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Short communication

Photocatalytic efficiency enhancement of plasma-sprayed TiO_2 coatings under external bias voltage

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Abstract

TiO_2 coatings were prepared on stainless steel by plasma spraying. The photocatalytic efficiencies of as-sprayed coatings were evaluated through the photo mineralization of methylene blue. External bias voltages applied to the coatings have shown an enhancement of the photocatalytic efficiency reducing the recombination of photogenerated electron–hole pairs. A more efficient photocatalytic reaction would take place when a higher external bias is imposed, because the force of recombination suppression is strengthened when the external bias is higher. The highest photocatalytic efficiency enhancement was about 46%.

Keywords: D. TiO_2; Plasma spraying; Photocatalytic efficiency; External bias

1. Introduction

TiO_2 photocatalyst has attracted a great deal of attention in environmental wastewater treatment in the past decade [1–5]. However, one of the limiting factors that control the efficiency of photocatalysis is the quick recombination between photo-induced charge carriers in semiconductor particulate systems [6,7]. Efforts have been made by several researchers to retard such a recombination of holes and electrons within the semiconductor particle and promote heterogeneous charge transfer at the semiconductor surface. Such efforts have included surface modification of the semiconductor with a noble metal [8,9] or other semiconductor [10,11] and an external bias imposed on TiO_2 membrane [12]. The external bias applied to the membrane pumps the photogenerated electrons through an external circuit into the cathode and leaves the holes in the TiO_2. Such effects may enhance the photocatalytic efficiency.

In order to evaluate the effect of external bias application, TiO_2 coatings were deposited on stainless steel by plasma spraying and a series of external bias were imposed on the coating when it was irradiated by UV lights.

2. Experimental

A commercial available TiO_2 (Degussa, P25) powder was used as raw materials which was agglomerated for plasma spraying. A 50 mm × 20 mm stainless steel slice was used as the substrate. An A-2000 atmospheric plasma spraying equipment (Sulzer-Metco, Switzerland) was used, with Argon as the primary plasma gas and hydrogen as the secondary gas. The actual spraying parameters are illustrated in Table 1. The thickness of as-sprayed coating is about 40 μm. Fig. 1 shows the schematic diagram of a photocatalytic reactor. A mercury lamp (125 W, peak wavelength is 365 nm) was used for the photocatalysis. The TiO_2 coating substrate was connected to the anode of a DC power supply. A blank stainless steel slice (60 mm × 25 mm) with one hundred thirty three meshes (diameter: 1 mm) opposite to the coating was connected to the cathode. The distance between them was 5 mm. The photocatalytic efficiencies of as-sprayed coatings under

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Table 1
Plasma spraying parameters

Argon flow rate (slpm)	80
Hydrogen flow rate (slpm)	6
Arc current (A)	303
Arc voltage (V)	76
Spraying distance (mm)	100

different bias (0 V, 5 V, 10 V, and 15 V) were evaluated through the photo mineralization of methylene blue (MB) solution (50 mL, 10 mg/L), with deionized water as the solvent. The methylene blue concentration in the solution was determined with a Shimadzu UV-1601PC UV–vis spectrophotometer.

3. Results and discussion

Fig. 2 shows the photocatalytic performance of as-sprayed coatings under different bias (0 V, 5 V, 10 V, and 15 V). When no bias was imposed on the coating, the photocatalytic efficiency only reached 65.3% in 90 min. But when an external bias was imposed on the coating, the photocatalytic efficiency was enhanced dramatically. Under different bias 5 V, 10 V, and 15 V, the photocatalytic efficiency reached 61.6%, 65.7%, and 76.2% in just 30 min, respectively. At the same time, the photocatalytic efficiency without external bias is only 27.0% after 30 min. The highest efficiency after 90 min is 95.3% when the coating was imposed a 15 V bias. So, the best photocatalytic efficiency enhancement is about 46%.

To investigate the effect of different bias on restraining the photo-induced carriers from recombination, the voltage–current curves were recorded when the coating was immersed in pure deionized water. The electrode was connected in the same way as it was done in the photocatalytic reaction. When the coating was irradiated by UV lamp, electrons were ousted from the valence band to

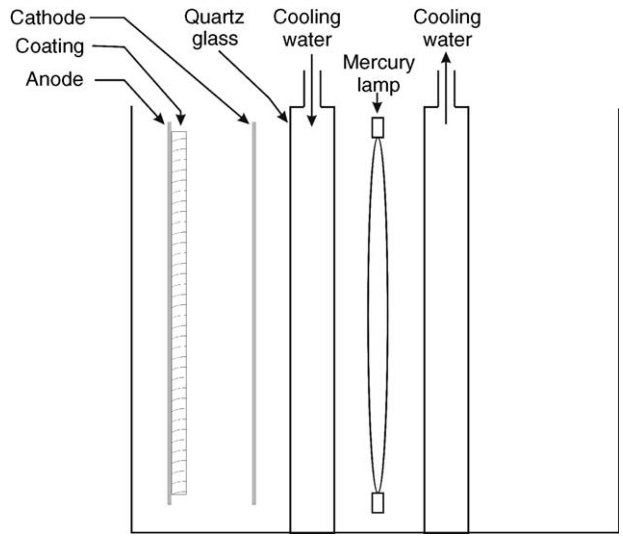

Fig. 1. Experimental apparatus for the photocatalytic reaction.

