

# Energy storage ability and photocathodic protection

## properties of $\text{TiO}_2$ - $\text{WO}_3$ system

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**Abstracts:**  $\text{TiO}_2$  /  $\text{WO}_3$  and  $\text{TiO}_2$  -  $\text{WO}_3$  coatings can be charged with reductive energy under UV irradiation. In this work,  $\text{TiO}_2$  /  $\text{WO}_3$  coating is compared with  $\text{TiO}_2$  -  $\text{WO}_3$  coating in terms of energy storage ability and photocathodic protection property. The self-discharging time of the  $\text{TiO}_2$  /  $\text{WO}_3$  coating is slower than that of the  $\text{TiO}_2$  -  $\text{WO}_3$  coating. The slow discharging may be suitable for an anticorrosion application for metal. In the case where  $\text{TiO}_2$  /  $\text{WO}_3$  coating electrode is electrochemically charged at  $-0.34$  V ( vs. SCE) for 1 h, it can maintain a good cathode protection for type 304 stainless steel for 6 h in the dark, while the  $\text{TiO}_2$  -  $\text{WO}_3$  coating electrode can only maintain a good cathode protection for less 0.5 h in the dark.

**Keywords:** energy storage; photocathodic protection; coating;  $\text{TiO}_2$  /  $\text{WO}_3$ ;  $\text{TiO}_2$  -  $\text{WO}_3$

### 1. Introduction

The applications of the  $\text{TiO}_2$  coatings for photocathodic protection of steels under UV illumination have been reported [1-6]. The reason why this field has attracted considerable interest is that  $\text{TiO}_2$  coating functions as a non-sacrificial anode when used for cathode protection of steel. However, the pure  $\text{TiO}_2$  coating cannot be used in the dark, because it suffers from the well-known charge recombination problem. The shortcomings of a plain  $\text{TiO}_2$  coating can also be circumvented by coupling another semi-conductor that has a different energy level as that of  $\text{TiO}_2$ , which accepts photogenerated electrons from the semiconductor under light illumination and donates those electrons to carry on some electrochemical reactions after the light is turned off. Based on the principle, in the past several years, there

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have been a number of studies related to  $\text{TiO}_2$  coupled with a semiconductor, such as  $\text{WO}_3$  [7-10] or  $\text{SnO}_2$  [11-14] or  $\text{MoO}_3$  [15] or phosphotungstic acid [16] or  $\text{Ni}(\text{OH})_2$  [17] or  $\text{Sb}_2\text{O}_5$  [18], etc. Such as, Ngaotrakanwivat [7-10] demonstrated that crystalline  $\text{WO}_3$  could serve as an energy storage material, when it was combined with  $\text{TiO}_2$  as a semiconductor. The  $\text{TiO}_2$ - $\text{WO}_3$  separately coating could provide cathode protection for type 304 stainless steel for 4 h in the dark after it was irradiation by UV illumination for 1 h, which exhibited more discharge properties than the  $\text{TiO}_2$ - $\text{WO}_3$  composite coating[7]. Subasri reported that an ITO glass coated with  $\text{SnO}_2$  –  $\text{TiO}_2$  film [11] and  $\text{SnO}_2$  /  $\text{TiO}_2$  film [12] had a good storage electrons ability. In addition, we have reported that type 304 stainless steel coated with  $\text{TiO}_2$  /  $\text{Sb}_2\text{O}_5$  bilayer coating could be protected from corrosion in 3 wt % NaCl solution, even after UV light was turned off [18].

In this work,  $\text{TiO}_2$  /  $\text{WO}_3$  and  $\text{TiO}_2$  -  $\text{WO}_3$  coatings were prepared on type 304 stainless steel by sol-gel method, respectively.  $\text{TiO}_2$  /  $\text{WO}_3$  coating is compared with  $\text{TiO}_2$  -  $\text{WO}_3$  coating in terms of energy storage ability and photocathodic protection property. First, electron storage behaviors for both coatings are investigated by electrochemical method. Then, the anticorrosion performances for both coatings are tested. Last, Surface morphology, structure and properties of the both coatings are characterized by scanning electron microscope (SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).

