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Influence of Silver Doping on Photocatalytic Activity of Liquid-Flame-Sprayed-Nanostructured TiO_2 Coating

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Silver ion was added to liquid feedstock to deposit Ag^+-doped-nanostructured TiO_2 photocatalytic coatings through liquid-flame spraying. The coating microstructure was characterized by x-ray diffraction (XRD). The photocatalytic performance of coatings was examined by photodegradation of acetaldehyde. The XRD analysis showed that the phase structure of coatings was not significantly influenced by the silver ion doping. However, a shift was found for XRD peaks of anatase TiO_2. The photocatalytic activity of the TiO_2 coatings increased and then decreased with the increase of dopant concentration. The photocatalytic activity of doped coatings was higher than that of pure TiO_2 coating, regardless of the dopant concentration. The enhancement of photocatalytic performance of doped coatings is attributed to co-doping of Ag^+ ion and metallic Ag.

Keywords photocatalyst, nanocrystalline material, TiO_2, liquid-flame spray, ion doping, silver ion

1. Introduction

The TiO_2 photocatalysis is an attractive low-temperature, energy-saving approach, and it has promising applications to the destruction of environmental-undesirable chemical contaminants, such as wastewater treatment and air purification (Ref 1-6). Photon-induced electrons and holes created in TiO_2 semiconductor under UV illumination migrate to the surface. Those electrons and holes serve as redox sources, which react with adsorbed reactants, leading to the destruction of pollutants. In order to increase quantum yield in photocatalysis, TiO_2 powders and coatings have been modified by selective surface treatments such as surface chelation, surface derivatization, and noble metal loading including platinization, and by selective metal ion doping of the crystalline TiO_2 matrix (Ref 7-10).

Metal ion dopants in TiO_2 have been reported to enhance the photocatalytic activity of TiO_2 photocatalyst. For all ion dopants, there exists an optimal dopant concentration, a deviation which leads to a decrease in photoreactivity (Ref 7). Many of experimental studies were carried out to investigate the effect of metal ion doping on the photocatalytic properties (Ref 7-13).

Noble metal loading is also reported to benefit the photocatalytic performance of TiO_2 photocatalyst. Ag is often loaded on the TiO_2 surface by a solution method or photochemical process (Ref 14). Ag clusters or ultra-fine particles are believed to be an electron scavenger, therefore improving charge separation and oxygen-reduction efficiency (Ref 14). The enhancement of photocatalytic activity is significantly influenced by the percentage of Ag loading (Ref 14-16). When the Ag loading is high, the activity is decreased due to the covering on the active sites of TiO_2 surface by many Ag clusters (Ref 14).

Liquid-flame spray was utilized to deposit nanostructured TiO_2 coating, as well as some other thermal spray technique, such as plasma spray, HVOF, and cold spray (Ref 12, 13, 17-26). Among those thermal spray approaches, liquid-flame spray is one-step method, which includes the formation and deposition of TiO_2 materials in the spraying, while in other spray methods TiO_2 spray materials are used as feedstock (Ref 12, 13, 17-26).

In this article, Ag^+-doped TiO_2 photocatalytic coatings were deposited through liquid-flame spraying by adding Ag^+ into a liquid feedstock. The dependence of photocatalytic activity on Ag^+ dopant concentration was studied to reveal the role of Ag^+ doping in the photocatalytic performance.

2. Experimental

2.1 Materials

Butyl titanate ($Ti(OC_4H_9)_4$) (Jinshan, Shanghai, China) was employed as the liquid precursor, in order to form a

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TiO_2 deposit. Butyl titanate was diluted in an analytically pure ethanol (Ante, Suzhou, China) to make the solution with a concentration of 30% for spraying. Ag^+ was introduced by adding $AgNO_3$ (Hongyan, Tianjin, China) to the liquid feedstock. The ion dopant concentration was controlled to be within a range from 0.005 up to 0.5 at.%. Stainless steel plate samples with dimensions of 105 mm × 25 mm × 1.5 mm were employed as substrates for the coating deposition. Prior to spraying, the substrate was blasted with 24 mesh alumina grits.

