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Cellulose/$CaCO_3$ nanocomposites: Microwave ionic liquid synthesis, characterization, and biological activity

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ABSTRACT

The purposes of this article are to synthesize the biomass-based hybrid nanocomposites using green method in green solvent and evaluate its biological activity. In this paper, microwave-assisted ionic liquid method is applied to the preparation of cellulose/$CaCO_3$ hybrid nanocomposites in the alkali extraction cellulose using $CaCl_2$ and Na_2CO_3 as starting reactants. The ionic liquid acts as the excellent solvent for absorbing microwave and the dissolution of cellulose, and the synthesis of cellulose/$CaCO_3$ nanocomposites. The influences of reaction parameters such as the cellulose concentration and the types of solvent on the products were investigated. The increasing cellulose concentration favored the growth of $CaCO_3$. The morphologies of $CaCO_3$ changed from polyhedral to cube to particle with increasing cellulose concentration. Moreover, the solvents had an effect on the shape and dispersion of $CaCO_3$. Cytotoxicity experiments demonstrated that the cellulose/$CaCO_3$ nanocomposites had good biocompatibility and could be a candidate for the biomedical applications.

1. Introduction

Cellulose/$CaCO_3$ nanocomposites have been receiving considerable attention thanks to their combining the advantages of cellulose and $CaCO_3$ (Dalas, Klepetsanis, & Koutsoukos, 2000; Fimbel & Siffert, 1986; Shen, Song, Qian, & Yang, 2010; Subramanian, Maloney, & Paulapuro, 2005; Vilela et al., 2010). Cellulose is a representative of natural polysaccharides on the earth, which can be applied in materials, chemical, energy, etc. As a typical biomineral that is abundant in both organisms and nature, $CaCO_3$ is known to have biological activities of protein-adhesive properties, cell compatibility, and hard tissue compatibility. In the literature, $CaCO_3$ was used as drug-support with hydrocortisone phosphate at the maximum amount of 7.5 wt% (Ikoma et al., 2007). Cellulose/$CaCO_3$ nanocomposites would be a promising material for biomedical applications. Many efforts have been placed on the fabrication of the cellulose/$CaCO_3$ nanocomposites. The research of the interaction of $CaCO_3$ (calcite) with cellulose fibers in aqueous medium was first reported by Fimbel and Siffert in 1986 (Fimbel & Siffert, 1986). Then, the kinetics process of the $CaCO_3$ deposition on cellulose substrate was researched by Dalas et al. (2000). After that, Subramanian et al. (2005) reported the coprecipitation of $CaCO_3$ as filler in papermaking. Calcium carbonate was performed in the presence of methyl cellulose and two kinds of hydroxyethyl cellulose (Zhang, Yang, & Tian, 2009). Ciobanu, Bobu, & Ciolacu (2010) reported in situ cellulose fibers loading with calcium carbonate by three different methods. Cellulose/$CaCO_3$ nanocomposites were prepared by the controlled reaction of $CaCl_2$ with dimethylcarbonate ($(CH_3)_2CO_3$) in alkaline medium in the presence of cellulose fibers (Vilela et al., 2010). More recently, Gebauer et al. (2011) prepared the transparent hybrid of nanocrystalline cellulose (NCC) and amorphous calcium carbonate (ACC) nanoparticles with tunable composition, homogeneity and anisotropy by controlling the interactions between NCC and ACC. Stoica-Guzun et al. (2012) investigated the effect of ultrasonic irradiation on the calcium carbonate deposition on bacterial cellulose membranes using $CaCl_2$ and Na_2CO_3 as starting reactants. Moreover, Serra, de Lourdes, & Robles (2003) researched the compatibility of agglomerated mixtures of calcium carbonate and microcrystalline cellulose. Hilder and Batchelor (2010) used attenuated total reflectance infra-red spectroscopy to determine the surface concentration of calcium carbonate filler contents in cellulose matrices. In previous study, the research group synthesized cellulose/$CaCO_3$ nanocomposites using the cellulose solution, $Ca(NO_3)_2{\cdot}4H_2O$ solution, and $Na_2SiO_3{\cdot}9H_2O$ solution by hydrothermal method (Jia, Li, Ma, Sun, & Zhu, 2012b). The influences of different cellulose types about the alkali extraction cellulose and microcrystalline cellulose on the cellulose/$CaCO_3$ composites were compared study via microwave-assisted method (Ma, Fu, Sun, & Jia, 2012).

Microwave-assisted ionic liquid method has been accepted as a promising green technology by combining the advantages of

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microwave heating and ionic liquid. In previous literature, rapid progress has been made in the synthesis of inorganic nanomaterials such as tellurium nanorods and nanowires (Zhu, Wang, Qi, & Hu, 2004), $PbCrO_4$ and Pb_2CrO_5 rods (Wang & Zhu, 2005), iron oxide hollow spheres (Cao & Zhu, 2009), $ZnFe_2O_4$ nanoparticles (Cao, Zhu, Cheng, & Huang, 2009), TiO_2 nanocrystals (Ding et al., 2007), CaF_2, MgF_2, and SrF_2 hollow microspheres (Xu & Zhu, 2012), ect, via microwave-assisted ionic liquid method. More recently, the research group fabricated cellulose-based nanocomposites including cellulose/calcium silicate nanocomposites (Jia, Li, Ma, & Sun, 2011a; Jia, Li, Ma, Sun, & Zhu, 2011b), cellulose/carbonated hydroxyapatite (Ma, Jia, Li, & Sun, 2011), and cellulose/F-substituted hydroxyapatite nanocomposites (Jia, Li, Ma, & Sun, 2012a) by microwave-assisted ionic liquid method. As far as we know, the synthesis of cellulose/$CaCO_3$ nanocomposites by microwave-assisted ionic liquid method has not been reported yet.

