

Rechargeable zinc oxide / carbon nano-structures

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A simple solution growth process was employed to deposit ZnO nanowires on carbon nanotubes and nano-structured carbon paper. Vertical ZnO nanowires formed on the carbon paper with a hexagonal orientation. On the carbon nanotubes, the ZnO nanowires and platelets integrated as an agglomerated sphere. Electric charge flow was measured in both structures upon probe contact, and would decay over several hours. A mechanical perturbation was found to recharge the structure, which was attributed to the piezoelectric ZnO nanowires. Continuous as well as intermittent vibration coupled with an electrochemical storage mechanism to create a perpetual current source.

key words: zinc oxide, carbon nanotube, piezoelectric, nanowire.

Introduction

Nanostructured ZnO and C are fundamental building blocks in two seemingly disparate applications: charge-storage and piezoelectric energy harvesting. The major energy storage devices are batteries and capacitors as well as supercapacitors, which bridge the characteristics of batteries and capacitors. A supercapacitor can store energy through a capacitive process, such as an electrochemical double layer capacitor (EDLC), or through a Faradaic battery-like reaction termed a pseudocapacitor.

An EDLC generates a double layer capacitance by charge separation at an interface between an electrolyte and a high surface area electrode such as activated carbon, carbon nanotubes (CNTs) or similar materials. EDLCs have large power densities by the fast absorption/desorption kinetics of protons but the energy density is limited [1, 2]. Recently, Kalpana *et al.* proposed combining the double layer capacitance of large surface area nano-carbon aerogel with the Faradaic capacitance of ZnO [3]. This carbon aerogel/ZnO composite showed high electrochemical reversibility and capacitive characteristics in a KOH electrode.

A lithium ion battery operates by transferring the lithium ions into and out of the carbon based electrode. The maximum charge is ultimately limited by the maximum storage of one lithium atom for every six carbon atoms in the standard graphite electrode. Substituting carbon nanotubes as the electrode increases the storage to one charged lithium atom for every three carbon atoms.

There has been a surge of interest in converting residual energy sources into useful electrical power particularly

for self-powered systems [4]. Numerous sources exist for energy harvesting with the two most accessible being vibrations from engines and mechanical movement from normal human activity [5]. Promising work by Wang and Song has shown that a mechanical deflection of a ZnO nanowire with a metal electrode creates a large piezoelectric DC current [6]. The Schottky barrier between the ZnO nanowires and tungsten metal probes described in this article replicate the Schottky rectifying behavior first demonstrated with a metal AFM tip by Wang and Song [5, 6], which was eventually scaled to a large area sawtooth Si electrode coated with a thin Pt layer [7].

The physics of the piezoelectric effect dictate that charge is only produced when a perturbation, e.g., vibration, is present. There are applications such as transmitters, receivers, sensors, actuators, in telemetry, and MEMS devices where it is necessary to have energy on-demand or in irregular bursts. Thus, a simple piezoelectric device is not sufficient as it is necessary to accumulate the piezoelectric energy in a rechargeable battery or supercapacitor. This has been demonstrated at the system level by hard wiring a battery to a piezoceramic lead-zirconate-titanate piezoelectric device [8, 9].

The focus of this study is a ZnO/carbon structure, which can couple charge-storage and energy harvesting mechanisms integrated at the nano-scale. Similar to most semiconductor crystals, ZnO is preferentially deposited on structurally comparable single-crystal substrates. This constraint is an application design limitation as single crystal substrates are inherently inflexible. In this document, a batch solution method was employed to deposit ZnO nanowires on carbon paper and nanotubes, which are inherently flexible.

Experimental

In this study, ZnO nanowires were deposited in aqueous solutions in a Parr pressure restricted chamber. Scaling this

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batch process was accomplished by a linear increase in reactant volume and vessel size. Prior to growth the carbon paper was washed in methanol and deionized water. The carbon nano-structures were immersed in a solution of 5 ml zinc acetate in water (0.001 M), 10 ml NaOH in water (0.01 M), and 1 ml ethylene glycol at 130 °C. The Parr chamber allowed a higher temperature for growth with a lower concentration of reactants to produce ZnO nanowires with high aspect ratios particularly at the initial stages of growth. Still, similar results could be produced in partially open Teflon beakers. Residual NaOH and $\text{Zn}(\text{OH})_2$ as a paste are common byproducts of this reaction. This dense paste acted as a binder for the nanostructures and no attempt was made to wash this paste following the reaction. Structural characterization was performed with a Panalytical X'pert X-ray diffraction (XRD) system and a LEO Field Emission Scanning Electron Microscope (SEM).