2.2 Deposition of the Coating

A liquid-flame-spraying torch was employed to deposit TiO_2 coatings, and the details of the torch design could be found elsewhere (Ref 18). Typical spraying conditions are shown in Table 1. Propane was used as fuel gas. Oxygen was employed as the atomizing gas. During the coating deposition, the spray torch was manipulated by a robot (Motoman, Kitakyushu, Japan) and traversed at a relative speed of 500 mm/s to the substrate.

2.3 Characterization of the Coating

An x-ray diffraction (XRD) system (Rigaku D/max-2400, Tokyo, Japan) was used to characterize the crystalline structure of the deposits using Cu Kα radiation operated at 40 kV and 100 mA at a scanning speed of 10°/min and 2°/min for 2θ. Peak area was used to estimate the anatase content in the nanostructured coating (Ref 13, 19). The grain size in the pure TiO_2 and Ag^+-doped TiO_2 coatings was estimated by Scherrer equation (Ref 19).

The photocatalytic performance of TiO_2 coatings was evaluated through photodegradation of acetaldehyde under UV illumination with a dominant wavelength of 360 nm. An experimental setup was assembled to carry out the photodegradation (Ref 18, 19). A 110 mL quartz cuvette (26 mm-ID × 220 mm-high) was used as a photocatalytic reactor. The UV light intensity at coating surface was about 1 mW/cm^2. The acetaldehyde concentration in the reactor was determined by gas chromatography (GC) (Agilent 6890, CA, USA).

The photocatalytic activity was estimated through fitting the change of the relative concentration of acetaldehyde with photodegrading time based on the following Langmuir-Hinshelwood principle (Ref 19, 20),

$$\ln\left(\frac{C_0}{C}\right) = \frac{t}{\tau} \qquad \text{(Eq 1)}$$

where C is the acetaldehyde concentration, C_0 the initial acetaldehyde concentration, t the irradiation time, and τ is the time constant of photocatalytic degradation. According to Eq 1, the smaller the value of τ, the better the photocatalytic performance of the coating. In the present study, the photocatalytic activity of TiO_2 photocatalyst was defined as the reciprocal of τ.

Table 1 Parameters of liquid-flame spraying

Propane pressure, MPa	0.1
Propane flow, L/min	7.3
Oxygen pressure, MPa	0.5
Oxygen flow, L/min	43
Atomizing gas (oxygen) pressure, MPa	0.3
Atomizing gas (oxygen) flow, L/min	42
Spray distance, mm	150
Feed rate of liquid feedstock, mL/min	10

3. Results

3.1 Microstructure of the Ag^+-Doped TiO_2 Coating

During liquid-flame spraying of TiO_2 coating, the TiO_2 in the coating resulted from the reaction of butyl titanate in the high temperature spraying flame (Ref 18, 19). The deposited TiO_2 coating presented a nanoporous structure which resulted from the stacking of nanoparticles (Ref 18, 19). Figure 1 shows XRD patterns of pure TiO_2 coating and Ag^+-doped TiO_2 coatings with dopant concentrations from 0.005 to 0.5 at.%. It is clearly revealed that the Ag^+-doped TiO_2 coatings were mainly composed of anatase phase. In addition, small fraction of rutile phase was also found in the coatings. The diffraction peaks of α-Fe and γ-Fe phases in the substrate were also detected because of the limited thickness of the sprayed coatings. A shift of the (101) diffraction peak of anatase phase to smaller diffraction angle occurred for Ag^+-doped coatings. Figure 2 shows the XRD patterns of pure TiO_2 coating and Ag^+-doped TiO_2 coatings obtained at a low scanning speed of