## 2 experimental

### 2.1 Preparation of the coatings

$\text{TiO}_2$  sol was prepared from tetra-n-butyl titanate( $\text{Ti}(\text{OBu})_4$ ) by sol-gel method as follows: firstly 30 ml ethanol and 1 ml ethyl acetoacetate (EAcAc) were mixed at room temperature, then 10 ml  $\text{Ti}(\text{OBu})_4$  was added and the solution was continuously stirred for 30 min, and finally 1 ml distilled water and 0.5 ml  $\text{HNO}_3$  as well as 10 ml ethanol were carefully added to the solution which was kept stirring for 2 h.

$\text{WO}_3$  sol was prepared by oxidation with hydrogen peroxide according to the following process: firstly 50 ml  $\text{H}_2\text{O}_2$  (30%) was carefully added to 10 g W powders (purity, 99 %), then 50 ml ethanol and a small amount of triethanolamine were added

to the solution and it was continuously stirred and refluxed for 5 h at temperature 80 °C.

TiO<sub>2</sub>-WO<sub>3</sub> sol was prepared by the following process: firstly the appropriate amount of (NH<sub>4</sub>)<sub>2</sub>WO<sub>4</sub> solution (W / Ti = 3 %) was added to TiO<sub>2</sub> sol. Then, the solution was kept stirring for 2 h.

Type 304 stainless steel (2 cm × 5 cm) was polished as a substrate. The stainless steel substrate was polished to a mirror finish with Al<sub>2</sub>O<sub>3</sub> powders and ultrasonically cleaned in acetone, ethanol and still water for 30 min, respectively. The TiO<sub>2</sub>/WO<sub>3</sub> coating was prepared by successive coating with WO<sub>3</sub> and TiO<sub>2</sub>. The WO<sub>3</sub> underlayer was prepared from WO<sub>3</sub> sol solution by dip-coating method. The substrate was annealed at 400 °C for 1 h. The average thickness of WO<sub>3</sub> coating was 120 nm (measured by SEM). The TiO<sub>2</sub> overlayer (average thickness measured by SEM, ca. 80 nm) was then prepared from TiO<sub>2</sub> sol solution in a similar way. In addition, TiO<sub>2</sub>-WO<sub>3</sub> coating was prepared from TiO<sub>2</sub>-WO<sub>3</sub> sol solution in a similar way. The average thickness of the composite coating was controlled with 80 nm (measured by SEM).

## 2.2 Characterization

The surface morphologies of the both coatings were characterized by scanning electron microscope (SEM) using LEO 1530 microscope with 15 kV accelerating voltage of the electron beam at various magnifications. The phase analysis of all samples was carried out using a D/max- $\theta$  A X-ray diffractometer by employing Cu K $\alpha$  as the incident radiation. The X-ray diffraction (XRD) patterns of the samples were collected over a  $2\theta$  range from 10° to 80° at a scan rate of 5°/min. The composition of both coatings were obtained with X-ray photoelectron model (XPS) with Al as the X-ray source and with 15 kV working voltage and 150 W working power.

## 2.3 Photo-electrochemical measurement

Each electrochemical experiment was performed in a three-electrode cell using a CHI660 electrochemical measurement system. All the measurements were done at room temperature in 3 wt% aqueous NaCl in an electrochemical cell equipped with a quartz glass window. A saturated calomel electrode (SCE) served as the reference

electrode. A stainless steel plate (8 cm × 8 cm) with a rectangular hole about 2 cm × 2 cm served as the reference electrode. TiO<sub>2</sub>/WO<sub>3</sub> and TiO<sub>2</sub>-WO<sub>3</sub> coatings electrodes were used as working electrodes (2 cm × 2 cm), respectively. The variations of open circuit potential (OCP) and the polarization curves of the two electrodes in the presence and absence of UV illumination were investigated, respectively. The potential swept amplitude was from 0 V to 0.5 V and the scan rate of 0.005 V/s for the polarization measurements. A 125 W high pressure Hg lamp with wavelength 365 nm was used as the source of irradiation.

