Anticorrosion of WO$_3$-Modified TiO$_2$ Thin Film Prepared by Peroxo Sol-Gel Method

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Abstract

The aim of this study was to develop a method to prepare WO$_3$-TiO$_2$ film which has high anticorrosion property when it was coated on type 304 stainless steel. A series of WO$_3$-modified TiO$_2$ sols were synthesized by peroxo-sol gel method using TiCl$_4$ and Na$_2$WO$_4$ as the starting materials. TiCl$_4$ was converted to Ti(OH)$_4$ gel. H$_2$O$_2$ and Na$_2$WO$_4$ were added in Ti(OH)$_4$ solution and heated at 95˚C. The WO$_3$-TiO$_2$ sol was transparent, in neutral (pH~7) solution, stable suspension without surfactant, nano-crystallite and no annealing is needed after coating, and very stable for 2 years in stock. WO$_3$-TiO$_2$ sol was formed with anatase crystalline structure. These sols were characterized by XRD, TEM, and XPS. The sol was used to coat on stainless steel 304 by dip-coating. The WO$_3$-TiO$_2$ was anatase in structure as characterized by X-ray diffraction. There were no WO$_3$ XRD peaks in the WO$_3$-TiO$_2$ sols, indicating that WO$_3$ particles were very small, possibly incorporating into TiO$_2$ structure, providing the amount of WO$_3$ was very small. The TiO$_2$ particles were rhombus shape. WO$_3$-TiO$_2$ had smaller size area than pure TiO$_2$. The SEM results showed that the film coated on the glass substrate was very uniform. All films were nonporous and dense films. Its hardness reached 2 H after drying at 100˚C, and reached 5 H after annealing at 400˚C. The WO$_3$-TiO$_2$ film coated on 304 stainless steel had better anticorrosion capability than the unmodified TiO$_2$ film under UV light illumination. The optimum weight ratio of TiO$_2$: WO$_3$ was 100:4.

Keywords

Anticorrosion, Photocatalyst, Nanocoating, WO$_3$-TiO$_2$, Coating, Sol-Gel Method, Nanomaterial

1. Introduction

TiO$_2$ has been well-known to be the good material for anticorrosion [1]. Yuan
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and Tsujikawa [2] coated TiO2 onto type 304 stainless steel, and reported that
TiO2 could protect the inner substrate stainless steel. The similar effects were
reported by Tatsuma et al. [3] under UV light and γ-ray irradiation. They re-
ported a photoelectrochemical anticorrosion system about TiO2-WO3. This re-
search revealed an energy storage system with a sufficient capacity, which using
WO3 as an electron storage pool to receive the photogenerated electrons from
TiO2 conduction band. This system can promise that it can be effective in the
dark for a while [3]. Adding WO3 into TiO2 can promote the anticorrosion ca-
pability under visible light irradiation [4]-[15]. However, most of previous st u-
dies used powder form or sol in acidic solution [4] [14] [15] [16] [17]. The
powder WO3-TiO2 cannot be used to coat on substrate. The acidic sol is difficult
to handle and cannot coat on some substrates. In previous studies, one of the
authors has developed a peroxo-sol gel method to prepare TiO2 sol. It is very
stable and transparent after coating on substrate. None of previous literature was
reported on WO3-TiO2 sol prepared by peroxo-sol gel method.

The aim of this study was to develop a method to prepare WO3-TiO2 sol by
peroxo sol-gel method. The WO3-TiO2 sol was 1) transparent, 2) in neutral
(pH=7) solution, 3) stable suspension without surfactant, 4) nano-crystallite and
no annealing is needed after coating, 5) very stable for 2 years in stock. We also
tried to find the optimum doping amount of WO3, and to investigate its effect on
anticorrosion after coating on stainless steel type 304.

2. Experimental

2.1. Preparation of WO3-Modified TiO2 Sols

Na2WO4 was purchased from Aldrich. The detail procedure of preparing
WO3-modified TiO2 sol is as follows. The preparation method was the same as
synthesis of pure TiO2 sol, as reported in the previous studies [18]. The only dif-
ference was that Na2WO4 and H2O2 were added in the heating step at 95˚C for 6
h under magnetic stirring. 6 h later, the transparent light yellow WO3-TiO2 sol
was obtained. The molar ratio of TiO2: H2O2 was 1: 6 and the weight ratio of
WO3: TiO2 was 0.5:100, 1:100, 2:100 and 4:100, respectively. Ti(OH)4 and
Na2WO4 were converted to WO3-TiO2 crystallites at 95˚C in the presence of
H2O2. It should be noted that there was no surfactant was added. The sol was
very stable even after 2 years in stock.

