Influence of substrate on the hydrophilicity and photocatalytic properties of TiO$_2$ nano-layers

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2013 Phys. Scr. 88 025604

(http://iopscience.iop.org/1402-4896/88/2/025604)

View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 141.5.34.42
The article was downloaded on 25/07/2013 at 12:35

Please note that terms and conditions apply.
Influence of substrate on the hydrophilicity and photocatalytic properties of TiO$_2$ nano-layers

S Kimiagar$^1$, A Nahal$^2$, M R Mohammadizadeh$^3$ and T Ghods Elahi$^4$

$^1$ Department of Physics, Central Tehran Branch, Islamic Azad University, Tehran, Iran
$^2$ Photonic Materials Research Laboratory, Department of Physics, College of Science, University of Tehran, 14399-55961 Tehran, Iran
$^3$ Superconductivity Research Laboratory (SRL), Department of Physics, College of Science, University of Tehran, 14399-55961 Tehran, Iran
$^4$ School of Physics, Institute for Research in Fundamental Sciences (IPM), Tehran, Iran

E-mail: nahal@khayam.ut.ac.ir

Received 5 November 2012
Accepted for publication 1 July 2013
Published 25 July 2013
Online at stacks.iop.org/PhysScr/88/025604

Abstract

The influence of substrate materials on the hydrophilicity and photocatalytic properties of TiO$_2$ thin films, prepared by the sol–gel spray pyrolysis method is investigated. In this regard, thin gold or copper films on glass, Ag-ion-exchanged glass and bare glass were used as substrates for TiO$_2$ thin films. It is found that in comparison to other samples, a TiO$_2$ thin film on the copper/glass substrate demonstrates the most efficient hydrophilicity property, while gold/glass substrate is the best in regards to photocatalytic behavior. The smaller band gap, larger grain size and roughness of the thin films show better photocatalyticity. In our case, we observed that, for gold/glass substrate a more condensed film causes a higher recombination rate of electron–hole pairs, which in turn decreases the hydrophilicity property of the samples.

PACS numbers: 68.08.Bc, 82.65.+r, 82.30.Rs

(Some figures may appear in colour only in the online journal)

1. Introduction

The low cost preparation process, non toxicity, chemical and structural stability have resulted in the TiO$_2$ thin films becoming one of the most investigated photocatalyst materials [1, 2]. Titanium dioxide has an interesting reaction to humidity and light, which makes it a popular material with considerable applications. TiO$_2$ coating also has hydrophilicity properties. At the same time, the photocatalytic property of the TiO$_2$ layer causes degradation of organic pollutants on the surfaces. In this way, rainfall could result in the cleaning of surfaces [3]. There are well known various applications for the self-cleaning properties of the TiO$_2$ thin films, such as self-cleaning glass windows, the self-cleaning of cars’ corpus or the surfaces of walls in hospital operation rooms [4].

Bulk TiO$_2$ has a relatively large band gap: 3.2 eV [5, 6], which is in the UV-region of the electromagnetic spectrum. This region includes only 5% of the whole electromagnetic spectrum [7], which causes difficulties for its application as a photocatalyst material. Irradiating the semiconductor photocatalyst TiO$_2$ layer by UV-light results in the transition of electrons from the valence band to the conduction band, accompanied by the creation of a hole in the valence band. However, in the excited state, the electron and the hole could be recombined again and release energy. Any manipulation, which may increase the lifetime of the electron–hole pairs, or their population, could enhance the photocatalytic and hydrophilicity properties of the TiO$_2$ layer. Doping TiO$_2$ by metallic or nonmetallic materials could elongate the electron–hole pairs’ lifetime and consequently, enables it to operate as an efficient photocatalyst agent in the visible region of the spectrum [8–12] because of the reduction in the recombination rate of the pairs.

