Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

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To cite this article: W. Halim, A. Moumen, S. Ouaskit & N. Errien (2016) Photocatalytic properties of TiO_2/ZnO thin film, Molecular Crystals and Liquid Crystals, 627:1, 49-55, DOI: 10.1080/15421406.2015.1137152

To link to this article: http://dx.doi.org/10.1080/15421406.2015.1137152

Published online: 13 May 2016.

MOL. CRYST. LIQ. CRYST.
2016, VOL. 627, 49–55
http://dx.doi.org/10.1080/15421406.2015.1137152

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Photocatalytic properties of TiO_2/ZnO thin film

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ABSTRACT
TiO_2, ZnO and ZnO/TiO_2 thin films have been prepared by radio frequency magnetron sputtering method under different temperatures. Their photo catalytic activities have been investigated. The structural of the thin films were characterized by X-ray diffraction and Raman spectroscopy. The photo catalytic activities of TiO_2 and ZnO/TiO_2 samples were evaluated by the photo decomposition of methylene blue. We note that the structural proprieties of the thin films showed a perfect crystallization along the (002) for ZnO, Rutile (110) for TiO_2 and Anatase (101) for TiO_2. The experimental results show that the bilayer ZnO/TiO_2 were the most efficient photo catalysts compared to the layer of TiO_2. This increased catalytic effect can attributed to the interface between the ZnO layer and the TiO_2 one, which modify significantly the chemical potential of the bilayer.

KEYWORDS
TiO_2; ZnO; ZnO/TiO_2; thin films; photo catalytic activity; RF magnetron sputtering

I. Introduction

The degradation of organic pollutants in water by photo catalysis, using semiconductors has been the subject of great study interest [1–5]. TiO_2 semiconductor, with energy band gap of 3.2 eV(Anatase phase), has very effective photo degradation activity because of its high efficiency, strong oxidizing power, low cost, inertness, non toxicity, low photo quantum efficiency and stability [6–9]. The recombination rate of the generate electro-hole pairs in the bulk semiconductor materials lowers their photo catalytic efficiency [1]. Coupled semiconductor photo catalysts may increase the photo catalytic efficiency by increasing the efficacy of charge separation and increasing the energy range of photo excitation [12–14]. Recently, there have been a number of studies associated to TiO_2 couples with a metal oxide, like ZnO [15, 16], for the aim of improving TiO_2 photo catalytic activity, ZnO was chosen as a buffer layer because of its high transparency, it has a similar band gap (3.2, 3.4 eV at room temperature) to TiO_2 thin films [11]. Some publications show that ZnO has attracted significant extend interest in the last decade [10]. Actually, ZnO is an excellent alternative photo catalyst with good photo catalytic activity; certainly it is not stable as titanium dioxide [17–19]. In the present work, a radio-frequency magnetron sputtering method was applied to synthesize ZnO, TiO_2 and ZnO/TiO_2 thin films under different temperatures. Their phase and crystal structure were characterized by X-ray diffraction and Raman spectroscopy. Subsequently, the photocatalytic

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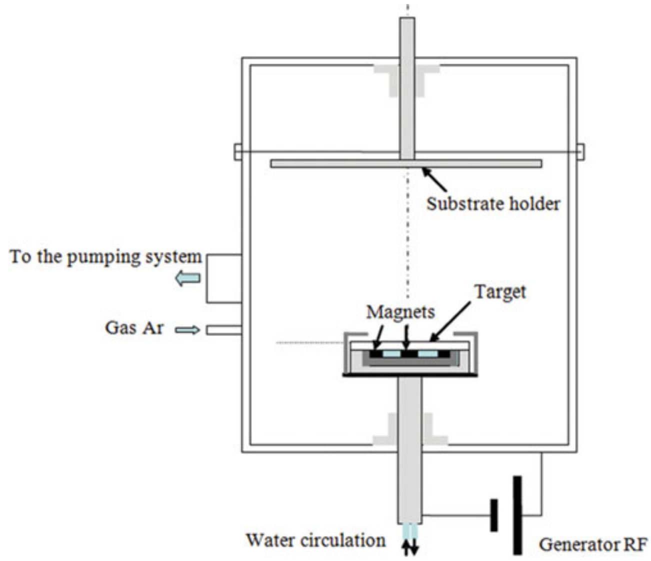

Figure 1. Drawing initial sputtering device.

activity of TiO_2 and ZnO/TiO_2 was evaluated by measuring the photo degradation of methylene blue under visible irradiation.