2.2. Preparation of WO3-TiO2 Films

WO3-TiO2 films were prepared by dip-coating method using the as-prepared
WO3-TiO2 sols. The substrate was type 304 stainless steel. The total coating sur-
face area of the substrate was 40 cm². Before coating, the substrate was cleaned
by neutral abrasives and distilled water for several times, and then dried in an
oven at 50˚C. The substrate was vertically soaked into the as-prepared sol for 2
min, then pull out with the constant speed of 60 cm/min for 6 times. The thick-
ness of WO3-TiO2 films was kept around 120 nm. After coating, it was heated at
400˚C. The number in parentheses means the weight percentage of WO₃ in the sample (Figure 1).

2.3. Characterization

2.3.1. X-Ray Diffraction (XRD)
The sample was prepared by drying the WO₃-TiO₂ sol at 100˚C for 2 days to obtain the powder form. The sample was calcined at 400˚C for 2 h. The crystalline structure of the as-prepared WO₃-modified TiO₂ powder was performed using Simens D500 powder diffractometer using CuKα radiation (λ = 1.5405 Å) at a voltage and current of 40 kV and 40 mA, respectively.

2.3.2. Scanning Electron Microscopy (SEM)
The morphology and thickness of films were observed by Hitachi-3000 with tungsten lamp at acceleration voltage of 10 kV and emission current of 81,000 nA. The SEM sample was prepared by cutting the coated glass substrate into 0.5 cm × 0.5 cm piece with a diamond knife first and then coated with platinum to increase its conductivity.

2.3.3. Transmission Electron Microscopy (TEM)
The morphology and structure of WO₃-TiO₂ sol were observed by TEM (JEM-2000 EX II) operated at 160 kV or 200 kV. The TEM sample was prepared by dipping the carbon-coated copper grid (200 meshes) (Ted Pella) into as-prepared sol for 3 times.

2.4. Anticorrosion Test

The following methods were used to investigate the effect of WO₃-TiO₂ coating on anticorrosion capability of stainless steel 304.

2.4.1. The State of Corrosion
One of the methods to examine the state of the metal substrate is to place the coated substrate in a 3 - 5 wt% aqueous sodium chloride (NaCl) solution to carry...
out the salt spray test which is based on ASTM B-17. To speed the test, 5 wt% sulfuric acid aqueous solutions was used in this study. The state of the coated substrates was examined every 2 h. The weight of the substrates was measured every test and the corrosion degree (mg/dm²·day) and erodibility (mm/year) were calculated.

\[
\text{Corrosion degree (mg/dm}^2\cdot\text{day}) = \frac{\Delta W}{S \times H} \times 24 \times 10^5
\]

\[
\text{Erodibility (mm/year)} = \frac{W_1 - W_2}{d \times S} \times \frac{365 \times 24}{H} \times 10 = \frac{\Delta W}{d \times S \times H} \times 87600
\]

where \( W_1 \) is the weight before soaking into acidic solution (before testing) (g), \( W_2 \) is the weight after soaking into acidic solution (after rusting) (g), \( \Delta W \) is the difference between \( W_1 \) and \( W_2 \) (g), \( d \) is density (g/cm³), \( S \) is surface area (cm²), and \( H \) is testing time (h).

2.4.2. Four-Point Probe

Four-point probe is the most commonly used instrument to measure the sheet resistance. As long as adding constant current into two probes, simultaneously measuring the voltage difference between the two probes, the sheet resistance can be calculated.

The resistivity and sheet resistance were calculated by the following equation:

\[
R = \frac{\rho}{R_s} = \frac{l}{w} = \frac{\rho}{R_s} \frac{l}{w}
\]

where \( R \) is resistance values (Ω), \( \rho \) is resistivity (Ω·cm), \( l \) is the length of specimen (cm), \( w \) is the width of specimen (cm), \( t \) is the thickness of specimen (cm), and \( R_s \) is sheet resistance (Ω/unit area).

2.4.3. Cyclic Voltammeter

The cyclic voltammeter is an instrument that can control the potential, and it can detect the current of electrochemical reaction. In the beginning, the electrode was washed by ultrapure water. The electrode was put in a beaker which contained 5 wt% NaCl solution. The OCP (Open Circuit Potential) was tested firstly and then the scanning potential range was set from −0.8 V to 0.6 V. The scanning rate of set potential was 0.05 V/s, and the scanning circles were 9. The method to analyze the effect of anticorrosion is electric polarization curve. The upper curve is anodic polarization and the lower one is the cathodic polarization curve. The anodic polarization curve represents the reduction of hydrogen during the whole experiment, \( i.e., 2H^+ + 2e^- \rightarrow H_2 \). The cathodic polarization curve shows the oxidation of metal, \( i.e., M \rightarrow Mn^+ + ne^- \). \( E_{corr} \) represents the potential that working electrode starts corrosion. The \( I_{corr} \) represents the corrosion current, which is the corrosion rate.

