

# Electrophoretic deposition of nano-ceramics for the photo-generated cathodic corrosion protection of steel substrates

Ji Hoon Park<sup>\*</sup>, Kyoo Young Kim and Jong Myung Park

Graduate Institute of Ferrous Technology  
Pohang University of Science and Technology (POSTECH)  
San 31, Hyoja-Dong, Pohang, 790-784, Korea

<sup>\*</sup> Presenter : jihun@postech.ac.kr

Presented at the 16<sup>th</sup> International Coating Science and Technology Symposium,  
September 9-12, 2012, Midtown Atlanta, GA

Corrosion is a destructive result of chemical reaction between a metal or metal alloy and its environment. Protective coatings are frequently employed in order to protect the steel from the corrosion. Among these, zinc coatings are most widely employed because of their good barrier property and sacrificial anodic performance. However, lifetime of the zinc coatings for the corrosion protection is limited. To overcome the drawback, inorganic TiO<sub>2</sub> coating has been extensively studied because it is electrochemically stable and it can be utilized as a photo-generated non-sacrificial anode [1, 2]. Under the ultraviolet (UV) illumination, TiO<sub>2</sub> can generate photo-electrons and then the generated electrons can inject to the metal via the conduction band. As a result, the open circuit potential of the metal can be shifted toward more negative potentials than the corrosion potential of the metal itself. Despite of its fascinating performance, pure TiO<sub>2</sub> coating suffers from the facile charge recombination reaction and, moreover, it cannot function photo-actively in the dark condition. Combination of other materials, which could separate the photo-electron from the TiO<sub>2</sub> and then store the electrons, will be the most promising way to overcome the drawbacks of pure TiO<sub>2</sub> coating. Tatsuma et al. demonstrated that WO<sub>3</sub> can store photo-electrons and subsequently release the photo-electrons in dark condition [3,4]. Many different materials are also demonstrated as electron storing materials, such as SnO<sub>2</sub> [5], Cu<sub>2</sub>O [6] and MoO<sub>3</sub> [7]. In this study, WO<sub>3</sub> was employed because it is mostly well-known photo-electron storing materials. In addition, electrophoretic deposition (EPD) was utilized to deposit TiO<sub>2</sub>-WO<sub>3</sub> nanoparticle on the stainless steel substrate (SUS 304). Electrophoretic deposition is achieved by coagulation of charged particles in a liquid suspension under an applied electric field. Recently, EPD has been intensively employed to fabricate the nano-structured functional ceramics composite layer because of its fascinating advantages such as versatility for application, cost effectiveness and simplicity. Especially, the uniform nano-structured packing ceramic film can be easily formed on steel substrate by electrophoretic deposition. In this study, TiO<sub>2</sub> (Degussa P25, particle size 25 nm, anatase and rutile mixture of 8:2) and WO<sub>3</sub> (particle size 90 nm) were used for the electrophoretic deposition. TiO<sub>2</sub> and WO<sub>3</sub> particle were dispersed in isopropyl alcohol (IPA) together with a particle charging additive (0.05M phosphoric acid di-butyl ester). The solutions of different particle concentration were prepared: TW 0 (TiO<sub>2</sub> 30 g·L<sup>-1</sup> + WO<sub>3</sub> 0 g·L<sup>-1</sup>), TW 20 (TiO<sub>2</sub> 24 g·L<sup>-1</sup> + WO<sub>3</sub> 6 g·L<sup>-1</sup>), TW 40 (TiO<sub>2</sub> 18 g·L<sup>-1</sup> + WO<sub>3</sub> 12 g·L<sup>-1</sup>), TW 60 (TiO<sub>2</sub> 12 g·L<sup>-1</sup> + WO<sub>3</sub> 18 g·L<sup>-1</sup>). The prepared suspensions were ultrasonicated for 1 hour to obtain a homogeneous dispersion of nano particles. The electrophoretic deposition (EPD) was performed at constant voltages of 30 V for 1 min. The distance between the substrates and counter electrodes was 15 mm. Then, the deposited specimen was dried at 60 °C in convection drying oven. The surface

