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# Photoinduced superhydrophilicity of TiO<sub>2</sub> thin film with hierarchical Cu doping

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## Abstract

Hydrophilic Cu–TiO<sub>2</sub> thin films with a gradient in the Cu concentration were prepared on glass by layer-by-layer dip-coating from TiO<sub>2</sub> precursors. The effects of the Cu doping on the structure and properties of TiO<sub>2</sub> self-cleaning thin films are discussed. The Cu gradient markedly affects the hydrophilicity of the films, with the water contact angle significantly reduced compared with those of the pure or uniformly doped TiO<sub>2</sub> thin films. This enhanced hydrophilicity is explained by the more efficient absorption of the solar light and by the reduced recombination of photoexcited electrons and holes in the TiO<sub>2</sub> films containing a gradient of Cu dopants.

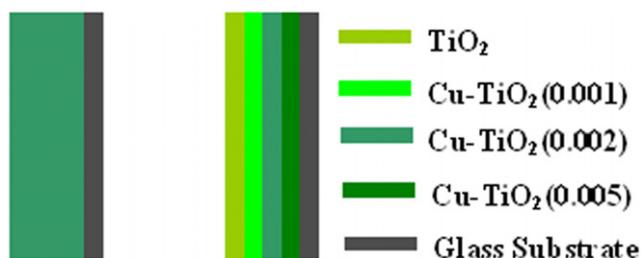
Keywords: Cu-TiO<sub>2</sub>, hydrophilicity, gradient, doping, film

## 1. Introduction

As an n-type semiconductor with a wide energy bandgap, titanium dioxide has been studied for potential applications in photocatalysis [1], photoelectrochemistry [2], dye-sensitized solar cells [3, 4], and so on. In 1997, Wang *et al* [5] first reported the preparation of highly hydrophilic TiO<sub>2</sub> surfaces using UV illumination, which provided self-cleaning and antifogging properties to this material. It is yet unclear how the interaction with UV light creates a hydrophilic surface [6]. Several papers suggest that clean TiO<sub>2</sub> is intrinsically hydrophilic. Under ambient conditions, its surface is contaminated, but hydrophilicity can be restored by the photocatalytic oxidation of organic contaminants [7, 8]. It is now well accepted that the mechanism of photoinduced hydrophilicity is quite different from that of conventional photocatalysis. The accepted mechanism of photoinduced hydrophilicity on TiO<sub>2</sub> is as follows: first, absorption of UV photons results in the generation of electrons in the conduction band and holes in the valence band. While electrons reduce Ti(IV) cations to Ti(III), holes migrate to the TiO<sub>2</sub> surface

where they oxidize the bridging O<sup>2-</sup> anions. The latter reaction leads to the expulsion of an O atom followed by the adsorption of water molecules at the resulting vacancy site, thereby producing new OH groups and increasing the hydrophilicity of the surface [9–13].

However, the practical application of self-cleaning of TiO<sub>2</sub> is limited because only a small (UV) portion of the solar spectrum is absorbed by TiO<sub>2</sub> owing to its large bandgap (3.0–3.2 eV), and because the undesired recombination of photoexcited electrons and holes hinders the photoinduced hydrophilicity. Therefore, much effort has been spent to modify the electronic properties of TiO<sub>2</sub>, to extend its optical absorption edge into the visible-light region and enhance its hydrophilicity. For this purpose, TiO<sub>2</sub> was doped with N [14], S [15], C [16], Cu [17], Fe [18], V [19] and other elements. Sakai *et al* [20] reported the N and S codoping of TiO<sub>2</sub> anatase thin films by radio-frequency sputtering; the resulting films show a greater photoinduced hydrophilic activity than the undoped TiO<sub>2</sub> even under fluorescent light. Chou *et al* [21] found that polyethylene terephthalate plates coated with TiO<sub>2-x</sub>N<sub>x</sub> thin films exhibit a lower water contact angle



**Figure 1.** Schematics of the Cu-TiO<sub>2</sub>(0.002) thin film (left) and Cu-TiO<sub>2</sub>(GC) thin film (right).

than noncoated plates when the surface is illuminated with UV and visible light. Li *et al* [22] prepared Ti<sub>1-x</sub>V<sub>x</sub>O<sub>2</sub> films by sol-gel dip-coating and found excellent hydrophilicity under visible light for  $x = 0.15$ .