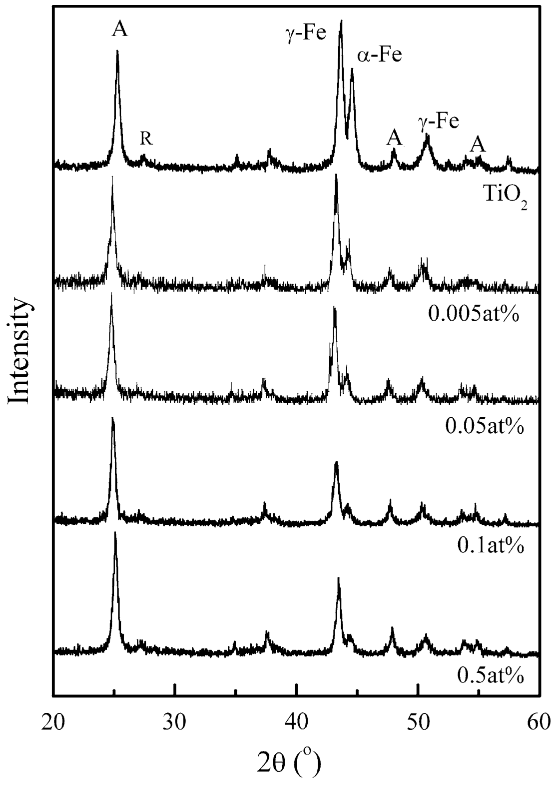

Fig. 1 XRD patterns of pure TiO_2 coating and Ag^+-doped TiO_2 coatings with dopant concentrations from 0.005 to 0.5% (A is referred to anatase phase and R to rutile phase)

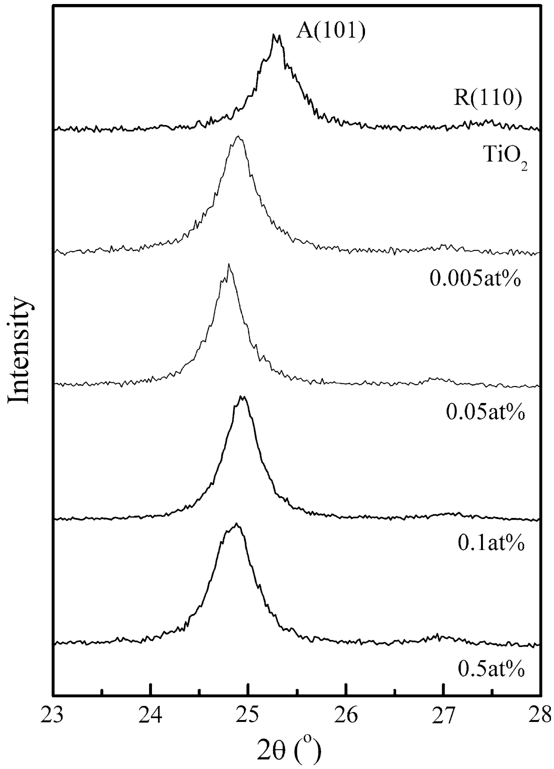

Fig. 2 XRD patterns of pure TiO_2 coating and Ag^+-doped TiO_2 coatings obtained at a low scanning speed of 2°/min for 2θ (A is referred to anatase phase and R to rutile phase)

Table 2 Grain size and anatase content in pure TiO_2 and Ag^+-doped TiO_2 coatings

Dopant concentration (at.%)	0	0.005	0.05	0.1	0.5
Grain size, nm	15	19	22	21	18
Anatase content, %	95	96	95	94	92

2°/min for 2θ. The left shift of the (101) diffraction peak was 0.3-0.5° for the coatings with Ag^+ dopant concentration of less than 0.5 at.%. The grain size and anatase content of pure TiO_2 coating and Ag^+-doped TiO_2 coatings are shown in Table 2. It is found that both grain size and anatase content in the TiO_2 coatings were not significantly influenced by Ag^+ doping.