II. Experimental

1. *Experimental procedure and setup*

ZnO, TiO_2 and ZnO/TiO_2 thin films were deposited by a radio-frequency magnetron sputtering at a frequency of 13.56 MHz on SiO_2 substrates under different temperatures. For TiO_2 films, the purity of Ti target was (99.97%) and its diameter was 50 mm. The target used for deposition of ZnO target was (99.99%) with diameter of 25 mm. The prepared SiO_2 substrates were ultrasonically cleaned in alcohol and acetone for 15 min. The substrate was placed parallel to the sputtering target surface with a substrate target distance of 100 mm (see Fig. 1). Before each run, the targets were pre-sputtered in argon for 30 min to remove any surface contamination of titanium and zinc targets. ZnO film was deposited at chamber pressure of 0.1 mbar and base pressure of $1.8–10^{-6}$ mbar. After that TiO_2 film was prepared in a mixture of high-purity argon (40 sccm) and oxygen (10 sccm), and the working Ar pressure was 0.008 mbar and the base pressure of the chamber was $5*10^{-8}$ mbar and supplied power to the magnetron was about 2000 W. The sputtering time was 30 and 60 min for ZnO films and TiO_2 films, respectively. After the deposition, some samples were annealed in air atmosphere at 500°C and 600°C for 1h.

2. *Characterization techniques*

The structural characterization of the deposited samples was carried out by X-ray diffraction (XRD, Panalytical X'pert X-ray diffractometer). XRD was performed in $\theta-2\theta$ mode using monochromatic Cu-Ka (I = 30 mA and V = 40 KV) with a wavelength of $\lambda = 1.540560$ Å radiation. The Raman spectra were recorded on an Xplora spectrometer. The wavelength of the laser light was 638 nm. The photo catalytic performance of prepared films was evaluated by degradation of methylene blue (C16H18N3S) dissolved in aqueous solution with an

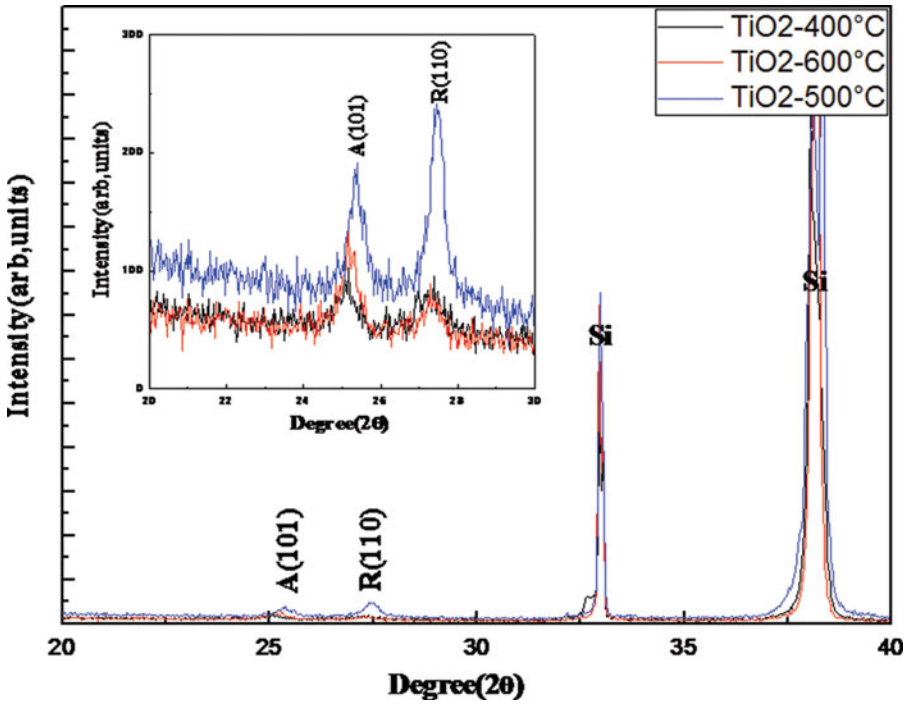

Figure 2. X-ray diffraction pattern of TiO2.

initial volume of 50 ml. All the photo catalysis experiments were performed at room temperature. For the photo catalytic reaction, each pollutant solutions were irradiated by 13.2 W lamp (which consists of mostly visible light spectrum in the range of 350–900 nm) in the presence of photo catalyst. TiO_2, ZnO and ZnO/TiO_2 films were dipped in pollutants solution and stirred in dark for 30 min to establish adsorption equilibrium between the solution and the catalysts.