morphology was observed using scanning electron microscopy (SEM, Hitachi SU-6600). Before SEM observations, the samples were coated with 10 nm of Pt/Pd. Furthermore, in order to investigate the cathodic protection ability of EPD coating layers, free corrosion potential ( $E_{\text{corr}}$ ) measurements were carried out under the UV irradiation with a Gamry Reference 600 with PCI4 Controller. 200W mercury-xenon lamp was employed as an ultraviolet (UV) light source. The optical properties of the electrodes were also characterized with a UV–vis diffuse reflectance spectrophotometer (Shimadzu UV2450). The X-ray diffractometer (XRD, D8 Advance, Bruker AXS) analysis using CuK $\alpha$  radiation was conducted to determine the actual ratio of deposited concentration of each type of ceramic particles on 304 stainless steel. Figure 1 shows SEM micrograph of the electrophoretically deposited layers on 304 stainless steel from the suspension of pure TiO<sub>2</sub> (TW 0) and TiO<sub>2</sub>-WO<sub>3</sub> hybrid solution with the different concentrations of 20 % WO<sub>3</sub> (TW 20), 40 % WO<sub>3</sub> (TW 40) and 60 % WO<sub>3</sub> (TW 60) of total weight of particles. As shown in SEM micrograph, TiO<sub>2</sub> and WO<sub>3</sub> nanoparticles were successfully deposited by electrophoretic motion of charged particle under the constant applied voltage. There was no noticeable homo-aggregation of the same kind of particle in the co-deposited layer. In other words, TiO<sub>2</sub> and WO<sub>3</sub> particle were homogeneously blended and uniformly deposited on the stainless steel substrate. The film thickness of each layer was around 10  $\mu\text{m}$ . In addition, X-ray diffractometer (XRD) analysis was performed to confirm the WO<sub>3</sub> concentration in the electrophoretically deposited layer. Figure 2 shows the variation of the XRD patterns of the deposited layer on the stainless steel from the different WO<sub>3</sub> concentrations of suspension. From XRD pattern, it can be demonstrated that the particle concentrations of WO<sub>3</sub> in the deposited layers on the stainless steel are proportional to the WO<sub>3</sub> concentrations of the suspensions.

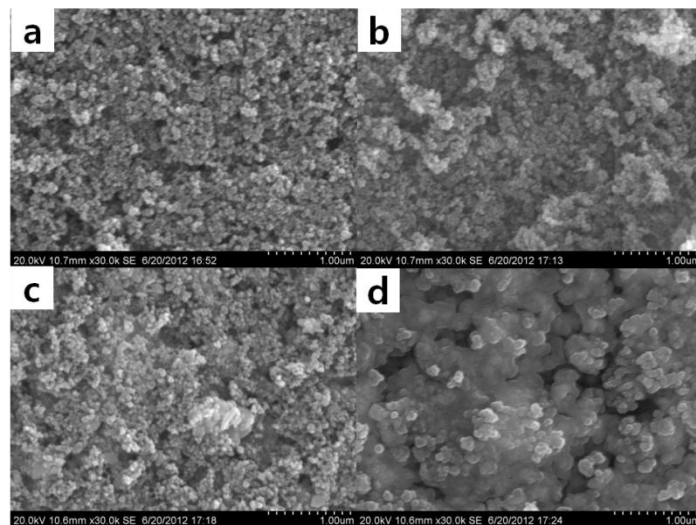


Figure 1. SEM micrograph of electrophoretic deposited layers on 304 STS with TW 0 (pure TiO<sub>2</sub>) (a) and TiO<sub>2</sub>-WO<sub>3</sub> hybrid layer with different particle concentrations of TW 20 (20 % WO<sub>3</sub>) (b), TW 40 (40 % WO<sub>3</sub>) (c) and TW 60 (60 % WO<sub>3</sub>) (d) of total weight of particles.

The optical absorption spectra of the electrophoretically deposited layers with different WO<sub>3</sub> concentrations are shown in Figure 3 (a). The spectra for these samples have similar shapes with absorption peak in the range of 300 to 400 nm, which is due to the charge transfer process from valence band to conduction band in TiO<sub>2</sub> particles (anatase 3.2 eV & rutile 3.02 eV). However, the absorption edges of the deposited layers with different WO<sub>3</sub> concentration are a little bit different (Figure 3(b)). Compared with the TW 0 (pure TiO<sub>2</sub>), WO<sub>3</sub> co-deposited samples possessed lower optical absorption edges. The higher WO<sub>3</sub> concentration, the more obvious the red shift of the sample is. For determining energy band gaps, the graph of optical absorption edge  $(ah\nu)^{1/2}$  versus energy of photo  $(h\nu)$  was plotted as given in Figure 3 (b). The estimated band gap was decreased with

increasing  $\text{WO}_3$  concentration. The reduction of band gap energy of co-deposited sample would be originated by the hybridization of smaller  $\text{WO}_3$  band gap (2.8 eV).

