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# Photoluminescent zinc oxide polymer nanocomposites fabricated using picosecond laser ablation in an organic solvent

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ABSTRACT

Nanocomposites made of ZnO nanoparticles dispersed in thermoplastic polyurethane were synthesized using picosecond laser ablation of zinc in a polymer-doped solution of tetrahydrofuran. The pre-added polymer stabilizes the ZnO nanoparticles in situ during laser ablation by forming a polymer shell around the nanoparticles. This close-contact polymer shell has a layer thickness up to 30 nm. Analysis of ZnO polyurethane nanocomposites using optical spectroscopy, high resolution transmission electron microscopy and X-ray diffraction revealed that oxidized and crystalline ZnO nanoparticles were produced. Those nanocomposites showed a green photoluminescence emission centred at 538 nm after excitation at 350 nm, which should be attributed to oxygen defects generated during the laser formation mechanism of the monocrystalline nanoparticles. Further, the influence of pulse energy and polymer concentration on the production rate, laser fluence and energy-specific mass productivity was investigated.


## 1. Introduction

One of the most versatile materials in nanotechnology is zinc oxide (ZnO), a semiconductor with a great application potential in optics, energy conversion and biomedicine. The particular optical properties of ZnO nanoparticles render them interesting as a material for electro-optical or optical devices [1,2], photovoltaic applications [3,4], and lasing materials [5,6]. ZnO has a wide band-gap energy of 3.37 eV at room temperature, and exciton binding energy of 60 meV. The photoluminescence spectra of ZnO consists of several emission bands in the UV [7] and the visible region violet [8], blue [9], green [10,11], yellow and orange-red [12]. The origins of these different defect emissions are not understood completely, but some hypotheses have been suggested to explain the mechanism of different defect emissions [13].

Furthermore, ZnO nanoparticles are bioactive, due to their capacity to release Zn ions which are known to support wound healing, or to provide anti-infectivity [14,15]. Consequently, ZnO nanoparticles can be used as bioactive metal ion sources to develop new drug release systems or medical devices.

To utilize such biomedical or optical properties, the inorganic nanoparticles have to be embedded into a carrier material, particularly an organic polymer. Such nanocomposites fascinate by their synergy of different materials and have gained growing attention in recent years [16]. Nevertheless, the most widespread methods to generate ZnO nanoparticles are conducted in alcoholic solutions [17,18] which are not compatible with many nonpolar or semipolar polymers. However, the synthesis of ZnO nanoparticles in nonpolar organic solvents is much more challenging. By using amphiphilic polymers as a stabilization agent, some progress has been made [19], but general applicability is not yet guaranteed.

A more general approach to nanoparticles dispersed in various solvents is nanoparticle fabrication using pulsed laser ablation in liquid. This versatile technique has attracted growing interest for a number of materials and liquids during the last two decades [20–23]. The synthesis of ZnO nanoparticles using laser ablation in an aqueous solution was intensively studied during the last years [24–30]. The addition of surfactants like sodium dodecyl sulfate (SDS) allows control of oxidation and formation of layered Zn nanocomposites. Those nanocomposites include different phases like Zn, ZnO, ZnDS or $Zn(OH)_x$ in core–shell structures, indicating that growth mechanisms and subsequent capping reactions with solvents and additives control the chemical nature of the product.

Recently, we reported on pulsed laser ablation of zinc in tetrahydrofuran (THF), and the effect of spatially or temporally separated laser pulses on the ablation efficiency [31]. However, the chemi-

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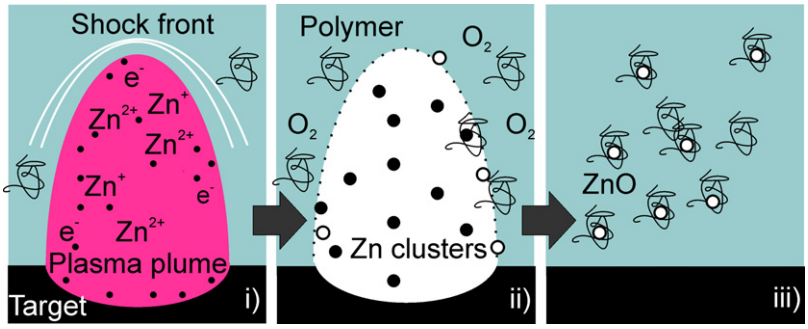


**Fig. 1.** Simplified formation mechanism of nanocomposites by laser ablation in liquid: (i) Laser-induced cavitation bubble, material ejection and formation of a zinc plasma; (ii) Bubble collapse, formation of zinc clusters and nanoparticles; (iii) Oxidation to zinc oxide nanoparticles, in situ conjugation with dissolved polymer.

cal nature and optical properties of nanoparticles generated using pulsed laser ablation of zinc in an organic solvent are still unclear.

In this article, we present an experimental study of picosecond laser ablation of zinc in polymer-doped tetrahydrofuran, and the characterization of the nanoparticles and nanocomposites generated. Further, we investigated the effect of a dissolved polymer as in situ stabilization agent to synthesize nanocomposites, and its impact on the production rate and efficiency.

