Polyaniline micro-rods based heterojunction solar cell: Structural and photovoltaic properties

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The present paper reports the fabrication and photovoltaic characterization of pure and dodecyl benzene sulfonic acid (DBSA)-doped polyaniline (PAni) micro-rods polymer/n-Si heterojunction solar cells, and also the morphological and structural properties of pure and micro-rods PAni doping with DBSA. The device shows a strong photovoltaic behavior with a maximum open-circuit voltage V_{oc} of 0.83 V, a short-circuit current J_{sc} of 14.72 mA cm^{-2}, fill factor FF of 0.54 resulting in an estimated device efficiency η of 6.13% under simulated solar light with the intensity of 100 mW/cm^2. The results indicate that the Au/DBSA-doped PAni micro-rods/n-Si heterojunction structure might be promising for the solar cell applications. © *2012 American Institute of Physics.* [http://dx.doi.org/10.1063/1.4772019]

Conductive polymers or, more precisely, intrinsically conductive polymers (ICPs)/electroactive polymers are organic polymers that conduct electricity.[1] The discovery of conducting polymers opened up many new possibilities for devices combining unique optical, electrical, and mechanical properties. Micro/nano-structured (tubes, fibers, rods, hollow, etc.) poly-aniline (PAni) is one of the most intensively studied conductive polymers, which have been explored for use in optical and electrical applications. It has demonstrated a significant potential for technological applications due to its high electrical conductivity associated to its simple and economical production routes, possible processibility, and relatively high environmental stability.[2] Another positive aspect is the fact that PAni is very inexpensive and, best of all, is compatible with silicon (Si) planar technology. PAni is the only conducting polymer whose properties not only depend on the oxidation state but also on its protonation doping level and also on the nature of dopants. These properties make the PAni a promising candidate for fundamental study of potential device applications such as solar cell, light emitting diodes, transparent electrodes, gas and humidity sensing, and many more in nanotechnology applications.[3–5] In particular, the role of the PAni polymer in the solar cell device design was dual: providing an interface with *n*-type Si for photo-carriers separation and hole collection through the polymer film to the external electrode.

The great potential of PAni is, however, masked by its serious disadvantages such as non-solubility in common solvents, infusibility, and hence poor process ability. For many years, attempts have been made to modify its solubility[6] of which the most widely adopted strategy is to dope PAni with organic acids such as dodecyl benzene sulfonic acid (DBSA).[7] Upon acid doping, the electrical conductivity of undoped PAni increases, depending on the dopant.[8] Herein, we report fabrication and

characterization of high quality micro-rod PAni/n-Si heterojunction solar cell. We have also investigated the surface topology and structural properties of the pure and DBSA-doped PAni. Additionally, its photovoltaic response was tested under the solar illumination. The various parameters of solar cell such as open circuit voltage, short circuit current, fill factor, efficiency, and incident monochromatic photon-to-current conversion efficiency (IPCE) have been obtained.

In the synthesis of polyaniline samples, aniline, DBSA, and hydrochloric acid (HCl) were mixed and then periodic acid (H_5IO_6) was added to this mixture and stirred at room temperature for 10 h. A dark green colloidal solution was obtained upon addition of the oxidant. The amounts of H_5IO_6 and HCl used in all polymerizations were 1.0 mmol. All the resulting dark green polymers were then filtered. The colloidal polymer samples were subjected to multiple rinsing procedures with distilled water to remove any residual monomers, oxidant, and HCl, and were then dried under vacuum.

In this work, an n-type silicon (phosphorus-doped) single crystal silicon wafer, pre-polished on one side and having a (100) orientation, thickness of 400 μm, and 1–10 Ω cm resistivity, was used as a substrate. For the fabrication process, the Si wafer was degreased through the RCA cleaning procedure. The RCA cleaning procedure has three major steps to be used sequentially: (I) Organic clean: removal of insoluble organic contaminants with 10 min boiling in $NH_4OH + H_2O_2 + 6H_2O$ solution. (II) Oxide strip: removal of a thin silicon dioxide layer where metallic contaminants may accumulate as a result of (I), the oxide on the front surface of the substrate was removed in HF:H_2O (1:10) solution and finally the wafer was rinsed in de-ionized water for 30 s. (III) Ionic clean: followed by a 10 min boiling in $HCl + H_2O_2 + 6H_2O$ solution. Next, it was subjected to a drying process in N_2 atmosphere for a prolonged time. Following the drying process, high-purity gold (99.9%) was thermally evaporated from the tungsten filament onto the whole back surface of the n-Si wafer under a pressure of 10^{-7} Torr. In order to

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obtain a low-resistivity ohmic back contact, Si wafer was sintered at 580 °C for 3 min in N_2 atmosphere.

