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Morphology control and optical properties of organic nanostructures based on thermotropic liquid crystalline benzoylated bacterial cellulose

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ABSTRACT

Organic nanostructures with different morphologies (nanoplatelets, nanotubes, and nanoparticles) of thermotropic liquid crystalline benzoylated bacterial cellulose (BBC) have been prepared with a reprecipitation method by dropwising tetrahydrofuran (THF) solution of BBC into water. The BBC concentration in THF proves crucial for the shapes of assembled BBC nanostructures. These novel BBC nanostructures exhibit apparent UV–vis blue-shifted in absorption peaks and enhanced fluorescence intensity up to 30–60 times compared with THF dilute solution of BBC. The formation mechanism of different nanostructures was tentatively proposed based on the BBC molecular structure.

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1. Introduction

Organic nanomaterials for luminescence have been widely used in optical and optoelectronic field because of their unique optical, electro-optical and optoelectronic properties as well as their potential applications in nanoscale devices (Halik et al., 2004; Kind, Yan, Messer, Law, & Yang, 2002; Law et al., 2004; Wang, Gudiksen, Duan, Cui, & Lieber, 2001). Nanotubes (Zhang et al., 2007a; Zhao, Yang, & Yao, 2006b), nanowires (Zhang et al., 2008; Zhao, Xiao, Yang, Peng, & Yao, 2006a), nanobelts, nanoribbons (Zhang, Zhang, Zou, Lee, & Lee, 2007b), and nanoparticles (An, Kwon, Jung, & Park, 2002; Zhao, Fu, Hu, Peng, & Yao, 2007) have been prepared by organic small molecules or low molecular weight compounds (Balakrishnan et al., 2005; Liu et al., 2006; Yamada, Okujima, & Ono, 2008; Zhao, Peng, Fu, Ma, & Yao, 2008a; Zhao et al., 2008b). It is well known that the fabrication of organic nanomaterials have spurred considerable interest and great significance totally different from those of their inorganic counterparts.

Up to the present, among all the methods to fabrication nanostructures, such as micro-emulsion method (Debuigne, Jeunieau, Wiame, & Nagy, 2000), laser irradiation technique (Tamaki, Asahi, & Masuhara, 2002), and so forth, reprecipitation is favored for its simple processes, no templates or surfactant. Brian et al. have used the reprecipitation method with the mechanism of synergistic dipole–dipole and hydrogen-bonding interactions to assemble organic nanowires and nanoplatelets of 8-[[*p*-[bis(ethyl)amino]phenyl]azo]-isobutylflavin (Jordan et al., 2008). Nakanishi et al. prepared microcrystals of perylene and polydiacetylene by the simple reprecipitation method and found that polydiacetylene microcrystals were a new type of materials for third-order non-linear optics (Kasai, Oikawa, Okada, & Nakanishi, 1998; Oikawa et al., 2000; Oshikiri et al., 1999). Fu and coworkers have also used the method to find that 1-phenyl-3-((dimethylamino)styryl)-5-((dimethylamino)phenyl)-2-pyrazoline nanoparticles possess special size dependence in their optical properties (Fu & Yao, 2001).

Herein we report a facile homoplastic approach to control the growth of the benzoylated bacterial cellulose (BBC) which is a typical thermotropic liquid crystalline material (Wang, Luo, Peng, & Pei, 2008). Meanwhile, there is amazingly discovered that it is not only a class of liquid crystalline material but also a class of photochromic polymer. With the reprecipitation by dropwising tetrahydrofuran (THF) solution of BBC into water, the BBC molecules were found to self-assemble into nanoplatelets, nanotubes, and nanoparticles at designed condition. The shapes are quite crucial to the optical properties of these novel BBC structures.

2. Experiment section

2.1. The preparation of BBC

BBC was prepared based on our previous paper (Wang et al., 2008). In a typical synthetic procedure, nitrobenzene and bacterial cellulose powder (12 mL/g,) were mixed. After standing for half an

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hour at room temperature, the above mixture was added by benzoyl chloride (8 mL/g) and pyridine (5 mL/g). The final mixture was heated at 125 °C for 20 h to form a homogenous solution. The solution was subsequently poured into bulky ethanol. The BBC was precipitated as a solid from the solution. The obtained BBC was separated by filtration, alternatively washed with ethanol and acetone, and finally dried at 70 °C. Saponification method was used to determine the degree substitution (DS) of BBC. The DS of used BBC in this paper is 1.5. The synthesized compound was confirmed with POM, DSC, WAXD and FTIR.

