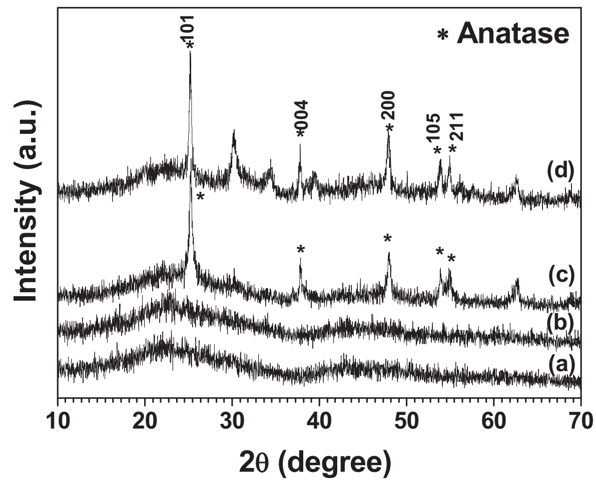

Fig. 1. XRD patterns of the hybrids prepared using (a) and (b) LiCl/DMAc solution and (c) and (d) NaOH/urea solution by hydrothermal method at 180 °C for 24 h: (a) and (c) tetra-n-butyl titanate (5 mL); (b) and (d) tetra-n-butyl titanate (1 mL).

3. Results and discussion

3.1. The phases, morphologies, and microstructures of hybrid

The inorganic antimicrobial materials included Ag, Cu, ZnO, TiO_2, etc. Among of these antimicrobial materials, Ag has the best antimicrobial activity. As a noble metal, Ag is more expensive than the other inorganic antimicrobial materials. Cu has biological toxicity and ZnO has relatively weak antimicrobial activity. TiO_2 might be a promising antibacterial candidate for the applications in antimicrobial field due to its excellent antimicrobial properties, the highest stability, and low price. Furthermore, the key problems

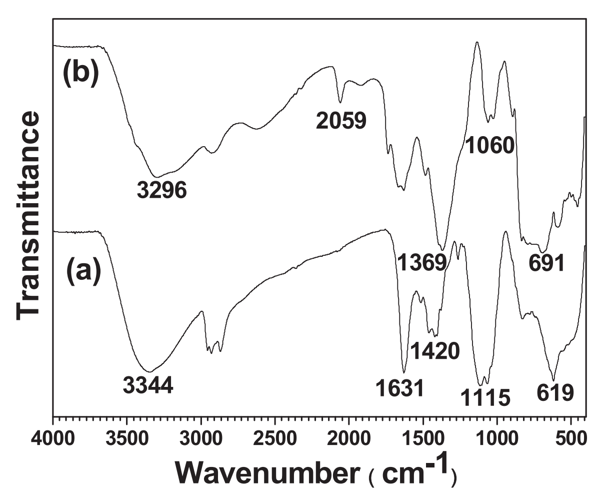

Fig. 2. FTIR spectra of the hybrids: (a) using LiCl/DMAc solution and (b) using NaOH/urea solution.

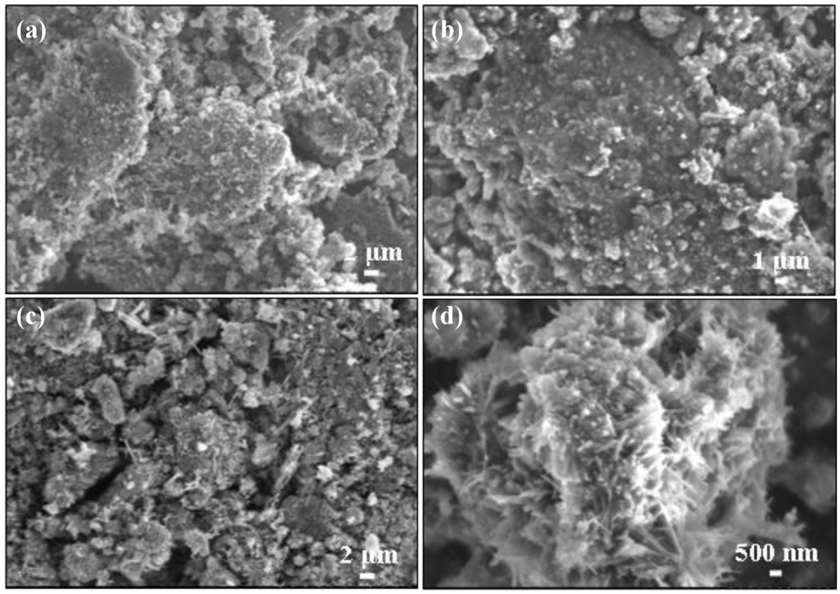

Fig. 3. SEM micrographs of the hybrids from cellulose and TiO_2 using NaOH/urea solution: (a) and (b) tetra-n-butyl titanate (5 mL); (c) and (d) tetra-n-butyl titanate (1 mL).