## 2. Experimental

ZnO nanocomposites were produced using laser ablation of a Zn target in THF with different concentrations of thermoplastic polyurethane (TPU) as a liquid media. A detailed description of the applied set-up can be found elsewhere [31]. In brief, a zinc plate (GoodFellow, purity 99.5%) was fixed on a vertical flat bracket in front of a laser beam in a Teflon chamber filled with a 30 mL solution of THF with specific concentration of TPU (Elastogran, Elastollan 1190A), which was continuously stirred. Ablation was performed for 10 min using a commercially available picosecond-pulsed laser (Trumpf TruMicro 5250, 25 W power, 515 nm wavelength, pulse duration about 7 ps, 125 μJ maximal pulse energy and up to 200 kHz repetition rate). The targets were irradiated using a fixed spiral scan pattern (diameter 5 mm, interline distance 50 μm) using a scanner optics (Scanlab HurrySCAN II-14) which allows scanning an area of 16 mm × 16 mm after passing a telecentric f-theta lens of 56 mm focal length. The lateral scan speed in the focal area on the substrate was 3.30 m/s leading to an interpulse distance of 100 μm at a fixed repetition rate of 33.3 kHz. Different pulse energies from 25 to 125 μJ, and different concentrations of TPU up to 0.5 wt.% were selected.

The nanocomposites were characterized using various techniques. For electron microscopy, a droplet of the colloid was evaporated on a TEM grid, and analyzed using different operational modes of electron microscopes (Jeol JEM-2100F and Fei Quanta 400). Optical absorption spectroscopy was used after fabricating thin films with an ultraviolet–visible spectrometer (Shimadzu 1650 PC,). For observing the photoluminescence emissions of nanocomposites, two samples were prepared, using ablation for an hour at a pulse energy of 125 μJ in the liquid with 0.4 wt.% TPU concentration, and measured at room temperature with a fluorescence spectrophotometer (Hitachi F-4500 with Xe lamp, excitation wavelength was 350 nm (3.65 eV)). X-ray diffraction was carried out using a commercial diffractometer (Stadi P Stoe using Cu $K_\alpha$ radiation ($\lambda$ = 0.154 nm)). Further, for each experiment, the ablated mass was determined by weighing the substrate before and after the ablation process (Sartorius M3P), with an accuracy of 0.001 mg.

For calculating laser fluence, the ablation spot diameters were measured in two different directions on the surface using an optical microscope (Leitz CMM 3000) with an accuracy of 0.1 μm. Though a single laser pulse was not visible using an optical microscope, the target surface was irradiated with a varying total number of pulses (100, 400 and 2000 pulses). Linear extrapolation of the data allowed calculation of a single laser pulse spot size.

## 3. Results and discussion

### 3.1. Chemical and optical properties of laser-generated nanocomposites

The formation of nanocomposites using laser ablation in a polymer-doped solution is subject to different, subsequent processes. A simplified sketch of a possible mechanism based on the recent literature is shown in Fig. 1. First, there is a high-temperature and high-pressure zinc plasma which is produced in the solid–liquid interface after interaction between the pulsed laser energy and the metal target. Ultrasonic and adiabatic expansion of the hot zinc plasma leads to cooling of the zinc plume and formation of zinc clusters [22,25,26]. The zinc clusters formed are affected by the liquid and solved molecules like oxygen. It is well known that pulsed laser ablation of zinc in pure aqueous solutions yields zinc oxide nanoparticles, whereas the addition of anionic surfactants like sodium dodecyl sulfate (SDS) can be used to control the state of oxidation [25]. Hence, laser ablation of zinc in an organic polymer-doped solution may lead to different products, compared to laser ablation in pure THF. The reaction of dissolved TPU with nascent Zn clusters might protect against oxidation by capping reactions, as well as to stabilize against agglomeration. Furthermore, in an organic solvent, the concentration of oxidizing agents like water or oxygen may be much lower.

Thus, we analyzed the chemical structure of the resulting nanocomposites using different spectroscopic methods. The UV/VIS absorption spectra of TPU nanocomposite films in Fig. 2 shows an absorption band at 360 nm (3.37 eV). Since the ZnO exciton absorption peak is located at about 360 nm, it indicates the formation of ZnO subsequent to laser ablation of Zn. The plasmon resonance peak of Zn at about 240 nm [25] could not be observed, because of the strong absorption band of TPU starting below 300 nm. Hence, it is questionable whether the oxidation reaction is complete or only partial.

Thus, we performed X-ray diffraction (XRD) of laser-generated nanocomposites which can be seen in Fig. 3. All peaks in the XRD pattern obtained can be assigned to the hexagonal structure of bulk ZnO with lattice constants of $a$ = 0.3249 nm and $c$ = 0.5206 nm. This indicates that laser ablation of Zn leads to fully oxidized ZnO nanoparticles. High resolution transmission electron microscopy (TEM) of laser-generated nanoparticles shown in Fig. 4 supports this interpretation. The TEM images clearly show observable lattice planes, indicating a crystalline structure for the whole particle. A