

Electro-induced hydrophilicity of hydrogen plasma bombarded Ag/TiO₂ nanostructure

Yaser Abdi¹, Salimeh Kimiagar^{2*}
Aliakbar Chahe³

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Abstract

Electro-induced hydrophilicity of the Ag/TiO₂ nanostructure has been reported in this study. In this work hydrogen plasma bombarded Ag/TiO₂ nanostructure was created using a sequential process including chemical vapor deposition and plasma bombardment. X-ray diffraction and X-ray photoelectron spectroscopy were used to analyze structure and chemical states of the sample. The prepared Ag/TiO₂ heterostructure has enhanced visible-light-induced hydrophilicity comparing to pure TiO₂. The electro-induced hydrophilicity of the samples was also examined by creating the comb like electrodes on the prepared Ag/TiO₂. A super-hydrophilic surface was achieved by applying an electric bias voltage on the electrodes.

Key words: Nanostructures, Thin films, plasma, X-ray diffraction, Surface properties.

1. Introduction

Because of their photo-catalytic activity, chemical stability and mechanical hardness, titanium dioxide (TiO₂) nanoparticles received much attention in recent years. Photocatalytic reactions of TiO₂ nanoparticles proceed under UV light radiation with photon energy greater than its band gap (3.20 eV) [1]. Antibacterial activity and self-cleaning property of the TiO₂ nanoparticles have been also studied [2,3]. It is very interesting that

TiO₂ nanoparticles show enhanced hydrophilicity beside their photocatalytic activities, even though the mechanisms are completely different [4].

One challenge, which has been studied [5-8], is shifting the materials absorption spectra from UV into the visible light region so the majority of the solar spectrum can be used as a light source. The large surface area of the porous nano-particulate films leads to increase light absorption efficiency and electron-hole generation [9]. On the other hand, system efficiency is limited by recombination of the electron-holes at the surface boundaries [10]. In recent years, the effects of dopants and deposited metals on photocatalytic activity of TiO₂ have been widely investigated [11-14]. It has been shown that usage of Ag in TiO₂ structure prevents the fast recombination of electron-hole pairs [11]. The recombination rate decreases by trapping the photo-generated carriers in Ag/TiO₂ composite.

In this study we have reported fabrication of Ag nanoparticles embedded in TiO₂ matrix with enhanced hydrophilicity. Formation of Ag/TiO₂ was carried out by a hydrogen bombardment system. Wettability of the fabricated Ag/TiO₂ nanostructure was measured under visible light. Also hydrophilicity of the obtained nanostructure under an applied electric bias voltage was examined in this work. The oxidation and reduction potentials of silver nanoparticles are low. Such behavior leads to an easy reduction and oxidation reaction within the Ag/ TiO₂ suitable for electrochemical application. We believe that electro-induced hydrophilicity of the Ag/TiO₂ nanoparticles can be attributed to the electrochemical activity of the Ag nanoparticles which leads to formation of OH⁻ and increasing the wettability.

2. Experimental details

Fabrication process was started by cleaning the substrate by the standard Radio Corporation of America (RCA) method (NH₄OH:H₂O₂ : H₂O solution with volume ratio of 1:1:5), rinsed in deionized water. Using an atmospheric pressure chemical vapor deposition (CVD) system TiO₂ layer was deposited on 2×2 cm² soda lime glass substrate at a temperature of 300°C [15]. TiCl₄ was used as the main precursor to form titanium dioxide. Argon gas was used for delivery of the solution from a bubbler into the chamber. Ar flow rates during the deposition were kept at 200 sccm.

1 . Nano-Physics Research Laboratory, Department of Physics, University of Tehr an, Tehran, Iran

2 .*Nano-Physics Research Laboratory, Department of Physics, Central Tehran Branch, Islamic Azad University, Tehran, Iran. Corresponding author: kimia@khayam.ut.ac.ir

