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Effect of Cu^{2+} Doping on Photocatalytic Performance of Liquid Flame Sprayed TiO_2 Coatings

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Cu^{2+} was added to liquid feedstock to deposit ion doping TiO_2 photocatalytic coatings through liquid flame spraying. The coating microstructure was characterized by x-ray diffraction (XRD), transmission electron microscopy, and x-ray photoelectron spectroscopy (XPS). The photocatalytic performance of coatings was examined by photodegradation of acetaldehyde. The XRD analysis shows that the crystalline structure of coatings is not significantly influenced by Cu^{2+} doping. The photocatalytic activity of the TiO_2 coatings is enhanced by Cu^{2+} doping. It is found that a high concentration of Cu^{2+} doping decreases the activity. The XPS analysis shows that the adsorbed oxygen concentration is increased with the increase of Cu^{2+} dopant concentration and decreases with a further increase of dopant concentration. The enhancement of photocatalytic activity can be attributed to the adsorption ability of oxygen and other reactants on the surface of doping TiO_2 coatings.

Keywords ion doping, liquid flame spray, nanocrystalline material, photocatalyst, surface adsorption, TiO_2

1. Introduction

TiO_2 photocatalysis is an attractive low-temperature, energy-saving approach with promising applications to the destruction of environmentally undesirable chemical contaminants, such as waste-water treatment and air purification (Ref 1-6). The basic principle of semiconductor photocatalysis involves photon-generated electrons and holes migrating to the surface and serving as redox sources. These redoxes react with adsorbed reactants, leading to the destruction of pollutants. The photocatalytic efficiency of TiO_2 depends, in part, on the relative degree of branching of the reactive electron-hole pairs into interfacial charge-transfer reactions (Ref 7). 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 platinization, and by selective metal ion doping of the crystalline TiO_2 matrix (Ref 7-10).

Several metal ion dopants in TiO_2 have been reported to enhance the photocatalytic activity of TiO_2 photocatalysts. Among the investigated ions, Fe^{3+} has been shown to be the best dopant to increase photocatalytic efficiency (Ref 7). For all ion dopants, there exists an optimal dopant concentration, a deviation from which leads to a decrease in photoreactivity (Ref 7). As the concentration is lower than the optimal value, photoreactivity increases with increasing dopant concentration because the number of trapping sites increases with the increase of dopant concentration (Ref 7). The optimal concentration values for different ion dopants are different from one to another. Even for the same ion dopant, the optimal concentration is influenced by many factors such as particle size (Ref 11). Therefore, it is difficult to theoretically predict the optimal dopant concentration. Experimental studies are needed to investigate the effect of metal ion doping on photocatalytic properties (Ref 7-13).

In this article, the deposition of Cu^{2+}-doped TiO_2 photocatalytic coatings was carried out through liquid flame spraying by adding Cu^{2+} into liquid feedstock. The dependence of photocatalytic activity on Cu^{2+} doping was studied to reveal the role of Cu^{2+} doping in the photocatalytic performance.

2. Experimental

2.1 Materials

Butyl titanate [$Ti(OC_4H_9)_4$] (Jinshan, Shanghai, China) was used as a liquid precursor to form TiO_2 matrix through liquid flame spraying. Butyl titanate was diluted in ethanol (Ante, Anhui, China) to make the solution for spraying. Cu^{2+} was introduced by adding $Cu(NO_3)_2 \cdot 3H_2O$ (Fengchuan, Tianjin, China) to the liquid feedstock. The ion dopant concentration was controlled to be within a range from 0.001 to 0.1 at.%. Stainless steel plate with dimensions of 105 × 25 × 1.5 mm was used as a substrate for coating deposition. Prior to spraying, the substrate was sand-blasted with alumina grit.

2.2 Deposition of the Coating

A liquid flame spray torch was used to deposit TiO_2 coatings. Details of the torch can be found elsewhere (Ref 14). Spraying

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Table 1 Liquid flame-spraying conditions

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

conditions are given in Table 1. During coating deposition, the spray torch was manipulated by a robot (Motoman, Kitakyushu, Japan) and traversed at a relative speed of 500 mm/s with respect to the substrate.

