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Enhanced photocatalytic performance of cementitious material with TiO₂@Ag modified fly ash micro-aggregates

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ABSTRACT

A TiO₂ photocatalyst is coated on the surface of a zeolite fly ash bead (ZFAB) to improve its dispersability and exposure degree in a cement system. The application of Ag particles in TiO₂/ZFAB modified cementitious materials is to further enhance the photocatalytic performance. Various Ag@TiO₂/ZFAB modified cementitious specimens with different Ag dosages are prepared and the characteristics and photocatalytic performance of the prepared samples are investigated. It is observed that the multi-level pore structure of ZFAB can improve the exposure degree of TiO₂ in a cement system and is also useful to enhance the photocatalytic efficiency. With an increment of the amounts of Ag particles in the TiO₂/ZFAB modified cementitious samples, the photocatalytic activities increased first and then decreased. The optimal Ag@TiO₂/ZFAB modified cementitious sample reveals the maximum reaction rate constant for degrading benzene ($9.91 \times 10^{-3} \text{ min}^{-1}$), which is approximately 3 and 10 times higher than those of TiO₂/ZFAB and TiO₂ modified samples, respectively. This suggests that suitable Ag particles coupled with a ZFAB carrier could effectively enhance the photocatalytic effects and use of TiO₂ in a cement system. Thus, ZFAB as a carrier could provide a potential method for a high efficiency engineering application of TiO₂ in the construction field.

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1. Introduction

The self-cleaning and purification abilities of building materials are two important developmental directions of green building, which can not only promote the diversified development of constructions, but can also provide an opportunity for the applications of new materials in building units [1–4]. To mitigate the effect of air pollutants, such as nitrogen oxides, volatile organic compounds, and so forth, the cementitious building material, which comes into direct contact with these pollutants, has attracted much attention. The issue is how to widely and effectively apply functional units, such as TiO₂ pho-

tocatalysts, to cementitious materials, which can subsequently be used to purify air pollutants [5–9]. In the past 10 years, photocatalytic cementitious materials have been used in practical engineering by either directly spraying TiO₂ photocatalysts on the surface of cementitious materials or intermixing the photocatalysts into the raw materials [10–14]. However, two problems need to be addressed for the high efficiency and stable application of TiO₂ photocatalysts in cementitious material systems. First, the dispersability and exposure degree of nano TiO₂ should be improved in the cement matrix. Second, the quantum efficiency or visible light activity of TiO₂ photocatalysts needs to be enhanced for the effective use of solar

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energy. This can be achieved by many methods such as non-metal and metal doping [15–18].

In our previous work, we have reported that loading nano TiO_2 on the surface of a porous aggregate (expanded shale) is an effective method to improve the dispersability and exposure degree of nano TiO_2 in cement systems [19]. This method can avoid the negative influences of cement hydrates on photocatalysts, thus is beneficial for photocatalysis. Unlike expanded shale, the micron-scale fly ash bead (FAB) is very compatible with cement-based materials and is a good source of raw materials. It can form a similar zeolite pore structure by using a facile excitation, and these pores are usually less than 50 nm (mesopores or micropores), which play important roles in adsorption and the diffusion of reaction gas molecules [20–24]. Based on these features, the photocatalytic behavior of TiO_2 /zeolite fly ash beads (ZFABs) may be different to TiO_2 /porous expanded shale in a cement system.

Hence, in this study, to promote the high efficiency application of TiO_2 photocatalysts in practical engineering, we propose a novel Ag@TiO_2 /ZFAB modified cementitious material, which can simultaneously enhance the light use, the dispersability and exposure degree of nano TiO_2 in a cement system. The structure and properties of the prepared photocatalytic cementitious material were characterized, and the activity for benzene degradation through photocatalysis was investigated.

2. Experimental

2.1. Materials

FABs were obtained from Yangluo power plant with the same composition as that in Ref. [25]. Ordinary Portland cement 42.5(C) (P-O 42.5 type according to GB175-2007) was provided by Huaxin Cement Co., Ltd. $\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$ (tetrabutyl orthotitanate, TBOT), $\text{CH}_3\text{CH}_2\text{OH}$, NaOH, HNO_3 (68 wt%), AgNO_3 and other routine chemicals were purchased from Shenshi Chem. All of the chemicals were of analytical grade. Doubly distilled water was used in the experiments.

