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Enhanced photovoltaic conversion of ZnO/PANI/NiOx heterostructure devices with ZnO nanorod array

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Abstract

An n-i-p type of organic-inorganic hybrid bifacial solar cells was constructed with a ZnO/polyaniline/NiOx heterostructure, in which vertically aligned ZnO nanorods (ZnONd) were synthesized by a facile electrochemical deposition process and act as an electron-transport layer. Semitransparent p-type semiconducting NiOx films were utilized as a hole-transport layer. Devices based on the ZnONd considerably outperform those employing ZnO thin films. The contact and electrical properties of NiOx can be carefully tuned through controlling the deposition parameters as well as surface treatments. Intimate contact between NiOx with PANI, created by in situ electrochemical polymerization, greatly improves the charge movement. Furthermore, an O2-plasma treatment of the NiOx film has a significant impact on the performance of polyaniline/ZnOx hybrid photovoltaic devices, reflected by the enhancement in the fill-factor and efficiency. The power conversion efficiency of the ZnONd/PANI/NiOx device under the optimized O2 plasma condition can reach up to 2.79% under AM1.5 illumination.

1. Introduction

Organic-inorganic hybrid photovoltaic devices have been attracting tremendous interest recently [1, 2], as they can enjoy the merits of both organic and inorganic materials in a single energy-harvesting device. The hybrid solar cells exhibit many advantages such as lightweight, low-cost roll-to-roll fabrication, applicability on flexible surfaces, and scalable solar power conversion. Current challenges of organic-inorganic hybrid solar cells lie in the improvement of efficiency, the development of materials for light-harvesting (light absorption/conversion), and charge transporting (hole-transport layer HTL or electron-transport layer ETL), stability, and so on [3].

As an organic light-absorbing material, the conductive conjugated polymer can provide an increased overlap on the solar spectrum and a proper energy level offset with an electron acceptor [4]. These properties allow to increase photocurrent and photovoltage, and consequently improve the performance of organic photovoltaics (OPVs). As one of the environmentally friendly and chemically stable energy polymers [5, 6], polyaniline (PANI) can be easily synthesized by either electrochemical polymerization or chemical oxidative polymerization [7]. In the electrochemical polymerization approach, the initiation and termination of the polymerization process can be well controlled for a purer material, while the chemical oxidative polymerization method holds promise for better productiveness, thus lowering the final cost.

An n-type semiconductor ZnO exhibits high electric conduction and carrier mobility for transporting electrons [8], therefore, organic-inorganic hybrid solar cells by combining polyaniline with ZnO nanorods can undoubtedly yield a phenomenal synergistic effect on electronics and optoelectronics [9, 10]. Particularly, ZnO nanorods (ZnONd) have garnered enormous attention because of their excellent electro-optic properties and promising potential applications in electronics, spintronics [11], optics [12], optoelectronics [13], light-emitting...
diodes [14], and photovoltaic devices [15]. For instance, a single layer ZnO/PANI inorganic/organic hybrid structure can be merely fabricated on a glass substrate by coating a polyaniline film on a ZnO thin film [16]. Its rectifying behavior indicates the formation of a diode, and the obtained heterojunction is very sensitive to UV illumination. Meanwhile, the interaction of ZnO with PANI molecular chains exhibits a wavenumber upshifting of the characteristic FTIR peaks of PANI, and a smaller dielectric constant [17], as compared with a pristine PANI film.

As far as organic-inorganic photovoltaics is concerned, the interface between a transparent electrode and an organic active layer plays a very important role in the power conversion performance. An ideal interfacial material is required to strengthen the electric field across an active layer so that electron-hole excitons can be dissociated and charge extraction is facilitated at the contact. The requirement for an interfacial material is that the valence band edge of the hole-transport layer must lay above the valence band edge of polyaniline such that holes can bubble up from polyaniline to the hole-transport layer through the interface, while a conduction band edge must lay above that of polyaniline to reject electrons. Its hole-mobility must be swift enough to prevent holes’ accumulation at the interface [18]. Therefore, it is extremely critical to employ a proper hole-transport layer in organic photovoltaic devices, which could ameliorate an interface between indium tin oxide (ITO) glass and polyaniline. It has proven to be a challenge to identify the right choice of hole-transport layer material. As an important metal oxide, Ni oxide films exhibit excellent electrochemical stability and large spin optical density. Additionally, they can be manufactured with various possibilities. In nonstoichiometric NiO, both Ni vacancies and O interstitials can contribute to the stable p-type conductivity [19, 20] with high hole mobilities of 28.56 and 11.96 cm$^2$/Vs respectively [21]. Simultaneously, NiO$_x$ has a wide bandgap of 3.7 eV for good optical transparency of visible light, [22] allowing for its widespread high technological applications [23, 24]. Thanks to all these merits, NiO$_x$ has been intensively applied in durable dye-sensitized photocathodes [25].