3 . Nano-Physics Research Laboratory, Department of Physics, University of Tehr

Oxygen was also introduced into the chamber by a separate inlet with flow rate of 400sccm. In this process 200 nm crystalline TiO₂ nano-structured layer was formed on the substrate. As contact metal for electro-induced activity, 300nm thickness of Ag layer was deposited on the TiO₂ coated substrate. Ag layer was then patterned by standard photolithography to obtain desired comb-like electrodes with spacing between the electrodes of 500 μ m and line width of 100 μ m. Photolithography was performed using a mercury lamp as UV light source, Shipely 1813 positive resist as photoresist. Ag electrodes were used for applying the voltage within the sample. Subsequently, a thin layer of Ag with a thickness of 20 nm was deposited on the prepared samples. Deposition of Ag layers were carried out by a physical vapor deposition system at a base pressure of 3×10^{-6} Torr and at temperature of 200°C. Deposition rate was kept at 3Å/s. System vacuum was performed by a rotary mechanical pump and diffusion pump. The prepared samples were then placed in the DC plasma bombardment system in the presence of H₂ at a pressure of 7 Torr. Hydrogen plasma was applied on the samples with a power density of 3W/cm² at a temperature of 350°C for 30 minutes to form Ag nano-islands. In the plasma bombardment process, accelerated ions of plasma transfer kinetic energy to the surface and the Ag grains are formed during plasma treatment.

Morphological investigation of the nanostructures was studied by a field emission scanning electron microscopy (FESEM). Phase formation and crystalline properties of the samples were characterized by an x-ray diffractometer 'XRD' (Philips PW 1130.90) in the 2 θ range from 20° to 100° operating at 40 kV accelerating voltage and 40mA current. XRD analysis was carried out by Cu K α (1.54Å) x-ray source in grazing geometry.

The components of the structure were determined by X-ray photoelectron spectroscopy (XPS) using Gammatdata-scienta ESCA 200 hemispherical analyzer equipped with an Al K α (1486.6 eV) X-ray source.

The wettability of the samples was evaluated by measuring the contact angle of distilled water. The picture of water drop on the surface was captured by a digital camera and imported to the measurement software (TESCAN Measurement) to measure the angle between the distilled water curve

and the sample surface. Contact angle was measured under a mercury lamp with maximum radiation at 365 nm wavelength as the UV source and halogen lamp as a visible light source. Irradiation power density of UV and visible light was 100mW/cm² at the sample position.

To investigate the effects of applied voltage on the hydrophilicity of the prepared Ag/TiO₂ nanostructures the contact angle measurement was carried out again by applying a voltage between the comb-like electrodes.

3. Results and discussion

Figure 1.a shows SEM image of the TiO₂ nanostructure on the glass substrate. As shown in this figure uniform cabbage-like nanostructures were formed on the substrate. Formation of Ag nanoparticles on the TiO₂ coated sample, after the hydrogen bombardment step, can be seen in SEM image of figure 1.b. The clearly observable spherical particles in this figure with a typical diameter ranging from 50 to 100nm are Ag

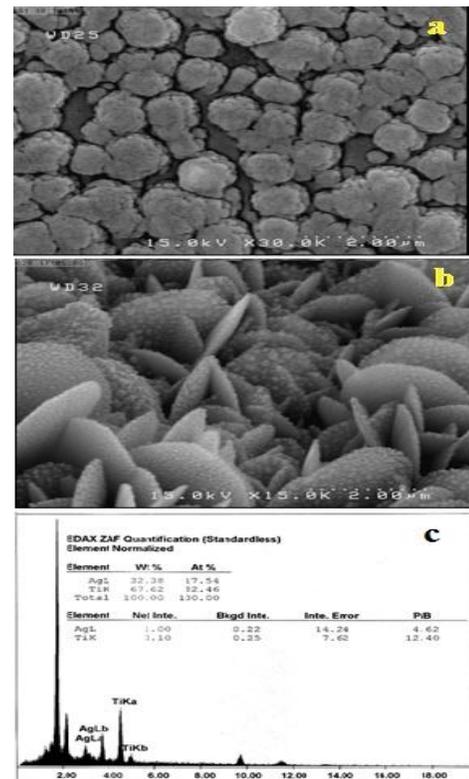


Figure 1. SEM images of the prepared TiO₂ nanostructures before (a) and after (b) the formation of Ag nano-particles. Part b demonstrates a magnified view showing the cabbage like TiO₂ coated by Ag nanoparticles. Part c is EDX analysis of the sample showing the presence of Ag nanoparticles on the TiO₂.

nanoparticles on cabbage like TiO₂. Part c of this figure is energy dispersive x-ray (EDX) analysis of the sample showing the presence of Ag nanoparticles on the TiO₂.