On the other hand, the substrate temperature and doping with different impurities has a strong influence on the
phase transition of the TiO$_2$ layers and therefore on their physical and chemical properties. Some groups [13–18] have reported doping the TiO$_2$ layer with metals leads to a narrowing of the band gap for photo-excitation, which decreases the excitation energy threshold, resulting in increasing the population of the generated electron–hole pairs. Other research groups [19–21] have reported that metal dopants could act as slow electron–hole pair recombination centers. Therefore, the photocatalytic properties of TiO$_2$ layers increase in this case.

On the basis of the above-mentioned points, we have investigated the effect of the substrate material on the hydrophilicity and photocatalytic properties of TiO$_2$ thin films, which could help to find the optimum and more efficient conditions for application purposes. In this regard, four types of thin film systems were prepared: (i) TiO$_2$/glass; (ii) TiO$_2$/Ag-ion-exchanged glass; (iii) TiO$_2$/Cu/glass and (iv) TiO$_2$/Au/glass.

2. Experimental details

2.1. Sample preparation methods

2.1.1. Substrates. The silver-ion-exchanged substrates were prepared using soda-lime type glasses. For the preparation of one-side ion-exchanged glass, the precisely cleaned surface of a glass slide was covered with a fine powder of uniform and homogeneous mixture of NaNO$_3$ and AgNO$_3$ salts, with a weight ratio of AgNO$_3$/NaNO$_3$ in the salt mixture as 4/96%. Then, the samples were placed into an electrical oven ($T_{\text{max}} = 1200 \, ^\circ\text{C}$) in atmosphere pressure for 210 min ion-exchange time at a fixed temperature $T = 400 \, ^\circ\text{C}$. During the ion-exchange process some of the silver ions of the molten salt exchange with some Na$^+$ ions of the glass matrix as a result of diffusion [22]. After the cooling process, the samples were washed by diluted HCl and distilled water [23].

Gold and copper thin films were prepared by co-deposition of RF-sputtering and RF-PECVD with $f \sim 13$ MHz, chamber pressure $p \sim 10^{-5}$ mbar, at room temperature on glass substrates. Deposition was done during 15 min with RF power of 180 W and an initial gas pressure of 0.035 mbar. The thickness of the gold and copper thin films obtained was $\sim 20$ nm. The details of the coating method are given in [24]. Subsequently, the prepared metal thin films could be used as different substrates for the TiO$_2$ layers and thus change their hydrophilicity and photocatalytic properties.

2.1.2. TiO$_2$ layers. As the sol–gel method is simple and at the same time gives a highly pure and homogeneous layer [25], we have used it for the preparation of TiO$_2$ thin films on different substrates. Thereby, a container including 20 cm$^3$ of ethanol was placed into an ice-water bath on a magnetic stirrer. Afterwards, TiCl$_4$ was added drop by drop until the produced vapor fades. In the next step, 20 cm$^3$ of distilled water was added drop by drop. At final stage (after 20 min aging) the produced sol was sprayed on the heated substrate ($T_0 = 300 \, ^\circ\text{C}$) with a total of 90 min deposition time. Using the above-mentioned method we prepared four kinds of layers: (i) TiO$_2$/glass; (ii) TiO$_2$/Au/glass; (iii) TiO$_2$/Cu/glass and (iv) TiO$_2$/Ag-ion-exchanged glass. During the entire time of the film deposition process, relative humidity and room temperature were 25 $\pm$ 2% and 30 $\pm$ 1 $^\circ\text{C}$, respectively.

Annealing the samples was performed in two steps; in the first step, samples were heated for 1 h at $T_1 = 150 \, ^\circ\text{C}$, and in the second step they were heated at $T_2 = 300 \, ^\circ\text{C}$ for an additional 1 h.

