TiO_2 assisted sensitivity enhancement in photosensitive nanocrystal skins

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Solution-processable semiconductor nanocrystals (NCs) have been widely used to create novel devices for the photovoltaic, light-emission, light-detection and biosensing applications. They are good candidates especially to develope more efficient and novel optoelectronic devices owing to the high absorption cross-section, spectral tunability, deposition easiness and low cost properties. In recent years, NC integrated photodetectors have been developed to be used in large-area light-sensing applications [1]. These NC-based photodetectors have the ability to convert an optical signal to an electrical signal using the NCs as the optical absorbers. These low-cost devices were initially operated on the basis of charge collection, where an electric field imposed on the detector dissociates the photogenerated excitons into electrons and holes, in which an electric current is produced [2]. On the other hand, as an alternative device structure, we have recently developed the light-sensitive nanocrystal skin (LS-NS) [3]. These LS-NS platforms, which were fabricated over areas up to 48 cm^2, are operated on the basis of photogenerated potential buildup, as opposed to conventional charge collection. In operation, close interaction of the monolayer NCs of the LS-NS with the top interfacing contact, while the bottom one is isolated using a high dielectric spacing layer, results in highly sensitive photosensing in the absence of external bias application. Furthermore, NC monolayer of the LS-NS makes the device semi-transparent with sufficient absorption, while reducing the noise generation and dark current. In our other recent work, we also reported that, by using a thick photoactive NC layer, a much lower photovoltage buildup was observed in the LS-NSs and it was attributed to the self-absorption effect [4]. In addition, we demonstrated the sensitivity increase in the LS-NSs via the absorption enhancement of NC film with the integration of plasmonic nanoparticles [5]. However, the localized plasmonic resonance band strongly limits the observed enhancement factor and the resultant operating wavelength range. Furthermore, in the absence of an external bias in the LS-NSs, each exciton tends to remain in the NC layer, where it was created, and recombine with the photogenerated holes that accumulate at the top interfacing contact, which causes also lower voltage buildup in the device. To overcome all these problems, in this study, we propose a thin TiO_2 layer as the electron-accepting material and demonstrate the first account of electron transfer in NC-based light-sensitive skins, which leads to significant broadband sensitivity enhancement in the active device architecture. Here, we prove that favorable conduction band offset aids in transferring photogenerated electrons from a monolayer of NCs to an electron-accepting layer, which is ultimately useful for photosensing platforms and the next generation of light-sensing NC devices.

To fabricate our LS-NS devices, we first synthesized CdTe NCs in solution by using the standard procedure in the literature. We also deposited a 50 nm thick HfO_2 film on top of a deeply cleaned ITO layer (80 nm) coated on a glass substrate. We then continued our fabrication by depositing a 10 nm thick TiO_2 layer on the HfO_2 layer by using atomic layer deposition technique for the both layers. After that, we deposited the as synthesized NCs via layer-by-layer self-assembly method with a computerized dip-coating system. Subsequently, we laid a very thin (15 nm) transparent Al contact layer on top of the NC monolayer with a thermal evaporation system. To measure the photovoltage buildup vs time characteristics of our devices, we utilized a parameter analyzer and a Xenon light source with a monochromator. During the operation, each device was connected to a shunt resistor and the ITO contact was grounded. We performed optical power measurements using a multi-function optical power meter. To eliminate the slight absorption of the TiO_2 layer, all devices were illuminated from the Al side. Device architecture for the proposed LS-NSs with the energy band diagrams of the layers is depicted in Figure 1. With this platform, we showed how electron transfer to a thin TiO_2 film in light-sensitive NC skins enhances the photosensitivity of the device. We observed substantial improvements in photosensitivity over a broadband spectral range (350-475 nm), with an approximately 22% enhancement as observed from Figure 2a, 2b and 2c. To develop a deep understanding and further support the existence of the charge transfer from the NCs to the TiO_2 layer, we also conducted time-correlated single-photon counting measurements. Polymer layer deposited between the NC layer and the TiO_2 layer was varied to demostrate the change in charge transfer efficiency. Decay curves obtained via these time resolved fluorescence experiments were analyzed by fitting with both 3-

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exponential and 1/e fitting analyses. The resultant efficiencies calculated from the decay lifetimes supported the existence of electron transfer from the NCs layer to the TiO_2 layer in the LS-NS (Figure 2d).

