Chapter 13
Wetting and Photoactive Properties of Laser Irradiated Zinc Oxide – Graphene Oxide Nanocomposite Layers

A. Datcu, A. Pérez del Pino, C. Logofatu, A. Duta, and E. György

Abstract Laser irradiation of zinc oxide (ZnO) – graphene oxide (GO) nanocomposite layers obtained by the drop-casting method has been carried out using a frequency quadrupled Nd:YAG ($\lambda = 266$ nm, $\tau_{FWHM} \cong 4$ ns, $\nu = 10$ Hz) laser source in air at atmospheric pressure or in controlled nitrogen atmosphere. The dependence of the morphology and chemical composition of the layers on the incident laser fluence, the number of accumulated laser pulses, and the ambient atmosphere has been studied. A significant improvement of the wetting and photoactive properties of the laser processed layers was attributed to nitrogen incorporation. The kinetics of the variation of the water contact angle when the samples are submitted to laser irradiation in nitrogen atmosphere is faster than that of the samples irradiated in air, the surfaces becoming super-hydrophilic under UV light irradiation.

Keywords Zinc oxide-graphene oxide nanocomposite layers • Laser irradiation • Superhydrophilicity • Wettability • Photoactive properties

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13.1 Introduction

For industrial applications, one of the most exciting sub-fields of nanotechnology is nanocatalysis focused on the photoactive properties of materials [1]. Much attention has been paid to the development of novel materials displaying more than one interesting property. Among the photoactive materials, those based on zinc oxide (ZnO) have deserved special attention due to its potential ability to form multifunctional materials, combining its semiconducting features (ZnO is a wide band-gap semiconductor) with a high thermal and chemical stability, and good transparency in the infrared-visible spectral region [2]. Due to these attractive properties ZnO is widely investigated, being a promising material for many applications in optoelectronics, gas sensors, transducers, filters, catalysts, as well as in biomedical fields due to its biocompatible properties [3]. Furthermore, transition metal oxides, and in particular ZnO, have peculiar wetting and photoactive properties [4]. It was found that their typical hydrophobic or slightly hydrophilic character changes to highly hydrophilic upon UV light irradiation [5]. Several products have already been designed based on this phenomenon, e.g. self-cleaning construction materials or anti-fogging surfaces [6]. As reported, the original hydrophobic character of the films recovers after storage in the dark [4]. Thus, the control of wetting contact angle even in the absence of UV light presents a challenge of this field, providing the possibility to wash the surface contaminants where UV light cannot be ensured. An option to obtain highly hydrophilic ZnO nano-composite is to combine it with other highly hydrophilic materials, such as graphene oxide (GO) [7] which offer the possibility to tailor the water contact angle. Motivated by this idea, we herein report on a study of UV laser irradiation in air and controlled nitrogen atmosphere, the incident laser fluence and the number of subsequent laser pulses, on the surface morphology and photoactive properties of ZnO/GO nanocomposite thin films by monitoring the water wetting angle evolution under UV light irradiation.

13.2 Experimental

Preparation of ZnO/GO Nanocomposites Films A 100 μl dispersions of 1 wt.% ZnO nanoparticles (NPs) and 0.5 wt. % GO plates in distilled water was deposited by the drop-casting method on the surface of 10×10 mm^2 (001) SiO_2 quartz substrates and dried in air at atmospheric pressure and at 60 °C during 30 min.

Irradiation of the Obtained Sample The reaction chamber where the sample was placed was evacuated down to a residual pressure of 10^{-4} Pa. The laser irradiation of the films was performed with a Nd:YAG ($\lambda = 266$ nm, $\tau_{FWHM} = 4$ ns, $\nu = 10$ Hz) laser source. The number of subsequent laser pulses was chosen in the range of 10–2,000. The incident laser fluence was set at 10, 30, 50 or 100 J/cm^2. The irradiations were performed in air at atmospheric pressure or nitrogen at a pressure of 2×10^4 Pa.

Characterizations Morphological properties of the deposited thin films were investigated by field emission scanning electron microscopy (FE-SEM) with the aid of a QUANTA FEI 200 FEG-ESEM system. Energy dispersive X-ray spectroscopy (EDX) analyses were carried out using an EDS Thermo Scientific Ultra Dry silicon drift X-ray detector controlled by NORAN System 7 software. The hydrophilic properties of the films were determined by measuring the contact angle of distilled water using an OCA-20 contact angle system from DataPhysics Instruments. A 3 μL volume liquid drop was placed in 0.5 μL/s steps on the surface of the ZnO/GO composite thin films. Contact angles were measured during 5 min time interval, the data were recorded with one second step.

