Si/PEDOT:PSS core/shell nanowire arrays for efficient hybrid solar cells

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A solution filling and drying method has been demonstrated to fabricate Si/PEDOT:PSS core/shell nanowire arrays for hybrid solar cells. The hybrid core/shell nanowire arrays show excellent broadband anti-reflection, and resulting hybrid solar cells absorb about 88% of AM 1.5G photons in the 300–1100 nm range. The power conversion efficiency (PCE) of the hybrid solar cell reaches 6.35%, and is primarily limited by direct and indirect interfacial recombination of charge carriers.

Inorganic semiconductor nanowires have been actively pursued for solar cell applications in recent years due to high crystallinity and purity, direct electrical pathways and fast electronic transport. In particular, Si nanowires have been extensively investigated because of good absorption profile overlap with the solar spectrum. Furthermore, arrays of Si nanowires prepared from chemical vapor deposition, wet chemical etching or dry etching feature wide-band low reflectivity and highly efficient light absorption due to strong light trapping effects. In contrast to the 200–300 μm thick Si layer needed to ensure adequate light absorption in planar crystalline Si solar cells, the active layer thickness of Si nanowire array solar cells can be reduced to 3–5 μm, significantly reducing the material cost. In addition, the nanowire based core/shell photovoltaic junction leads to a charge carrier conduction mode different from that in conventional planar Si solar cells. Photogenerated charge carriers diffuse a short distance on the nanowire radial direction, which is orthogonal to the direction of incident light, to reach the photovoltaic junction and thus leading to high separation efficiency of the charge carriers. Due to the short carrier diffusion pathway for separation, core/shell nanowire solar cells can tolerate higher material defects and allow the utilization of lower quality Si, which further reduces materials cost. Up to now, the difficulty lies in the preparation of efficient core/shell nanowire photovoltaic junctions in a simple way. To this regard, photoelectrochemical (PEC) cells, in which a conformal photovoltaic junction at the solid–liquid interface is conveniently formed, have also been exploited. But ionic conduction in liquid is orders of magnitude slower than electronic transport in solid semiconductors, so the overall efficiency of PEC cells is typically not ideal.

Organic polymer materials exhibit tunable optoelectronic properties and can be solution processed onto various substrates, and thus are increasingly used in organic/inorganic hybrid solar cells. Many organic polymers such as poly(3-hexylthiophene) (P3HT) and poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS) for organic/inorganic hybrid core/shell nanowire array structured solar cells have been demonstrated. However, the PCEs of these devices are typically in the range of 0.01–2.7%, with the best performance of 5.8% obtained from GaAs-based hybrid devices. Further studies are still necessary to build hybrid core/shell nanowire arrays for efficient photovoltaic conversion.

In this communication, we report Si nanowire array based organic/inorganic hybrid solar cells, in which the Si/PEDOT:PSS core/shell photovoltaic junction is conveniently formed for the separation of charge carriers. We notice a recent report on hybrid solar cells obtained by directly pressing Si nanowires arrays into wet PEDOT:PSS coated ITO glass, resulting in a high PCE of 5.09%. In contrast, our approach involves conformally coating Si nanowire arrays with a thin PEDOT:PSS layer by a solution filling and drying method. The Si/PEDOT:PSS core/shell nanowire arrays show excellent broadband anti-reflection. The resulting hybrid solar cells absorb about 88% photons in the 300–1100 nm wavelength range from the AM 1.5G light, and exhibit PCE up to 6.35%. In addition, the potential of Si/PEDOT:PSS core/shell nanowire arrays for photovoltaic conversion is evaluated and the limiting factor of device performance is attributed to direct and indirect interfacial recombination of charge carriers.

As illustrated in Fig. 1(a), Si/PEDOT:PSS core/shell nanowire arrays and hybrid solar cells are fabricated in four steps. Firstly, Si nanowire arrays are prepared from n-type Si (100) wafer (1–10 μm) by using silver-assisted chemical etching followed by nitric acid and hydrofluoric acid washing to remove the silver catalyst and the silicon dioxide layer, respectively. Secondly, a drop of PEDOT:PSS solution (PH1000, H. C. Starck, Germany) does not wet the PEDOT:PSS coated ITO glass, resulting in a high PCE of 5.09%. Thirdly, the sample is dried at 120 °C for 10 min to form the hybrid core/shell nanowire array. Lastly, hybrid solar cells are fabricated by making front and back contacts to the Si/PEDOT:PSS core/shell nanowire arrays. A 500 nm thick aluminum...
layer is thermally evaporated onto the back side of the Si wafer as the back contact, and the front contact is prepared by covering the sample with a PEDOT:PSS coated ITO glass, followed by drying at 120 °C for 30 min in an oven.