2.2. Nanostructure fabrication

A solution of BBC in THF at varied concentration of 0.5×10^{-3}, 0.75×10^{-3}, and 2×10^{-3} g/mL were separately taken 0.2 mL and injected into deionized water (5 mL) and vigorously stirred for 5 min. The THF/water solutions were left undisturbed for 6 h, during which the nanostructures with different morphologies were formed gradually.

2.3. Scanning electron microscopy

Samples were dropped onto silicon wafers and the solvent was left to evaporate at corresponding temperature. The dried samples were coated with a thin gold layer for the SEM observation. The SEM images were observed with TM-1000 (Hitachi, Japan) and LEO S440 (Leica Cambridge LTD, UK) microscope.

2.4. Transmission electron microscopy

Samples for transmission electron microscopy (TEM) were conducted on JEM 2010(JEOL, Japan) microscope.

2.5. UV/Vis absorption spectroscopy

Solutions of BBC in THF at varied concentration were separately taken 0.2 mL and injected into deionized water (5 mL) and vigorously stirred for 5 min. The THF/water solutions were left undisturbed for 6 h, and then recorded on the UV-3150 spectrophotometer made in Shimadzu Company of Japan.

2.6. Fluorescence emission spectra

The fluorescence spectra of BBC with different morphologies in the solution and assembled on the silicon wafers were obtained with the excitation wavelength of 250 nm with a PE-LS55 spectrofluorimeter (PerkinElmer, America).

3. Results and discussion

3.1. The morphologies of BBC nanostructures

BBC/THF solution (0.2 mL) with concentration of 0.5×10^{-3} g/mL was injected into deionized water (5 mL) and vigorously stirred for 5 min. The sample was subsequently allowed to stand for 6 h at 16 °C. The nanoplatelets occurred (Fig. 1a). The nanoplatelets exhibit hexagonal morphology with the thickness of a few hundred nanometers (Inset of Fig. 1a). Increase of the BBC concentration to 0.75×10^{-3} g/mL leads to the formation of nanotubes (Fig. 1b). The nanotubes are of several micrometers in length. The corresponding TEM image reveals that the nanotube is multi-walled with open tip, which is formed by sheets via rolling (Fig. 1c). Further increase of the concentration to 2×10^{-3} g/mL results in the nanoparticles (Fig. 1d). The strikingly different morphologies of