2.2. Characterization of the samples

The average thickness of TiO$_2$ thin films on the bare glass substrate was about 65 nm, which was measured by the profilometry method (Dektak 3 version 2.13 instrument). For all of our different produced substrates the same coating method and same amount of TiO$_2$ were applied. It should be mentioned that from results of our atomic force microscopy (AFM) studies, one can find that the particle size of our films are bigger than the thickness of the TiO$_2$ layer. In a later section we will show that the produced metallic films have a granular structure, resulting in the formation of granular TiO$_2$ films which is made from the particles with an oblate spheroid shape. To be exact, generally the diameter of our produced TiO$_2$ film particles are larger than their thickness, which determines the average thickness of the produced TiO$_2$ films.

The samples structure characterization was performed by means of: (i) x-ray diffraction (XRD), by Philips PW-1390 diffractometer using a Cu $K_\alpha$ radiation with a scan rate of 4$\,\text{min}^{-1}$ over a range of 10–70$^\circ$; and (ii) AFM, which was performed by NT-MDT in semi-contact mode. The AFM data were analyzed by NOVA software.

In order to investigate the influence of substrate material type on the photocatalytic properties of the TiO$_2$ layer, 0.5 molar methylene blue (MB) was used as pollution on the surface of the samples. The influence of UV irradiation on the MB and its decomposition was studied by measuring the transmission spectra of the samples at wavelength $\lambda = 660$ nm (the maximum absorption of MB) using a UV–Vis spectrophotometer, Buach & Lamb 710.

To measure the hydrophilicity of the samples, a CCD camera (Proline UK) was used to acquire images of the droplet in order to measure the contact angle of the droplets on the surfaces of different samples. The contact angles were measured with $\pm 1^\circ$ precision. The volume of each droplet was $\sim 20 \, \mu\text{l}$. The effect of irradiation duration time on the contact angle of droplets was investigated by photography after irradiating the samples by a UV-lamp with $P_{\text{max}} = 1 \, \text{mW cm}^{-2}$ at the sample position.

3. Results

In figure 1 the results of the XRD measurement are shown. One can see that, the annealing of our samples results in dominating of the anatase phase, and there is no considerable peaks related to impurities. Since the annealing process for all of our samples was the same, we assumed that the ratio of rutile/anatase phase structures has not changed for different substrates.

Results of the AFM study of the produced TiO$_2$ layers on different substrates are shown in figures 2–4 for Ag-ion-exchanged glass, TiO$_2$/Au/glass and TiO$_2$/Cu/glass
samples, respectively. As previously mentioned, the produced TiO$_2$ films have a granular structure, which could be related to the fact that our metallic substrates are very thin (~20 nm), resulting in the formation of island-like metallic films. Consequently, we measured the roughness and grain size evaluation of our different substrate materials, using AFM images, which are presented in table 1. The grain size in the plane of the samples could be different from the thickness of the particles. This point indicates an oblate spheroid shape of the grains. It can be seen from table 1, the roughness and grain size of the TiO$_2$ coating on the Au/glass substrate is the largest and decreases for the Cu/glass one. It is obvious for a simple glass substrate that the roughness of TiO$_2$ is very low and at the same time, the size of the TiO$_2$ grains is the smallest in comparison to the cases where the glass substrate was coated by Au or Cu thin films. As is shown later in figure 7, except for the Ag-ion-exchanged glass substrate, an increase in roughness of the samples is accompanied by an improvement in the photocatalytic properties of the samples.

Tables 1. Roughness and particle sizes of the samples extracted from AFM images.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Roughness (nm)</th>
<th>Average particles' diameter in the plane of the sample (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$/Au/glass</td>
<td>29</td>
<td>138</td>
</tr>
<tr>
<td>TiO$_2$/Cu/glass</td>
<td>20</td>
<td>106</td>
</tr>
<tr>
<td>TiO$_2$/Ag-ion-exchanged glass</td>
<td>13</td>
<td>106</td>
</tr>
<tr>
<td>TiO$_2$/glass</td>
<td>3</td>
<td>41</td>
</tr>
</tbody>
</table>