In this article, we report the synthesis of the cellulose/$CaCO_3$ nanocomposites by microwave-assisted ionic liquid method using $CaCl_2$ and Na_2CO_3 as starting reactants. The alkali extraction cellulose was used as matrix and the biological activity of cellulose/$CaCO_3$ nanocomposites was evaluated by cytotoxcity experiments. The influence of alkali extraction cellulose concentration on the cellulose/$CaCO_3$ nanocomposites was investigated. Moreover, the effects of the solvents such as ethylene glycol, *N,N*-dimethylformamide, and NaOH/urea on the products were also researched. In comparison to the previous reports (Jia et al., 2012b; Ma et al., 2012), this article develops a green strategy to fabricate the cellulose-based materials in green solvent. Furthermore, it opens up new opportunities for the high value-added applications of cellulose.

2. Experimental

2.1. Preparation of cellulose/$CaCO_3$ nanocomposites by microwave-assisted ionic liquid method

All chemicals were of analytical grade and used as received without further purification. All experiments were conducted under air atmosphere. A typical synthesis experiment for the alkali extraction cellulose was carried out as follow: The holocellulose sample was extracted by 10% KOH aqueous solution with a solid to liquid ratio of 1:25 ($g\,mL^{-1}$). The mixture was maintained at 25 °C for 16 h. After the treatment period, the insoluble residues were separated from the solution by filtration, washed with distilled water until the pH of filtrates was neutral, and then dried at 60 °C. Finally, the alkali extraction cellulose was obtained.

The synthesis of cellulose/$CaCO_3$ nanocomposites was carried out as follow: 0.162 g alkali extraction cellulose (5 wt%) was added into BmimCl (3.240 g) under vigorous stirring at 130 °C for 10 min by microwave heating to obtain a homogeneous cellulose solution. Then, 0.110 g $CaCl_2$ and 0.106 g Na_2CO_3 were added into the above cellulose solution under vigorous magnetic stirring. The solution was heated to 130 °C for 30 min by microwave heating. The microwave oven used for sample fabrication was purchased from Beijing Xiang-Hu Science and Technology Development Reagent Co., Ltd., which was equipped with the magnetic stirring system and a water-cooled condenser outside the microwave cavity. The resulting precipitate was separated from the solution by centrifugation, washed by water and ethanol several times and dried at 60 °C for further characterization.

For comparison, the samples were also obtained by microwave heating at 130 °C for 30 min using 10 wt% and 2 wt% cellulose solution, which were fabricated by adding 0.324 g and 0.065 g alkali extraction cellulose into BmimCl (3.240 g), respectively. Moreover, the influences of types of cellulose solution on the products were investigated. 0.162 g alkali extraction cellulose was added into 20 mL of ethylene glycol, *N,N*-dimethylformamide, and NaOH/urea, respectively, and kept the other conditions the same.

2.2. Characterization

X-ray powder diffraction (XRD) was performed in 2θ range from 10° to 70° on a Rigaku D/Max 2200-PC diffractometer with Cu $K\alpha$ radiation ($\lambda = 0.15418$ nm) and graphite monochromator at ambient temperature. Fourier transform infrared (FTIR) spectroscopy was carried out on Thermo Scientific Nicolet iN10 FTIR Microscope (Thermo Nicolet Corporation, Madison, WI, USA), which was equipped with a liquid nitrogen cooled MCT detector. Dried samples were ground and pelletized with BaF_2 and the spectra were recorded in the range of 4000–670 cm^{-1} at 4 cm^{-1} resolution and 128 scans/sample. Scanning electron microscopy (SEM) images were obtained with a Hitachi 3400 N scanning electron microscopy. All samples were Au coated prior to examination by SEM. The energy-dispersive X-ray spectra (EDS) attached to the scanning electron microscopy was used to analyze the compositions of sample.

2.3. Cell cytotoxicity

The human gastric carcinoma cells (SGC-7901) that were cultured in a RPMI-1640 medium supplemented with 10% fetal bovine serum (FBS) and 1% penicillin-streptomycin at 37 °C for 48 h, were used for cell viability test. Then, the cells were seeded in 96 well flat-bottom microassay plates at a concentration of 1×10^4 cells/mL and cultured for 24 h. The sterilized samples (the cellulose/$CaCO_3$ nanocomposites) were added into wells at the concentration from 0.1, 1, 10, 100 to 500 μg/mL, and were co-cultured with cells for 48 h. The sample free tissue culture plate was used as a control. Cell viability was quantified by 3-(4.5-Dimethylthiazol- 2-yl)-2,5-diphenyltetrazolium bromide (MTT) assay, and the data are representative as mean value of five parallel experiments.