of the inorganic antimicrobial materials in applications were the dispersion and the washable of inorganic particles. The hybrids from cellulose and TiO_2 were obtained using cheap cellulose as matrix and support, which had advantages of decreasing the price of antimicrobial materials, increasing the ability of washable, and improving the antimicrobial activity.

Fig. 1c shows the X-ray powder diffraction (XRD) pattern of the sample synthesized using 10 mL cellulose solution (the dissolution of MCC in NaOH/urea solution) and 5 mL tetra-n-butyl titanate by a hydrothermal method at 180 °C for 24 h. One can see that the sample consisted of the characteristic peaks of anatase (JCPDS 21-1272). No obvious peaks of cellulose were observed, which due to the strong peak intensity of anatase. When the tetra-n-butyl titanate concentration was decreased from 5 to 1 mL, the major phase was still anatase and the peaks of impurities at $2\theta = 30.2°$ and $34.5°$ were observed (Fig. 1d). This result indicated that the tetra-n-butyl titanate concentration was important for the fabrication of hybrid from cellulose and TiO_2. However, no peaks of TiO_2 were observed by using the tetra-n-butyl titanate and cellulose solution (Fig. 1a and b), which was obtained by the dissolution of MCC in LiCl/DMAc solution, indicating that the obtained TiO_2 was amorphous or no TiO_2 was obtained in hybrids. Based on the results of XRD, one can conclude that the types of cellulose solution had an effect on the phase of the hybrids.

Fig. 2 provides the FT-IR spectra of the typical cellulose-based hybrid. When hybrid was synthesized by the dissolution of MCC in NaOH/urea solution, the bands at about 3296, 1369, 1060, and 691 cm^{-1} were attributed to the characteristic peaks of MCC

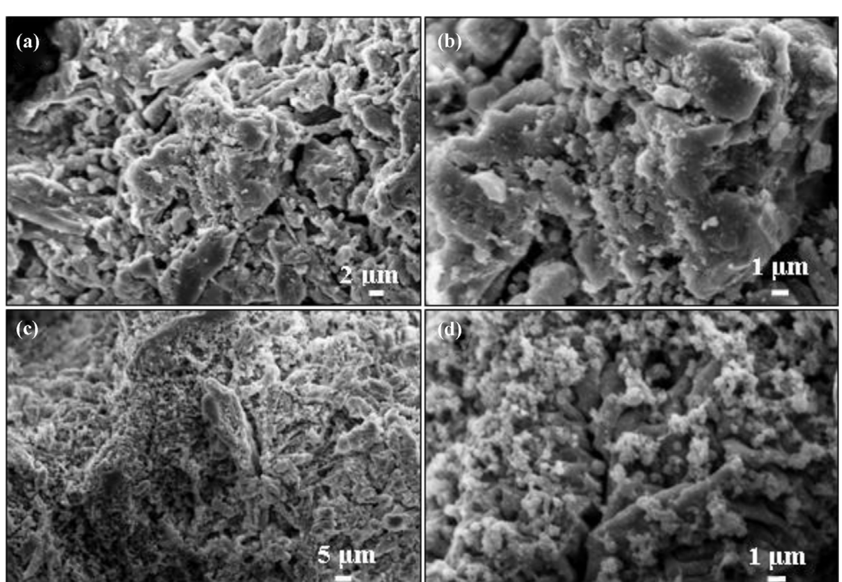

Fig. 4. SEM micrographs of the hybrids using LiCl/DMAc solution: (a) and (b) tetra-n-butyl titanate (5 mL); (c) and (d) tetra-n-butyl titanate (1 mL).

