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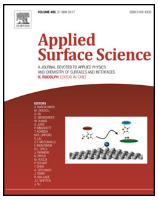

Full Length Article

BiOBr@SiO_2 flower-like nanospheres chemically-bonded on cement-based materials for photocatalysis

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ABSTRACT

Endowment of photocatalytic property on the surface of concrete structure can contribute to the self-cleaning of the structure and purification of the polluted environment. We developed a nanostructured BiOBr@SiO_2 photocatalyst and innovatively used for surface-treatment of cement-based materials with the hope of attaining the photocatalytic property in visible-light region and surface modification/densification performances. The SiO_2 layer on the flower-like BiOBr@SiO_2 helps to maintain a stable distribution of the photocatalyst, as well as achieving a chemical bonding between the coating and the cement matrix. Results showed that the color fading rate of during the degradation of Rhodamine B dye of the BiOBr-cem sample is 2 times higher compared with the commonly studied C, N-TiO_2-cem sample. The photo-degradation rates of samples BiOBr-cem and BiOBr@SiO_2-cem are 93 and 81% within 150 min, respectively, while sample BiOBr@SiO_2-cem reveals a denser and smoother surface after curing for 28 days and pore-filling effect at size within 0.01–0.2 μm when compared with untreated samples. Moreover, additional C-S-H gel can be formed due to the pozzolanic reaction between BiOBr@SiO_2 and the hardened cement matrix. Both advantages of the BiOBr@SiO_2 favor its application for surface-treatment of hardened cement-based material to acquire an improved surface quality, as well as durable photocatalytic functionality.

1. Introduction

Photocatalytic property has been intensively used to develop environment friendly construction and building materials in recent years. Photocatalysts have been mixed into cement-based materials to endow self-cleaning, air purifying and antimicrobial, properties [1–7]. Among them, self-cleaning property has gained considerable interests, for example, the famous self-clearing "Dives in Misericordia" in Rome has drawn particular attention due to its white surface after years of service. For air purifying, indoor pollutants, such as volatile Organic Compounds (VOCs), are considered to be as the targets, because most of VOCs are toxic and increasingly generated in urban and industrial areas. Propylene is a main component of VOCs and automobile exhaust, which will caused that the plants on the road have no ability to grow properly. It should be emphasized that the most efficient application of photocatalysts is on the surfaces of concrete, at where it is more capable of receiving light, and much lower cost can be resulted, comparing with the incorporation method.

As a popular photocatalytic material, TiO_2, usually in the anatase crystallographic form, has been widely utilized on the surface of the cement-based materials due to its promising photocatalytic property, chemical stability, and reasonable price [8–12]. When irradiated under suitable light (with a wavelength of 385 nm or shorter), anatase TiO_2 with the band gap ($E_g \sim 3.2$ eV) is activated. However, when irradiated under solar light, only in the UV region, which is about 4% of the energy, can be utilized. Thus to utilize solar light more effectively, more highly active photocatalysts are desired and has received considerable research attention.

BiOX (X = Cl, Br, I), a family of promising photocatalysts of a tetragonal matlockite structure is attracting great interests due to its superior photocatalytic properties under visible light [13–24]. Among them, BiOBr is more intensively studied due to its relatively low band gap, high stability and superior photocatalytic performance [25,26]. Ai's group prepared BiOBr microspheres with efficient air purifying property for the removal of NO under visible light [27]. Yu et al. fabricated BiOBr nanomaterials with hierarchical morphology and effectively removed organic dyes (methylene blue) from wastewater [28].

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Table 1
Major chemical compositions of cement.

Constituent	CaO	SiO_2	SO_3	Al_2O_3	MgO	Na_2O	TiO_2	Fe_2O_3	K_2O
Mass (wt.%)	65.44	20.09	4.07	2.55	1.77	0.71	0.33	0.25	0.24

Another key issue concerning the application of photocatalysts on the surface of cement-based materials is the treatment technique. Normally, spray coating, sputtering and sol-gel dip-coating methods have been used [29–32] in all these cases, the substrate was directly coated with photocatalysts, i.e., absorption of the photocatalysts on the surface, leading to a weak bonding between the photocatalyst and the matrix and resulting in a poor durability of the photocatalytic property [11]. Polymer like epoxy has also been used as a bonding agent to increase the adhesion, but the poor weather resistance of the organic binder weakens the durability. For an ideal bonding, the inorganic adhering material should be considered. As a surface treatment agent, SiO_2 will react with cement matrix and result in calcium silicate hydrate (C-S-H) gel [33,34], which exhibits a potential to serve as a surface modification/densification candidate. Mendoza et al. [35] used SiO_2 layer as a binding constituent between mortar and the photocatalyst of TiO_2, although a relatively better adhesion of TiO_2 to the cement was reported, scratches/cracks were observed, leading to a weak bonding. Lu et al. [36] synthetized TiO_2/SiO_2 hydrosol which was compactly coated on the surface of fiber reinforced cement. However, SiO_2 sol in the system can stabilize the TiO_2 hydrosol. TiO_2 may also be bonded to the SiO_2 layer leading to the enhancement of adhesion. Jafari and his group [37] reported nanosized hybrids of TiO_2/SiO_2 for surface-treatment of cement-based materials. In his system, SiO_2 act as a cohesion agent and fix the TiO_2 particles on the support substrate. Although an improved cohesion and photocatalytic activity were reported, the reaction mechanism was not well understood.

