

Effect of crystal structure on photoinduced superhydrophilicity of copper grafted TiO₂ nanostructure thin film

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Abstract. In this work, copper grafted titanium dioxide (rutile and brookite) thin films were deposited on glass substrates using the dip-coating method. Field emission scanning electron microscopy and X-ray photoelectron spectroscopy were used to evaluate the surface morphology and properties of the film surfaces. The water contact angle on the film surfaces during irradiation and storage in a dark place was measured by a contact angle analyser. The results indicate that copper grafted titanium dioxide brookite thin film showed higher hydrophilicity than copper grafted titania rutile thin film.

Keywords. Copper grafted TiO₂; crystal structure; superhydrophilicity.

1. Introduction

Titanium dioxide (TiO₂) exists in three crystalline structures: rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic). Rutile is a stable form, whereas anatase and brookite are metastable and are readily converted to rutile when heated (Paola *et al* 2008). The photocatalytic property of TiO₂ is known to be more effective with anatase phase than rutile phase but studies on TiO₂ with brookite phase as a photocatalyst have been uncommon since it is relatively hard to produce artificially (Kim *et al* 2006). Masahiro and Hidenori (2000) reported that brookite phase TiO₂ may function as a more effective photocatalyst than anatase phase under weak light or in the area of visible rays. Shibata *et al* (2004) mentioned that brookite phase TiO₂ thin film shows high photoinduced hydrophilicity and high photocatalytic activity compared with rutile and anatase.

However, TiO₂ thin films become superhydrophilic only under ultraviolet irradiation. When ultraviolet light is turned off, the superhydrophilicity disappears. To shorten the time required for making TiO₂ thin films superhydrophilic and to make them remain superhydrophilic in a dark place, various metals and oxides have been used as a dopant to produce surface defects and photocatalytic properties for the degradation of organic pollutants (Guan and Yin 2005). Several researchers have reported that metal doping could work as a recombination centre for electron–hole pairs and decrease the photocatalytic activity (Lopez *et al* 2009). Recently, it has been reported that surface modification of TiO₂, such as metal loading, is effective in inhibiting the recombina-

tion of photogenerated electron–hole pairs by increasing the charge separation and improving the photoreactivity of TiO₂ (Celik *et al* 2006). Among the metals loaded to improve the photocatalytic activity of TiO₂, copper is the most desirable due to its low cost. Irie *et al* (2008) reported that Cu-grafted TiO₂ rutile has higher photocatalytic activity than that of unmodified TiO₂ for the oxidative decomposition of 2-propanol. Furthermore, they found that Cu grafting extended the photoabsorption region from UV to the visible region (410–450 nm) without affecting the bandgap of TiO₂ (Shibata *et al* 2004). However, effect of crystal structure on the photoinduced superhydrophilicity of copper grafted TiO₂ thin film has not been investigated yet. In the present study, the photoinduced super hydrophilicity of copper grafted brookite and rutile TiO₂ thin films deposited on the glass substrates were investigated.

2. Experimental

First, grafting of copper (0.1 wt%) onto TiO₂ was performed. The procedure for preparation of copper grafted TiO₂ was performed as follows (Eshaghi and Eshaghi 2011): (i) an aqueous solution of CuCl₂·2H₂O in a concentration of 0.0468 mol L⁻¹ was prepared, (ii) a 1 g portion of TiO₂ was suspended in 100 mL water, (iii) the volume of CuCl₂ solution which contains 0.1 wt% of Cu to TiO₂ was added to the suspension, (iv) the suspension was stirred magnetically at 80–90 °C for 1 h and (v) copper grafted TiO₂ was recovered by centrifugation, washed three times with water and dried at 120 °C overnight.

