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Removing algae with CoO_2-doped TiO_2 coatings on foamed glass

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Commercial nano-sized TiO_2 powder (P25) coated with commercial CoO_2 powder by a sonochemical method was immobilized on foamed waste-glass substrates using plasma spraying coating technology. The immobilized TiO_2-CoO_2 coatings were applied to treat both green tide and red tide samples under the illumination of an UV light. Their photocatalytic characterizations were evaluated as functions of the number of residual algae, the transmission as well as the pH value with illumination time. It was found that the plasma sprayed 1 mol% CoO_2-doped TiO_2 nanostructured coatings on foamed waste-glass showed higher photocatalytic activity, which was effective to treat the green tide and red tide samples.

Key words: Plasma spraying, TiO_2-CoO_2 coating, Photocatalytic activity, Foamed waste-glass, Algae.

Introduction

Over the last few decades, the coastal regions throughout the world have experienced incidences of algal blooms, which are harmful or otherwise toxic because of their potential threat to humans as well as marine organisms, owing to accelerated eutrophication from human activities and certain oceanic processes [1]. In order to reduce the fisheries damaged by the red and green tides and protect the ecological environment, suitable countermeasures should be taken. Recently, photocatalytic technology has been attracting much interesting in the field of environmental engineering applications. Photocatalytic reactions of nano-semiconductors are ideal and powerful to eliminate pollutants in air and water [2]. When the light irradiate TiO_2, the energy of the OH radical created (120 cal/mol) is larger than the combination energy of organic compound (100 cal/mol), so the an organic compounds were easy to decomposed, which can destroy the enzyme and which is related to the respiration or coenzyme such as coenzyme A in the germ cell, which can also intercept an increase of germ or mold.

Moreover, if the materials which have good compatibility with germs or molds can be attached on photocatalyst surfaces, or complexed with a photocatalyst, the effect on germ or mold removal is obvious [3]. Nano-sized TiO_2 particles are an ideal photocatalyst due to their chemical stability, non-toxicity and high reactivity for the elimination of pollutants in air and water [4]. Under UV light irradiation, electrons can be excited from the valence band of TiO_2 materials to the conduction band, leaving photo-generated holes in the valence band [5]. Photo-generated electrons and holes play an important role in photocatalytic degradation of pollutants.

In this study, we attempt to enhance the removal of red/green tide and diatoms with plasma sprayed CoO_2-doped TiO_2 coatings deposited on foamed waste-glass substrates by plasma spray coating technology.

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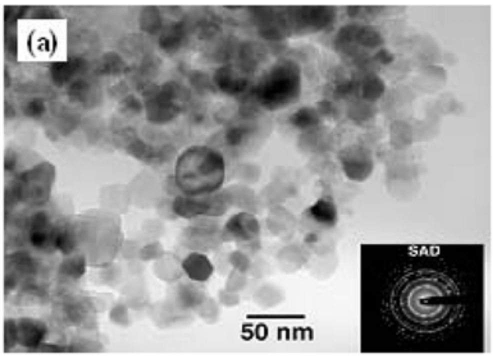

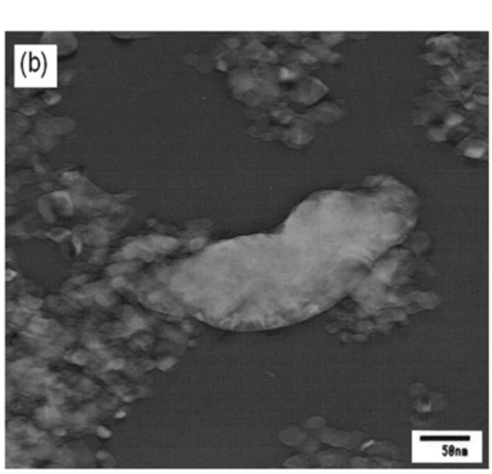

Fig. 1. TEM micrographs of (a) nanostructure P25 TiO_2 powder and (b) CoO_2 doped TiO_2 powder prepared by a sonochemical method.