Immediately after the surface cleaning procedures, a number of PAni solutions were coated by the spin coating method (ten times) on the front surface of the n-Si wafer, and vapoured by itself for drying of solvent in N_2 atmosphere for 2 h in room temperature. In order to obtain a rectifying contact on the front surface of n-Si coated with PAni, a high-purity gold layer (99.9%) was thermally evaporated from the tungsten filament using a shadow mask on the surface in a high vacuum under the pressure of 10^{-7} Torr. Rectifier dot contacts have a circular geometry with a diameter of about 1.0 mm (diode area $= 7.85 \times 10^{-3}$ cm^2). Thus, Au/pure PAni/n-Si/Au and Au/DBSA-doped PAni micro-rod/n-Si/Au heterojunction solar cell was obtained.

Before DC conductivity measurements, dry pellets were prepared from powdery polymer material under a pressure of 5 ton cm^{-2}. The conductivity values of polymers were measured using a four-probe electrical conductivity measuring device (Entek Electronic) at room temperature. Gold-plate probes were used to avoid any errors caused by ohmic contacts. The resistivity of the samples was measured at five different positions, and at least two pellets were measured for each sample: an average of 10 readings was used for conductivity calculations. The electrical conductivity values of pure and DBSA-doped PAni were found as 0.002 and 0.01 S/cm, respectively. Thus, the conductivity values increase with the doping of the DBSA concentration. Also, thickness of the pure and DBSA-doped PAni was measured as 161 and 279 nm, respectively, using ellipsometry.

X-ray diffractions (XRD) and morphological characteristics of the powdered polymer samples were recorded using a Rigaku D/MAX-2200 diffractometer and Zeiss Evo-50 scanning electron microscopy, respectively. The current–voltage (*I-V*) characteristics of the heterojunction solar cell under dark and light were performed with a Keithley 4200 semiconductor parameter analyzer. The light source was a 100 mW/cm^2 xenon lamp (Oriel) with an Oriel filter to simulate the AM1.5 solar spectrum.

The PAni and DBSA-doped PAni polymers were dried under vacuum and then their XRD spectra were recorded in Figs. 1(a) and 1(b), respectively. As shown in the XRD patterns, the transition from amorphous to crystalline phase can be seen (sharp reflections indicate good crystallinity). This case indicates that DBSA also influences the polymer crystallite. Fig. 1(a) demonstrates several sharp peaks approximately at 9.80, 17.03, 18.45, 20.51, 23.06, 24.19, and 25.04 corresponding to crystal plane (001), (012), (003), (100), (020), (110), and (111), respectively. We do admit that the XRD pattern for the DBSA-doped-PAni is not similar to the reported one of PAni,[9–12] probably due to the difference of preparing method and the effect of DBSA in media. Furthermore, it is known from the literature[9–12] that the XRD of PAni clearly suggests that the system is generally amorphous. The appearance of a large number of sharp diffraction peaks upon doping with DBSA shown in the diffractogram patterns of our sample (Fig. 1) suggests significant crystallization of PAni on protonation. From the result, we can draw a conclusion that DBSA-doped-PAni is high crystalline material.