To date, the most reported hybrid devices have not been satisfactorily optimized for any specific active layer components employed through the treatment of contact materials to minimize losses in the carrier and in potential at the charge-extraction interfaces. In this work, ZnO and NiO$_x$ were utilized as an electron-transport layer and hole-transport layer, respectively, to construct PANI-based n-i-p type hybrid bifacial photovoltaic devices. The innovative inverted architecture with opposite charge collecting layers is constructed. The NiO$_x$ layer is introduced to avoid contact between the ITO and the active organic material (polyaniline), so that current leakage can be reduced. The purpose of this project is to look into the hole-extracting behaviors of NiO$_x$ on an ITO glass as an electrode and electrons collecting by the ZnO electrode. The question that how NiO$_x$ as a hole-extraction layer improves efficiency for solar cells will be explored. To understand how the interfaces affect the efficiency of ZnO/PANI composite-based solar cells, the NiO$_x$ films will be treated with oxygen plasma, as oxygen plasma treatment can reportedly reduce the work function and increase the mobility of electrons in the NiO$_x$ layer [26, 27]. The effects of oxygen plasma treatment on the homogeneity of NiO$_x$ electrode and its electronic and optical properties, and consequently photovoltaic performance will be explored.

2. Experimental details

2.1. Materials preparation
An electrochemical method was adopted to grow NiO$_x$ on ITO glass (1 × 2 cm$^2$, a working electrode). 0.01 M nickel hydrate was dissolved in a solvent made of 50 ml DI water and methanol 50 ml. A zinc-plated steel paper clip was used as a counter electrode and a gold wire as a reference electrode. A voltage – 2 volt was applied for 5 min. A schematic description of an electrochemical cell had been reported in the previous work [28]. The NiO$_x$/ITO glass was annealed at 500 °C for 120 min and treated by O$_2$ plasma for HTL application.

Aniline monomer was distilled twice under reduced pressure before use. Polyaniline was synthesized on the above prepared NiO$_x$/ITO glass by dissolving 1 M of aniline monomer in 1 M sulfuric acid by a galvanostatic method with a constant voltage of 3 V. The amount of electrodeposited polyaniline was calculated by weighing the working electrode before and after electrochemical deposition.

A ZnO thin film (ZnO$_{TY}$) was deposited on an ITO glass (as a working electrode) by an electrochemical method. A proper amount of zinc nitrate was dissolved in (50:50) ethanol:deionized water to make a 0.05 M Zn(NO$_3$)$_2$ solution and set at 60 °C, then a 2.5 V potential was applied between the working and reference electrodes for 5 min. To grow ZnO nanorods on the ITO glass substrate, the as-prepared ZnO$_{TY}$/ITO film was submerged in a mixing aqueous solution of 0.01 M zinc nitrate and 0.01 M hexamethyamine at a temperature of 90 °C for at least 60 min, then washed with deionized water and dried in a nitrogen flow.

2.2. Photovoltaic device fabrication by the sandwiching technique
An ITO/ZnO$_{TY}$/PANI/NiO$_x$/ITO bifacial photovoltaic device was fabricated by sandwiching the as-deposited PANI thin film on top of NiO$_x$/ITO with ZnO$_{TY}$/ITO in a face-to-face position as shown in figure 1(a). Another
cell with the configuration of ITO/ZnO<sub>Nd</sub>/PANI/NiO<sub>x</sub>/ITO was built by depositing ZnO<sub>Nd</sub> on top of ZnO<sub>TF</sub>/ITO glass and electrochemical-polymerizing a PANI thin film on NiO<sub>x</sub>/ITO glass, then sandwiching them. The schematic diagram of the bifacial solar cell is displayed in figure 1(b).