To make Cu loaded TiO₂ thin film, Cu loaded TiO₂ colloidal sol was prepared by ball milling: The Cu loaded TiO₂ paste solution was prepared by dissolving Cu-grafted

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TiO₂ powder (0.5 g) in water (4.5 ml) and surfactant (POIZ, 50 mg). To prepare a paste solution and to avoid the formation of larger titania agglomerates in the sol, ZrO₂ balls (5 g) were dissolved in the above solution and the solution was milled for 3 h (500 rpm). After that, ZrO₂ balls were removed from the solution and volume of the paste solution was increased to 100 ml using deionized water. This procedure was repeated for the preparation of colloidal TiO₂ sol solution.

Before coating, the glass substrates were ultrasonically cleaned in acetone and ethanol for 15 and 20 min, respectively. The films were obtained by a dip coating method and

withdrawn at the speed of 5.33 cm/min. Then, the films were air dried for 5 h and heated in air at 500 °C for 1 h.

Field emission scanning electron microscopy (FE-SEM; JEOL) was used to study morphology of copper grafted TiO₂ thin film. The surface chemical composition of the film samples was analysed by X-ray photoelectron spectroscopy (XPS; JEOL JPC-9010MC) using an MgK α source (1253.6 eV). The X-ray source was operated at 10 kV with a current of 10 mA. XPS spectra were calibrated with respect to a carbon-1s peak at 284.6 eV (Sharma *et al* 2006). The oxygen-1s peak of the films was deconvoluted using a Gaussian-20% Lorentzian function after subtraction of

