Structured SWNTs and Graphene for Solar Cells

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Abstract

We propose the concept of structured single-walled carbon nanotubes (SWNTs) for the applications of heterojunction solar cells and dye-sensitized solar cells (DSSCs). The structure of SWNTs was controlled and modified by a simple water vapor treatment, which was originally developed by our group. Compared with the graphene-Si solar cell and the SWNT-Si solar cell using the random-oriented SWNT film, the pristine micro-honeycomb structured SWNT-Si solar cell shows a significant improvement in terms of fill factor and the greater potential to obtain high power conversion efficiency (PCE). Moreover, the performance of the pristine micro-honeycomb structured SWNT-Si solar cells is stable in ambient condition. In addition, the PCE and fill factor of the DSSC with the micro-honeycomb structured SWNT counter electrode are 3.90% and 0.61, respectively, which are comparable to those of the DSSC with Pt as the counter electrode. This result shows that the micro-honeycomb networked SWNTs provide a low-cost alternative to replace Pt in DSSCs.

Keywords: Single-walled carbon nanotubes, Micro-honeycomb, SWNT-Si solar cell, Dye-sensitized solar cell, Graphene

1. Introduction

Single-walled carbon nanotubes (SWNTs) and graphene are emerging nanocarbon materials for solar cell applications. Indeed, SWNTs possess outstanding electronic, optical, mechanical and thermal properties and can be further exploited for photovoltaic and photo-electrochemical cells, serving as photovoltage generation sites, photoelectrochemical reaction scaffolds and electrodes, *etc*. The SWNT-Si solar cells[1-5] with high power-conversion efficiency (PCE) have emergent technological impact, owing to their high efficiency and structural simplicity. Dye-sensitized solar cells (DSSCs)[6] have the advantages of relatively high PCE values and low production cost. Single-walled carbon nanotubes and graphene are considered as good candidates to replace Pt as the counter electrodes of DSSCs which demand high conductivity and catalytic activity.

However, the superior nanoscale properties of individual SWNTs are far from fully exploited. Many efforts have been made for bridging the gap between their superior nanoscale properties and the less impressive micro/macroscale performance.[7] Carefully designed morphology of SWNTs would help to efficiently organize the charge generation, separation and transport at the interfaces of SWNT-Si solar cells and DSSCs. Self-assembly

is a simple and low-cost way for building nanomaterials and has been used for nanowires, nanopillars and multiwalled carbon nanotubes.[8-10] However, the self-assembly of SWNTs is very difficult because of their very small diameters and superhydrophobicity.

In this research, a novel water vapor treatment process has been proposed to build vertically aligned SWNTs (VA-SWNTs) into a self-assembled hierarchical micro-honeycomb network (μ-HN) for the applications of SWNT-Si solar cells and DSSCs. Graphene was also synthesized for the use of graphene-Si solar cells. Compared with the SWNT-Si solar cell with the random-oriented SWNT film and the graphene-Si solar cell, the SWNT-Si solar cell with the μ-HN SWNT film has a higher fill factor (FF) and greater potential to obtain high power conversion efficiency (PCE). The μ-HN SWNT film was also applied to the DSSC as the counter electrode. The impedance spectra of the DSSCs with the μ-HN SWNT film counter electrode and Pt counter electrode were compared to discuss the feasibility of the μ-HN SWNT film counter electrode for DSSCs.

2. Experimental Details

Both the SWNTs and graphene were synthesized from ethanol by chemical vapor deposition (CVD). Vertically-aligned SWNTs were grown on Co/Mo dip-coated Si/SiO_2 substrates using our conventional alcohol catalytic CVD (ACCVD) process.[11] The bimetallic catalysts were reduced in

the Ar/H_2 environment at 800 ºC for 10 min. Ethanol was flowed at 450 sccm at 1.3 kPa, resulting in the growth of SWNTs. The length of the VA-SWNT films was controlled as 5 μm. Graphene was grown on a copper substrate by the low pressure CVD method. [12] The copper foil was heated in the Ar/H_2 environment at 1000 ºC for 20 min to remove the copper oxide and smooth the surface. The ethanol was flowed at 10 sccm diluted by 300 sccm Ar/H_2 at 300 Pa. The grain size of the graphene is about 10 μm.