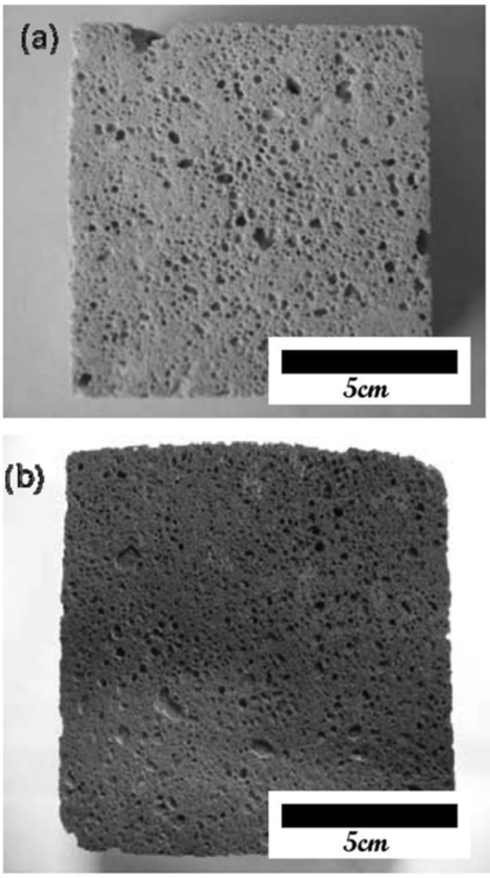

Fig. 2. Foamed waste-glass sample (a) before plasma spray coating and (b) after plasma spray coating.

Experimental Procedure

A commercial nano-sized TiO_2 powder (P25, 20-50 nm, Degussa, Germany) and CoO_2 powder (Junsei, Japan) were mixed, and treated by a sonochemical method. TEM micrographs of P25 TiO_2 powder and CoO_2-doped TiO_2 powder are shown in Fig. 1. The CoO_2-doped TiO_2 powder was utilized to deposit photocatalytic coatings by plasma spraying coating technology. Foamed waste-glass substrates with dimensions of 10 × 10 × 3.4 cm^3 were used. The samples were dark blue and had various porosities. Figure 2 shows a foamed waste-glass sample of before and after plasma spray coating.

The purification test was carried out at room temperature (25 °C). The coating sample was put into a batch reactor with 6 liters of green or red tide and 2 liter of nutritious water. The illustration of the batch reactor was well described in the previous work [6]. Two 30 W A-type UV lights (400 nm) lamps were used in this work. The number of residual algae, transmission as well as pH value of the water was measured at regular intervals.

Results and Discussion

In this study, two types of tests (TiO_2-1 mol%CoO_2, TiO_2-10 mol%CoO_2) were carried out for the red tide,

