Use of ZnO nanorods grown atomic force microscope tip in the architecture of a piezoelectric nanogenerator

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The piezoelectric potential output has been studied using a ZnO nanorods (NRs) grown atomic force microscope (AFM) tip in lieu of the normally used AFM tip. The ZnO NRs were synthesised on the AFM tip and on the fluorine-doped tin oxide (FTO) glass substrate using the aqueous chemical growth method. The as-grown ZnO NRs were highly dense, well aligned and uniform both on the tip and on the substrate. The structural study was performed using X-ray diffraction and scanning electron microscopy techniques. The piezoelectric properties of as-grown ZnO NRs were investigated using an AFM in contact mode. In comparison to the AFM tip without ZnO NRs, extra positive voltage peaks were observed when the AFM tip with ZnO NRs was used. The pair of ZnO NRs on the AFM tip and on the FTO glass substrate together worked as two oppositely gliding walls (composed of ZnO NRs) and showed an enhancement in the amount of the harvested energy as much as eight times. This approach demonstrates that the use of the AFM tip with ZnO NRs is not only a good alternative to improve the design of nanogenerators to obtain an enhanced amount of harvested energy but is also simple, reliable and cost-effective.

1. Introduction: Owing to increasing use of energy, it is highly desirable to explore/improve different resources of energy to fill the gap between the demand for and the supply of energy. One possible approach that has the potential to fill (partially) this gap is the use of nanostructures to modify/design/develop self-powered nanodevices that can harvest their operating energy from the environment. Since all the systems that exist at present are fully dependent on a power source (normally a small-sized battery), it is extremely worthwhile to keep the size of the battery as small as possible. However, the reduced size of the battery will affect its lifetime. Therefore, the key requirement is to build such self-powered nanosystems that are not only able to scavenge their desired energy from the environment but also work independently with an uninterrupted supply of energy. Scientists and researchers have tried hard to explore different ways and means to harvest energy from the environment just by converting mechanical, vibrational or thermal energy into electricity [1]. This type of energy becomes more important when the available sources of energy are expensive or insufficient. Designing a nanogenerator (NG) in such a way that it can convert mechanical energy into electric energy by utilising the piezoelectric effect is an approach that has been developed in the recent past [2–4]. This kind of piezoelectric NG would not only be helpful for developing new nanodevices but can be utilised to build self-powered systems as well. This is why in recent years a lot of work has been done, first to fabricate these NGs, and then to improve their performance either by enhancing/increasing their efficiency in terms of harvested energy or by minimising the cost or by improving their reliability etc.

In this connection, Wang's group has presented quite a few novel approaches, some of which are highlighted here. Wang *et al.* [3] replaced the normal atomic force microscope (AFM) tip with an ultrasonic wave to actuate all the ZnO nanowires (NWs) at the same time to improve the power generation capabilities. Xu *et al.* [5] have used a flat plate type electrode to bend/deflect a maximum number of ZnO NWs in one instance to obtain more output, because a flat shape has more surface area than a tip. Qin *et al.* [6] exhibited a fibre-based NG in which two pieces of fibre were used to grow ZnO NWs and then on one piece a gold layer was deposited to form Au-coated ZnO NWs, so it can serve as the top electrode. Finally, the ZnO NWs grown sides were entangled on one another to make relative brushing between two ZnO NWs grown fibre pieces to improve the output response. Hsu and Chen [7] also made a brush-like NG for improving piezoelectricity by using two pieces of flexible polyethylene terephthalate (PET) substrate, one with ZnO NWs and the other with Pt/ZnO NWs to work as the electrode. Xu *et al.* [8] also made a four-layered NG by stacking four pieces of substrate over one another to form a four-layered brush-like architecture. They utilised Si as substrates and grew ZnO NWs on both sides of the substrate to make a layered brush in which every top piece acted like an array of AFM tips. All these studies showed significant enhancement in the generated amount of piezoelectricity. In this Letter, partial modification has been done in the design of NGs to enhance the output energy from the as-grown ZnO NRs. We synthesised ZnO NRs on the rectangular shaped cantilevers of the probe (known as the AFM tip) and used ZnO NRs grown FTO glass substrate, so they can work together as two oppositely gliding walls (composed of ZnO NRs) at the time of the scan measurement of the sample.

