

# Unit 11 “Nanotechnology and nanometrology”

## Two-steps formation of ZnO-loaded TiO<sub>2</sub> nanotube array films with enhanced photocatalytic performance

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### Abstract

Recent results are reported on the investigation of the optical properties of ZnO-loaded TiO<sub>2</sub> nanotubes array layers. TiO<sub>2</sub> nanotubes layers formed by electrochemical anodization of the Ti surface were subsequently loaded with controllable amounts of ZnO, originating from a magnetron sputtering source. Structural and optical analyses of the ZnO-TiO<sub>2</sub> composite films with different ZnO coverage were carried out to further investigate the electronic properties of the composite films. The results are discussed in terms of the occurrence of the ZnO-TiO<sub>2</sub> heterojunctions and the bandgap modification. These effects increase the photocatalytic yield and activation duration of the films.

### Introduction

TiO<sub>2</sub> semiconductors feature peculiar advantages as photocatalytic materials, in spite of two main drawbacks, which diminish their area of applications: (a) less than 5% of the energy of the incident solar radiation can be harvested for surface photoactivation, and (b) the high recombination rate of photo-generated electron-hole pairs in pristine titania reduces the photocatalytic yield of the surface. A red-shift of the absorption edge of titania by doping with various chemical elements was reported extensively [1]. To increase the lifetime of the charge carriers, one can manipulate their spatial separation, such as inside p-n junctions, which can be formed on the TiO<sub>2</sub> surface by growing ultra-thin oxide islands of materials with convenient band gap (WO<sub>3</sub>, ZnO, etc.) [2, 3]. Besides enhanced charge separation, our current results point to the alteration of the band gap of ZnO/TiO<sub>2</sub> nanocomposites, and suggest a synergic effect in terms of widening the photoactivation range.

### Materials and Methods

The synthesis of the samples is described in detail elsewhere [3]. Briefly, on top of the anodized TiO<sub>2</sub> nanotube layers, ultra-thin ZnO thin films with gradually increasing thickness were deposited by RF magnetron sputtering. ZnO films coverage was adjusted *via* growth duration, from 10 to 30 min, with a step of 10 min. A Shimadzu LabX XRD-6000 diffractometer was used for structural characterization, while the diffuse reflectance spectra (DRS) were recorded (within the 200 – 1100 nm wavelength range) using an Analytik Jena Specord 210 Plus spectrometer, equipped with a collecting integrating sphere, at an angle of 8°.

## Results and Discussion

The X-ray diffraction patterns of the TZN\_x samples are presented in Fig. 1, where TZN stands for ZnO/TiO<sub>2</sub> layers, and x – for the ZnO deposition time (in minutes). Two distinct diffraction peaks are evident, at  $2\theta = 25.30^\circ$  and  $27.43^\circ$ , corresponding to the reflections on the anatase A(101) and rutile R(110) planes. The diffraction peaks at  $2\theta = 35.05^\circ$ ,  $38.42^\circ$ ,  $40.16^\circ$ , and  $52.98^\circ$  originate in the reflections on the Ti planes, namely T(100), T(002), T(101), and T(102), respectively. The intensity of the A(101) peak decreases with the increase of the amount of ZnO coverage. The average crystalline grain size in the TiO<sub>2</sub> nanotube wall, derived from the A(101) signal, fluctuates between 28.9 nm and 27.3 nm.

Fig. 2 shows a detail of the UV–Vis absorbance spectra (within the 350 – 500 nm range) of the same samples, where a noticeable shift in the absorption edge of the ZnO-loaded films occurs. The band gap energy ( $E_g$ ) was determined using the equation  $E_g = 1240/\lambda_g$  (eV), where  $\lambda_g$  is the absorption edge wavelength, which was obtained from the intercept of the tangent of the absorption curve with the abscissa.

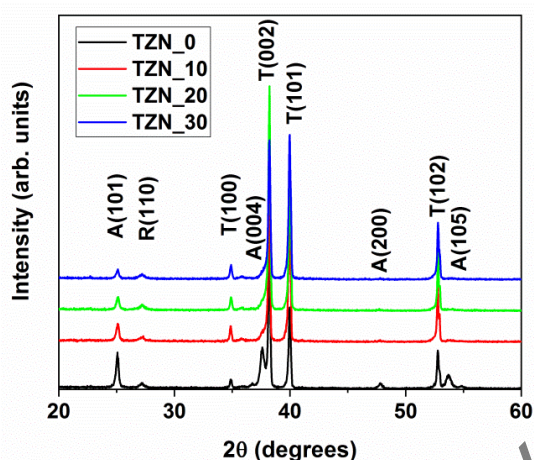


Fig. 1. X-ray diffraction patterns of the TZN\_x samples

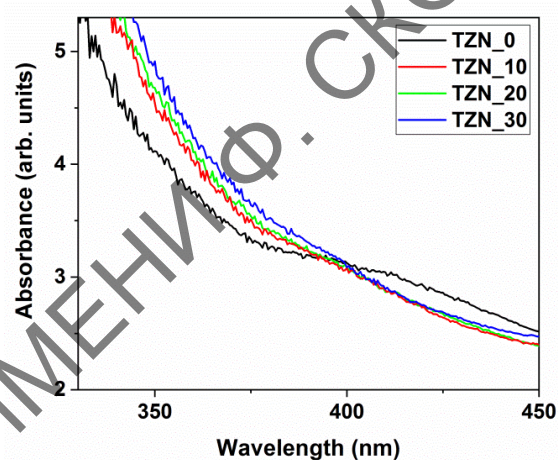


Fig. 2. Absorbance spectra of the investigated samples

The calculated band gap energy ( $E_g$ ) for the four ZnO loading conditions decrease from  $E_g = 3.25$  eV (for TZN\_0) to 3.16 eV (for TZN\_30). We ascribed this alteration to the dual effect of local doping of titania with Zn species and structural changes (anatase-to-rutile ratio) in the interface region.

## Conclusion

ZnO/TiO<sub>2</sub> heterojunctions have been fabricated by sputtering ZnO films on top of anodized TiO<sub>2</sub> nanotube array layers. Anatase and rutile crystalline phases with different ratios were detected in the nanotube volume. A slight decrease of the crystalline grain size in the sample with a higher amount of ZnO thin film was noticed. As demonstrated by the DRS data, loading ZnO material on top of TiO<sub>2</sub> nanotubes results in shifting the absorption edge of materials by 2.76 percent, most probably as the effect of local modification of crystallinity and chemical environment.

Based on cyclic voltammetry and surface wettability techniques, future research is foreseen to evaluate the potential synergic effect of the heterojunctions development as a path for higher-performance photocatalytic applications.

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## References

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mixed in the diluted lemon acid (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>) and glycerol C<sub>3</sub>H<sub>8</sub>O<sub>3</sub> (volume ratio 1:4) solution to form a Fe precursor solution. The solution was continuously stirred for 30 min at 50°C to completely dissolve the ferric nitrate. Bi and Sm precursor solution was obtained through a similar process. Secondly, Fe precursor solution was mixed with Bi and Sm precursor solution