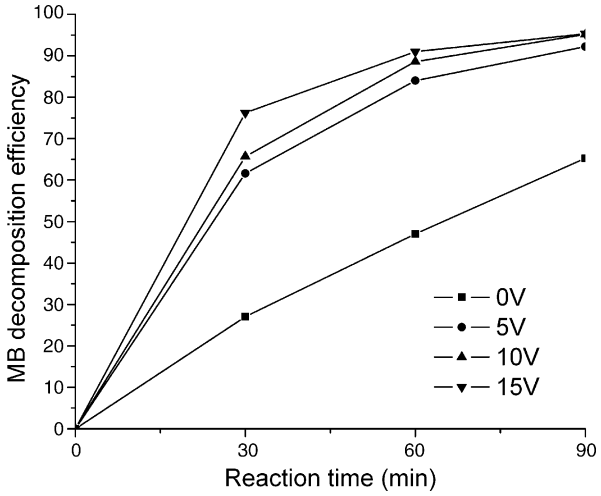

Fig. 2. Photocatalytic performance of as-sprayed coating.

the conduction band. According to Shockley [13], electrons depart from holes and form a current in the electric field. The left holes will generate more oxidant radicals, such as $OH^{\bullet}$ [14]. This behavior would be beneficial to the enhancement of the photocatalytic efficiency.

Fig. 3(a) and (b) show the current-potential curves of the coating immersed in pure deionized water under UV irradiation and dark condition. Curve (c), obtained by subtracting curve (b) from curve (a), is also shown in Fig. 3. Curve (b) indicates that the relationship between the dark voltage and the dark current is approximately linear. This implies that the current may mainly arise from the conductivity of the deionized water. The electronic structure of unexcited TiO_2 is characterized by a filled valence band and an empty conduction band [15], so there is no any electron of conduction band that contributes to the current in curve (b). After the coating was irradiated by UV lights, the current increases as shown in Fig. 3(a). When the coating was replaced with a blank stainless steel slice, there was no

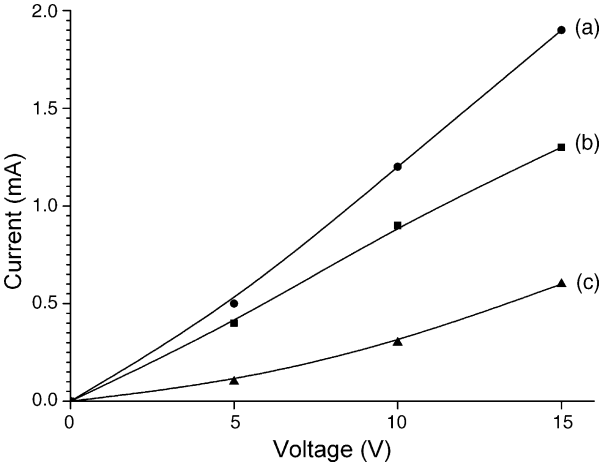

Fig. 3. Voltage–current curves of as-sprayed coating in pure deionized water under: (a) UV irradiation, (b) dark condition, and (c) curve in (a) − curve in (b).

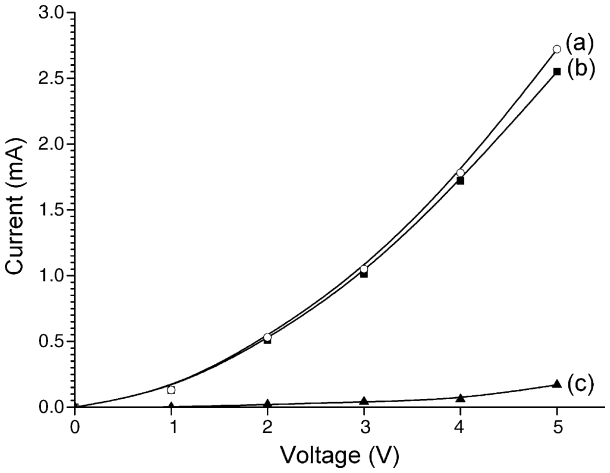

Fig. 4. Voltage–current curves of the membranate coating under: (a) UV irradiation, (b) dark condition, and (c) curve in (a) − curve in (b).

difference between the current under UV irradiation and dark condition at each voltage. This means that the UV light cannot influence the conductivity of the deionized water to make any contribution to the current increase. Based on this analysis, the increase of curve (a) compared to curve (b), viz. curve (c) may be composed of two sections. One section is the photo-induced electrons injection to the substrate due to the electric field. Another section is the increase of the current in the liquid because the conductivity of the deionized water would descend when more ion radicals have formed. An experiment also has been done to check the truth of the field induced charge carriers separation. A nanoscaled gold membrane was vaporized on the surface of the TiO_2 coating. The substrate and the membrane were connected to the anode and the cathode, respectively. As a consequence, the field direction is identical with that in the foregoing experiment. The current-potential curves of the membrane coating under UV irradiation and dark condition are shown in Fig. 4(a) and (b), respectively. Curve (c), obtained by subtracting curve (b) from curve (a), represents the photo-induced current. The increase of the photo-induced current means that more photo-induced carriers have separated from each other. So it can be concluded that the external bias could inhibit the recombination of photo-induced carriers and the number of separated carriers would increase when the external bias increases. This is consistent with the foregoing results.

4. Conclusions

TiO_2 coatings were prepared on stainless steel by the plasma spraying technique. The photocatalytic efficiencies of as-sprayed coatings under different bias were evaluated through the photo mineralization of methylene blue. The external bias can improve the photocatalytic efficiency of as-sprayed coatings effectively by restraining the photo-induced carriers from recombination. The number of electrons that depart from holes would increase when the external bias imposed on the coatings increases. The highest photocatalytic efficiency enhancement was about 46% when a 15 V external bias was imposed on the coating.

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