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Photocatalytic activity of Portland cement loaded with 3D hierarchical Bi_2WO_6 microspheres under visible light

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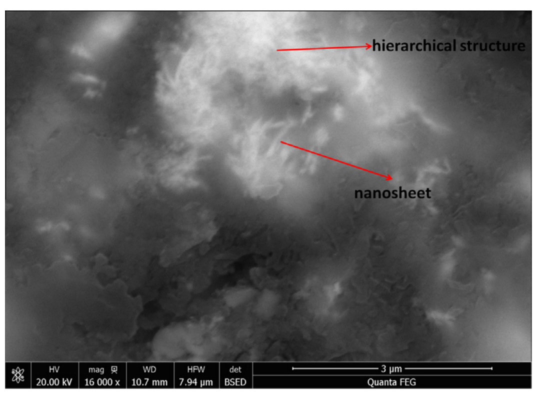
HIGHLIGHTS

- 3D hierarchical Bi_2WO_6 microspheres were incorporated into Portland cement.
- 3D hierarchical structure remained on the surface of cement after hydration.
- Bi_2WO_6 photocatalytic cement can remove the pollutants under visible light efficiently.
- Catalysts cementitious materials are exposed to solar light widely.

GRAPHICAL ABSTRACT

3D hierarchical structure of Bi_2WO_6, the nanoplate and nanosheets facilitate the adsorption of organic gas. Interestingly, the hierarchical microsphere, the nanoplate and nanosheets did not aggregate together after stirring but distributed equably in the cement matrix.



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ABSTRACT

In this work, photocatalytic cement was prepared by loading Bi_2WO_6 microspheres with Portland cement. 3D hierarchical Bi_2WO_6 microspheres were synthesized by self-assembly of 2D nanosheets and nanoplates firstly. Interestingly, Backscattered Electron (BSE) images showed Bi_2WO_6 hierarchical structure remained unchanged on the surface of hydration cement. The nanoplate and nanosheets which fell off from the Bi_2WO_6 microspheres distributed evenly on the surface of the hydration products. As to the inner structure of Bi_2WO_6/cement, a porous structure was observed and Bi_2WO_6 particles were located evenly in the pores. This result was in favor of enhancing photocatalytic performance and gas adsorption. The 15 wt% Bi_2WO_6/cement showed the highest photocatalytic activity, which can degrade the HCHO completely within 80 min under visible light. XRD and hydration heat results showed that Bi_2WO_6 hardly influences the hydration process. However, when the Bi_2WO_6 dosage was increased to beyond 15%, the hydration process was deterred and hydration heat decreased, which may influence the durability of the cement matrix.

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1. Introduction

Cementitious materials are predominantly used in building construction due to their high strength, good durability, mold ability, and environmental-friendly properties. Combination of photocatalysts together with construction and building materials was expected to provide a new method for the removal of air pollutants [1–4]. Generally, the photocatalyst is loaded or mixed with cementitious material. When the photocatalyst is exposed to solar light, it can absorb photon energy and promote electrons to jump from the valence band to the conduction band. The activation of the electrons produces holes and electrons (h^+ and e^-). Some radicals, e.g. OH^-, HO_2^-, O^{2-} and O^- can be produced in the presence of h^+ and e^-. They can further react with air pollutants, resulting in the degradation of these substances.

The development of photocatalysts in recent years has established a solid foundation for comprehensive applications in the field. Among the available photocatalysts, TiO_2 has been extensively investigated and commercially applied in several fields [5,6]. However, the drawback of TiO_2 limits its wide application. Due to the band gap of anatase (3.2 eV), TiO_2 needs to be activated under UV light. The electron–hole recombination rate of TiO_2 photocatalyst was considered to be another application bottlenecks.

Bismuth tungstate (Bi_2WO_6) is a new kind of photocatalyst for of removing environmental pollutants and hydrogen production from splitting water using solar energy. Bi_2WO_6 is characterized with high stability, nontoxicity, especially narrow band gap (~2.8 eV) and good photocatalytic performance. Bi_2WO_6 can produce photo-generated electrons and degrade the pollutants under visible light [7–9]. Therefore, Bi_2WO_6 can be potentially incorporated into cementitious materials and potentially remove polluted gas.

The other important advantage of Bi_2WO_6 was particle size for the application in photocatalytic cementitious material. The particle size of Bi_2WO_6 is about 3 μm, which is similar to size of micro-aggregate in cement. In the loading process, the surface of photocatalysts with a smaller size (300 nm TiO_2) might be covered and the absorption of pollutants and photocatalytic efficiency decrease. The properties of Bi_2WO_6 can overcome this drawback. The incorporation of Bi_2WO_6 into cementitious material is advantageous to gas diffusion, adsorption and degradation on surface of photocatalysts.

In this work, we present a novel Bi_2WO_6 structure on the cement surface with high photocatalytic performance. Formaldehyde (HCHO) was used as a target pollutant to study the photocatalytic efficiency. The effect of Bi_2WO_6 on thermal change and crystal in hydration process of Portland cement was monitored after loaded with Bi_2WO_6 particles.

