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High-bendability flexible dye-sensitized solar cell with a nanoparticle-modified ZnO-nanowire electrode

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We report a high-bendability flexible dye-sensitized solar cell (DSSC) based on a ZnO-nanowire photoelectrode, which was fabricated on polyethylene terephtalate/indium tin oxide substrate by low-temperature hydrothermal growth. Nanowire morphology shows preferable in crack resistance due to its efficient release of bending stress. The ZnO-nanowire film can be bended to an extreme radius of 2 mm with no crack observed. Flexible DSSCs based on this kind of ZnO-nanowire photoelectrodes showed good bending stability. With a ZnO-nanoparticle modification on the nanowires, the flexible DSSC fabricated showed a much improved power conversion efficiency. Meanwhile, the good bendablility of this nanoparticle-modified nanowire electrode is maintained. The results demonstrate that high quality ZnO nanowires fabricated by the low-temperature method is promising for efficient and flexible plastic solar cells. © *2008 American Institute of Physics.* [DOI: 10.1063/1.2905271]

Flexible solar cells based on plastic substrates are lightweight, thin, and bendable. They can be produced at low cost and can be easily integrated in a curved form, suitable for portable and wearable applications. Recently, there is an increased interest in developing flexible dye-sensitized solar cells (DSSCs) with nanostructured metal-oxide (such as TiO_2 or ZnO) films fabricated on flexible substrates.[1–8] Typically, nanoparticles are connected to form a mesoporous film on a plastic substrate by low-temperature processes such as sintering,[9] mechanical pressing,[10] hydrothermal crystallization,[11] electrophoretic deposition,[12] microwave irradiation[13] or film transfer.[14] However, the poor necking of nanoparticles arising from the low-temperature heat treatment makes the film more fragile thus limiting the bendability and efficiency of the flexible DSSCs. Bendability of the photoanode film is very important for flexible DSSCs. Especially, in the electrolyte-based DSSCs with a thick (~ 8 μm) nanocrystalline film (required by large dye loading) as the photoelectrode, achieving good bendablility without cracking and peeling off of the photoelectrode film is really a challenge. The bending stress in a mesoporous network has to be released through network deformation leading to cracks or peeling [see the schematic shown in Fig. 1(a)]. Improvements in efficiency of flexible DSSCs were achieved,[14–17] but few sought improvements by tackling the mechanical stability issue of the flexible photoelectrodes and the DSSCs constructed.

ZnO is a large wide band gap (>3 eV) semiconductor with high electronic carrier mobility.[18] ZnO-nanowire array with large surface area is a promising option for the photoanode of DSSCs, although the power conversion efficiency (PCE) of DSSCs based on ZnO nanowires on indium tin oxide (ITO) glass is relatively low ($\sim 2\%$) due to poor dye loading and other unknown reasons.[19–22] Nevertheless, the low-temperature and low-cost fabrication of ZnO nanowires by solution process (hydrothermal method) makes it attractive and especially suitable for flexible devices and roll-to-roll mass production.[23] For flexible electronics applications, orderly aligned nanowires can efficiently release the bending stress in the film through the gap (between nanowires) adjustment [Fig. 1(b)]. So far, there is no report of applying hydrothermal ZnO nanowires on plastic polyethylene terephtalate (PET)/ITO substrate for efficient flexible DSSC fabrication.

In this letter, we report a flexible DSSC based on ZnO-nanowire film on plastic substrate. The highly bendable ZnO-nanowire film on PET/ITO substrate was fabricated by low-temperature hydrothermal growth. To improve the performance of the flexible DSSC, ZnO nanoparticles were filled in the gaps (between nanowires) and attached to the nanowires, resulting in a doubled efficiency while retaining good mechanical stability.

ZnO-nanowire films were grown on PET/ITO substrates by a hydrothermal method at low temperature.[23] In brief, a thin layer (~ 30 nm) of ZnO seeds was deposited on a cleaned PET/ITO substrate by spin coating a gel solution contain 0.2% (weight/volume) ZnO nanoparticles (10 nm) in
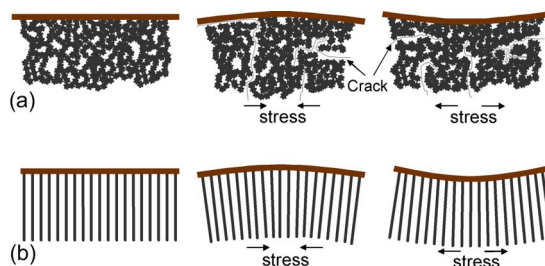

FIG. 1. (Color online) Schematic shows of the bending stress release in nanocrystalline films of nanowire array and mesoporous network. (a) Mesoporous network and its bending form. Bending stress cause network deform leading to cracking or peeling. (b) Nanowire array and its bending form. Bending stress released through the gap adjustment.