After the ACCVD synthesis, the VA-SWNTs were exposed to vapor from a hot water reservoir, and subsequently dried in the ambient environment. The uniform VA-SWNT array (Figure 1a) was aggregated into hexagonal frames (intermediate stage shown in Figure 1b) after the first water vapor treatment. By repeating this treatment 20 to 30 times, the VA-SWNT array gradually evolved into a μ-HN (Figure 1c). The liquid-solid interaction induced by the condensation and subsequent evaporation of water is the building tool used to engineer the morphology of VA-SWNTs into a self-assembled μ-HN. [2] The μ-HN is a hierarchical hexagonal-shaped three-dimensional network that consists of vertical cross-linked SWNT walls and a randomly networked SWNT bottom. Elongating the vapor exposure time resulted in a collapsed HN structure which is very close to the random network. One the other hand, decreasing the water reservoir temperature would make honeycomb structure porous. [2] Figure 1d shows the cross-sectional view of the micro-honeycomb structure with a hierarchical three-dimensional network of SWNTs formed by the water vapor treatment.

Additionally, the morphology of the as-synthesized single-layer graphene is shown in Figure 2.

The schematics of the fabricated SWNT-Si solar cell and graphene-Si solar cell are shown in Figure 3a and Figure 3b, respectively. The SWNT-Si solar cells and the graphene-Si solar cells were fabricated by respectively transferring SWNTs and graphene onto the 3 mm × 3 mm bare Si contact window. Each bare Si contact window was surrounded by a 200-nm-thick SiO_2 as the insulating layer and a 100-nm-thick Pt electrode. The 10-nm-thick Ti and 50-nm-thick Pt layers were subsequently sputtered onto the back of the Si substrate as the rear contact.

The schematic of the DSSC with the μ-HN SWNT film as counter electrode is shown in Figure 3c.The DSSC is composed of photoelectrode, electrolyte and counter electrode. The photoelectrode was fabricated using fluorine tin oxide (FTO) glass and a layer of nanocrystalline TiO_2 particles with thickness of 10 μm. The photoelectrode was heated to 450 ˚C for 30 min and annealed in air. It was then immersed into 0.3 mM N719 solution in ethanol for 24 h. The N719-incorporated electrode was carefully rinsed by ethanol. Both the μ-HN SWNTs and Pt were used as counter electrodes for making comparison. Each DSSC was fabricated by placing the photoelectrode on the counter electrode with a 50-μm-thick scotch tape as the spacer. The redox electrolyte was introduced into the cell through a slit by the capillary force.

3. Results and Discussion

The current density–voltage (*J*-*V*) characteristics of the SWNT-Si solar cells fabricated using μ-HN SWNTs were obtained under 100 mW/cm^2 AM 1.5G illumination (Newport Co.), as shown in Figure 4a. The pristine μ-HN SWNT-Si solar cell has the highest fill factor (FF) of 72%, with an ideality factor of 1.71 in the range of 300 mV to 500 mV bias. This ideality factor is the lowest reported so far. The PCE value of 5.91% was obtained immediately after the fabrication, and it gradually increased to 6.04% after three weeks in ambient condition.[2] The PCE of μ-HN SWNT-Si heterojunction solar cell boosted to 10.02% after 2.4 M nitric acid doping, as shown in Figure 4a. The *J*-*V* characteristic of the SWNT-Si solar cell using 90%-transparency random-oriented SWNT film was also measured as a control group. [13] This SWNT film made by aerosol technique has state-or-art high transparency and conductivity because of the optimized bundle size and long bundle length. The SWNT-Si solar cell using a pristine random-oriented SWNT film exhibited the highest short-circuit photocurrent(J_{sc})owing to the high transparency of the SWNT film.[13] In addition, the fabricated graphene-Si Schottky solar cell had the PCE of 1.50% and the FF of 21%. Its J_{sc} and open-circuit photovoltage (V_{oc}) were 15.5 mA/cm^2 and 460 mV, respectively, as shown in Figure 4b.

The FF represents the quality of a solar cell, and is one of the three parameters characterizing solar cell performance along with V_{oc} and J_{sc}. The

significant improvement in terms of FF over the SWNT-Si solar cell with the random-oriented SWNT film and the graphene-Si solar cell as well as the previously reported values[3-5] is attributed to the hierarchical μ-HN which simultaneously enhances the carrier separation, collection and transport. The mechanism schematic of the micro-grid configuration is shown in Figure 5. These dense and cross-linked SWNT walls in the μ-HN act as efficient conduction pathways, serving as micro-grid electrodes to collect the charge carriers generated from the adjacent micro-honeycomb cells. The micro-grid configuration in the μ-HN significantly shortens the minimum carrier diffusion path, resulting in a more efficient photocurrent collection.