The sample was tested on a glass slide with two flat-tip probes. The probe station was enclosed in a metal dark box, which acted as a Faraday cage. The current was zero if the probes were lifted, which was also ensured by the high input impedance of the electrometer. There were two types of current fluctuations: a long time constant discharge that occurred on the hour time scale, which is attributed to an electrochemical discharge effect; and a weaker noise, which is attributed to the intermittent formation of reverse Schottky contacts.

Results

The electron micrograph of as-received carbon nanofoam (aerogel) paper (Marketch International Inc.) in Fig. 1(a) and (b) shows platelets of carbon nanofoam firmly attached to random carbon fibers, interspersed with micro and nano-scale porosity. Subsequent ZnO deposition produced a dense packing of vertical nanowires as observable in Fig. 1(c) and (d). The solution growth of the ZnO nanowires

proceeded rapidly with large areas of the carbon paper covered after 10 minutes of growth. A deposition time beyond approximately 1 hour yielded a packed array of ZnO nanowires approximately 10 mm in length.

A similar process was used to deposit ZnO nano-structures interwoven into agglomerated single-wall carbon nanotubes. The initial stages of growth seeded ZnO nanorods on the carbon nanotube bundles. Additional growth time formed an agglomerated mass of ZnO nanorods, carbon nanotubes, and residual NaOH and $\text{Zn}(\text{OH})_2$ paste (Fig. 2).

Samples of the ZnO/CNT and ZnO/C-paper structures were placed in a probe station. The measured samples were approximately 0.01 grams. As discussed by Wang and coworkers, the critical metric for the piezoelectric effect is the number of nanowires interacting with the metal contact [6, 7]. Electrical current between the two probes was measured using an HP4140 pA-meter or a Keithley 6517 electrometer. Both instruments were programmed to measure current at 1 s intervals with 0 V bias applied on the probes. All measurements were performed in darkness.

The measured current from a ZnO/CNT bundle is presented on Figs. 3(a) and (b) and that from a ZnO/C-paper structure is pictured in Fig. 3(c). A typical sample would initiate with a current in tens of micro-Amps range at hundreds of micro-Volts. If the sample remained isolated, the current would decay over several hours. When the probes or, as displayed in Fig. 3, the chuck was vibrated the current would dramatically jump to a higher level that was not necessarily limited by the magnitude of the original current.

A continuous vibration applied to the ZnO/CNT bundle created a constant or slightly increasing current source as seen in Fig. 3(b). Similar experiments conducted for a measurement time of several weeks showed a similar constant current source in air, N_2 ambient, as well as in vacuum.

Similar results were generated from the ZnO/C-paper structure. Fig. 3(c) depicts the current response of a 0.01 g ZnO/C-paper sample in low vacuum. In the current exper-

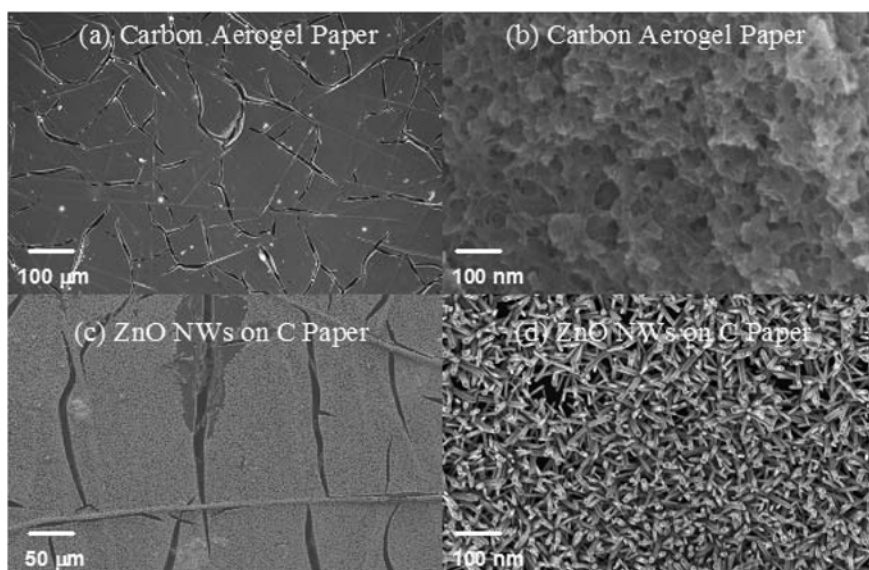


Fig. 1. Electron micrographs of (a,b) as-received carbon paper with (c,d) hydrothermal ZnO nanowires.