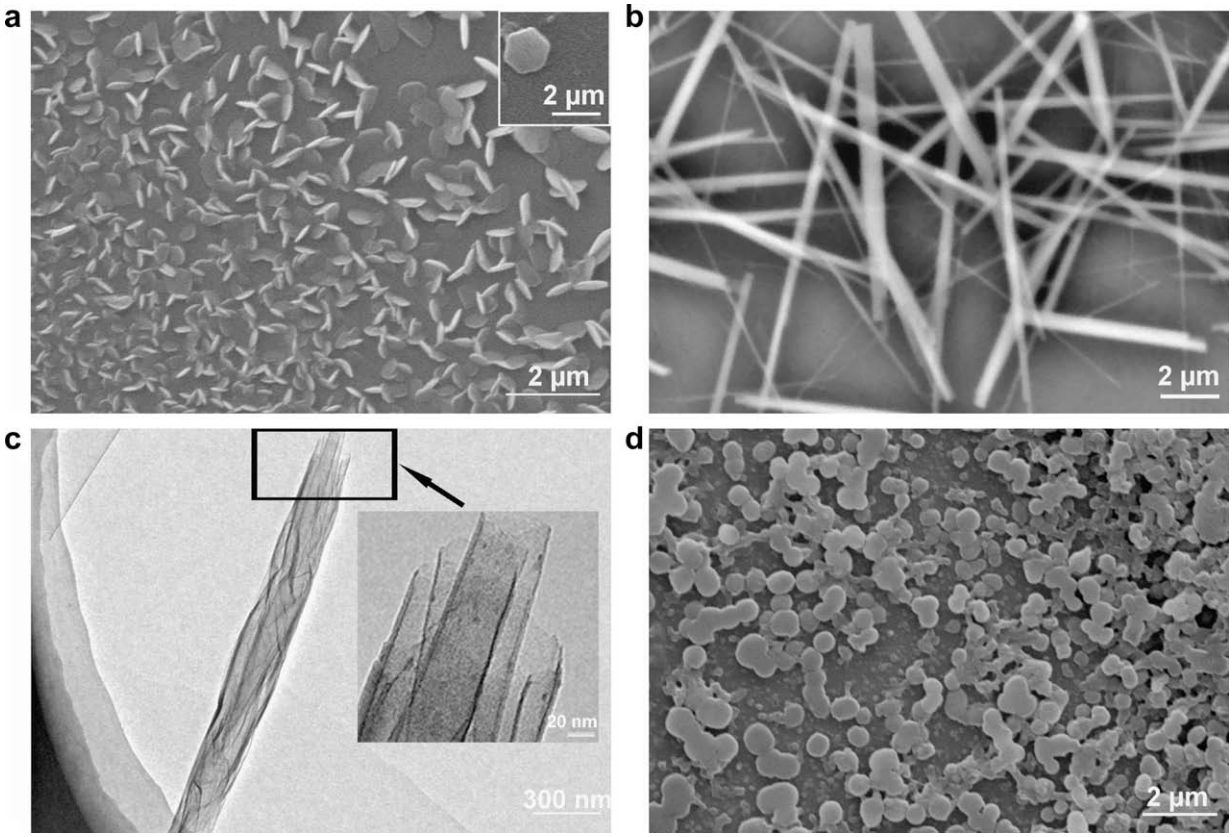

Fig. 1. Electron microscopy images of BBC. (a) SEM image of edge-shaped nanoplatelet (inset a flat hexagonal platelet, supporting information); (b) SEM image of nanotubes; (c) TEM image of the nanotubes (inset the magnifying one of the selected tip section); and (d) SEM image of round nanoparticles.

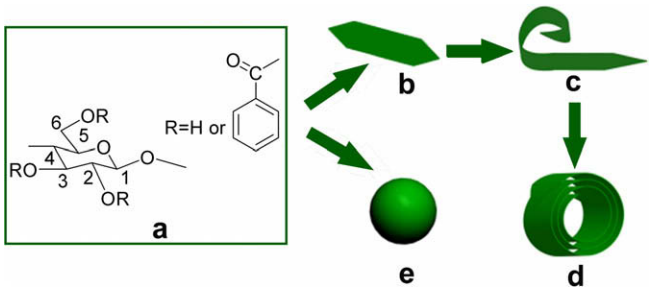

Fig. 2. The typical schematic illustration of the fabrication processes of BBC nanostructures with different morphologies: (a) the molecular structure of BBC; (b) the hexagonal nanoplatelet; (c) a nanoscroll extension of hexagonal nanoplatelet; (d) nanotube formation through rolling hexagonal nanoplatelet; (e) the nanoparticle.

BBC indicate that the concentration is crucial for the self-assembly of the BBC molecules.

The formation process of the unique BBC nanostructures with different morphologies is schematically illustrated in Fig. 2. As many –OH groups exist in BBC (Fig. 2a), we believe that the hydrogen-bonding and van der Waals interaction among the BBC molecules may be the driven force for the nanostructure formation. Several theories have been proposed for formation of nanotubes (Shimizu, Masuda, & Minamikawa, 2005; Yan et al., 2008). The bending and roll-up of a thin layer to form tube is a thermally driven process. (Feldman, Wasserman, Srolovitz, & Tenne, 1995; Tenne, Margulis, Genut, & Hodes, 1992). We think that the present BBC nanotube was generated by scrolling of the extended hexagonal nanoplatelet (Fig. 2c).

3.2. UV absorption spectrum

As a conjugated polymer, Fig. 3 shows that the UV–visible absorption spectrum of BBC/THF dilute solution exhibits one peak at 278 nm (curve A), which may originates from intramolecular charge transfer from the HOMO of the donor part to the LUMO of the acceptor (Horiguchi, Shirai, Matsuoka, & Matsui, 2002). With reprecipitation of the BBC from THF by adding water, the peak blue-shifted to 235 nm (curve B) for nanoparticles, 238 nm (curve C) for nanotubes, 242 nm (curve D) for nanoplatelets. The peak shift may be due to the increased solvent polarizability, intermolecular H-bonding effects and intermolecular dipole–dipole interactions forces of BBC (Blanco, Gasull, & Ferretti, 2003; Cui et al., 2008; Ghanadzadeh, Zeini, Kashef, & Moghadam, 2009). Meanwhile, the shape-dependent peak location may be attributed to different packing fashion of the BBC molecules.