2.2. Preparation

The preparation method for TiO_2 /ZFAB is the same as that in our previous report [25]. The typical preparation route was as follows. 10 mL of TBOT was dissolved in 15 mL absolute ethanol, followed by stirring for 30 min at 40 °C. Then, the mixture solution was added to another mixture solution containing 100 mL of deionized water, 0.8 mL of HNO_3 (68%) and 15 mL of absolute ethanol, with a speed of 1–2 drop/s. The suspension solution was continuously stirred for 48 h, and then a desired amount of ZFAB particles (10 g), which were prepared according to the method of Refs. [26,27] with 4 h activation time at 90 °C, were added into the prepared TiO_2 hydrosols solution with stirring for 2 h. Finally, TiO_2 /ZFAB photoactive admixtures were obtained by drying the prepared materials at 105 °C for 24 h.

The surface spraying-photo reduction method was used to prepare the photocatalytic cementitious materials. First, the

pure cement slurry was produced with a water/cement (W/C) mass ratio of 0.4, then the slurry was cast into molds (Φ 160 mm $\times$ 50 mm) and aged for 1 h. Consequently, 5 g of TiO_2 /ZFAB powder was sprayed on the surface of the fresh slurry (5 wt%), and aged for 3 d at room temperature. Subsequently, a certain amount of AgNO_3 water solution ($C_{\text{AgNO}_3} = 5.0 \times 10^{-3}$ mol/L) was sprayed on the surface of the TiO_2 /ZFAB modified cementitious sample, and the prepared sample was irradiated using a 300 W high pressure Hg lamp (China, Shanghai Yaming, GYZ, $\lambda_{\text{nm}} > 340$ nm, which had a light spectrum with peaks at approximately 365, 400, 440, 550, and 580 nm) for 1 h. After that, the sample was washed with 65% ethanol-water solution (volume ratio), and finally dried at 65 °C for 12 h. The sprayed amounts of Ag particles were set as 0.23, 0.70, 1.4, 2.34 and 3.28×10^{-4} wt% of the TiO_2 /ZFAB mass. The different Ag@TiO_2 /ZFAB modified cementitious samples were denoted by the mass fraction of Ag to TiO_2 /ZFAB ($\text{Ag wt\%@TiO}_2/\text{ZFAB}$). The mass of Ag was calculated by the AgNO_3 spraying amounts. For comparison, photocatalytic cementitious specimens with 5 g TiO_2 particles, which were obtained by drying the TiO_2 hydrosols in the oven at 65 °C for 48 h, were also prepared under identical conditions.

2.3. Characterization

Scanning electron microscopy (SEM, S-4800) was used to observe the surface morphology. Ultraviolet-visible (UV-vis) diffuse reflectance spectra were recorded in the diffuse reflectance mode (R) and transformed to absorption spectra. A Lambda 35 (PerkinElmer) spectrometer equipped with a Lab-sphere RSA-PE-20 integration sphere and MgO as a standard was used. An X-ray photoelectron spectrometer (XPS, V. G. Scientific. Ltd; Al K_α) was used to obtain the element states. The N_2 adsorption-desorption isotherm was measured on an ASAP 2020 instrument (Micromeritics, USA). The phase composition was determined by X-ray diffraction (XRD, PHILIPS P W 3040/60X'PertPRO) using a Cu K_α ray source at a scanning speed of 8°/min and scanning range of 10° to 70°.

2.4. Photocatalytic performance

The photocatalytic performance of the prepared cementitious samples was evaluated in a closed cylindrical stainless steel gas-phase reactor (3.5 L) with a quartz window. Gaseous benzene was used as a model of a pollutant, and a 300W high pressure Hg lamp with 1.6 mW/cm² UV light (320–400 nm) irradiance on the sample surface was used as a light source for photocatalysis. The detailed test steps were as follows. 2 μL of benzene liquid was injected into the reactor, and then allowed to stand for approximately 10 min to allow the injected benzene to evaporate into the gaseous state (the initial concentration of gaseous benzene was $(200 \pm 20) \times 10^{-6}$, which was detected by gas chromatography). When the concentration of gaseous benzene achieved an adsorption/desorption equilibrium in the dark (60 min), the lamp was turned on to begin the photocatalytic degradation measurement. The concentration of gaseous benzene was measured every 15 min by a gas chro-

matograph (GC2020, Hengxin, which was equipped with a flame ionization detector, a methane converter). The degradation rate (ω), reaction rate and the reaction half-life ($t_{1/2}$) of gaseous benzene were calculated using the following formulas.