TiO<sub>2</sub> thin films were homogeneously doped in most previous studies. In this work, we fabricated a TiO<sub>2</sub> thin film with a gradient of Cu doping by layer-by-layer dip-coating technique. This allowed us to overcome the above-mentioned two limitations by absorbing more sunlight and reducing the recombination of photoexcited electrons and holes. To illustrate the effect of the Cu gradient, we deposited a series of undoped and homogeneously Cu-doped TiO<sub>2</sub> films by the sol-gel method. By varying the concentration of Cu, we conducted a systematic study on the factors that affect the hydrophilicity of doped TiO<sub>2</sub> films. The hierarchical Cu doping shows a remarkable effect on the final hydrophilicity, indicating that the self-cleaning performance can be further improved by carefully designing the TiO<sub>2</sub> film structure.

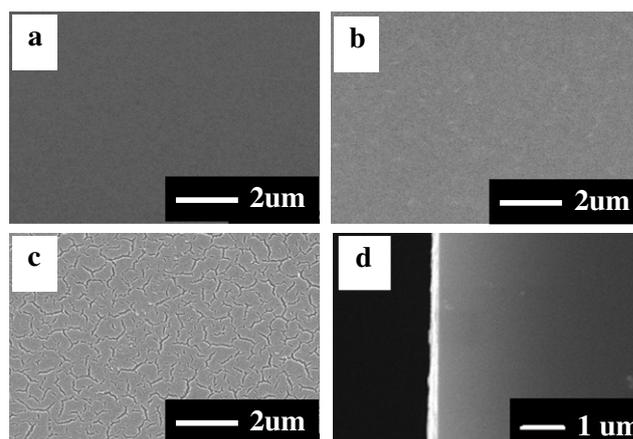
## 2. Experimental details

### 2.1. Preparation of TiO<sub>2</sub> and Cu-doped TiO<sub>2</sub> (Cu-TiO<sub>2</sub>) sols

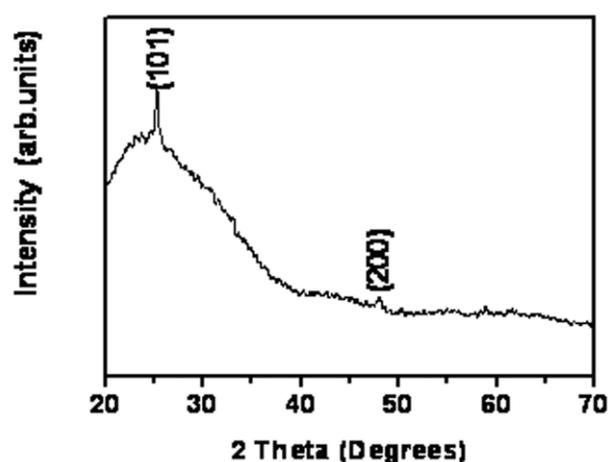
Cu-TiO<sub>2</sub> sols were synthesized at room temperature in the following manner: tetrabutyl orthotitanate (Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>) was dissolved in a mixture solution of 35 ml of ethanol and a small amount of diethanolamine (NH(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>) as chelating agent. The molar ratio of NH(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub> : Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub> was 1 : 1. After magnetic stirring for 2 h, the obtained solution was hydrolyzed by the addition of a mixture of ethanol and deionized water containing a certain concentration of cupric nitrate (Cu(NO<sub>3</sub>)<sub>2</sub>) and stirred for another 2 h. Finally, a series of transparent sols with different Cu concentrations was obtained.