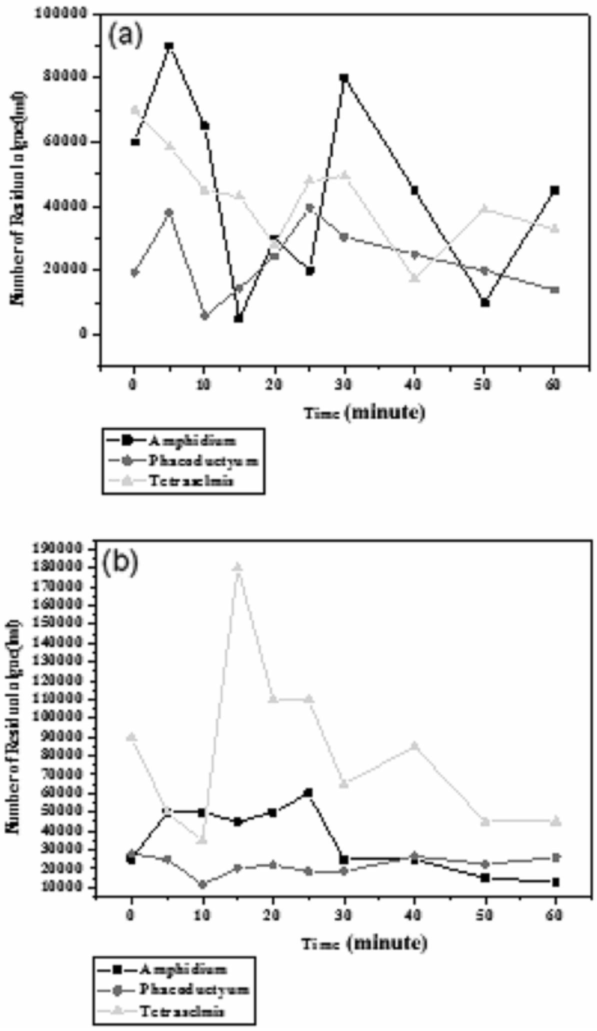

Fig. 3. Variation of the number of residual of the red tide (Amphidinium), green tide (Tetraselmis) and diatoms (Phaeoductyum) with illumination time from coatings with sonochemical powder: TiO_2-1 mol%CoO_2, and (b) TiO_2-10 mol%CoO_2.

green tide and diatoms. Figure 3 shows the variation of residual red, green tide and diatoms with illumination time from plasma sprayed coating samples.

According to these results, red, green tide and diatoms have different behaviors. The coated sample with TiO_2-1 mol% CoO_2, which was applied to the green tide, gradually removed large quantities as time went on.

The other sample removed a good quantity of green tide for the first 20 minutes, but from that time a slight increase of green tide germs was found. The exact reason for this result is not clear, but the coated sample with TiO_2-1 mol%CoO_2 was expected to effect only the first stage. In the case of the red tide for all the samples, all the red tide was removed in the first stage.

Figures 4 and 5 show the variation of the transmittance of the red tide, green tide and diatoms samples with illumination time from plasma sprayed coated samples.

The two types of coated samples were very similar to the variation of the numerical value, and the numerical

