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Environmentally stable/self-powered ultraviolet photodetectors with high sensitivity

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Here, we demonstrate self-powered ultraviolet photodetectors that are capable of generating opposite current flow when illuminated at different wavelengths. The photodetectors are composed of n-ZnO/Polyaniline (PANI) p-n and PANI/ZnGa2O4 type-II heterojunctions and operate without any need for external power source. Devices display superior stability in ambient conditions within months. Results provide opportunities for developing devices for optical recognition. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4824204]

Photodetectors are key elements of optoelectronics in imaging techniques, signal processing, and sensing applications.1–3 In the past several decades, many oxide semiconductors such as ZnO, TiO2, and SnO2 have been investigated for photodetectors in the UV spectral range.4–7 However, most of the investigated photodetectors are photovoltaic type photodetectors that need external bias voltage as the driving force to generate photocurrent, which will limit the size of the nanodevice and its independent working system.8 To reduce the device size and achieve independence, alternative routes have been proposed and demonstrated.8–12 In fact, p-n junction between p-type and n-type semiconducting materials has a build-in potential difference which has the ability to control the directional movement of the photogenerated electrons and causes the generation of photocurrent. More specifically, when ZnO is used in a p-n junction geometry, electric fields built in the junction (depletion) region prevent recombination of photo-excited electron-hole pairs, efficiently separate the photo-generated carriers.13–15 Alternatively, type-II heterojunction geometry is another method to separate the photo-generated electron-hole pairs for generated photosensitivity. Because type-II band alignment results in collection of electrons mostly on one constituent, and the holes accumulate on the other constituent. Recent theoretical and molecular dynamics studies have shown that the type-II junction is ideal for photovoltaic and photoconductive devices as it provides long-range photo-generated charge separation.16–18 So far, studies have been carried out to induce or enhance the UV photo-conductance and sensitivity of metal-oxide devices; however, these devices typically require a constant voltage bias to function. Moreover, the reported devices displayed poor UV selectivity.19–22

In this work, we present p-n and type-II heterojunctions based UV photodetectors operating at zero applied voltage with superior UV wavelength selectivity. The designed photodetectors connect two different kinds of junctions, allowing to change the direction of the current flow responding to 254 and 365 nm, respectively. The internal field built at the heterojunction interface(s) efficiently separates photogenerated electron-hole pairs, yielding current within the circuit, and therefore the end product functions at zero applied bias voltage without any need for external power source.

A schematic diagram of the photodetector heterojunction is shown in Figure 1(a). In this device geometry, an n-type ZnO/Polyaniline (PANI)/ZnGa2O4 heterostructure constitutes the active part of the device. Here, ZnO nanorods were grown on indium tin oxide (ITO) glass by a hydrothermal process with average length of ~1.0 μm and diameter of ~70 nm (see supplementary material, Figure S1(a)32). The ZnGa2O4 layer was spin coated on a separate ITO substrate from as-grown nanocrystals that were 5–6 nm in size (supplementary material, Figure S1(c) TEM images32). The ITO substrate served as the transparent conducting electrodes to connect the ZnO nanorods and ZnGa2O4 nanocrystals through an external circuit. The ZnO and ZnGa2O4 layers were separated by a thin layer (~2.0 μm thick) of PANI nanofibers with average diameter of ~85 nm grown by interfacial polymerization (supplementary material, Figure S1(b)).23 Here, the ZnO layer on the PANI forms the p-n junction, and the electric field developed at the interface separates the electron-hole pairs that are created by the incident UV light. In the mean time, the valence band edge (VB) and conduction band edge (CB) of ZnGa2O4 are both below that of the PANI, respectively, and this type-II junction results in electron transfer from PANI to ZnGa2O4 under the UV illumination. Since ZnO and ZnGa2O4 have a bandgap of 3.2 eV (Refs. 24 and 25) and 5.0 eV, respectively, the heterostructure has UV selectivity for wavelength onset at 365 nm and 254 nm.