$$\omega\% = c/c_0 \quad (1)$$

$$\ln(c/c_0) = -kt \quad (2)$$

$$t_{1/2} = (\ln 2)/k \quad (3)$$

where c_0 and c are the concentrations of the initial and remaining benzene, respectively; k is the reaction rate; t is the light application time.

3. Results and discussion

3.1. Physiochemical properties

Fig. 1 shows the XRD patterns of the prepared TiO_2 and TiO_2/ZFAB samples. It can be determined that the prepared TiO_2 photocatalyst had an anatase crystal structure along with a small amount of brookite crystal, which is consistent with a previous report [28]. Furthermore, the XRD pattern of TiO_2/ZFAB clearly shows that TiO_2 particles were successfully coated on the ZFAB surface. The results also revealed that the prepared ZFAB carrier contained three types of zeolites (sodalite, Na-P1 and Na-X zeolites), indicating that the prepared material had a multi-level pore structure [27,29]. As shown in Fig. 2, the N_2 adsorption-desorption isotherm of TiO_2/ZFAB is of type IV according to the BDDT (Deming and Teller) classification, and has one hysteresis loop at a relative pressure ranging from 0.43 to 1, indicating that the prepared material has a mesoporous structure [5]. The pore size distribution curve (inset in Fig. 2) revealed that the prepared TiO_2/ZFAB mainly contained meso- and macro-porous structures. This multi-level pore structure is considered to be useful in the photocatalytic process, which could improve the capacity of adsorption and diffusion of the reactant molecules.

Fig. 3 shows the surface structures of TiO_2/ZFAB and $\text{Ag}@\text{TiO}_2/\text{ZFAB}$ modified cementitious samples. Fig. 3(a) and (b) shows that the sprayed TiO_2/ZFAB particles displayed a good exposure degree on the surface of the cement matrix, and the supported TiO_2 particles can also be observed. Fig. 3(c)

Fig. 1. XRD patterns of the prepared TiO_2 and TiO_2/ZFAB samples.

Fig. 2. N_2 absorption-desorption and pore size distribution (inset) isotherm of TiO_2/ZFAB sample.

Fig. 3. SEM images of TiO_2/ZFAB and $\text{Ag}@\text{TiO}_2/\text{ZFAB}$ modified cementitious samples. (a, b) TiO_2/ZFAB ; (c, d) $\text{Ag}0.23 \times 10^{-4} \text{ wt}\%@\text{TiO}_2/\text{ZFAB}$; (e) $\text{Ag}1.4 \times 10^{-4} \text{ wt}\%@\text{TiO}_2/\text{ZFAB}$; (f) $\text{Ag}3.28 \times 10^{-4} \text{ wt}\%@\text{TiO}_2/\text{ZFAB}$.

shows that the deposition process of the Ag particles had no influence on the surface structures of the prepared cementitious sample. At the same time, Fig. 3(d) and (e) shows some white particulate matter with diameters of 30–150 nm, which was identified as metallic Ag particles [30]. The high magnification image of Fig. 3(e) (inset) also shows that the deposited Ag particles had a good contact with TiO_2 particles. As the amount of Ag deposition was increased, its distribution on the surface of TiO_2/ZFAB became more and more intense, and the particle size also increased (Fig. 3(d) and (f)). The largest Ag particle size reached approximately 200 nm on the surface of the $\text{Ag}3.28 \times 10^{-4} \text{ wt}\%@\text{TiO}_2/\text{ZFAB}$ modified cementitious sample, which was attributed to the self-aggregation effect of Ag particles.

Fig. 4. The XPS spectra of the $\text{Ag}3.28 \times 10^{-4} \text{ wt\%} @ \text{TiO}_2/\text{ZFAB}$ modified cementitious sample. (a) Full spectrum; (b) High magnification of Ag 3d.