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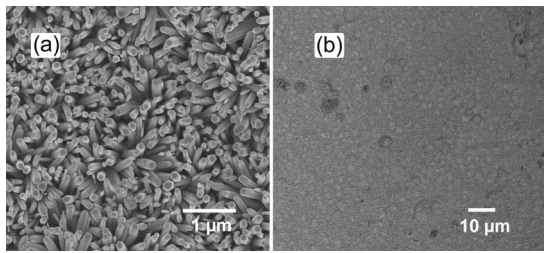[c)] Electronic mail: logq@ime.a-star.edu.sg.

FIG. 2. SEM images of the ZnO nanowires grown on flexible PET/ITO substrates by hydrothermal synthesis. (a) As prepared; (b) after bending 2000 cycles with bending radius of 5 mm.
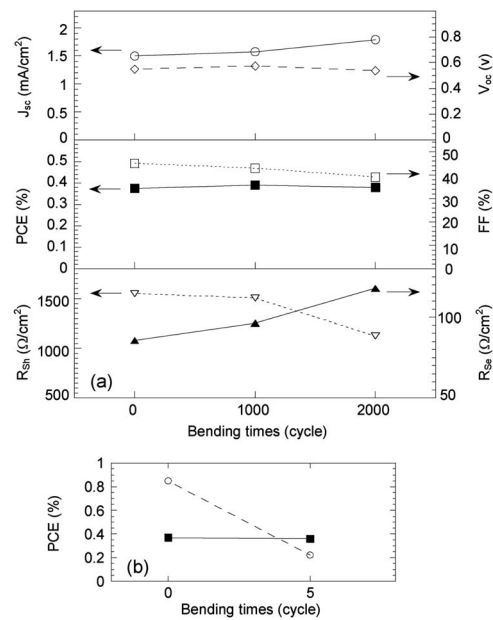

FIG. 3. (a) The photovoltaic performances (J_{sc}, V_{oc}, FF, PCE, R_{sh}, and R_{se} resistances) of DSSCs fabricated as a function of bending times on ZnO-nanowire substrates (bending was conducted before the fabrication of DSSC). (b) Comparison of the PCEs before (0 cycle) and after (5 cycles) bending of DSSCs fabricated using a ZnO-nanowire film (rectangle) and a ZnO-nanoparticle film (circle) (bending was conducted after the fabrication of DSSC).

methanol with $0.05M$ acetic acid (HAc). After drying at 80–90 °C for 1 h, the substrate was immersed in an 80 ml zinc acetic (20 mM) aqueous solution with a small amount of ammonia (28%, Wako Chemicals, 2–5 ml) in a bottle with autoclavable screw cap. Then, the solution was kept at 85 °C for 12 h, with solution refreshed every 2 h.

Figure 2(a) shows the scanning electron microscopy (SEM) image of ZnO nanowires on PET/ITO substrate. The ZnO nanowires are uniform with average diameter and length of about 190 nm and 7 μm, respectively. To test the mechanical bendability of the flexible nanowire substrates, the film was manually bended to an extreme bending radius of 2 mm for several cycles and was further bended 2000 cycles with bending radius of 5 mm using a bending machine. After bending, there are no visible cracks or signs of peeling off in the film [Fig. 2(b)], demonstrating a highly bendable ZnO-nanowire film with excellent mechanical stability.

As a comparison, we also prepared nanoporous ZnO films on PET/ITO substrates by squeegee printing the paste of ZnO nanoparticles with a low-temperature process.[17] The paste was prepared by mixing 5.0 g ZnO powder (20 nm, Wako) and 8 ml HAc ($0.1M$) aqueous solution by mortar grinding. After several cycles of bending test with a bending radius of 10 mm, visible cracks and peeling off could be clearly seen in the porous ZnO film (not shown here).