### 2.2. Preparation of TiO<sub>2</sub> and Cu-doped TiO<sub>2</sub> (Cu-TiO<sub>2</sub>) films

Dip-coating method was used to deposit the sol on a clean glass substrate and the drawing rate was 6 cm min<sup>-1</sup>. The coated films were then dried in an oven at 100 °C for 30 min. This coating process was repeated several times until the required thickness was obtained. By using sols with different Cu/Ti mole ratios, a series of coatings with different Cu concentrations (0.005, 0.002, 0.001



**Figure 2.** SEM images of Cu-TiO<sub>2</sub>(GC) films prepared using the tetrabutyl orthotitanate concentrations of (a) 0.3 mol l<sup>-1</sup>, (b) 0.5 mol l<sup>-1</sup> and (c) 0.8 mol l<sup>-1</sup>. (d) The cross-sectional SEM image for the 0.5 mol l<sup>-1</sup> film.

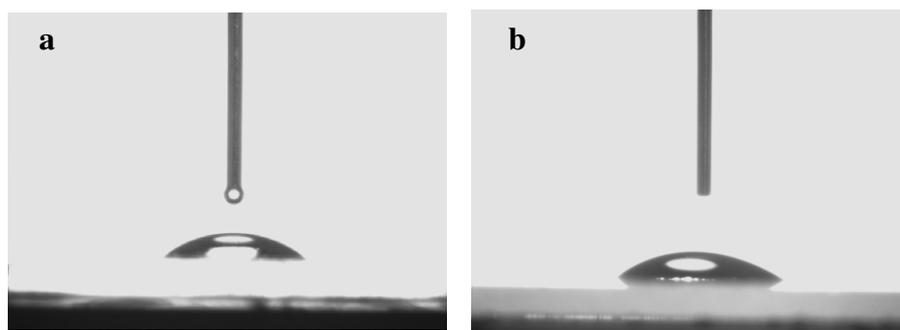


**Figure 3.** XRD pattern of a Cu-TiO<sub>2</sub>(GC) film.

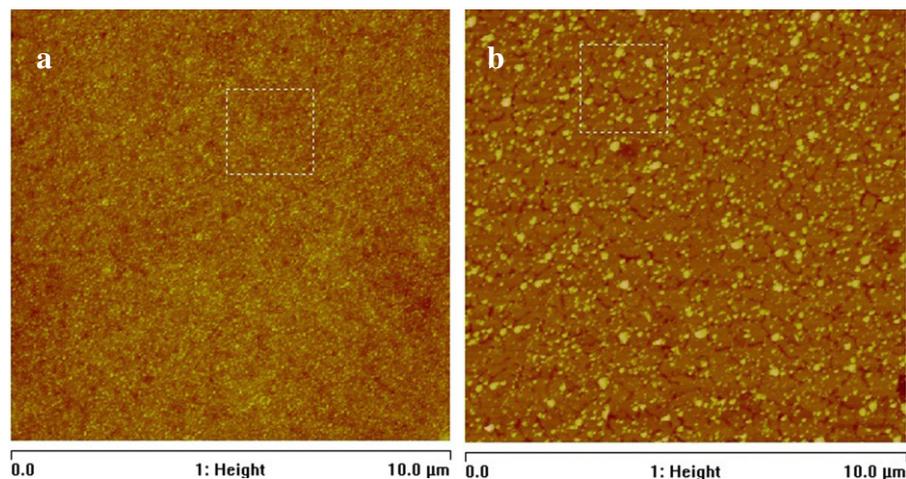
and 0) were sequentially formed on a glass substrate, yielding a gradient-coating structure, Cu-TiO<sub>2</sub>(GC). For comparison, TiO<sub>2</sub>, Cu-TiO<sub>2</sub>(0.001), Cu-TiO<sub>2</sub>(0.002) and Cu-TiO<sub>2</sub>(0.005) films with similar thicknesses were also prepared using one Cu-TiO<sub>2</sub>( $x$ ) sol, where  $x = 0.001, 0.002$  or 0.005 is the Cu mole fraction in the sol. The schematics of the film structure are shown in figure 1. After drying at 100 °C for 1 h, the films were calcined in air at temperatures up to 500 °C and a heating rate of 2 °C min<sup>-1</sup>. Before deposition, the glass substrates were ultrasonically rinsed for 15 min in acetone, isopropyl alcohol and then in absolute ethanol.

