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Journal of Polymer Science B, Hoboken : John Wiley and Sons, v. 52, n. 4, p. 333-337, Feb. 2014
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Fabrication of Zinc Oxide Nanowires/Polymer Composites by Two-Photon Polymerization

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Received 26 August 2013; revised 7 November 2013; accepted 11 November 2013; published online 29 November 2013

DOI: 10.1002/polb.23418

ABSTRACT: We present an approach to fabricate ZnO nanowires/polymer composite into three-dimensional microstructures, based on two-photon polymerization direct laser writing, a fabrication method that allows submicrometric spatial resolution. The structural integrity of the structures was inferred by scanning electron microscopy, while the presence and distribution of ZnO nanowires was investigated by energy dispersive X-ray, Raman spectroscopy, and X-ray diffraction. The optical

properties of the produced composite microstructures were verified by imaging the characteristic ZnO emission using a fluorescence microscope. Hence, such approach can be used to develop composite microstructures containing ZnO nanowires aiming at technological applications. © 2013 Wiley Periodicals, Inc. *J. Polym. Sci. Part B: Polym. Phys.* **2014**, *52*, 333–337

KEYWORDS: composites; microstructure; NLO

INTRODUCTION Zinc oxide (ZnO) has been exploited as a promising material for optoelectronic devices operating in the blue-to-near-UV spectral region.¹ In addition to its wide-bandgap (~ 3.3 eV),² high-quality nanostructures can be readily obtained from ZnO,^{3,4} prompting use of this material for nanoscale optoelectronic devices.^{5–10} Recently, for instance, a decrease of the deep-level emission and an increase of the near band-edge emission, dominated by a surface exciton, has been shown when ZnO nanowires are embedded in polymers.¹¹ The dimension of ZnO nanowires allows, in principle, the fabrication of micrometric ZnO nanowires/polymer composites aiming at device integration. Although standard methods, such as cast and spin coating, can be used to produce ZnO nanowires/polymer composites in the form of films, such approaches do not allow the fabrication of three-dimensional (3D) microstructures due to the lack of spatial resolution. Hence, it is interesting to develop 3D microfabrication methods for producing composites based on ZnO nanowires/polymer with high spatial resolution.

In this article, we report on the fabrication of 3D microstructures of ZnO nanowires/polymer composite by using the two-photon polymerization (2PP). Direct laser writing by 2PP has been demonstrated to be a powerful method to fabricate complex microstructures, with applications in different areas such as mechanical actuators,^{12–14} data storage,^{15,16} photonics,^{17–19} and biology.^{20–24} In 2PP, the nonlinear nature of the absorption confines the polymerization to the vicinity of the laser focus, enabling microfabrication by moving the laser beam through the unpolymerized resin.²⁵ Due to the nonlinear nature of the light-matter interaction and to the energy threshold required for the polymerization, fabrication with a resolution below the diffraction limit can be achieved.^{26–28} The approach presented here to produce microstructures of ZnO nanowires/polymer composite is based on the incorporation of ZnO nanowires in the polymeric resin prior the 2PP. We show that the ZnO nanowires are well preserved in the fabricated 3D microstructures, and that they are distributed throughout the bulk. The obtained

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results also indicate that the presence of ZnO nanowires does not impair the morphology or integrity of the final structures. In addition, we demonstrate that the photoluminescence of the ZnO nanowires are still found in the composite microstructures.

EXPERIMENTAL

ZnO nanowires employed in this work were prepared by a hydrothermal technique from aqueous solutions of zinc nitrate hexahydrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] and potassium hydroxide. These two solutions were then slowly mixed together in a larger glass beaker under constant stirring at room temperature until a transparent solution was obtained. This transparent solution was placed on a hot plate at 80°C for about 4 h. After the reaction, a milky white precipitation of ZnO nanowires was collected from the beaker and washed several times with deionized water and ethanol. The obtained nanowires were 1–3 μm long and with diameter of ~ 100 nm.