3. Results and discussion

The regenerated cellulose was obtained using ionic liquid as the solvent for the dissolution of alkali extraction cellulose and its XRD pattern was shown in Fig. 1a. One can see that the regenerated cellulose assigned to the crystalline cellulose type II (Togawa & Kondo, 1999). The cellulose/$CaCO_3$ nanocomposites were obtained

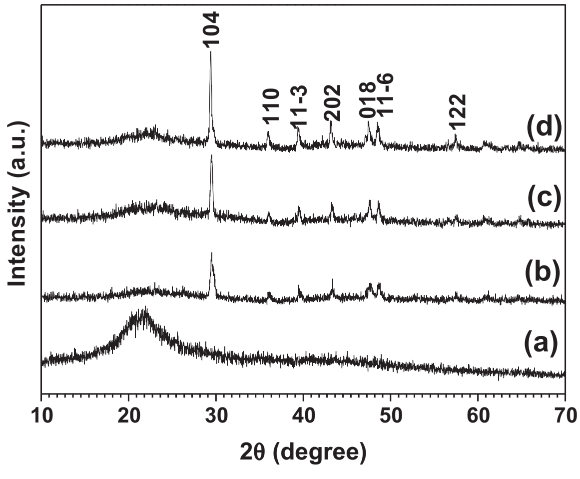

Fig. 1. XRD patterns of the cellulose/$CaCO_3$ nanocomposites prepared in ionic liquid by microwave heating using different cellulose concentrations at 130 °C for 30 min: (a) the control; (b) 2%; (c) 5%; and (d) 10% (by weights).