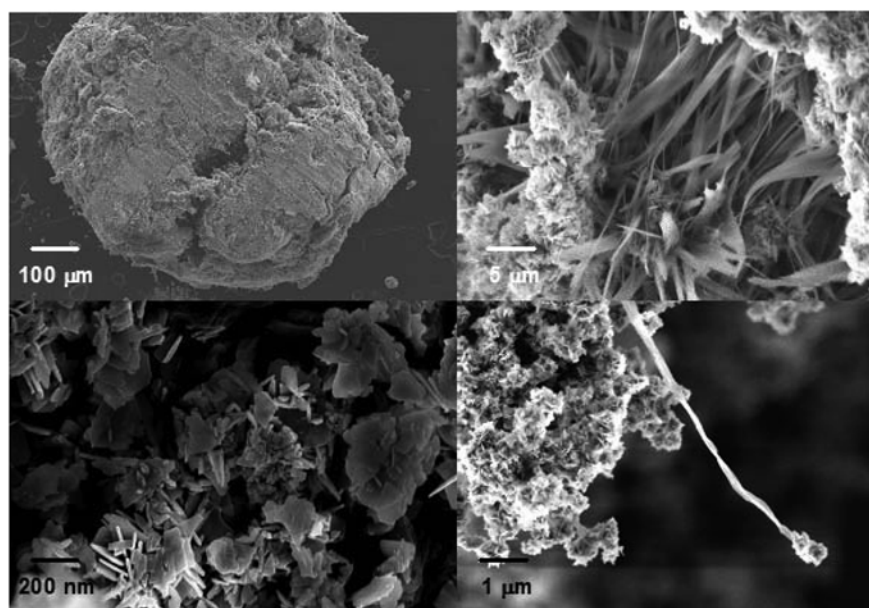


Fig. 2. Electron micrographs of ZnO nanocrystals deposited into bundles of single-wall carbon nanotubes. A paste of residual NaOH and $\text{Zn}(\text{OH})_2$ bound the nanorods and platelets of ZnO with the carbon nanotube bundles into mm to cm sized spheres.

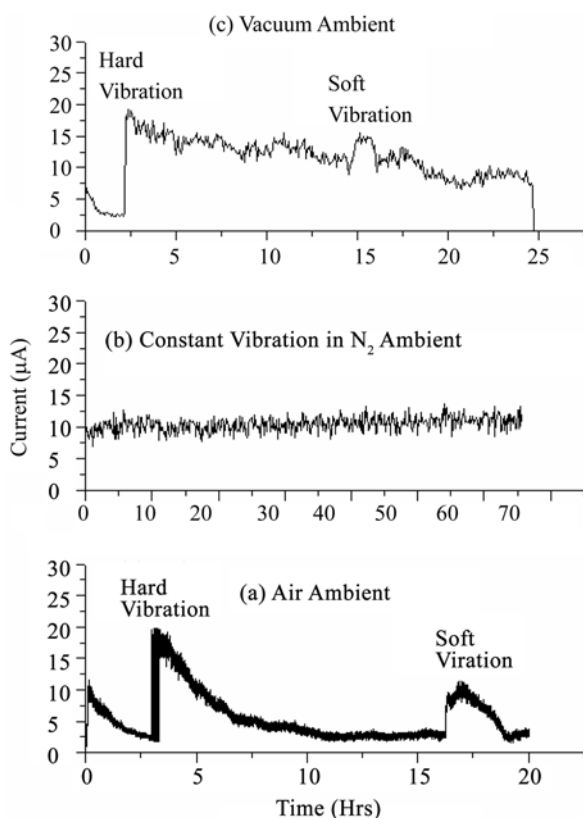


Fig. 3. (a) Current response of ZnO/CNT (a) bundle to background vibration in an air ambient. The sample shows a self-charging effect proportional to the level of mechanical perturbation. (b) Current response of the same bundle as (a) to a constant background vibration in a N_2 ambient. (c) Current response of ZnO/C-paper structure in a vacuum. Termination of the vibration in all samples and measurements resulted in a several hour decay in the current.

imental set-up, the suction of the vacuum system created a low level background vibration that distorted the decay

mechanism observed in Fig. 3(a). Still, a singular or constant vibration would always boost the current level even in vacuum. Additionally, no degradation in charge storage was observed after disconnecting the sample for several weeks as the subsequently measured current levels remained comparable.