### 2.3. Characterization

The morphology of the films was observed using a Philips XL-30 environmental scanning electron microscope (ESEM). Atomic force microscopy (AFM) was employed to observe the surface morphology and roughness of these films. X-ray diffraction (XRD) patterns were acquired with a Rigaku D/max-2500 setup using Cu K $\alpha$  radiation ( $\lambda = 0.154059$  nm). Optical transmittance was examined with



**Figure 4.** Water contact angles of  $\text{TiO}_2$  and  $\text{Cu-TiO}_2(\text{GC})$  films before illumination (a)  $\text{TiO}_2$ — $37.7^\circ$  and (b)  $\text{Cu-TiO}_2(\text{GC})$ — $29.3^\circ$ .



**Figure 5.** AFM images of (a)  $\text{TiO}_2$  and (b)  $\text{Cu-TiO}_2(\text{GC})$  films.

a DU-8B UV/vis double-beam spectrophotometer, and the hydrophilicity of the films was measured by observing the water contact angle under xenon lamp irradiation with an intensity of  $100 \text{ mW cm}^{-2}$ . To collect accurate data, five samples were measured for each  $\text{Cu-TiO}_2(x)$  film.

### 3. Results and discussion

Figure 2 shows SEM images of  $\text{Cu-TiO}_2(\text{GC})$  films prepared using a tetrabutyl orthotitanate concentration of 0.3, 0.5 or  $0.8 \text{ mol l}^{-1}$ . Cracks become more evident at higher precursor concentration. The deposited thickness per dip increases with the viscosity of the sol, which is also affected by the tetrabutyl orthotitanate concentration. The shrinkage stress develops in a film upon drying, and cracks can be observed when it exceeds a threshold value. Crack-free morphology is observed for the 0.3 and  $0.5 \text{ mol l}^{-1}$  films. The film thickness was estimated as 300 nm from the cross-sectional SEM image for the  $0.5 \text{ mol l}^{-1}$  film shown in figure 2(d).

Figure 3 shows the XRD pattern of the  $0.5 \text{ mol l}^{-1}$   $\text{Cu-TiO}_2(\text{GC})$  film annealed at  $500^\circ\text{C}$  for 1 h. The broad signal at low angles originates from the glass substrate. The peaks at  $2\theta = 25.4^\circ$  and  $47.6^\circ$  correspond to the (101) and (200) reflections of the anatase  $\text{TiO}_2$  structure, respectively. No copper-related peaks are visible, indicating the formation of a solid solution in the  $\text{Cu-TiO}_2(x)$  films. We believe that

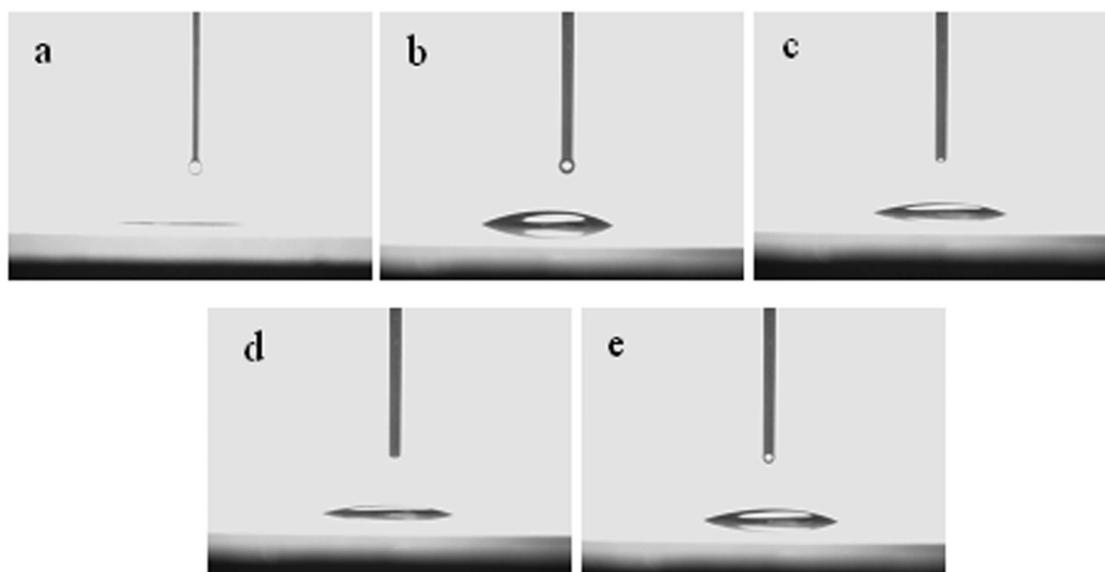
all the Cu is incorporated into  $\text{TiO}_2$  as dispersed ions rather than cupric oxide crystallites.