To verify the structural characteristics of the Ag/TiO₂ nanostructure XRD analysis was carried out. Figure 2 shows the XRD results of the prepared nanostructures. Curve (a) of this figure is the XRD result of the TiO₂ coated

sample. The appeared peaks in this figure are associated with the crystalline planes of anatase and rutile phases of TiO₂. Part b of this figure shows the XRD result of the sample after the formation of Ag nanoparticles. Some peaks associated with the crystalline planes of Ag can be seen in this figure indication the formation of Ag crystalline structure in the TiO₂ matrix. Peaks shift is clearly observed in the XRD results. We have reported in our previous work [16] that TiO₂ structure changes in the plasma treatment process. It may be due to atomic diffusion and recrystallization.

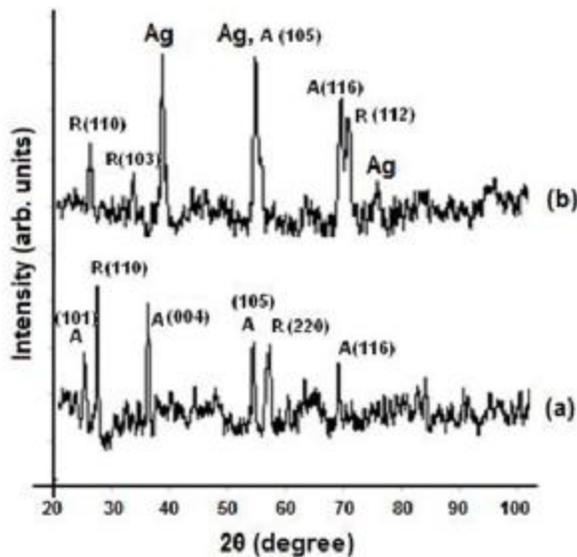


Figure 2. XRD patterns of the prepared TiO₂ nanostructures before (a) and after (b) the formation of Ag nano-particles. The peaks corresponding to anatase and rutile phases of TiO₂ are denoted by A and R, respectively. Numbers in parentheses indicate the orientation of crystal planes.

To investigate the chemical state of the Ag/TiO₂ nanostructure XPS analysis was utilized. Figure 3 shows high-resolution XPS spectra of Ag, Ti and O core level of the prepared Ag/TiO₂. As can be seen from part a of this figure, the Ag(3d_{5/2}) and

Ag(3d_{3/2}) bands of the sample were found at binding energies of about 368.3 and 374.1 eV, respectively. The energy splitting value is 5.8 eV for the 3d doublet of Ag and can be attributed to formation of nonmetallic Ag nanoparticles [17], indicating the formation of Ag-Ti and Ag-O bonds. Such peak shift was reported in previous works [18].

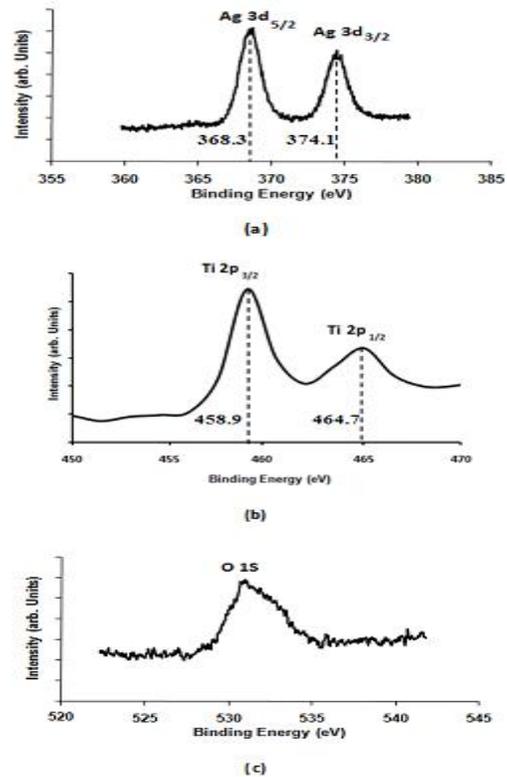


Figure 3. XPS spectra of a: Ag (3d), b: Ti(2p) and c: O(1s) core level of the Ag/TiO₂ nanostructure

The spectra of the Ti (2p) and O (1s) regions are shown in part b and c. The bands centered at binding energies of 464.7 and 458.9eV were attributed to the Ti (2p_{1/2}) and Ti (2p_{3/2}) indicating a predominant state of Ti⁴⁺, respectively [18]. The slitting between bands which is found to be 5.8 eV in this result shows a bit difference comparing with the normal state of Ti⁴⁺ in the anatase TiO₂ [19]. Part c of this figure shows XPS spectra of the O(1s) core level of the sample.