Besides of the SWNT-Si and graphene-Si solar cells discussed above, DSSCs are another low-cost and high-efficiency solar cells which have been drawing research interest recently. The conventional counter electrode of DSSC is Pt which is not cost-effective and earth-abundant. In this study, we further applied the easily fabricated μ-HN SWNT film to the DSSCs. The *J-V* characteristics measured under AM1.5G illumination of the DSSCs using μ-HN SWNT film and Pt as counter electrodes are compared in Figure 6a. The PCE and FF of the DSSC with μ-HN SWNT film electrode are 3.90% and 0.61, respectively, which are comparable to those with Pt counter electrode. Additionally, the impedance spectra of the DSSCs using μ-HN SWNT film and Pt as counter electrodes were compared in Figure 6b for evaluating the corresponding counter electrode and whole solar cell. The internal resistance of the μ-HN SWNT film counter electrode is comparable

to that of the Pt counter electrode, demonstrating the applicability of the μ-HN SWNT film to the counter electrode of DSSCs. Although Figure 6b shows that the Pt counter electrode plays a relative better role on the entire solar cell performance than the μ-HN SWNT film counter electrode, it is worth mentioning that there is still room for the improvement of the morphology of the μ-HN SWNT film. We believe that the honeycomb structured SWNT film is very promising for replacing Pt as a counter electrode for DSSCs.

4. Conclusion

We have demonstrated the great potential of structured single-walled carbon nanotubes for the applications of heterojunction solar cells and DSSCs. The FF of the SWNT-Si solar cell was increased notably by honeycomb structuring. Moreover, the μ-HN SWNT film could also be used to replace Pt as the counter electrode of DSSCs. We believe that the μ-HN SWNT film obtained by the simple water vapor treatment is very promising for the practical applications of solar cells in future.

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Figure captions

Figure 1. SEM images of (a) as-grown vertically aligned single-walled carbon nanotubes; (b) intermediate stage of the micro-honeycomb formation after the first vapor exposure; (c) stable micro-honeycomb network formed after 20 to30 iterations of the water vapor treatment; (d) cross-sectional view of the micro-honeycomb network.

Figure 2. SEM image of as-grown graphene.

Figure 3. (a) Schematic of SWNT-Si solar cell. (b) Schematic of graphene-Si solar cell. (c) Schematic of dye-sensitized solar cell.

Figure 4. (a) *J-V* curves of SWNT-Si solar cells using μ-HN SWNT films before and after nitric acid doping measured under AM1.5G 100 mW/cm^2 irradiation, compared with that of SWNT-Si solar cell using high-transparency random-oriented SWNT film. (b) *J-V* curve of graphene-Si heterojunction solar cell measured under AM1.5G 100 mW/cm^2 irradiation.

Figure 5. Mechanism schematic of improved performance of SWNT-Si solar cell using μ-HN SWNT film.

Figure 6. (a) *J-V* curves of DSSCs using μ-HN SWNT film and Pt as counter electrodes measured under AM1.5G 100 mW/cm^2 irradiation. (b) Nyquist plot of impedance spectra of DSSCs

using μ-HN SWNT film and Pt as counter electrodes.