To further identify the deposition states of Ag particles on the TiO_2/ZFAB surface, the XPS spectrum of $\text{Ag}3.28 \times 10^{-4} \text{ wt\%} @ \text{TiO}_2/\text{ZFAB}$ modified cementitious sample is presented in Fig. 4. The full spectrum of the modified cementitious sample mainly displayed Ca, Si, O, Al, Fe, Ti, C, and Ag elements, indicating that Ag particles were successfully deposited on the surface of the sample. The C 1s peak at 285.0 eV was mainly caused by CaCO_3 and other hydrocarbons in the cementitious sample. Fig. 4(b) shows the high resolution spectra of Ag 3d. It was found that Ag 3d presents in the characteristic peaks at 368.0 and 374.0 eV, which is consistent with Ag $3d_{5/2}$ and Ag $3d_{3/2}$ binding energies, respectively. According to the research of Lei et al. [31], the above combination of peaks corresponds to the metal Ag^0 characteristic peaks.

Fig. 5 presents the UV-vis diffuse reflectance spectra of the TiO_2/ZFAB and $\text{Ag}3.28 \times 10^{-4} \text{ wt\%} @ \text{TiO}_2/\text{ZFAB}$ modified cementitious samples. As shown in Fig. 5, all samples displayed an obvious absorption in the 200–380 nm region, which was attributed to the absorption of TiO_2 . The TiO_2/ZFAB modified cementitious sample presented some response in the visible light region owing to the light absorption of grey Portland cement and the zeolite fly ash beads. However, the absorption

Fig. 5. UV-vis diffuse reflectance spectra of TiO_2/ZFAB (1) and $\text{Ag}3.28 \times 10^{-4} \text{ wt\%} @ \text{TiO}_2/\text{ZFAB}$ (2) modified cementitious samples.

contribution of the Ag-modified sample in the visible light region can be further identified by comparing both UV-vis curves, in which the Ag modified sample exhibited a distinctly higher absorption than that of the unmodified sample. This suggests that the presence of Ag could enhance the visible light response of TiO_2 . The surface plasmon resonance (SPR) absorption peak of Ag particles, located at greater than 500 nm, may be attributed to their shape and size effects. According to the report of Linic et al. [32], the SPR absorption peak and wavelength of Ag particles depend on their size and shape, and the large particles will result in the absorption peak shifting in the high wavelength direction. As shown in Fig. 3, the Ag particles presented the largest size and nonuniform distribution as the amount of Ag deposition was increased to $3.28 \times 10^{-4} \text{ wt\%}$.

3.2. Photocatalytic performance and mechanism

Figs. 6 and 7 show the photocatalytic removal rates and reaction rates of gaseous benzene on various sample surfaces. As can be seen from Fig. 6, as the amount of Ag deposition was increased, the removal rate of gaseous benzene first increased

Fig. 6. The photocatalytic removal rates of gaseous benzene on various cementitious samples surface.

Fig. 7. The photocatalytic reaction rates of gaseous benzene on various cementitious samples surface.

