# Photoinduced Superhydrophilicity in $TiO_2$ Thin Films Modified with $WO_3$

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Tungsten oxide-modified $TiO_2$ thin films were formed on a glass substrate by sol-gel and dip coating processes using acetyl acetone as a chelating agent. The hydrophilic properties of the thin films were investigated with illumination of UV light. The dependence of water contact angle on material composition and morphology of the film is established with SEM image and AFM profile. The surface morphology was controlled with the change of precursor concentration. 0.01 M of tungsten oxide-modified $TiO_2$ have shown the highest hydrophilicity after UV-irradiation. The effect of composition on photoinduced hydrophilicity of the $WO_3$-$TiO_2$ films was also investigated. The films were characterized by XRD, SEM, AFM and XPS.

**Key Words :** Hydrophilicity, Water contact angle, $TiO_2$ thin films, $WO_3$

## Introduction

Titania has been intensely studied for its applications in the fields of photocatalysis, solar energy conversion, paints, cosmetics, etc. Among them, the decomposition of organic molecules using $TiO_2$ as a photocatalyst is well established.[1] However; the less attended but equally important application is based on photoinduced hydrophilicity. The water contact angel ($\theta$) of 0 degrees under UV radiation is reported in the literature.[2,3] The possibility of monitoring hydrophilicity suggests the applications such as air and water pollution control,[4] antifogging and self-cleaning glasses.[5] The important properties of $TiO_2$ are correlated with the photo generated electron hole pair and their interactions with chemical species before their recombination.[6] For the efficient use of photogenerated charge carriers, basic $TiO_2$ matrix is modified by additives. Such modification may change its structure and morphology simulteneously. Use of charge carriers for the desired chemical action or efficient removal of those which are detrimental to desired reaction, through such modifications is well established.[7-10]

Miyauchi *et al.* have studied $TiO_2$ layer on $WO_3$ layer to show that $WO_3$ layer facilitates the enhancement in photogenerated hydrophilicity, even with very weak UV illumination.[11] This observation leads to the conclusion that $WO_3$ is also an active species in the mechanism of achieving hydrophilicity. Su *et al.* used $WO_3$ doping in $TiO_2$ to form novel composition for varistor applications. The proposed model suggests the segregation of excess additive at the grain boundaries which contributes to the desired properties.[12] Rampaul *et al.* showed that the photocatalytic properties as well as the super hydrophilicity of $TiO_2$-$WO_3$ compositions are due to the dispersion of $WO_3$ phase in $TiO_2$ phase, without forming a solid solution. They proposed that the efficient charge separation causes an improvement in these properties.[13]

Thus, the introduction of $WO_3$ in $TiO_2$ modifies the surface morphology which is exploited for the applications in various fields like catalysis, varistor devices etc. However, there are very few reports which make use of surface morphological modifications for the improvement in hydrophilicity of $TiO_2$ based material, although hydrophilicity due to charge separation has been recognized in the references in a very large number.[13,14]

The surface morphology is also strongly decided by the material processing parameters. Therefore, the preparation method for the material becomes important. With this background, we report the investigation on the photohydrophilicity of $WO_3$-$TiO_2$ films, deposited by sol gel and dip coating methods.

## Experimental Section

**Preparation of thin films.** All the chemicals were used as received from Aldrich. Double distilled deionized water is used throughout the chemical processing. Compositions of $TiO_2$/$WO_3$ for film formation were prepared by adding Titanium (IV) isopropoxide and Tungsten (VI) chloride with the molar ratio 19 : 1 in ethyl alcohol to make 0.01 M solution. Acetyl acetone was added to the solution to stabilize it.[15] The resulting solution was stirred in air atmosphere for two hours for hydrolysis and condensation to occur. The glass substrates were pretreated with a freshly prepared ($H_2SO_4$/$H_2O_2$ = 3 : 1, v/v) solution at 70 °C for 15 min, rinsed with deionized water and dried under nitrogen flow. The films were deposited by dip coating in an ambient atmosphere. The dip- withdrawal speed was maintained at 8 mm/min with dip time of 1 min. When required, the procedure was repeated to increase the film thickness. The uniform films thus formed by dip coating were finally annealed at temperatures in the range 350-500 °C at a heating rate of 2 °C/min in air. For comparison, pure $TiO_2$

and $WO_3$ films were formed under same conditions.

