Enhanced infrared light harvesting of inorganic nanocrystal photovoltaic and photodetector on graphene electrode

Chih-Cheng Lin,1 Di-Yan Wang,1 Kun-Hua Tu,1 You-Ting Jiang,2 Meng-Hsiang Hsieh,1 Chia-Chun Chen,2,3 and Chun-Wei Chen1,a)

1Department of Materials Science and Engineering, National Taiwan University, Taipei 10617, Taiwan
2Department of Chemistry, National Taiwan Normal University, Taipei 11677, Taiwan
3Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan

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We demonstrate an enhancement of infrared light harvesting of inorganic PbS nanocrystal photovoltaic and photodetector devices based on the transparent graphene electrode. Due to high infrared transparency of the graphene electrode with respect to indium tin oxide (ITO), the infrared photoresponse of the graphene-based device is superior to the ITO-based counterpart, in spite of a higher sheet resistance of the graphene electrode. The outstanding infrared characteristics of the devices based on the graphene electrode make it a promising candidate for infrared optoelectronic applications such as solar cells, imaging and sensing, or optical communication. © 2011 American Institute of Physics. [doi:10.1063/1.3605682]

Since one third of the Sun’s power reaching the Earth lies beyond 1000 nm, the solution to harvest the incident photons with wavelengths in the infrared (IR) spectral region becomes crucial to further improve the photovoltaic efficiencies. In the past decade, many advances have been realized in the synthesis of efficient infrared photovoltaic materials of organic polymer1,2 or inorganic nanocrystals (NCs)3–6 in the applications of IR solar cells or IR imaging and sensing. Nevertheless, the use of the conventional transparent conductive electrode of indium tin oxide (ITO) is still problematic in IR photovoltaic or photodetector devices due to its poor transparency with wavelengths beyond 1000 nm,7 which largely limits the light harvesting efficiency. In addition, the price of ITO has increased by an order of magnitude over the last decade due to the scarcity of In. Therefore, an alternative electrode material to replace the ITO with high IR transparency is very important in the development of infrared optoelectronic devices.

Graphene, a two dimensional (2D) monolayer of sp²-bonded carbon atoms arranged in a honeycomb lattice has demonstrated an excellent carrier transport arising its unique 2D energy dispersion.8 It has shown substantial advantages, such as high transparency and excellent electrical and thermal conductivity, and superior mechanical flexibility and has been proposed as the potential material for the next-generation large-scale multifunctional transparent electrode.9 One of the unique properties of graphene over ITO as a transparent electrode is that it can persist very high transparency over a wide range of wavelengths from visible to IR regions.10 To date, many reports have been focused on the applications of the transparent graphene electrode in the visible wavelength range while the exploration of the graphene electrode in IR optoelectronics is still lacking. In this article, we would like to demonstrate that the IR photoresponses of photovoltaic or photodetector devices using the inorganic PbS nanocrystals deposited on the graphene electrode. The outperforming IR photoresponse of the device based on the graphene electrode due to its high IR transparency makes it a promising candidate for IR optoelectronic applications.

For the fabrication of the graphene electrode, we first synthesized the graphene films on copper (Cu) foils following the chemical vapor deposition processes.11 Graphene films were transferred from Cu foils to the glass substrate by using the roll-to-roll production method reported by Bae et al.9 Since a single layer of graphene does not have sufficiently high sheet conductivity, we have to stack multilayers of graphene on the glass substrate to obtain the electrode with optimal conductance and transparency. To further improve the conductivity of graphene, p-type doping was performed by soaking the graphene film into nitric acid (65 wt. %) solution for 3 min and drying it with nitrogen flow.9 The sheet resistances of the graphene films were found to decrease with increasing number of layers (one to eight layers), as shown in Fig. 1(a). The thin films consisting of one, two, and three layers of graphene deposited on the glass substrate were also shown in the inset of Fig. 1(a). The optical transmittance of the graphene electrodes with different stacked layers were shown in Fig. 1(b) and high transparency of graphene from 400 nm to 1800 nm can be clearly observed. The transmittance is reduced about 2–3% as each layer of graphene was added.12 In addition, the surface roughness of the graphene electrodes were also found to increase with increasing number of transferred graphene layers (not shown), which may deteriorate the device performance. Upon optimization of sheet resistance, transmittance, and surface roughness of the graphene electrodes, we used the three-layer graphene, which has sheet resistance of 165 Ω/sq. and a transmittance of 80% at 500 nm and of 85% at 1500 nm for the following fabrication of IR photovoltaic and photodetector devices. For the referenced ITO electrode with a sheet resistance of 15 Ω/sq., the transmittance is about 87% at 500 nm while it decreased significantly with wavelengths beyond 1000 nm, showing a transmittance of 42% at 1500 nm. Although the sheet resistance of the graphene electrode is still higher than that of ITO, the excellent infrared
transparency of the graphene electrode provides the opportunity to enhance light harvesting of IR optoelectronic devices. The atomic force microscope (AFM) topological image of the three-layer graphene film was shown in Fig. 1(c) and the corresponding workfunction mapping image examined by the scanning Kelvin probe microscope (SKPM) was also shown in Fig. 1(d), with an average workfunction value of about 4.86 eV, close to that of a typical ITO electrode.\textsuperscript{13}