13.3 Results and Discussion

SEM images of a ZnO/GO composite reference thin film obtained by the drop-cast method are shown in Fig. 13.1. The ZnO NPs partially cover the micro sized GO sheets (Fig. 13.1a). The higher amplification FE-SEM image (Fig. 13.1b) reveals that the ZnO NPs have a homogeneous size distribution with an average diameter around 20 nm (Fig. 13.1b).

The drop-cast samples were submitted to laser irradiation in air at atmospheric pressure (Fig. 13.2) and in controlled nitrogen atmosphere at a pressure of 2×10^4 Pa (Fig. 13.3). In air, at the lowest laser fluence value of 10 mJ/cm^2, and 1,000 pulses a melting of the ZnO NPs takes place followed by the formation of hundreds of nm sized interconnected grains (Fig. 13.2a), while for the GO sheets no morphological changes can be observed in the FE-SEM images (Fig. 13.2b) under the same irradiation conditions. Inter-connected molten aggregates of ZnO NPs can also be observed at a higher laser fluence of 30 mJ/cm^2 but a lower number of pulses

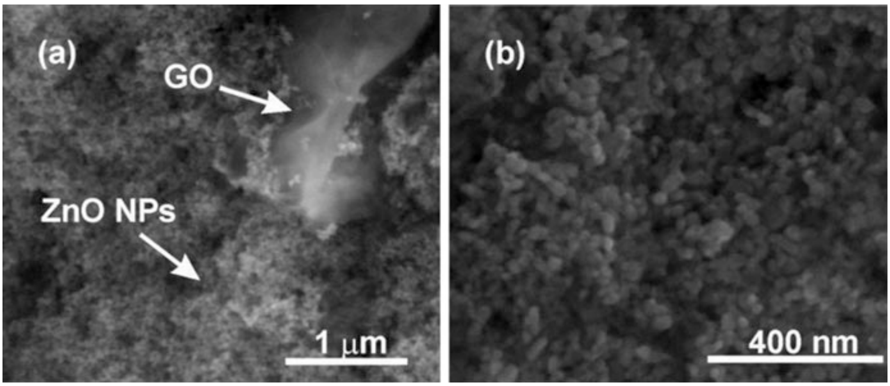

Fig. 13.1 FE-SEM images of a composite reference thin film consisting of ZnO NPs and GO plates