The resin we used to prepare the ZnO nanowires/polymer composite is composed of a mixture of tris(2-hydroxyethyl)isocyanurate triacrylate and ethoxylated(6) trimethylolpropane triacrylate. While the first one provides hardness to the structure, the later reduces polymerization shrinkage,²⁹ improving the quality of the final structure. As the photoinitiator for the polymerization process we used ethyl-2,4,6-trimethylbenzoyl phenylphosphinate, commercially known as Lucirin TPO-L.^{22,29} The monomers are mixed to the photoinitiator, added in 3 wt % to the monomers.²² To the photosensitive resin we added ZnO nanowires in a proportion of 0.5–5 wt %, and stirred for 2 h to properly mix the components, yielding a viscous liquid that is used for the photopolymerization.

The 2PP microfabrication is carried out using 100-fs pulses at 800 nm from a Ti:sapphire laser oscillator operating at 86 MHz. The laser beam is focused into the sample using a microscope objective with numerical aperture (NA) of 0.85. The energy per pulse used for the fabrication is 0.5 nJ, measured before the objective. The laser is scanned in the x - y direction by a pair of galvo mirrors, while the sample's axial (z) positioning is performed by a motorized stage. After the laser fabrication via 2PP, the sample is immersed in ethanol to wash away the unsolidified resin, leaving behind only the hardened microstructure on the glass slide.

The morphology and relative elemental concentration of the fabricated microstructures were analyzed by scanning electron microscopy (SEM; JEOL microscope, model JSM 6510) coupled with an energy dispersive X-ray spectrometer (EDX; Thermo Scientific UltraDry X-ray detector). The microstructures on the glass slide were placed on a metallic stub and subsequently coated with gold by a table-top sputter coater (Leica EM SCD 050). The structural characterization of pure ZnO nanowire powder and a film with the same composition of the microstructure containing ZnO (2 wt %), were carried out by a X-ray diffractometer (Shimadzu, XRD-6000 model)

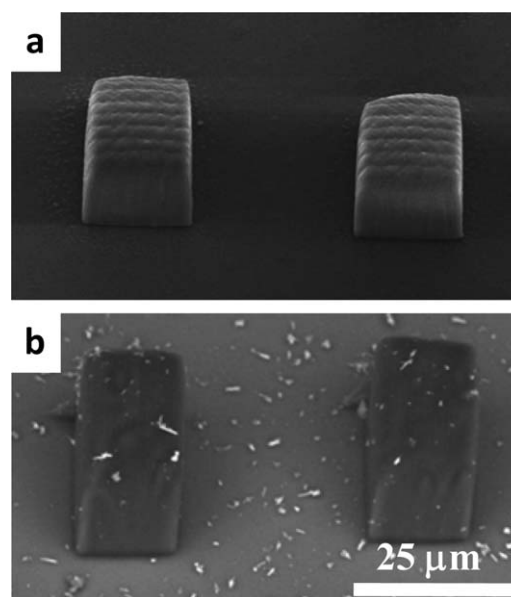


FIGURE 1 SEM images of 2PP ZnO nanowires/polymer composite microstructures containing 0.5 (a) and 1.0 (b) wt % of ZnO nanowires. The scale bar is the same for both samples.

in θ – 2θ mode, operating at 30 kV and 30 mA, Cu $K\alpha$ radiation, operating in step-scanning mode with a fixed time of 4 s and a scan of 0.02° . The emission spectra of microstructures were obtained by a portable spectrometer coupled to an optical microscope, which uses as excitation a He-Cd laser operating at 325 nm.

The Raman scattering spectra of the ZnO nanowire powder, the fabricated microstructures and films with the same composition of the microstructures were obtained using a micro-Raman Renishaw spectrograph, model in-Via, coupled to a Leica microscope objective of $50\times$ (NA 0.75). The system is equipped with 1800 and 1200 grooves/mm gratings, CCD detector and a computer-controlled three-axis-encoded (xyz) motorized stage to take point-by-point Raman maps with a minimum step of 1 μm . Excitation laser line at 632.8 nm was used.