3.2 Photocatalytic Property of the Ag^+-Doped TiO_2 Coating

Figure 3 shows the change of acetaldehyde concentration with reaction time using pure TiO_2 and Ag-doped TiO_2 coatings. It can be found from Fig. 3 that all coatings were active for photodegradation of acetaldehyde. When a pure TiO_2 coating was used as photocatalyst, 70% of the acetaldehyde was photocatalytically decomposed in 90 min. However, acetaldehyde can be degraded much faster by Ag^+-doped TiO_2 coatings in the same period than that by pure TiO_2 coating. For the Ag^+-doped TiO_2 coating at 0.005-0.05 at.%, more than 95% of acetaldehyde can be decomposed in 90 min.

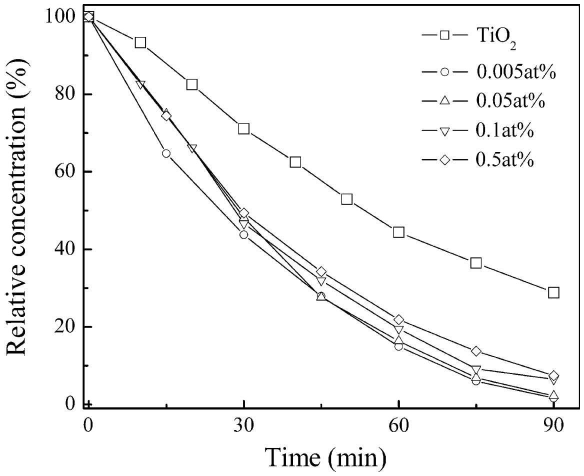

Fig. 3 Change of acetaldehyde concentration with reaction time using pure TiO_2 and Ag-doped TiO_2 coatings

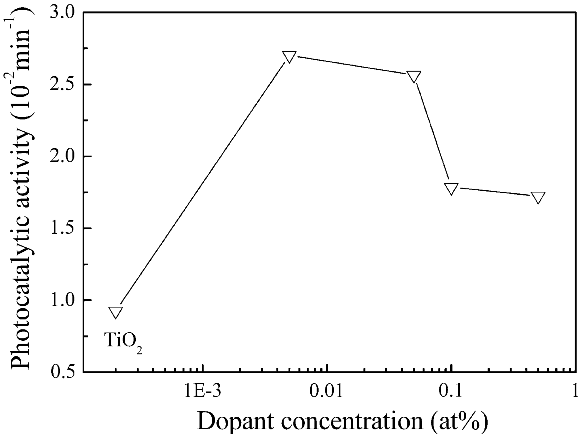

Fig. 4 Effect of Ag^+ dopant concentration on photocatalytic activity

3.3 Influence of Ag^+ Concentration on Photocatalytic Activity

Figure 4 shows the influence of Ag^+ dopant concentration on photocatalytic activity. For pure TiO_2 coating, the activity was 0.93 min^{-1}. The activity was significantly enhanced by Ag^+ doping. The activity of the 0.005 at.% Ag^+-doped TiO_2 coating was enhanced to 2.6 min^{-1}, which was thrice that of pure TiO_2 coating. Furthermore, the activity tend to decrease with a further increase of dopant concentration more than 0.05 at.%. The activity of 0.1 and 0.5 at.% Ag^+-doped TiO_2 coatings were still two times higher than that of pure TiO_2 coating.

4. Discussion

From XRD analysis results, it could be found that the phase structure in the liquid-flame-sprayed-nanostructured TiO_2 coatings was not significantly influenced by the low concentration Ag^+ doping from 0.005 to 0.5 at.%. The grain size of the anatase phase was also not influenced by the Ag^+ doping. Those results are consistent with our previous results on Cu^{2+}-doped TiO_2 coatings (Ref 13). Although some other literature (Ref 27) reported that the phase structure and phase transformation were influenced by Ag^+ doping at dopant concentration of 0.5-20 at.%, the present study clearly revealed that the phase structure was not influenced by Ag^+ doping in the present conditions. This is possibly because the dopant concentration is much lower than those reported.