The FE-SEM image of PAni and DBSA-doped-PAni polymers was shown in Figs. 2(a) and 2(b), respectively. As
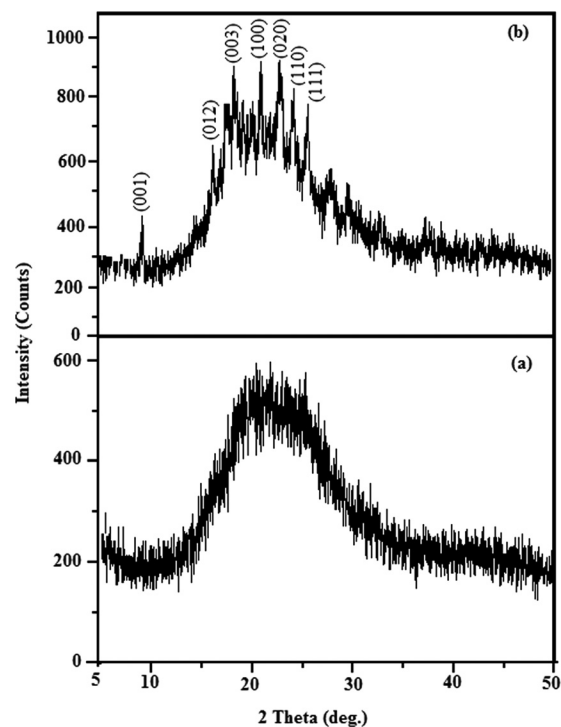

FIG. 1. X-ray diffractogram patterns of (a) pure PAni, (b) DBSA-doped-PAni, respectively.
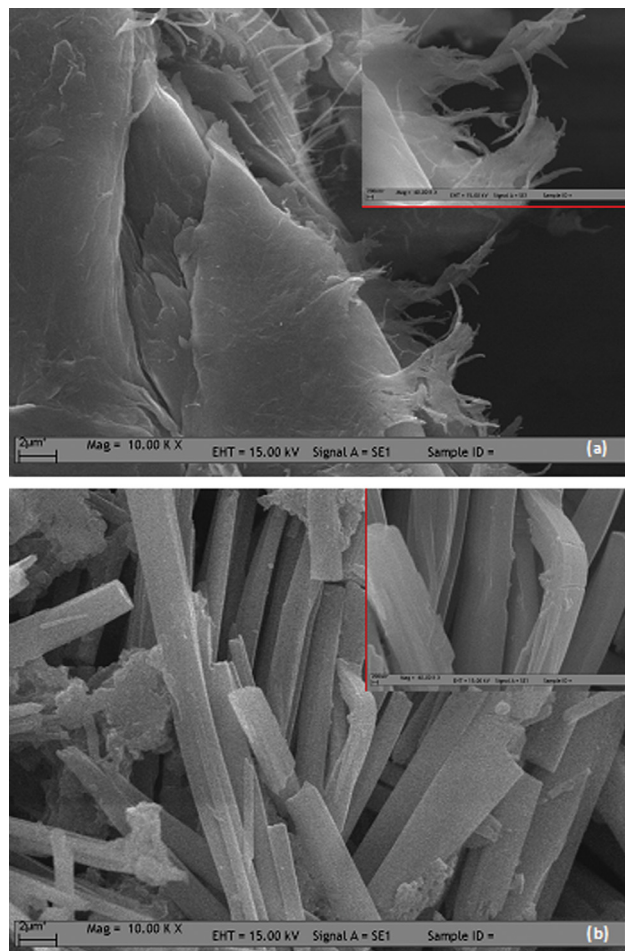

FIG. 2. FE-SEM image of (a) pure PAni, (b) DBSA-doped-PAni, at 10 $k\times$ magnification (2 μm), respectively. In the inset of figure, surface topography of these samples at 40 $k\times$ magnification (200 nm).

shown in FE-SEM photographs, when the DBSA is doped into the PAni, new existing polymer transforms into rod structure. Fig. 2(b) shows that the average diameter is around $1–2\,\mu m$ and the length is $5–10\,\mu m$, yielding an aspect ratio (length/diameter) of ~ 5. It can be seen that the product consists of lots of micro-rods which are lateral to smooth surfaces. Large surface area of the rod shaped structures facilitates good absorption of the incident light and the length of the rods enables effective separation and transfer of the photo-generated charges. In addition to this, the FE-SEM image further indicates that the large quantity of the PAni micro-rod products can be achieved via the method. It is a well known fact that the rods show dramatically enhanced performance over conventional PAni applications such as in solar cells.