and then decreased. The $\text{Ag}1.40 \times 10^{-4} \text{ wt\%}@\text{TiO}_2/\text{ZFAB}$ modified cementitious sample displayed the optimal photocatalytic effect, where the removal rate of gaseous benzene on its surface reached approximately 98.9% after 180 min of irradiation, while the TiO_2/ZFAB modified cementitious sample only degraded approximately 46% of the gaseous benzene. However, when the deposition amount of Ag particles was further increased from 1.40×10^{-4} to $3.28 \times 10^{-4} \text{ wt\%}$, the removal rates of gaseous benzene were significantly reduced. This suggests that the application amounts of Ag particles in the TiO_2/ZFAB modified cementitious sample were in the optimal range. Greater or less than this optimal range would affect the photocatalytic performance of the material. Owing to the Schottky barrier effect, the modification by the Ag nanoparticles (NPs) will lead to the migration of photo-generated electrons (e^-) from excited TiO_2 to the surface of Ag NPs, and the photo-generated holes (h^+) in TiO_2 will simultaneously transfer to its surface to result in electron-hole separation, and the subsequent improvement of the quantum efficiency of the material (Fig. 8). Additionally, Ag NPs can produce a moderate amount of $e^- \text{-Ag}_{\text{NPs}}^+$ owing to the SPR effect. The separated e^- , h^+ or Ag_{NPs}^+ could react with the adsorbed molecules, such as O_2 , H_2O , and so forth, for generating reactive oxygen species (ROS) like OH , HO_2 , O_2^- , H_2O_2 , and O_2^1 , all of which have been clearly confirmed to be generated on irradiated TiO_2 [33–36]. These ROS all act as strong oxidation reagents for degrading benzene molecules, thus modification of the Ag NPs could further enhance the photocatalytic performance of the material (from 0.23 to 1.40 wt% Ag modification amounts). However, because the Ag particles occurring on the TiO_2 layer are negatively charged, the excessive Ag NPs (from 1.40 to 3.28 wt% Ag modification amounts) can significantly trap the holes in the interfacial region, which can strongly decrease the holes concentration [31]. At the same time, the superfluous Ag particles can also shade the irradiation of the light, which is detrimental to the photocatalysis, thus decreasing the photocatalytic performance of material.

To quantify the photocatalytic effects, the photocatalytic re-

Fig. 8. Schematic of the photocatalytic mechanism of the $\text{Ag}@\text{TiO}_2/\text{ZFAB}$ modified cement sample.

action rates and reaction half-times of gaseous benzene were determined (Fig. 7), and the results are listed in Table 1. As shown in Fig. 7, all modified cementitious samples displayed higher reaction rates for degrading gaseous benzene than that of the pure TiO_2 sprayed sample, indicating ZFAB is able to improve the photocatalytic performance of TiO_2 in a cement system. This is because ZFAB can enhance the exposure degree of TiO_2 , as well as its reaction sites, to gas molecules (Fig. 8). After modification with Ag NPs, the reaction rates of TiO_2/ZFAB modified cementitious samples are enhanced. The $\text{Ag}1.40 \times 10^{-4} \text{ wt\%}@\text{TiO}_2/\text{ZFAB}$ modified sample reveals the maximum reaction rate constant for degrading benzene ($9.91 \times 10^{-3} \text{ min}^{-1}$), which is approximately 3 and 10 times higher than those of the TiO_2/ZFAB and TiO_2 modified samples, respectively. This means that the degradation of benzene requires a shorter time on the surface of this sample. For instance, the removal half-time for benzene on the surface of the $\text{Ag}1.40 \times 10^{-4} \text{ wt\%}@\text{TiO}_2/\text{ZFAB}$ modified sample was 69.9 min, while that of the TiO_2/ZFAB modified sample was 210 min. As shown in Table 1, the photocatalytic efficiency of all samples can be represented in the order of $[(\text{Ag}1.40 > \text{Ag}0.70 > \text{Ag}2.34 > \text{Ag}0.23 > \text{Ag}3.28) \times 10^{-4} \text{ wt\%}@\text{TiO}_2/\text{ZFAB} > \text{TiO}_2/\text{ZFAB} > \text{TiO}_2]$ modified cementitious sample $>$ no catalyst (gas phase benzene + light). This suggests that suitable Ag particles coupled with a ZFAB carrier could effectively enhance the photocatalytic ef-

Table 1

The photocatalytic reaction rate constants and reaction half-times for gaseous benzene on various modified cementitious sample surfaces under irradiation.

Sample	k/min^{-1}	$t_{1/2}/\text{min}$	R^2
No catalyst	2.05×10^{-4}	—	0.99
TiO_2	9.75×10^{-4}	710.9	0.99
TiO_2/ZFAB	3.30×10^{-3}	210.0	0.99
$\text{Ag}0.23 \times 10^{-4} \text{ wt\%}@\text{TiO}_2/\text{ZFAB}$	7.09×10^{-3}	97.7	0.96
$\text{Ag}0.70 \times 10^{-4} \text{ wt\%}@\text{TiO}_2/\text{ZFAB}$	8.01×10^{-3}	86.5	0.98
$\text{Ag}1.40 \times 10^{-4} \text{ wt\%}@\text{TiO}_2/\text{ZFAB}$	9.91×10^{-3}	69.9	0.98
$\text{Ag}2.34 \times 10^{-4} \text{ wt\%}@\text{TiO}_2/\text{ZFAB}$	7.26×10^{-3}	95.5	0.97
$\text{Ag}3.28 \times 10^{-4} \text{ wt\%}@\text{TiO}_2/\text{ZFAB}$	6.12×10^{-3}	113.2	0.98

fects of TiO_2 in a cement system.