The sandwiching technique to fabricate a heterojunction has proven very successful, although it has not been extensively adopted compared with an alternative technique — the subsequent deposition of two layers [29, 30]. The electropolymerization of PANI facilitates intimate contact with ZnO<sub>TF</sub> or ZnO<sub>Nd</sub>. ZnO<sub>Nd</sub> could increase the junction area and conveniently result in a good back ohmic contact. The subsequent deposition requires to immerse ZnO<sub>TF</sub> or ZnO<sub>Nd</sub> in an electrolyte, which would dissolve ZnO because of sulfuric acid, leading to the degradation. A similar issue exists in the evaporation technique in which an ohmic contact is fabricated by depositing a metal onto a PANI surface, which could degrade the PANI surface. For most solar cells, it is common to use one ITO electrode and one metal electrode with different work functions, so that the power conversion efficiency could be improved if an appropriate metal electrode is used. Here two ITO electrodes were used in the solar cells in order to turn it out to be a bifacial solar cell. With a transparent rear side, bifacial solar cells can absorb light from both the front and rear sides. Hence, they can produce more electricity than conventional monofacial solar cells. The additional advantage of using two ITO electrodes is to save the fabrication cost.

2.3. Characterizations
The morphology of the as-prepared ZnO nanorods and NiO<sub>x</sub> coating was examined by scanning electron microscopy (SEM, Philips XL 30 FEG). The crystalline structures of materials were characterized using XRD in Bragg-Brentano geometry on Rigaku Ultima IV with Cu Kα radiation. The UV–vis-NIR spectra of the coatings were collected in a transmission mode on a LAMBDA 750 UV–vis spectrophotometer with a 23 W mercury arc UV lamp (365 nm) for illumination. The photoluminescence (PL) spectra were obtained by a Horiba Jobin Yvon 320 spectrometer with a 325 nm excitation wavelength at room temperature. Raman scattering spectroscopy was performed on an HR800 spectrometer in the backscattering configuration, which is equipped with a charge-coupled detector and a He-Ne laser of 633 nm wavelength was used as an excitation source. Raman shifts were calibrated by using the 521 cm<sup>−1</sup> peak of a silicon wafer. The electrochemical impedance spectra (EIS) of the devices were measured in a frequency range of 0.05 Hz – 1 MHz under an alternative signal of 5 mV. The impedance measurements were carried out at 0.3 V. The current density–voltage (J-V) characteristics both in the dark and under AM1.5 illumination (100 mW cm<sup>−2</sup>) were recorded by a Keithley 2400 Source Meter, in which current was continuously measured as a function of voltage. The devices were irradiated in an area of 1 × 1 cm<sup>2</sup> under a small-area class-B solar simulator (PV Measurements, Inc).

3. Results and discussions

3.1. Morphology and structure: SEM and XRD
The morphology of NiO<sub>x</sub>, PANI films, and ZnO<sub>Nd</sub> was examined by SEM. Figure 2(a) displays the morphology of NiO<sub>x</sub> porous texture leading to get large cavities on an ITO glass, similar to the structure as reported in the literature [31]. The NiO<sub>x</sub> film has good uniformity with little agglomeration. It can be seen that the surface of the ITO glass was completely covered by a NiO<sub>x</sub> film with good homogeneity. Figure 2(b) reveals that the PANI film was entirely blanketed by a granular-shaped PANI layer. The green color of the PANI film indicates that the polymer thin film is conductive emeraldine. As disclosed in figure 2(c), ZnO<sub>Nd</sub> arrays vertically grew on the substrate with a density of

![Figure 1. Schematic diagrams of (a) ITO/ZnO<sub>TF</sub>/PANI/NiO<sub>x</sub>/ITO and (b) ITO/ZnO<sub>Nd</sub>/PANI/NiO<sub>x</sub>/ITO solar cells.](image-url)
about 60 nanorods per \( \mu m^2 \), and each ZnONd has a hexagonal structure with a preferential c-axis growth. The diameter of the ZnONd ranges from 40 nm to 120 nm. The thickness of the ZnONd layer is approximately 700 nm.