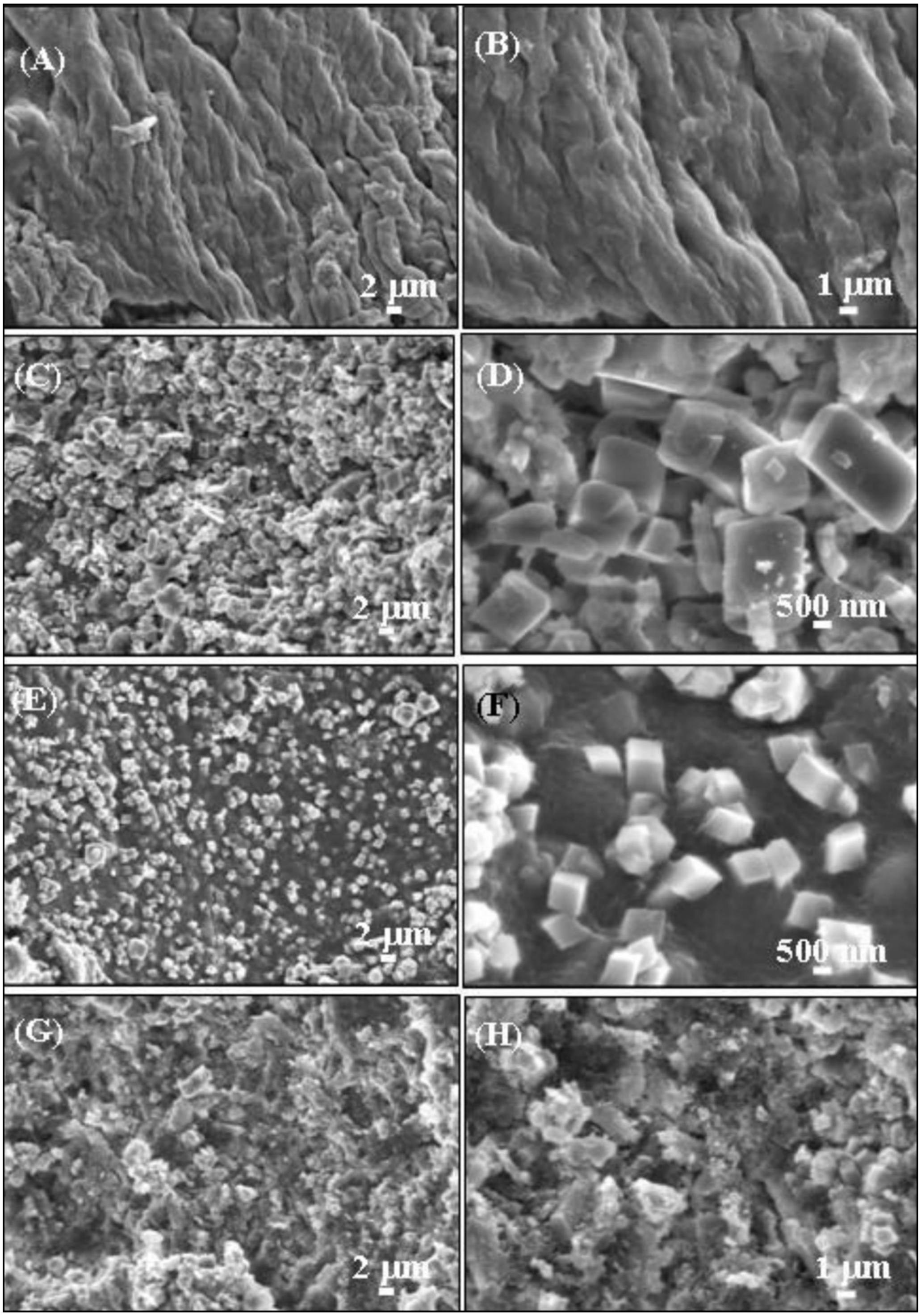

Fig. 2. SEM images of the cellulose/$CaCO_3$ nanocomposites prepared in ionic liquid by microwave heating using different cellulose concentrations at 130 °C for 30 min: (A,B) the control; (C,D) 2%; (E,F) 5%; and (G,H) 10% (by weights).

using alkali extraction cellulose solution, $CaCl_2$, and Na_2CO_3 by microwave-assisted ionic liquid method. When the alkali extraction cellulose concentration was 2 wt%, the XRD pattern of the sample was indexed to a single phase of well-crystallized calcite with the hexagonal structure (JCPDS 47-1743) (Fig. 1b). No other phases such as aragonite or vaterite were observed. The diffraction peaks of regenerated cellulose were not obviously observed due to the strong peaks intensity of $CaCO_3$. In the literature, the mixed phases of calcite and aragonite were obtained via hydrothermal method using $Ca(NO_3)_2{\cdot}4H_2O$ and $Na_2SiO_3{\cdot}9H_2O$ as starting reactants in NaOH/urea solution (Jia et al., 2012b). The phase of poor-crystallized calcite was synthesized by microwave-assisted method in the alkali extraction cellulose using $CaCl_2$ and Na_2CO_3 as starting reactants in NaOH/urea solution (Ma et al., 2012). In this study, the peaks intensities were stronger than those in the literature (Ma et al., 2012). This result indicated that the addition of ionic liquid favored the crystallinity of calcite. When the cellulose concentration was increased from 2 wt% to 5 wt%

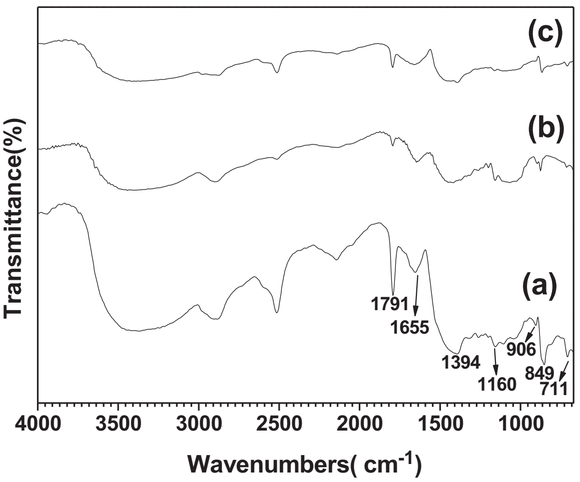

Fig. 3. FTIR spectra of the cellulose/$CaCO_3$ nanocomposites prepared in ionic liquid by microwave heating using different cellulose concentrations at 130 °C for 30 min: (a) the control; (b) 2%; (c) 5%; and (d) 10% (by weights).

to 10 wt%, the samples had similar XRD patterns (Fig. 1c and d), compared with Fig. 1b, indicating that the same phase of calcite was obtained. One can clearly observe that the peak intensity dramatically increased with increasing alkali extraction cellulose concentration, implying that the increasing cellulose concentration favored the growth of $CaCO_3$ in cellulose/$CaCO_3$ nanocomposites. It was well known that the heating time and relatively reaction concentration had an effect on the crystallinity of inorganic materials. There are a few reports about the crystallinity of calcite inducing by cellulose concentration. This phenomenon is a very interesting result, demonstrating that a strong interaction existed between calcite particles and the cellulose matrix, which provided an experimental example for better understanding of the interaction mechanism between inorganic materials and cellulose.

The regenerated cellulose has fiber-like shape with clear surface, as shown in Fig. 2A and B. No particles were observed at the surface of alkali extraction cellulose. Some pores existed in the alkali extraction cellulose fibers, which maybe favor the composition of $CaCO_3$ particles. However, the microcrystalline cellulose displayed irregular short fiber-like shape (Jia et al., 2012a). When the alkali extraction cellulose concentration was 2 wt%, $CaCO_3$ with polyhedral-like shape were disappeared on the surface of cellulose (Fig. 2C and D). Magnified micrograph of the composites was shown in Fig. 2D, from which one can clearly see the polyhedral-like shape of calcite. When the alkali extraction cellulose concentration was increased to 5 wt%, $CaCO_3$ crystals with cube-like shape were embedded in the cellulose matrix (Fig. 2E and F). Cube is the typical shape of calcite. This result demonstrated that the samples were not simple mechanical mixtures of alkali extraction cellulose and $CaCO_3$. This result was consistent with the above XRD results, indicating the interaction between calcite particles and the cellulose matrix. It is generally agreed that the interaction mechanism of inorganic materials and polymer included absorption, weak interactions, and the chemical bonds. However, it is still a significant challenge to found a simple method to explore the intrinsic interaction mechanism. When the alkali extraction cellulose concentration was increased to 10 wt%, $CaCO_3$ particles were dispersed on the surface of cellulose (Fig. 2G and H). From Fig. 2, one can clearly observe the change process of morphology from polyhedral to cubes to particles. Moreover, the size of $CaCO_3$ on the surface of cellulose decreased with increasing cellulose concentrations. When the cellulose concentration was 5 wt%, the dispersion of $CaCO_3$ on the surface of cellulose was better than others. In the previous