In the past few years, different piezoelectric materials like ZnO, GaN, CdS and ZnS were tested to make an efficient and low-cost NG. Among these piezoelectric materials, ZnO has captured a lot of attention from researchers/scientists for developing piezoelectric devices, because of the following three rare attributes of ZnO. Firstly, ZnO is a typical piezoelectric and pyroelectric material that is more than useful to develop energy conversion devices. Secondly, ZnO is known to be a green/environment friendly and biocompatible material; therefore it can be utilised even in biomedical sciences [9]. Finally, ZnO has the most diverse configurations of nanostructures (NSs) such as nanowires, nanorods (NRs), nanoflakes, nanodisks, nanoflowers, nanotubes [3, 10–12] and so on. To prepare the desired ZnO NSs, there exist many approaches including low and high temperatures [13, 14]. The relatively low temperature (< 100°C) aqueous chemical growth (ACG) method is better than other methods because a very low growth temperature is more suitable for soft/foldable substrates such as common paper, textile fabrics, flexible plastic and aluminium foil [15]. Furthermore, this method is relatively simple to adopt and of low cost, therefore it can also be used in bulk production.

A number of techniques have been used so far to measure the piezoelectric response from the grown ZnO NRs including interferometry [16], scanning tunnelling microscopy [17], scanning probe microscopy [18] and AFM [19] or piezoresponse force microscopy [20]. In this Letter, the scan measurements were performed by using AFM in contact mode.

2. Experimental: All chemicals including hexamethylenetetramine [$C_6H_{12}N_4$] (purity 99.90%), zinc acetate dihydrate [Zn $(CH_3COO)_2{\cdot}2H_2O$] (purity 99.98%) and zinc nitrate hexahydrate [Zn $(NO_3)_2{\cdot}6H_2O$] (purity 99.99%) along with fluorine-doped tin oxide (FTO)-coated glass substrate were purchased from Sigma-Aldrich, Sweden, and used without any further purification. In addition, silicon-made tipless probes (NT-MDT NSG11 series) having two cantilevers on opposite sides with a gold-coated reflective side (back side) were purchased from NT-MDT, Russian Federation, and used in the experiments.

To avoid any kind of contamination during the substrate/tipless probes cleaning and then the synthesis of ZnO NRs, all the experimental work has been conducted in clean room environment. The synthesis of n-type ZnO NRs both on the FTO glass substrate and on cantilevers of Si-made tipless probes was performed using the low-temperature ACG method. The cleaning of the FTO glass substrate was performed via an ultrasonic bath with acetone and isopropanol, respectively, for 5 min each, then washed with deionised water, and dried by a flow of nitrogen gas. The probes were carefully rinsed through acetone and isopropanol, respectively, then gently washed with deionised water and dried in air. A seed solution of zinc acetate dihydrate was deposited on the substrate and probes to act as the nucleation site for well-aligned ZnO NRs. The seed solution was deposited using the spin-coating technique. This procedure was repeated twice at about 3000 rpm for 30 s each time and after that the samples were annealed at 100°C for 10–15 min to have good adhesion of the seed particles. The deposition of the seed solution on the probes was performed by dipping them in the seed solution for a while and then taken out. Finally, the FTO-coated glass substrates and the probes decorated with ZnO particles were placed in a beaker containing an equimolar (0.075) solution of zinc nitrate hexahydrate and hexamethylenetetramine. The beaker was then kept in a preheated electric oven at 95°C for 5–6 h. After completion of the growth duration, the substrate and the probe were washed carefully with deionised water to remove residual solid particles from the surface. Finally, the samples were dried in air at room temperature.

For coating of the platinum layer on the Si-made tipless probe decorated with ZnO NRs, the thermal evaporation technique was utilised. A 20 nm-thick layer of platinum was evaporated on the probe at a pressure of 2×10^{-7} T. The Pt coating has two advantages. First, it is suitable for increasing the conductivity of the electrode and secondly, to make a Schottky contact with the ZnO. It is well known that the coating material must be conductive to have a Schottky contact between the coating material and ZnO.

