Nanostructures based on ZnO and TiO$_2$ oxides produced by PLD in open air

A Dikovska$^{1,4}$, M Gancheva$^2$, Ru Nikov$^1$, G Avdeev$^3$, R Iordanova$^2$ and N Nedyalkov$^1$

$^1$Institute of Electronics, Bulgarian Academy of Sciences, 72 Tsarigradsko Chaussee, Sofia 1784, Bulgaria
$^2$Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev str., Bl. 11, 1113 Sofia, Bulgaria
$^3$Rostislaw Kaischew Institute of Physical Chemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev str., Bl.11, 1113 Sofia, Bulgaria

E-mail: dikovska@ie.bas.bg

Abstract. We report on the fabrication of highly porous metal-oxide nanostructures by pulsed laser deposition performed in air at atmospheric pressure. The depositions were performed by ablating synthesized ZnO and a mixed target of ZnO and TiO$_2$ as initial materials. The attention was focused on the structure, morphology, optical and photocatalytic properties of the as-deposited nanostructures of the ZnO-TiO$_2$ system. The technology applied leads to the formation of nanostructures composed of nanoparticles. The as-prepared samples possess a high transmittance in the visible and near IR region with an optical band gap in the range of 3.1 – 3.2 eV. It was demonstrated that the as-deposited ZnO and ZnO-TiO$_2$ nanostructures degrade Rhodamine B up to 43 – 44% after 300-min UV irradiation.

1. Introduction

Due to their remarkable physical and chemical properties, semiconductor oxides are among the most widely studied materials in view of applications, such as gas sensors, transparent electrodes, catalysts etc. [1]. One approach to improving the functionality of these materials is producing a nanostructured morphology [2]. Recently, pulsed laser deposition (PLD) in air at atmospheric pressure (in open air) proved to be a promising technique for inexpensive and easy fabrication of highly porous nanostructures composed by nanoparticles [3–6]. In such an environment, the ns-laser ablation leads to the formation of nanoparticles and nanoparticle’ aggregates in the plasma plume close to the target due to the fast condensation of the ablated material [7]. This technology allows the fabrication of high-purity nanostructures since no chemicals are used. Another advantage of this technology is the use of simple equipment, i.e., no vacuum system is necessary.

Another approach to modifying and improving the performance of a semiconductor oxide is by forming a compound or a composite with other oxides. ZnO is one of the most promising and reliable

$^4$ To whom any correspondence should be addressed.
materials due to its specific properties, namely, optimal conductivity, low toxicity, low cost, chemical and thermal stability, as well as capability of being grown easily in a variety of nanostructures [8]. TiO$_2$ is well known as a good candidate for degrading environmental contaminants due to its high photocatalytic activity, non-toxic nature, stability in aqueous solutions and a relatively low cost [9]. However, as has been previously reported, very fast recombination of electron-hole pairs takes place in a single semiconductor (such as TiO$_2$ and ZnO), which significantly reduces the photocatalytic efficiency of these materials. Since TiO$_2$ and ZnO both have excellent properties and similar band gap energy, this drawback can possibly be overcome by combining these two semiconductor oxides to enhance their photocatalytic efficiency. Recently, the coupled photo-catalyst ZnO/TiO$_2$ has been studied extensively and the results showed that the photocatalytic activity of ZnO/TiO$_2$ was higher than that of the single oxide [10]. Siwińska-Stefańska et al. reported a binary oxide system TiO$_2$-ZnO (9:1) that exhibited a high photocatalytic activity, namely, 95% after a 180-min irradiation, in the decomposition of C.I. Basic Violet [10, 11]. However, the easy and low-cost fabrication of composite metal-oxide photocatalysts in an environmentally friendly manner using conventional equipment is still a challenge.

In this work, highly porous nanostructures based on ZnO were fabricated by PLD in open air. We studied the effect of introducing a small amount of TiO$_2$ into the ZnO target on the structure, morphology and optical properties of the deposited samples. Preliminary results on the photocatalytic properties of the as-prepared nanostructures are also presented.

2. Experimental

The metal-oxide nanostructures were produced by PLD in air at atmospheric pressure (in open air). The targets used in the depositions were composed of pure ZnO (99.99 %) and a mixture of 10 wt% TiO$_2$ (99.99 %) in ZnO (99.99 %). The ablation process was carried out by nanosecond laser pulses emitted by a Nd:YAG (Lotis LS-2147) laser system oscillating at its fundamental wavelength (λ = 1064 nm). The target was rotated by an electric motor to prevent its perforation during prolonged laser irradiation. The ablated material was deposited on Si (100) or SiO$_2$ (001) substrates. The distance between target and substrate was fixed at 10 mm. The samples were deposited at a laser fluence of 10 J/cm$^2$. The PLD process lasted 10 min at a pulse repetition rate of 10 Hz.