After confirming the good bendability of ZnO nanowires on PET/ITO, DSSCs were fabricated using the as-prepared and the bended ZnO-nanowire substrates. To fabricate DSSCs, the ZnO-nanowire electrodes were firstly treated by oxygen plasma for 2 min. Then, the substrates were immersed in a ethanolic solution containing 0.2 mM *cis*-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)-ruthenium(II) bis-tetrabutylammonium (N719, Solaronix) for 1 h for dye loading. The flexible DSSCs were fabricated by assembling a dyed ZnO-nanowire electrode and a Pt coun-terelectrode fabricated by e-beam evaporation of a 400 Å Pt on a PET/ITO substrate. The two electrodes were bonded together by ~60 μm thick double-sided tape (Scotch 3*M*) which also served as spacer and sealer. Before bonding, the gel electrolyte composed of $0.1M$ I$_2$, $0.1M$ LiI, $0.5M$ ter-butylpyridine, $0.6M$ 1-hexyl-3-methylimidazolium iodide (HMII), and 5 wt % SiO$_2$ powder (12 nm, Degussa) in methoxy-acetonnitrile was dropped and dispersed on the dyed ZnO-nanowire area. The active cell area was typically ~0.3 cm^2. Photovoltaic test for all DSSCs was conducted under a simulated AM1.5G illumination with a light intensity of 100 mW/cm^2.

Figure 3(a) shows the short circuit current (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF), PCE, shunt (R_{sh}), and

series (R_{se}) resistances of DSSCs fabricated as a function of substrate bending times (bending was conducted before the fabrication of DSSC). The shunt and series resistances are defined as $R_{sh} = dV/dI_{(V=0)}$ and $R_{se} = dV/dI_{(I=0)}$. It can be seen from Fig. 3(a) that there is no distinct decrease in J_{sc} and V_{oc} after 2000 cycles of bending. However, slightly degradation in FF (decrease), R_{sh} (decrease), and R_{se} (increase) with the increase of bending times is observed in these DSSCs. Thus, the repeated bending will influence the electric properties of the nanowire electrode. However, the influence is small and there is only slight decrease in the total energy conversion efficiency (PCE) [Fig. 3(a)]. The bending of the flexible DSSCs based on both the ZnO-nanowire photoanode (as pre-pared by hydrothermal) and a nanoparticle photoanode (by squeegee printing of ZnO paste) were also tested and com-pared. Figure 3(b) compares the PCEs before (0 cycle) and after (5 cycles) bending (with a bending radius of 5 mm) of DSSCs fabricated using a ZnO-nanowire film (rectangle) and a ZnO-nanoparticle film (circle). It can be seen from Fig. 3(b) that the PCE of nanowire-based DSSC (rectangle) shows no obvious decrease after bending of the device. How-ever, the PCE of nanoparticle-based DSSC (circle), despite its higher initial value, significantly decreases after device bending.

Though the bendability is better than that of the nanowire-based DSSC, the photovoltaic performance of this device is much lower compared to the nanoparticle-based DSSC [Fig. 3(b)], which is due to the lower surface area and lower dye loading.[19–22] To overcome the low efficiency caused by low surface density of nanowire electrodes, a com-bination of nanowire and nanoparticle morphology was fur-ther adopted in our experiment. After the nanowire growth, the ZnO nanoparticles were filled in the gaps (between nano-wires) attaching the surface of the nanowires by spin coating a ZnO-nanoparticle solution containing 1.6 g ZnO powder
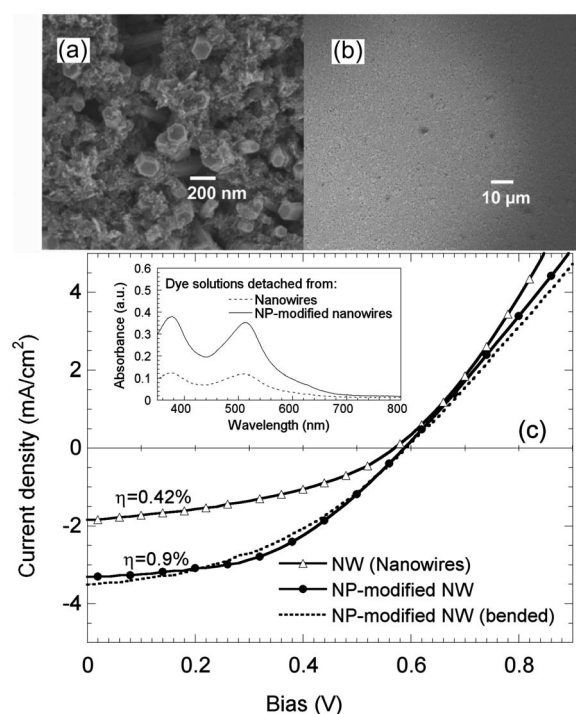
FIG. 4. SEM of ZnO nanoparticle (NP) modified ZnO nanowires (with ZnO nanoparticles filled in the gaps and attaching the surface of the nanowires) before (a) and after (b) bending 1000 cycles (with bending radius of 5 mm). (c) Current-voltage (*I-V*) characteristics of DSSCs constructed using ZnO nanowires (triangle) and NP-modified ZnO nanowires (circle), and the *I-V* curve (dashed) of the NP-modified ZnO-nanowire DSSC after bending to 5 mm radius for 5 cycles (under illumination: 100 mW/cm², AM1.5G). Inset: absorptions of dye solutions containing dyes from ZnO-nanowire film (solid) and NP-modified ZnO-nanowire film (dashed), respectively. The dye solutions were prepared by detaching dye molecule from 1 cm² ZnO film (nanowires or NP-modified nanowires) into 8 ml KOH (0.1 mM) aqueous solution.