The crystalline structure of PANI-NiO\(_x\) and ZnONd films were characterized using XRD and displayed in figure 3. The ZnONd possesses the Wurtzite crystal structure (a space group of \( P63mc \), JCPDS file 36-1451) with cell constants of \( a = 3.25 \) Å, \( c = 5.21 \) Å, which correspond to \(100\), \(002\), \(101\), \(102\), \(110\), \(103\), and \(112\), respectively. The minor peak around 28.5 degrees comes from the substrate ITO glass. In the x-ray diffraction pattern of PANI-NiO\(_x\) film, the diffraction peaks at 37.4, 43.3, and 63.1 degrees can be assigned to the reflections of single-phase cubic structure of NiO\(_x\) (JCPDS file 73-1523) with diffracting planes \(111\), \(200\), and \(220\), respectively. The crystallite size of the NiO\(_x\) is estimated to be around 30 nm by using Scherrer’s formula. The presence of the two broad diffraction peaks in the XRD pattern of PANI-NiO\(_x\) film observed at \(2\theta = 21.5^\circ\) and \(25.6^\circ\) suggests that PANI is partly crystallized in the PANI-NiO\(_x\) film. This indicates that NiO\(_x\) in PANI matrix facilitates the crystallization of PANI through the interfacial interactions between PANI and NiO\(_x\).

3.2. Optical properties: PL, UV–vis-NIR, and Raman
To probe the electronic structure of ZnONd, NiO\(_x\), and PANI, the photoluminescence (PL) response curves of ZnONd, PANI, and NiO\(_x\) were measured, as shown in figure 4(a). ZnONd exhibits much stronger UV emission than the visible emission. The UV peak mainly originates from the recombination of free exciton through an exciton–exciton collision process\([32]\). Based upon the peak, the optical band gap of ZnO nanorod was calculated with 3.25 eV (381 nm). The visible luminescence of ZnO nanorod mainly originates from different defect states such as oxygen vacancies and Zn interstitials \([33]\). Oxygen, in general, exhibits three types of charge states of oxygen vacancies such as \(V_{00}, V_{0+1}, \) and \(V_{0+2} \). The oxygen vacancies are located below the bottom of the conduction band in the sequence of \(V_{00}, V_{0+1}, \) and \(V_{0+2} \), from top to bottom. The peak around 537 nm can be related to the singly ionized oxygen vacancy. The green emission is caused by the recombination of a photogenerated hole with a singly ionized charged state of the specific defect. The shallow acceptor levels are created at 0.3 eV and 0.4 eV above the top of the valance band due to zinc vacancy (\(V_{Zn}\)) and oxygen interstitial (O\(_i\)), respectively. Again, Zinc

Figure 2. The top view SEM images of (a) the NiO\(_x\)/ITO glass, (b) PANI and (c) ZnONd.

Figure 3. The XRD pattern of PANI-NiO\(_x\) and ZnONd films.
interstitial (Zn$_i$) produces a shallow donor level at 0.5 eV below the bottom of the conduction band [34, 35]. The emission at 381 nm can be assigned to the recombination of an electron at Zn$_i$ and a hole in the valence band. The origin of photoluminescence can be many sources such as quantum confinement and surface states, and photoluminescence spectroscopy is usually used to measure the band-gap energy of semiconductors. The emission characteristics of NiO$_x$ discloses one broad major emission peak around 2.92 eV (427 nm) and another weak peak at 2.28 eV (543 nm). The main peak associated with two feeble shoulders is attributed to the electronic transition of Ni$^{2+}$ ions. The optical absorption study reveals the existence of several transitions at energies below the bandgap of NiO$_x$. The electron energy loss spectroscopy (EELS) and spin-polarized electron energy loss spectroscopy (SPEELS) also confirm the transition of 3d$^8$ electrons in NiO$_x$ [36]. The luminescence peak of NiO$_x$ results from the electronic transition of the cationic state, which can be exploited as a good emitter of 427 nm (2.91 eV) wavelength.