Figure 4 shows the water contact angles of the  $\text{TiO}_2$  and  $\text{Cu-TiO}_2(\text{GC})$  thin films before illumination. The respective values,  $37.7$  and  $29.3^\circ$ , indicate that the samples are not hydrophilic. The lower value for the  $\text{Cu-TiO}_2(\text{GC})$  film may be ascribed to its higher roughness, as revealed by the AFM images in figures 5(a) and (b). Higher roughness can enhance the hydrophilicity according to the Wenzel equation [22]:

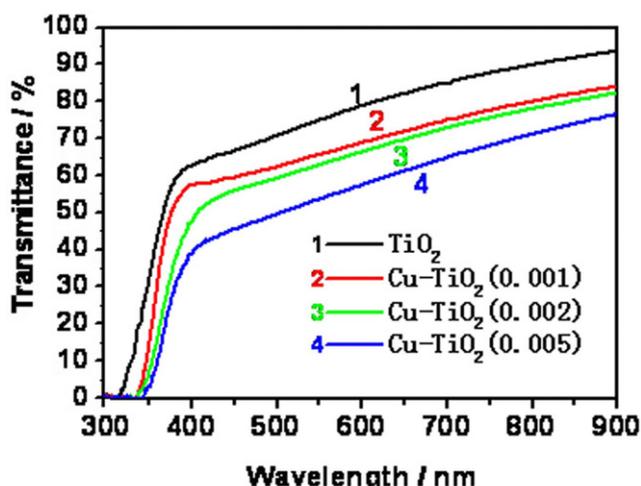
$$\cos \theta^* = \gamma \cos \theta, \quad (1)$$

where  $\gamma$  is the film surface roughness,  $\cos \theta$  is the classical contact angle calculated with the Young's equation and  $\theta^*$  is the measured contact angle.

Figure 6 shows the water contact angles of the studied films after irradiation with a xenon lamp for 1 h at an intensity of  $100 \text{ mW cm}^{-2}$ . It can be seen that the water contact angles are  $3.3$ ,  $14.4$ ,  $8.7$ ,  $6.9$  and  $9.8^\circ$  for  $\text{Cu-TiO}_2(\text{GC})$ ,  $\text{TiO}_2$ ,  $\text{Cu-TiO}_2(0.001)$ ,  $\text{Cu-TiO}_2(0.002)$  and  $\text{Cu-TiO}_2(0.005)$  films, respectively. It is noteworthy that the water contact angle of the  $\text{Cu-TiO}_2(\text{GC})$  film is 4.4 times smaller than that of the  $\text{TiO}_2$  film and 2 times smaller than that of the  $\text{Cu-TiO}_2(0.002)$  film. The absolute value of  $3.3^\circ < 10^\circ$  indicates that superhydrophilicity was induced in the  $\text{Cu-TiO}_2(\text{GC})$  film by the xenon lamp irradiation. These results demonstrate the superior hydrophilic properties of



**Figure 6.** Water contact angles of the studied films after illumination: (a) Cu-TiO<sub>2</sub>(GC)—3.3°, (b) TiO<sub>2</sub>—14.4°, (c) Cu-TiO<sub>2</sub>(0.001)—8.7°, (d) Cu-TiO<sub>2</sub>(0.002)—6.9° and (e) Cu-TiO<sub>2</sub>(0.005)—9.8°.