RESULTS AND DISCUSSION

Figure 1 displays scanning electron micrographs (tilted view) of the composite microstructures fabricated by 2PP, containing 0.5 (a) and 1.0 (b) wt % of ZnO nanowires. As it can be seen, for the 1% sample, residual ZnO nanowires can be seen on the substrate as well as on top of the microstructure, even after the washing procedure. The cubic structures have a lateral dimension of ~ 20 μm , with a resolution of ~ 800 nm. Such structures were fabricated using pulse energy of 0.5 nJ, measured before the 0.85-NA objective. For pulse energies below 0.2 nJ we have not observed 2PP. The structures have high definition and physical integrity, which demonstrates that the presence of ZnO nanowires does not affect the 2PP process, and indicates that the method presented here is suitable for fabricating 3D microstructures based on ZnO nanowires/polymer composite.

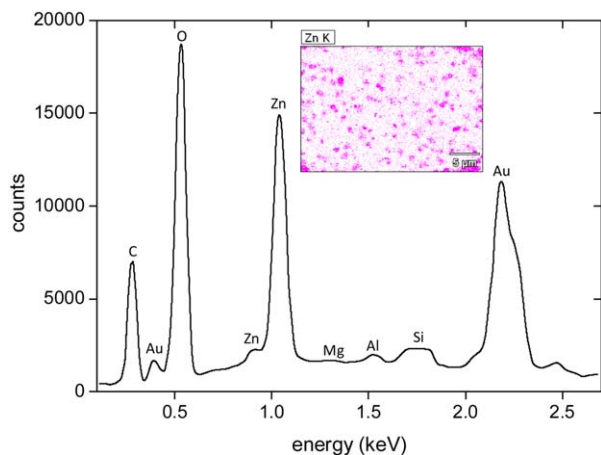


FIGURE 2 EDX mapping of a composite microstructure containing 5 wt % of ZnO nanowires. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

EDX analyses of the fabricated composite microstructures were carried out to verify the presence of the ZnO nanowires in its composition. Figure 2 presents the EDX spectrum of a microstructure containing 5 wt % of ZnO nanowires. As it can be seen, the spectrum indicates the presence of C, Au, O, Zn, Mg, Al, and Si. The presence of C atoms is due to the acrylic resin used for the microfabrication process, while the Au peak arises from the metallic coating used for the SEM measurements. The peak at ~ 1.0 keV in Figure 2 confirms the presence of Zn in the microstructure, suggesting that ZnO nanowires are retained within the structure. The inset in Figure 2 exhibits an EDX mapping of the microstructure obtained from the intensity of the signal at 1.0 keV (corresponding to Zn emission). The result reveals that ZnO is distributed throughout the entire microstructure, although the distribution is not uniform as seen by the presence of aggregates.

Figure 3 shows the X-ray diffraction pattern obtained for a film with the same composition of the microstructure containing ZnO (a) and for ZnO nanowire powder (b). The set of diffraction peaks observed in Figure 3 indicate the hexagonal wurtzite-type crystalline structure (according to Joint Committee on Powder Diffraction Standards card number 036-1451) of the ZnO nanowires, that belongs to the C_{6v}^4 ($P6_3mc$) space group, with lattice parameters of $a = 3.249$ Å and $c = 5.206$ Å. We observe a broad peak signal from 30° to nearly 60° for the film sample (a), which is attributed to the disordered crystalline structure of the polymeric phase.

To further verify the presence of ZnO nanowires in the microstructures, as well as to investigate possible interactions between the polymerized resin and ZnO nanowires, we measured the Raman spectrum of a microstructure prepared with neat resin as well as with the composite microstructure containing 2 wt % of ZnO nanowires, as shown in Figure 4. For comparison, in Figure 4 we also show the Raman spectrum for the ZnO nanowire powder. All Raman spectra were obtained at room temperature. As can be seen in

