CdSe/ZnS (Core/Shell) Quantum Dots Multi-walled Carbon Nanotubes (MWCNTs) on a Stainless Steel as a Photoanode in Solar Cells

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Abstract: Multi-walled carbon nanotube (MWCNT) forests grown on a stainless steel substrate were used as a photoanode in CdSe/ZnS (core/shell) quantum dot (QD) sensitized solar cells (QDSSCs). QD-treated MWCNTs on the conductive metal stainless substrate showed a higher power conversion efficiency (PCE) of 0.014% than those grown on a doped silicon substrate with a PCE of 0.005% under AM 1.5 sunlight intensity (100 mW/cm²). This higher efficiency can be attributed to the lower sheet resistance of 0.0045 Ω/sq for the metal substrate than the value of 259 Ω/sq for doped silicon. Additionally, the relationship between the reflectance of as-grown CNT and PCE is also examined. QDSSC fabricated from CNT of lower reflectance of 1.9 % at a height of 25 μm showed a better efficiency because the lower reflectance indicates the scattering of light repeatedly into deeper CNT forest resulting in higher absorption which indicates a higher surface area of CNTs to adsorb much amount of QDs on CNT forests, resulting in the higher PCE.

1 INTRODUCTION

The extraordinary mechanical, chemical, and electronic properties of carbon nanotubes (CNTs) make them outstanding materials for energy applications (Iijima 1991; Dong et al. 2011; Zhu et al. 2008). A major challenge in solar cell applications is the development of modified CNT structures for use as transparent electrodes (Cui et al. 2013). The modified CNT structure is expected to be a good material for use as a counter electrode or photo-anode (Cui et al. 2013) with semiconducting quantum dots (QDs) in order to harvest a broader range of light from the ultraviolet (UV) to the infrared (IR) (Hickey et al. 2000). We have reported a significant increase in optical total reflectance using a structural modification of CNT honeycombs (Udorn et al. 2016), which will increase the utility of CNT honeycomb structures in high-efficiency solar cells. QD-decorated CNTs exhibit efficient charge transfer from photo-excited QDs to the CNTs (Harenza et al. 2002). QD sensitized solar cells (QDSSCs) have attracted considerable interest from researchers because their power conversion efficiency (PCE) may exceed the Shockley and Queisser limits (Watanabe et al. 2011; Miller et al. 2012). In particular, QDs can harvest a broad range of optical wavelengths by multiple exciton generation (MEG), thus improving the photovoltaic efficiency (Péchy et al. 2001; Barve et al. 2012; Mar et al. 2011). Optical absorption by QDs fabricated from materials such as CdS (Yu et al. 2012), CdSe (Tian et al. 2013), and CdSe/ZnS (Baek et al. 2014) is intrinsically tunable from the UV to the near-IR due to the particle-size dependence of the bandgap. A major advantage of QDs as light sensitizers compared with conventional dyes is that electron recombination is suppressed, thereby improving the efficiency of QDSSCs (Hoke et al. 2012; Li et al.
One dimensional (1D) wires, of e.g., TiO2 (Zarazúa et al. 2011; Guijarro et al. 2009), ZnO (Li et al. 2013; Zhang et al. 2009), and Si (Takahashi 2011; Jeyakumar et al. 2013) have been extensively used for electron transfer from QDs to electrodes. In particular, CNTs have arisen as a superior candidate 1D wire electrode material for QDSSC (Dong et al. 2011; Malara et al. 2011; Peng et al. 2011) because of their large surface area, high conductivity, high aspect ratio, and chemical stability. Due to their excellent electrical and thermal conductivity, flexible metal substrates can reduce both the sheet resistance and production cost of solar cells (Kang et al. 2006; Miettunen et al. 2008; Ma et al. 2004). To the best of our knowledge, there are no reports of QDSSCs in which QD-treated CNT forest photoanodes are fabricated on a metal substrate.

In this study, CNT forests grown on stainless steel serving as a photoanode for CdSe/ZnS core/shell QDSSCs are investigated as a means of improving photovoltaic efficiency. The efficiency was compared for samples of QDSSCs on a metal stainless steel substrate, QDSSCs on a doped silicon substrate, and QDSSCs with a photoanode of randomly oriented CNT (buckypaper) films on a metal stainless steel substrate. The relationship between the optical total reflectance of as-grown CNTs and the PCE was investigated.