The photo-absorption ability of the Ag/TiO₂ nanostructure was compared with pure TiO₂. Figure 4 represents the achieved results. As shown in this figure the transmission intensity of the Ag/TiO₂ decreases at wavelengths below the 600

nm. It shows that, increasing the visible light absorption leads to enhancement in photo induced hydrophilicity of the Ag/TiO₂ under the visible.

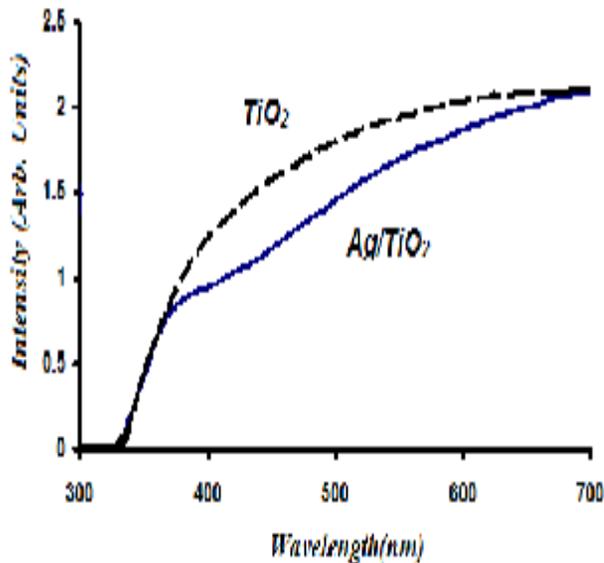


Figure 4. a): Transmission spectra of prepared TiO₂ and Ag/TiO₂ showing the photo-absorption of Ag/TiO₂ in the visible range.

Hydrophilicity of the prepared samples under visible light was evaluated by measuring the contact angle of distilled water on the sample surface. Figure 5 demonstrates the results of this measurement. This figure shows the contact angle of the water drop versus time on the TiO₂ layer and Ag/TiO₂ nanostructures. Substrate temperature during the irradiation is very important. We measured the substrate temperature during the irradiation. Measurement shows a 3°C increasing in the substrate temperature. As shown in this figure the Ag/TiO₂ nanostructure shows a significant activity under visible light while hydrophilicity of the TiO₂ layer does not change considerably under visible light. It means that Ag/TiO₂ can be excited under visible light. Visible light absorption by surface plasmon resonance of Ag nanoparticles is thought to induce electron transfer to TiO₂ resulting in charge separation and thus activation by visible light [20, 22]. Therefore, Ag-TiO₂ nanocomposites can be a promising material for visible light induced photocatalytic applications.

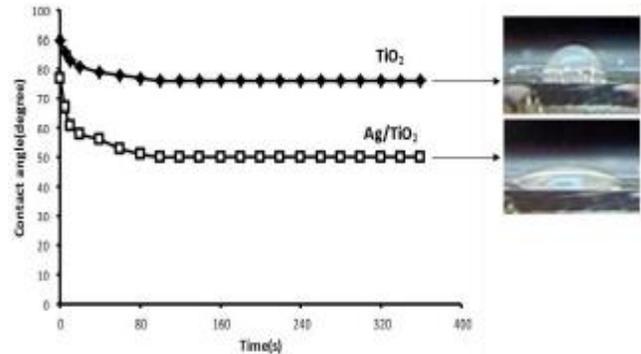


Figure 5. Contact angle measurement of distilled water on the TiO₂ and Ag/TiO₂ nanostructures under visible light exposure.

For investigation of the electro-induced activity of the fabricated structure 50 and 100V were applied on the Ag electrodes. Electric current between the electrodes was 150μA and 300μA, respectively. Figure 6 and 7 show the electro-induced wettability of the sample. Figure 6 shows a significant enhancement in visible light induced wettability of the Ag/TiO₂ by applying voltage between the electrodes. Inset in figure 6 is optical image of the sample containing the Ag electrodes. We believe that ionization ability of the Ag nanoparticles [23] is responsible for this enhancement. Ionization of H₂O molecule on the nano-structured surface increases the