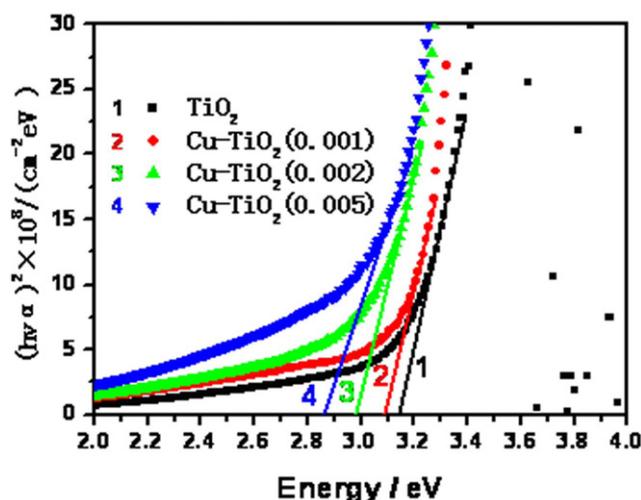


**Figure 7.** Optical transmittance spectra of the studied films.

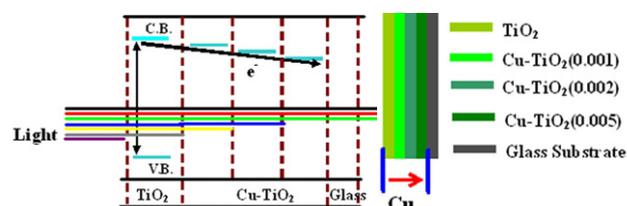
the Cu-TiO<sub>2</sub>(GC) thin film. No clear relation was found between the water contact angle and Cu content in the Cu-TiO<sub>2</sub>(0.001–0.005) films, which will be investigated in the future.

To understand the hydrophilicity enhancement in the Cu-TiO<sub>2</sub>(GC) film, we measured the optical transmittances of the TiO<sub>2</sub>, Cu-TiO<sub>2</sub>(0.001), Cu-TiO<sub>2</sub>(0.002) and Cu-TiO<sub>2</sub>(0.005) films (see figure 7). While all the spectra have similar shapes, the absorption edge shifts to the longer wavelengths with increasing Cu content. This redshift can be attributed to the formation of a new Ti<sub>1-y</sub>Cu<sub>y</sub>O<sub>2</sub> phase through the replacement of Cu atoms by Ti atoms in the TiO<sub>2</sub> crystal lattice [19, 22, 23]. This reduces the distance between Ti and O atoms, facilitating the transfer of photoexcited electrons from the O<sub>2p</sub> to Ti<sub>3d</sub> orbitals in TiO<sub>2</sub>.

The absorption coefficient  $\alpha$  relates to the transmittance  $T$  and film thickness  $d$  as  $\alpha = -\ln(T)/d$ , and the dependence of the absorption coefficient  $\alpha$  on the photon energy  $h\nu$  near