2. Materials and methods

2.1. Materials

Portland cement 42.5, (P·O 42.5 type according to GB175-2007) with a Blaine fineness of 340 cm^2/g and surface density of 3.08 g/cm^3, was acquired from Huaxin Cement Co., Ltd. The chemical composition of cement in wt% is as follows: CaO: 60.26, SiO_2: 21.00, Al_2O_3: 8.12, Fe_2O_3: 2.33, MgO: 1.28, SO_3: 1.98. $Bi(NO_3)_3·5H_2O$ and $Na_2WO_4·2H_2O$ was purchased from Sigma. Distilled water was used in all experiment.

2.2. Synthesis of Bi_2WO_6

The hydrothermal method was used to synthesize Bi_2WO_6. In a typical procedure, 3.881 g $Bi(NO_3)_3·5H_2O$ and 1.319 g $Na_2WO_4·2H_2O$ was mixed in 70 ml deionized water. The pH value of the mixture was adjusted to 2 by HNO_3. Then the mixture was stirred vigorously at room temperature. Finally, the mixture solution was treated at 160 °C for 24 h in Teflon-lined stainless steel autoclave. The resulted precipitates were recovered by centrifugation, rinsed with deionized water and ethanol repeatedly. The precipitate powder of Bi_2WO_6 was finally dried at 70 °C for 8 h.

2.3. Characterization of Bi_2WO_6

The synthesized powders were characterized by X-ray diffractometer (XRD, PHILIPS P W 3O4O/60X'PertPRO) with a Cu Kα ray source. The morphology and particle size were characterized by Scanning Electron Microscopy (Quanta FEG 450) with Backscattered Electron (BSE).

2.4. Preparation of photocatalytic cement paste

Ordinary Portland cement, water and synthesized Bi_2WO_6 were mixed using a standard Lab mixer for 2 min with a revolution speed of 62 ± 5 r/min, and another 2 min with a revolution speed of 126 ± 10 r/min, according to the Chinese national standard GB/T 1346-2011, to prepare the photocatalytic cement paste. The water/powder ratio was kept at 0.30 and the amount of photocatalysts added was 5%, 10%, 15%, and 20% of the total weight of cement. A smooth and well blended paste was obtained and cast into molds (diameter 16 cm, thickness 5 mm). After that, the samples were cured in an environmental chamber (20 ± 1 °C, RH ⩾ 90%) for 7 days. The hardened pastes were then removed from their molds for further tests.

2.4.1 Characterization of photocatalytic cement

The crystalline phases of samples were determined by X-ray diffractometer (XRD, PHILIPS P W 3O4O/60X'PertPRO) with a Cu Kα ray source. SEM-BSE was used to observe the morphology of 10% Bi_2WO_6/cement samples.

2.5. Photocatalytic performance

The photocatalytic performance was evaluated by the removal of gaseous formaldehyde (HCHO) in a closed cylindrical glass gas-phase reactor (2.35 L). The light source was iodine tungsten lamp (300 W, FoShan lighting, main wavelength ⩾760 nm) with a UV filter for removing UV light. The as-prepared Bi_2WO_6/cement paste was placed in the dish and the distance between the lamp and the paste was 15 cm. 2 μl of HCHO solution was injected in the reactor by a syringe and the mixture was then completely evaporated into gas. The initial concentration of HCHO in the reactor is about 0.28 mg/L. HCHO were sampled every 10 min and the concentration was measured by acetylacetone spectrophotometric method (GB 13179-19). In a typical procedure, formaldehyde with a known amount was mixed with acetyl acetone. A new yellow compound was formed and by this standard curve was established. The concentration of formaldehyde is proportional to absorbance at the wavelength of 413 nm. The concentration of unknown formaldehyde can be calculated by the obtained curve.

The removal efficiency of HCHO was evaluated as follows:

$$\eta\% = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

where C_t and C_0 are the concentrations of the primal and remaining HCHO, t is the light illumination time.

2.6. Determination of hydration heat

The hydration heat was measured by a TAM air isothermal microcalorimeter (Thermometric AB, Sweden), which was equipped with eight twin calorimetric channels, of which one side was used for the sample and the other for a static reference. In the conduction calorimeter, all the heat produced is transferred through a thermopile to heat sink which is maintained at a constant temperature. When a heat energy change occurs in the sample, a small temperature difference arises (relative to the heat sink) which forces the heat to flow.

Six groups of samples were to add in the calorimeter to monitor the thermal curves (water/cement ratio: 0.30; the amount of photocatalysts: 0, 5%, 10%, 15%, 20% of the total weight of cement).

3. Results and discussion

The synthesized products were characterized by SEM in Fig. 1. Fig. 1(a, b and c) shows SEM images with different magnification suggesting Bi_2WO_6 microspheres hold three levels of structure. The entire 3D hierarchical Bi_2WO_6 microspheres were built by 2D nanosheets and Bi_2WO_6 nanoplates were composed by rectangle nanoplates. The average sizes of Bi_2WO_6 microspheres, nanosheets and nanoplates were about 2.5 μm, 0.5 μm and 50 nm respectively. It has been proposed that the formation of a 3D hierarchical structure might involve a three-step process: self-aggregation, Ostwald-ripening and self-assembly [10]. In this synthesis, tiny particles