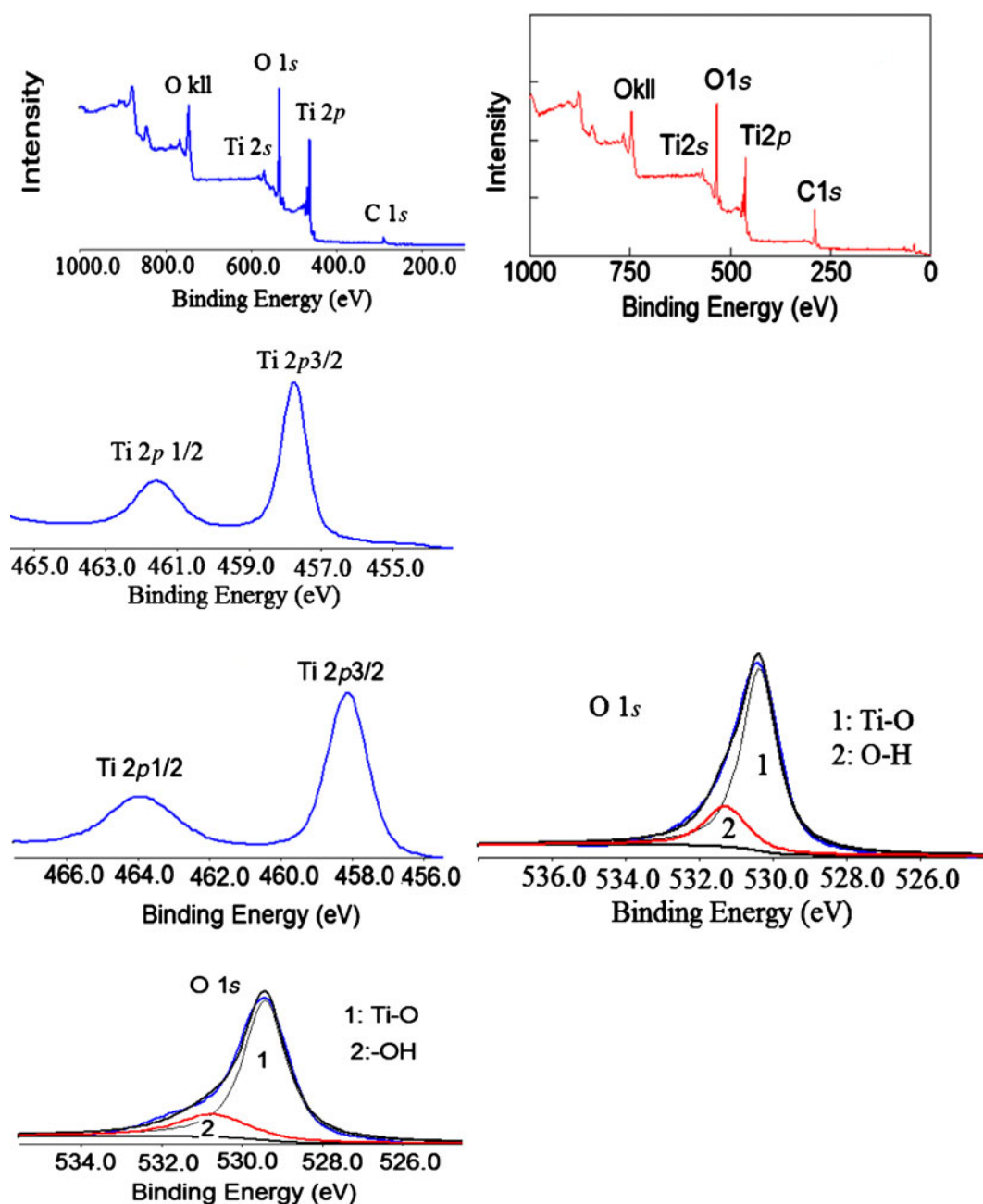


Figure 1. Low and high-resolution XPS spectra of Cu-grafted TiO₂ thin film, (right) Cu rutile and (left) Cu brookite.

the background by the Shirley method. The photoinduced hydrophilicity of the films was evaluated by measuring the contact angle of a water droplet on the film surfaces (Kyowa Interface Science Drop Master 500). A droplet was injected onto the surface using a 1 μ L microinjector. The water contact angle was averaged from five measurements. UV-visible light was irradiated to the samples by a xenon lamp (300 W, 300–500 nm). In the stage of photoinduced hydrophilicity measurements, samples were stored in a drying oven (Fine, FVO-10) at 100 °C for at least 12 h before photoirradiation. After irradiation and contact angle measurements, the films were stored in dark to check the recovery of the contact angle.

3. Results and discussion

Figure 1 shows low and high-resolution XPS spectra of a copper grafted brookite and rutile TiO₂ thin films. The high resolution spectrum showed that the binding energies of Ti 2p 3/2 brookite and rutile were observed at 458.1 and 458.2, Ti 2p 1/2 brookite and rutile in 463.8 and 463.9 eV, respectively with a separation of 5.7 eV between the two peaks. This is a typical characteristic of the four-valent titanium (Ti⁴⁺) state in TiO₂ (Meng *et al* 2004; Ge *et al* 2006; Mei *et al* 2006). In addition, the Ti 2p XPS peak is sharp and strong, indicating that the titanium element exists mainly as the chemical state of Ti⁴⁺ in the films (Meng *et al* 2004). Therefore, XPS spectrum confirms that the film contains only titania.

We could not detect any peak for copper in the XPS spectra. This case was also reported by Lopez *et al* in their work (Lopez *et al* 2009). They showed that in the samples with 0.1 copper wt%, the XPS equipment did not detect the Cu 2p spectrum, which was most probably due to the low content of copper in the sample.

XPS is one of the most useful methods for measuring the hydroxyl group content on film surfaces. In literature, the O 1s peak was often believed to be composed of several different oxygen species, such as lattice oxygen, oxygen on reduced titanium (Ti³⁺), oxygen connected to surface carbon species, hydroxyl groups and adsorbed water (Jensen *et al* 2005).

In the present study, the obtained XPS peaks were assigned to lattice oxygen (peak 1) and surface hydroxyls (peak 2), for convenience, and their contents were estimated by deconvolution using two pseudo-Voigt functions as shown in figure 1. The hydroxyl content for TiO₂ and copper grafted TiO₂ was calculated and indicated in table 1.

Table 1. Hydroxyl group content on film surfaces (R: rutile, B: brookite).

Sample	TiO ₂ R	Cu/TiO ₂ R	TiO ₂ B	Cu/TiO ₂ B
Hydroxyl group %	14	20	17	26

According to table 1, it can be seen that copper grafting increases the density of surface hydroxyls on the TiO₂ surface and brookite phase has higher hydroxyl content than rutile. These differences in the hydroxyl density are discussed in relation to the results of superhydrophilicity in the following section.