Figures 5–6 show the variation of transmittance and reflectance spectra of the films. The surface plasmon resonance peak position of the TiO$_2$/Cu/glass sample ($\lambda = 580$ nm [26]) for the copper islands thin film is shown in figure 5. The reflectance spectra of the films (figure 6) show an increasing of the reflectance in longer wavelengths for all samples in comparison to the bare glass. In other words, in our case spectral interval for the absorption of incident light is improved toward the visible region of the spectra, which could be taken as an advantage for adding a metallic thin film on the glass substrates.
If $C_0$ represents the concentration of MB at time $t=0$ and $C$ represents the concentration of MB at time $t$, there is a relation as [27]

$$\frac{C}{C_0} = \frac{\ln(T_0/T_m)}{\ln(T_0/T_i)},$$

(1)

where $T_0$ is the transmission coefficient of the layer without pollution, $T_i$ is the transmission coefficient with pollution at time $t=0$, and $T_m$ is the transmission coefficient of the sample with pollution at time $t$. In this way, by measuring the transmission coefficient in determined exposure time (in our case every 10 min) and calculating the quantity $C/C_0$, one can follow the decomposition process. A small value of $C/C_0$ means an improvement of the photocatalytic properties, which could be related to a larger surface for chemical reactions or to longer electron–hole recombination times. An increase in the roughness of the samples’ surfaces could result in increasing chemical reactions. In order to obtain adequate data, all experiments explained in this report were repeated several times.

The photocatalytic decomposition of MB is shown in figure 7. As it can be seen, with increasing exposure time the quantity of $C/C_0$ decreases, which is a measure of photocatalytic properties. That is, the better the photocatalytic properties, the faster MB decomposition. From figure 7 one can conclude that the best photocatalytic properties are obtained for the TiO$_2$ layer on the gold and copper substrates.

To investigate the effect of irradiation by UV light on samples’ hydrophilicity, we measured the variation of the contact angle with the UV exposure time for different samples (figure 8). Our results indicate that hydrophilicity for TiO$_2$/Cu/glass system is the best and for TiO$_2$/Au/glass sample is the worst.

### 4. Discussion

In order to determine the band gap energy for the produced samples, we calculated a $(\alpha h\nu)^{0.5}$ versus $(h\nu)$ diagram (figure 9), where $\alpha$ is the absorption coefficient and $h\nu$ is the energy of the incident photons. By drawing the tangential line of the linear part of the produced curves, we obtain band gap energies [28] of the samples, which are presented in table 2.

The Ag-ion-exchanged sample is different from the other samples due to the micrometer depth of silver diffusion in the glass, which leads to a bulk material behavior for the silver ion-exchanged substrates. On the other words, depending on the duration time and temperature at which the ion-exchange occurs, the thickness of the ion-exchanged layer of the glass substrate would be between a few up to

![Figure 5. Transmission spectra of TiO$_2$ thin films on different substrates.](image)

![Figure 6. Reflection spectra of TiO$_2$ thin films on different substrates.](image)

![Figure 7. Influence of exposure time of different samples, irradiated by the UV source ($P_{max} = 1$ mW), on the decomposition of MB.](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$/Au/glass</td>
<td>$3.4 \pm 0.9 \times 10^{-3}$</td>
</tr>
<tr>
<td>TiO$_2$/Cu/glass</td>
<td>$3.5 \pm 10^{-3}$</td>
</tr>
<tr>
<td>TiO$_2$/glass</td>
<td>$3.7 \pm 10^{-3}$</td>
</tr>
<tr>
<td>TiO$_2$/Ag-ion-exchanged glass</td>
<td>$3.2 \pm 0.8 \times 10^{-3}$</td>
</tr>
</tbody>
</table>
The bigger band gap is accompanied by a droplet of water showing a droplet of water, and for the TiO\textsubscript{2}, it can be seen that adding a metallic thin film on the glass substrate leads to still lower transmittance in the whole visible spectrum. It means that in this case because of a reduction in band gap energy, the worst photocatalytic properties of the samples. Therefore, Cu doping as a substrate of the TiO\textsubscript{2} can lead to an efficient charge separation by trapping or removing electrons from the TiO\textsubscript{2} grains. Afterward, OH radicals would be produced, which in turn stimulate the enhancement of the photocatalytic properties [29]. In our experiments and as shown in figures 5 and 6, the addition of a thin Au film on the glass substrate leads to still lower reflectance at the longer wavelength and at the same time, low transmittance in the whole visible spectrum. It means that in this case because of a reduction in band gap energy, most of the incident light is absorbed which results in better photocatalytic properties for the TiO\textsubscript{2} thin film, should be calculated differently for the TiO\textsubscript{2}/Ag-ion-exchanged glass system. As can be seen from table 2 and figure 8 the bigger band gap is accompanied by the worst photocatalytic properties of the samples.