The morphology and the structure of Si/PEDOT:PSS core/shell nanowire arrays are characterized by electron microscopy. The cross-sectional field emission scanning electron microscope (FE-SEM) image in Fig. 2(a) shows that nanowires with a uniform height of about 2.9 μm are vertically aligned on the Si substrate. Transmission electron microscope (TEM) micrographs in Fig. 2(b) and (c) clearly indicate that the hybrid nanowire consists of a single-crystalline Si core and an amorphous organic shell. The organic shell layer conformally coats the Si core with a thickness of about 10–20 nm.

Light-trapping capability of Si/PEDOT:PSS core/shell nanowire arrays and corresponding hybrid solar cells are measured by optical reflectance spectra using a Lambda 950 UV-VIS-NIR spectrometer. The spectra in Fig. 3 show strongly suppressed optical reflection of the Si/PEDOT:PSS core/shell nanowire arrays compared to planar Si wafer. The reflectance is lower than 5% over the range of 300–900 nm. The broadband anti-reflection effect may be attributed to scattering and diffraction of incident light within sub-wavelength scaled nanowire arrays. While the reflectance of the hybrid solar cell is slightly higher than that of nanowire arrays due to the ITO glass front cover, it is still lower than 10% in the primary solar spectrum range of 500–950 nm. Since there is no transmission through the thick Si substrates, photons not reflected are all absorbed. We derive a light-trapping ratio (η) of the Si/PEDOT:PSS core/shell nanowire array and the hybrid solar cell in the 300–1100 nm wavelength range using eqn (1).

\[
\eta = \frac{\int_{300}^{1100} (1 - R(\lambda))(I_{\text{AM1.5G}}(\lambda))/(hc/\lambda)d\lambda}{\int_{300}^{1100} (I_{\text{AM1.5G}}(\lambda))/(hc/\lambda)d\lambda}
\]
in which \( R(\lambda) \) is the reflectance, \( \lambda \) is the wavelength, \( I_{\text{AM1.5G}}(\lambda) \) is the AM 1.5G solar spectrum, \( h \) is the Planck constant, and \( c \) is the speed of light. The results reveal that about 95% and 88% of the photons in the 300–1100 nm wavelength range from the AM 1.5G light are absorbed by the Si/PEDOT:PSS core/shell nanowire array and the hybrid solar cell, respectively. The light-trapping properties of the hybrid nanowire array and the hybrid solar cell without any anti-reflection coating are similar to, if not better than, that of Si pillar arrays with micrometre-scaled diameters.\(^4\)

The photovoltaic performance of the hybrid solar cell is measured under 100 mW cm\(^{-2}\) AM 1.5G illumination (Newport Inc., New Jersey, USA) using a Keithley 2635 source meter. Fig. 4(a) shows the current density–voltage (\( J-V \)) characteristics of the hybrid solar cell, which exhibits an open circuit voltage (\( V_{\text{OC}} \)) of 0.46 V, a short circuit current density (\( J_{\text{SC}} \)) of 21.6 mA cm\(^{-2}\), a fill factor (FF) of 0.64, and an overall PCE of 6.35%. In spite of the simple preparation method, the device has achieved the highest efficiency reported so far in organic/inorganic hybrid solar cells.\(^{18,25}\)

The Si/PEDOT:PSS core/shell nanowire arrays could potentially realize even higher efficiency for photovoltaic conversion. Based on the light absorption profile of the hybrid solar cell, and assuming one electron–hole pair per every absorbed photon and no recombination (i.e. 100% internal quantum efficiency), we calculate an upper limit of the photogenerated current density (\( J_{\text{ph}} \)) using eqn (2).\(^{26}\)

\[
J_{\text{ph}} = q \int_{300 \text{ nm}}^{1100 \text{ nm}} \left[ 1 - R(\lambda) \frac{I_{\text{AM1.5G}}(\lambda)}{(hc/\lambda)} \right] d\lambda 
\]

where \( q \) is the elementary charge, to be 38 mA cm\(^{-2}\). Furthermore, previous studies on planar Si/polymer Schottky junctions revealed that such organic/inorganic heterojunctions could produce photovoltages approaching their theoretical limit, which is determined by materials properties such as doping and carrier mobility of the Si.\(^{27,28}\) Considering the Si wafer used in our study, the theoretical upper limit of \( V_{\text{OC}} \) achievable in the Si/PEDOT:PSS junction is about 0.56 V.\(^{28}\) Taking into account the measured FF of 0.64, the nominal upper limit of attainable PCE is 13.6%. Current device performance indicates that there is still much room for improvement.

