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The hierarchical porous structure of substrate enhanced photocatalytic activity of TiO_2/cementitious materials

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HIGHLIGHTS

- The hierarchical porous FMOC substrate with good light transmittance was prepared.
- Through a facile method synthesized FMOC/TiO_2 catalyst with desirable microstructure.
- Hierarchical structure provided more active TiO_2 sites and large catalysis areas.
- Reaction rate of FMOC/T12 was estimated to be about 3.87 times higher than MOC/T12.
- TiO_2 exhibited an excellent re-use performance on surface of porous magnesium cement.

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ABSTRACT

Although the use of TiO_2 photocatalyst on cementitious materials for air purification has been developing rapidly in the last decades, the photocatalytic effect of TiO_2 is significantly diminished due to the low specific surface areas, poor gas diffusion and light transmission performance of cementitious substrates. This paper presents a novel hierarchical porous structure magnesium cementitious/TiO_2 photocatalyst (FMOC/TiO_2) to improve the photocatalytic effect and utilization rate of TiO_2 in cementitious materials. The results revealed that the hierarchical porous structure of substrate was beneficial to the dispersion of TiO_2, which provided more active TiO_2 sites and large catalytic areas. The good gas diffusion and light transmittance performance of substrate improved the photocatalytic effect and utilization rate of TiO_2 particles. The reaction rate of gaseous acetone in FMOC/T12 ($\varnothing 50 * 3$ mm) surface was measured to be about 3.87 times higher than MOC/T12 ($\varnothing 50 * 3$ mm). Additionally, FMOC/T12 ($\varnothing 50 * 3$ mm) also exhibited an excellent re-use performance.

1. Introduction

The wide application of cementitious materials offers the mediums of using photocatalytic materials to solve the problem of urban air pollutants [1–3]. Nano-TiO_2 is the most generally used photocatalyst in this field due to relatively inexpensive, chemically stable and high photocatalytic activity features. It could provide antimicrobial, self-cleaning and air purifying properties for construction materials [4,5]. The applications of TiO_2 in cementitious materials involve mixing with binding materials or coating on the existing buildings. However, the photocatalytic effect of TiO_2 is significantly diminished due to the low specific surface areas and the negative influence of ionic species of cementitious materials. [6–8]. Moreover, because of the low gas diffusion and light transmittance of cement pastes, the utilization of catalyst within the matrix might be reduced thoroughly [9–11].

In recent years, some methods have been attempted to eliminate those problems, such as improving substrate roughness [12], doping high adsorption porous materials [13,14] and incorporating recycled glass cullets in cementitious materials [10,15]. These approaches enhanced the specific surface areas and light transmittance of cement pastes, therefore inducing the large contacting areas of active TiO_2 with light and air pollutants, which could improve the activity of materials. On the basis of above, it can be concluded that the macro/microstructural features and light transmittance of cementitious substrate have obviously influence on activity of TiO_2 [16,17]. The more active TiO_2 sites, more light and gas channels can lead to high photocatalytic efficiency due to the interface reaction property of photocatalysis. Some studies

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also pointed out that the design of interface macro/microstructure of cementitious substrate could enhance the photocatalytic effect of TiO_2 catalyst [14,18–20]. Although these are important achievements, a more detailed information about cementitious substrate with high specific surface areas, more active sites, good gas diffusion and light transmittance features should be further studied. On the other hand, a reasonable composition and structure of cementitious substrate are essential to catalyst for weakening the influence of ionic species [21]. Magnesium oxychloride cement (MOC) is the mixtures of MgO powder and $MgCl_2$ solutions of a certain concentration. It has two well crystallized needle-like phases ($Mg_3Cl(OH)_5{\cdot}4H_2O$ and $Mg_2Cl(OH)_3{\cdot}4H_2O$) after hardening [22]. Therefore, the microstructure composition of MOC matrix is mainly the need-like hydration phases in appropriate proportions. Importantly, its microstructure features could be regulated easily by MgO/$MgCl_2$ molar ratios and introducing foams [23,24]. This may be beneficial to the design of gas diffusion and light transmittance channels. Meanwhile, the relatively simple structure and low ionic species of MOC could weaken the negative effect of substrate on TiO_2 photocatalyst.