2.3 Characterization of the Coating

An x-ray diffraction (XRD) system (D/max-2400; Rigaku, Tokyo, Japan) was used to characterize the crystalline structure of the deposits using Cu-Kα radiation, and was operated at 40 kV and 100 mA at scanning speeds of 10 and 2°/min for 2θ. Peak area was used to estimate the anatase content in the nanostructured coating using the following equation (Ref 15, 16):

$$C_A = \frac{A_A}{A_A + 1.265 \cdot A_R} \cdot 100\% \qquad \text{(Eq 1)}$$

where C_A is the anatase content in the TiO_2, and A_R and A_A are the areas covered by rutile peak (110) and anatase peak (101), respectively, in the XRD pattern. The morphology of the primary particles in the TiO_2 coating was examined by transmission electron microscopy (JEM-200CX; JEOL, Tokyo, Japan). The x-ray photoelectron spectroscopy (XPS) was carried out with the XPS system (MK-II; VG, London, UK), using Mg Kα radiation with energy of 1253 eV operated at 15 kV and 250 W.

2.4 Evaluation of the Photocatalytic Activity

The photocatalytic performance of TiO_2 coatings was evaluated through the photodegradation of acetaldehyde under ultraviolet (UV) illumination with a dominant wavelength of 360 nm. An experimental setup was assembled to carry out the photodegradation (Ref 16, 17). A 110 mL quartz cuvette (internal diameter 26 mm, height 220 mm) was used as a photocatalytic reactor. The UV light intensity at the coating surface was ~1 mW/cm^2. The acetaldehyde concentration in the reactor was determined by gas chromatography (model 6890; Agilent, Santa Clara, CA).

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 16, 17):

$$\ln\left(\frac{C_0}{C}\right) = \frac{t}{\tau} \qquad \text{(Eq 2)}$$

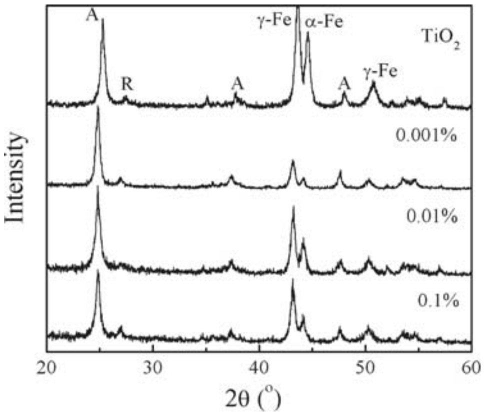

Fig. 1 XRD patterns of Cu^{2+}-doped TiO_2 coatings

where C is the acetaldehyde concentration, C_0 is the initial acetaldehyde concentration, t is the irradiation time, and τ is the time constant of photocatalytic degradation. According to Eq 2, the smaller the value of τ, the better the photocatalytic performance of the coating. In the current study, the photocatalytic activity of the TiO_2 photocatalyst was defined as the reciprocal of τ.

3. Results

3.1 Influence of Cu^{2+} Doping on the Crystalline Structure of the Coating

Figure 1 shows the XRD patterns of Cu^{2+}-doped TiO_2 coatings. It can be found that TiO_2 is composed of both an anatase phase and a fraction of a rutile phase. Quantitatively, the calculation yielded an anatase content of 95% in the coatings. The phase structure of the TiO_2 is not significantly influenced by ion doping when the dopant concentration is <0.1%. It was also found that the shift of the (101) diffraction peak of the anatase phase to a smaller diffraction angle occurred with Cu^{2+} doping. Figure 2 shows the XRD patterns of the pure TiO_2 coating and the Cu^{2+}-doped TiO_2 coatings obtained at a low scanning speed of 2°/min for 2θ. The shift of the (101) diffraction peak was 0.5° for the coatings with a Cu^{2+} dopant concentration of <0.1%.

Figure 3 shows the morphologies of the nanosized particles within the pure TiO_2 coating and the Cu^{2+}-doped TiO_2 coating. The primary particle size in the coatings ranged from 10 to 30 nm. It was clearly revealed that the primary particle size was not significantly influenced by the Cu^{2+} doping at a dopant concentration of <0.1%.

3.2 Influence of Cu^{2+} Doping on Adsorbed Oxygen on TiO_2 Surface

Figure 4 shows the O1s XPS spectra of the Cu^{2+}-doped TiO_2 coatings with different dopant concentrations. The O1s region is composed of two peaks (Ref 18). The first contribution is the crystal oxygen in TiO_2, such as Ti-O. The other is the surface adsorbed oxygen in the form of, for example, an hydroxyl group and O_2.