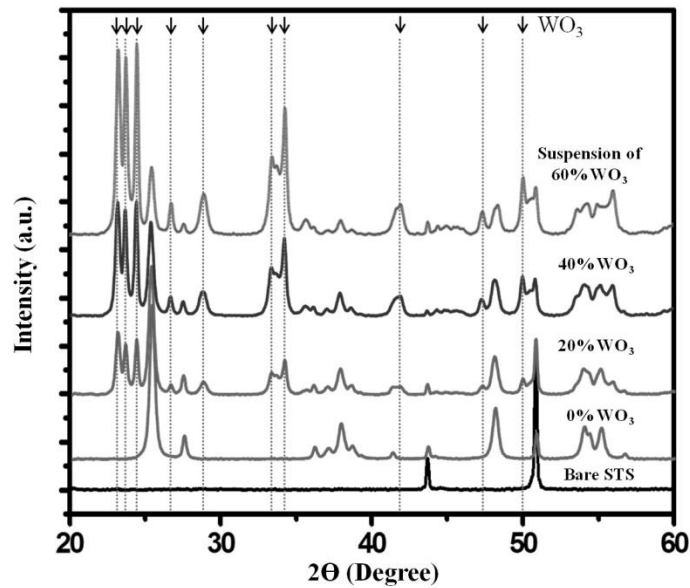


Figure 2. The variation of XRD patterns of electrophoretically deposited layers on 304 stainless steel with different  $\text{WO}_3$  concentrations in the suspensions.

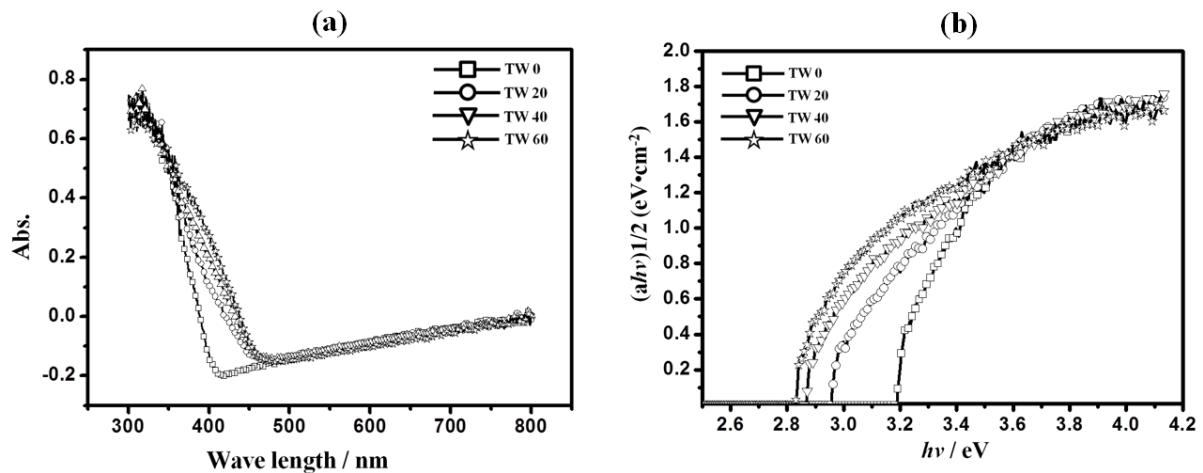


Figure 3. (a) The optical absorption spectra and (b) the optical absorption edge  $(ah\nu)^{1/2}$  versus energy of photon ( $h\nu$ ) of electrophoretically deposited layer on the stainless steel with different  $\text{WO}_3$  concentrations.

Figure 4 shows the open circuit potential changes of electrophoretically deposited  $\text{TiO}_2\text{-WO}_3$  layer on the stainless steel in 3.5 wt. % NaCl solution upon UV light on-off. Under the UV irradiation, the open circuit potential of the electrophoretically deposited stainless steel immediately dropped down in the range of  $-0.5 V_{\text{SCE}}$  and  $-0.7 V_{\text{SCE}}$ . However, the increase of the  $\text{WO}_3$  concentration caused the slowdown of the rate of potential drop. The free corrosion potential of bare 304 stainless steel was about  $-0.1 V_{\text{SCE}}$ . Thus it is assumed that, under the ultraviolet (UV) illumination, the deposited layer would generate photo-electrons and then the generated electrons would be injected to the metal via the conduction band. Therefore, the open circuit potential of the electrodeposited stainless steel was shifted to more negative values than its own corrosion potential. Obviously, all deposited layers with different ratios of  $\text{TiO}_2/\text{WO}_3$  provided a cathodic protection ability to the stainless steel. However, soon after light