### 3. Results and Discussion

#### 3.1 Photo-electrochemical performance

First, electron storage behavior of TiO<sub>2</sub>/WO<sub>3</sub> and TiO<sub>2</sub>-WO<sub>3</sub> coatings are examined. Fig. 1 illustrates the potential changes for those coatings. During the UV irradiation, TiO<sub>2</sub>/WO<sub>3</sub> and TiO<sub>2</sub>-WO<sub>3</sub> coatings can keep their potentials more negative than the corrosion potential of type 304 stainless steel, indicating that these substrates are maintained under a photocathode protection condition. Moreover, the TiO<sub>2</sub>-WO<sub>3</sub> coating electrode shifts more negative value than that of the former, indicating the former may have less photo-electrochemical performance than that of the latter. The cause of the difference photo-electrochemical performance may be the difference surface area of WO<sub>3</sub> on surface of those coatings. This is discussed further below. After the potential application, the colors of those coatings are changed to blue, suggesting that those coatings are reduced. It is known that WO<sub>3</sub> (transparent) is electrochemically reducible to a tungsten bronze, and the charging process should be as follows



After the UV light is turned off, the OCP of the electrodes is gradually shifted to the positive direction due to the reoxidation by O<sub>2</sub>. This is a so-called self-discharging process. That is to say, M<sub>x</sub>W( )<sub>3</sub> is gradually reoxidized to W( )O<sub>3</sub> by giving electrons to oxidation state matters or dissolved oxygen. As can also be seen from Fig.1, those coatings are irradiated by UV illumination for 1 h, TiO<sub>2</sub>/WO<sub>3</sub> coating electrode can be maintained cathode protection for more than 6 h, which is

longer than that of the  $\text{TiO}_2$  -  $\text{WO}_3$  coating. That is to say, the  $\text{TiO}_2$  /  $\text{WO}_3$  coating shows longer self-discharging time than does the  $\text{TiO}_2$  -  $\text{WO}_3$  coating, indicating that the former may have greater capacity than the latter. This may be because the content of  $\text{WO}_3$  of the  $\text{TiO}_2$  /  $\text{WO}_3$  coating is much more than that of the  $\text{TiO}_2$  -  $\text{WO}_3$  coating, so that much more the photogenerated electrons from  $\text{TiO}_2$  are stored by  $\text{WO}_3$  in the former.

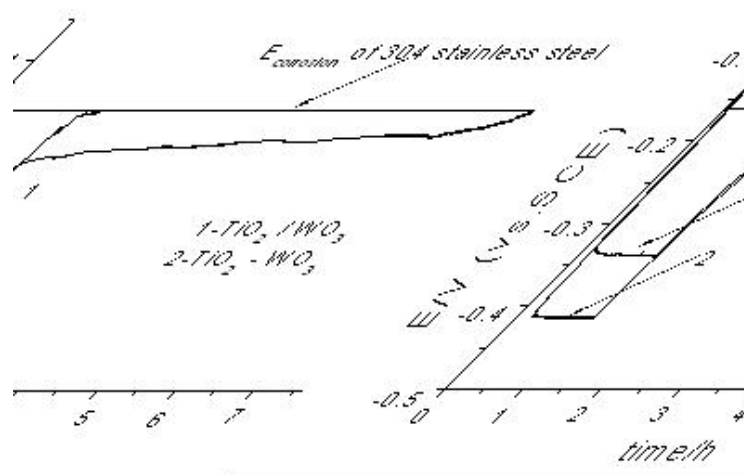


Fig.1. Potential changes of the photo-electrochemically charged  $\text{TiO}_2$  /  $\text{WO}_3$  and  $\text{TiO}_2$  -  $\text{WO}_3$  coatings in 3 wt% aqueous NaCl.

