On enhancing capability of tribocharge transfer of ZnO nanorod arrays by Sb doping for anomalous output performance improvement of triboelectric nanogenerators

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We have been concentrating on developing novel and functional materials, enabling the development of alternative renewable energy harvesting technology with high efficiency in the lab. For example, Triboelectric nanogenerator (TENG) is an emerging green energy generator, converting ubiquitous mechanical energy into electricity through triboelectricity. The working mechanism combines triboelectric charges produced by materials rubbing against each other during stressing and charge induction during releasing. But the output power is still low, limited by the capability of charge transfer during triboelectricity. As semiconductors can readily be doped to modify surface chemistry, we demonstrate that ZnO nanorod (NR) arrays doped into p-type with Sb can drastically enhance the output performance of TENG.

The p-type characters of all the Sb-doped ZnO NRs are confirmed and the hole carrier concentration is estimated to range from $2.83 \times 10^{15}$ to $1.87 \times 10^{18}$ cm$^{-3}$. Fig. 1 summarizes the output performance of a series of TENGs made of ZnO NR arrays with various Sb doping concentrations rubbing against PDMS and nylon. Surprisingly, the output voltage and current of p-type ZnO NR arrays are remarkably enhanced from undoped n-type ZnO by 24 (from 0.5 V to 12 V) and 5.5 ($2.0 \times 10^{-8}$ A/cm$^2$ to $1.1 \times 10^{-7}$ A/cm$^2$) times, respectively, in giving up electrons to negatively charged PDMS. This contradicts to the perception in that drawing electrons toward PDMS should only be facilitated by n-type doping, rather than p-type characters. Contrarily, the triboelectric output performance of ZnO NR arrays is degraded by Sb doping when rubbing against positively charged nylon. This demonstrates surface modification of a semiconductor material by doping can cause tremendous impact on the output performance of TENG.
Fig. 1. Summary of the output voltage, current density and tribocharge density of various TENGs, rubbing against PDMS and nylon.

Therefore, according to the tendency of losing or receiving electrons upon frictions, the relative position of doped ZnO NR in the triboelectric series is proposed in Figure 2. These results show the viability of a material to be tuned by doping in occupying a large section of the triboelectric series, expanding the degree of freedom for device design and material choice.

The abnormal phenomena are ascribed to the formation of electron accumulation layers upon Sb doping through substitution of Zn$^{2+}$ with Sb$^{3+}$, resulting in surface downward band bending to render as n-type characteristics. Sb$^{3+}$ dominantly residing at the surface regions is identified by x-ray photoemission spectroscopy. It has been well proposed that Sb$^{5+}$ is responsible for the p-type characteristics in the bulk, while Sb$^{3+}$ of similar size (0.76Å) may directly substitute for Zn sites forming either Sb-O bonds, acting as donors for n-type behavior at the surface. The surface band bending is confirmed by ultra-violet photoemission spectra. More strikingly, the shell regions of all
the Sb-doped ZnO NR arrays are characterized to be more n-type than the undoped ZnO NR arrays. Ultimately, Figure 3 proposes the detailed energy band diagram of both the un-doped and Sb-doped ZnO NRs before contact with PDMS, depicting how electrons as tribocharges populated in the conduction band can transfer to the surface states of PDMS during rubbing. Consequently, the more p-type ZnO NR arrays doped with Sb presenting with more surface states are inclined to donate more electrons from the surface electron accumulating layer upon electrification in response to its lower work function, and thus enhancing triboelectric output power dramatically.

Fig. 3. Proposed possible surface energy downward bending diagrams and tribocharges transfer for the TENG made of (a) undoped ZnO NR arrays and (b) Sb-doped ZnO NR arrays against PDMS before contact.

Finally, the working mechanism of the TENG is proposed in Figure 4 to describe contact charging and electrostatic induction. This work demonstrates a viable and facile method to modify surface potential of semiconductors simply by doping with great ability to tune the relative position of the same material in the triboelectric series. This work opens a new dimension in designing TENG with more freedom to select the best combination of material assemble with ease.
Fig. 4. Schematic illustration of working mechanism of triboelectric nanogenerator made of PDMS against undoped/ Sb-doped ZnO NR arrays under a cycled external compressive and releasing force. (If PDMS is replaced by Nylon, all of the signs shown in the schematic diagram are reversed)