The light emission of the PANI film after the absorption of electromagnetic radiation is shown in figure 4(a). A photoluminescence peak of around 427 nm (2.91 eV) is very close to the reported bandgap of PANI [37, 38]. Broad visible emission is observed where two main peaks can be identified (500 and 440 nm), in good agreement with the results reported by other groups [39, 40]. The growth of PANI on NiO$_x$ reduces the luminescence intensity of both NiO$_x$ (ultraviolet and visible emission) and PANI. Although the additional non-radiative recombination channels from structural defects associated with lattice corruption by PANI deposition at NiO$_x$/PANI interface act as traps, some reduction of photoluminescence intensity still results. The eliminated PL intensity is primarily attributed to the efficient charge transfer processes between NiO$_x$ and PANI, as a result of the band alignment in the structure. Indeed, the band alignment of two materials is type-II, such that in a ZnO/PANI/NiO$_x$ device, the photogenerated electrons transfer from PANI to the conduction band of ZnO, and the photogenerated holes transfer from the valence band of PANI to that of NiO$_x$. Therefore, it can be concluded that the growth of PANI on NiO$_x$ promotes the separation of photoexcited free carriers towards the cathode.

Figure 4(b) depicts the optical absorbance spectra of NiO$_x$, PANI, and ZnO$_{34d}$ from UV to NIR range. The optical absorption in the UV–vis–NIR range plays an important role in photovoltaic conversion. The transmittance spectra of the polyaniline film demonstrate three absorption peaks around 345, 465, and 667 nm. The absorptions around 345 and 465 nm correspond to the $\pi-\pi^*$ transitions in the benzenoid rings, while the

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**Figure 4.** (a) The photoluminescence spectra of ZnO$_{34d}$, PANI, and NiO$_x$. (b) Optical absorbance spectra of ZnO$_{34d}$ films, NiO$_x$, the polyaniline film on ITO glass.
band at 667 nm is usually ascribed to the absorption of excitons located in the quinoid ring [41]. The peak around 290 nm represents the $\pi-\pi^*$ electron orbital transition along the backbone of PANI chains. The optical absorbance spectrum of ZnONd in figure 4(b) suggests that ZnONd has an absorption edge around 350 nm. The spectrum of NiO$_x$ indicates a strong absorption band centered at 390, 435, 505 nm, and broad absorption bands around 618 and 790 nm (figure 4(b)).

Based on the optical absorbance curve, the optical band gap ($E_g$) energy can be estimated from the Tauc plot [42] by plotting the graph between $(\alpha h\nu)^n$ versus photon energy ($h\nu$). The energy band gap value is given by extrapolating the straight-line portion of the $(\alpha h\nu)^n$ curves to zero absorption coefficient value through the following equation [43]:

$$\alpha h\nu = B(h\nu - E_g),$$

where $h\nu$ is the photo energy, $\alpha$ is a material constant and $n$ is either 2 for a direct bandgap material or ½ for an indirect bandgap material. As the value of $n = ½$ does not produce any meaningful data for the bandgap energy, it suggests that PANI, NiO$_x$, and ZnONd are semiconductors with direct bandgap [44]. Following the equation and setting $n = 2$, the corresponding band gaps for NiO$_x$, ZnONd, and PANI are estimated to be around 3.75 eV, 3.21 eV, and 2.82 eV, respectively. It is noteworthy that NiO$_x$ and ZnONd films are semitransparent in the visible region, which makes them good optical windows for the hybrid n-i-p solar cells.

The Raman scattering spectra of both pure NiO$_x$, PANI, and PANI-NiO$_x$ composites are shown in figure 5. The pristine NiO$_x$ features several characteristic bands. After being mixed with PANI, no new peaks appear on the doped PANI with NiO$_x$. Therefore the general structure of the polymer still retains the same without deformation. The weak peaks in the range from 420 cm$^{-1}$ to 560 cm$^{-1}$ and from 520 cm$^{-1}$ to 1600 cm$^{-1}$ are the TO and LO phonon modes, respectively. The stronger second-order peaks are assigned to 2TO ($\sim$1200 cm$^{-1}$), 2LO (1350 cm$^{-1}$), and a combination of TO + LO (1100 cm$^{-1}$) phonon modes, [45] which is in good consistency with the literature [46]. The second-order 2 M peak around 1580 cm$^{-1}$ originates from two Brillouin zone (BZ) edge magnons, likely X or Z points, propagating with opposite momenta [47]. The Raman scattering spectrum of PANI recorded using 633 nm excitation exhibits many bands in the wavenumber range of 1100–1700 cm$^{-1}$ corresponding to the stretching modes of different bonds [48]. Raman band at 1600 cm$^{-1}$ is attributed to the C–C stretching vibration of the benzene ring. The band at 1500 cm$^{-1}$ originates from the N–H deformation vibrations. The band at 1340–1354 cm$^{-1}$ yields information about the benzene ring. The band at 1245 cm$^{-1}$ can be associated with the C–N stretching mode of the polaronic unit [49]. The intense band observed around 1170 cm$^{-1}$ is related to C–H vibrations of aromatic rings. The band from 100 to 400 cm$^{-1}$ gives information about the deformation vibrations of the benzene rings [50]. The bands at 874, 812, and 420 cm$^{-1}$ are in-plane and out of plane vibrations of the ring of protonated emeraldine form of PANI [51].