Fig.2 shows the polarization curves of  $\text{TiO}_2$  /  $\text{WO}_3$  and  $\text{TiO}_2$  -  $\text{WO}_3$  coatings electrodes in the presence and absence of UV irradiation, and of bare type 304 stainless steel in the dark in 3 wt% aqueous NaCl, respectively. The corrosion potential of the type 304 stainless steel is -0.16 V (vs. SCE). The photopotentials of  $\text{TiO}_2$  /  $\text{WO}_3$  and  $\text{TiO}_2$  -  $\text{WO}_3$  coatings are displaced to more positive values in comparison with bare 304 stainless steel in the dark. As a result, those coatings are able to act as optimal barrier layers to metallic substrates without a photo effect. In addition, the photopotential of -0.41 V (vs, SCE) is obtained for  $\text{TiO}_2$ -  $\text{WO}_3$  coating, which is more negative than that of  $\text{TiO}_2$  /  $\text{WO}_3$  under UV irradiation. The difference in the photopotentials of those coatings may be the difference surface area of  $\text{TiO}_2$  on surface of those coatings. Moreover, the two of electrodes yield higher anodic currents when compared to bare type 304 stainless steel under UV irradiation. It can be attributed to the creation of a part of the photogenerated electrons from the two of



coatings. Generally, the occurrence of a positive stable potential is related to the presence of a higher corrosion resistance layer. That is to say, the two of coatings offer better corrosion protection under the free corrosion potential condition.

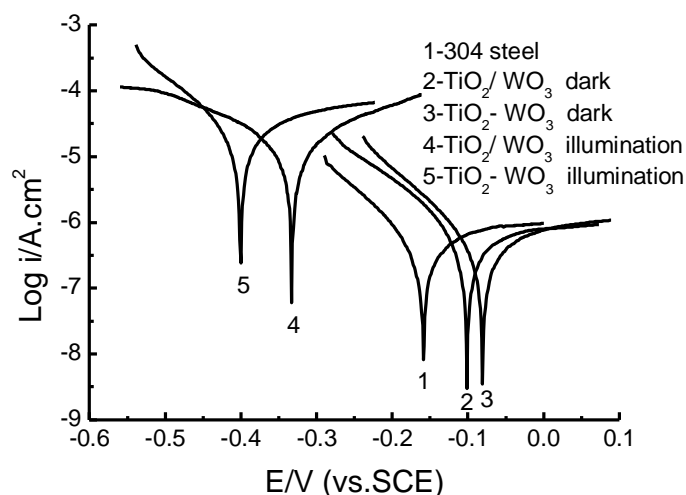


Fig.2. Tafel curves of a type 304 stainless steel electrode in the dark, and  $\text{TiO}_2 / \text{WO}_3$  and  $\text{TiO}_2 - \text{WO}_3$  coatings electrodes under UV illumination on and off

### 3.2 Phase structure

Fig.3 shows SEM images of the prepared  $\text{TiO}_2 / \text{WO}_3$  and  $\text{TiO}_2 - \text{WO}_3$  coatings. It is apparent that the  $\text{TiO}_2 / \text{WO}_3$  coating is continuous and uniform, and the shape of these particles is irregular (see Fig.1a). In comparison with the  $\text{TiO}_2 / \text{WO}_3$  coating, the surface of the  $\text{TiO}_2 - \text{WO}_3$  coating is more uniform and compact (see Fig.1b). In addition, the particles of the  $\text{TiO}_2 - \text{WO}_3$  coating are smaller than those in the  $\text{TiO}_2 / \text{WO}_3$  coating. This degradation must give rise to the photo-electrochemical performance increase.