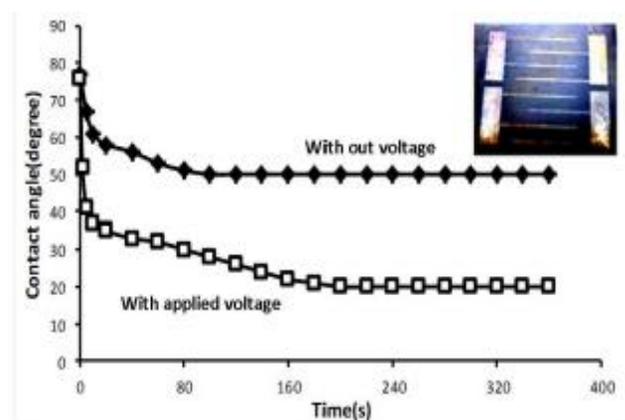


Figure 6. Contact angle measurement of distilled water on the Ag/TiO₂ nano-structure under visible light by applying 100V bias voltages on the electrodes.

quantum efficiency of the photo-induced hydrophilicity [24]. Figure 7 represents contact angle measurement of Ag/TiO₂ in dark with

different applied voltage. Results confirm the electro-induced wettability of the prepared structure.

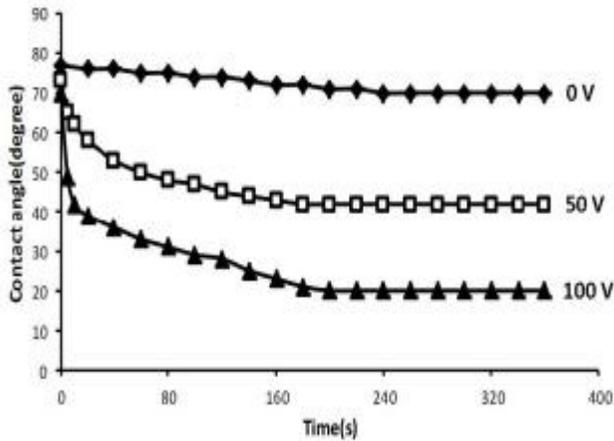


Figure 7. Contact angle measurement of distilled water on the Ag/TiO₂ in dark by applying different voltages showing the electro-induced hydrophilicity of the sample.

As schematically shown in Figure 8, formation of the Ag nano particles on the TiO₂ (as a semiconductor) allows formation of isolated Schottky barriers [25]. Schottky barriers serve as efficient electron traps to avoid electron-hole recombination leading to increase hydrophilicity of the surface. Electron-hole generation (accumulation of negative charges on the Ag nanoparticle surface and positive

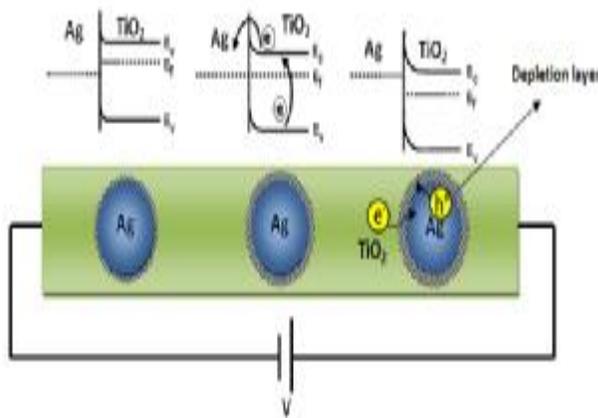


Figure 8. Schematic of electro-induced electron-hole generation in the Ag/TiO₂ structure.

charges in TiO₂) due to applied voltage in such Schottky nano-diodes is responsible for electro-induced hydrophilicity of the Ag/ TiO₂. I-V

characteristic of the Ag-TiO₂ (shown in figure 9) confirms formation of Schottky junction.

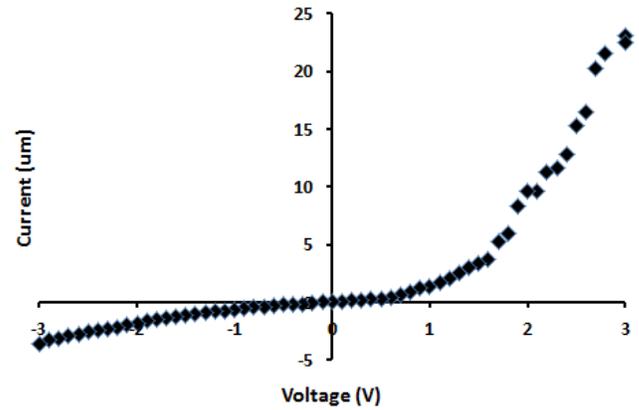


Figure 9. Electrical characteristic of the Ag/TiO₂ heterojunction showing the Schottky junction related rectifying behavior.