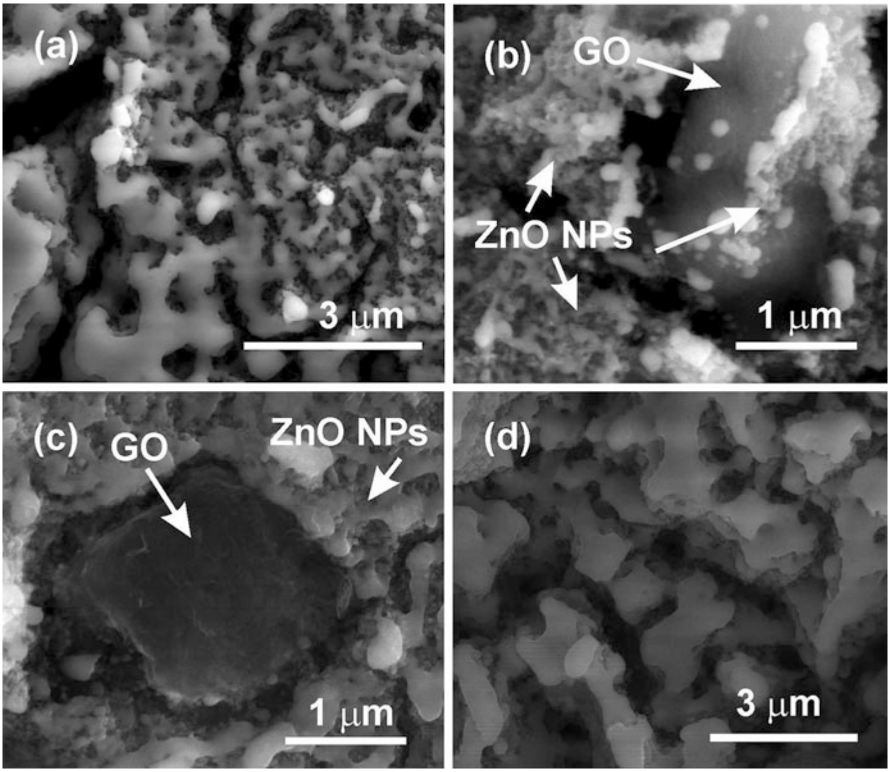

Fig. 13.2 FE-SEM images of ZnO/GO composite thin films irradiated in air at (**a**, **b**) 10 mJ/cm^2 laser fluence and 1,000 subsequent laser pulses, and 30 mJ/cm^2 laser fluence with (**c**) 100 or (**d**) 1,000 subsequent laser pulses

(Fig. 13.2c). With the accumulation of the laser pulses the dimensions of the inter-connected molten aggregates increases (Fig. 13.2d). However, with the increase of the laser fluence value to 50 mJ/cm^2 vaporization of the irradiated material takes place even at 10 subsequent pulses only.

It is well-known that laser-induced melting and vaporization thresholds are significantly reduced for multi-pulse irradiation as compared to single-shot thresholds. This interesting phenomenon, in the literature referred to as incubation effect, can be explained by the changes in absorption of the incident laser radiation caused by the creation of radiation-induced defects on the surface of the irradiated material [8].

In parallel experiments the ZnO/GO drop-cast samples were irradiated in controlled nitrogen atmosphere (Fig. 13.3). In nitrogen atmosphere both the incident laser fluence and the number of laser pulses necessary for the onset of the melting process are higher as compared to the experiments performed in air. For an irradiation with 50 mJ/cm^2 fluence and 2,000 subsequent pulses the melting of ZnO NPs takes place followed by the formation of inter-connected structures (Fig. 13.3a) similar to those observed when the irradiations were conducted in air.

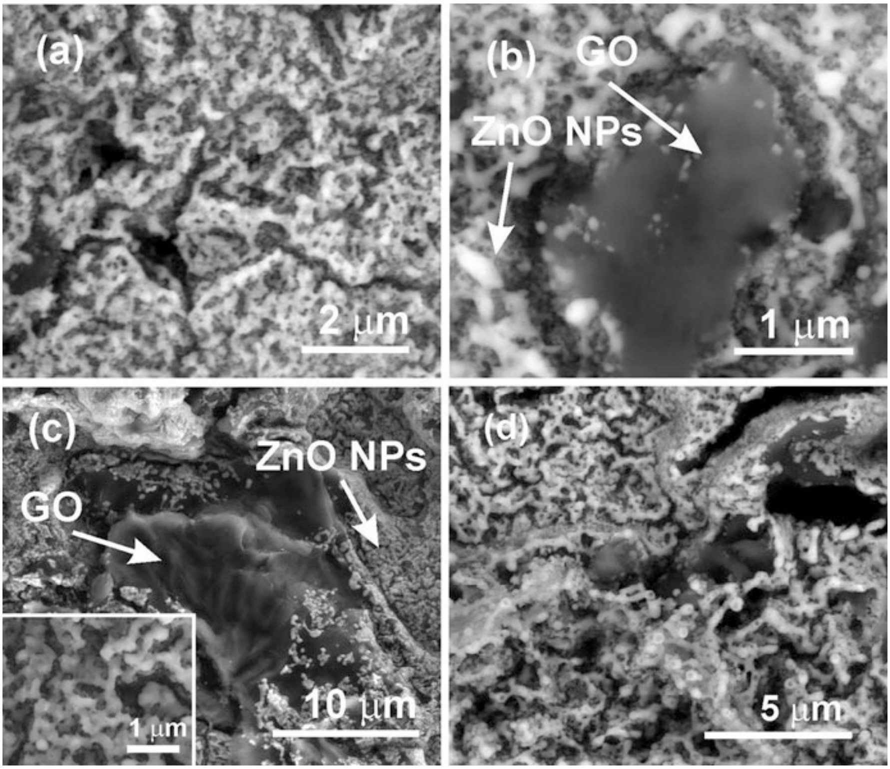

Fig. 13.3 FE-SEM images of ZnO/GO composite thin films irradiated in 2×10^4 Pa nitrogen atmosphere at (**a**) 50 mJ/cm^2 laser fluence and 2,000 subsequent laser pulses and 100 mJ/cm^2 laser fluence and (**b**) 10, (**c**) 1,000, or (**d**) 2,000 subsequent laser pulses

At a laser fluence of 100 mJ/cm^2 melting of the ZnO NPs can be observed even at 10 subsequent laser pulses (Fig. 13.3b). An increase of the number of pulses leads to a network-like structure consisting of large, hundreds of nm sized particles (Fig. 13.3c, d) formed most probably by the coalescence of molten ZnO NPs.