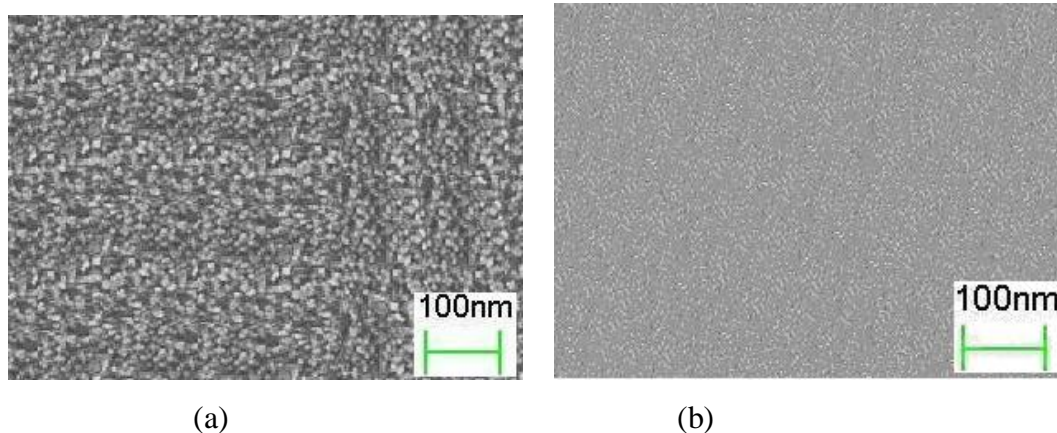


Fig.3. SEM images of the  $\text{TiO}_2 / \text{WO}_3$  coating (a) and  $\text{TiO}_2 - \text{WO}_3$  coating (b)

The Raman spectra for the  $\text{TiO}_2 / \text{WO}_3$  and  $\text{TiO}_2 - \text{WO}_3$  coatings are shown in Fig.4.

It is known that  $\text{TiO}_2$  photocatalyst in anatase phase has much higher photocatalytic properties than in other phases. Anatase in photoanode may also be important for the photocathodic protection effect because this effect came from the photoelectrochemical reactions on  $\text{TiO}_2$  photocatalysts. It is obvious that  $\text{TiO}_2 / \text{WO}_3$  coating is made up of anatase  $\text{TiO}_2$  and  $\text{WO}_3$ . In compare with  $\text{TiO}_2 / \text{WO}_3$  coating, the  $\text{TiO}_2 - \text{WO}_3$  coating is only made up of anatase  $\text{TiO}_2$ , and no  $\text{WO}_3$  characteristic peaks are shown in it. It may be due to too small  $\text{WO}_3$  particles in it. This can be further verified by XPS analyses. In addition, the peak intensity and peak width of anatase  $\text{TiO}_2$  in the  $\text{TiO}_2 - \text{WO}_3$  coating turn stronger and wider, which indicate that the particles size becomes smaller.

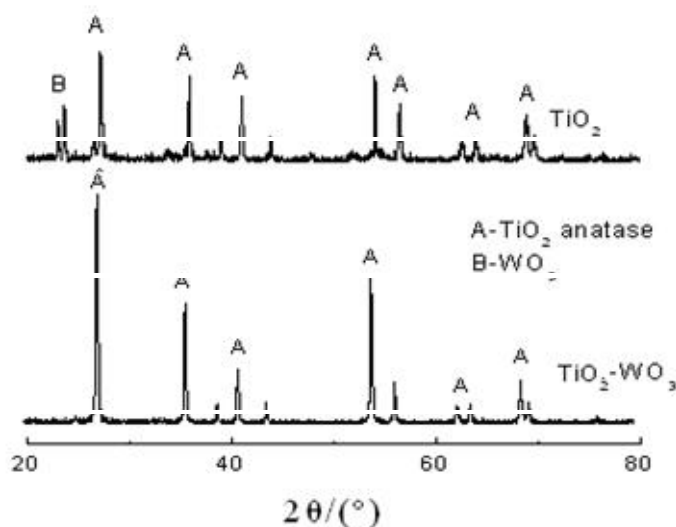


Fig.4.XRD spectra of the  $\text{TiO}_2 / \text{WO}_3$  and  $\text{TiO}_2 - \text{WO}_3$  coatings