AFM measurements were performed using an Si-made probe (with and without ZnO NRs) coated with a platinum layer in contact mode. The silver (Ag) bottom electrode was grounded by using Ag paste and the AFM tip was used as the Schottky contact during the 1–5 measurements. The spring constant of the tip was about 0.6–1 N/m, maintaining a force (0.6–3 µN) between the cantilever and the sample's surface. The scan speed was 30 µm/s and the scan direction was perpendicular to the cantilever. The direction of the current is from the cantilever to the ZnO NRs (confirmed by the positive output voltage). To avoid the leakage current, an operational amplifier having a gain bandwidth product of about 1.8 MHz was used to keep the sample at ground potential. Throughout the AFM scan measurements external voltage has not been allowed.

The mechanism of the piezoelectric generation is based on two things. One is the piezoelectric effect [21] describing the coupling between the dual (piezoelectric and semiconducting) properties of ZnO and the other is the rectifying behaviour of the Schottky contact between the platinum-coated AFM tip and the ZnO NR [22]. The piezoelectric effect transforms the mechanical strain into ionically polarised charges, which creates a piezoelectric potential in the NR to regulate the carrier transport process. On the other hand, the Schottky barrier drives the current in the direction where the Schottky barrier is at forward bias. Hence, if thousands of NRs are generating electricity at the same time, then the Schottky barrier sums up all and drives them in the same direction [3]. When the AFM tip starts to bend the NR, the Schottky contact becomes reversely biased between the ZnO NR and the Pt-coated AFM tip, because ZnO has less electron affinity than the work function of Pt. The Pt–ZnO interface acts as a gate to stop the backward movement of electrons. However, when the tip touched the compressed side of the NR, the Schottky contact becomes forwardly biased and the external electrons were allowed to move across the Pt–ZnO interface that results in finding an external current.

A field emission scanning electron microscopy (FESEM) model LEO 1550 Gemini microscope running at 15 kV was used to investigate the morphology of the grown ZnO NRs. The crystal quality has been assessed by the X-ray powder diffraction (XRD) technique using a Phillips PW 1729 powder diffractometer equipped with Cu Kα radiation ($\lambda = 1.5418$ Å) having a generator voltage of 40 kV and a current of 40 mA. The piezoelectric generation from the ZnO NRs was recorded using an AFM (Digital Instruments Multimode AFM, The Netherlands) and a custom-made transimpedance amplifier along with stiff platinum-coated probes (NT-MDT NSG11/Pt, Russian Federation) with and without ZnO NRs.

3. Results and discussion: The schematic diagram in Fig. 1*a* describes the dimensions of the probe along with the cantilevers that were used to grow the ZnO NRs. The rectangular cantilever had a tetrahedral shape with an apex angle of 70°. There are two cantilevers on both sides of the probe denoted as L_A and L_B as shown in Fig. 1*a*. These cantilevers with and without ZnO NRs were used for the measurements and named as the Pt/ZnO tip and the bare (without ZnO NRs) Pt tip, respectively, in the later discussion for clarity. Fig. 2*b* is the high-magnification SEM image of the cantilever of the AFM tip before the growth of ZnO NRs. Fig. 2*c* shows the low-magnification SEM image of the AFM tip prior to growth.

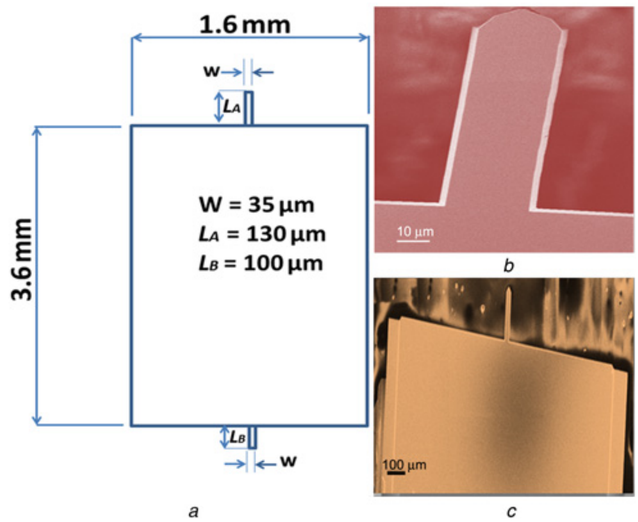

Figure 1 *Schematic diagram showing dimensions of used cantilever, and high- and low-magnification SEM images of cantilever of AFM tip prior to growth*
a Schematic diagram
b, *c* SEM images