From these characteristics, we have extracted typical photovoltaic cell values as the open-circuit voltage (V_{oc}), the short-circuit current (J_{sc}), the fill factor (FF), and the external photovoltaic yield (η), which are key parameters in evaluating the performance of solar cells.

These parameters were calculated by equations below,

$$FF = \frac{J_{mm} \cdot V_{mm}}{J_{sc} \cdot V_{oc}} = \frac{P_{mm}}{J_{sc} \cdot V_{oc}}, \tag{1}$$

$$\eta = \frac{P_{mm}}{P_{in}} \times 100\,\% = \frac{FF \cdot J_{sc} \cdot V_{oc}}{P_{in}} \times 100\,\%, \tag{2}$$

where P_{mm} and P_{in} are the maximum power generated by solar cell at a voltage V_{mm} and current J_{mm} and input power, respectively.

The fill factor, FF, is the ratio of maximum power point, and the energy conversion efficiency of solar cell, η is the comparison of maximum power point of cell, P_{mm} to input light from source, P_{in}.

The dependence of the current density upon voltage is shown in Fig. 3 for a pure PAni and DBSA-doped PAni/n-Si heterojunction solar cell structure measured under tungsten illuminations through the PAni intensity of 100 mW/cm^{-2}. The pure and DBSA-doped-PAni based micro scaled heterojunction
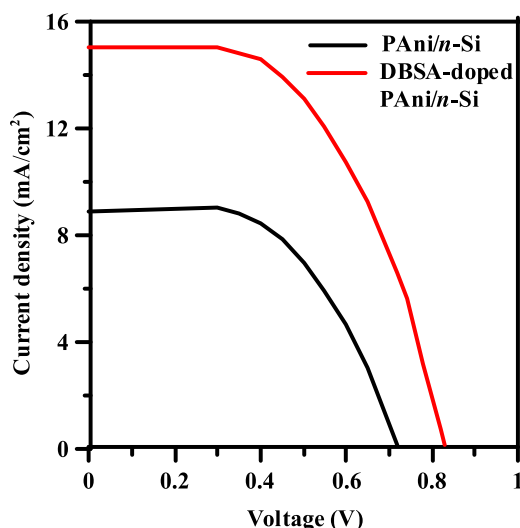

FIG. 3. Current density as a function of voltage across pure PAni and DBSA-doped micro-rod PAni/n-Si heterojunction solar cell under illumination.

device shows a strong photovoltaic behavior with a maximum open-circuit voltage V_{oc} of 0.71 and 0.83 V, a short-circuit current J_{sc} of 8.89 and 14.72 mA/cm^2, fill factor FF of 0.50 and 0.54 resulting in an estimated device efficiency η of 3.32% and 6.13%, respectively. The efficiency of the solar cell using the DBSA dopant was markedly higher than the pure PAni polymer. This is due to a higher intensity, the uniform growth geometry of microrods and broader range of the light absorption of DBSA-doped PAni micro-rods, and the greater interaction between PAni micro-rods and n-Si lead to a better charge transfer. Also, electron transport in crystalline rods is expected to be several orders of magnitude faster than percolation through a amorphous network. This could facilitate an electron transfer from PAni micro-rods to the n-Si surface and could account for better performance of DBSA dopant material. Our result is acceptable when compared with some previously published data. Namely, Wang and Schiff[5] reported that typical cell parameters for the PAni/n-Si heterojunction solar cell under simulated solar light with the intensity of 100 mW/cm^2 had the following values: $V_{oc} = 0.51$ V and $J_{sc} = 17 \text{ mA/cm}^2$. Tan *et al.*[13] obtained a value of $V_{oc} = 0.32$ V and $J_{sc} = 0.09 \text{ mA/cm}^2$ for 4-DBSA-doped-PAni in chloroform structure under 100 mW/cm^2 illumination. Zaidan *et al.*[14] obtained a value of $J_{sc} = 45\,\mu A$ cm^{-2} and $V_{oc} = 400$ mV, and solar cell efficiency $\eta = 0.3\%$ illuminated of 100 mW/cm^2. The addition of polyacrylamide (PAM) into the PAni was reported by Bejbouji *et al.*,[15] and the best power conversion efficiency was obtained as $\eta = 2.49\%$ with the value of $J_{sc} = 8.74\,\mu A/cm^2$, $V_{oc} = 0.56$ V, and $FF = 0.51$ by irradiating 100 mW/cm^2 simulated sunlight. Sorkhabi *et al.*[16] have constructed a composite device based on polyaniline-copoly9u (butyl acrylate/vinyl acetate) (PAni-poly-BuA/Vac), and found the following values: $\eta = 0.001\%$, $J_{sc} = 2.0\,\mu A/cm^2$, $V_{oc} = -12$ mV, and $FF = 0.28$ under the intensity of 100 mW/cm^2. Also, Au/PAni/GaAs metal-insulator-semiconductor (MIS) solar cell was fabricated by Mangal *et al.*[4] and the values of the open circuit voltage and short circuit current at air mass (AM) 1.0 are measured to be 0.45 mA and 1.07 V, respectively. The notable values of our device can be attributed to the difference in preparing method, the effect of DBSA as a dopant, and mostly the presence of microrods in the structure. The rods act as wires because when they absorb light of a specific wavelength they generate electrons. These electrons flow through the rods until they are collected by the electrode where they are combined to form a current and are used as electricity.

