

Photocatalytic sol-gel TiO₂ coatings on steel substrate: effect of surface treatment of coated steel substrate on the photo-catalytic activity

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There has been much effort to utilize the solar energy in a chemical reaction because the so-called photocatalysis is very economic and environmentally friendly technique. A photocatalyst is the material capable of utilizing sunlight to convert the gaseous materials, decompose the pollutants and split water to produce hydrogen. TiO₂ has been most widely used due to its low cost, high stability and most efficient photoactivity. TiO₂ photocatalyst can be applied on the various substrates such as glass, quartz, tile, stainless steel and paper [1-3]. However, galvanized steel (GI) has been rarely studied as a substrate for immobilizing a photocatalyst. GI has many advantages such as good mechanical property, high anticorrosion performance and good material reliability. In this study, GI was employed for the substrate of TiO₂ photocatalyst. In addition, the sol-gel method was used in order to immobilize TiO₂ layers on the substrate. The crystalline TiO₂ powder (Degussa P-25) was incorporated into a precursor sol in order to enhance the photocatalytic activity of TiO₂ films. Nevertheless, TiO₂ has a wide bandgap of 3.2 eV, so it can only absorb the UV portion of the solar spectrum [4]. To utilize a larger fraction of the solar spectrum, TiO₂ should be modified to make the bandgap smaller. Recently, it has been reported that TiO₂ mixed with rare earth elements, such as La, Nd, Eu and Ce, showed photoactivity in the visible light [5-7]. Among them, Ce showed the best activity in visible region consistently when mixed with TiO₂ [8, 9]. For that reason, cerium oxide layer was deposited on GI surface as an interfacial layer of TiO₂ photocatalytic film. In the study, the effect of cerium conversion coatings on the photocatalytic activity of TiO₂ layer was mainly discussed. The effect of incorporation of commercial crystalline TiO₂ particle (P-25) into TiO₂ sol-gel layer was also evaluated.

Cerium oxide interfacial layer was formed by applying the cerium conversion coating on galvanized steel. The ingredient of the solution and specific formation method for the cerium conversion coating are shown in Table 1. In order to prepare the photocatalytically active galvanized steel, All chemicals to prepare TiO₂ powder modified sol (PMS) were used as received, which include titanium iso-propoxide (TTIP, Aldrich, 97%), iso-propanol (IPA, Sam Chun Chemical, 99.8%) polyethylene glycol (PEG, Aldrich, MW:300), de-ionized water,

nitric acid (60%) and P-25 powder. The precursor solution consisted of 70 g TTIP, 50g IPA and 9g PEG. The solution was stirred at room temperature for approximately 1 hour. Then the pre-mixed solution containing 30g IPA, 2g nitric acid and 4 g of de-ionized water was added drop-wise under vigorous stirring. Subsequently, P-25 powder was incorporated into a precursor sol solution. The loading concentrations of P-25 powder were 0, 10, 20, 40 and 80 $\text{g}\cdot\text{L}^{-1}$. After aging the solution at room temperature for 1 day, the pre-cleaned galvanized steel substrates were coated with P-25 powder modified TiO_2 sol-gel solution using a dip-coater. The dipping time was 5 minutes and the withdrawing speed of the sample was $2\text{m}\cdot\text{min}^{-1}$. The dip-coated specimens were dried at 65°C for 1 hour and then calcined at 300°C for 2 hour.

Solution			Dipping time at RT (min)	Drying Time at RT (hr)
$\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ (mM)	pH	H_2O_2 (g/L)		
10	3.8	30	30	12

Table 1. Formation method for the cerium oxide interfacial layer.

The surface morphologies of the sample were observed by a scanning electron microscopy (SEM, Hitachi SU-6600). Figure 1 shows SEM surface morphology of specimens with the different loading concentration of P-25 powder. As increasing the loading concentration, the agglomerated TiO_2 particle was clearly appeared on the surface of the sol-gel film. Many cracks were observed in all substrates. The crack formation of TiO_2 films could not be avoided because of the internal stress increase and film volume shrinkage upon thermal treatment. The cracks were mainly formed at valley areas in rough surface of galvanized steel because of relatively thicker film in the areas. On the other hand, the incorporation of crystalline TiO_2 particle was helpful to form a crack-less film. It seems to be due to the stress relaxation in the interface between particle and film matrix. However, the high concentration of P-25 powder deteriorated the sol-gel film integrity and thus forming a crack again.