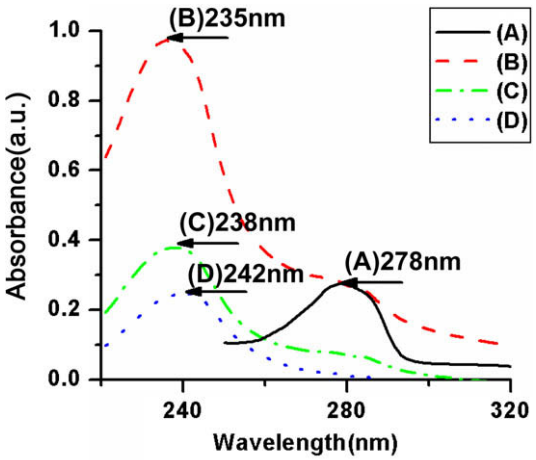

Fig. 3. UV absorption spectrum of (A) dilute BBC/THF solution (0.5×10^{-3} g/mL); (B) nanoparticles; (C) nanotubes; (D) nanoplatelets.

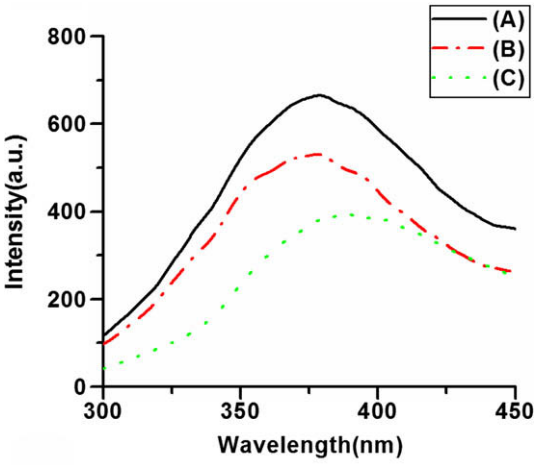

Fig. 4. Fluorescence emission spectra of BBC nanostructures in solution (A) nanotubes; (B) nanoparticles; (C) nanoplatelets. Excitation wavelength at 250 nm.

3.3. Fluorescence emission spectra

The fluorescence properties of BBC nanostructures with different morphology in solution were shown in Fig. 4., compared to that BBC in dilute THF is of scarcely fluorescence characteristics. In contrast, the produced nanoplatelets, nanotubes, and nanoparticles display apparent fluorescence peaks at 383, 375, and 393 nm, respectively, and the fluorescence intensities were increased over 30–60 times compared with that of BBC in dilute THF. Meanwhile, the intensity order of the nanostructures is nanotube > nanoparticle > nanoplatelet. The reason for the considerably enhanced fluorescence intensity may be explained that with the formation of the BBC nanostructures, decrease of the intermolecular vibration due to the rigid plane and possibilities of collisional deactivation are both beneficial for creation of fluorescence (Tasic & Parmenter, 2004; Hu et al., 2008). Meanwhile, the increased polarity of the solvent upon injection of BBC in THF solution into water is also favorable for enhancement of the fluorescence intensity. In addition, the morphology-dependent location of the fluorescence peak may also originate from different stacking fashions of BBC molecules.

The fluorescence emission spectra of different morphologies with BBC nanostructures assembled on the silicon wafers were measured. It can be seen that the prominent feature of the emission spectra of the nanostructures were similar to the as-prepared samples in the solution. There is no distinct change in the peak position and intensity compared to the solution stabilized for 6 h. It can support the information that the nanostructures were formed in the solution and what on the silicon wafers remained to be BBC. Furthermore, the luminescence intensity is nanotube > nanoparticle > nanoplatelet, all of them are much stronger than the corresponding quantity of BBC powder. Significantly, such morphology-dependent optical properties may provide a novel approach to engineer new optoelectronic devices.

4. Conclusion

Control of the concentration of BBC in THF which reprecipitates in water allows us to obtain the different morphology of nanoplatelets, nanotubes, and nanoparticles. These novel BBC nanostructures exhibit apparent UV–vis blue-shift in absorption peaks and

enhanced fluorescence intensity up to 30–60 times compared with THF dilute solution of BBC. This work also explores the potential to apply the material for creation morphology-dependent functional nanosystems on optoelectronic devices.

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