Figure 2 shows FE-SEM images of the films. It can be seen that the crystals nucleated from the thin films are homogeneous; the average particles sizes for the rutile and brookite are 15–25 nm and 10–20 nm, respectively.

Figure 3 shows water contact angle (WCA) results on the TiO₂ and copper grafted TiO₂ thin film surfaces under irradiation and storage in the darkness. Changes in the WCA, as a function of irradiation time, showed that the surface of Cu-grafted brookite and rutile TiO₂ films turned superhydrophilic (WCA < 5°) after 75 min and 150 min irradiation, respectively whereas the unmodified TiO₂ thin films became superhydrophilic after a long time of irradiation (240 min for TiO₂ brookite and 300 min for TiO₂ rutile). When thin

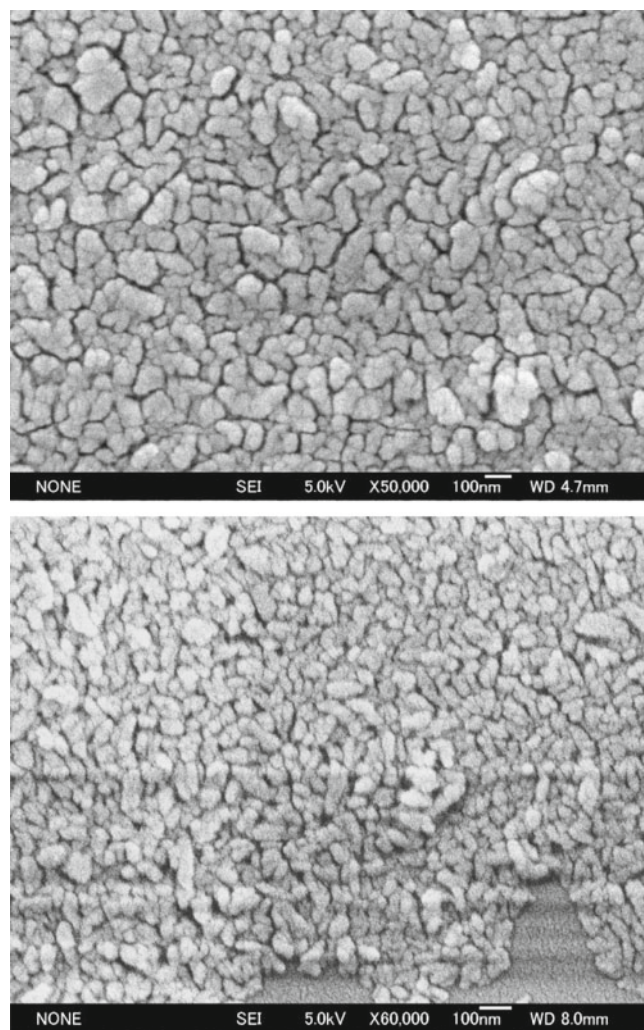


Figure 2. FE-SEM images of Cu grafted films (upper) rutile and (lower) brookite thin films.