III. Results and discussion

1. *X-Ray diffraction*

The phase composition of the prepared samples has been identified by XRD analysis (Fig. 2). The two composites are crystalline and have the diffraction peak at $2\theta = 34.428°$ marked by its miller index (002) corresponding to ZnO, indicating that the phase of ZnO was wurtzite (hexagonal structure, a = 3.2499 Å, b = 3.2499 Å, c = 5.2066 Å, density = 5.67g/cm^3). In addition to that, the sample deposited at 200°C exhibits higher peak intensity than that of sample deposited at 20°C.

Figure 3 represents the XRD pattern of TiO2 thin films at different temperatures. The peaks observed at 25.23° in all TiO_2 films corresponds to (101) plane of Anatase phase of TiO_2 (tetragonal structure, with the lattice parameters: a = 3.7971 Å, b = 3.7971 Å, c = 9.5790 Å and a density of 3.84 g/cm^3). In addition, broad peaks due to Rutile (tetragonal structure with lattice parameters: a = 4.6083 Å, b = 4.6083 Å, c = 2.9737Å and a density of 4.2g/cm3) TiO_2 are also observed at 27.37° correspondents to (110). This shows that mixed phase of Anatase-Rutile is present in the TiO_2 films deposit at 400°C. The film annealed at 600°C has a greater intensity than that deposited at 400°C. When annealing temperature is 500°C, it shows that the thin films crystallize. This is reflected by an increase of the diffracted intensity of the planes

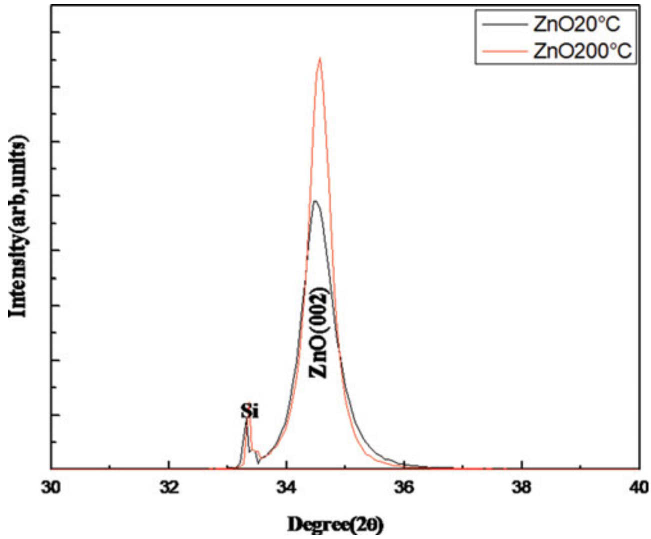

Figure 3. X-ray diffraction pattern of ZnO.

(101) and (110), which is probably due to the growth and the preferential orientation of the crystallite size.

Figure 4 shows the XRD spectra of ZnO/TiO_2 thin films obtained before and after calcinations. We observed the presence of a peak at 34.5° corresponding to (002) plane of ZnO for all the samples. From 400°C, we see the emergence of two peaks at 27.37°, 39.72° corresponding to (110) and (200) planes which suggest the formation of Anatase TiO_2. Beyond 500°C, there is onset of Anatase phase at 25.24° with an increase in the amplitude and the occurrence of

