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Synthesis of ZnO rod arrays on aluminum recyclable paper and effect of the rod size on power density of eco-friendly nanogenerators

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ABSTRACT

In this work, we demonstrated a novel and effective approach on the use of low-cost electrodes, an eco-friendly substrate and zinc oxide (ZnO) micro or nanorods (MRs or NRs, respectively) for building triboelectric devices (TENGs). The reported strategy focuses on using low-cost materials and fabrication processes. For the first time and without any pre-treatment, an aluminum recyclable paper from the milk carton (named ARP) was used as a substrate and TENG bottom electrode. A systematic study on the growing of ZnO structures on ARP by chemical bath deposition has been carried out. We found that the ZnO rods size, and resistivity of the TENG upper electrode considerably influence the power density of the device. Such sustainable, low-priced ZnO-based TENGs can produce up to 1.6μW/cm^2 output power density when operated at 50 Hz. The fabrication of an eco-friendly nanogenerator demonstrates the possibility of manufacturing low-cost, flexible, and large-area energy harvesting devices for future applications.

1. Introduction

In the last years, researchers have started looking for new devices able to harvest different kinds of wasted mechanical energies from the environment and effectively convert such energies into electricity [1,2]. In this scenario, nanogenerators have emerged as a promising technology to produce electric power enough to drive some small functional devices, like light-emitting diodes (LEDs) and sensors, at low costs [3–6].

Among the existing types of nanogenerators for this purpose, the piezoelectric (PENGs) and triboelectric (TENGs) ones are those that have been receiving increased attention in the last decade [3–10]. In PENGs, the deformation of nanostructures by mechanical energy causes negative and positive charge separation generating an electric current [6,8–10]. In TENGs, on the other hand, the charges are generated by triboelectric effect (viz. contact and induction electrification) when two different materials are brought in contact and rubbed [2–5,7]. Briefly, during the contact in the triboelectric effect, each material develops a charge of opposite polarity [4]. The magnitude and polarity of the generated static charges are sensitivity to material composition, contact surface and the environmental [11].

TENGs show the advantage of providing high-output energy density with simple structures and easier packaging. Moreover, TENGs afford the possibility of using a variety of materials [7] for their fabrication, including flexible and transparent substrates [4,5]. Although TENGs have been intensively studied, issues related to the energy loss occurring during the power-generation process still need to be overcome for more effective applications. In this context, ZnO nanostructures stand out as an excellent material to be used in TENGs inasmuch as they may increase the device surface area and improve the performance by reducing the energy loss [6].

ZnO is a wide band-gap (3.37 eV) semiconductor compound with excellent charge carrier transport properties and high crystalline quality [12,13]. ZnO nanostructures show high piezoelectric and pyroelectric coefficients and large electromechanical coupling [6]. The piezoelectricity in ZnO nanostructures (e.g., nanowires, nanorods) comes from the lack of a center of symmetry in wurtzite structure. In addition to such excellent electrical properties, ZnO nanostructures with distinctive morphologies are relatively easy to grow on different substrates, including flexible ones, by using low temperature and low-cost methodologies [14].

One of such interesting routes is the low-temperature ZnO synthesis in aqueous solution, a pioneer the Vayssieres publication [14]. This method has no restriction in respect to the kind of substrate employed, as long as it is not completely water-soluble. This opens up lots of possibilities for using low-cost flexible substrates to grow ZnO nanostrucutres, for exempla paper – the cheapest and most abundant existing flexible substrate [7]. The synthesis of ZnO on paper substrates and bacterial cellulose substrates with no need of surface modification has been successfully reported by us in a previous work [15].

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Flexible, lightweight triboelectric devices are particularly interesting for applications for powering portable electronics through low power consumption. From previous works, a wide variety of flexible substrates have been tested for this purpose, which include the use of Kapton, PET (polyethylene terephthalate) [9,16], PVC(polyvinyl chloride), PET/ITO (indium-tin oxide) [4], and PDMS (polydimethylsiloxane) [17]. However, these substrates are costly in comparison with paper, so the development of low-price device becomes compromised. Aiming to overcome this issue, the use of packaging cardboard as a substrate for solar cells toward self-sustainable intelligent packaging was reported recently as a proof-of-concept [18]. Nevertheless, one of the limitations in this case was the evaporation of aluminum (Al) contact an e-beam system, which does not contribute to a cost-effective device fabrication process.

To tackle the issue of developing a more affordable electronics, we demonstrate a cost-effective route to manufacture flexible, lightweight large-area nanogenerators based on ARP.

In this work, aluminum recyclable paper (ARP), readily obtained from a milk carton, with no need of additional surface treatments was used as the substrate and bottom electrode of ZnO-based TENGS. The device development involved the establishment of the ideal conditions for growing ZnO nanostructures on ARP, as our first target. Second, we used the ZnO micro and nanorods (here, namely MRs and NRs, respectively) to build TENGs devices as a proof-of-concept. We also tested different materials for the device upper electrode, such as copper foil or platinum/PTE. The evaluation of such experimental conditions is important as the size of ZnO rods and the characteristics of the upper electrodethe govern on the response of the triboelectric device.

