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Novel near infrared reflective pigments based on hollow glass microsphere/ $BiOCl_{1-x}I_x$ composites: Optical property and superhydrophobicity

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ABSTRACT

In this work, $BiOCl_{1-x}I_x$ coated hollow glass microsphere was synthesized as a novel near infrared reflective pigment for superhydrophobic cool roof coatings. $BiOCl_{1-x}I_x$ microflowers or microspheres were deposited on hollow glass microspheres using a simple chemical liquid deposition method. The morphologies of $BiOCl_{1-x}I_x$ were found to differ drastically by varying the molar ratio of Cl to I. The color of the composite pigments changed from white to red and the band gap decreased from 3.16 eV to 1.87 eV as the increased content of I. The near infrared solar reflectance of the composite pigment was as high as 0.947. An approximately 8 °C decrease in outer surface temperature was obtained for the heat box coated with the composite pigments. With the help of the micro/nano-scale surface roughness of hollow glass microsphere/ $BiOCl_{1-x}I_x$ composites, a superhydrophobic coating with a contact angle of 156.1° could be obtained. The superhydrophobic cool coating showed good antifouling property when they were fouled by the slurry solution containing montmorillonite and Rhodamine B. Moreover, the prepared superhydrophobic coatings exhibited long term stability and ultraviolet durability. Therefore, such superhydrophobic cool coatings with antifouling property is able to work for a longer time by preventing the contamination for building thermal insulation.

1. Introduction

The urban heat island phenomenon (UHI) describes how densely packed urban areas are warmer than surrounding rural regions [1]. UHI increases the peak electricity demand for cooling, intensifies the emission of pollutants from power plants, and deteriorates indoor and outdoor thermal comfort conditions [2]. Recent studies have shown that for each degree of temperature increase caused by UHI, the increase of the peak electricity load during the summer period varies between 0.45% and 4.6% [3]. In order to overcome this challenge, several experimental and numerical studies have been performed in order to develop mitigation solutions and passive cooling strategies [4–13]. Cool roof coatings with high near infrared (NIR) reflectance used in the urban environment present a significantly lower surface temperature and contribute to reducing the heat gain of the buildings and mitigating the urban heat island [5,14–19]. Therefore, the design and creation of novel NIR reflective materials for building energy-saving applications would be of great value.

To maintain maximum cooling energy saving efficiency throughout the service lifetime, cool coatings should retain their original NIR reflectance as long as possible. However, the initially high reflectance of a cool coating can be reduced by soiling process including deposition of atmospheric black carbon, dust, and organic and inorganic particulate matter, as well as microbiological growth [20]. It was reported that the solar reflectance of existing white-coated roofs decreases approximately 15% in the first year due to dirt accumulation, followed by a 2% annual decline in subsequent years [21]. Thus, it would be of great value to develop cool coatings with antifouling property. Superhydrophobic coating has been reported to exhibit excellent self-cleaning property and antifouling property [22,23]. However, little work concerning about the superhydrophobic cool roof coatings has been reported [24].

In this paper, we developed a novel approach for the design of superhydrophobic NIR reflective coatings using hollow glass microspheres/$BiOCl_xI_{1-x}$ composite pigments, as shown in Fig. 1. Due to the hollow structure of hollow glass microspheres (HGM), HGMs exhibit a lower thermal conductivity than that of clay, calcite and zeolite [25]. Thus, coating of $BiOCl_{1-x}I_x$ on the surface of HGMs leads to a composite material with low thermal conductivity and high NIR reflectance. $BiOCl_xI_{1-x}$ micro/nanostructures were deposited on the surfaces of HGMs by a simple chemical liquid deposition method. The phase composition, microstructure and optical properties of HGM/ $BiOCl_xI_{1-x}$ composite pigments were investigated. Moreover, the thermal

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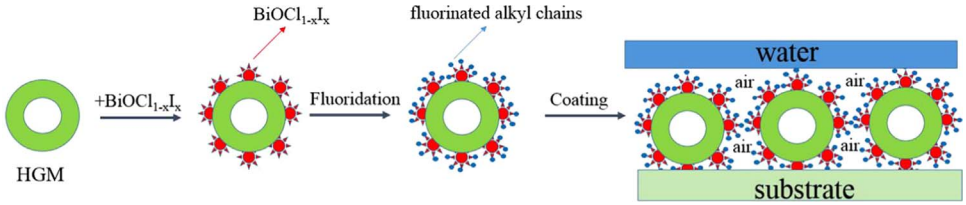

Fig. 1. Schematic illustration of the fabrication of superhydrophobic cool films derived from HGM/ $BiOCl_{1-x}I_x$ composites through a facile brush technique process.

insulation property, superhydrophobic property and antifouling property of the cool coatings composed of HGM/ $BiOCl_xI_{1-x}$ composite pigments were reported for the first time.

2. Experimental

2.1. Materials

All the reagents in the present work were analytical grade and used without further purification. Deionized water was used for preparing solutions in the experiments. HGMs were supplied by Sinosteel Maanshan New Material Technology Co. Ltd. The spherical shapes of the HGMs could be observed from Fig. 2. The diameter of the HGMs are of 5–50 μm. In the XRD pattern of the pristine HGMs, only a broad peak at around 23° is shown, which is the characteristic peak of amorphous SiO_2.