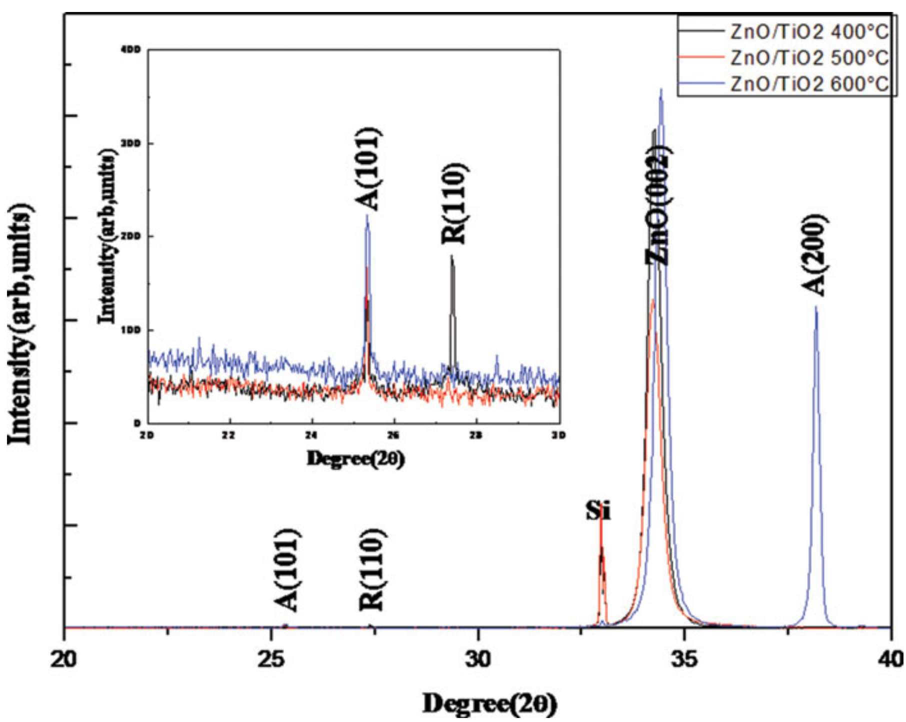

Figure 4. X-ray diffraction pattern of ZnO/TiO2.

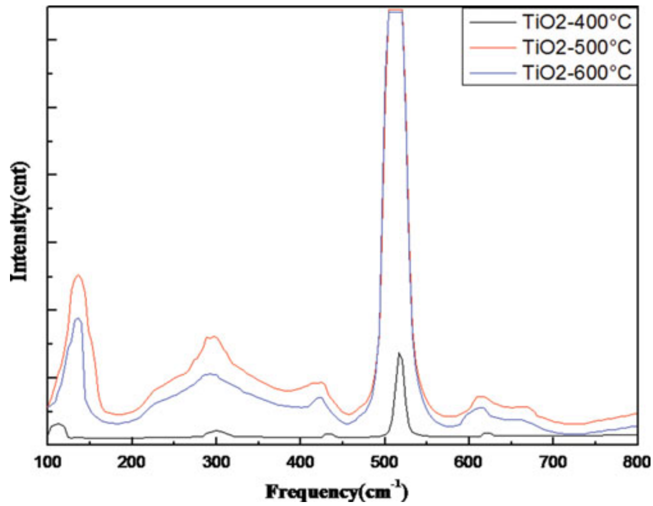

Figure 5. Raman spectroscopy of TiO2.

the Rutile phase at 39.7° corresponds to the plane (200). The observed peak at 25.24° can be attributed to the characteristics of the Rutile phase. A better crystallization of Anatase TiO_2 is observed when the annealing temperature is about 600°C.

2. *Raman spectroscopy*

Figure 5 shows the Raman spectra of ZnO films prepared at two temperatures. The observed peaks at 102 and 427cm^{-1} corresponding to the vibration modes of the ZnO phase. The crystalline film of ZnO deposited at 200°C is better than that deposited at 20°C.

Raman spectra were acquired and presented in Fig. 6 for TiO_2 thin films. It was reported that peaks at 142, 396, 518 and 632 cm^{-1} were characteristic peaks of Anatase TiO_2 [20]. The peak at 572 cm^{-1} is attributed to some species of silica substrate. In addition to these three bands of the Anatase phase, broad peaks centered at 614 and 811 cm^{-1} due to the Rutile phase is also evident in all the films of TiO_2 indicating the presence of a mixed Anatase-Rutile phase

