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Fabrication of UV-blocking nanohybrid coating via miniemulsion polymerization

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Abstract

A novel convenient approach to fabricate ZnO@polystyrene nanohybrid coating on cotton fabrics is reported. The as-prepared core–shell nanohybrid coating was characterized by scanning electron microscope (SEM), transmission electron microscope (TEM), energy dispersive X-ray (EDX), and UV-blocking. The cotton fabrics treated in this study provided ultrahigh UV protection and superior wash fastness. Therefore, this new nanohybrid material and its synthesis method are highly potential to various functional treatments of flexible surfaces.

Keywords: Nanohybrid coating; In situ polymerization; Miniemulsion

1. Introduction

Recently, much interest in organic/inorganic nanohybrids has developed in the field of material science [1–4]. Nano-ZnO, as an important inorganic material, exhibits low dielectric constant, large electromechanical coupling coefficient, high luminous transmittance, high catalysis activity, intensive ultraviolet and infrared absorption, etc. Therefore, nano-ZnO can potentially be applied to catalysts, gas sensors, semiconductors, varistors, piezoelectric devices, field-emission displays, and UV-shielding materials [5–11]. However, designing and modifying fabrics by nano-ZnO for high protection against UV radiation (UV-R, both UVA and UVB, falls into the regions of 400–315 and 315–280 nm, respectively, of the solar spectra) is a relatively new application. Few literatures in this area could be found, and they also showed lower UV-blocking activity or worse wash fastness [12,13]. Because nano-ZnO with enormous aspect ratio is apt to coagulate, and there would not exist chemical bonding forces between inorganic ZnO and organic fibers, but just weaker physical adsorptions. In this regard, encapsulation of nano-ZnO by polymer is suggested to the fabrication of protective coating on cotton fabrics, which will result in better performance, uniformity and affinity. Several methods have been reported to achieve the encapsulation of inorganic particles, such as heterophase polymerization [14,15], heterocoagulation [16,17], and layer-by-layer self-assembly process [18–20]. But the meticulous pretreatment of the particles, ambiguous particle nucleation mechanism and kinetic process in these methods heavily complicate the structure formation and morphology control of the nanohybrids. The dispersion of inorganic particles directly into the hydrophobic monomer phase, followed by miniemulsification of the oil in water to form submicron droplets and their subsequent polymerization is proposed to provide several advantages over the above methods [21–23]. In a miniemulsion, the monomer droplets with inorganic cores become the dominant site for particle nucleation, thereby bringing about the effective encapsulation [24–26].

In this paper, the ability to carry out particle nucleation in miniemulsion droplets will be shown leads to an efficient encapsulation of nano-ZnO by polystyrene (PS). For the preparation of the miniemulsion, two steps have to be controlled: First, the already hydrophobic particulate ZnO has to be dispersed in the monomer phase, using a surfactant system 1 with lower HLB value. It is due to that the stable dispersion of inorganic ZnO nanoparticles in the hydrophobic monomer medium requires the adsorption of a dispersing agent at the solid/oil interface. Then, this common mixture is miniemulsified in the

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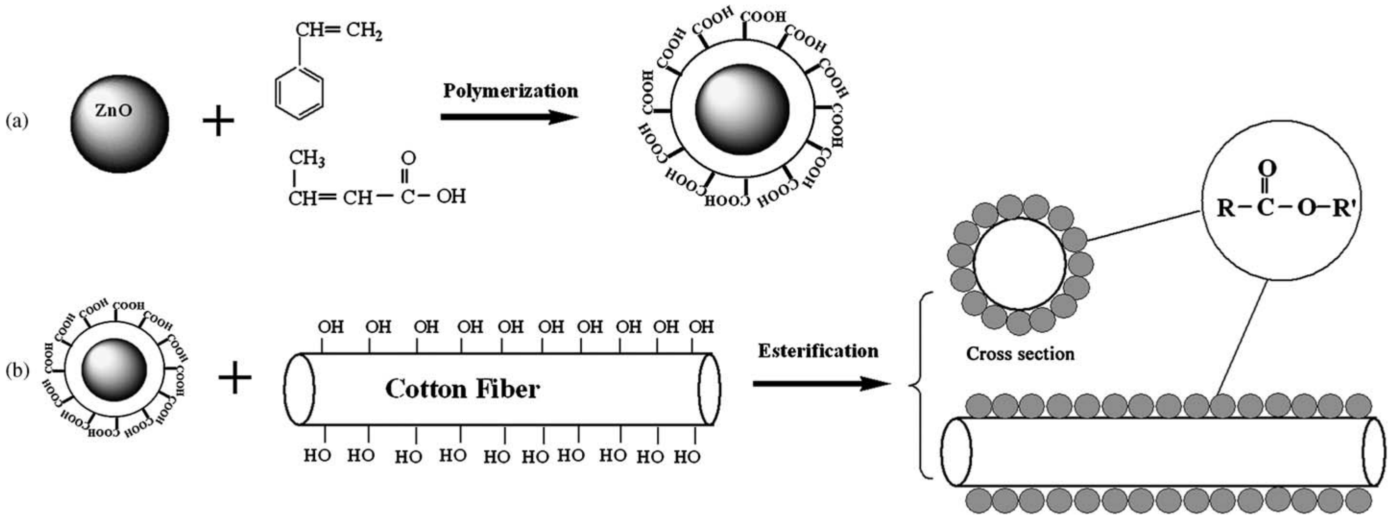