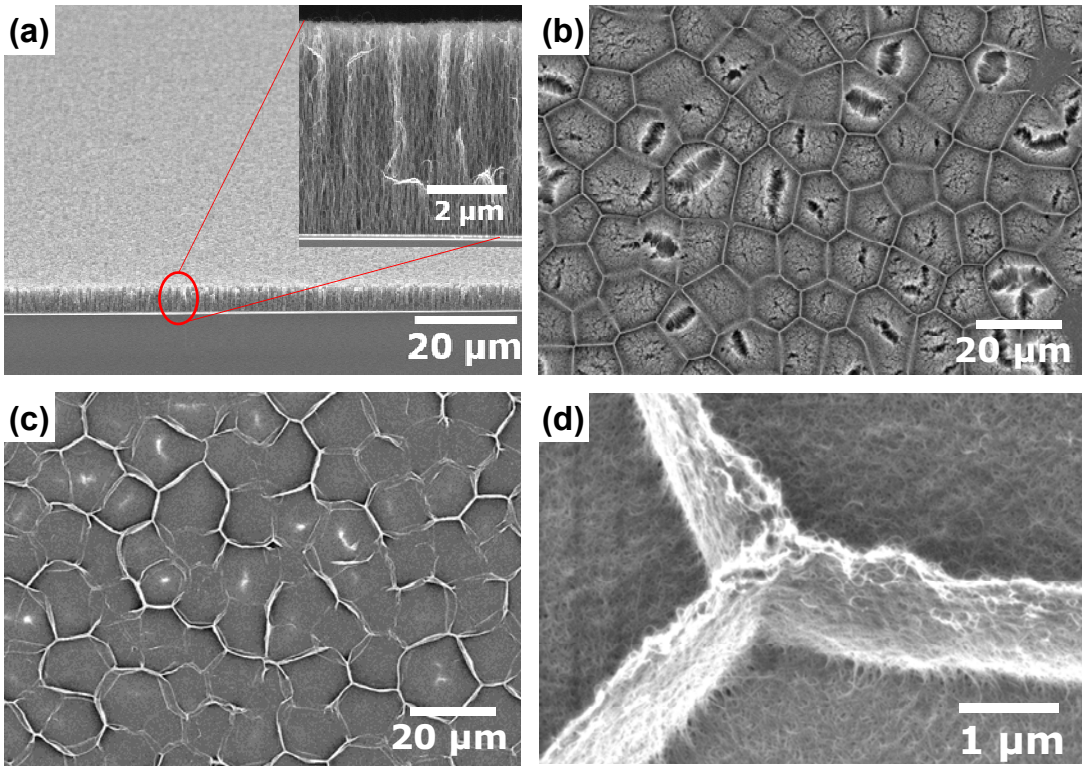
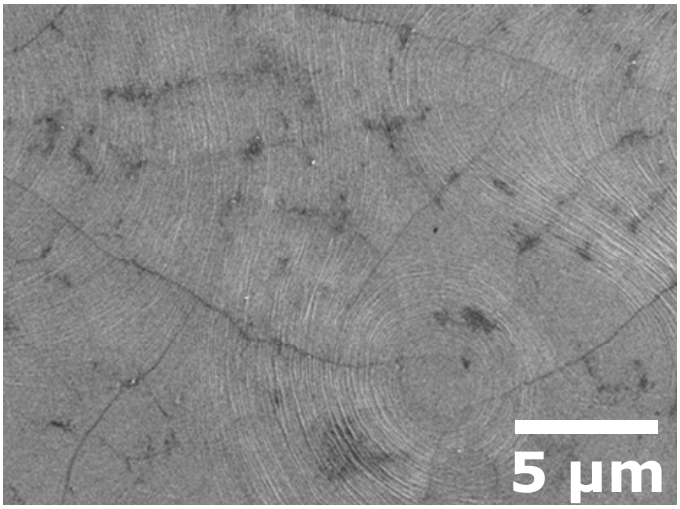


Figure 1. Cui et al.



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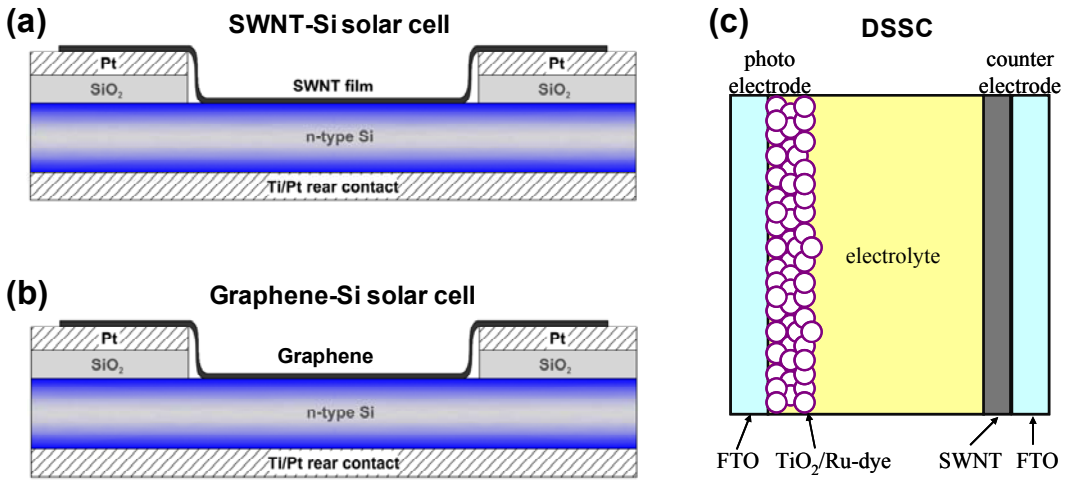