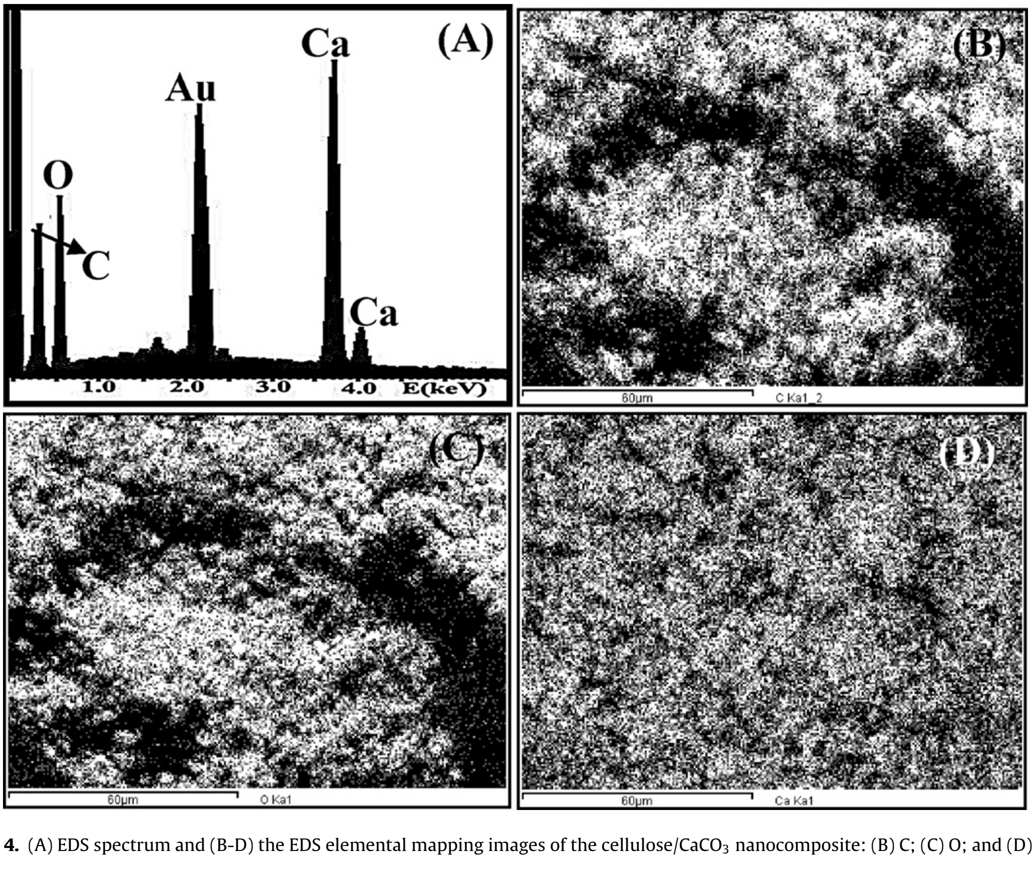

Fig. 4. (A) EDS spectrum and (B-D) the EDS elemental mapping images of the cellulose/$CaCO_3$ nanocomposite: (B) C; (C) O; and (D) Ca.