The stability is important for the practical application of a prepared material. In this case, the recyclability of the optimal $\text{Ag@TiO}_2/\text{ZFAB}$ modified photocatalytic cementitious material was investigated by repeating the degradation of gaseous benzene experiment three times. At the end of the first photocatalytic cycle, the sample was removed and irradiated under a UV-C lamp (Philips, 36 W, $\lambda_{\text{max}} = 254 \text{ nm}$) for 24 h to completely decompose the adsorbed gaseous benzene molecules. Subsequently, the next cycle was started under the identical conditions.

As shown in Fig. 9(a), the removal rate of gaseous benzene reached approximately 96.3% after three cycles, indicating the $\text{Ag@TiO}_2/\text{ZFAB}$ modified photocatalytic cementitious material exhibits a good stability. However, considering the carbonation influence of the cementitious material on $\text{Ag@TiO}_2/\text{ZFAB}$ composites, the long-term photocatalytic performance of the material requires further evaluation. As was shown in our recent report [37] for the removal of gaseous benzene, the photocatalytic efficiency of the TiO_2/ZFAB modified cementitious material decreased by approximately 11% after 28 d of accelerating carbonation (marked as 28d AC, Fig. 9(b)), which is an excellent improvement compared with the efficiency of the specimen prepared with pure TiO_2 , indicating ZFAB could enhance the long-term photocatalytic performance of TiO_2 in a cement system. This enhancement arises from the high adsorption of ZFAB being able to decrease the amount of cement hydration products formed (high Ca/Si ratio C-S-H gel and $\text{Ca}(\text{OH})_2$ crystals) on the ZFAB/ TiO_2 surface. The long-term photocatalytic performance behavior of the $\text{Ag@TiO}_2/\text{ZFAB}$ modified photocatalytic cementitious material is expected to be the same as the reported material, as the Ag modification simply enhances the use of light for the TiO_2/ZFAB modified photocatalytic cementitious material.

Fig. 9. Stability evaluation of the $\text{Ag}1.40 \times 10^{-4} \text{ wt\%TiO}_2/\text{ZFAB}$ (a) and TiO_2/ZFAB (b) modified cementitious sample. Irradiation time 180 min.

4. Conclusions

A novel $\text{Ag@TiO}_2/\text{ZFAB}$ modified cementitious material was prepared to enhance the light use, dispersability and exposure degree of nano TiO_2 in a cement system. The structure and properties of the prepared photocatalytic cementitious material were characterized, and the activity for benzene degradation by photocatalysis was investigated. It was observed that the multi-level pore structure of ZFAB can improve the exposure degree of TiO_2 in a cement system, and is also useful to enhance its photocatalytic efficiency and stability. The presence of Ag particles in TiO_2/ZFAB modified cementitious materials could further enhance the photocatalytic activity for the removal of gaseous benzene. With increasing the amount of Ag particles, the photocatalytic performance of the prepared cementitious samples increased first and then decreased. Specifically, the $\text{Ag}1.40 \times 10^{-4} \text{ wt\%TiO}_2/\text{ZFAB}$ modified cementitious sample exhibited the maximum reaction rate constant for degrading benzene ($9.91 \times 10^{-3} \text{ min}^{-1}$), which is approximately 3 and 10 times higher than that of the TiO_2/ZFAB and TiO_2 modified samples, respectively. This suggests that suitable Ag particles coupled with the ZFAB carrier could effectively enhance the photocatalytic effect of TiO_2 in a cement system.

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Graphical Abstract

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A variety of Ag@TiO₂/ZFAB modified cementitious materials are prepared. Coupling suitable Ag particles with a ZFAB carrier is shown to effectively enhance the photocatalytic effects and use of TiO₂ in a cement system.