To understand the limiting factors of the device performance, \( J-V \) characteristics of the device in the dark are measured. As shown in Fig. 4(b), the dark \( J-V \) curve shows a typical rectifying behavior. Similar to organic bulk heterojunction solar cells, the dark \( J-V \) relation of the organic/inorganic hybrid nanowire solar cell consists of three regimes.\(^{29,30}\) A simple equivalent circuit model including a diode, a series resistor and a shunt resistor is often used to describe the \( J-V \) characteristic, with an analytical expression described by eqn (3).\(^{30}\)

\[
J = J_0 \left\{ \exp \left[ \frac{q}{nkT} (V - JAR_s) \right] - 1 \right\} + \frac{V - JAR_s}{AR_{\text{sh}}}
\]

in which \( k \) is the Boltzmann constant, \( T \) is the absolute temperature, \( J \) is the current density, \( V \) is the applied voltage, \( J_0 \) is the reverse saturation current density, \( n \) is the diode ideality factor, \( A \) is the effective area of the solar cell, \( R_s \) is the series resistance, and \( R_{\text{sh}} \) is the shunt resistance. At an intermediate positive bias regime, the current is dominated by the rectifying diode. At low and high positive bias regimes, the current is controlled by the shunt resistance and series resistance, respectively. From the best fitting of the diode dominated region to \( \ln (J) = \ln (J_0) + (q/nkT)V \), we obtain an \( n \) of 2.1 and a \( J_0 \) of 3.26 \( \mu\)A cm\(^{-2}\). The high \( n \) is consistent with previously reported values for Si nanowire core–shell p–n junction solar cells,\(^2\) and indicates a high interfacial state density in the hybrid solar cell.\(^{14}\) The interfacial states may arise from the dangling bonds at the surface of Si nanowires, surface roughness due to wet chemical etching and the large interfacial area of the hetero-junction due to small size of the Si nanowires. The high interfacial state density suggests that a severe direct recombination may occur at the Si/PEDOT:PSS interface, thus resulting in a low \( J_{\text{SC}} \).

The reverse saturation current density obtained from the fit \( J_0 \) is two to three orders of magnitude higher than that of the planar Si/ PEDOT:PSS heterojunction and those reported for planar Si p–n+ junction solar cells and Si micron pillar p–n+ junction solar cells.\(^{32}\) Using \( J_0 = 3.26 \mu\)A cm\(^{-2}\), \( n = 2.1 \), \( J_{\text{ph}} = J_{\text{SC}} = 21.6 \text{ mA cm}^{-2} \) and equation\(^{30}\) \( V_{\text{OC}} = (nkT)/\ln [(J_{\text{ph}}/J_0) + 1] \) for our hybrid solar cell, we obtain a \( V_{\text{OC}} \) of 0.48 V, which is very close to the experimental value of 0.46 V. The high \( J_0 \) suggests high probability of minority carriers (electrons) in Si crossing the Si/PEDOT:PSS barrier via thermionic or tunneling emission mechanisms to indirectly recombine with minority carriers (holes), thus resulting in the lower \( V_{\text{OC}} \). The high \( J_0 \) in Si/ PEDOT:PSS nanowire array solar cells can be attributed to the large
specific Si/PEDOT:PSS interfacial area in the devices. In contrast to planar Si/polymer hybrid solar cells\cite{27,28} where the small specific interface area and low interfacial electron transfer velocity result in high \( V_{OC} \), Si/PEDOT:PSS nanowire solar cells exhibit lower \( V_{OC} \) because of large specific interface area.

Electrical loss due to series and shunt resistances could potentially also affect the photovoltaic conversion of solar cells. We calculate an ideal FF of the hybrid solar cell in the absence of parasitic series or shunt resistance using experiential eqn (4)\cite{53}.

\[
FF = \frac{V_{OC} - \ln \left( \frac{V_{OC} + 0.72}{V_{OC}} \right)}{V_{OC} + 1}
\]  

(4)

where \( V_{OC} = \frac{q}{nkT} \) is the normalized open circuit voltage. Using \( n = 2.1 \) and \( V_{OC} \) of 0.46 V, we obtain an ideal FF of 0.66 for the hybrid solar cell. If the series resistance or the shunt resistance affects the photovoltaic performances of the hybrid solar cell significantly, the calculated ideal FF will be much higher than the real value. In the device above, the experimental FF of 0.64 is close to the ideal value of 0.66, suggesting that the electrical loss in the current device is not significant.

Therefore, future efforts to optimize the hybrid nanowire solar cells need to focus on decreasing direct and indirect interfacial recombination of charge carriers. For example, the Si nanowire surface could be passivated to reduce interfacial states mediated direct recombination in order to improve \( J_{SC} \); and hole-conducting but electron-blocking interfacial layers could be introduced to reduce the reverse saturation current density and improve \( V_{OC} \). In the mean time, \( V_{OC} \) of the Si/PEDOT:PSS nanowire solar cells is dependent on the doping density of the Si materials.\cite{29} Therefore, the \( V_{OC} \) of the hybrid silicon solar cell can also be optimized via proper doping of Si.

In conclusion, a solution filling and drying method has been demonstrated to fabricate Si/PEDOT:PSS core/shell nanowire arrays for efficient hybrid solar cells. The fabricated hybrid solar cells show excellent light trapping capability and exhibit PCE up to 6.35%. The device performance is primarily limited by interfacial recombination of charge carriers, but there is still much room for improvement. Future investigations on passivation of the Si nanowire surface and introduction of hole-conducting but electron-blocking interfacial layers may further optimize these promising devices.

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Notes and references