(Fig. 2b), demonstrating the existence of MCC in the hybrids. The band at 691 cm^{-1} was also assigned to the vibration of Ti—O bonds in anatase. The FT-IR spectrum of sample synthesized by the dissolution of MCC in LiCl/DMAc solution had similar peaks at 3344, 1420, 1115, and 619 cm^{-1} in Fig. 2a, compared with Fig. 2b. There were slight differences between the peaks intensity between the FT-IR spectra (Fig. 2). Based on the XRD and FT-IR results, one can demonstrate that the hybrid from cellulose and TiO_2 had been successfully synthesized by the hydrothermal method.

Fig. 3 displays the SEM images of typical hybrid from cellulose and TiO_2 synthesized by the dissolution of MCC in NaOH/urea solution. When the ratio of tetra-n-butyl titanate to cellulose solution was 1:2, one can see that the TiO_2 nanoparticles were dispersed in the cellulose matrix (Fig. 3a and b). When the ratio of tetra-n-butyl titanate to cellulose solution was decreased to 1:14, the particles and fiber-like morphologies were observed, as shown in Fig. 3c and d. However, a few particles dispersed on the surface of cellulose were observed by the dissolution of MCC in LiCl/DMAc solution (Fig. 4a and b). Furthermore, when the tetra-n-butyl titanate concentration was decreased to 1 mL, the size of particles increased (Fig. 4c and d). These results implied that the tetra-n-butyl titanate concentration and the types of solvent not only had an influence on the phase of the cellulose-based hybrid, but also had an effect on the size and morphology of the cellulose-based hybrid.

3.2. The thermal stability and antibacterial activity of hybrid

The thermal stabilities of the hybrid from cellulose and TiO_2 were investigated with TGA and DTA, as shown in Fig. 5. The total weight loss of sample synthesized by the dissolution of MCC in NaOH/urea solution was 17.0% and the exothermic peaks at about 299.8, 460.0, and 527.7 °C were observed in the DTA curve (Fig. 5b). However, the total weight loss of sample synthesized by the dissolution of MCC in LiCl/DMAc solution was 55.8% and the exothermic peaks at about 242.5, 480.0, and 560.6 °C were oberved in the DTA curve (Fig. 5a). The total weight loss of this sample was more than that of Fig. 5b, indicating that the TiO_2 concentration in this sample was higher than that of Fig. 5b. These results implied that the cellulose solution by the dissolution of MCC in NaOH/urea aqueous solution favored the hybrid of cellulose and TiO_2.

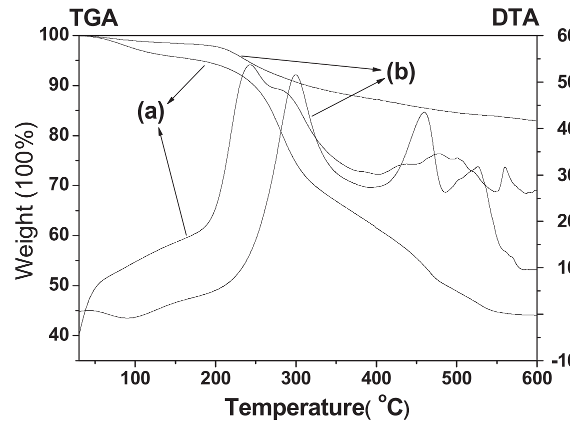

Fig. 5. TGA and DTA curves of the hybrids: (a) using LiCl/DMAc solution and (b) using NaOH/urea solution.

The antibacterial activity of the hybrid from cellulose and TiO_2 was shown in Fig. 6. Pure microcrystalline cellulose was used as control. One can see that no inhibition zone was observed, as shown in the control of Fig. 6, indicating that the pure cellulose had not antimicrobial activities. Cellulose was used as matrix for the dispersion of TiO_2 crystals. The synthesis of hybrid from cellulose and TiO_2 by introduce of cellulose decreased the price of antibacterial materials. The inhibition zone of the sample synthesized by the dissolution of MCC in LiCl/DMAc solution for *E. coli* was 2.5 mm (Fig. 6a), conforming that the TiO_2 had antimicrobial activity. However, there was no obvious inhibition zone for *S. aureus* in Fig. 6b. These results demonstrated that the antimicrobial activity against *E. coli* was higher than that against *S. aureus*, which might be due