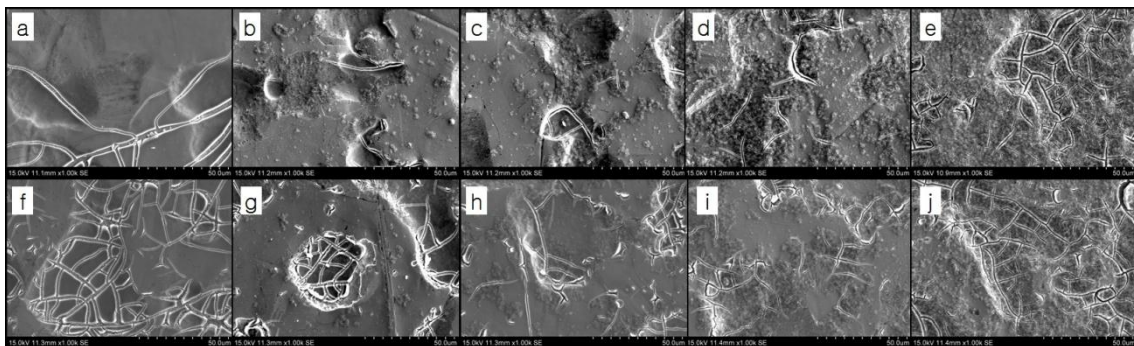


Figure 1. SEM microscopy of the surface of TiO_2 film made from (a) non CeCC(Cerium conversion coating)-PMSGM $0\text{ g}\cdot\text{L}^{-1}$; (b) non CeCC-PMSGM $10\text{ g}\cdot\text{L}^{-1}$; (c) non CeCC-PMSGM $20\text{ g}\cdot\text{L}^{-1}$; (d) non CeCC-PMSGM $40\text{ g}\cdot\text{L}^{-1}$; (e) non CeCC-PMSGM $80\text{ g}\cdot\text{L}^{-1}$; (f) CeCC-PMSGM $0\text{ g}\cdot\text{L}^{-1}$; (g) CeCC-PMSGM $10\text{ g}\cdot\text{L}^{-1}$; (h) CeCC-PMSGM $20\text{ g}\cdot\text{L}^{-1}$; (i) CeCC-PMSGM $40\text{ g}\cdot\text{L}^{-1}$ and (j) CeCC-PMSGM $80\text{ g}\cdot\text{L}^{-1}$

The optical absorption spectra of P-25 modified sol-gel film coated on bare-GI and cerium

conversion coated GI are shown in Figure 2. The spectrum shows an absorption onset at 380 nm for P-25 modified sol-gel layer. The higher the loading of P-25 particle, the higher the absorption of UV light (below 380 nm) is. Obviously, the photocatalytic film formed on the cerium conversion coated GI showed a red shift. CeO_2 is an n-type semiconductor whose bandgap is around 2.8 eV. Therefore, the cerium oxide layer would be responsible for the observed red shift about 50 nm. The coupled semiconductor ($\text{TiO}_2\text{-CeO}_2$) mechanism for the visible light activity was illustrated in Figure 3.

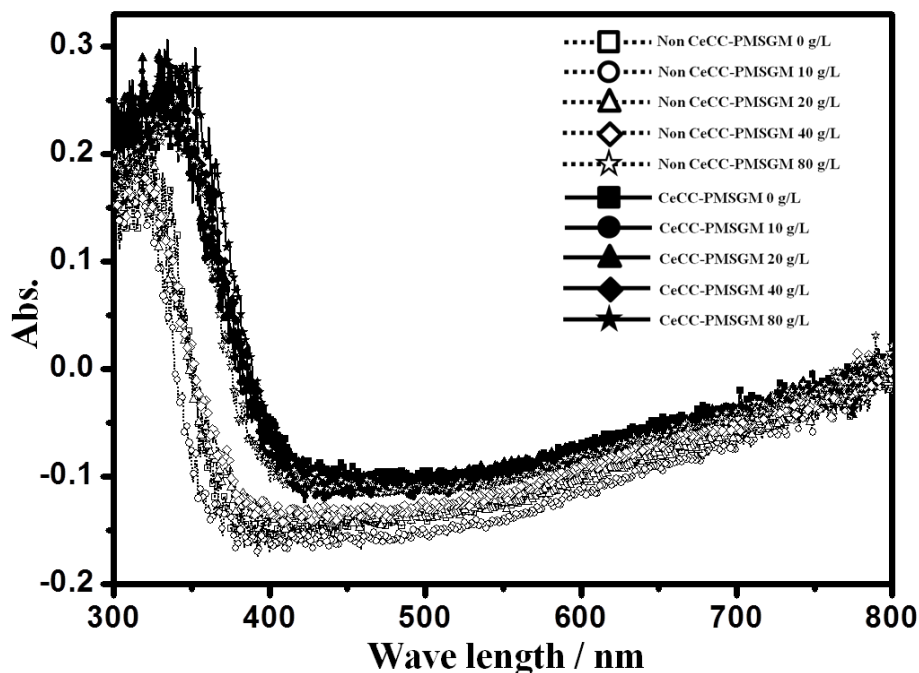


Figure 2. Optical absorption spectra of P-25 modified sol-gel TiO_2 film coated on bare-GI (dotted lines) and cerium conversion coated GI (solid lines).