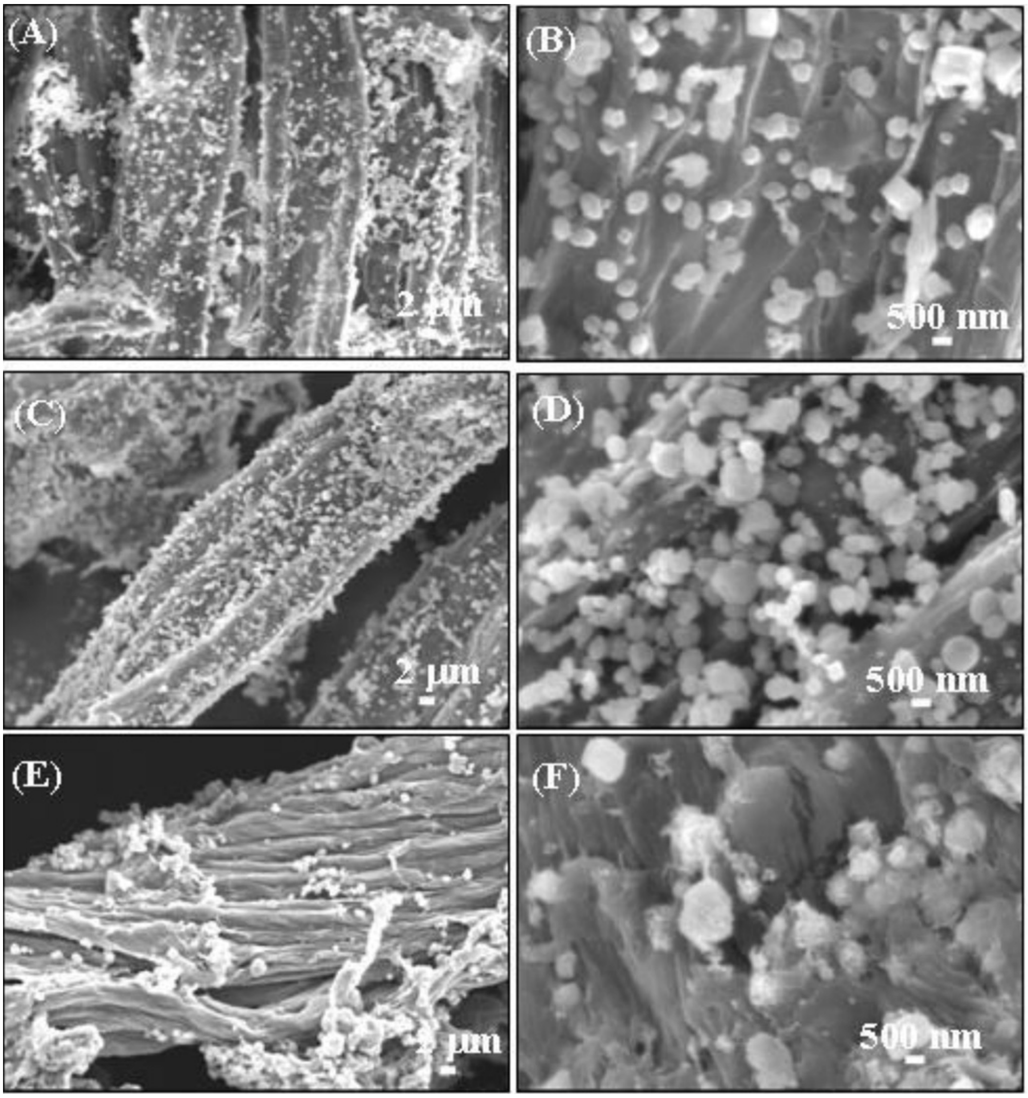

Fig. 5. SEM images of the cellulose/$CaCO_3$ nanocomposites prepared in different solvents by microwave heating at 130 °C for 30 min: (A,B) *N,N*-dimethylformamide; (C,D) ethylene glycol; and (E,F) NaOH/urea.

article, the $CaCO_3$ particles dispersed in the alkali extraction cellulose matrix were observed via microwave-assisted method using $CaCl_2$ and Na_2CO_3 as starting reactants in NaOH/urea solution (Ma et al., 2012). Therefore, the cellulose concentrations had influence on the shape and dispersion of cellulose/$CaCO_3$ nanocomposites. The cellulose was used as matrix, which had many hydroxyl groups. The reaction system changed with the increasing cellulose concentration, inducing the fabrication of CaCO3 crystals with different shapes and dispersion in the cellulose matrix.

FTIR analysis is a useful technology to examine the crystal structure and groups of the products. The FTIR spectra of all the cellulose/$CaCO_3$ nanocomposites fabricated using 2 wt%, 5 wt%, and 10 wt% alkali extraction cellulose concentrations by microwave-assisted ionic liquid method at 130 °C for 30 min were shown in Fig. 3. The FTIR spectra of all the obtained nanocomposites displayed the typical bands of cellulose at 1160 cm^{-1} (the C-O in cellulose) and $CaCO_3$ at around 1394 cm^{-1} ($\nu_{3\text{-}3}$ $CO_3{}^{2-}$ and $\nu_{3\text{-}4}$ $CO_3{}^{2-}$) (He, Huang, Liu, Chen, & Xu, 2007; Nelson & Featherstone, 1982). The bands at 711 cm^{-1} and 849 cm^{-1} were assignable to characteristic peaks of calcite (Donners et al., 2000). The typical band of aragonite was not observed (Naka, Keum, Tanaka, & Chujo, 2000), further indicating that the pure phase of calcite was

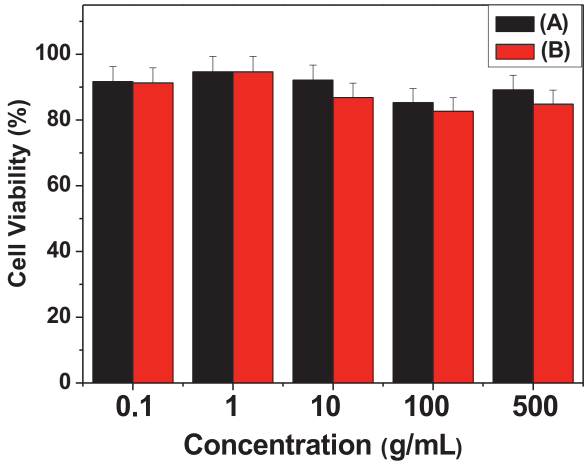

Fig. 6. Viabilities of normal human fibroblasts incubated with the cellulose/$CaCO_3$ nanocomposites: (A) using ethylene glycol and (B) using ionic liquid. They were determined by survival cells per well relative to that of untreated cells. The error bars stand for standard deviations.

