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One-step synthesis of ZnO decorated CNT buckypaper composites and their optical and electrical properties

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ABSTRACT

ZnO/CNT composites were prepared using ZnO nanoparticles and tetrapods synthesized by the Laser Assisted Flow Deposition method. The co-operative behaviour between these two materials may give rise to the production of advanced functional materials with a wide range of applications in electronics and optoelectronics. Despite some degree of aggregation in the case of the nanoparticles, scanning electron microscopy images evidence that the produced ZnO structures are well dispersed in the CNT buckypapers. Independent of the ZnO morphology the samples resistivity was shown to be of the order of $\sim 10^{-1}\ \Omega$ cm while in the case of the electron mobility, the composite with tetrapods reveals a lower value than the ones obtained for the remaining samples. Well-structured ZnO luminescence was observed mainly in ultraviolet highlighting the high optical quality of the produced structures. The temperature dependence of the luminescence reveals a distinct trend for the composites with ZnO tetrapods and ZnO nanoparticles.

1. Introduction

Zinc oxide is a wide bandgap semiconductor ($E_g \sim 3.4$ eV) with important technological applications in several fields like optoelectronics, UV sensors, thin film transistors, energy conversion or biomedicine [1–8]. Among other characteristics, the large free exciton binding energy (~60 meV), the low production cost and good thermal stability make the ZnO material an attractive metal oxide semiconductor.

ZnO is a versatile functional material that can be grown in different morphologies (e.g. particles, rods, tetrapods, springs, helixes, belts) with sizes ranging from micro to nano scale [9–11]. Several techniques have been employed to grow this semiconductor like colloidal synthesis [12], chemical vapour deposition [13], molecular beam epitaxy [14], thermal evaporation [9], hydrothermal synthesis [15], among others. Due to its high vapour pressure and the fact that this material does not melt, instead decomposes into its atomic components at the temperature of 1977 °C, at atmospheric pressure, the flux methods have been extensively studied [16]. Laser Assisted Flow Deposition (LAFD) proved to be a very efficient method to grow ZnO samples with high crystalline and optical quality [17–19]. This laser assisted synthesis method comprises the local heating of the ZnO precursor by a focused high power laser, and subsequent thermal decomposition of ZnO at its melting temperature. The generated gases are transferred to the low temperature regions, after the reaction of the zinc with the oxygen to form ZnO products. Different ZnO morphologies (microrods (MR), nanoparticles (NP) and tetrapods (TP)) can be obtained in the as-grown samples as a result from different kinetics/thermodynamics local conditions at different regions of the growth chamber [18,20].

ZnO potential for some applications can also be improved by forming composite structures. Therefore, the synergetic combination with other materials has been intensively investigated due to the possibility of the modulation of their properties [21]. The research on the modification of semiconductors with noble metal ions, for instance, as is the case of silver or gold, has gained a significant interest in different areas like photocatalysis, sensing, surface-enhanced Raman or biomedicine, showing very remarkable prospects [21–23]. For instance, one of the most important limitations of the ZnO nanostructures in photocaltalytic or photovoltaic applications is the high recombination rate of photoinduced charge carriers. One efficient method to overcome this problem is to deposit noble metals, as silver, on the surface of the semiconductor

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[24]. The photogenerated electrons are then transferred from the conduction band to the metal particle while the holes remain in the semiconductor surface, improving the charge separation.

Carbon nanotubes (CNTs) show unique chemical, electrical and mechanical properties that have been explored in a wide range of technological applications at nanoscale [25]. As such, CNTs are auspicious materials for the development of functional nanocomposites [26]. CNTs can preserve their morphology and structure even when mixture with a high amount of other nanostructure due to their great mechanical properties. In this sense, different semiconductor nanostructures have been used to produce CNT composites by several methods [27].

CNT buckypaper is a self-supported membrane with entangled CNTs forming a flexible structure with chemical–physical stability and similar properties to those seen in nanotubes alone [28], offering the advantage of easy application as flexible electronic devices [29]. Constituting a functional component in various applications buckypapers can be used as permeable membranes, capacitors, electrodes for fuel cells, reinforcement in composite materials, among others [30–34]. This approach could be used as an effective method to create composites of CNTs with metal oxide nanoparticles with suitable properties to give rise new materials with tailoring properties [29,35]. ZnO appears as a good candidate to be incorporated in CNT buckypapers since this material enlarges the photon absorption region, increasing the photoconversion efficiency of the generated photocurrent [29]. Earlier works already proved that the UV-induced photoconductive behaviour and the photocurrent generation of ZnO/CNT structures revealed functional interaction between both phases giving a quantum efficiency of 1% in unbiased photoconductivity measurements [36]. The ZnO/CNT heterojunctions can have a charge transfer efficiency of up to 90%. Additionally, the ZnO intrinsic recombination of photoinduced electron–hole pairs is reduced, enhancing charge separation and transport properties [37].