Hence, the objective of present paper is to provide a new design and production method of TiO_2/cementitious photocatalytic materials, which could improve the utilization and photocatalytic effect of TiO_2 photocatalyst. By using magnesium oxychloride cement and foaming agent, the hierarchical porous magnesium cementitious material were produced at an appropriate MgO/$MgCl_2$ ratio to improve the active site, gas diffusion and light transmittance of substrate. Then, a series cementitious/TiO_2 photocatalysts were synthesized through the negative pressure-co-stirring method. The physical and chemical properties of materials like the coating times, coating areas, pore structure, and the photocatalytic performance towards gaseous acetone removal were studied in detail. X-ray diffraction (XRD), optical microscopy (OM) with image analysis, scanning electron microscopy (SEM), N_2 adsorption–desorption isotherms, and energy dispersive X-ray spectroscopy (EDS) analytical methods were employed to investigate the crystalline phase composition, pore structure, morphology and photocatalytic mechanism of materials.

2. Material and methods

2.1. Materials

Light burnt magnesium oxide with 85.2% MgO, 1.4% CaO, 3.8% SiO_2, 0.3% Al_2O_3, 0.2% Fe_2O_3, and 9.1% loss on ignition (mass fraction, technical grade) was used. Magnesium chloride (98% $MgCl_2{\cdot}6H_2O$, A.R) was purchased from Liaoning (Ying Kou Co., Ltd.), Shenyang Province, China. Foaming agent with solid content of 36%, specific gravity of 1.16 g/cm^3, PH of 9–10, was purchased from Henan Province (Yongtai Co. Ltd., technical grade), China. The main component of foaming agent is bone glue protein, which is suitable for FMOC densities ranging from 0.2 g/cm^3 to 1.6 g/cm^3 [25]. TiO_2 (P25, 87% anatase and 13% rutile) and other chemicals (A.R) were provided by Shenshi Chem.

2.2. Preparation of porous magnesium cementitious substrate

Porous magnesium cementitious (FMOC) substrate was prepared as follows, 43 g MgO powder was added into 57 g $MgCl_2$ water solution ($w\%$ = 27.4%), then, added 3 ml foaming agent, stirring about 5 min to form the FMOC slurry, the density of slurry was about 0.35–0.40 g/cm^3. Casted the FMOC slurry into silicone moulds, which were sealed with polyethylene film, each sample was cured in the temperature at (20 ± 1) °C and relative humidity at (60 ± 5)%. The molar ratio of MgO:$MgCl_2$:H_2O was 5:1:14 for producing incompact and porous cell walls. For comparison, the sample of un-entraining foaming agent was prepared by the same method (MgO:$MgCl_2$:H_2O = 5:1:14, mark as MOC). After 28 day, the samples were cut into slices of 3 mm thick. The cut surface of every slice was polished slightly by abrasive cloth, and then cleaned by compressed air and placed in the oven at 65 °C.

2.3. Preparation of FMOC/TiO_2 photocatalyst

The negative pressure-co-stirring method was used to prepare the FMOC/TiO_2 photocatalyst. FMOC substrate was put in the vacuum flask, and loading 0.1 MPa vacuum; 10 g P25 powder was added in 1000 mL of water, and ultrasonic dispersed 30 min, then the suspension solution was pumped into the vacuum flask; meanwhile, a stirring device was used to keep the homogeneous suspension solution; the solution temperature was (30 ± 2) °C. After that, the FMOC/TiO_2 precursors were washed, and then dried at 85 °C in oven for 12 h. Finally, the FMOC/TiO_2 samples were obtained. For comparison, the reaction times and sizes were 1 h, 12 h and ∅50 * 3 mm, ∅70 * 3 mm respectively. The samples denoted as FMOC/T*n* (T stood for TiO_2, *n* stood for different reaction times). MOC/TiO_2 sample with 12 h coating time was prepared by the same method. The P25 sample was prepared by using the same dimension ground glass (∅50 * 3 mm, 0.1 mol/L NaOH ultrasonic washing 30 min, and drying at 85 °C in oven for 2 h) as a substrate, then, the same coating method and conditions were used. The schematic of preparation routes and the product images were shown in Fig. 1. FM phase is hydration products of FMOC, light source is 3 W LED lamp, and sample is FMOC/T1 of 3 mm thick.