**Characterization.** The X-Ray Diffraction (XRD) patterns were obtained using Philips 1730 X-ray diffractometer with Cu Ka radiation. The Ultraviolet-Visible (UV-Vis) absorption spectra of the films were recorded on a spectrophotometer (UV-2500PC, Shimatzu Co., Kyoto Japan). Surface morphology and film thickness was measured using Scanning Electron Microscopy (SEM) on Philips XL-30 microscope and surface profile was studied on Atomic Force Microscope (AFM, Ls, Park Instrument). X-ray Photoelectron Spectroscopy (XPS) was studied on ESCALAB-MKII (VG Scientific Ltd England) Equipped with Mg K$\alpha$ source (1256.3 eV) and calibrated with C 1S (284.6 eV). The contact angle measurements were performed at room temperature using a commercial contact angle meter (CA-X, Kyowa Interface Science, Saitama, Japan) with an experimental error of $\pm$ 1 $^{\circ}$C. To observe the effect of radiations on hydrophilicity, the films were initially stored in dark for 5 days. Contact angle measured and there after exposed to UV irradiation of 40 mW/cm$^2$ for 10 hours using Hg-Xe lamp with an optical fiber coupler, employing a filter to obtain light with a wavelength centered at 365 nm. A water jacket was employed to eliminate IR radiation. The contact angle of water was evaluated as a measure of hydrophilicity.

### Results and Discussion

The main feature of the present study is the application of simple chemical method to achieve superhydrophilicity in the films of $TiO_2$ under UV irradiation. The main points to which we pay special attention in this study are the following: (a) Addition of $WO_3$ to $TiO_2$ matrix makes the films hydrophilic after exposed to UV radiations; (b) The contact angle, on exposure to UV, was the lowest for film composition, $TiO_2/WO_3$ molar ratio = 19 : 1; (c) 0.01 M concentration of the precursor is optimum to get the best results with respect to hydrophilicity of the film. All these observations are explained by considering the characterization and contact angle study of these films.
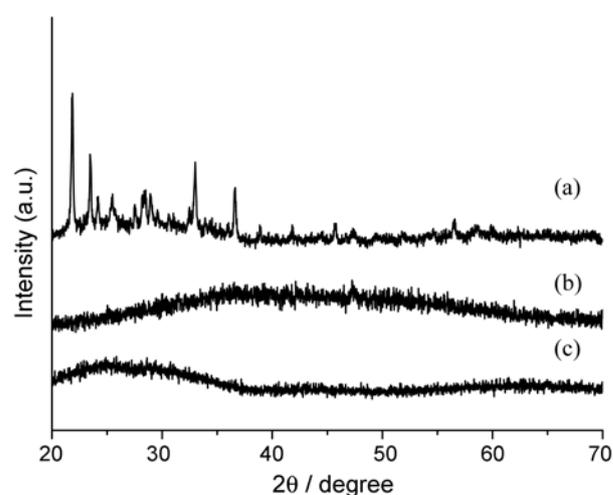


**Figure 1**. XRD patterns of calcined (a) $WO_3$, (b) $TiO_2$ and (c) $WO_3$-$TiO_2$ thin films at 500 $^{\circ}$C by dip-coating method.

