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# Influence of $TiO_2$ film on photo-catalytic property of enamels

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**Abstract**

$Ti(OC_4H_9)_4$–$C_2H_5OH$–$H_2O$ was used as matrix solution of titanium dioxide ($TiO_2$) film. Through sol–gel process, enamels were coated with $TiO_2$ film. Using methyl-orange as the simulative pollutant solution of photo-catalytic efficiency, we studied photo-catalytic activities of the enamels with and without $TiO_2$ film. Crystal structure and microstructure of the $TiO_2$ film were analyzed by means of scanning electron microscope (SEM) and X-ray diffract meter (XRD). Results showed that the photo-catalytic efficiency was greatly improved by the $TiO_2$ film coated on the enamel surface, and crystal of the $TiO_2$ film was anatase with imperfect crystal structure at the baking temperature of 450 °C. The $TiO_2$ film consisted of a lot of very small particles (0.01–0.05 μm and/or 10–50 nano), those particles had very small size and very large surface dimension as well as very high chemical activity, which made $TiO_2$ film have excellent photo-catalytic degradation.


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## 1. Introduction

Since photo-catalytic function of $TiO_2$ was discovered in 1972, titanium dioxide has been widely used in the field of pollutant degradation, virus killer and environment protection [1–5]. It has the advantage of not only high photo-catalytic activity, but also good acid resistance, low cost and no poison, which makes it become one of the best photo-catalytic agents [6,7].

A lot of research works on substrate materials for $TiO_2$ film, such as glasses, porcelains, fibers and metals, have been done [8–10]. So far, glasses coated with $TiO_2$ film have been manufactured and used for automobile wind-screen with pollutant degradation and self-cleaning properties. But no report on $TiO_2$ film on enamels with the same properties has been published. In fact, steel sheet enamels have been widely used as decorating materials inside and outside buildings, subway stations and tunnels [11,12], and enamel materials have also been used as boilers and vessels for food and water [13,14]. With the photo-catalytic property, these decorating materials and enamel vessels could be self-cleaned or cleaned very easily as well as virus killer.

Since enamels are different from glasses and porcelains in chemical composition, structure and properties, specially, the soften point temperature and surface structure, it will influence the coating technology and the $TiO_2$ film structure as well as the photo-catalytic property [3,12,13].

In view of the potential pollutant degradation and self-cleaning properties of $TiO_2$ film on enamels, we made enamels with $TiO_2$ film by sol–gel process, and observed their photo-catalytic properties. We also study the photo-catalytic mechanisms by investigating the microstructure and the crystal structure of the $TiO_2$ film with the help of scanning electron microscope (SEM) and X-ray diffract meter (XRD).

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## 2. Experimental details

### 2.1. Preparation of $TiO_2$ sol solution

The proportion of $Ti(OC_4H_9)_4$:$C_2H_5OH$:$H_2O$ must be controlled to prepare stable sol solution [6,15]. First, solution S1 and S2 were made respectively. Solution S1 was made by mixing 1 mol $Ti(OC_4H_9)_4$, 9 mol $C_2H_5OH$ (Eth) and 0.5 mol acetyl-acetone (AcAc), and solution S2 was the mixture of 0.2 mol $HNO_3$, 9 mol $C_2H_5OH$ and 2 mol $H_2O$. During S1 was stirred by an electric magnetic stirrer, S2 was dribbled into S1 slowly. After the mixture was completed, the electric magnetic stirrer continued to work on the solution for 2 h. After that, the solution was kept in standstill for 24 h. The stable $TiO_2$ sol solution was then made.

### 2.2. Preparation of $TiO_2$ film on enamels

A $TiO_2$ opaque enamel sheet was used as the substrate material. Chemical composition of the enamel is shown in Table 1.

Size of the substrate enamel sheet was $50 \times 50 \times 1$ mm. The enamel sample was immerged in 10% HCl solution for 30 min, then rinsed with de-ion water and washed in acetone solution with supersonic wave. After that, it was rinsed with de-ion water for the second time. The treated enamel sample was dried at 80 °C for 1 h, and the substrate enamel sample without $TiO_2$ film E1 was then made.