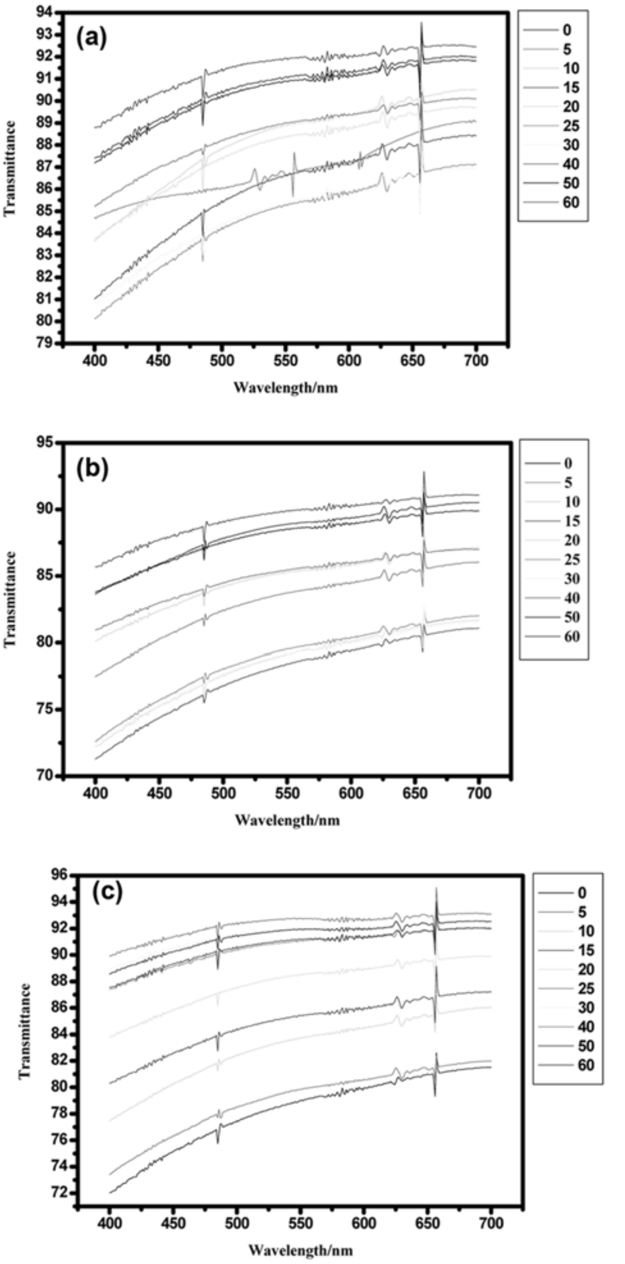

Fig. 4. Variation of the transmittance of the (a) red tide (Amphidinium), (b) diatoms (Phaeoductyum) and (c) green tide (Tetraselmis) with illumination time from coatings with sonochemical powder: TiO_2-1 mol%CoO_2.

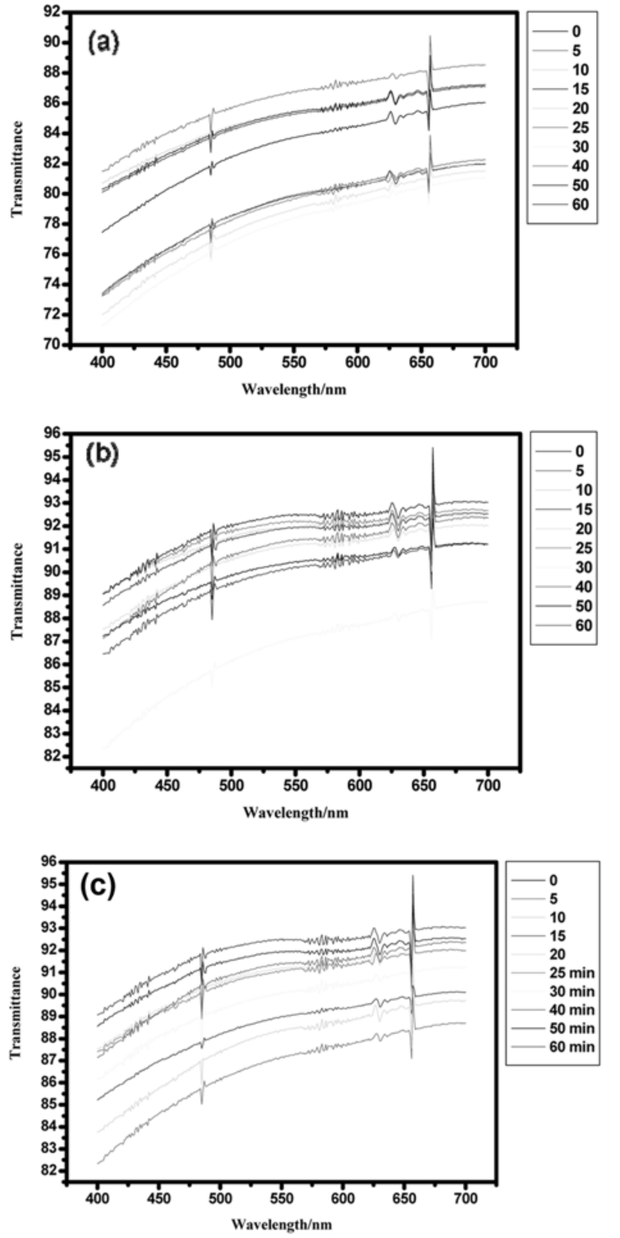

Fig. 5. Variation of the transmittance of the (a) red tide (Amphidinium), (b) diatoms (Phaeoductyum) and (c) green tide (Tetraselmis) with illumination time from coatings with sonochemical powder: TiO_2-10 mol%CoO_2.

value following the variation of the transmittance for 1 hour was extremely large. The variation of the numerical value was similar, but the coated sample with TiO_2-1 mol% CoO_2 showed a higher transmittance compared to that of the TiO_2-10 mol% CoO_2 sample. This result indicates a remarkable photocatalytic activity for the first 20 minutes and then a slow change as time went on.