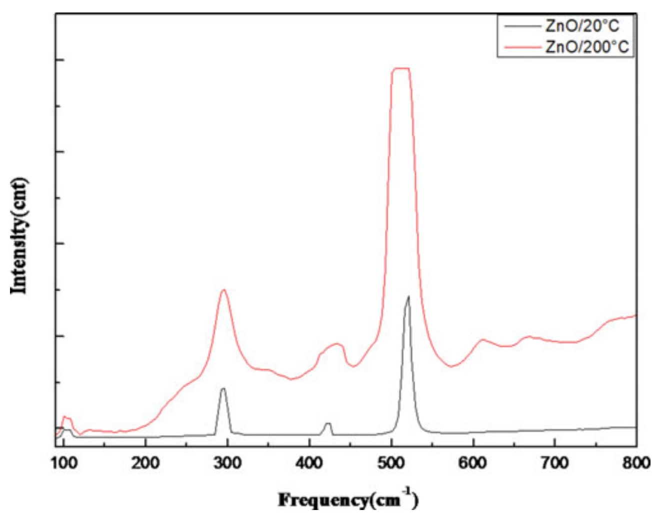

Figure 6. Raman spectroscopy of ZnO.

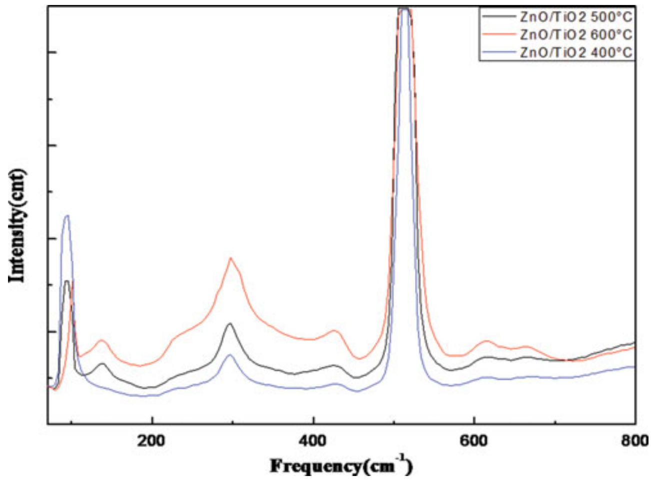

Figure 7. Raman spectroscopy of ZnO/TiO2.

on the surface. With the increase of temperature, the peaks of Anatase become more intense. A better crystallization of Anatase TiO_2 is formed when the temperature of annealing is 500°C.

Raman measurement of ZnO/TiO_2 bilayer film exhibits both ZnO and TiO_2 structure, such as the TiO_2 film exhibits a Rutile and Anatase structure, as show in Fig. 7. Therefore, it is presumed that another new phase may be presented. As a result, it is considered that high temperature can lead to the formation of substances and phases different from the Anatase TiO_2. Owing to the low intensity of vibration peaks of ZnO/TiO_2 compared with the TiO_2 film, it can be deduced that annealing temperature destroyed the crystalline of the TiO_2 film.

3. *Evaluation of photo catalytic activity*

The photo catalytic activities of TiO_2 and ZnO/TiO_2 thin films have been investigated. Fig. 8 presents the photo catalytic degradation of aqueous methylene blue in presence of the TiO_2 and ZnO/TiO_2 films. Under application on the surface of the film the electron-hole pairs is produced, then they will move through the film surface causing the degradation of methylene

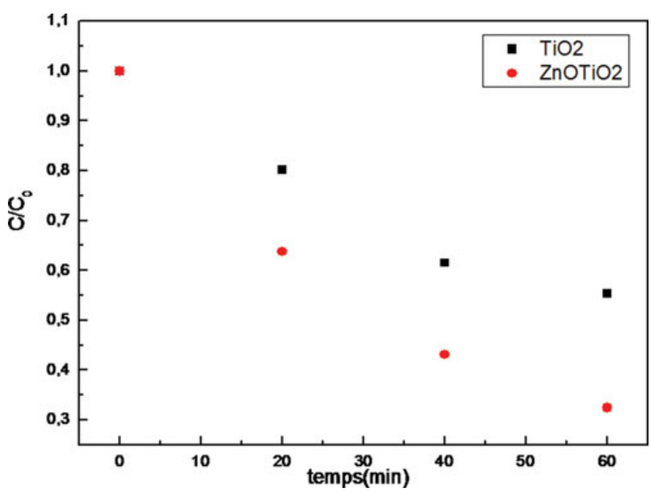

Figure 8. Photocatalytic degradation of MB in an aqueous solution of films.

blue molecules. As shows in Fig. 8, the degradability of methylene blue dye has stronger photo catalytic activity in the presence of ZnO/TiO_2 thin films compared to the TiO_2 deposited without ZnO layer. This can be attributed to less protection of TiO_2 layer and it's less crystalline without using ZnO layer.

