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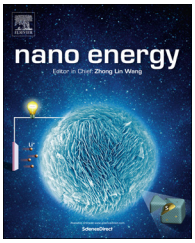

RAPID COMMUNICATION

Flexible piezoelectric energy nanogenerator based on ZnO nanotubes hosted in a polycarbonate membrane

Stefano Stassi[a,1], Valentina Cauda[b,*,1], Carminna Ottone[a,b], Angelica Chiodoni[b], Candido Fabrizio Pirri[a,b], Giancarlo Canavese[a]

[a]*Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 24, Torino 10129, Italy*
[b]*Center for Space Human Robotics@PoliTo, Istituto Italiano di Tecnologia, Corso Trento 21, Torino 10129, Italy*

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Abstract
Highly oriented zinc oxide (ZnO) nanotubes were synthesized in a porous polycarbonate (PC) matrix, leading to a highly flexible ZnO-PC composite able to work as efficient energy nanogenerator. The crystalline direction of the ZnO *c*-axis is obtained parallel to the membrane surface, thus advantageous for the exploitation of composite under bending stresses. Three different pore sizes of the templating PC membranes were successfully employed, i.e., having nominal pore diameter 30, 50 and 100 nm, thus obtaining three different ZnO one-dimensional nanostructures supported into the PC membrane. The ZnO-PC nanogenerators were successfully tested both under compressive and bending strains, showing an influence of the ZnO nanotube size on the output voltage. Using the 100 nm pore PC membrane, a maximum output voltage of 1.15 V, a maximum current of 100 μA and a maximum output power density of 287.5 mW/cm^3 were reached, being these values among the highest reached in zinc oxide-based piezoelectric nanogenerators. Such remarkable results make the nanostructured ZnO-PC composite a promising material for energy harvesting applications.

Introduction

Zinc oxide (ZnO) is a prominent example of both piezoelectric and semiconductor material. The enhancement of these properties by exploiting ZnO nanostructuration spread

*Corresponding author. Tel.: +39 011 0903436.
E-mail address: valentina.cauda@iit.it (V. Cauda).
[1]These authors have equally contributed to the work.

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its application as functional material in a wide variety of different fields, including nanosensors [1-3], thermoelectric devices [4], third-generation solar cells [5-7], energy storage [8], electrochemical water splitting devices [9,10], and field-effect transistors [11,12]. Moreover ZnO nanowires (NWs) recently pioneered a new branch of research and devices called piezoelectric nanogenerators, widely studied in the last period [13-15]. Indeed the combination of the piezoelectric and semiconducting properties of zinc oxide enables to convert mechanical deformations into electric potential with the purpose to harvest energy from the surrounding environment. This concept was firstly introduced by Wang in 2006 [16] measuring the voltage generated deforming a single ZnO NW with a platinum-coated Atomic Force Microscopy (AFM) tip, and further broadly developed on arrays of self-standing ZnO NWs [13,17], ZnO nanocomposites [18,19] and several other ZnO nanostructures. Generally, the amount of converted energy is small, i.e., in the order of μW up to few mW, however enough for supplying MEMS sensors, implantable medical devices or even wearable electronics, up to charging mobile phone batteries.

In general zinc oxide nanostructures and in particular nanowires (NWs) and nanotubes (NTs) can be grown using several different techniques, mostly leading to a high crystalline quality and an elevate reproducibility of the material. The most reported ones included chemical-vapor-deposition (CVD) [20,21], physical-vapor-deposition (PVD) [22], electrochemical deposition [23-25], hydrothermal synthesis [13,26-28], and sol-gel templating approach [29-31]. In particular this last method is generally applied using anodic alumina membranes as hosting matrix [24,29,30,32], with the advantage of being very simple and high throughput. It leads however to the formation of polycrystalline NWs or NTs with low quality in terms of morphology. In addition, the corrosion of the alumina membrane during the chemical synthesis and its intrinsic fragility pose also not negligible problems [1]. To overcome these challenges, it reported the use of polycarbonate (PC) membranes as templating matrix, adopting, as synthesis technique for ZnO material, the electrochemical deposition [23,24,33-35] or physical templating-assisted sol-gel route [36]. However, none of the previously cited works went a step further the synthetic process and tested the functional properties and potentialities of these composite systems, focusing only on the NTs growth mechanisms and varying different synthetic parameters.