Figure 1 shows the X-ray diffractogram of the films of pure $TiO_2$, Pure $WO_3$ and $TiO_2$-$WO_3$ composite, deposited on glass substrate and subsequently heat treated at 500 $^{\circ}$C for 2 hours. The $WO_3$-$TiO_2$ composite film was prepared from 0.01 M concentration of the precursors. The diffractogram of this film represents all compositions prepared under various conditions since they showed identical diffractograms. Analysis of the diffractogram for $WO_3$ shows that it crystallized in triclinic phase, in agreement with literature.[16] $TiO_2$ and other composites do not get crystallized in the experimental conditions under study. The non crystalline nature of $WO_3$ in the compositions is not surprising considering its low fraction in the compositions.[17] $TiO_2$ does not crystallize, most probably, because of the insufficient temperature and time of calcination of the films. Another probable reason for $TiO_2$ not crystallizing is that $WO_3$ prevents the process of crystallization. It is reported that $WO_3$-$TiO_2$ system does not form solid solution.[18] $WO_3$ phase is segregated on the surface of the $TiO_2$ particles thus preventing their growth.
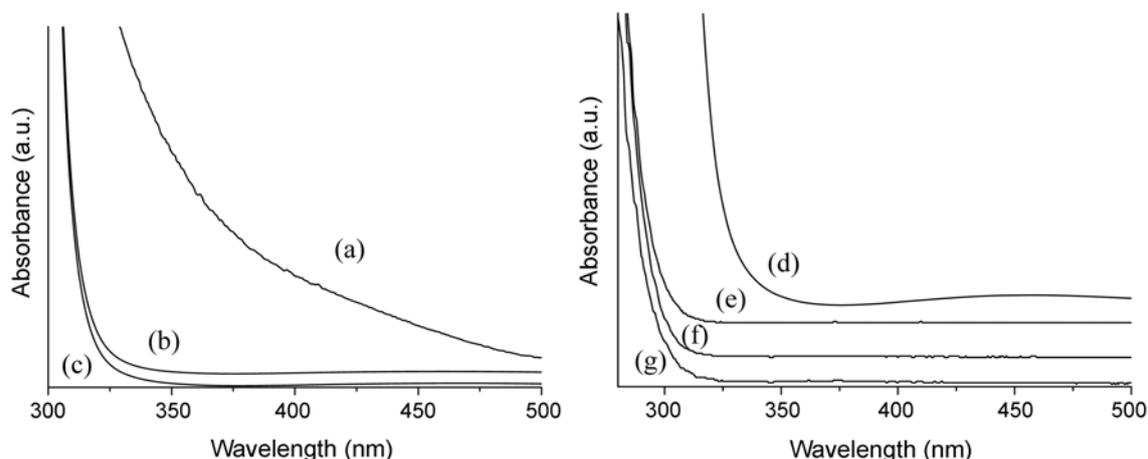


**Figure 2**. UV-visible absorption spectra of (a) $WO_3$, (b) $TiO_2$ and (c) $WO_3$-$TiO_2$ thin films with the precursor concentration of 0.01 M, and $WO_3$ -$TiO_2$ thin film with the precursor concentration of (d) 0.01, (e) $0.2 \times 10^{-3}$, (f) $0.1 \times 10^{-3}$ and (g) $0.5 \times 10^{-4}$ M at 450 $^{\circ}$C on glass.

Figure 2 shows the UV absorption spectra of $WO_3$-$TiO_2$ thin films formed by dip- coating process for various compositions along with the absorption spectra of pure $TiO_2$ and $WO_3$ thin films for comparison. The cut off wavelength is in general blue shifted. Since the particle growth of both phases is restricted as would be revealed from our SEM observations, the shift can be attributed to quantum size effects. Alternatively, the amorphous $WO_3$ is reported to have higher band gap[19] corresponding to the shift observed in the present study. It may be noted that the major phase of $TiO_2$ influences the absorption spectra in all the binary compositions. This seems to be consistent with our SEM observations where no separate existence for $WO_3$ is seen. In fact, this point suggests that $WO_3$ either becomes a part of $TiO_2$ lattice or gets segregated on $TiO_2$ grain boundary. Another important observation from the optical absorption is that higher the precursor concentration for film formation, the absorption edge is red shifted for the corresponding composite film. An important point of this study to be noted is that with the addition of $WO_3$ to the composite, the absorption in the UV spectral region is decreased. This observation suggests that $WO_3$ phase does not have independent existence in the composite.