3.3. Electric properties: impedance spectroscopy
To further clarify the charge transport process at the interface of a heterostructure, the dielectric properties of the devices were measured by impedance spectroscopy as a function of frequency in the dark. Impedance spectroscopy can provide charge transport information in materials’ bulk phase (e.g. conductivity, dielectric

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**Figure 5.** Raman spectrum of NiO$_x$, PANI, and PANI-NiO$_x$, under 633 nm excitation at room temperature.
constant) as well as at their inner/outer interfaces (e.g. capacitance of the interfacial region and derived quantities). The Nyquist spectra for different ZnO/PANI/NiOx solar cells were depicted in figure 6. The dependence of frequency on the impedance for the electrochemical systems was analyzed by modeling the electrical properties into their equivalent circuits as shown in the insets of figure 6. The Nyquist spectrum exhibits a semicircle pattern in the frequency range from 0.05 Hz to 1 MHz in both samples, but a non-negligible difference in the impedance (radius) of the semicircles was observed, indicating distinct charge transfer processes at the interfaces of ZnO/PANI/NiOx. The recombination resistance at the interface could be estimated by the diameter of the semicircle in an intermediate frequency. The large-radius semicircle of ZnOTF/PANI/NiOx devices suggests the difficulty in collecting charges, leading to more severe recombination and shorter electron lifetime. The high quantity and crystallinity of ZnONd grown on the ITO can promote the charge transfer at the ZnONd/PANI interface, which would suppress recombination and increase electrons’ lifetime.

3.4. Photovoltaic properties: effects of plasma and annealing treatments

The dark I-V characteristics of two different heterojunction configurations (ZnO\textsubscript{Nd}/PANI/NiO\textsubscript{x} and ZnOTF/PANI/NiO\textsubscript{x}) were investigated. All devices show nonlinear rectifying characteristics in the dark. The typical double-diode behavior is attributed to the formation of an effective dipole at the NiO\textsubscript{x} thin film/PANI interface and the other is between ZnO\textsubscript{Nd}/PANI [52]. The reverse current illustrates a gradual increase which is a feature of the heterojunction diode. The forward current shows an exponential behavior in the following form:

$$I = I_0 \exp\left(\frac{qV}{nkT}\right)$$

where $I_0$ is the saturation current, $V$ is the bias voltage, $q/kT$ is the thermal energy and $n$ is the ideality factor (emission coefficient), which describes how closely the diode’s behavior matches that predicted by theory, assuming that the p-n junction of a diode has an infinite plane and no recombination occurs within the space-charge region. The curve fitting results show that the rectification behavior value and the ideality factor for ITO/ZnOTF/PANI/NiO\textsubscript{x}/ITO are 21 and 1.8, respectively. For ITO/ZnO\textsubscript{Nd}/PANI/NiO\textsubscript{x}/ITO, the rectification behavior value is 25 and the ideality factor 1.2.