It is known that the presence of metal particles with TiO\textsubscript{2} can lead to an efficient charge separation by trapping or removing electrons from the TiO\textsubscript{2} grains. Afterward, OH radicals would be produced, which in turn stimulate the enhancement of the photocatalytic properties [29]. In our experiments and as shown in figures 5 and 6, the addition of a thin Au film on the glass substrate leads to still lower reflectance at the longer wavelength and at the same time, low transmittance in the whole visible spectrum. It means that in this case because of a reduction in band gap energy, most of the incident light is absorbed which results in better photocatalytic properties for the TiO\textsubscript{2} thin film, should be calculated differently for the TiO\textsubscript{2}/Ag-ion-exchanged glass system. As can be seen from table 2 and figure 8 the bigger band gap is accompanied by the worst photocatalytic properties of the samples.

As is shown in figure 7 for the TiO\textsubscript{2}/Cu/glass system the photocatalytic properties are better than that for the TiO\textsubscript{2}/glass system. It is possible that Cu could reduce to a metallic state (Cu\textsubscript{0}) to act as a co-catalyst [30]. It has also been reported that the copper species are mixture of metallic (Cu\textsubscript{0}) and ionic copper (Cu\textsuperscript{+} and Cu\textsuperscript{2+}). When we irradiate such a film by UV light the copper ions could be reduced to metallic ones, and metallic copper could be oxidized to ions by photogenerated electron–hole pairs, respectively [31]. Therefore, Cu doping as a substrate of the TiO\textsubscript{2} layer could improve the photocatalytic properties of the sample (figure 7), but its band gap energy is bigger than that for Au. Thus as can be seen from figure 7, the photocatalytic properties of the TiO\textsubscript{2}/Cu/glass system are not as good as the TiO\textsubscript{2}/Au/glass system, but it is much better than the bare glass substrate. It is reported that the photocatalytic properties of the samples can be influenced by the crystal structure, effective surface area, size distribution, porosity, band gap and hydroxyl radical concentrations [32, 33]. A small particle size provides a greater effective surface area and reduces the electron–hole pair recombination rate, which results in improving the photocatalytic properties [34]. For TiO\textsubscript{2} photocatalysts, an additional improvement is reported for nanoparticles smaller than 5 nm due to quantum size effects [35]. In our case, on the basis of our experimental data, due to an average size of a few 10 nm order of magnitude, the quantum size effects could be negligible as important influencing candidate parameters on the photocatalytic properties.

Figure 8. Variation of contact angles of water droplet versus exposure time for different samples irradiated by the UV source (P\textsubscript{max} = 1 mW). The inset-photo in figure 8 shows a droplet of water on a TiO\textsubscript{2}/Au/glass system and its contact angle.