(20 nm, Wako) and 2% Ti isoproxide in 8 ml methanol solution with 0.02M HAc. Here, Ti isoproxide and HAc were used to facilitate and fasten the attachments of ZnO nanoparticles on nanowire surface, and also the connections between particles. The SEM image of the ZnO-nanoparticle (NP) modified nanowire film is shown in Fig. 4(a). It can be seen from Fig. 4(a) that the ZnO nanoparticles are uniformly filled in the gaps and tightly attached to the nanowires. Figure 4(b) shows the surface SEM image of the NP-modified nanowire film after 1000 cycles of bending test with bending radius of 5 mm. No visible crack is seen [Fig. 4(b)], demonstrating the good mechanical stability of this NP-modified nanowire film. As expected, the NP-modified nanowire film should have larger surface area for more dye loading. The inset of Fig. 4(c) shows the absorption spectra of two solutions containing dyes from a nanowire film and a NP-modified nanowire film, respectively. The dye solutions were prepared by detaching dye molecule from 1 cm² nanowire film or NP-modified nanowire film into 8 ml KOH (0.1 mM) aqueous solution. It can be seen from the inset of Fig. 4(c) that the peak absorption (at 510 nm) of the dye solution from the NP-modified nanowire film is more than twice higher than that from the nanowire film, proving a much increased surface area and dye loading for NP-modified nanowire film. Figure 4(c) shows the *I-V* characteristics of DSSCs constructed using ZnO nanowires (triangle) and NP-modified ZnO nanowires (circle), under AM1.5G illumination. It can be seen from Fig. 4(c) that both the photocurrent and the fill factor show much

improvement in the NP-modified nanowire DSSC. The PCE (0.9%) of NP-modified nanowire DSSC increased by ~110% as compared to that of the nanowire-based DSSC (0.42%). The improvement is due to the increased surface area and dye loading in NP-modified nanowire film. More importantly, the bending stability of the NP-modified DSSC is maintained. The *I-V* curve of the same NP-modified DSSC after bending to 5 mm radius for 5 cycles is also presented in Fig. 4(c) (dashed), which is no much difference from the unbent one (circle).

In conclusion, a highly bendable ZnO-nanowire film on PET/ITO substrate was fabricated by low-temperature hydrothermal growth at 85 °C. The film shows good mechanical stability at an extremely small bending radius of 2 mm. The good mechanical bendability is due to the cracking-resistant nanowire morphology. Flexible DSSC based on this kind of ZnO-nanowire photoelectrode showed better stability compared to nanoparticle-based DSSC after bending. With ZnO nanoparticles modified ZnO nanowires, the power conversion efficiency of the flexible DSSC increased by ~110% due to the increased surface area and dye loading, meanwhile, retaining the good bendability. The results demonstrate that modified ZnO nanowires fabricated by the low-temperature hydrothermal method is promising for efficient and flexible plastic solar cells.

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