The IPCE is an important characteristic of a photovoltaic device. It is defined as the number of electrons generated by light in the external circuit divided by the number of incident photons as a function of excitation wavelength as in the following equation:[17]

$$IPCE(\lambda) = \frac{Photocurrent\,density}{Wavelenght \times Photon\,flux}$$
$$= LHE(\lambda) \times \varphi_{inj} \times \eta_c, \tag{3}$$

where $LHE(\lambda)$ is the light-harvesting efficiency at wavelength λ, φ_{inj} is the quantum yield, and η_c is the efficiency for the collection of electrons.
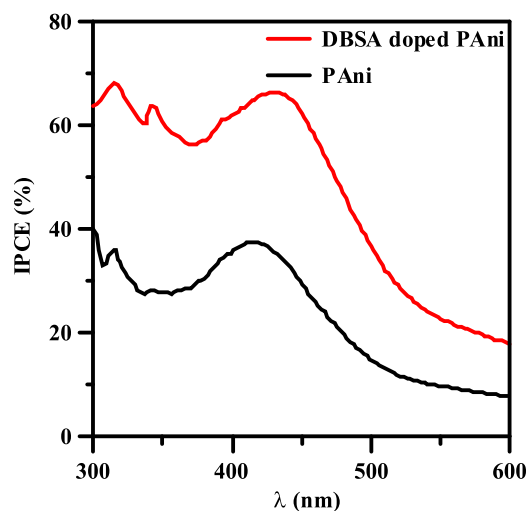
FIG. 4. IPCE(λ) spectra for pure PAni and DBSA-doped micro-rod PAni/n-Si heterojunction solar cell.

Fig. 4 shows the photocurrent action spectra, $IPCE(\lambda)$, for pure and DBSA-doped PAni heterojunction solar cell. The maximum IPCE values of these solar cells used by pure and DBSA-doped PAni are about 36% and 66% at the same wavelength (430 nm), respectively. It was shown that the IPCE of solar cell is effectively improved by doping DBSA material.

In conclusion, we have fabricated a PAni micro-rods based heterojunction solar cell on an n-type Si wafer. Lots of sharp diffraction peaks upon doping with DBSA shown in the diffractogram patterns refer a polycrystalline structure. Some photovoltaic parameters of the pure PAni and DBSA-doped PAni micro-rod/*n*-Si heterojunction solar cell such as open-circuit voltage V_{oc}, a short-circuit current J_{sc}, fill factor FF, energy conversion efficiency η, etc., under illumination have also been evaluated. DBSA-doped PAni gave significantly high photocurrent voltages with reasonable efficiency

compared to the pure PAni and other studies. This could be due to better interaction between the DBSA-doped PAni and the surface of *n*-Si. The obtained values refer a strong photovoltaic behavior, which is attributed to the presence of micro-rods. These results emphasize the applicability or suitability of DBSA-doped PAni micro-rods grown on appropriate substrate using chemical solution method for the fabrication of efficient and low-cost optoelectronic devices, particularly solar cell.

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