was turned off, the open circuit potential recovered to the original value (the free corrosion potential of stainless steel). The higher the  $\text{WO}_3$  concentration in the deposited layer, the more delayed the time of potential recovery was. Namely, it was due to the electron storage ability of  $\text{WO}_3$ . Tatsuma et al. demonstrated that  $\text{WO}_3$  can store photo-electrons under light and subsequently release the photo-electrons in dark condition. The longer recovery time of potential means the longer corrosion protection of 304 stainless steel in dark condition. In the case of TW 60 sample, the open circuit potential of electrophoretically deposited 304 stainless steel maintained below the corrosion potential of the stainless steel substrate for 5 hours.

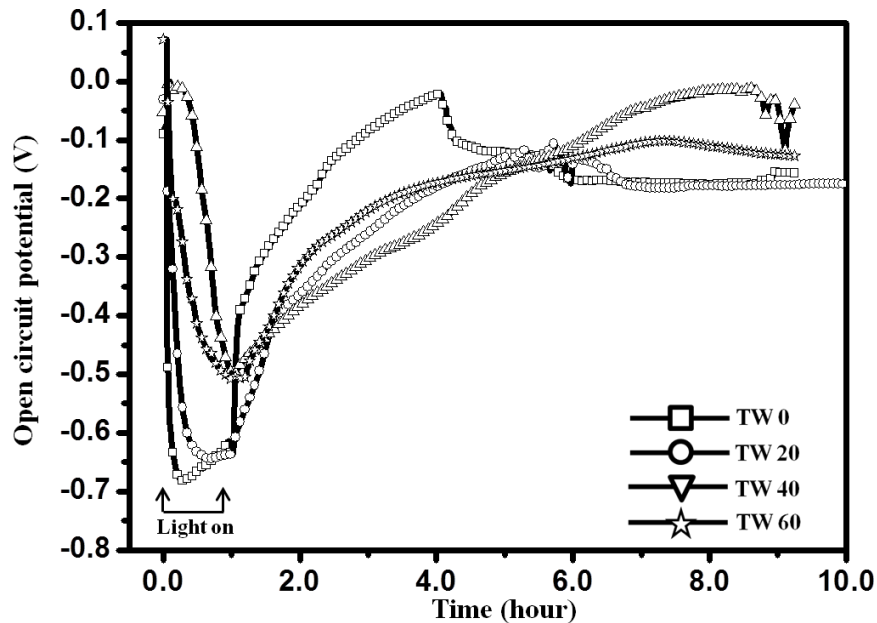


Figure 4 Effect of  $\text{WO}_3$  concentration of EPD layer on the changes of open circuit potential of  $\text{TiO}_2\text{-WO}_3$  particle deposited 304 STS in the 3.5 wt.% NaCl solution under UV irradiation.

In conclusion, in this study,  $\text{TiO}_2\text{-WO}_3$  hybrid layer successfully deposited on 304 STS via an electrophoretic deposition method in the applied voltage of 30V for 1 min. The  $\text{TiO}_2\text{-WO}_3$  co-deposited layer was stable in the aqueous NaCl solution. Moreover, it was demonstrated that  $\text{TiO}_2\text{-WO}_3$  electrodeposited layer can protect the 304 stainless steel both under UV irradiation and in dark (light off) condition. The increase of  $\text{WO}_3$  content in the deposited layer brought about the delay of potential recovery time in dark condition.

- [1] J. Yuan and S. Tsujikawa, *J. Electrochem. Soc.*, 142, 3444 (1995).
- [2] T. Imokawa, R. Fujisawa, A. Suda and S. Tsujikawa, *Zairyo-to Kankyo*, 43, 482 (1994)
- [3] T. Tatsuma, S. Saitoh, Y. Ohko, A. Fujishima, *Chem. Mater.*, 13, 2830 (2001)
- [4] T. Tatsuma, S. Saitoh, P. Ngaotrakanwivat, Y. Ohko, A. Fujishima, *Langmuir*, 18, 7777 (2002)
- [5] R. Subasri, T. Shinohara, *Electrochem. Commun.*, 5, 897 (2003)
- [6] J.P. Yasomanee, J. Bandara, *Sol. Energy Mater. Sol. Cells*, 92, 348 (2008)
- [7] Y. Takahashi, P. Ngaotrakanwivat, T. Tatsuma, *Electrochim. Acta*, 49, 2025 (2004)