3 RESULTS AND DISCUSSIONS

Figures 1(a), (b), (c) display a top-view of FE-SEM micrographs of as-grown on a silicon substrate, the stainless steel substrate, and CNT buckypaper films on the stainless steel substrate, respectively. Inserted images of Fig.1(a), (b) and (c) show a cross-sectional image of as-grown on silicon substrates, on the stainless steel, and CNT buckypaper films, respectively. As can be seen in Figs. (a) and (b), the as-grown CNTs on the stainless steel shows an inconsistent height where as-grown CNTs on the silicon substrate shows a higher density and a consistent height. Meanwhile, CNT buckypaper films which were simply prepared by dipping vertically-aligned CNTs into a methanol solution for 5 min show a highly-packed randomly oriented CNTs as shown in an inset of Fig. 1(c). After QDs treatment, the self-assembly patterns can be formed, an inset of Fig. (b') shows a highly-magnified image of highly-packed CNTs where honeycomb-like patterns are formed on a silicon substrate as shown in Fig. 1(a').

The performance of the different substrates, patterns, and different heights is analysed by a sheet resistance, a series resistance, optical total reflectance, and power conversion efficiencies (PCE) as shown in Table 1. As-grown CNTs with a height of 25 µm on a stainless steel substrate with a sheet resistance of 0.0045 Ω/sq and an optical total reflectance of 1.9% at 560 m exhibit the highest PCE of 0.014%. Meanwhile, as-grown CNTs on a
Figure 1: Top-view FE-SEM images of (a) as-grown CNTs on silicon substrate, (b) as-grown CNTs on stainless steel substrate, (c) CNT buckypaper films on stainless steel substrate. The insets show cross-sectional images. CdSe/ZnS QDs-treated on (a') as-grown CNTs on silicon substrate, (b') as-grown CNTs on stainless steel substrate, (c') CNT buckypaper films on stainless steel substrate. The insets show high-magnification images.

Table 1: Properties of QD-treated CNTs on a silicon substrate, and CNT buckypaper films on the stainless steel substrate, and QDs-treated CNTs on the stainless steel with various heights.

<table>
<thead>
<tr>
<th></th>
<th>Sheet resistance (Ω/sq)</th>
<th>Series resistance (Ω/sq)</th>
<th>Total reflectance at 560 nm (without QDs)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>$\eta$ (PCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>QD-treated CNTs on silicon substrate</td>
<td>259</td>
<td>33K</td>
<td>0.98%</td>
<td>0.067</td>
<td>0.21</td>
<td>38.6%</td>
<td>0.005%</td>
</tr>
<tr>
<td>QD-treated CNT buckypaper films on stainless steel</td>
<td>0.0046</td>
<td>14 K</td>
<td>4.3%</td>
<td>0.068</td>
<td>0.32</td>
<td>42.9%</td>
<td>0.009%</td>
</tr>
<tr>
<td>QD-treated 17-µm CNTs on stainless steel</td>
<td>0.0047</td>
<td>13K</td>
<td>4.1%</td>
<td>0.050</td>
<td>0.38</td>
<td>56.7%</td>
<td>0.011%</td>
</tr>
<tr>
<td>QD-treated 25-µm CNTs on stainless steel</td>
<td>0.0045</td>
<td>13K</td>
<td>1.9%</td>
<td>0.057</td>
<td>0.45</td>
<td>52.2%</td>
<td>0.014%</td>
</tr>
<tr>
<td>QD-treated 33-µm CNTs on stainless steel</td>
<td>0.0043</td>
<td>14K</td>
<td>2.2%</td>
<td>0.049</td>
<td>0.40</td>
<td>65.6%</td>
<td>0.013%</td>
</tr>
<tr>
<td>QD-treated 41-µm CNTs on stainless steel</td>
<td>0.0043</td>
<td>13K</td>
<td>2.2%</td>
<td>0.056</td>
<td>0.39</td>
<td>54.4%</td>
<td>0.012%</td>
</tr>
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</table>

silicon substrate with a higher sheet resistance of 259 Ω/sq exhibit a PCE of 0.005%. The 2.8 times higher PCE for the former sample can be attributed to the higher conductance of the substrate. The PCE for QD-treated CNTs on the stainless steel substrate is 1.6 times higher than that for CNT buckypaper films on the same metal stainless steel substrate, which can be attributed to the higher number of QDs adsorbed on the surface of the CNTs. QD-treated CNTs on the stainless steel substrate had heights of 17, 25, 33 and 41 µm, and the PCE was the highest, at 0.014%, for a height of 25 µm. For the taller CNTs, the lower PCE could be explained by the fact that the electron transport path was longer than the electron diffusion length, leading to increased recombination of electrons and holes (Wei et al. 2014), and hence a lower efficiency.

