Giant Enhancement in UV Response of ZnO Nanobelts by Polymer Surface-Functionalization

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Zinc oxide (ZnO) is one of the most important nanomaterials for nano-optoelectronics,1 sensors,2 transistors,3,4 and nanoelectronics.5,6 Because of the unique piezoelectric and semiconducting dual properties, ZnO nanowires (NWs) and nanobelts (NBs) are the fundamental material for nanogenerators,7,8,9 and focused ion beam (FIB) microscopy.10 Surface functionalization is one of the widely used methods to enhance the electric transport properties of different 1D nanostructures.11,12 Because of the special physical and chemical properties of the attached chemical species, devices based on ZnO NWs/NBs demonstrate unique and interesting physical and chemical properties of the attached chemical species, devices based on ZnO NWs/NBs demonstrate unique and interesting properties.13,14 In this paper, absorbance, functionalization and focused ion beam (FIB) microscopy.11 Surface functionalization is one of the widely used methods to enhance the electric transport properties of different 1D 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Figure 1. (a) Normalized conductance responses of a single functionalized ZnO NB device (see inset) upon UV illumination being turned on and off: bare ZnO NB without coating (green line, magnified by 10000), PS-co-MAc-coated ZnO NB (dark line, magnified by 1000), PSS-coated ZnO NB (red line), PSS polymer only (blue line, magnified by 500). Inset is an SEM image of a typical device. The applied voltage remained at 1 V for all of the measurements. (b) UV absorption spectra of PSS (red line), PS-co-MAc (dark line), PNIPAM (blue line), CMC (green line). Inset is an SEM image of a polymer-coated ZnO NB sample.

Soci et al.\(^9\) have proposed that the high sensitivity UV detection of ZnO NW was due to the presence of oxygen-related hole-trapping states at the NW surface. This process can also be applied to explain our observation. The first layer of coated polymer is cationically charged PDADMAC. The free electrons might be trapped by the positively charged sites at the surface. Upon UV illumination, these immobilized electrons can trap the photon-generated holes and thus reduce the electron–hole recombination rates in ZnO NB and increase the carrier lifetime. This mechanism accounts for the enhanced UV response for ZnO NB coated with PS-co-Mac, PNIPAM, and CMC.

The above mechanism may not be sufficient to account for the huge increase in photoresponse of the PSS-coated NBs. From Figure 1b, the UV absorption spectrum of PSS has a peak at around 260 nm, which is coincidently close to the applied UV source wavelength. We proposed that this absorption peak and the related molecular energy states in PSS play a significant role for enhancing the photon response. Although the first layer of ZnO NB surface is covered by PDADMAC, it is well-known that the monolayer adsorption usually cannot reach 100% coverage. Therefore, the remaining surface could be covered by the next adsorbed layer of PSS, as shown in Figure 2b. We now consider the area that PSS is remaining surface could be covered by the next adsorbed layer of polymer. If the ground energy state of the PSS is at the level directly interfacing with ZnO and lower in energy than the valence band of ZnO, it is likely that the electron in the valence band of ZnO NB is excited to the ground state of PSS, which subsequently transits to the conduction band of ZnO (step 2). This “hopping” process may largely enhance the transition probability of the valence electrons in ZnO to its conduction band, resulting in a large increase of electron–hole pairs (Figure 2a).

Figure 2. (a) Schematic illustration of the electron–hole generation process with facilitation of transition states from the molecular energy states in PSS. (b) Schematic illustration of photon-induced carrier transportation process in a ZnO NB by UV illumination.

The role played by PSS is to serve as a hopping-state or bridge for the electron transfer. As discussed above, the as generated holes are trapped at the NB surface by the PDADMAC, while the electrons are transported through the NB core, (Figure 2b). Therefore, the conjunction of electron–hole pair generation in ZnO with the assistance of PSS and surface-hole trapping effect by PDADMAC may largely prevent the electron–hole recombination, resulting in a huge increase in the photoconductance of PSS-coated ZnO NB.

In conclusion, by coating ZnO NB using a polymer that exhibits a large UV absorption peak, the UV induced photoconductance increases by 5 orders of magnitude. This huge increase in photoconductance is suggested owing to an electron–hole generation process as assisted by the energy states in the polymer. Therefore, with coating UV sensitive polymers, the UV response of ZnO NB was greatly enhanced. This study sets the foundation for increasing the sensitivity of UV detectors based on ZnO. The result suggests that, by selecting polymers with different wavelengths of UV absorption, UV detectors with a large range of wavelengths and super-high sensitivity can be fabricated using arrays of ZnO NWs and NBs functionalized using different polymers. This discovery can have outstanding applications in photonics and optoelectronics.

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Supporting Information Available: UV response of PNIPAM and CMC-coated ZnO NBs. Response of PSS-coated ZnO NB to 523 and 680 nm wavelength. This material is available free of charge via the Internet at http://pubs.acs.org.

References

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