Additionally, the deposition of metal nanoparticles onto the TiO₂ surface and hence the intimate interfacial contacts may lead to the formation of structural defects and trap states within the TiO₂ band gap [26]. Visible light absorption and visible light induced hydrophilicity of the Ag/TiO₂ may come from such structural defects and trap states.

4. Conclusion

Ag/TiO₂ nanostructure was successfully grown on glass substrates. An atmospheric pressure cabbage-like nanostructure. Structural studies using CVD method was used to fabricate crystalline TiO₂ XRD confirmed formation of Ag and TiO₂ crystalline phases. XPS spectra showed the Ag(3d_{5/2}) and Ag(3d_{3/2}) bands of the sample at binding energies of 368.3 and 374.1 eV, which have a bit difference with typical core level of Ag(3d) (368.1 and 374.25 eV). Also the Ti (2p_{1/2}) and Ti(2p_{3/2}) bands are centered at binding energies of 464.7 and 458.9eV. Comparing with the typical core level of Ti (2p_{3/2}) band at 459.1 a little shift is shown in this band. These little shifts in typical core levels of Ag (3d) and Ti(2p) indicate the diffusion of the Ag in TiO₂ structure. Due to this heterostructure formation photo-absorption intensity of the fabricated Ag/TiO₂ increased in the range of visible light wavelengths. Hydrophilicity of the Ag/TiO₂ was compared with the corresponding activity of pure TiO₂ as well. The tests under visible light showed that the

Ag/TiO₂ heterostructure has enhanced visible-light-induced hydrophilicity. The electro-induced hydrophilicity of the samples was also examined by creating the comb like electrodes on the prepared Ag/TiO₂. Contact angle measurement in dark confirmed the pure electro-induced hydrophilicity of the sample. Enhancement in the hydrophilicity of TiO₂ using electric voltage encouraged us to use this approach in other applications based on catalytic activity of TiO₂ such as antibacterial, anti-fogging air and water purification.

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References

- [1] F.D. Duminica, F. Maury, R. Hausbrand, Growth of TiO₂ thin films by AP-MOCVD on stainless steel substrates for photocatalytic applications, *Surface & Coatings Technology* 201 (2007) 9304-9308.
- [2] P. Evans, D.W. Sheel, Photoactive and antibacterial TiO₂ thin films on stainless steel, *Surface & Coatings Technology* 201 (2007) 9319-9324.
- [3] A.G. Rincon, C. Pulgarin, Bactericidal action of illuminated TiO₂ on pure Escherichia coli and natural bacterial consortia: post-irradiation events in the dark and assessment of the effective disinfection time, *Applied Catalysis B: Environmental* 49 (2004) 99-112.
- [4] A. Fujishima, T.N. Rao, D.A. Tryk, Titanium dioxide photocatalysis, *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* 1 (2000) 1-21.
- [5] J.R. Bolton, Solar photoproduction of hydrogen: A review, *Solar Energy* 57 (1996) 37-50.
- [6] V. M. Aroutiounian, V. M. Arakelyan, G. E. Shahnazaryan, Metal oxide photoelectrodes for hydrogen generation using solar radiation-driven water splitting, *Solar Energy* 78 (2005) 581-592.
- [7] M. Gratzel, Dye-sensitized solar cells, *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* 4 (2003) 145-153.
- [8] M. Ashokkumar, An overview on semiconductor particulate systems for photoproduction of hydrogen, *International Journal of Hydrogen Energy* 23 (1998) 427-438.
- [9] F. Cao, G. Oskam, G. J. Meyer, P.C. Searson, Electron transport in porous nanocrystalline TiO₂ photoelectrochemical cells, *Journal of Physical Chemistry* 100 (1996) 17021-17027.
- [10] P.E. deJongh, D. Vanmaekelbergh, Trap-Limited Electronic Transport in Assemblies of Nanometer-Size TiO₂ Particles, *Physical Review Letter* 77 (1996) 3427-3430.
- [11] K.D. Kim, D.N. Han, J.B. Lee, H.T. Kim, Formation and characterization of Ag-deposited TiO₂ nanoparticles by chemical reduction method, *Scripta Materialia* 54 (2006) 143-146.
- [12] H.M. Sung, J.R. Choi, H.J. Hah, S.M. Koo, Y.C. Bae, Comparison of Ag deposition effects on the photocatalytic activity of nanoparticulate TiO₂ under visible and UV light irradiation, *Journal of Photochemistry and Photobiology A: Chemistry* 163 (2004) 37-44.
- [13] J. Keleher, J. Bashant, N. Heldt, L. Johnson, Y. Li, Photo-catalytic preparation of silver-coated TiO₂ particles for antibacterial applications, *Journal of Microbiology and Biotechnology* 18(2002) 133-139.
- [14] L.A. Brook, P. Evans, H.A. Foster, M.E. Pemble, A. Steele, D.W. Sheel, H.M. Yates, Highly bioactive silver and silver/titania composite films grown by chemical vapour deposition, *Journal of Photochemistry and Photobiology A: Chemistry* 187 (2007) 53-63.
- [15] B. Arvan, A. Khakifirooz, R. Tarighat, S. Mohajezadeh, A. Goodarzi, E. A. Soleimani, and E. Arzi, Atmospheric pressure chemical vapor deposition of titanium dioxide films from TiCl₄, *Mater. Sci. Eng. B* 109 (2003) 17-23.
- [16] Y. Abdi, M. Khalilian, E. Arzi, Enhancement in photo-induced hydrophilicity of TiO₂/CNT nanostructures by applying voltage, *J. Phys. D: Appl. Phys.* 44 (2011) 255405.
- [17] J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben, *Hand Book of X-ray Photoelectron Spectroscopy*, Physical Electronics, Inc., Eden Prairie, MN, 1992.
- [18] O. Akhavan, Lasting antibacterial activities of Ag-TiO₂/Ag/a-TiO₂ nanocomposite thin film photocatalysts under solar light irradiation, *Journal*