2. Experimental

2.1. Materials

The aluminum recyclable paper (ARP) was obtained from a regular milk carton package (tetrapak®). Zinc acetate dihydrate 98%, $Zn(Ac)_2{\cdot}2H_2O$, Zinc nitrate hexahydrate 98%, $Zn(NO_3)_2{\cdot}6H_2O$, hexamethylenetetramine (HMTA) 99% were purchased from Sigma-Aldrich. An ethanolic solution (Ethanol absolute from Sigma Aldrich 98%) of zinc acetate dehydrate (Sigma-Aldrich) was used to prepare the nucleation layer by spray deposition.

Copper foil (Cu) was purchased from 3 M (Metal 1181 6035–11), and the platinum (Pt) film on PET was deposited by sputtering. The deposition of the 100 nm Pt film on PET substrate (Sigma Aldrich®) was performed in a Balzers (BA510) DC sputtering system in the LNNano Microfabrication Laboratory. The Pt film was deposited under a pressure of 2×10^{-7}mbar and at room temperature. The Pt film thickness was monitored by a quartz crystal microbalance sensor in the deposition chamber. The resistivity of the Pt/PET and Cu was measured by using Thin Film Devices, Inc. FPP-2000, presenting values of 5.3 $Ohm.sq^{-1}$ and 0.005 Ohm. sq^{-1}, respectively.

2.2. Growth of ZnO nanostructures on ARP

ZnO micro and nanostructures were synthesized directly on the ARP substrate without any surface treatments on the carton. Chemical bath deposition (CDB) synthesis was used for growing ZnO rods. The details for the ZnO structures growth on ARP are discussed in the following.

2.3. Preparation of the ARP substrate

ARP mainly consists of three layers: paperboard, an Al layer and a polyethylene film (PE) (Fig. 1a). Thus, to use the aluminum layer as the bottom electrode, it is required to remove the polyethylene film. The polyethylene film was mechanically peel off using tweezers (Fig. 1b), preserving the Al layer underneath. After that, ARP substrate was rinsed with acetone to eliminate any residual polymer adhered to the surface. Following, ARP substrate was immersed in a 1 mol L^{-1} sodium hydroxide (NaOH) solution for three minutes to promote hydrophilic characteristics to the surface and, consequently, better wetting of the zinc acetate ethanolic.

2.4. Seeding layer deposition by ultrasonic spray

A seeding layer based on zinc acetate ethanolic solution was deposited on ARP by ultrasonic spray coating method. An *ExactaCoat Ultrasonic Coating System - Sono-Tek microspray* (Fig. S1), and a 10 mM zinc acetate $Zn(Ac)_2$ ethanolic solution was used during deposition. Table S1 shows a summary of the parameters of deposition used here.

2.5. Synthesis of ZnO micro and nanostructures on ARP substrate

ZnO micro and nanostructures were grown over the seeded ARP by chemical bath deposition (CBD). $Zn(NO_3)_2{\cdot}6H_2O$ and HMTA were mixed in a 10 mM equimolar aqueous solution [15]. The reagents and the substrate were put in a Teflon cup and the CBD process was carried out in neutral pH at 95 °C for 2 h (Fig. S2). To complete the process, the substrates were withdrawn from the solution, rinsed with deionized water and dried in air at 90 °C using a hot plate.

2.6. Characterization

The surfaces of the bare ARP and ZnO coated substrates were characterized by scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), and atomic force microscopy (AFM). The SEM images and EDS were obtained through an Inspect F50- SEM from FEI by using 5 kV and 12 μA. The XRD results were obtained by using a Shimadzu-XDR 7000 diffractometer with a copper tube CuKα (α = 1.54060 Å), a graphite monochromator, and operated at a power of 40 kV and 30 mA. Nanosurf AFM was used to image the surface topography in the noncontact/phase contrast mode. A surface profiler (Dektak 150) was used to measure the thickness of the layer.

The resistivity of the Al layer on the ARP was obtained by using the four points method and a Keithley 4200-SCS equipment.

To test the triboelectric devices, we employed a special structure designed and built as described by Shieh et al. [19]. In the Test System, the sinusoidal signals are supplied by Wavetek Datron model 29 A signal generator. The signal is amplified by a Sonata Sonasom AM/FM stereo audio amplifier. The device response is monitored by a Taktronix TDS2014B oscilloscope that provides the voltage supplied by the device. The audio amplifier provides vibration on the Test System allowing the device strikes against a planar surface and bending due to its flexibility. The device compression against a planar surface enables the contact and separation of charges on the electrode surface. All triboelectric devices were built with a contact surface area of 4.4 × 4.4 cm, using the configuration showed in Fig. 1.e. All TENGs measurements were driven with a load of 10 MΩ. The TENGs were tested in different frequencies to find out the maximum electrical response.

3. Results and discussion

3.1. Characterization of the ARP substrate

From SEM and AFM characterization, the ARP substrate exhibited a homogeneous surface with apparently low roughness (Fig. 1c and d). EDS confirms the presence of Al on the card. XRD analysis shows well-defined peaks corresponding to the Al structure (Fig. S3.a and Fig. S3.b, respectively (111), (200), (311)).

Additional AFM analyses provided roughness values (root-mean-square, R_{ms}) of the 115.3 nm and 615 nm for scanned areas having $3 \times 3\ \mu m^2$ and $10 \times 10\ \mu m^2$, respectively (Fig. 1d and Fig. S3c).

The electrical measurements on the ARP surface show an average