3. Results and Discussion

3.1. Characteristics of WO₃-TiO₂ Sol

WO₃-TiO₂ sol was light yellow transparent sol containing WO₃-TiO₂ nanoparticles dispersed in water. The yellow color was due to the presence of small
amount of titanium peroxide [18]. If one decreased the amount of H₂O₂ in preparation, the color became light yellow. The pH values of TiO₂ and WO₃-TiO₂ sols are listed in Table 1. The pH value of TiO₂ sol was 8.7. Adding WO₃ in TiO₂ sol decreased the pH value very slightly because the tungsten precursor was acidic and its amount was very low.

3.2. XRD

The XRD patterns of all the samples are shown in Figure 3. The result in Figure 3 represents the anatase TiO₂ diffraction peaks located at 2θ = 25.4102°, 37.9658°, 48.1227°, 62.7199°, and 75.2245° corresponding to the anatase phase of (101), (004), (200), (204), and (215). The as-prepared TiO₂ had low intensity peaks for anatase, as shown in Figure 2(b), because the TiO₂ crystallites were very small, in agreement with literature data [14] [15] [16] [17] [18]. Figure 3 shows the XRD patterns of WO₃-TiO₂ samples. The diffraction peaks of these patterns coincide with the characteristic peaks of anatase TiO₂ and did not match any diffraction peak of WO₃. This is because the amount of WO₃ in WO₃-TiO₂ sample was very small. The characteristic peaks of WO₃. H₂O are at 2θ = 25.7164°, 35.1076°, and 52.7672°. In order to check whether the diffraction peaks of WO₃ appeared in W-TiO₂ samples or not, we added more amount of W precursors in the sample. Figure 5 shows the XRD pattern of 1 wt% WO₃-modified TiO₂ using H₂WO₄ as the precursor. There were no WO₃ XRD peaks in Figure 5. Tatsuma et al. [3] reported that WO₃ was highly dispersed in the bulk phase of TiO₂ particles and a new solid such as WO₃ was not formed. Our results are in accord.

Table 1. The pH values of the as-prepared sols.

| Sample | pH value |
|--------|----------|
| TiO₂   | 8.78     |
| WT (0.5)| 8.78    |
| WT (1) | 8.68     |
| WT (2) | 8.43     |
| WT (4) | 8.32     |
Figure 3. XRD patterns of (a) TiO$_2$; (b) WT (10); (c) WT (100); and (d) WO$_3$.

3.3. SEM

The structure of TiO$_2$ and WO$_3$-TiO$_2$ films were examined by SEM. The top-view surface structure and cross-section view of the as-prepared thin film are shown in Figure 4. Each sample had very uniform and smooth surface of film on the top of substrate, indicating that dip coating is a good way to prepare the thin film. The surface of TiO$_2$ film was smoother than those of WO$_3$-TiO$_2$ samples. All films were nonporous and dense films. Its hardness reached 2 H after drying at 100˚C, and reached 5 H after annealing at 400˚C.

3.4. TEM

The morphology of as-prepared WO$_3$-TiO$_2$ sols was analyzed by TEM and HRTEM. HRTEM image in Figure 5(a) shows that the TiO$_2$ particles were rhombus shape with the major axis and minor axis of 30 - 50 nm and 15 - 30 nm, respectively. Figure 5 also shows the morphology and particle size of the as-prepared WO$_3$-TiO$_2$. Comparing with pure TiO$_2$ sol, the particle sizes of WO$_3$-TiO$_2$ was smaller than that of TiO$_2$. It is in agreement with the literature data reported by Tryba et al. [19]. No WO$_3$ particles were observed and one can conclude that W atoms were incorporated into the structure of TiO$_2$, providing that the concentration of W precursor was low. In conclusion, we have successfully developed a method to prepare WO$_3$-TiO$_2$ sample.

3.5. Anticorrosion Test

The samples were loaded in the 5 wt% sulfuric acid solution to test their anticorrosion capabilities. The results are shown in Table 2 and Table 3. Table 2 shows the results tested for 24 h and Table 3 shows the results tested for 48 h.
Figure 4. Top-view SEM images of the surface structure of (a) TiO₂ film; (b) WT (0.5) film; (c) WT (1) film; (d) WT (2) film; (e) HT (10) film and (f) HT (100) film.