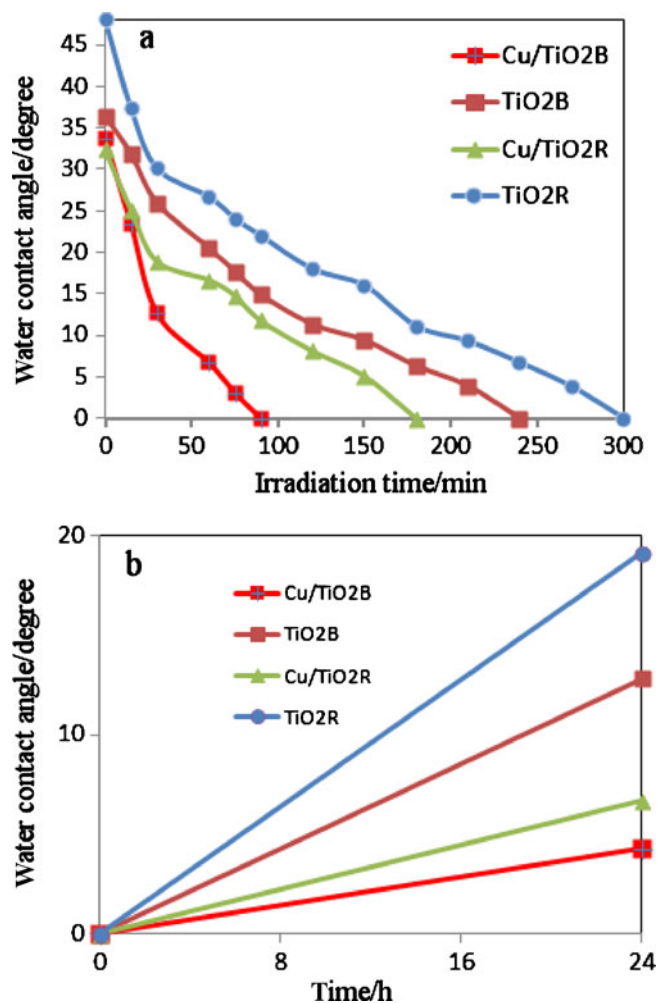


Figure 3. Water contact angle on TiO₂ and Cu-grafted TiO₂ surfaces during irradiation (a) and after storage in dark (b).

films were stored in the dark, the surfaces converted to a hydrophobic state, and rate of the hydrophobic conversion of the Cu-grafted brookite TiO₂ was slower than that of the rutile TiO₂. Thus, the WCA measurements indicated that crystalline structure had significant effect on the hydrophilicity of copper grafting TiO₂ thin films both under irradiation and storage in the dark.

Several papers on the studies of photoinduced superhydrophilicity of TiO₂ have been published (Wendt *et al* 2005; Kontos *et al* 2007; Ohdaira *et al* 2007; Chen and Poon 2009). When TiO₂ is irradiated with an UV light, photoexcited electrons and positive holes are produced in the conduction and valence bands, respectively and it has been proposed that certain redox reactions induced by the photoexcited electrons and holes may produce extra hydroxyl groups on the surface, which induces superhydrophilicity. It is also reported that the photoinduced superhydrophilicity of TiO₂ thin films depends on various parameters such as the electron–hole recombination rate, surface hydroxyl group density, crystal structure, surface active area and porosity or surface contamination (Carp *et al* 2004).

Table 2. Potential of VB, CB of TiO₂ and redox potential of Cu (II)/Cu (I), (Shibata *et al* 2004; Kontos *et al* 2007).

Parameter	Potential vs SHE at pH = 0 (V)
Top VB (B)	+3.00
Bottom CB (B)	−0.65
Top VB (R)	3.0
Bottom CB (R)	0.0
Cu (II)/Cu (I)	+0.16