2.2. Preparation of HGM/ $BiOCl_xI_{1-x}$ composite pigments

To improve the surface activities of the glass microspheres, the surface of HGMs was modified with sodium hydroxide solution. 25 g of HGMs was dispersed with 1 L of sodium hydroxide solution (10 wt%). The batch was then stirred for 12 h. Last, the particles were separated, washed with distilled water, and dried at 90 °C for 24 h.

To prepare the HGM/ $BiOCl_{1-x}I_x$ (x = 0, 0.25, 0.5, 0.75, 1) composite pigments, stoichiometric amounts of KCl and KI were dissolved in a mix solution of water and ethanol and then $Bi(NO_3)_3{\cdot}5H_2O$ was added into this solution under magnetic stirring. Subsequently, the modified HGMs were dispersed into the solution. The pH value of the slurry was adjusted to 7.0 using ammonium hydroxide. The slurry was then stirred for an additional 120 min at 25 °C. Finally, the precipitate was collected, filtered and dried at 70 °C for 12 h.

2.3. Surface modification of HGM/ $BiOCl_xI_{1-x}$ composite pigments

To hydrophobize the composite pigments, the pigments were treated by (Heptadecafluoro-1,1,2,2-tetrahydrodecyl) trimethoxysilane (FAS). FAS can be used to functionalize metal oxides from hydrophilic to hydrophobic. The process by which functionalization occurs is illustrated in Fig. 1. The exposed long-chain fluoroalkyl group of the FAS molecules result in a hydrophobic particle surface. Approximately 4 g of particles were added to a 40 mL n-hexane solution. The mixture was stirred vigorously for 30 min. Next, 1 g of FAS were added to the batch. The slurry was stirred for an additional 3 h. Finally, the precipitate was collected and dried at 60 °C for 24 h.

2.4. Fabrication of superhydrophobic coating

0.3 g of polystyrene resin was added to 9.7 g of butyl acetate, and stirred for 3 h to obtain the polystyrene/butyl acetate solution. 0.6 g of FAS modified particles were added to the solution. The slurry was stirred for 30 min. Then, the slurry was coated onto a glass substrate or an aluminium plate by a wire bar coater. The thickness of the wet coating layer is about 120 μm. Finally, the coated glass was dried at ambient temperature.

2.5. Characterization

Morphological observations and identification of chemical composition were performed with scanning electron microscope EV018 (Zeiss) equipped with an energy-dispersive X-ray spectrometer (EDX). Crystalline structure of as synthesized composite pigments was characterized by a PANalytical X'Pert Pro diffractometer. The UV–Vis–NIR diffuse reflectance spectra of the samples was measured using a Lambda950 spectrophotometer (PerkinElmer). The chemical composition and the valence states of the constituent elements were analyzed by X-ray photoelectron spectroscopy (XPS) (ESCALAB 250, Thermo-VG Scientific). Surface roughness and morphologies of the coatings were evaluated by a surface profilometer (BMT Expert 3D) in the tapping mode. Static water contact angles were measured by the sessile drop method using a Contact Angle System OCA40.

The thermal insulation efficiency of the prepared superhydrophobic films was carried out in a self-designed set-up (Fig. 3). The heat box was insulated with polystyrene foam and equipped with an infrared lamp (OSRAM, 250 W). The coated aluminium plates were placed at the top of the heat box. The outer surface temperature of the aluminium plates was recorded by a digital thermometer.

To demonstrate the antifouling property of the prepared

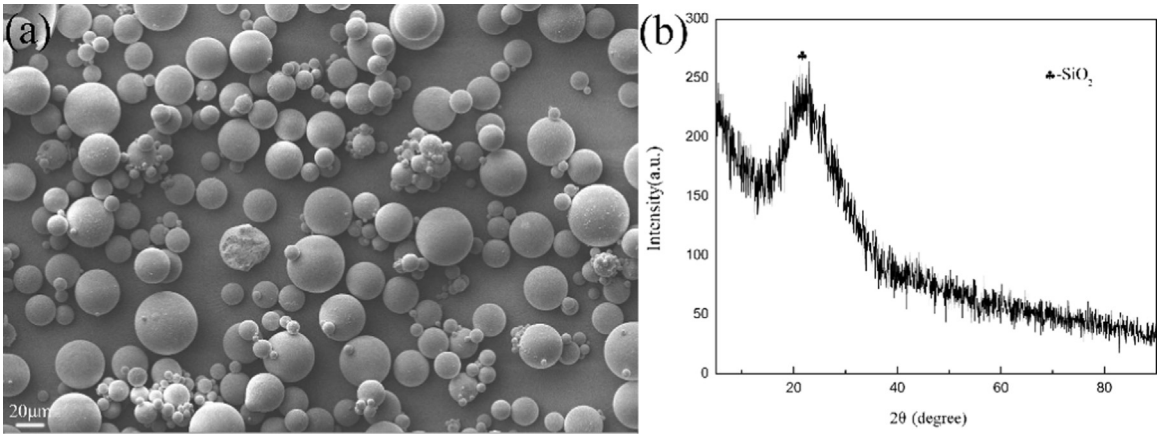

Fig. 2. SEM micrograph and XRD pattern of HGMs.