Table 2. Weight loss of various samples in the 5 wt% sulfuric acid solution after 24 h.

| Coating    | weight before test (g) | weight after test (g) | Rate of corrosion \(\times10^5\) (g/cm²·min) |
|------------|------------------------|-----------------------|------------------------------------------|
| Bare substrate | 9.0930               | 6.9609                | 12.339                                   |
| TiO₂       | 9.0989                | 7.4859                | 9.334                                    |
| WT (0.5)   | 9.0942                | 7.5393                | 8.998                                    |
| WT (1)     | 9.0778                | 7.5759                | 8.692                                    |
| WT (2)     | 9.0733                | 7.4347                | 9.483                                    |
| WT (4)     | 9.0635                | 7.4322                | 9.440                                    |
| WO₃        | 9.1027                | 7.3400                | 10.201                                   |
Table 3. Weight loss of the sample in 5 wt% sulfuric acid solution after 48 h.

| Sample         | weight before test (g) | weight after test (g) | rate of corrosion $\times 10^{-5}$ (g/cm²·min) |
|----------------|------------------------|-----------------------|-----------------------------------------------|
| Bare substrate | 9.0975                 | 5.7162                | 19.57                                         |
| TiO₂           | 9.0945                 | 6.3181                | 16.07                                         |
| WT (0.5)       | 9.0990                 | 6.2845                | 16.29                                         |
| WT (1)         | 9.0504                 | 6.3375                | 15.70                                         |
| WT (2)         | 9.0725                 | 6.2969                | 16.06                                         |
| WT (4)         | 9.0458                 | 6.3673                | 15.50                                         |
| WO₃            | 9.0741                 | 6.2388                | 16.41                                         |

The bare sample without coating had very low resistance to corrosion. One can see in Table 2 that sample WT (1) had the lowest weight loss by corrosion, indicating that it had the best anticorrosion performance among all the samples. Instead, WO₃ sample had low anticorrosion capability. Table 2 and Table 3 also show that the weight losses of all the samples coated with WO₃-TiO₂ films were almost the same. The difference was small because the short time test was used. The results indicated that TiO₂ has good anticorrosion property. Adding suitable amount of WO₃ in TiO₂ improved the anticorrosion property of TiO₂. WO₃ can store the electrons generated by TiO₂ under light irradiation [6]. It also can improve the separation of electron-hole pairs, resulting in high anticorrosion capability [10] [11] [15].

Anticorrosion property of the sample was examined by four-point probe to
determine the conductivity of the test specimen. If the conductivity of the specimen is high, the oxidative capacity is high, and its ability of anticorrosion is low. By applying an electric potential (1 V) and current (0.4 A) to the sample, the conductivity was zero in each sample, except the bare 304 stainless steel as shown in Table 4, indicating that all samples with coating had high anticorrosion property in the presence of and absence of light illumination.

3.6. Analysis by Cyclic Voltameter

The corrosion resistance and the behavior of materials were evaluated by the potentiostatic and potentiodynamic polarization methods. Figure 6 shows that the I-V curves of all samples were very smooth in the range between $-0.6$ V and $-0.05$ V. It illustrates that no obvious electrochemical reactions occurred in this region. This result has been initially applied to explain that coating onto the substrate would retard the electrochemical reactions.

Figure 6 shows that WT (4) sample had the lowest current density and TiO$_2$ sample had the highest current density. High current density infers low anticorrosion property. Figure 6 shows that the best sample had the weight ratio of TiO$_2$: WO$_3$ of 100:4. The amounts of charge of all samples are listed in Table 5. The higher the amount of charge means the lower the anticorrosion capability.

The results show that all of the samples had better anticorrosion capability than the unmodified TiO$_2$.

![Figure 6. The I-V curve of coated W-modified TiO$_2$ sol onto type 304 stainless steel. From top to bottom are TiO$_2$, WT (1), WT (2), and WT (4).](image)

**Table 4.** The experimental values of four-point probe for all samples.

| Sample           | With light irradiation   | Without light illumination |
|------------------|--------------------------|----------------------------|
| Bare 304 stainless steel | 1.002 V, 0.260 A        | 1.002 V, 0.260 A           |
| TiO$_2$          | X                        | X                          |
| WT (0.5)         | X                        | X                          |
| WT (1)           | X                        | X                          |
| WT (2)           | X                        | X                          |

“X” means that the conductivity was zero.
4. Conclusions

A series of WO₃-modified TiO₂ sols with various WO₃ contents were synthesized by peroxo sol-gel method. The as-prepared WO₃-modified TiO₂ sols were transparent with very light yellow color. The sols were very stable even after 2 years. The sol was used to coat on 304 stainless steel by dip coating for anticorrosion test. Its hardness reached 2 H after drying at 100°C, and reached 5 H after annealing at 400°C.

The crystalline phase of TiO₂ in sol was anatase. There were no WO₃ XRD peaks in the WO₃-TiO₂ sols, indicating that WO₃ particles were very small, possibly incorporating into TiO₂ structure, providing the amount of WO₃ was very small. The TiO₂ particles were rhombus shape. WO₃-TiO₂ had smaller size area than pure TiO₂. The SEM results showed that the film coated onto glass substrate were very uniform. The WO₃-TiO₂ coating on 304 stainless steel had better anticorrosion capability than the unmodified TiO₂ coating. The optimum weight ratio of TiO₂: WO₃ was 100:4.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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