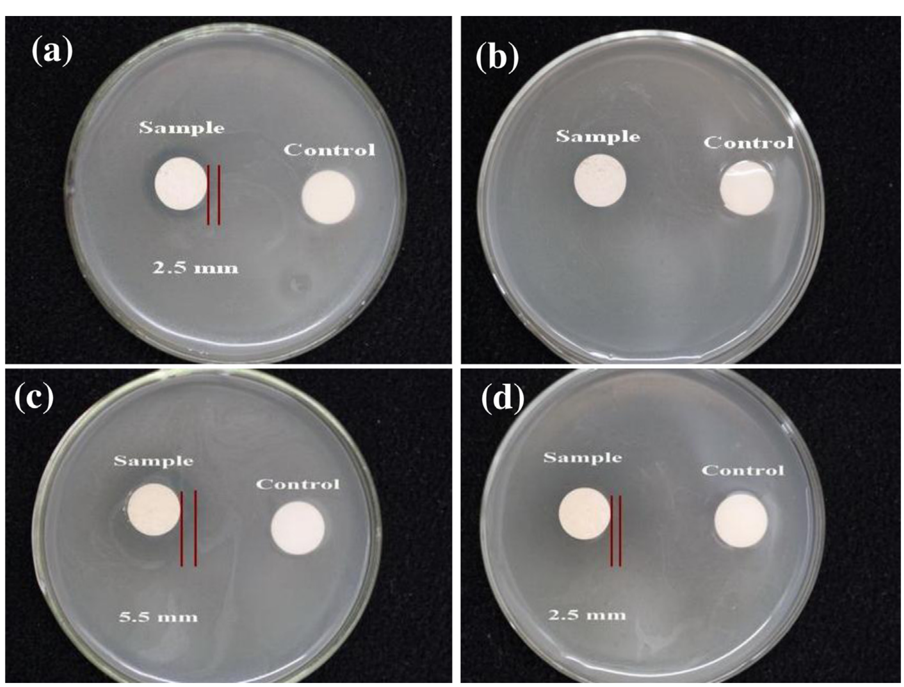

Fig. 6. Antimicrobial activities of the hybrids: (a) and (b) using LiCl/DMAc solution; (c) and (d) using NaOH/urea solution. *(a) and (c) is for *E. coli*; (b) and (d) is for *S. aureus*.

to the difference in cell walls between Gram-negative and Gram-positive bacteria (Feng et al., 2000). The inhibition zones of the hybrid from cellulose and TiO_2 (synthesized by the dissolution of MCC in NaOH/urea solution) for *E. coli* and *S. aureus* were 5.5 mm and 2.5 mm, respectively (Fig. 6c and d). Based on the results of antimicrobial activities, one can conclude that the sample synthesized by the dissolution of MCC in NaOH/urea solution had a better antibacterial effect, compared with sample synthesized by the dissolution of MCC in LiCl/DMAc solution, indicating that the sample fabricated by the dissolution of MCC in NaOH/urea solution favored the improvement of antibacterial effect.

3.3. TiO_2 crystals by calcination the hybrid

Based on the TGA and DTA results, the 600 °C was chosen as the calcination temperature for the completed decomposition of cellulose. The TiO_2 crystals were obtained by calcination the hybrid precursors. The according XRD patterns were shown in Fig. 7A. When the hybrid synthesized by dissolution the MCC in LiCl/DMAc solution were applied as precursors, no obviously peaks of TiO_2 were observed (Fig. 7A(a)). However, when the hybrid synthesized by dissolution the MCC in NaOH/urea solution were applied as precursors, the sample was indexed to well-crystallized rutile with a tetragonal structure (JCPDS 21-1276) (Fig. 7A(b)). In comparison with anatase, it is well known that rutile is a thermodynamically stable phase of TiO_2. During the calcination process, the cellulose was decomposed and the anatase was transformed to rutile at high temperature. FT-IR spectra show that the absorptions are present at the same positions for all the samples, but the differences of peaks intensities are observed (Fig. 7B). The absorptions below 800 cm^{-1} are assigned to the vibrations of Ti—O bonds. The weak peak at 1741 cm^{-1} indicated the presence of water. The adsorption peaks at 1599 and 1507 cm^{-1} were attributed to C—H vibrations of hydrocarbons. The absorptions between 1000 and 1200 cm^{-1} are assigned to the C—O vibration. SEM images showed that the particles were abounded on the surface of fibers (Fig. 8a and b). One can suggested that the fibers were the carbon materials from the thermal decomposition of cellulose. Rutile nanoparticles were dispersed on the irregular block matrix (Fig. 8c and d). The rutile nanoparticles were highly agglomerated from magnified micrograph of the products.