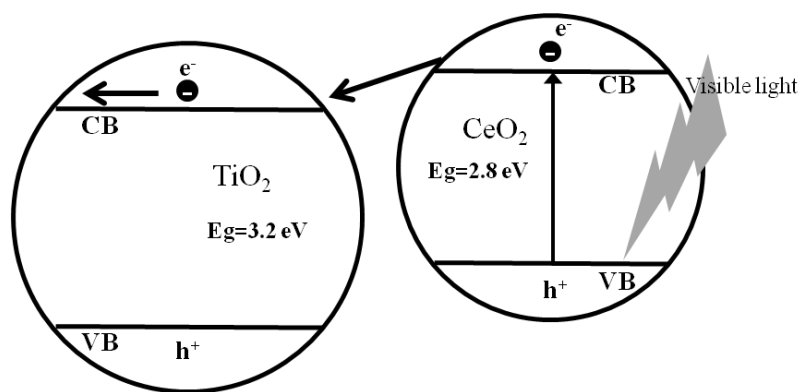


Figure 3. The coupled semiconductor ($\text{TiO}_2\text{-CeO}_2$) mechanism for the visible light activity.

The photocatalytic activity of the coated sample was evaluated by measuring the rate of photodegradation of methyl orange in aqueous solution. The photo-induced degradation of methyl orange was monitored in the presence of coated sample under the ultra-violet (UV) light source (200W mercury xenon lamp) for 4 hour. The photocatalytic activities of P-25 modified sol-gel film on GI with different particle loading concentration are shown in Figure 4. It can be demonstrated that the photocatalytic activity was enhanced with increasing P-25

particle loading concentration. Moreover, the existence of the cerium oxide interfacial layer formed GI sample provided better photocatalytic activity. The result is good agreement with the UV-visible light absorption behaviors of the sample. In other word, the enhancement in the photocatalytic activity may come from the hetero-junctions of $\text{TiO}_2\text{-CeO}_2$ in the coupled photocatalysts as explained in Figure 3. In conclusion, high P-25 powder loading of TiO_2 coating layer on GI in combination with the CeO_2 interfacial layer showed the best photocatalytic activity.

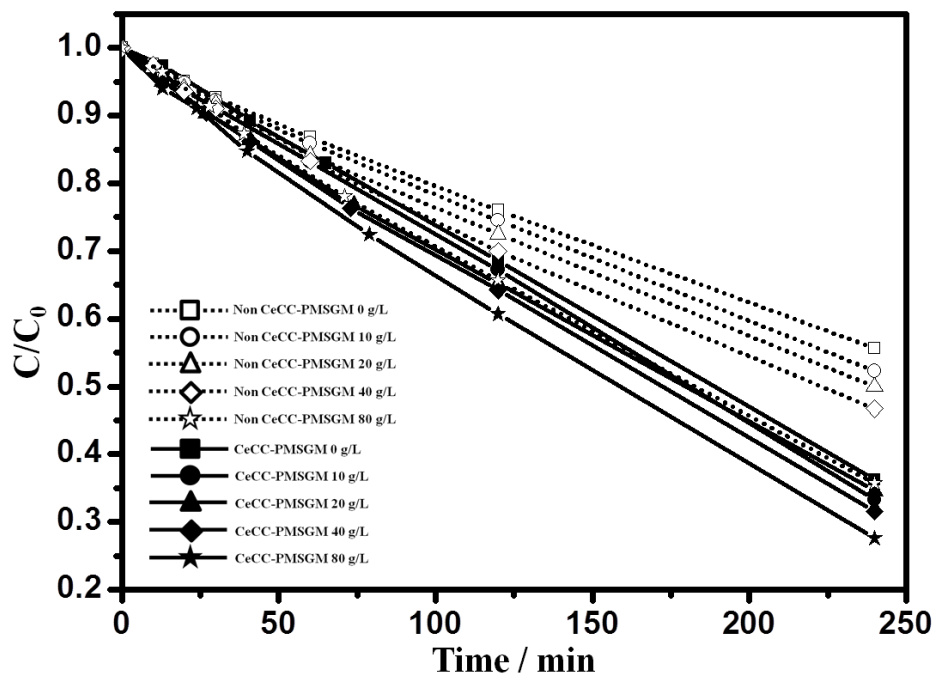


Figure 4. The degradation rate of methyl orange solution in UV light with P-25 modified sol-gel TiO_2 film coated on bare-GI (dotted lines) and cerium conversion coated GI (solid lines).

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