For the fabrication of IR photovoltaic and photodetector devices, we used the low band-gap PbS quantum dots as the photoactive layer material. The solution-processed solar cells consisting of lead chalcogenide (PbX) quantum dots have recently demonstrated an excellent infrared photovoltaic performance with unique advantages of tunable absorption characteristics by the quantum confinement effect\textsuperscript{14} and enabling the large-area low-cost fabrications.\textsuperscript{15–17} The device consisting of a Schottky-junction structure of Al/PbS/PEDOT:PSS/graphene electrode is shown schematically in Fig. 2(a). The thickness of the PbS NC active layer is about 100 nm. The PEDOT:PSS layer was incorporated into the NCs solar cell to reduce the interfacial roughness between the anodic electrode and active layer.\textsuperscript{18} For comparison, the device using the ITO electrode was also fabricated as the referenced cell. Since the as-synthesized PbS quantum dots were usually capped with insulating oleic acid ligands, we performed the ligand exchange treatment by using the 1,2-ethanedithiol to remove the oleic acid ligand.\textsuperscript{19,20} Fig. 2(b) shows the transmission electron microscopy (TEM) image of uniformly distributed PbS quantum dots with a size of about 6 nm in diameter and the high resolution TEM (HRTEM) image (inset) revealed that the d-spacing value was \(0.296\) nm corresponding to the (200) plane of the rock salt structure of PbS. Next, the cyclic voltammetry measurement\textsuperscript{21,22} was performed to obtain the lowest unoccupied molecular orbital level of PbS nanocrystals as shown in Fig. 2(c). The corresponding highest occupied molecular orbital level of PbS NCs was further obtained by subtracting the measured band gap of 0.86 eV, resulting from a well-defined excitonic absorption peak centered at 1530 nm as shown in the inset of Fig. 2(c). The corresponding energy levels of the respective layers of the device with a structure of Al/PbS/PEDOT:PSS/graphene electrode were thus summarized in Fig. 2(d), where the graphene electrode acts as an anode to collect holes and the cathode of Al is for collecting electrons.

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<th>Photovoltaic performances of PbS solar cells fabricated on the different anodic electrode under various illuminations.</th>
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<td><strong>J_{sc}(mA/cm^2)</strong></td>
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<td>ITO electrode (AM 1.5)</td>
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<td>ITO electrode (500 nm)</td>
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<td>ITO electrode (1500 nm)</td>
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<td>Graphene electrode (AM 1.5)</td>
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The current density-voltage (J-V) characteristics and external quantum efficiencies (EQEs) of the PbS Schottky-junction solar cells based on the graphene and ITO electrodes were plotted in Fig. 3(a). Although the ITO-based control device exhibits a higher power conversion efficiency (PCE) of 1.02% than 0.61% of the graphene-based device under simulated AM 1.5 (100 mW/cm²) illumination (inset), the two devices demonstrate different EQE spectral responses at different ranges of incident wavelengths. As the illuminated wavelengths were shorter than 1060 nm, the ITO-based PbS solar cell has higher EQE values than the graphene-based device, mainly attributed to a lower sheet resistance of ITO. By contrast, the graphene-based PbS solar cell shows larger EQE values at wavelengths beyond 1060 nm due to the high IR transparency of graphene, in spite of its higher sheet resistance. The result can be further supported from the measured current density-voltage characteristics of these devices under monochromatic illumination at wavelengths of 500 and 1500 nm, respectively. For the devices under visible light illumination of 500 nm (incident power 2.519 mW/cm²), the ITO-based PbS solar cell yields a better power conversion efficiency of 2.28% compared to 0.97% of the graphene-based PbS solar cells [Fig. 3(b)]. While the devices were illuminated at wavelength of 1500 nm (0.368 mW/cm²), the graphene-based PbS solar cell exhibits a PCE of 1.20%, which is higher than the 0.55% of the ITO-based solar cell as shown in Fig. 3(c). Table I summarizes the photovoltaic performances of the PbS solar cells fabricated on the different anodic electrodes. The outperforming IR photovoltaic response of the graphene-based device further suggests its potential application in IR photodetection or sensing. Fig. 4(a) shows the responsivity $R$ deduced from the EQE spectra between 1100 and 1800 nm of the graphene-based and ITO-based PbS photodiodes operated at different reverse bias conditions. The responsivity $R$ of the graphene-based and ITO-based PbS devices are 0.112 and 0.076 A/W at $\lambda = 1530$ nm and increase to 0.69 and 0.50 A/W at bias of $-1$ V, respectively. The photocurrent response of the devices under IR illumination ($\lambda = 1530$ nm) were found to increase linearly with light power as shown in Fig. 4(b). The high IR transparency of the graphene electrode thus makes it an excellent candidate in the IR optoelectronic device applications. Optimization in the conductivity of the graphene electrode by chemical doping, defect reduction, etc., will lead to a further improvement of the device performance.

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