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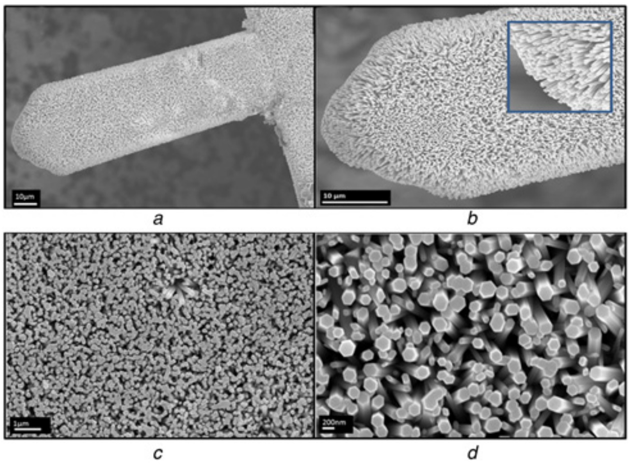

Figure 2 *SEM images of ZnO NRs grown on AFM tip and on FTO glass substrate*
a Low-resolution image of AFM tip
b High-resolution image of AFM tip
c Low-resolution image of FTO glass substrate
d High-resolution image of FTO glass substrate

Fig. 2 shows the SEM images of ZnO NRs grown on the cantilever (tip) of the AFM probe and on the FTO glass substrate with different magnifications. Fig. 2*a* is a low-magnification SEM image of ZnO NRs grown on the cantilever (tip) and Fig. 2*b* is a relatively much higher resolution image of the same. It is clear from the Figures that the cantilever (tip) is completely covered with highly dense and well-aligned ZnO NRs. The inset of Fig. 2*b* shows the top view of as-grown ZnO NRs. It can be seen from the inset that all the NRs have hexagonal faces and the average length and diameter of these NRs is about 1–1.5 and 80 nm, respectively. Typical SEM images of the as-grown ZnO NRs on the FTO glass substrate are shown in Figs. 2*c* and *d*. Fig. 2*c* is a low-magnification SEM image of ZnO NRs measured at 1 μm and it can be seen that the NRs are highly dense and uniformly distributed on the surface of the substrate. Fig. 2*d* is a high-resolution image measured at 200 nm depicting that the NRs are grown with hexagonal faces and are perpendicular to the substrate as well. The size of the NRs is almost uniform with a diameter of ∼150–200 nm and a length of ∼1–1.2 μm.

Fig. 3 reveals the crystalline study of as-grown ZnO NRs, investigated using the XRD technique. All the diffraction pattern peaks appeared in the spectra, indicating the crystalline quality of ZnO as per JCPDS Card No. 36–1451. The relatively high (002) peak at