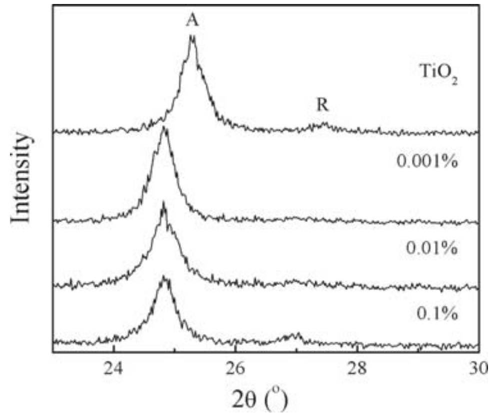

Fig. 2 XRD patterns at low scanning speeds of Cu^{2+}-doped TiO_2 coatings

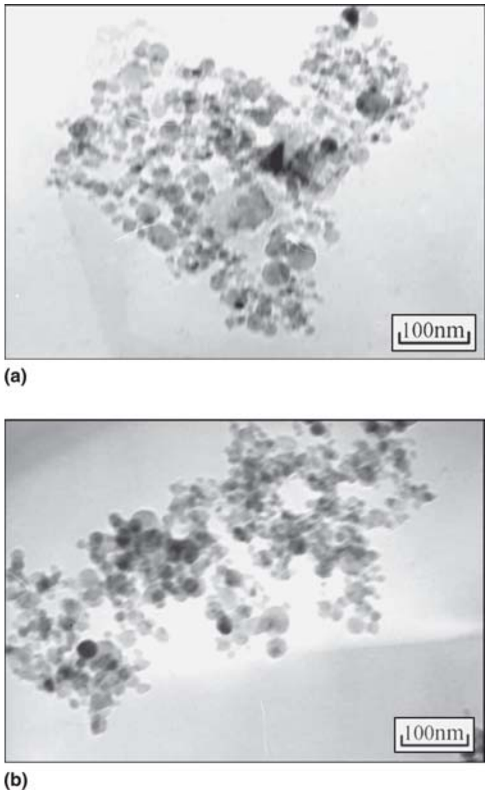

Fig. 3 Morphologies of nanoparticles in pure TiO_2 coating and Cu^{2+}-doped TiO_2 coating. (a) TiO_2; (b) $0.1\%Cu^{2+}/TiO_2$

Table 2 shows the areas of the two peaks obtained through deconvolution of the O1s XPS spectra for the pure TiO_2 coating and those for the Cu^{2+}-doped TiO_2 coatings at different dopant concentrations. The ratio of O_A to O_L represents the ratio of adsorbed oxygen to crystal oxygen in TiO_2 coatings. It is clearly seen from Table 2 that the ratio of O_A to O_L is significantly enhanced by Cu^{2+} doping at a relatively low dopant concentration. However, a dopant concentration >0.01% results in the decrease of the ratio of O_A to O_L.

3.3 Influence of Cu^{2+} Doping on the Photoreactivity

Figure 5 shows the influence of the Cu^{2+} dopant concentration on the photocatalytic activity of the as-sprayed TiO_2 coatings. It can be found that the photoreactivity is significantly increased from 1×10^{-2}/min for pure TiO_2 coating to 3.2×10^{-2}/min for the Cu^{2+}-doped TiO_2 coating with a dopant concentration of 0.005%. It was found that 0.005% was the optimal dopant concentration for Cu^{2+} in the current study. As the dopant concentration became higher than the optimal value, the photoreactivity decreased. The photoreactivity of Cu^{2+}-doped coatings became even lower than that of the pure TiO_2 coating as the dopant concentration was >0.01%.

4. Discussion

The present results showed that the photoreactivity of liquid flame-sprayed TiO_2 coatings can be enhanced by Cu^{2+} doping. The photoreactivity is influenced by doping concentration. There exists an optimal dopant concentration for the photocatalytic activity. The optimal dopant concentration of Cu^{2+} was 0.005 at.% in the current study.

Phase structure is one factor used to determine the photocatalytic reactivity of TiO_2 coating deposited by liquid flame spraying. The anatase phase presents superior photoreactivity over the rutile phase when TiO_2 is used as a photocatalyst (Ref 16, 17). When anatase TiO_2 synthesized by liquid flame spraying is annealed at a temperature higher than 500 °C, the phase transformation of the anatase particle to rutile phase occurs preferably at the TiO_2 particle surface (Ref 16, 17). The photocatalytic activity of the annealed TiO_2 is decreased to the same level as that of rutile TiO_2 (Ref 16, 17).