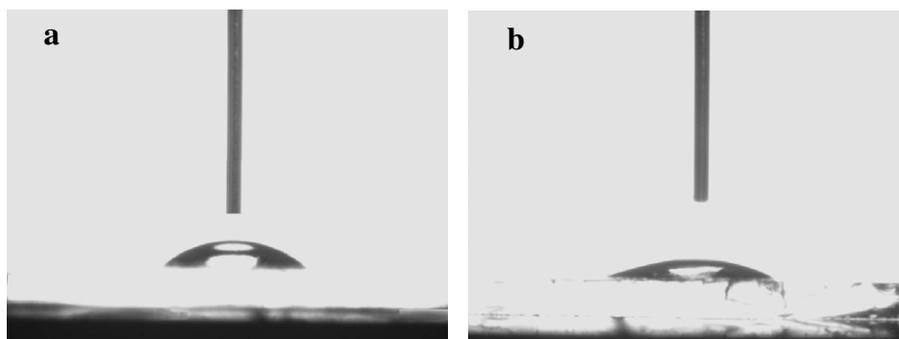


**Figure 8.** Determination of the bandgap values  $E_g$  in Cu-TiO<sub>2</sub>( $x$ ) films.



**Figure 9.** Schematic of energy level and light absorption in the Cu-TiO<sub>2</sub>(GC) thin film.

the absorption edge in semiconductors takes the form  $\alpha h\nu = k(h\nu - E_g)^m$ . Here,  $E_g$  is the optical bandgap and  $k$  and  $m$  are constants;  $m = 1/2$  for materials with an allowed direct energy gap, such as TiO<sub>2</sub>. Using the above equations, we calculate the bandgaps of the TiO<sub>2</sub> and Cu-TiO<sub>2</sub>(0.005) films



**Figure 10.** Water contact angles of  $\text{TiO}_2$  and  $\text{Cu-TiO}_2(\text{GC})$  films under xenon lamp irradiation passed through a UV cutoff filter: (a)  $\text{TiO}_2$ — $34.2^\circ$  and (b)  $\text{Cu-TiO}_2(\text{GC})$ — $15.5^\circ$ .

as 3.16 and 2.86 eV, respectively. As shown in figure 8, the bandgap gradually shrinks with increasing Cu content in  $\text{TiO}_2$ , which may be responsible for the improved hydrophilicity of the  $\text{Cu-TiO}_2(\text{GC})$  thin film. This film contains layers having different bandgaps and therefore absorbs a wider spectrum of light than the other studied films as illustrated in figure 9. To further test the utilization of visible light by the  $\text{Cu-TiO}_2(\text{GC})$  thin film, the water contact angles of the  $\text{TiO}_2$  and  $\text{Cu-TiO}_2(\text{GC})$  films were evaluated under xenon lamp irradiation passed through a UV cut-off filter as shown in figure 10. A comparison of figures 4 and 10 reveals a stronger decrease in the water contact angles with irradiation for the  $\text{Cu-TiO}_2(\text{GC})$  film (from  $293^\circ$  to  $15.5^\circ$ ) than for the  $\text{TiO}_2$  film (from  $37.7^\circ$  to  $34.2^\circ$ ).

It is well known that besides the effect of solar light absorption, the hydrophilicity of traditional self-cleaning films also depends on the recombination of photoexcited electrons and holes. The bandgap gradient in the  $\text{Cu-TiO}_2(\text{GC})$  structure is advantageous in this respect because it facilitates the separation and thus reduces the recombination of photoexcited electrons and holes.

The above results demonstrate a remarkable effect of the  $\text{Cu-TiO}_2(\text{GC})$  structure on the hydrophilicity of thin films. This effect is twofold: firstly, the Cu gradient in  $\text{TiO}_2$  results in a hierarchical narrow-band structure, which can absorb a wider spectrum of solar light than undoped or uniformly doped  $\text{TiO}_2$ . Secondly, the photoexcited electrons and holes are easier to separate and transmit in  $\text{Cu-TiO}_2(\text{GC})$  owing to the sequential hetero-nanostructure resulting from the Cu concentration gradient.

#### 4. Conclusions

Hydrophilic  $\text{Cu-TiO}_2(\text{GC})$  thin films with a gradient Cu doping of  $\text{TiO}_2$  were deposited on glass by a layer-by-layer dip-coating method using  $\text{TiO}_2$  precursors. By varying the Cu concentration we systematically studied the parameters that influence the hydrophilicity of  $\text{TiO}_2$  thin films. The water contact angle was reduced by about 4.4 times in the  $\text{Cu-TiO}_2(\text{GC})$  film compared with that in the pure  $\text{TiO}_2$  film owing to the Cu gradient.

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