Figure 2(a) shows the total reflectance of as-grown CNTs on a silicon substrate, a CNT buckypaper film on a stainless steel substrate, and as-grown CNTs of various heights on a stainless steel substrate. For as-grown CNTs on the stainless...
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Figure 2: (a) Optical total reflectance of as-grown CNTs on a silicon substrate (red), CNT buckypaper films on the stainless steel substrate in various heights, (b) PCE vs. total reflectance.

Before QD treatment, the strong reflection at wavelengths shorter than 380 nm can be assigned to Rayleigh scattering, which provides a higher reflectance at shorter wavelength (Yu & Louis Brus 2001). The bandgap of CdSe \( E_g = 2.21 \text{ eV} \) is corresponded to 561 nm which is expected as an absorption edge of QDs. The CNT buckypaper films (black line) exhibit a higher total reflectance of more than 5% at 560 nm due to the highly packed CNTs serving as glassy carbon to strongly reflect light (Shabanet et al. 2014). As-grown CNTs on a silicon substrate (grey line) exhibit the lowest total reflectance of less than 2%, which can be attributed to the higher density of CNT forests. The CNT forest with a height of 25 µm has a lower total reflectance of 1.9% at a wavelength of 560 nm. This can be explained by multiple scattering of the incident light into the bottom of the CNT forest, so-called blackbody absorption (Mizuno et al. 2009). Figure 2(b) shows the relationship between the total reflectance and the PCE, which indicates that the lower total reflectance of the as-grown CNTs on the stainless steel gives a higher solar cell efficiency after QDSSC fabrication. Significantly, the PCE for QDSSCs with CNTs with heights of 25 µm on a stainless steel substrate, with the total reflectance of 1.9% (green symbols), has a maximum value of 0.014%. Also, as can be seen in Fig. 2(b), the lower total reflectance of 25 and 33 µm exhibits the better PCE. The lower total reflectance due to efficient absorption of light in CNTs leads to higher solar cell efficiency. The low total reflectance of CNT forests, by the mechanism of the repeated reflection of incident light into the CNT bottom region, indicates a higher CNT surface area, which is expected to adsorb a larger number of QDs, resulting in a higher PCE.

Figure 3 presents J–V curves for QDSSC cells of QD-treated CNTs on various heights on stainless steel substrates.

The low resistivity of the conductive substrate gives an increased open-circuit voltage, leading to improved solar cell efficiency. The QD-treated CNTs with heights of 25 µm exhibit a higher VOC of 0.45 volts and also slightly improves the VOC.
from 0.32 to 0.45 volts as compared with CNT buckypaper films. In addition, the energy barrier at the QDSSC/CNT interface can suppress interfacial recombination, leading to an increased VOC, which is expected for CNT forests directly grown on metal substrates. The increase in the PCE is an indication of improved charge collection and transport due to introducing the CNTs forest directly grown on the metal substrate at a significant specific height as an electrode scaffold in the photoanode.

4 CONCLUSIONS

This study reported the first QDSSCs with photoanodes of MWCNTs on a metal substrate, and found that the PCE for such QDSSCs on stainless steel substrates was three times higher than those on a low-resistive (0.15 Ω·cm), doped silicon substrate. A QD-treated MWCNT forest on a metal substrate was found to have a resistance of 0.0045 Ω/sq and exhibited a higher PCE of 0.014%, whereas QD-treated MWCNTs on a doped silicon substrate had a resistance of 259 Ω/sq and a lower efficiency of 0.005%. This difference could be attributed to the fact that the very low sheet resistivity of a metal substrate gives a higher electrical conductance leading to a higher cell efficiency. The relationship between the total reflectance of CNT forests and the PCE was investigated. It was shown that the lower total reflectance QD-treated CNT forest of 25-μm height achieved a higher PCE of 0.014%, likely due to the higher light absorption in the QDs. Although the efficiency is currently low compared with that of high-performance DSSCs or QDSSCs, the successful incorporation of QDs with a CNT forest on a conductive substrate as a photoanode for solar cells has been demonstrated for the first time.

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