In the present work, ZnO nanostructures were synthesized by sol-gel route into the pores of polycarbonate membranes (hereafter indicated as ZnO-PC), having three different pore diameters (i.e., 100, 50 and 30 nm), and for the first time it demonstrated their application as nanogenerators for mechanical energy harvesting. The advantages offered by this technique are the rapidity and the high-throughput of the synthetic procedure, forming, in one-single step, arrays of vertically aligned one-dimensional (1D) ZnO nanostructures supported in a flexible and insulating matrix. The obtained nanocomposite materials are thus quite easy to handle and can be straightforward used, without any further chemical or thermal treatments. In particular there is no need of removing the templating matrix, which is in contrast highly desired because it gives high flexibility and compactness to the whole sample, enabling the direct assembly or integration into devices for different applications. Here we present for the first time the piezoelectric characterization and application as energy harvester of the templated 1D ZnO nanostructures, exploiting the potential of having such inorganic nanomaterial vertically oriented in an extremely flexible hosting matrix. The ZnO-PC nanogenerators were successfully tested both under compressive and bending stresses, examining the effect of the PC matrix pore size, which is reflected on the diameter of the templated ZnO, toward the generated voltage. In the case of 100 nm composite nanostructure, we reached a maximum output voltage and current of 1.15 V and 100 μA, respectively, and a maximum output power density of 287.5 mW/cm^3, one of the highest reached in zinc oxide-based piezoelectric nanogenerators [15,37].

Experimental section

Synthesis of ZnO-templated 1D nanostructures

Track-etched porous polycarbonate membranes (Nucleopore from Whatmann, disc of 25 mm in diameter) having thickness of 5 μm and a nominal pore diameter of 100, 50 and 30 nm were immersed for 3 h at 88 °C in an hydrothermal growth bath composed by 25 mM zinc nitrate hexahydrate $Zn(NO_3)_2 \cdot 6H_2O$ (purity 98%, Sigma-Aldrich), 12.5 mM hexamethylenetetramine $C_6H_{12}N_4$ (HMT, purity 98%, Sigma-Aldrich), 5 mM polyethylenimine (PEI, average Mw ~800, Sigma-Aldrich), and 320 mM ammonium NH_4OH (28%, Sigma-Aldrich) in 100 mL bi-distilled water (from Direct-Q, a Millipore purification system), as reported for the synthesis of vertically aligned ZnO NWs [13]. After growth, the samples were thoroughly rinsed with bi-distilled water and dried with nitrogen flow. Gentle cleaning of the PC surface with 1 M HCl was carried out to remove the ZnO material deposited on the top of the surface. This procedure did not affect the nanostructures formed into the PC pores, as confirmed by the measurements reported below. The samples were named ZnO-PC100, ZnO-PC50, and ZnO-PC30 referring to the ZnO 1D nanostructures templated into the PC membranes having 100, 50 and 30 nm pores, respectively.

Material characterization

The morphology of the ZnO 1D nanostructures was investigated, after PC membrane dissolution in N-methyl pyrrolidone for 2 min, using both ZEISS Auriga and ZEISS Merlin Field Emission Scanning Electron Microscopes (FESEM). High Resolution Transmission Electron Microscopy (HRTEM) images were collected by an FEI Tecnai F20ST transmission electron microscope, operating at 200 kV. The ZnO-PC crystal structure was evaluated using a Panalytical X'Pert X-ray diffractometer in the Bragg-Brentano configuration. A Cu Kα monochromatic radiation was used as X-ray source, with a characteristic wavelength $\lambda = 1.54059$ Å.

Nanogenerator preparation and measurement

To collect the generated electric charges by the ZnO-PC samples, both surfaces of the membranes were first metalized with 50-nm thick platinum electrodes (by a Q150T sputter system form Quorum Technologies, operating at 50 mA and $1 \cdot 10^{-4}$ bar using a suited circular mask in order to avoid metallization at the membrane edges and