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TiO₂@Ag修饰的粉煤灰微集料增强水泥基材料光催化性能杨露^a, 高衣宁^b, 王发洲^{a*}, 刘鹏^b, 胡曙光^a^a武汉理工大学硅酸盐建筑材料国家重点实验室, 湖北武汉430070^b武汉理工大学化学化工与生命科学学院, 湖北武汉430070

摘要: 自清洁和空气净化能力是绿色建筑发展的两个重要方向, 它们不仅使建筑体向功能多样化方向发展, 而且为新材料的应用提供了平台. 因与大量城市环境污染物(氮氧化物, 挥发性有机化合物等)直接接触, 具有空气净化能力的光催化水泥基材料引起了人们广泛关注. 在过去几十年里, 通过使用直接喷洒到浆体表层或与水泥原材料预先共混的方法, 国内外已相继将TiO₂光催化材料应用到了一些实际工程中. 但TiO₂光催化剂在水泥基材料中高效和稳定发挥其性能仍需解决两个关键问题: (1)它在水泥基体中分散性和效能耐久性问题; (2)其量子效率和对可见光利用率问题. 对于后者, 目前的材料制备与改性方法, 如金属、非金属改性等已能获得量子效率和可见光活性都较好的TiO₂类光催化材料. 研究表明, 水泥水化产物(氢氧化钙、C-S-H凝胶等)的包覆、后期碳化所致气体和光线扩散孔隙的降低是导致TiO₂光催化剂在水泥基材料中耐久性和利用率差的可能原因. 我们前期报道了一种将纳米TiO₂催化剂预先负载到水泥基材料用的多孔粗集料表面, 然后将负载型催化剂整体引入到水泥基体中的催化剂应用方法, 发现该法能有效提升TiO₂催化剂在水泥基材料中的催化效率和耐久性. 微米级活性粉煤灰具有良好的水泥基材料兼容性, 通过采用简单的碱激发手段, 可形成孔径小于50 nm的介孔和微孔类沸石材料, 从而影响光催化材料的催化性能. 因此, 基于粉煤灰的特征, 为了进一步提高TiO₂催化剂在水泥基材料中的应用效率和催化耐久性, 我们采用碱激发法获得了大比表面和介孔结构的沸石类粉煤灰材料, 将其用于负载纳米TiO₂催化剂, 然后引入到水泥基体中, 制备了沸石类粉煤灰/TiO₂光催化水泥基材料, 同时研究了光还原Ag修饰对沸石类粉煤灰/TiO₂光催化水泥基材料的催化性能影响及其催化耐久性.

结果表明, 具有分级孔结构的沸石粉煤灰载体可有效提升纳米TiO₂光催化剂在水泥基体中的暴露度, 同时还增加了其对气相苯(200×10^{-6} 初始浓度)的光催化去除能力. 最佳Ag修饰量(1.4×10^{-4} wt%)沸石类粉煤灰/TiO₂光催化水泥样品对气相苯的光催化伪一级反应速率常数达到 $9.91 \times 10^{-3} \text{ min}^{-1}$, 分别是沸石类粉煤灰/TiO₂光催化水泥样品和纯TiO₂光催化水泥样品效能的3和10倍. 光催化稳定性结果发现, 在3次催化循环后, 样品对气相苯的光催化去除率仍能达到96.3% (180 min). 考虑到水泥基材料碳化是影响光催化剂使用耐久性的一个关键因素, 我们还评估了沸石类粉煤灰/TiO₂光催化水泥样品28 d加速碳化后的光催化性能. 结果表明, 经过加速碳化后, 样品对气相苯光催化去除率只降低了11%, 相比于同条件下纯TiO₂水泥样品性能, 其催化耐久性显著提高, 表明沸石类粉煤灰载体可有效提升TiO₂在水泥基体中的催化耐久性. 这可能是由于其高孔隙特性可降低周围水泥水化产物的形成量, 如高钙/硅比C-S-H凝胶及氢氧化钙结晶, 进而降低了这些水化产物碳化所带来的影响.

关键词: 光催化水泥基材料; 沸石粉煤灰; 光催化效果; 二氧化钛; 银修饰

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