Fig. 1. Schematic preparation of the nanohybrid coating on cotton fabric.

water phase, employing a surfactant system 2 with higher HLB to stabilize the monomer (polymer)/water interface. Thus, the oil phase comprised of ZnO nanoparticles was dispersed in water as miniemulsion droplets and subsequently polymerized using an oil-soluble initiator. On the other hand, in order to improve the affinity of nanohybrid coating on the cotton fabrics, chemical bonds have to be obtained between nanohybrids and cotton fibers. As a cellulosic fiber, the cotton surface is rich of hydroxy groups [27], which can form ester bonds with carboxyl groups by catalysis of sodium hypophosphite. Accordingly, methacrylic acid was selected as the comonomer, as illustrated in Fig. 1. The synthesis procedure, structure and UV-blocking property of the core–shell nanohybrids and coating were emphatically investigated in this study.

2. Materials and methods

2.1. Materials

The monomer styrene (St, 99%, International Laboratory, USA) and methyl acrylic acid (MAA, 99.5%, Acros Organics, USA) were distilled under reduced pressure to remove inhibitor and were stored at −5 °C before they were used. ZnO nanopowder (20–100 nm in diameter) was gift from Junye Nanotechnology Co. (Shenzhen, China). Poly(ethylene-alt-maleic anhydride) (PEMA), sodium lauryl sulfate (SLS, 95%), Igepal DM-970, 2,2-azobisisobutyronitrile (AIBN, 98%), sodium hypophosphite monohydrate ($NaH_2PO_2 \cdot H_2O$, 98%) were all purchased from Aldrich and used as received. Water was doubly distilled and deionized. The substrates (white tabby woven cotton fabrics) were scoured by nonionic detergent to remove the wax, grease, and other finishing chemicals from fabrics before coating. The scouring process was performed at 80 °C for 30 min.

2.2. Synthesis of nanohybrid coating

First, 3 g particulate ZnO was dispersed in the mixture of 100 g St, 5 g MAA, 3 g PEMA, and 1 g AIBN by ultrasonication for 5 min. The obtained oil phase was added into 1880 ml water dissolving with surfactants (2 g SLS and 0.4 g DM-970) and catalyst (5 g $NaH_2PO_2 \cdot H_2O$). After stirring for 5 min, the miniemulsion was prepared by ultrasonication for 15 min. To avoid polymerization due to heating, the mixture was cooled in an ice-bath during homogenization. After miniemulsification, 5 pieces of cotton fabrics (3 × 4 cm, 0.75 g/piece) were suspended in. The reaction was then carried out under a nitrogen atmosphere for 12 h at 68 °C with stirring. Finally, the cotton fabric samples were dried at 80 °C for 30 min and cured at 120 °C for 5 min for further esterification.

2.3. Instruments and characterizations

The structures and morphologies were investigated using a field emission scanning electron microscopy (FESEM, Leica Stereo-scan 440, operating at 20 kV) and a transmission electron microscopy (TEM, JEOL JEM 2010 operated at 200 kV). Energy dispersive X-ray microanalysis (EDX) was performed at 10 kV coupled to the FESEM. "Ultraviolet protection factor" (UPF) was measured by a Varian Cary 300 UV spectrophotometer according to the Australian/New Zealand Standard AS/NZS 4399:1996. Wash fastness was evaluated following the AATCC Test Method 61-1996 test No. 2A, using an AATCC Standard Instrumental Atlas Launder-Ometer LEF. One wash in Atlas Launder-Ometer LEF is equivalent to five home machine launderings according to AATCC test method. For easy understanding, we quote the equivalent number of home machine launderings in this paper.

3. Results and discussion

Fig. 2a shows a SEM image of the initial ZnO nanopowder used in this study. Fig. 2b shows a TEM image of the pure PS nanoparticles (absence of ZnO) with 20–100 nm in diameter. Some typical TEM images of the synthesized nanohybrids are shown by different magnifications in Figs. 2c–2e, respectively. In comparison with Fig. 2b, it is evident that almost all