2.4. Characterization

The crystalline phases of samples were determined by XRD (PHILIPS, PW 3040/60X'PertPRO) using Cu Kα ray source at the scanning speed of 8° min^{-1}. The macro-air void structures of FMOC/TiO_2 photocatalysts were analyzed by optical microscope (OM, OLYMPUS, CKX33-A12PHP) and statistical software (Image-Pro Plus 6.0 (IPP), all of the images were converted into binary form by IPP, and the air void parameters were analyzed based on the operation mode of Ref. [26]). The micromorphology of FMOC/TiO_2 photocatalysts was observed by SEM (HITACHI, S-4800). Energy dispersive spectroscopy (EDS) was recorded on S-4800 as its accessory. The N_2 adsorption–desorption isotherms were measured on an ASAP 2020 instrument (Micromeritics, USA). The relative light transmittance of sample was tested by irradiance meter (PHOTO-2000Z, Ever fine instrument). The irradiation intensity of light through the sample (I_s) was tested by using 125 W high pressure Hg lamp (the same light source with photocatalytic activity evaluation) as incident light source to irradiate the sample at the fixed distance (15 cm). Likewise, the irradiation intensity of the lamp (I_0) at the same distance also was tested. Finally, the relative light transmittance can be calculated by $I_s/I_0 * 100\%$.

The photocatalytic activities of FMOC/TiO_2 photocatalysts were evaluated by using acetone (A.R, 99.9%) as a test molecule in a closed cylindrical stainless steel gas-phase reactor (5.56 L) with a quartz window. The light source is a 125 W high pressure Hg lamp (China, Shanghai Yaming, GYZ, λ_{nm} > 340 nm, the light spectrum with peaks around 365, 400, 440, 550 and 580 nm), the distance between the lamp and the reaction samples was 15 cm. The intensity of UV light in the region of 320–400 nm on the surface of catalyst, which was measured with an UV-A radiometer (LUTRON, UV-A-365, Taiwan), is 0.96 mW/cm^2. This is corresponding to the sunlight UV level of central region of China (about 1.0–3.0 mW/cm^2 in summer daylight, and ~1.5 mW/cm^2 in winter daylight) [27]. In addition, the artificial light source can provide the same test conditions for comparing the photocatalytic activity of different samples. 2 μl of acetone liquid was injected in the reactor, and the mixture was irradiated by the light when the liquid acetone completely evaporated into gaseous. The samples were measured every 5 min by gas chromatograph (GC9560, Shanghai, Huaai, which equipped with a flame ionization detector, a methane converter, a Porapak R column and PEG20M column). The procedure for the recycled experiments of sample is as follows. After the first photocatalytic activity test, the reactor was opened to remove the degradation products with fresh air. Meanwhile, the sample was irradiated under UV-C lamp (Philips, 36 W, λ_{max} = 254 nm) at room temperature for 2 h to ensure the complete removal of acetone absorbed on the surface of photocatalyst. Then, covered the reactor again, 2 μl of acetone was injected in the reactor, and the Hg lamp was turned on to start the next test. The procedure was repeated for 5 times. Each test lasted for 50 min, and the initial concentration gaseous acetone was about 270 mg/m^3.

The degradation rate and reaction rate were calculated by the following formulas,

$$w\% = c/c_0 \tag{1}$$

$$Lnc/c_0 = -kt \tag{2}$$

where C and C_0 are the concentrations of the primal and remaining acetone, k is the reaction rate; t is the light application time.

3. Results and discussion

3.1. Physical chemistry properties of FMOC and FMOC/TiO_2

Fig. 2 shows that porous magnesium cementitious substrate has a hierarchical pores and network structure. It can be seen in Fig. 2(a) and (b), there were abundant macro-air pores within 300 μm in the sample. Interestingly, some micro-air pores within 50 μm in cell walls also can be observed clearly. Likewise, form Fig. 2(c) and (d), it was worthy to note that the hydration products of FMOC led to the formation of interlaced network and crystalline