IV. Conclusion

In this paper we investigated the effect of annealing and deposition temperature on the surface structure, phase formation and photo catalytic activities of TiO2, ZnO and ZnO/TiO2 thin films deposited on SiO2 substrates. It was found that:

- ZnO thin film deposited at 200°C has higher intensity of XRD compared to that of films deposited at 20°C.
- A better crystallization of Anatase TiO2 is observed when the annealing temperature is about 600°C.
- These results were confirmed also by Raman spectroscopy.

Our experiments as reported by Abdollahi Nejand et al. [21]. This increased catalytic effect can attributed to the interface between the ZnO layer and the TiO2 one, which modify significantly the chemical potential of the bilayer.

Acknowledgments

We acknowledge the financial support from CNRST-Maroc to Hassan II University of Casablanca (Project URAC10).

References

[1] Hoffmann, M.R., Martin, S.T., Choi, W.Y., Bahnemann, D.W. (1995). *Chem. Rev.*, *95*, 69.
[2] Suzuki, M., Ito, T., Taga, Y. (2001). *Appl. Phys. Lett.*, *78*, 3968.
[3] Kim, S., Fisher, B., Eisler, H.J., Bawendi, M. (2003). *J. Am. Chem. Soc.*, *125*, 11466.
[4] Schwitzgebel, J., Ekerdt, J.G., Gerischer, H., Heller, A. (1995). *J. Phys. Chem.*, *99*, 5633.
[5] Peralta-Zamora, P., de. Moraes, S.G., Pelegrini, R., Freire, M., Reyes, J., Mansilla, H., Duran, N. (1998). *Chemosphere.*, *36*, 2119.
[6] Fabbri, D., Prevot, A.B., Pramauro, E. (2006). *Appl. Catal. B Environ.*, *62*, 21.
[7] Asahi, R., Morikawa, T., Ohwaki, T., Aoki, K., Taga, Y. (2001). *Science.*, *293*, 269.
[8] Hernandez-Alonso, M.D., Fresno, F., Suarez, S., Coronado, J.M. (2009). *Science.*, *2*, 1231.
[9] Ozgur, U., Alivov, Y.I., Liu, C., Teke, A., Reshchikov, M.A., Dogan, S., Avrutin, V., Cho, S.J., Morkoc, H. (2005). *J. Appl. Phys.*, *98*, 041301.
[10] Fujishima, A., Rao, T.N., Tryk, D.A. (2000). *J. Photochem. Photobiol. C: Photochem. Rev.*, *1*, 1.
[11] Salem, I. (2003). *Catal. Reviews.*, *45*, 205.
[12] Liu, R., Ye, H., Xiong, X., & Liu, H. (2010). *Materials Chemistry and Physics.*, *121*, 432.
[13] Pozan, G. S., Isleyen, M., Gokcen, S. (2013). *Applied Catalysis B: Environmental.*, *140*, 537.
[14] Habib, M., Shahadat, M., Bahadur, N., smail, I., & Mahmood, A. (2013). *International Nano Letters.*, *3*, 1.
[15] Wang, C., Zhao, J.C., Wang, X.M., Mai, B.X., Sheng, G.Y., Peng, P.J., Fu, J.M. (2002). *Appl. Catal. B Environ.*, *39*, 269.
[16] Wang, C., Xu, B. Q., Wang, X. M., & Zhao, J. C. (2005). *J. Solid State Chem.*, *178*, 3500.
[17] Gaya, U. I., Abdullah, A. H., Hussein, M. Z., & Zainal, Z. (2010). *Desalination.*, *263*, 176.
[18] Han, J., Liu, Y., Singhal, N., Wang, L., & Gao, W. (2012). *Chemical Engineering.*, *213*, 150.
[19] Chekir, N., Benhabiles, O., Tassalit, D., Laoufi, N. A., & Bentahar, F. (2013). *3ème Conférence Internationale sur l'Eau.*, *18*, 20.
[20] Pattier, B. (2010). Étude des gels d'oxyde de titane entrant dans la fabrication de cellules photovoltaïques.
[21] Abdollahi Nejand, B., Sanjabi, S., Ahmadi, V. (2010). *Vacuum.*, *85*, 400.