The XRD results shown in Fig. 2 revealed that the phase structure of a liquid flame-sprayed TiO_2 coating is not influenced by Cu^{2+} doping. The as-sprayed TiO_2 coatings are mainly composed of anatase phase. The doping of Cu^{2+} did not change the phase structure; therefore, the increase in photoreactivity after doping cannot be attributed to phase change. Other factors must be involved.

Because photocatalytic performance is a surface property of TiO_2 particles, photocatalytic activity is significantly influenced by effective surface area. The effective surface area is decreased with the increase of primary particle size. However, the morphology of the primary particle shown in Fig. 3 revealed that the primary particle size was not significantly influenced by Cu^{2+} doping during liquid flame spraying.

For Cu^{2+}-doped TiO_2 coatings, the (101) diffraction peak presents a significant shift to a lower diffraction angle. This shift suggests that Cu^{2+} has entered the crystal structure. Because a Ti^{4+} ion is displaced by a Cu^{2+} ion, the distortion of the crystal cell occurs because the ionic diameters of Ti^{4+} and Cu^{2+} are 0.068 and 0.073 nm, respectively (Ref 7). Therefore, it is reasonable to consider that the shift of the diffraction angle is attributed to the distortion of the TiO_2 crystal lattice.

The XPS analysis of the doped coating revealed that the ratio of O_A to O_L was significantly enhanced by Cu^{2+} doping. This fact suggested that more hydroxyl group and O_2 are adsorbed on the TiO_2 particle surface with Cu^{2+} doping. The hydroxyl group on the particle surface comes from the chemically adsorbed H_2O

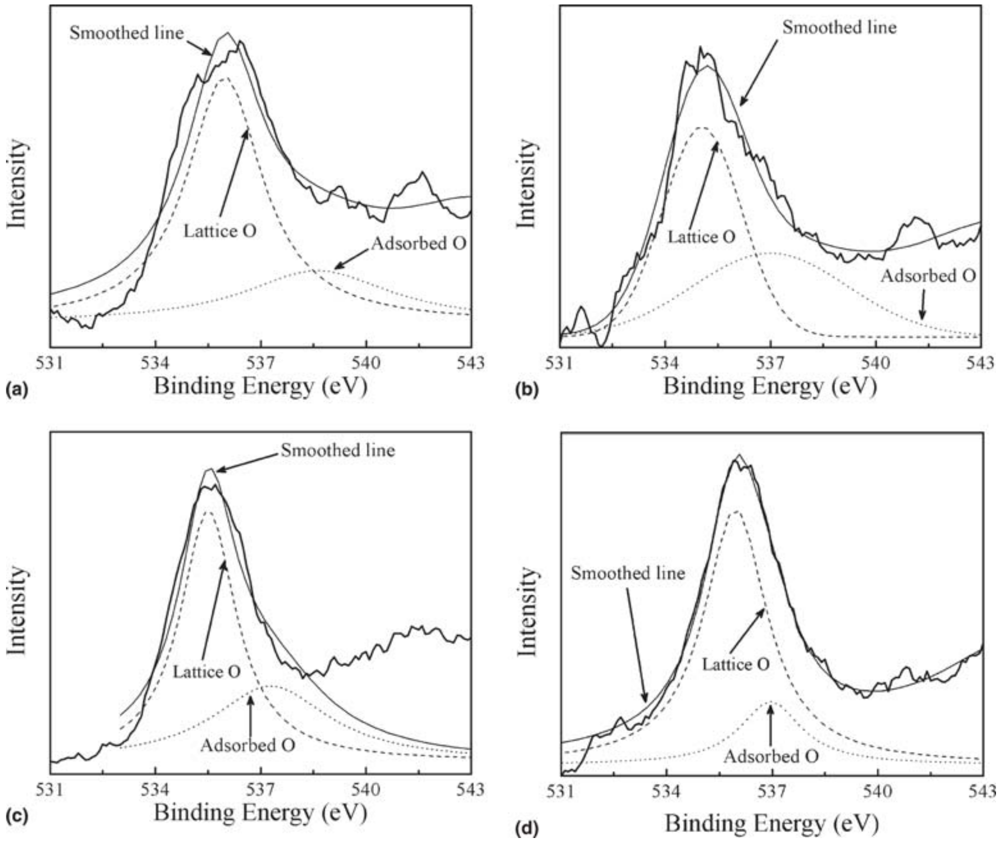

Fig. 4 O1s XPS spectra of Cu^{2+}-doped TiO_2 coatings: (a) TiO_2; (b) 0.001%Cu^{2+}/TiO_2; (c) 0.01%Cu^{2+}/TiO_2; and (d) 0.1%Cu^{2+}/TiO_2