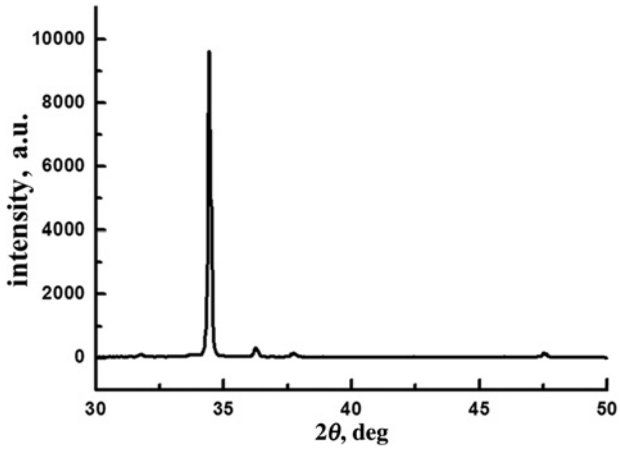

Figure 3 *XRD spectra of ZnO NRs grown on FTO glass substrate*

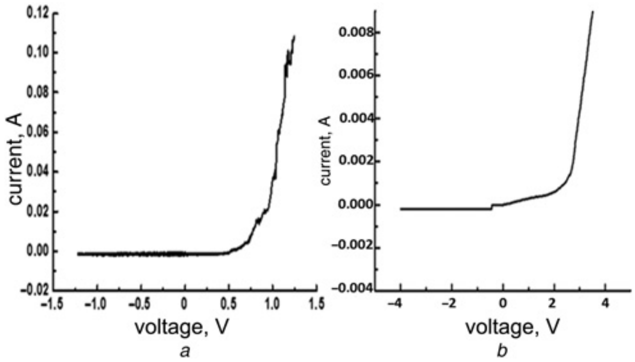

Figure 4 *Current–voltage (I–5) characteristics between ZnO NRs on FTO glass substrate and bare (without ZnO NRs) AFM tip and AFM tip with ZnO NRs*
a Bare AFM tip
b AFM tip with ZnO NRs

34.4° belongs to ZnO, demonstrating the wurtzite hexagonal phase of crystalline *c*-axis-oriented NRs, while other present peaks are just the reflections for ZnO. This study verifies the pure phase of ZnO NSs and no other crystallised phase was observed.

A current–voltage (I–5) measurement was performed before starting the scan measurements with the bare Pt tip to validate the presence of Schottky contact between the bare Pt tip and the ZnO. The result is shown in Fig. 4*a*. The same procedure was repeated when the bare Pt tip was replaced with the Pt/ZnO tip and the corresponding result is shown in Fig. 4*b*. Both Figures show typical Schottky-type behaviour.

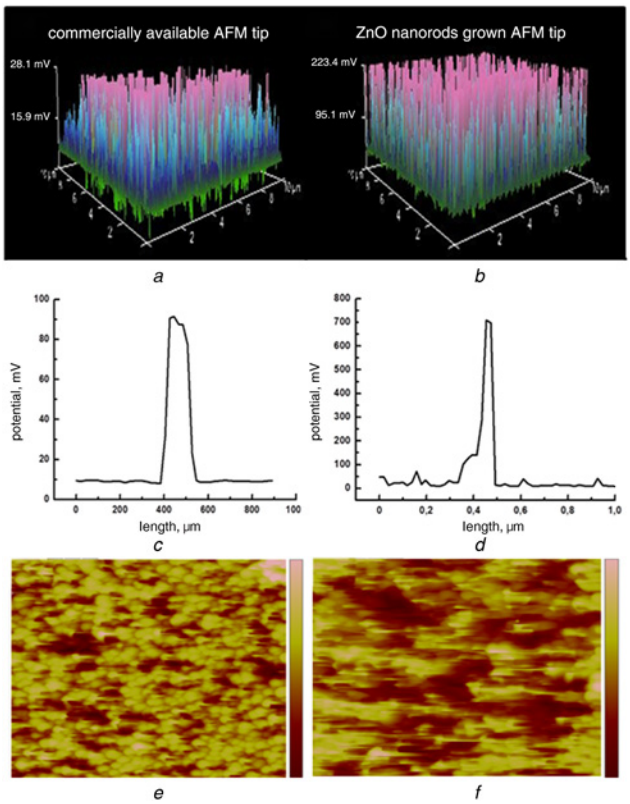

Figure 5 *3D plot of output voltage from ZnO NRs using AFM tip with and without ZnO NRs (Figs. 5a and b); tip scan using AFM tip with and without ZnO NRs (Figs. 5c and d); topography image using AFM tip with and without ZnO NRs (Figs. 5e and f)*

Before starting the AFM scan measurements a few steps were taken to avoid the artefacts (if any) in the measurements of the piezoelectric potential. First, the confirmation of the ZnO NRs coupling with the AFM setup; secondly, the presence of Schottky contact at one end of the ZnO NRs, and finally, the ZnO NRs must hold the linear superposition rule [23]. After a careful checking of these steps, we started to record the scan measurements.