Recently, our group envisaged fundamental studies on the synthesis and analysis of the physical properties of ZnO/CNT composites involving vertical aligned CNTs (VACNTs) decorated with ZnO nanostructures grown by LAFD [19]. As an extension of the preliminary work we now focus on the production of ZnO/CNT buckypapers composites to explore their fundamental properties for optical and electrical applications. For some applications, as it is the case of dye sensitized solar cells, during the device construction the introduction of a liquid electrolyte destroys the CNTs alignment compromising the integrity of the composite samples [38]. In this sense, using disordered CNTs in the form of buckypapers constitutes an advantage relative to the VACNTs. The combining semiconductor nature of the ZnO nanostructures with the excellent electric properties of CNTs in a flexible sample shows a great potential for application as an electrode for this type of solar cells.

In this work, the morphological, structural, optical and electrical properties of the synthesized ZnO/CNT composites are analysed and discussed. Since in composites the particles size and morphology constitute important parameters for the resulting material properties, the effect of ZnO morphologies (TP and NP) on CNT buckypaper composites properties were studied.

2. Experimental

The LAFD was performed on a modified laser floating zone (LFZ) growth chamber which comprises a 200 W CO_2 laser (Spectron) coupled to a reflective optical set-up producing a circular crown-shaped laser beam [39]. The laser beam was focused on the tip of the extruded cylindrical rods, previously prepared by mixing the ZnO powders (AnalaR, 99.7%) with polyvinyl alcohol (PVA, 0.1 g ml^{-1}, Merck). The produced ZnO structures are collected in a sample holder attached to the upper spindle of the LFZ system, above the feed rod as previously described [17–20,40].

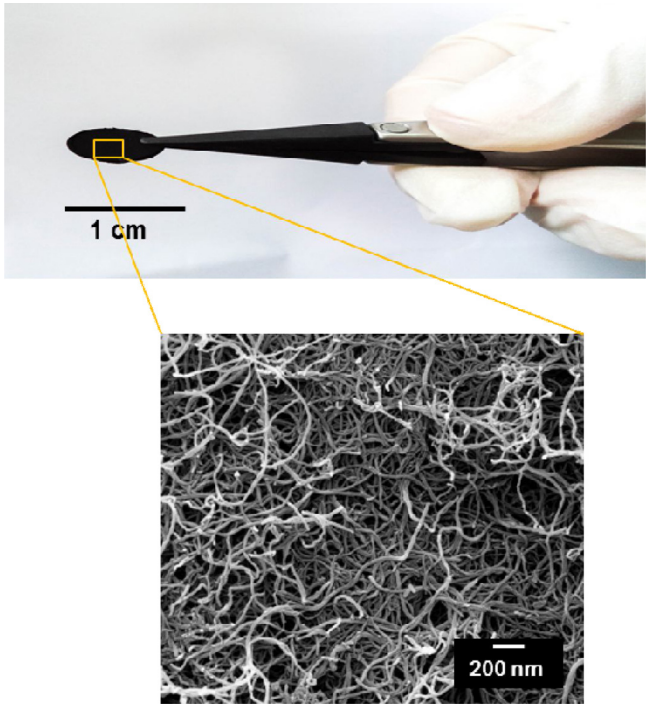

Fig. 1. Macroscopic and microscopic images of the produced buckypapers.

Functionalized multi-walled CNTs (NC3101), provided by Nanocyl supplier, were used to prepare the ZnO/CNT composites. The CNTs have an average length and diameter sizes of 1.5 μm and 9.5 nm, respectively, with a purity level of 95 wt.% and a 4 wt.% content of covalently bonded carboxylic groups (—COOH). ZnO/CNTs composites with a weight ratio of 4:1 were prepared in isopropyl alcohol (IPA, ≥99.8%, Sigma–Aldrich). The preparation procedure comprises essentially five steps: (1) CNT suspensions of 0.1 g l^{-1} start to be processed by high-speed shearing for 15 min (IKA T25-Ultra-Turrax, working at 20,500 rpm) with a shearing force of 96 Pa to eliminate big CNTs agglomerates; (2) afterwards, the CNT suspension was sonicated (Selecta, working at 60 kHz, 200 W) for 60 min to yield mixtures of individualized CNTs and small sized agglomerates (<3 μm) [41]. At the same time, both the suspensions of ZnO TP and nanoparticles NP with a fixed concentration of 1 g l^{-1} each were sonicated in the same conditions of those of the CNTs suspension to de-agglomerate possible ZnO clusters. (3) Next, the suspensions were mixed together and sonicated during 15 min to promote interactions of individual ZnO particles with CNTs. (4) The ZnO/CNT suspension was then dropped into a cylindrical mould of 10 mm of diameter placed onto a 0.22 μm pore size filter (hydrophobic PTEF, Millipore) to produce the buckypapers of ZnO and CNTs by vacuum filtration [42]. This was accomplished by coupling a rotary vacuum pump to a filter-Büchner funnel-Kitasato flask setting. For each CNT membrane of 10 mm of diameter about 12 ml of suspension was used. (5) Finally, the membranes were dried in an oven at 80 °C for 15 min. The final samples can be seen in Fig. 1. The composites thickness is around 100 μm for all the samples.

The crystallinity of the ZnO/CNT composites was determined by X-ray diffraction (XRD) analysis using a PANalytical's X'Pert PRO MRD X-ray diffractometer, with a monochromatic CuK_α radiation source (wavelength 1.540598 Å). XRD measurements were carried out from 20° to 60° (2θ), with a scanning step size of 0.016°.