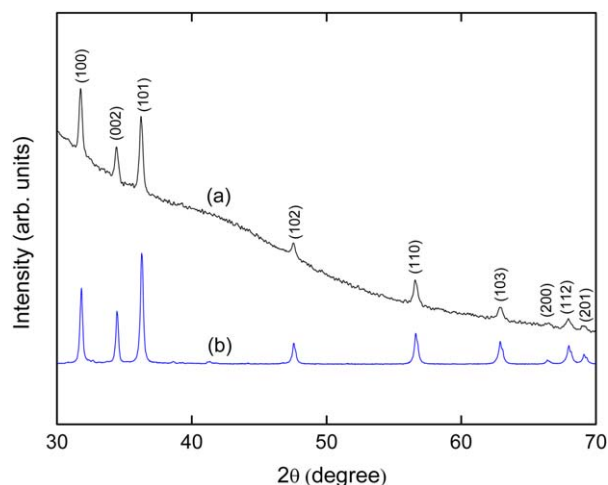


FIGURE 3 X-ray diffractograms of a (a) polymeric sample containing 1 wt % ZnO and (b) neat ZnO powder. The structure determined is that of zincite, with hexagonal crystal structure. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 4(a), the Raman spectrum for ZnO nanowire powder presents two strong peaks at 437 and 1062 cm^{-1} and low intensity ones at 378 and 537 cm^{-1} . The narrow band at 437 cm^{-1} has been assigned to the E_2 modes mainly related to Zn motion. The peak at 378 cm^{-1} (A_1 mode) indicates the presence of some degree of structural order-disorder in ZnO lattice, while the band at 537 cm^{-1} is the contribution of the $E_1(\text{LO})$ mode of ZnO associated with oxygen deficiency. Finally, the band at 1062 cm^{-1} is attributed to overtones and/or combination bands.³⁰ Figure 4 also shows the Raman spectra obtained for the neat resin microstructure (b) and for the ZnO nanowires/polymer composite microstructure (c), respectively. As it can be seen, in Figure 4(c) there is a peak at 1054 cm^{-1} , that is characteristic of the ZnO nanowires [see Fig. 4(a) peak at 1062 cm^{-1}], further confirming

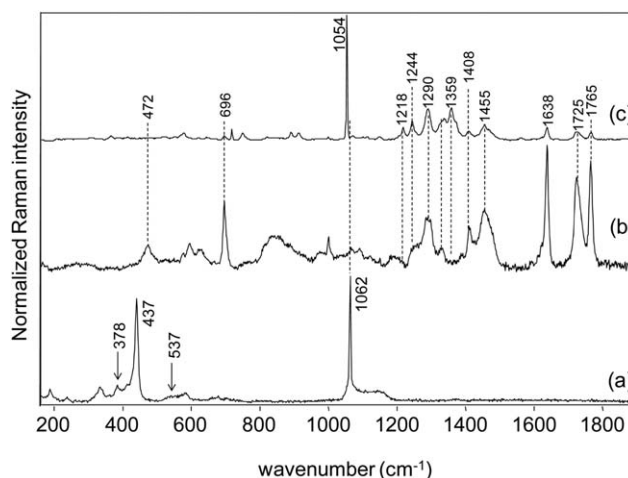


FIGURE 4 Raman spectra of the ZnO nanowires powder (a), neat resin microstructure (b) and composite microstructure with 2 wt % of ZnO nanowires (c).

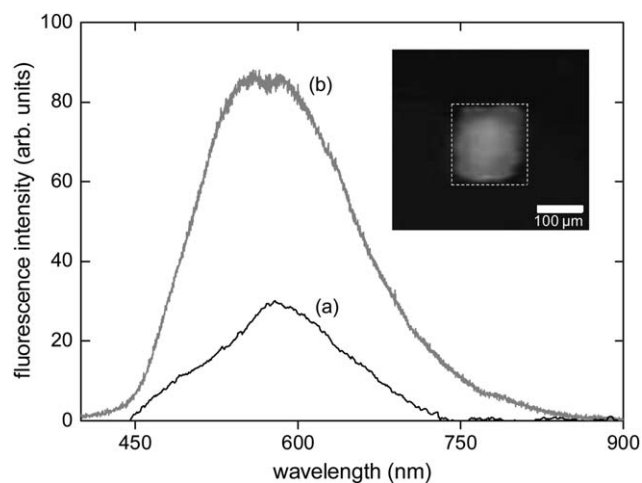


FIGURE 5 Emission spectra of the ZnO nanowires/polymer composite microstructure containing 5 wt % of ZnO nanowires (a) and for the ZnO nanowire powder (b). The inset shows the fluorescence image (top view) of a cubic microstructure containing ZnO.