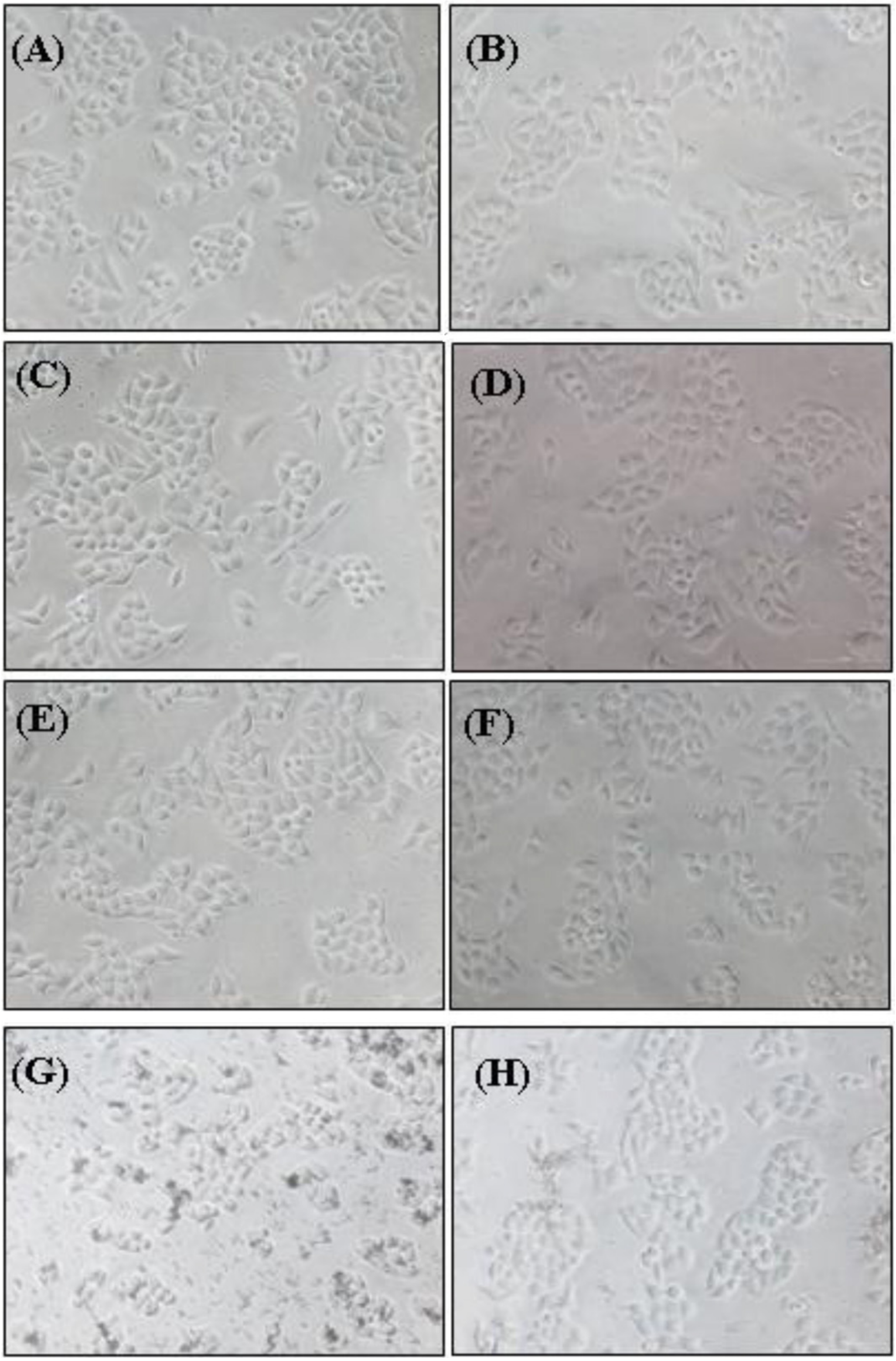

Fig. 7. Photo images of the cell incubated with the cellulose/$CaCO_3$ nanocomposites (A,C,E,G) using ethylene glycol and (B,D,F,H) using ionic liquid: (A,B) 0.1 μg/mL; (C,D) 1 μg/mL; (E,F) 10 μg/mL; (G,H) 500 μg/mL.

obtained. These results were also consistent with the above XRD results.

In order to investigate the dispersion of $CaCO_3$ on the alkali extraction cellulose matrix, the EDS spectrum and the EDS elemental mapping were tested. The EDS spectrum shows that the sample consisted of C, O, and Ca, the right compositions of cellulose/$CaCO_3$ composites (Fig. 4A). The Au peak came from the preparation procedure of samples prior to examination by SEM. The peak intensity of Ca was very strong, implying that the quantity of $CaCO_3$ existed in composites. Fig. 4B-D show the EDS elemental mapping images of C, O, and Ca, respectively, from which one can see that both of C, O, and Ca elementals had well-distribution.