Table 2 Ratio of O_A to O_L in TiO_2 coatings at different Cu^{2+} dopant concentrations

Cu^{2+}/TiO_2	Area of O_L	Area of O_A	O_A/O_L
0%	1870	643.1	0.344
0.001%	1468	1151	0.784
0.01%	1454	914.8	0.629
0.1%	3818	916.4	0.24

(Ref 16-21). Adsorbed H_2O can react with TiO_2 to form Ti-OH, such as, $H_2O + Ti–O–Ti \rightarrow 2Ti–OH$ (Ref 4). Figure 6 shows the effect of Cu^{2+} dopant concentration on the ratio of O_A to O_L and the photocatalytic activity of the coating. It was found that the ratio of O_A to O_L changes in the same direction as the photocatalytic activity changes with the dopant concentration.

Both the adsorbed O_2 and the hydroxyl group are beneficial to the enhancement of photocatalytic activity (Ref 22). It was reported that the rate constant for electron transfer to oxygen is the decisive factor determining the efficiency of the spontaneous photoelectrochemical process on semiconductor particles, where oxygen is the electron acceptor (Ref 22). Therefore, the photocatalytic reactivity will be increased with an increase of adsorbed O_2 at the particle surface. The increase of hydroxyl content on the TiO_2 surface through surface acid treatment is beneficial to the enhancement of photocatalytic activity (Ref 18). In addition, when the TiO_2 particle surface can adsorb more O_2 and H_2O, it may also have a higher ability to adsorb a larger amount of other reactants, which may also be beneficial to the increase of the photocatalytic activity. Therefore, it can be considered that the enhancement of photocatalytic activity by Cu^{2+} doping is attributed to the adsorption ability of oxygen and other reactants on the TiO_2 particle surface.

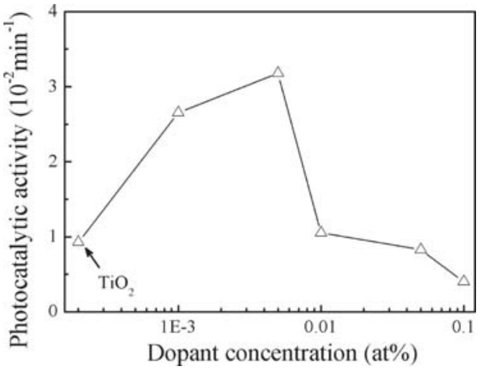

Fig. 5 Influence of dopant concentration on photoreactivity

5. Conclusions

Cu^{2+}-doped TiO_2 coatings were deposited through liquid flame spraying by adding Cu^{2+} into liquid feedstock. The XRD

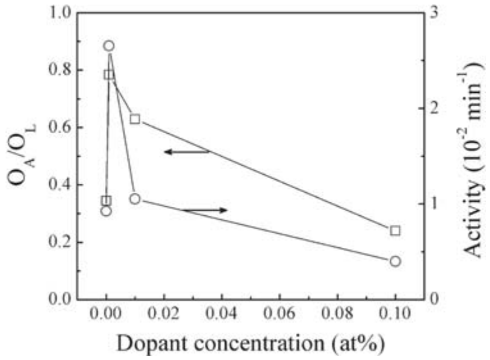

Fig. 6 Influence of Cu^{2+} dopant concentration on ratio of O_A to O_L and photocatalytic activity

analysis showed that both the phase composition and the grain size of the coatings were not significantly influenced by Cu^{2+} doping. The photoreactivity of the TiO_2 coatings can be enhanced by Cu^{2+} doping. The dopant concentration has a significant influence on the photocatalytic reactivity of the TiO_2 coating. The optimal dopant concentration of Cu^{2+} was 0.005 at.% in the current study. Doping at a higher concentration decreased the activity. The XPS analysis revealed that the adsorbed oxygen concentration was influenced by the Cu^{2+} dopant concentration. It was found that the increase of the adsorbed oxygen fraction with doping concentration coincides with the increase of photocatalytic reactivity. This fact suggests that the enhancement of photocatalytic activity is attributed to the increased adsorption ability of oxygen and other reactants on the particle surface of low-concentration Cu^{2+}-doped TiO_2 coatings.

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