Fig. 5*a* is a three-dimensional (3D) plot of the output voltage corresponding to the feedback signals generating from a scanned area of 10 μm × 10 μm over the ZnO NRs array through a bare Pt tip. The corresponding output voltage image was recorded when the AFM tip was scanning the NRs and the NRs were crouching back-to-back. The average recorded output voltage was 28.1 mV. Remember that the output peaks appearing in Fig. 5*a* correspond to the maximum deflection of the NRs. It is important to note that when the AFM tip deflected the NRs there was no output voltage and the potential was observed only when the maximum bending of the NRs was achieved. When the NRs lost their contact with the AFM tip, the potential becomes zero. This suggests that the output response was noticed as soon as the AFM scan was completed, as shown in Fig. 5*c*. The NRs were bent back-to-back during the scanning process and the recorded bending distance was shown in the topography image (Fig. 5*e*). The topography image is used to describe the presence of any change in normal force perpendicular to the substrate.

To observe the effect of the Pt/ZnO tip (NRs grown tip) in comparison with the bare (without NRs) Pt tip, we carried out an experiment without changing the parameters of the AFM equipment. Besides this, neither the sample nor the conditions have been changed and the experiment has been performed almost at the same time. We just replaced the bare Pt tip with the Pt/ZnO tip. Fig. 5*b* is a 3D output voltage image recorded by scanning the same area of the sample but with the Pt/ZnO tip. Most of the observed potential pulses were about 220–280 mV. The output signal exhibits much more potential pulses in comparison to that for the bare Pt tip. It is important to point out that the generated current is the addition of all those NRs that participate in giving the output power. However, the voltage is decided by a single NR, because all the NRs are ‘in parallel’. The average piezoelectric output response generated by the Pt/ZnO tip was recorded as 223.4 mV. This significant enhancement showed that the Pt/ZnO tip plays an important role in the enhancement of output response.

As the enhanced output voltage is based on the NRs that contributed to the generated amount of electricity, it can be achieved in two possible ways. One is to utilise all those ZnO NRs that have unvarying size and length and the other is to grow ZnO NRs on the AFM tip as shown in Fig. 1. In this work, we used the later approach, which showed that an enhancement in the output voltage would come with a coincident gain in the output current, which is directly related to the participated NRs.

It is well known that generally a sample having an area of 10 μm × 10 μm holds thousands of ZnO NRs and it can generate piezoelectricity in millivolts. These thousands of NRs on the Pt/ZnO tip and on the FTO glass substrate participated in the generated output in a haphazard form. Since each NR is supposed to be in a short-lived state, the average of these thousands of NRs possibly is in a firm state with an unchanging and uninterrupted output. This can be explained in terms of solar cells, in which one photon can only crumple one or possibly few electrons to make an electric pulse, but an uninterrupted current is possible if thousands of photons hit the cell in a haphazard manner. This example may help in understanding the enhanced output voltage presented in this Letter. Figs. 5*d* and *f* are the corresponding tip scan and topography profiles describing the same features as discussed for the bare Pt tip.

4. Conclusion: In this Letter, a new approach has been used to enhance/improve the performance of NGs in terms of output piezoelectricity. Well-aligned and highly dense ZnO NRs were synthesised on the cantilevers (tip) of the AFM probe and FTO-coated glass substrate, respectively. Two kinds of cantilevers were utilised in the experiments without changing any other parameters to distinguish the results. The bare (without ZnO NRs) Pt tip produced an average of 28.1 mV, whereas the Pt/ZnO tip results in 223.4 mV harvested energy. This approach is not only useful for enhancing the amount of harvested energy, but also has several other advantages as well. Firstly, the synthesis of ZnO NRs through the low temperature (< 100°C) ACG method is not only compatible for all kinds of substrates, such as flexible, foldable, soft and hard, but also cost-effective and environmentally friendly. Secondly, the rational growth of ZnO NRs does not require a consistent length and size, which minimises the complications of the growth process. Thirdly, the use of platinum as the coating material is not mandatory and in lieu of Pt any other conductive material (preferably low-cost) can be used; if and only if, it is making a Schottky contact with ZnO. Last but not least, it opens the door to the possibility of using two completely different piezoelectric materials at the same time, one for the AFM tip and other for the used substrate.

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