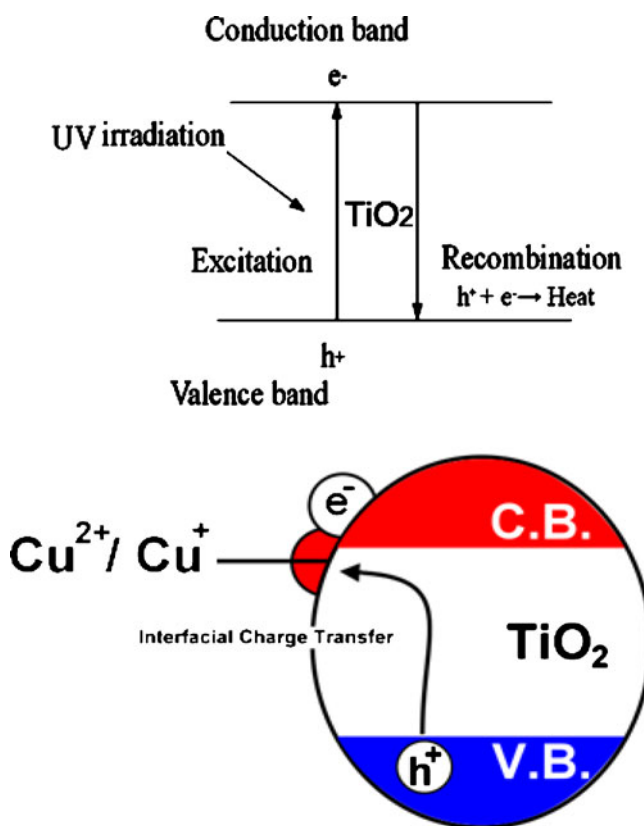


Figure 4. Copper grafting on TiO₂ surface (Irie *et al* 2008).

Since both photocatalytic oxidation of organic pollutants and photoinduced superhydrophilicity are initiated by electron–hole pairs, inhibition of recombination may enhance those reactions (He *et al* 2003). Therefore, in copper grafted TiO₂ thin films, copper ions might inhibit the recombination of photoinduced electron–hole pairs.

Before we investigated the photoinduced superhydrophilic mechanism of copper grafted TiO₂, it was necessary to investigate the interaction between Cu (II) and TiO₂ surface. It is well known that the basic unit of TiO₂ is TiO₆ octahedrons (Cui *et al* 2008). Towle *et al* (1999) discussed the adsorption of Co (II) ions on the surface of TiO₂. They mentioned that Co (II) adsorbs at sites corresponding to the Ti-equivalent positions in the TiO₂ structure. We can assume that a similar phenomenon occurs for Cu (II). Some Cu (II) ions can be

adsorbed at sites corresponding to the Ti- equivalent positions in TiO₂ and form CuO₆ octahedral. The effect of copper grafting on the photoinduced superhydrophilicity of TiO₂ is discussed in the following section.

Considering the conduction band bottom position and the standard electrode potential of a copper/copper ion redox couple (table 2), copper ions can behave as electron acceptors under UV-light irradiation. This also means that the interfacial charge-transfer excitation of electrons in the valence band of TiO₂ to copper ions can proceed. Then, copper species on the surface may catalyze electron transfer to molecular oxygen (Irie *et al* 2008; Li *et al* 2008).

Therefore, due to the interfacial charge transfer, Cu ions inhibit electron-hole recombination. The superhydrophilicity mechanism of copper grafted TiO₂ can be summarized in figure 4.

Furthermore, higher density of the surface hydroxyls on copper grafted TiO₂, as discussed in the preceding section, might be beneficial for increasing the rate of photoinduced superhydrophilicity and slowing the recovery as shown in figure 3.

In contrast, higher superhydrophilicity of brookite than rutile TiO₂ thin film can be related to conduction band bottom potential. The conduction band bottom potential of brookite TiO₂ lies at -0.65 V, which is more negative than that of rutile TiO₂. Thus, oxygen reduction is expected to process in brookite than rutile TiO₂ which produces more superoxide anion radicals. Therefore, brookite TiO₂ thin film shows higher hydrophilicity than rutile TiO₂ thin film.

It is proposed that surface acidity is an important factor in maintaining the superhydrophilicity of TiO₂ thin film in the darkness (Guan and Yin 2005). Paola *et al* (2004) showed that copper grafted TiO₂ has Lewis acid sites on the surface. Therefore, copper grafted TiO₂ can maintain a hydrophilic state for a long time in a dark place in comparison to TiO₂, since the hydroxyl groups on the surface are beneficial in maintaining the hydrophilicity, especially in a dark place.

4. Conclusions

In this study, the effect of copper grafting and crystalline structure on the surface properties of the TiO₂ thin films was investigated. The results indicated that copper grafted TiO₂ showed lowest water contact angle under irradiation and in the dark place than that of pristine TiO₂. In addition, the superhydrophilic results indicated that copper loading had significant effect on wettability of brookite TiO₂ than rutile TiO₂ thin film. Thus, surface modification and crystal

structure are important factors in the improvement of TiO₂ photoreactivity.

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