In Figure 1(b), we show the I–V characteristics measured from two independent n-ZnO/PANI and PANI/ ZnGa2O4 heterostructures without UV illumination in the dark room conditions. The I–V characteristics display typical rectifying behavior for both p-n and type-II junction separately up to 1 V applied bias. The observed rectifying behavior mainly stems from the fact that a p-n junction is formed at the p-PANI/n-ZnO interface. The forward bias I–V curve displays an exponential increase as a result of decrease in the width of depletion layer at the junction and changes in the
built-in potential (curve I). Similarly, the I-V characteristic measured at the PANI/ZnGa$_2$O$_4$ junction also shows nonlinear response since the VB = 3.28 eV and the CB = −1.42 eV of ZnGa$_2$O$_4$ are lower than the highest occupied molecular orbital (HOMO = 0.62 eV) and the lowest unoccupied molecular orbital (LUMO = −2.14 eV) of PANI, respectively. So, type-II heterojunction can form between PANI and ZnGa$_2$O$_4$. Such type-II band alignment results in collection of electrons mostly on the ZnGa$_2$O$_4$ side, and the holes accumulate on the PANI side, leading to the observed rectifying response in Figure 1(b) (curve II).

Figure 2(a) shows photocurrent curves generated across the UV photodetector for repetitive switching between 254 nm (~8 W, 11.8 × 10$^5$ μW/cm$^2$) and 365 nm (~8 W, 11.8 × 10$^5$ μW/cm$^2$) UV light illumination when the device is illuminated from the opposite sides, i.e., 365 nm wavelength light from the ZnO and 254 nm from the ZnGa$_2$O$_4$ side. The device was operated in dark ambient to prevent interference. Overall, the device displays excellent sensitivity to the UV light illumination. After several times of cycles, the on/off ratio and response time remain the same as the initial value, and the device exhibits an excellent durability and stability. After more than a month, when the photoresponse have been measured again, the device had still a steady light response as shown in Figure 2(a) (red line). Interestingly, the direction of photocurrent is reversed depending on the different wavelength of the UV light. We find that the 254 nm illumination generates a positive photocurrent, whereas 365 nm light illumination results in negative photocurrent (Figure 2(a)). Such current switching provides opportunities for developing a new generation photodetectors with excellent UV wavelength selectivity and sensitivity owing to the current switch properties. Illuminating 365 and 254 nm light both from the ZnGa$_2$O$_4$ side of the device displays similar characteristics as shown in Figure 2(c) as the ZnGa$_2$O$_4$ layer is mostly transparent to 365 nm light and the 365 nm light still generates excitons (e-h pairs) at the ZnO/PANI junction (Figure 2(c)). However, the current polarity is largely lost when the light is illuminated both from the ZnO side as a result of broad-range light absorption in the ZnO film but the devices still display remarkable photodetection capability (see supplementary material, Figure S3).