From figure 8 it can be seen that adding a metallic thin film on the glass substrate does not necessarily improve the samples’ hydrophilicity. As one can see for the TiO\textsubscript{2}/Au/glass system, the contact angle of the water droplets on the surface of the sample is much bigger than that of the TiO\textsubscript{2}/glass system which means that the hydrophilicity has declined for the TiO\textsubscript{2}/Au/glass system. On the other hand the contact angle of the droplets on the surface of the TiO\textsubscript{2}/Cu/glass system is much smaller than that of the TiO\textsubscript{2}/glass system. That is, depending on the material used for coating the glass substrate, different hydrophilic properties could be obtained. Although, the band gap of the TiO\textsubscript{2}/Au/glass sample is smaller than that of TiO\textsubscript{2}/Cu/glass, which should result in better hydrophilic properties, our experimental observations show reverse results. Therefore, other important parameters should be involved in the process which are able to neutralize the role of the band gap of our systems. In [36, 37] it is reported that the contact angle of a water droplet on a gold surface is about ~85°, which is larger than that of our case for TiO\textsubscript{2}/Au/glass (~80° before exposure).

If one compares the AFM results, shown in figures 3 and 4, there is an obvious difference in the amount of empty spaces (porosity) for two cases: TiO\textsubscript{2}/Au/glass and...
TiO$_2$/Cu/glass. Comparing the case where the Cu thin film is coated on the glass to the case where the Au thin film is coated, the TiO$_2$ film has higher porosity. It is reported that [38, 39, 40] more porosity results in better hydrophilicity, similar to our case. It seems that our produced TiO$_2$ thin films on the Cu coated glass have more porosity, which makes it more hydrophilic. This advantage suggests that for hydrophilic proposes, if one uses a Cu coated glass instead of a bare glass (as a substrate for TiO$_2$ layer) better results can be achieved.

It should be mentioned that the average Au grain size is bigger than the Cu grain size in our samples (table 1), which decreases the hydrophilicity. In other words, the relatively large size of the grains in the TiO$_2$/Au/glass samples, leads to a higher recombination rate for the photo-generated electron–hole pairs on the TiO$_2$/Au/glass surface [41, 42], making it a poor hydrophilic layer. This point also should be taken into account in the whole process as a competitive mechanism.

It is obvious that more precise and exact studies should be carried out to obtain quantitative interpretations about the role of porosity and its competition, with the influence of the band gap of the samples, which is out of range of the present work.

5. Conclusions

We have studied the influence of substrate material on the hydrophilicity and photocatalytic properties of TiO$_2$ nano thin films. Our experimental results indicate that the TiO$_2$/Au/glass system has better photocatalyst properties in comparison to the TiO$_2$/Cu/glass, TiO$_2$/Ag-ion-exchanged glass and the TiO$_2$/glass systems. We discussed it as a result of a lower band gap for the TiO$_2$/Au/glass system, which determines the electron–hole generation rate, the main parameter in the photocatalytic properties. We observed that among our samples, the TiO$_2$/Cu/glass sample shows the highest hydrophilicity. Our investigations leads us to conclude that, in the TiO$_2$/Au/glass samples, where the grains are more compact or the Au grains relatively are large, the number of recombination centers would be high enough to imperfect the hydrophilicity of the TiO$_2$/Au/glass system in comparison to the TiO$_2$/Cu/glass system. At the same time, our AFM analysis shows a more porous texture for the TiO$_2$/Cu/glass system, which (as reported in [39, 40]) plays essential role in the hydrophilicity of the sample.

Results of the present work emphasise that by adding a suitable layer on the glass substrate for the TiO$_2$ thin films, one can improve and control the photocatalytic and hydrophilic properties of the surfaces for different applications, such as the walls of operating rooms in hospitals or cars’ corpuses or buildings, which lead to reducing the expenses for cleaning or disinfection of such places.

Acknowledgments

We acknowledge the partial financial support by the Department of Physics Research Council of the University of Tehran. MRM thanks the Center of Excellence on the structure and properties of matter of the University of Tehran.

SK appreciates partial financial support of the Islamic Azad University, Central Tehran Branch.

References

[18] Penner S S 2006 Energy 31 33
Int. J. Heat Mass Transfer 140 1017


79 491


[40] Lindholm I and Jonsson I 1969 Electrochem. Soc. 116 1150

[41] Kamat P V 2002 Pure Appl. Chem. 74 1693