SEM image of $TiO_2$-$WO_3$ composites are shown in Figure 3. SEM of pure $TiO_2$ and Pure $WO_3$ films coated with the same precursor concentration (0.01M) are also given for comparison. It is seen that in the composition under consideration, both phases retard each others particle growth. With decreasing concentration of $WO_3$ composites, the particle size of $WO_3$-$TiO_2$ samples decreases. Also, the surfaces of the films become smoother with decreasing precursor concentration. The film formed from the precursor concentration of 0.01 M consists of particles having a certain structure, with sharp edges and corners with an irregular shape. The particle size is in the range of 25-30 nm which is much bigger as compared to the particle sizes observed in

other SEM images of films formed by using higher precursor concentration. The surface of this film obviously becomes rough due to non-close packing of particles with shapes having corners and edges. The surface phenomenon would be effective to higher depth as compared with smoother films. Further evidence for quantitative measurements of surface roughness were analyzed by AFM (Fig. 4). The same trend was observed as shown by SEM images. The RMS of roughness of these films were 8.8 nm of 0.01 M and 0.6 nm of $0.1 \times 10^{-3}$ M $WO_3$-$TiO_2$, respectively.

The water contact angle has been used as an index of hydrophilicity in the present study. It is reported in the literature that pure $TiO_2$ shows photo-induced hydrophilicity wherein contact angle on UV irradiation is lowered to 20°. To study the effect of precursor concentration, the films formed from three different precursor concentrations were stored in dark for 5 days and their water contact angles were measured. The same films were exposed to UV irradiation for 10 hours and its effect on water contact angle was recorded. Figure 5 depicts effect of UV irradiation on contact angle. The maximum effect is observed in the films of 0.01 M precursor concentration. The contact angle of water in the sample stored in dark is $30^0$ while after exposure to UV radiations it is $2^0$. It may be noted that contact angle is not lowered on exposure to UV radiations for the films with the same composition but which are formed by using 'dilute' precursor concentrations. The effect of morphology is highlighted by this observation.

The important observations of photo-induced hydrophilicity in this study are as follows: (a) Addition of $WO_3$ to $TiO_2$ improves the photo-induced hydrophilicity and, (b) precursor concentration of 0.01 M is more effective to form hydrophilic films than more 'dilute' concentrations. (c) Dip coated films show more consistent observations than those of spin coated films. In general, dip-coated films are likely to be more uniform than spin-coated films as there is likely to
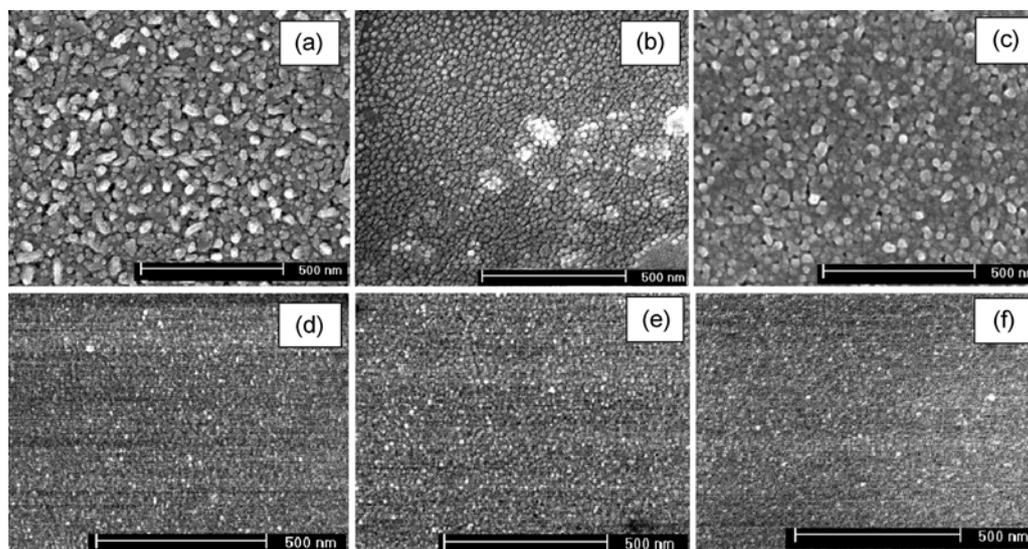