The morphology of the as-deposited samples was observed by scanning electron microscopy (SEM) using a LYRA I XMU system (Tescan). The crystalline structure and phase composition of the samples were explored by an Empyrean diffractometer (PANalytical) by glancing (3°) incidence X-ray diffraction (GIXRD) using CuKα radiation. The crystalline phases were identified using the PANICSD and COD database cards. The average crystal size and the quantitative phase composition of the samples were obtained by profile fitting of the existing phases using the HighScore Plus and ReX software [12,13]. The optical properties of the structures produced were analyzed based on their transmission spectra taken by an optical spectrometer (Ocean Optics HR 4000). The photocatalytic activity of the samples was evaluated by following the degradation of a model aqueous solution of Rhodamine B (Rhb) (10 ml, 20 ppm, pH 6) upon UV-light irradiation (λ$_0$ = 365 nm, 18 W). The suspension was stirred for 1 h to reach absorption-desorption equilibrium between the RhB and the photo-catalyst under dark conditions. The absorption spectrum of the decomposed dye was collected using a Carry 1E UV-visible spectrophotometer. The degradation rate was calculated as:

$$\text{Photodegradation rate} = \left(\frac{C_0 - C_t}{C_0}\right) \times 100,$$

where $C_0$ is the initial concentration at 0 min and $C_t$ is the concentration at time $t$.

3. Results and discussion

SEM images of the samples produced by PLD are presented in figure 1. In open air, the ablation process leads to a direct deposition of nanoparticles and nanoparticle aggregates formed in the plasma plume due to condensation resulting in the growth of a highly porous structure on the substrate, as we reported earlier [3–6]. Figure 1 (a) shows a SEM image of the sample produced by ablating a ZnO
target. As seen, the structure is highly porous and consists of aggregated nanoparticles. Figure 1 (b) is a SEM image of the sample deposited from a mixed target, namely, 10 wt% TiO$_2$ in a ZnO target. The sample’s morphology is similar to that of the sample deposited from a pure ZnO target. However, a higher porosity is observed compared with the pure ZnO sample.

Figure 1. SEM images of nanostructures deposited in open air by PLD from (a) ZnO and (b) ZnO-TiO$_2$ targets.

The XRD patterns of the ZnO and ZnO-TiO$_2$ nanostructures are presented in figure 2. The XRD pattern of the sample deposited from the pure ZnO target is shown in figure 2 (a). The pattern is indexed to a hexagonal structure of bulk ZnO (ICSD 98-002-6170) with an estimated ZnO crystallites size of about 30 nm. The XRD pattern of the sample deposited from the mixed ZnO-TiO$_2$ target is presented in figure 2 (b). The phase composition of the sample is identified as a combination of ZnO and dizinc titanium oxide (Zn$_2$TiO$_4$, ICSD 98-008-0851). The predominant phase is zinc oxide, with the ratio between ZnO and Zn$_2$TiO$_4$ being 85% to 15%. The average crystallite size of the ZnO and Zn$_2$TiO$_4$ phases is about 30 nm and 60 nm, respectively. It should be noted that no nitrogen impurities were detected in spite of the depositions being performed in air.

Figure 3 shows the UV–VIS transmission spectra of the samples deposited from pure ZnO and ZnO-TiO$_2$ targets. As seen, both samples are transparent in the visible spectral range. However, increasing the sample thickness shifts the absorption edge of both spectra to the longer wavelengths and decreases the optical transmission in the visible range as a whole (not shown). This

Figure 2. XRD patterns of samples deposited by PLD in open air from (a) ZnO and (b) ZnO-TiO$_2$ targets.
The result has to do with the increase of the scattering losses with the thickness in the porous 3D structure shown in figure 1. The optical band gaps of samples were calculated using Tauc’s equation:

\[ a h v = A (h v - E_g)^n, \]

where \( h \) is Planck’s constant, \( \alpha \) is the absorption coefficient, \( \nu \) is the photon frequency, \( A \) is a constant, \( E_g \) is the optical band gap and \( n = 1/2 \) is used for ZnO [14]. Based on this equation, the band gaps of the samples deposited from pure ZnO and from a ZnO-TiO\(_2\) target were estimated to be 3.22 eV and 3.14 eV, respectively, as illustrated in the inset of figure 3. Thus, a small amount of TiO\(_2\) introduced into a ZnO target leads to the deposition of samples with a narrower band gap compared to the one of pure ZnO, which is in good agreement with previous reports [15].