their presence in the composite microstructures. Besides the displacement of the peak $1062\text{--}1054\text{ cm}^{-1}$, it can also be noted in Figure 4 (c) the absence of the peak at 437 cm^{-1} , which clearly appears in the ZnO powder spectrum (a). Such change (suppression and displacement) has been attributed to a complex interaction between ZnO and the polymer matrix as reported in ref. 31, or to a resonance relationship between the excitation energy (laser line) and the ZnO structures in different forms such as solid, thin films and nanowires, which strongly affects the relative intensity of both longitudinal and transversal vibrational modes.³² In our case, an interaction of the ZnO nanowires with the polymer matrix seems to be more likely. Besides the excitation radiation at 632.8 nm is out-of-resonance with the ZnO nanowire absorption, an interaction ZnO-polymer matrix is consistent not only with the changes observed in the Raman spectrum of the ZnO when dispersed within the polymer matrix [spectra (a) and (c)] but also (and mainly) with the spectral differences found for the polymer matrix with and without ZnO nanowires, that is, spectra (c) and (b) respectively. For instance, in case of neat polymer matrix [spectrum (b)], the peaks between $1638\text{ and }1765\text{ cm}^{-1}$ are stronger than those between $1218\text{ and }1455\text{ cm}^{-1}$. However, the opposite is observed when ZnO nanowires are dispersed within the polymer matrix [spectrum (c)]. Drastic changes are also observed for the polymer peaks between $472\text{ and }696\text{ cm}^{-1}$ [spectrum (b)], which are practically vanished when ZnO nanowires are added to the polymer matrix [spectrum (c)].

Given the interest in the use of ZnO nanowires for optoelectronic and photonic devices, we used a fluorescence microscope to measure the luminescence of the fabricated microstructure. The excitation was carried out using a cw He-Cd laser operating at 325 nm , with an average power of 12 mW . Figure 5(a) shows the emission spectrum of the ZnO nanowires/polymer composite microstructure. Such spectrum

corresponds, in fact, to the emission of the microstructure containing ZnO nanowires subtracted from the one for a pure resin microstructure (without ZnO nanowires), taken in exactly the same conditions. Therefore, Figure 5(a) exhibits the emission originated only from the ZnO nanowires. As it can be seen in Figure 5(a), the microstructure presents an emission peak around 570 nm . For comparison, Figure 5(b) shows the emission spectrum of the ZnO nanowire powder obtained with the same optical experimental setup. This emission, also known as green photoluminescence, is attributed to deep defects in ZnO (oxygen vacancies).³³ It is worth mentioning that the emission spectrum presented for the composite microstructure [Fig. 5(a)] was obtained by subtracting the emission observed for the undoped microstructure, since the resin also presents a very weak luminescence at this region. The inset in Figure 5 displays the top view fluorescence image of a cubic ZnO nanowires/polymer composite microstructure containing 5 wt % of ZnO nanowires (as the one displayed in Fig. 1), in this case obtained using an excitation at 350 nm .

CONCLUSIONS

In summary, we present an approach for fabricating 3D ZnO nanowires/polymer composite microstructures. The fabricated structures present structural integrity, and the presence of ZnO nanowires was confirmed by EDX, Raman spectroscopy and XRD. Although the Raman spectrum strongly suggests an interaction between the ZnO nanowire and the polymerized acrylic resin, it appears not to influence the ZnO nanowires emission, as revealed by the characteristic emission observed for the sample under UV-excitation. Hence, direct laser writing by 2PP can be used to fabricate composite microstructures containing ZnO nanowires, which can be used to develop optical and optoelectronic devices.

ACKNOWLEDGMENTS

The research described in this article was supported by Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), and Conselho Nacional de Pesquisa e Desenvolvimento Tecnológico (CNPq) from Brazil. T. Voss acknowledges funding from the German Research Foundation (DFG) in the frame of the research unit FOR1616 (project Vo1265-6).

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