To understand the origin of the alternating photocurrent direction upon illumination with 254 and 365 nm UV light as shown in Figures 2(a) and 2(c), we first emphasize the fact that the external bias voltage of the device is not needed, which is fundamentally different from the UV detectors previously reported. In our device design, there are two heterojunctions, i.e., a p-n and a type-II junction, in the back to back connection configuration. Normally when UV light generates a large number of electron-hole pairs within the ZnO, they recombine very rapidly resulting in radiative or non-radiative recombination. The photocurrent can be generated by applying an external bias voltage, which separates...
the electrons and holes before they recombine. Therefore, most of existing ZnO based photodetectors rely on constant-voltage source to generate photo-response. On the contrary, in our structure the internal electric field generated at the n-ZnO/p-PANI interface separates the photo-generated electrons and holes, and the non-equilibrium electrons move to the ZnO layer, and holes move through the PANI layer to the type-II junction region. The photo-electrons collected in the ZnO pass through the external circuit and finally enter the type-II junction to neutralize the positive charge of holes (Figure 2(b) top). Conversely, when the type-II junction is illuminated with UV light, electron-holes pairs are generated and separated at the PANI/ZnGaO₂ junction, the electrons migrate to the ZnGaO₂ layer, and holes to the PANI layer. The electrons then move through the external circuit to the p-n junction, and neutralize with the holes (Figure 2(b), bottom). For these two heterojunctions, the moving direction of electrons is opposite to each other, so the short-circuit current direction is also opposite. Similarly, when the device is illuminated by the 365 and 254 nm light from the type-II junction (same side illumination), the 365 nm light mostly interact with the ZnO/PANI layer as the ZnGaO₂ film is nearly transparent to 365 nm light. As a result, the 365 nm still generates the negative current, whereas the 254 nm light is mostly absorbed at the ZnGaO₂/PANI junction generating positive current (Figure 2(c)). To confirm, we have measured the UV-Vis diffuse reflectance spectra of the ZnO and ZnGaO₂ used in fabrication of these devices. In Figure 3(a), the strongest absorption peak position of the ZnO is around 360 nm (curve II), and at this wavelength the absorption of ZnO is far greater than that of ZnGaO₂. Therefore, illuminating the device with 365 nm light may mostly pass through the ZnGaO₂ and create far greater electron-hole pairs in the ZnO/PANI junction, and as a result, the overall current flows from ZnO to ZnGaO₂ through the external circuit, yielding a negative photocurrent. On the other hand, the UV-Vis diffuse reflectance spectra of the ZnGaO₂ peaks range from 200–300 nm, so it does hardly response to the 365 nm UV light but responses to the 254 UV light. When the device is illuminated by the 254 nm light from the ZnGaO₂ side, electron-hole pairs are created at the ZnGaO₂/PANI junction generating positive photocurrent. And the band alignment of the PANI/ZnGaO₂ type-II heterojunction is shown in Figure 3(b). Since the absorption to 254 nm light is not as strong as that of ZnO layer (Figure 3(a)), some portion of the 254 nm light still interacts with the ZnO/PANI junction and generates counter current which reduces the magnitude of the positive current. As a result, our devices display larger negative current and the positive current value is smaller due to the interaction of 254 nm light with the ZnO/PANI layer.

In summary, we display the first n-ZnO nanowire/PANI/ZnGaO₂, (a p-n and a type-II heterojunction) based photodetector devices that are self-powered and showing excellent sensitivity to UV light at different wavelengths with complete current reversal capabilities. The devices show remarkable environmental stability. The current generated at the p-n junction and the type-II junction can be controlled by UV illumination at different wavelengths yielding remarkable sensitivity and current switch. Based on this effect, an UV photodetector that can identify different UV wavelengths when illuminated at the heterojunction devices be designed. The different photocurrent directions at 254 and 365 nm illumination are explained by the different efficiencies in photo-absorption, exciton generation and exciton separation of the two junctions. This effect provides opportunities for developing devices that are capable of digitally recognizing UV wavelengths at zero external voltage bias.

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See supplementary material at http://dx.doi.org/10.1063/1.4824204 for experimental details, SEM images of PANI nanofibers and ZnO nanorods, HRTEM images of ZnGa$_2$O$_4$ nanocrystalline, and XRD of ZnGa$_2$O$_4$ nanocrystalline and ZnO nanorods. The measure current across the device for different wavelength light source when illuminated from the ZnO side, FT-IR of PANI and EDX of ZnGa$_2$O$_4$ nanocrystalline. Figure S1: SEM images of PANI nanofibers (A) and ZnO nanorods (B), HRTEM images of ZnGa$_2$O$_4$ nanocrystalline (C). Figure S2: XRD of ZnGa$_2$O$_4$ nanocrystalline (A) and ZnO nanorods (B). Figure S3: The measure current across the device for different wavelength light source when illuminated from the ZnO side. Figure S4: FT-IR of PANI (A) and EDX of ZnGa$_2$O$_4$ nanocrystalline (B)].