**Figure 3**. SEM images of the (a) $TiO_2$, (b) $WO_3$ and $WO_3$-$TiO_2$ thin films with the precursor concentration of (c) 0.01 M, (d) $0.2 \times 10^{-3}$ M, (e) $0.1 \times 10^{-3}$ M and (f) $0.5 \times 10^{-4}$ M
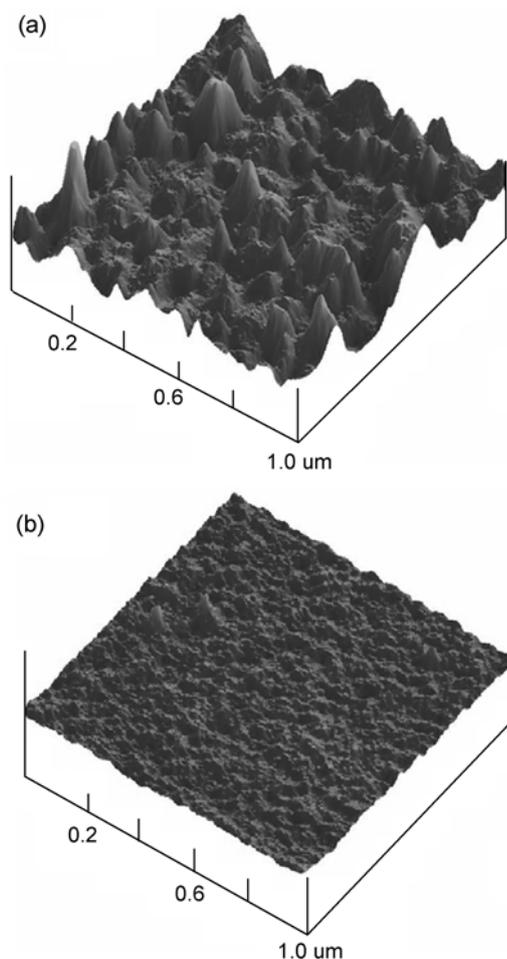
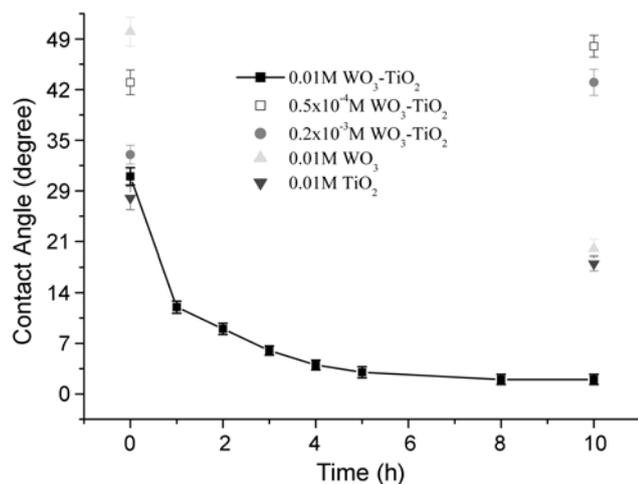**Figure 4**. Surface morphology of (a) 0.01 M and (b) $0.1 \times 10^{-3}$ M T of $WO_3$-$TiO_2$ thin films by AFM.



**Figure 5**. Changes of water contact angle of hydrophilic $TiO_2$, $WO_3$ and $WO_3$-$TiO_2$ films on a glass substrate with different concentration after UV irradiation for 10 h.

be concentration gradient of precursor composition along the length of the film coated by spin process.

The qualitative mechanism of photo-induced hydrophilicity has been reported in the literature for $TiO_2$ based
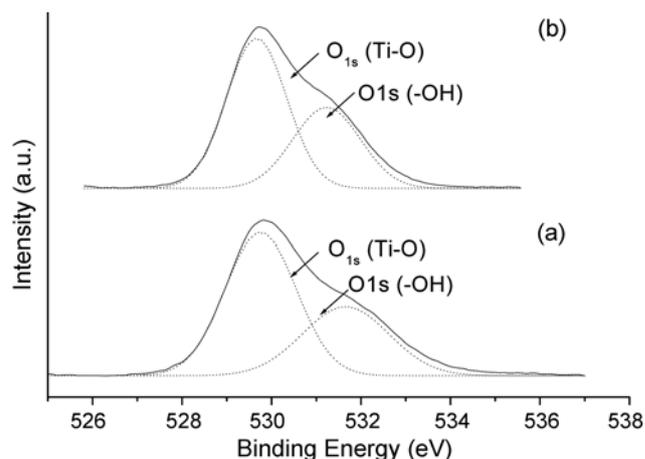