A substrate enamel sample E1 was dipped into the $TiO_2$ sol solution for 5 min, and raised by speed of 5 cm/min. After that, the enamel was dried at 80 °C for 40 min, and baked at 450 °C for 1 h. The enamel sample E2 with $TiO_2$ film was then made.

### 2.3. Observation on photo-catalytic properties of the enamel samples

Methyl-orange can be used as simulative pollutant solution to estimate photo-catalytic efficiency of the $TiO_2$ film on enamels according to references [16]. The concentration of the methyl-orange used in our work was 10 mg/L. The enamel samples E1 and E2 were put into two glass vessels with diameter of 100 mm, and 50 ml methyl-orange solution was added into the glass vessels, respectively. The enamel samples E1 and E2 were immerged in the solution for 1–13 h.

During the immerging, a 365 nm low-pressure mercury ultraviolet (UV) lamp (20 W UV light source) was positioned horizontally over twelve glass vessels with methyl-orange solution at about 80 mm distances. Four of them were with the enamel sample E1, four of them were with the enamel sample E2 and four of them were without the enamel sample. The temperature was $25 \pm 1$ °C.

Table 1
Chemical composition of the $TiO_2$ opaque enamel

| Chemical composition | $SiO_2$ | $Al_2O_3$ | $B_2O_3$ | $TiO_2$ | $K_2O$ | $Na_2O$ | $Na_2SiO_4$ | $P_2O_5$ |
|---|---|---|---|---|---|---|---|---|
| Weight percent | 43.8 | 1.0 | 18.0 | 18.5 | 1.0 | 8.5 | 7.0 | 2.2 |

With concentration of the methyl-orange solution changing, which was caused by the enamel samples, its color was changing at the same time. By observing the color of methyl-orange solution with those enamel specimens, the photo-catalytic efficiency of these enamel samples would be determined.

After the artificial radiation with different time, the simulative pollutant methyl-orange solution was tested by a spectrophotometer HACH DR/2010 at 455 nm.

### 2.4. The crystal structure and microstructure analysis

Microstructure of the $TiO_2$ film on enamel sample E2 was analyzed by using a scanning electron microscope (EPMA-8705QH, Japan) (SEM).

The $TiO_2$ film on enamel sample E2 was removed from the enamel and ground into powder. The powder was analyzed with an X-ray diffract meter (Ragaku D/max 2550, Japan) to investigate the crystal structure of the $TiO_2$ film on the enamel.

## 3. Results and discussion

### 3.1. Photo-catalytic activities

Relation between light absorption and concentration of methyl-orange at the 520 nm [16] is as follows:

$$A = 0.023 \times C + 0.011, \quad (1)$$

where $A$ is light absorption, $C$ is concentration of methyl-orange (in mg/L).

In accordance with Eq. (1), we calculated the concentration changing of the methyl-orange solution before and after the radiation of 365 nm.

The degradation rate of methyl-orange, which represents the photo-catalytic efficiency of the $TiO_2$ film on the enamels, can be determined by Eq. (2):

$$d = (Co - C)/Co \times 100\%, \quad (2)$$

where $d$ is degradation rate, $C$ is concentration after radiation, $Co$ is concentration before radiation.

Fig. 1 shows the relation between radiation time of the methyl-orange under UV lamp and degradation rate of the methyl-orange with and without the enamel specimens. The values on the Fig. 1 are the average of four specimens. It shows that the degradation rate of methyl-orange solution with different enamel specimens under the same radiation condition is different. Among the three methyl-orange solutions, the one with enamel E2 changed much faster than the other two. After radiation of 11 h, the degradation rate of the methyl-orange with sample E2 was over 80%, while that of the methyl-orange with sample E1 and without enamel sample were 40% and 20%, respectively. It indi-