In conclusion, we demonstrated the great broadband enhancement in the sensitivity of LS-NS via the transfer of photogenerated electrons to the TiO_2 layer. With the integration of TiO_2 as an electron acceptor, we achieved the decrease in the electron-hole recombination probability resulting in broadband sensitivity improvement across 350-475 nm and a significant photovoltage sensitivity improvement in the proposed nanostructure platform. We also observed that the controlled thickness between the CdTe monolayer and the TiO_2 layer enables the rise in sensitivity to the percentage values of 22%. Therefore, we think that these results are not only scientifically interesting but also technologically important and useful. These findings have significant implications for the future design of photosensing platforms and for moving toward the next generation of large-surface light-sensing devices based on semiconductor NCs, including smart transparent windows, light-sensitive walls and large-area optical detection systems.

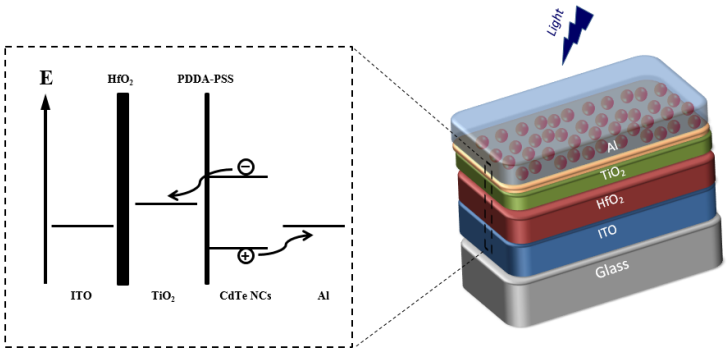

Figure 1. Schematic of the proposed LS-NS device with the energy band diagrams of CdTe NCs, TiO_2, ITO and Al. When the excitons are photogenerated, electrons are transferred to the TiO_2 layer while holes migrate to the Al layer.

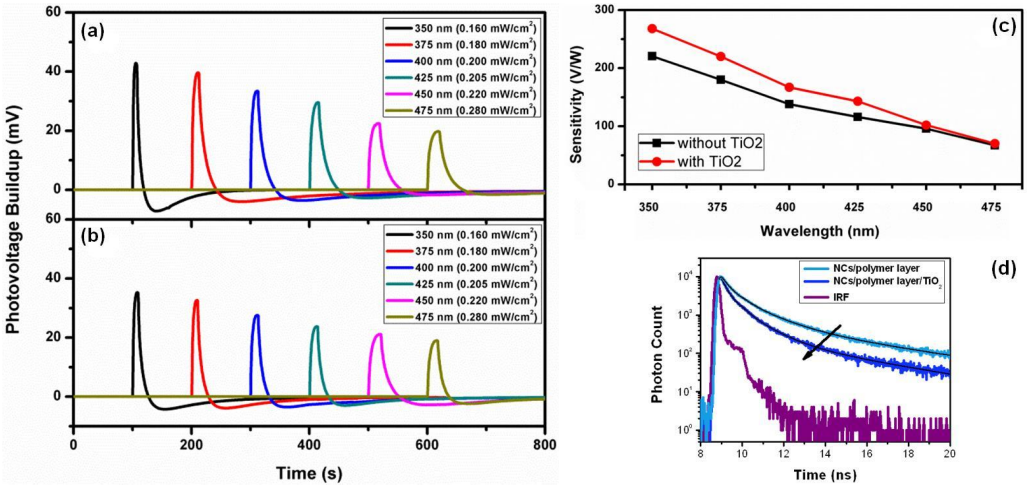

Figure 2. Photovoltage buildup at different excitation wavelengths for the LS-NS (a) with TiO_2 and (b) without TiO_2**.** (c) Demonstration of (c) device sensitivity enhancement at different excitation wavelengths and (d) time resolved fluorescence decay lifetime shortening of the LS-NS with and without TiO_2.

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