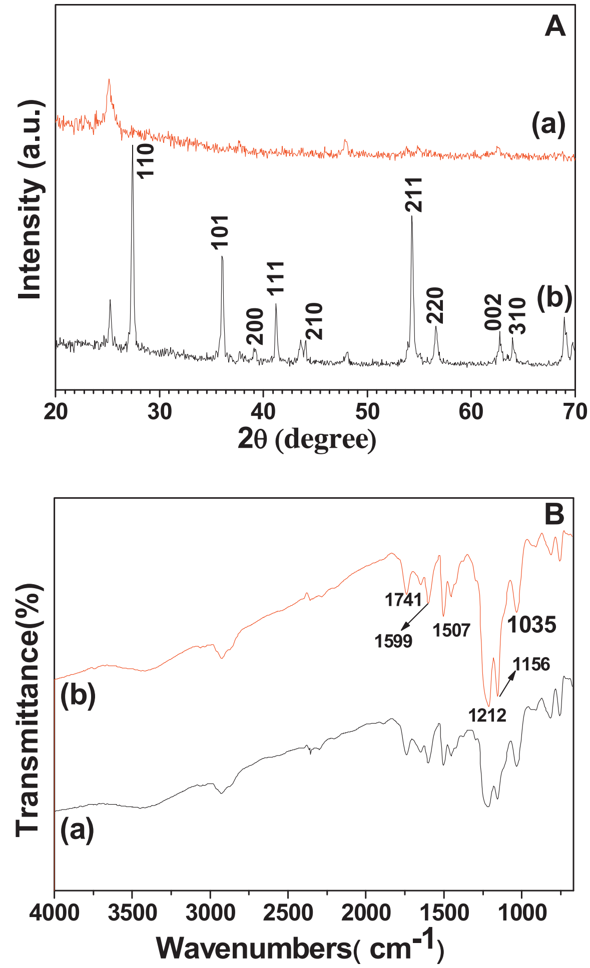

Fig. 7. (A) XRD patterns and (B) FTIR spectra of the products by calcination of the precursors at 600 °C for 3 h: (a) using LiCl/DMAc solution; (b) using NaOH/urea solution.

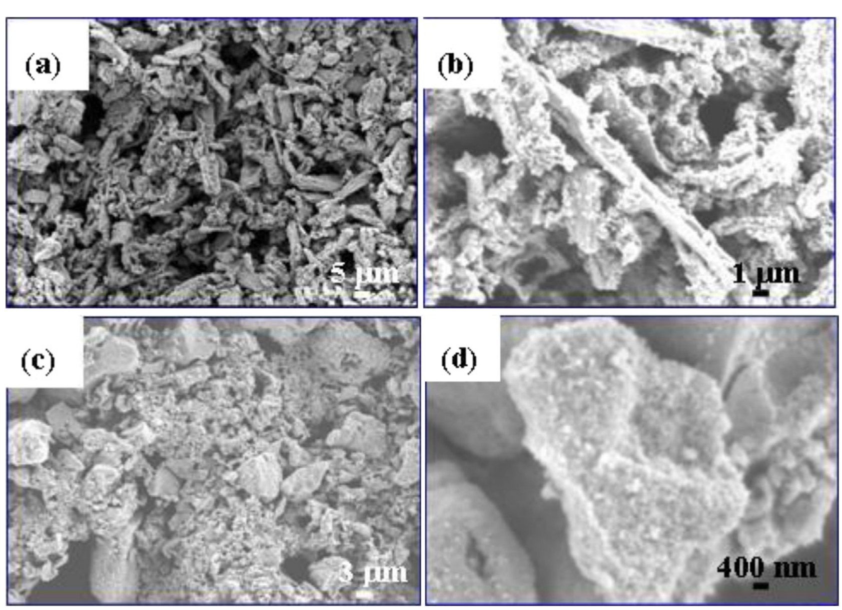

Fig. 8. SEM images of the products by calcination of the precursors at 600 °C for 3 h: (a) and (b) using LiCl/DMAc solution; (c) and (d) using NaOH/urea solution.

4. Conclusions

In summary, the hybrids from cellulose and TiO_2 with high antibacterial activity have been successfully synthesized by a hydrothermal method. The tetra-n-butyl titanate concentration and the types of solvent played an important role in the phase and shape of hybrid. This hybrid might be a promising antibacterial candidate for the applications in biomedical field. This synthetic strategy reported here opens a new window to the high value-added applications of cellulose.

Acknowledgments

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