**Figure 6**. Deconvoluted XP spectra of the O1s region for the surface of 0.01 M $WO_3$-$TiO_2$ film (a) before and (b) after UV irradiation.

materials.[3] $TiO_2$ has a band gap of 3.2 eV. When excited by UV radiations, electron hole pair is generated. Holes defuse to the surface and react with adsorbed oxygen, creating a defect site namely $Ti^{3+}$. It is known that such sites are favorable for dissociative adsorption of water. Oxygen adsorbed site is hydrophobic while dissociatively adsorbed water makes the site hydrophilic, thus UV radiations change hydrophobic site to hydrophilic one. However it is noted that oxygen adsorption is more stable state and therefore when the exciting source namely UV radiations are removed and the material is stored in dark, oxygen gets readsorbed so that the material recovers to its original state. If water contact angle is an index of hydrophilicity, then it is reasonable that on UV irradiation, the contact angle is lowered. In the dark, the material regains its normal state, showing high contact angle. The presence of $WO_3$ additives to $TiO_2$ matrix becomes the cause of further improvement in photo-induced hydrophilicity. $WO_3$ has a band gap of 2.8 eV. The conduction band (CB) and valance band (VB) are located slightly below the CB and VB of $TiO_2$, so that transfer of electrons from $TiO_2$-CB to $WO_3$-CB as well as transfer of holes from $WO_3$-VB to $TiO_2$-VB are favorable. Thus the separation of electron hole pair increases the possibility of holes diffusing to the surface, causing enhanced hydrophilicity as explained above.

Further support to the mechanism of enhanced hydrophilicity in our films from surface defects which dissociatively adsorb water is obtained from XPS observations. Figure 6 shows the high resolution XP spectra of O 1s region, for $WO_3$-$TiO_2$ film before and after UV irradiation. The 529.9 eV peak is assigned to Ti-O in $TiO_2$ and 531.9 eV peak is assigned to W-O in $WO_3$[20] and hydroxyl species. After UV irradiation, the intensity of the latter peak increases significantly. The hydroxyl contents can be reasonably determined from the ratio of the areas of 531.9 eV peak to the total area of two O 1s peaks.[21] It clearly shows that the hydroxyl content increases on UV irradiation .

Since water contact angle is a surface phenomenon, it is

natural that the morphology of the surface plays an important role. A significant change in these two types of films is shown in their SEM and AFM. The rough surface favors the desired property while smoother surfaces are not favorable (Fig. 4). The particle size of the smoother films is lower than the 'rough' film and therefore more surface area is available for surface-dominating property. These films are still inferior to 'rough' films. The probable reason is that during calcination the $WO_3$ phase segregates at the grain boundaries thus covering $TiO_2$ grains. This will lead to two effects: (a) less number of defects in $TiO_2$ phase namely $Ti^{3+}$ on the surface which is shown to be the cause of photo hydrophilicity and (b) less UV radiations reaching $TiO_2$. In the 'rough' films, on the other hand, $TiO_2$ phase gets exposed to radiations and also, UV irradiation may be more effective due to multi-reflections in films because of the angular nature of the surface of grains. Therefor the UV absorption in the smoother films is less than the 'rough' film as shown in Figure 2.

## Conclusions

A simple procedure to form photo hydrophilic films consisting of $TiO_2$ and $WO_3$ by dip coating method is described. The dip coating method is found to be superior to spin coating method. When coated by dip coating procedure with precursor composition of 0.01 M The films with molar composition of $TiO_2$ : $WO_3$ = 19 : 1 showed water contact angle in dark of 30°. On exposure to UV radiations for 5 hours, contact angle lowers to 2°, thus proving superhydrophilicity of these films.

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