Figure 13.4 shows a FE-SEM image of a ZnO/GO composite thin film irradiated in 2×10^4 Pa nitrogen with 100 mJ/cm^2 laser fluence and 1,000 subsequent pulses, and the corresponding EDX mapping of the element distribution (Zn, C, O, N) on a surface.

The difference of the surface composition is clearly visible in the C and Zn maps; the regions with more intense C signals corresponding to GO plates surrounded by ZnO NPs visible in the Zn signal. The O signal contains contributions both from the GO sheets and ZnO NPs as well as from the SiO_2 quartz substrate. On the other hand, the less intense N signal belongs to nitrogen incorporated during laser processing.

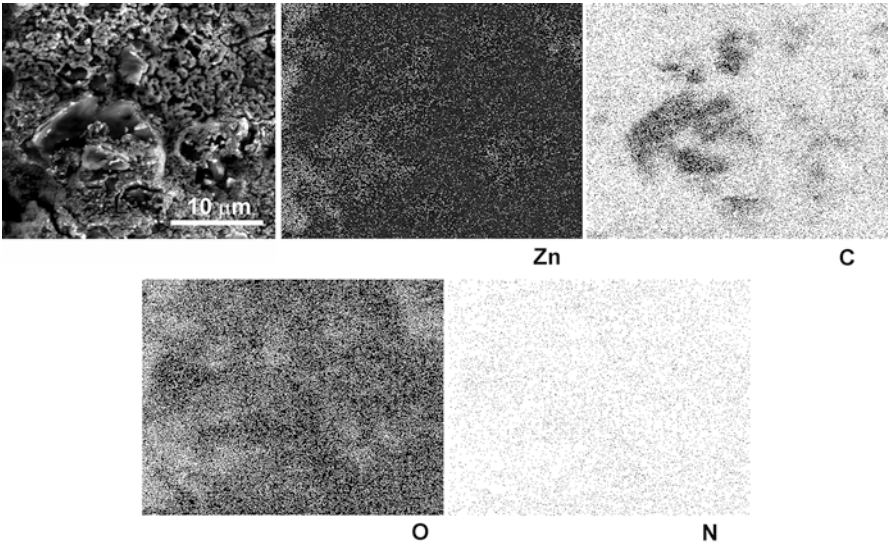

Fig. 13.4 FE-SEM image of a ZnO/GO composite thin film irradiated in 2×10^4 Pa nitrogen atmosphere with a fluence of 100 mJ/cm^2 and 1,000 subsequent pulses, and the corresponding EDX maps of the elements Zn, C, O, and N. The surface area of the FE-SEM image is 30×30 μm^2

The static contact angle values of ZnO/GO composites measured in the absence of UV light irradiation in air as well as nitrogen atmosphere are much lower than those characteristic for pure ZnO reported in the literature [4c, 8]. The reduction kinetics of the contact angle is approximately five times faster in the case of the samples irradiated in nitrogen as compared to those obtained in air, the surface becoming super-hydrophilic after only 1 min of UV light irradiation. The better performance of the samples submitted to laser treatment in nitrogen as compared to those irradiated in air is attributed to nitrogen inclusion in the films. The contact angle decrease on the UV illuminated surfaces is attributed to dissociative adsorption of water molecules on the photogenerated surface defective oxygen vacancy sites [4c]. It is known that N doping of metal oxides enhances the formation of oxygen vacancies [9].

13.4 Conclusions

The based ZnO/GO nanocomposite thin films were deposited by the drop-cast method using ZnO/GO aqueous dispersions. The drop-cast samples were submitted to laser irradiations using a frequency quadrupled Nd:YAG laser source in air and controlled nitrogen atmosphere. The results obtained for the laser processed composite layers for the water wetting angle evolution suggest that the incorporation of

GO in the ZnO thin films improves the photoactive properties after irradiation atmosphere in air and in nitrogen. A better performance is obtained in the case of thin film nano-composite ZnO/GO irradiated in nitrogen.

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