- of Colloid and Interface Science 336 (2009) 117-124.
- [19] O. Akhavan, M. Abdollahad, Y. Abdi, S. Mohajerzadeh, Synthesis of titania/carbon nanotube heterojunction arrays for photoinactivation of *E. coli* in visible light irradiation, *Carbon* 47 (2009) 3280–3287.
- [20] M. M. Hasan, A. B. M. Abdul Malek, A. S. M. A. Haseeb and H. H. Masjuki, Investigations on TiO₂ and Ag based single and multilayer films for window glazings, *Journal of Engineering and Applied Sciences* 5 (2010) 22-28.
- [21] Y. Tan, T. Tatsuma, Plasmon-induced photoelectrochemistry at metal nanoparticles supported on nanoporous TiO₂, *Chem. Commun.* 16 (2004) 1810.
- [22] M.K. Seery, R. George, P. Floris, S.C. Pillai, J. Photochem. Silver doped titanium dioxide nanomaterials for enhanced visible light photocatalysis, *Photobiol. A* 189 (2007) 258-263.
- [23] S.D. Sherrod, A.J. Diaz, W.K. Russell, P.S. Cremer, D.H. Russell, Silver Nanoparticles as Selective Ionization Probes for Analysis of Olefins by Mass Spectrometry, *Analytical Chemistry* 80 (2008) 6796–6799.
- [24] H. Limage, F.D. Tichelaar, R. Closset, S. Delvaux, R. Cloots, S. Lucas, Study of the effect of a silver nanoparticle seeding layer on the crystallisation temperature, photoinduced hydrophylic and catalytic properties of TiO₂ thin films deposited on glass by magnetron sputtering, *Surface & Coatings Technology* 205 (2011) 3774–3778.
- [25] Y. Lai, H. Zhuang, K. Xie, D. Gong, Y. Tang, L. Sun, C. Lin and Z. Chen, Fabrication of uniform Ag/TiO₂ nanotube array structures with enhanced photoelectrochemical performance, *New J. Chem.*, 34 (2010) 34 1335–1340.
- [26] P. Hu, G. Du, W. Zhou, J. Cui, J. Lin, H. Liu, D. Liu, J. Wang and S. Chen, Enhancement of Ethanol Vapor Sensing of TiO₂ Nanobelts by Surface Engineering, *Applied materials & interfaces* 2 (2010) 3263–3269.