To tackle with the above mentioned two key issues when making photocatalytic cement-based materials, advantages of the photocatalytic property of BiOBr under visible light and the binding effect of SiO_2 were taken by synthesizing BiOBr@SiO_2 and applied for surface-treatment of cement-baesed materials. To investigate the photocatalytic properties of photocatalytic cement-based materials, self-cleaning for the degradation of model organic pollutant and air purifying for VOCs, i.e., Rhodamine B (RhB), methyl orange (MO) dyes and propylene, have been carried out. The bonding and the surface modification effects of SiO_2 shell were studied using the mercury intrusion porosimetry (MIP), the scanning electron microscopy (SEM) and the X-ray photoelectrons spectroscopy (XPS).

2. Experimental

2.1. Materials

White Portland cement (WC, Aalborg Cement Company) was used in this work. The chemical compositions of WC are listed in Table 1. Bismuth nitrate, sodium chloride, sodium bromide, sodium iodide, urea and ethylene glycol and ethanol of chemical grade were purchased from China National Pharmaceutical Group Corporation (Sinopharm).

2.2. Synthesis of BiOBr@SiO_2

In a typical process of synthesizing BiOBr, 2 mmol $Bi(NO_3)_3{\cdot}5H_2O$ and 2 mmol NaBr were dissolved in 30 mL ethylene glycol and 20 mL water before vigorously stirred for 30 min. Then, the solution was heated at 160 °C for 12 h. The obtained precipitates were alternately washed for four times with ethanol and deionized water before dried at 60 °C.

Table 2
Experimental parameters of BiOBr@SiO_2.

Sample/parameters	BiOBr (g)	water (mL)	$NH_3{\cdot}H_2O$ (mL)	Ethanol (mL)	TEOS (mL)
BiOBr@SiO_2-1	0.5	20	1	20	30
BiOBr@SiO_2-2	0.5	20	1	20	60
BiOBr@SiO_2-3	0.5	20	1	20	120

The silica shell coating was obtained by the well-known Stöber method. BiOBr (0.5 g) were dispersed into water (20 mL) and stirred for 10 min at room temperature. Subsequently, 1 mL of $NH_3{\cdot}H_2O$ was added. Ethanol (20 mL) and TEOS (30 μL) mixture were dropped into the above solution under stirring for 12 h. After reaction, the suspension sample was stocked for next step. Experimental parameters were adjusted to investigate the influence of SiO_2 amount on the surface modification effect, and the detailed experimental data are listed in Table 2.

2.3. Cement paste preparation, curing and surface treatment

For preparing cement pastes, water-to-cement ratio of 0.35 was used in this work, and dry samples were mixed for 3 min and then wet-mixed for 5 min. Then the mixtures were molded in 4 cm × 4 cm × 16 cm molds and covered with plastic sheet and then demolded after 24 h curing. The samples were cured at 95% relative humidity and 20 ± 2 °C until test.

The samples were cut into pieces with the size of 4 × 4 × 2 cm which were dried at 45 °C for 1 day before being treated with BiOBr and BiOBr@SiO_2. Homogenous suspension of BiOBr (0.25 g) water (10 mL) and ethanol (10 mL) was prepared under stirring. The obtained BiOBr suspensions (2 mL) or BiOBr@SiO_2 suspensions (2 mL) were sprayed onto the faces (4 × 4 cm) of the hardened white cement paste sample, and named as BiOBr-cem and BiOBr@SiO_2-cem, respectively.

2.4. Photocatalytic degradation of RhB

The photocatalytic efficiency of the photocatalysts (BiOX) was evaluated via the RhB degradation under xenon lamp irradiation (500 W). The photocatalyst (0.01 g) dispersed in RhB solution (20 mL, 10 mg/L) was stirred for 30 min in the dark to reach the adsorption–desorption equilibrium. The concentration of RhB solution after the irradiation was tested using UV–vis spectrometer at a wavelength of 463 nm to evaluate the photocatalytic efficiency.

During the test, 1 mL of RhB solution (80 mg/L) was sprayed on the face (4 × 4 cm) of the treated sample. The RhB contaminated sample was then placed under xenon lamps (500 W). During the radiation operation, xenon lamp was cooled down using circulating water to keep the temperature at 25 ± 2 °C.

The variation of color before and after irradiations was measured by a portable spherical spectrophotometer (RM200, X-Rite). The results were expressed by the colorimetric coordinates of L^*, a^* and b^* in the CIE LAB system according to ISO 10526 [10]. The reading data of ΔE, the color variation, was calculated by the color coordinates according to the following equation (the Commission International de l'Éclairage): L^*- plots the lights from white to black, a^*- hues from red to green, and b^*- hues from blue to yellow [38,39].

$$\Delta E = \sqrt{\left(L_t^* - L_0^*\right)^2 + \left(a_t^* - a_0^*\right)^2 + \left(b_t^* - b_0^*\right)^2} \qquad (1)$$

$\triangle E$ was the color change before and after irradiation. The three coordinates, L_0^*, a_0^* and b_0^*, were the initial parameters of the RhB-contaminated sample before irradiation.L_t^*, a_t^* and b_t^* were the parameters after irradiation. These efficiencies of RhB removal ($R_{\triangle E}$

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