It was noticed that the (101) diffraction peak of anatase phase presented a significant shift to a lower diffraction angle. This shift suggests that Ag^+ has entered the crystal structure and consequently induced distortion in the crystal lattice. This fact is consistent with the results reported by Liu et al. (Ref 15). The ionic diameters of Ti^{4+} and Ag^+ are 0.068 and 0.126 nm, respectively (Ref 28). Comparing with Ti^{4+}, Ag^+ is a much larger ion. It is impossible for Ag^+ to act as interstitial ions in the TiO_2 matrix (Ref 28). Ag^+ within the TiO_2 matrix must replace Ti^{4+} in lattice sites (Ref 28). The difference of ion radius of Ti^{4+} from Ag^+ may lead to a distortion of anatase crystal lattice, which contributes to the left shift of anatase (101) diffraction peak.

Results of photocatalytic degradation clearly show that the activity was significantly enhanced by Ag^+ doping. The photocatalytic activity was increased to about thrice that of pure TiO_2 by a 0.005 at.% dopant concentration. Although a high concentration doping of more than 0.05 at.% led to a decrease in the activity, the activity of 0.1-0.5 at.% Ag^+-doped coatings were still about two times that of pure TiO_2 coating. Our previous results showed that the photoreactivity of the liquid-flame-sprayed TiO_2 coatings can be enhanced by Cu^{2+} doping, and the activity is significantly influenced by dopant concentration (Ref 13). The activity was increased with the increase of Cu^{2+} dopant concentration to 0.005 at.% and decreased with the further increase of the dopant concentration (Ref 13). The photoreactivity of Cu^{2+}-doped coatings became lower than the pure TiO_2 when the dopant concentration was higher than 0.01% (Ref 13). Comparing with Cu^{2+}-doped TiO_2 coatings, the Ag^+-doped TiO_2 coating presents a much different dependence of activity on the dopant concentration. This difference is attributed to the different forms of copper and silver within the doped coatings.

Copper in the TiO_2 coating is in the form of Cu^{2+} ion. Due to the high redox potential of Ag^+ ion, Ag^+ ion in the Ag^+-doped TiO_2 coating is easily reduced to metallic Ag atom by accepting an electron through photochemical approach (Ref 27, 29, 30). Therefore, both Ag^+ ion and metallic Ag were present in the Ag^+-doped TiO_2 catalyst, which had been approved by XPS and XRD analysis (Ref 27). Both Ag^+ ions and metallic Ag atoms benefit the photocatalytic performance of liquid-flame-sprayed TiO_2 coatings. Investigation of the metallic Ag load on the TiO_2 surface reveals that metallic Ag, which acts as an electron scavenger, improves charge separation and oxygen-reduction efficiency (Ref 14). Therefore, for high Ag^+ concentrations of 0.1-0.5 at.%, even if the Ag^+ ion doping cannot benefit the photocatalytic activity, the metallic Ag does benefit the photocatalytic activity. In brief, the enhancement of photocatalytic activity was attributed to the co-doping of Ag^+ ion and metallic Ag.

5. Conclusions

Silver ion was added in liquid feedstock to deposit Ag^+-doped nanostructured TiO_2 photocatalytic coatings through liquid-flame spraying. The XRD analysis showed that the Ag^+-doped TiO_2 coatings were composed of 95% anatase phase and a little faction of rutile phase. The left shift of the (101) diffraction peak of anatase TiO_2 suggested that Ag^+ entered the crystal lattice in the form of substitutional impurity. The photocatalytic activity of the TiO_2 coatings was thrice increased at a dopant concentration of 0.005 at.% and tended to decrease with the increase of dopant concentration. The photocatalytic activity of doped coatings was higher than that of pure TiO_2 coating even at a high dopant concentration up to 0.5 at.%. The enhancement of photocatalytic performance of Ag^+-doped coatings is attributed to co-doping effect of Ag^+ ion and metallic Ag.

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