![Graph showing transmission spectra](image)

**Figure 3.** Transmission spectra of samples produced by PLD in open air from (a) ZnO and (b) ZnO-TiO\(_2\) targets.

The photo-degradation of RhB was used as a model reaction to evaluate the photocatalytic activity of the materials prepared by monitoring the changes in the main absorption band at 555 nm of the dye. For comparison, a dye solution without a catalyst was exposed under the same conditions (figure 4 (a)).

![Graph showing decomposition of RhB](image)

**Figure 4.** Decomposition of the RhB during UV-light irradiation.
The photo-degradation of PhB in the presence of a catalyst, namely, ZnO or the nanocomposite ZnO-TiO₂, is illustrated in figure 4 (b) and (c), respectively. As seen, the RhB solution degradation is too slow and increases up to 43% and 44% after a 300-min irradiation in the presence of either catalyst. It should be noted here that introducing a small amount of TiO₂ into ZnO target leads to the preparation of a target with a higher ablation threshold compared with pure ZnO. Consequently, less material is deposited on the substrate than in the case of a ZnO target. The amount of material ablated from the mixed ZnO-TiO₂ target used for photo-degradation in this work was 0.07 mg for a 10-ml dye solution, a quantity substantially lower than the one used and reported in the open literature [11]. In order to obtain a better photocatalytic performance, the composition of the metal-oxide used should be optimized.

4. Conclusions
Highly porous composite samples consisting of nanoparticles or nanoaggregates were fabricated by laser ablation in air at atmospheric pressure of a ZnO target doped with 10 wt% TiO₂. The sample deposited from the ZnO-TiO₂ target possessed a higher porosity compared to pure ZnO sample; its crystalline phase composition was identified as a combination of the ZnO and Zn₂TiO₄ oxides. All samples were transparent in the visible and near IR range of the spectrum, while increasing their thickness decreased the optical transmission as a whole due to an increase in the scattering losses in the porous structure. A small amount of TiO₂ introduced into the ZnO target led to the deposition of samples with a narrower band gap compared to the one of pure ZnO. The samples prepared possess a photocatalytic activity even for relatively small amounts of photo-catalyst – around 0.07mg.

Acknowledgements
The authors acknowledge the financial support of project KP-06-N37/20 “Formation and physical properties of composite nanostructures of metal oxides and noble metals” under the Competition for Financial Support of Basic Research Projects – 2019 Program of the Bulgarian National Science Fund.

References
[1] Yu X, Marks T J and Facchetti A 2016 Nat. Mater. 15 383
[2] Korotcenkov G ed 2018 Metal Oxide Nanostructures: Synthesis, Properties and Applications (Elsevier)
[3] Nikov R G, Dikovska A O, Nedyalkov N N, Atanasov P A, Atanasova G, Hirsch D and Rauschenbach B 2017 Appl. Phys. A: Mater. Sci. & Proc. 123 657
[4] Atanasova G, Dikovska A Og, Dilova T, Georgieva B, Avdeev G V, Stefanov P and Nedyalkov N N 2019 Appl. Surf. Sci. 470 861
[5] Dilova T, Atanasova G, Dikovska A Og, Avdeev G V, Stefanov P and Nedyalkov N N 2018 Proc. SPIE 110470 110470G
[6] Dilova T, Atanasova G, Dikovska A Og and Nedyalkov N N 2020 Appl. Surf. Sci. 505 144625
[7] Amoruso S, Bruzzese R, Spinelli N, Velotta R, Vitiello M and Wang X 2003 Phys. Rev. B: Condens. Matter & Mater. Phys. 67 224503
[8] Wang J, Chen R, Xiang L and Komarneni S 2018 Ceram. Int. 44 7357
[9] Nakata K and Fujishima A 2012 J. Photochem. Photobiol. C: Photochem. Rev. 13 169
[10] Shifu C, Wei Z, Wei L and Sujuan Z 2008 Appl. Surf. Sci. 255 2478
[11] Siwińska-Stefanik K, Kubiak A, Piascecki A, Dobrowolska A, Czaczyk K, Motylekno M, Rafaja D, Ehrlisch H and Jesionowski T 2019 Appl. Surf. Sci. 463 791
[12] Degen T, Sadki M, Bron E, König U and Nérent D 2014 Powder Diffraction 29 S13
[13] Bortolotti M, Lutterotti L and Lonardelli I 2009 J. Appl. Cryst. 42 538
[14] Chahmat N, Souier T, Mokri A, Bououdina M, Aida M S and Ghers M, 2014 J. Alloys Comp. 593 148
[15] Upadhyay G K, Rajput J K, Pathak T K, Kumar V and Purohit L P 2019 Vacuum 160 154