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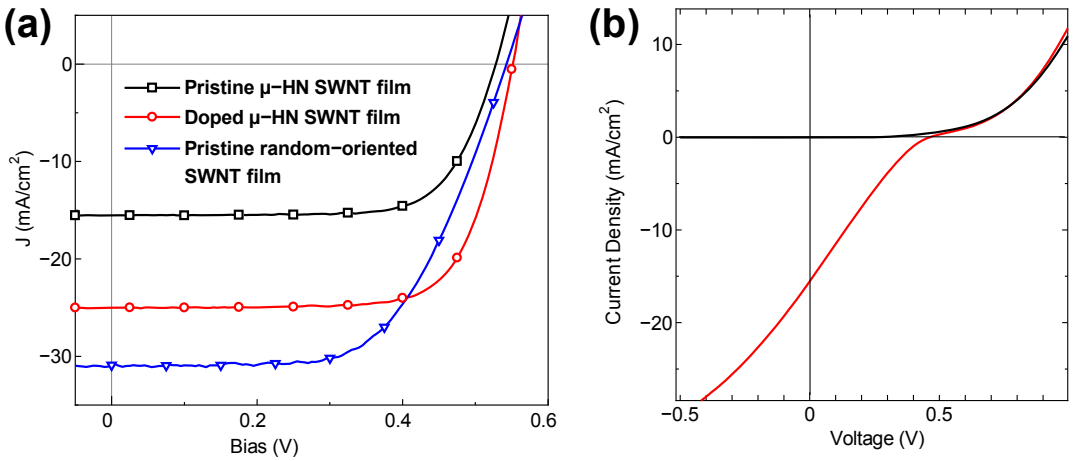

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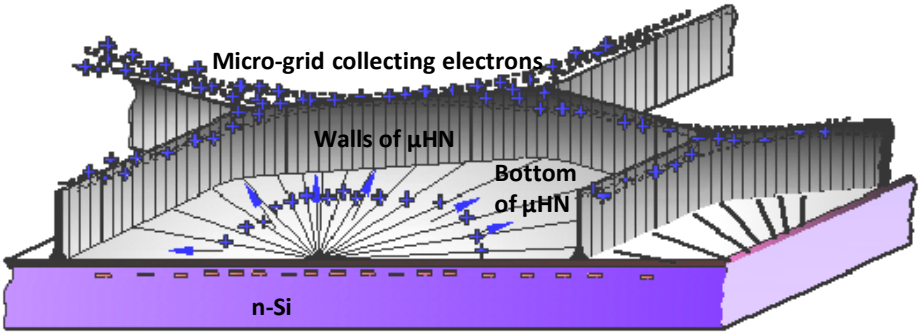


Figure 5. Cui et al.

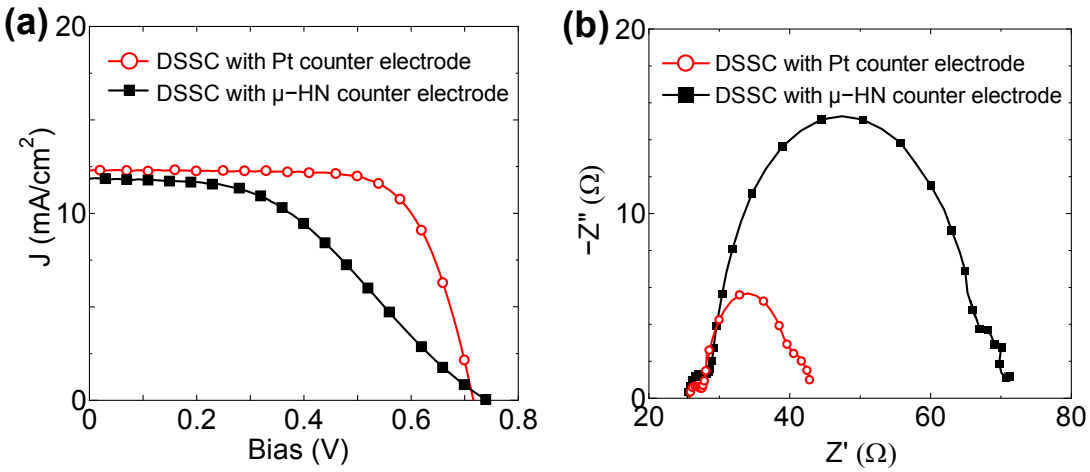
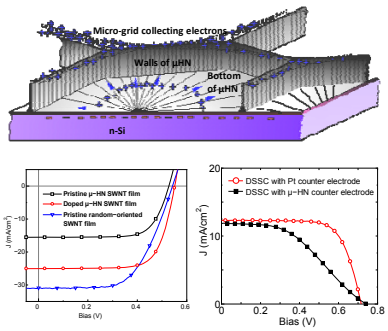


Figure 6. Cui et al.


Micro-grid collecting electrons
Walls of μHN
Bottom
of μHN
n-Si
Pristine μ-HN SWNT film
Doped μ-HN SWNT film
Pristine random-oriented
SWNT film
Bias (V)
DSSC with Pt counter electrode
DSSC with μ-HN counter electrode
J (mA/cm²)
Bias (V)

TOC graphic