In comparison with ionic liquid, the influences of the other solvents such as ethylene glycol, *N,N*-dimethylformamide, and NaOH/urea on the morphologies of cellulose/$CaCO_3$ nanocomposites were also conducted, as shown in Fig. 5. When *N,N*-dimethylformamide was used as solvent, the $CaCO_3$ spheres dispersed on the cellulose fibers were obtained (Fig. 5A and B). When ethylene glycol was used as solvent, a similar shape were observed and congregates of $CaCO_3$ increased (Fig. 5C and D). When the NaOH/urea solvent instead of ethylene glycol was used, $CaCO_3$ congregates with porous structure dispersed on the surface of cellulose fibers were observed and congregates of $CaCO_3$ decreased (Fig. 5E and F). Both the morphologies and dispersion of the $CaCO_3$ in cellulose/$CaCO_3$ nanocomposites were different from that of samples using ionic liquid, compared with Fig. 2. These results indicated that the solvents had an influence on the shape and dispersion of $CaCO_3$ in nanocomposites, which probably were related to the change of CO_3^{2-} source. All the solvents including ethylene glycol, *N,N*-dimethylformamide, and NaOH/urea have different characteristics, compared with ionic liquid. As a relatively weak organic base, *N,N*-dimethylformamide released NH_4^+ and provided a basic condition for the nucleation and growth of $CaCO_3$. Using NaOH/urea as solvent, urea acted as the CO_3^{2-} source and provided a basic condition for the synthesis of $CaCO_3$. Ethylene glycol had high viscosity, which restrained the nucleation and growth of $CaCO_3$ at relatively low temperature. The viscosity of the ethylene glycol rapidly decreased with the elevation of temperature by microwave heating, inducing the formation of $CaCO_3$. Moreover, the different crystal facets have different growth rates. The different additive had different adsorption ability on various facets, leading to the different growth rate for different crystal facet and the synthesis of $CaCO_3$ with different morphologies in nanocomposites.

As biomedical materials, biologically safe of the cellulose/$CaCO_3$ nanocomposites is very important for their application in biomedical field. Cell cytotoxicity of the cellulose/$CaCO_3$ nanocomposites was tested via 5-dimethylthiazol-2-yl-2,5- diphenyltetrazolium bromide (MTT) assay, as shown in Fig. 6. The cellulose/$CaCO_3$ nanocomposites synthesized by microwave-assisted ionic liquid method using the alkali extraction cellulose concentration (5%) was used as typical sample (Fig. 6B). For comparison, the sample synthesized via microwave-assisted method using the alkali extraction cellulose concentration (5%) in ethylene glycol was also provided (Fig. 6A). From Fig. 6B, one can see that the cell viability values were 91.34%, 94.64%, 86.88%, 82.68%, and 84.88% with the increasing cellulose/$CaCO_3$ nanocomposites concentrations from 0.1 to 1 to 10 to 100 to 500 μg/mL. Using ethylene glycol as solvent, when the cellulose/$CaCO_3$ nanocomposites concentrations were 0.1, 1, 10, 100, and 500 μg/mL, the cell viability values were 91.69%, 94.64%, 92.13%, 85.3%, and 89.18%, respectively, which were a little more than those of the cellulose/$CaCO_3$ nanocomposites synthesized in ionic liquid. Both of the samples had essentially no in vitro cytotoxicity and were comparable with the tissue culture plates. Photo images of the cell incubated with the cellulose/$CaCO_3$ nanocomposites using ethylene glycol and ionic liquid were also provided, as shown in Fig. 7. Morphology of cell was clearly observed. The cell disappeared or became sphere-like shape with increasing nanocomposite concentrations (Fig. 7A-F), indicating that high nanocomposite concentrations had a little effect on the shape of cell. When the cellulose/$CaCO_3$ nanocomposites concentration was 500 μg/mL, some cell disappeared or became sphere-like shape using ethylene glycol and ionic liquid (Fig. 7G and H), suggesting that the sample with high concentration had a little cytotoxicity. In view of the cell viability values (84.88% and 89.18%) in Fig. 6, one can still conclude that the as-prepared cellulose/$CaCO_3$ nanocomposites are safe biomaterial.

4. Conclusions

In summary, we have successfully synthesized the cellulose/$CaCO_3$ nanocomposites by microwave-assisted ionic liquid method using alkali extraction cellulose. XRD and FTIR results indicated that the nanocomposites of cellulose and calcite were obtained and the increasing cellulose concentration favored the growth of $CaCO_3$ in cellulose/$CaCO_3$ nanocomposites. SEM micrographs implied that the morphologies of $CaCO_3$ changed from polyhedral to cube to particle with the increasing cellulose concentration. The solvents also had an influence on the shape and dispersion of $CaCO_3$ in nanocomposites. Cytotoxicity experiments demonstrated that the cellulose/$CaCO_3$ nanocomposites had good biocompatibility. Hence, the as-prepared cellulose/$CaCO_3$ nanocomposites are promising for biomedical applications as a kind of safe biomaterial.

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