![Figure 6. Impedance spectra of (a) ZnO\textsubscript{TF}/PANI/NiO\textsubscript{x} and (b) ZnO\textsubscript{Nd}/PANI/NiO\textsubscript{x}. The insets display the equivalent electronic circuit.](image-url)
The I-V characteristics for the devices are shown in figure 7, and the photovoltaic parameters under AM1.5 illumination are summarized in table 1. The ZnONd/PANI/ NiOx solar cells exhibit a much higher power conversion efficiency than that of the ZnOTF/PANI/ NiOx, as reflected in the boosted short circuit current and fill-factor. It can be explained by two factors: (1) as an anti-reflection structure, the multi-scattering effect between the vertically aligned nanowires [53], the ZnONd array grown on ITO enhances the optical path of the incident light in them and significantly boost the photon absorption [54]; (2) the aligned 1D nanostructure is beneficial for improving the carrier collection of an active layer and increasing the fill-factor of photovoltaic devices, accordingly facilitating the enhancement in the external quantum efficiency of solar cells.

The surface treatment of the NiOx films also affects the photovoltaic performance of the ZnONd/PANI/ NiOx devices, as seen in figure 7(a). The increase in work function observed upon O2-plasma treatment is correlated with a significant decrease of hydroxide and carbonaceous species from the surface of the as-prepared NiOx films, accordingly enhancing the PANI’s adhesion towards the NiOx film. The valence band level of the NiOx film is deeper by about 0.15 eV [55], and the work function of NiOx reaches values up to 5.4 ± 0.02 eV after subjected to an O2 -plasma treatment. A distinct shift in the work function of the NiOx films immediately after the O2 plasma treatment brings the changes of permanent and temporary components in the electronic structure of the NiOx film [56].

For the device in which the surface of the NiOx films was plasma-cleaned, the series resistance at high forward bias indicates either a modest decrease in the conductivity of the NiOx or an increase in the contact resistance at the NiOx active layer interface. This is consistent with the decrease in short circuit current (Jsc) when there is no hole-transport layer. Thus, the surface plasma treatment significantly impacts the I-V characteristic

Table 1. The photovoltaic characteristics of ZnO/PANI/ NiOx devices.

| ZnO/PANI/ NiOx devices | Voc(V) | Jsc(mA cm⁻²) | FF(%) | Efficiency(%) |
|------------------------|--------|-------------|-------|--------------|
| ZnOTF device without O₂ plasma | 0.513  | 4.65        | 34.2  | 0.81         |
| ZnOTF device with O₂ plasma treatment | 0.537  | 4.63        | 46.3  | 1.15         |
| ZnONd device without O₂ plasma | 0.539  | 9.09        | 35.9  | 1.76         |
| ZnONd device with O₂ plasma treatment | 0.548  | 9.15        | 55.6  | 2.79         |

Figure 7. I-V characteristics of (a) ZnONd/PANI/ NiOx and (b) ZnOTF/PANI/ NiOx devices.
for the device of \( \text{ZnO}_{\text{Ndx}}/\text{PANI}/\text{NiO}_{\text{x}} \), apparent improvements were observed in the fill-factor and power conversion efficiency. The \( \text{ZnO}_{\text{Ndx}}/\text{PANI}/\text{NiO}_{\text{x}} \) device with optimal \( \text{O}_{2} \)-plasma treatment exhibits a power conversion efficiency of up to 2.79% (single-sided radiation value) under AM1.5 illumination.

4. Conclusion

Overall, \( \text{ZnO} \) and \( \text{NiO} \), thin films were employed as an electron-transport layer and a hole-transport layer in organic–inorganic hybrid \( \text{ZnO}/\text{PANI}/\text{NiO} \) heterostructure solar cells. The solar cells were prepared by an \( \text{in situ} \) electrochemical polymerization method and their properties were characterized with various techniques. The performance of heterojunction solar cells was evaluated. The \( \text{in situ} \) polymerization process can intensively contact \( \text{NiO} \) with PANI to improve charge movement through the blocking layer and reduce current leakage, thus enhancing the solar cells’ performance. A more homogenous electrode with better conductivity and lesser work function was achieved by \( \text{NiO} \) after an oxygen plasma treatment, leading to the increased mobility of electrons, which further improve the photovoltaic performance. The vertical alignment of \( \text{ZnO}_{\text{Ndx}} \) improves both the light trapping and the photo-carrier collection. Although a lot of work is still in need to enhance the solar cell performance, this comparative study indicates that the proper interface material has a significant impact on solar cells’ performance, which sheds light on the design for optimized photovoltaic devices with low cost, environmental friendliness, long-lasting, and flexibility.

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