Fig. 5 shows the XPS survey scan of the  $\text{TiO}_2 / \text{WO}_3$  and  $\text{TiO}_2 - \text{WO}_3$  coatings, in which only signals from Ti, W, O and C can be observed in those coatings. The carbon may mainly come from the surface contaminants. No signals steel from Fe, Co, Mn, or Ni, which are characteristic elements in stainless steel, can be detected in the XPS measurement. The results show that the stainless steel electrodes are entirely covered by the  $\text{TiO}_2 / \text{WO}_3$  and  $\text{TiO}_2 - \text{WO}_3$  coatings, respectively. In addition, table.1 shows that the content of W element in the  $\text{TiO}_2 / \text{WO}_3$  coating is more than that of in the  $\text{TiO}_2 - \text{WO}_3$  coating, which indicates a small amount of W ions diffusing to the  $\text{TiO}_2$  coating in the former.

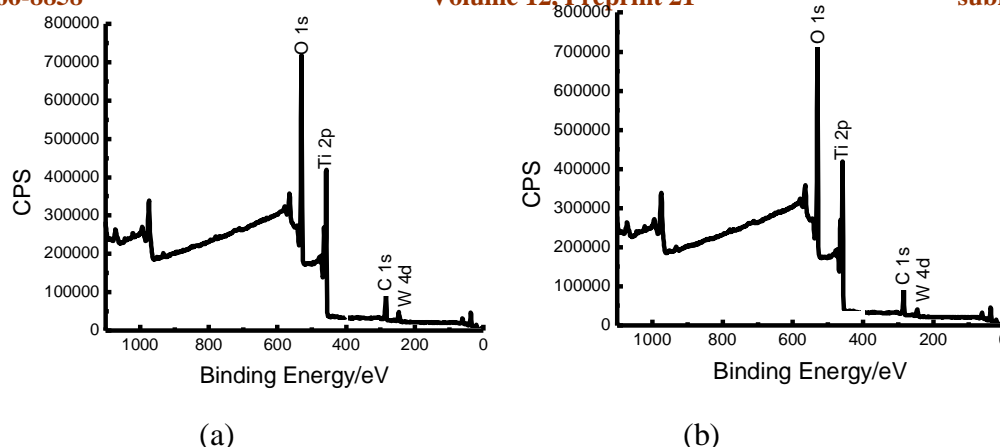


Fig.5 XPS survey spectra of  $\text{TiO}_2/\text{WO}_3$  coating (a) and  $\text{TiO}_2-\text{WO}_3$  coating (b)

Table. 1 Contents of  $\text{TiO}_2/\text{WO}_3$  coating and  $\text{TiO}_2-\text{WO}_3$  coating / %

element	Ti	W	O	C
$\text{TiO}_2/\text{WO}_3$ coating	17.898	0.149	51.301	28.945
$\text{TiO}_2-\text{WO}_3$ coating	17.902	0.073	50.989	28.497

#### 4. Conclusions

Continuous and uniform  $\text{TiO}_2/\text{WO}_3$  and  $\text{TiO}_2-\text{WO}_3$  coatings were prepared on type 304 stainless steel substrates by sol-gel method. Both coatings can be charged with reductive energy under UV irradiation. The self-discharging time of the  $\text{TiO}_2/\text{WO}_3$  coating is slower than that of the  $\text{TiO}_2-\text{WO}_3$  coating. Type 304 stainless steel with the  $\text{TiO}_2/\text{WO}_3$  coating can maintain cathode protection for 6 h in the dark after irradiation by UV irradiation for 1 h. The slow discharging may be suitable for an anticorrosion application.

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