Discussion

Various permutations in background ambient, time, and perturbation rate all showed the same trends in the electrometer testing, i.e., a large increase in current when exposed to a mechanical force. A perpetual current source created by constant vibration as seen in Fig. 3(b), is predictable based on the large piezoelectric coefficients of ZnO. Recently, Wang and coworkers have fabricated ZnO nanowire arrays on conducting substrates for just this purpose, i.e., converting mechanical vibrations into useable current sources [4-6]. In contrast, in this article, the approximate 3 h half-life of the current decay indicates coupling with an independent charge storage mechanism. The analysis of the exact mechanism is underway but the composition of these structures suggests an electrochemical effect. A possible Faradaic mechanism for charge release is by the $\text{Zn}|\text{ZnO(s)}|\text{NaOH(paste)}$ half-cell.

A force applied by the metal contact to the ZnO nanowire typically creates the arrangement depicted in Fig. 4(a). The uneven longitudinal strain distribution creates a piezoelectric-induced potential variation across the nanowire. The positive potential on the trailing edge of the wire creates a reverse bias Schottky barrier with the metal contact preventing electron flow. The only source for discharge is to drive the solid-state redox reaction involving generation of the Zn^{2+} ion within the paste electrolyte and intercalation of the Zn^{2+} ion (and possibly the OH^- ion) into open sites

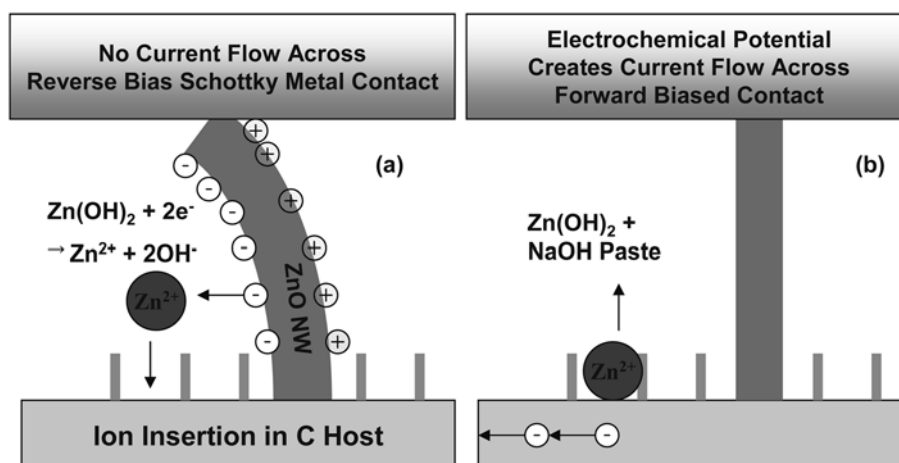


Fig. 4. Electrochemical insertion reaction driven by piezoelectric charge. (a) Electrons are unable to pass through contact under reverse bias, thus the charge drives the electrochemical insertion of mobile Zn^{2+} ions into interstitial sites and open ends in the carbon nanostructure. (b) Electronic and ionic conduction creates a current flow through the carbon and ZnO nanostructures.

in the nanostructured carbon host [10, 11]. In Fig. 4(b), the strain and, thus, piezoelectric-induced potential distribution is removed. Combined with the electrochemical potential present in the system, a forward biased Schottky contact is now present, which allows current flow through the carbon nanostructure and the n-type ZnO nanowire.

Wang and coworkers generated a vibration-induced electron current from ZnO nanowires by employing a specially designed zigzag contact [4-6]. With sufficient displacement, the inverted-V shape of this contact would slide across the nanowire tip to contact the leading edge of the nanowire. The negative potential at the leading edge created a forward biased Schottky contact, which allowed electron flow. Wang and Song measured no current flow when a flat contact was employed since this arrangement only formed reverse biased Schottky contacts with the trailing-edge of ZnO nanowires [6]. We were able to replicate this lack of current flow with a flat contact for a vibration applied to ZnO nanowires on glass slides [12]. The unique design presented in this article stores the piezoelectric energy as electrochemical energy with a characteristic long time release mechanism.

The charge creation and storage coupled mechanism of this structure is interesting in itself; however, the key result is the possibility to fabricate a piezoelectric charge storage device in immediate contact or close proximity to an active carbon electrode of a capacitor, supercapacitor or battery. Thus, this piezoelectric charge source could be located internal to the battery or supercapacitor package. The external behavior would be a package that converts intermittent ambient vibrations into a perpetually charge source.

Conclusions

This article shows that ZnO nanowires embedded in

carbon nanostructures can be fabricated by a simple solution process. Electrical measurements of these structures indicate a piezoelectric energy harvesting mechanism created a device capable of converting vibration energy into electrical energy. Within the same structure, an electrochemical effect is able to store this charge over several days and release the current over several hours.

Acknowledgement

The Research at Korea University was supported by the BK21 program.

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