The variation of the pH value for the red/green tide and diatoms samples with illumination time from plasma sprayed coated samples is shown in Fig. 6. Initially, the quality of the water showed an almost weak alkaline nature but the pH strongly increased to be more alkaline.

Conclusions

CoO_2-doped nano-sized TiO_2 powder, which was made by a sonochemical method, was immobilized on the foamed waste-glass by plasma spraying technology. By treatment of green tide and red tide samples, the photocatalytic characteristics of the plasma sprayed nanostructured TiO_2-CoO_2 coatings were evaluated as functions of the number of residual algae, light transmission as well as the pH value with illumination time. It's found that the plasma sprayed nanostructured TiO_2-1 mol%CoO_2 coatings on the foamed waste-glass showed higher photocatalytic activity, and was effective to treat the green tide and

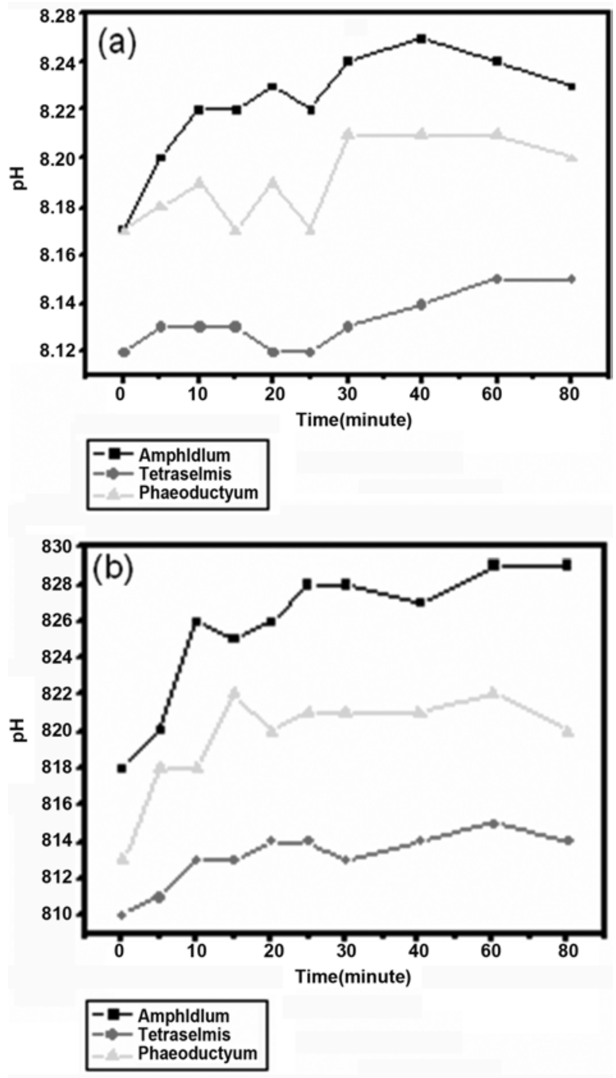

Fig. 6. Variation of pH value of the red tide (Amphidinium), green tide (Tetraselmis) and diatom (Phaeoductyum) with illumination time from coatings with sonochemical powder: (a) TiO_2-1 mol%CoO_2, and (b) TiO_2-10 mol%CoO_2.

red tide samples with UV light. When the sample was dipped, the water changes its pH from weakly alkaline to strong, because the foamed waste-glass is alkaline itself. This result indicates a possible application to the ocean bloom problem.

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