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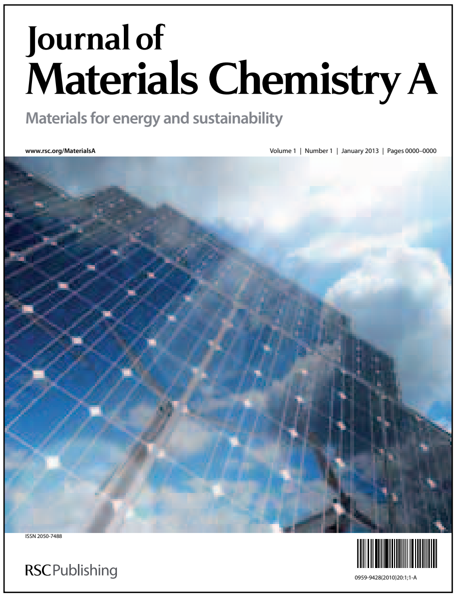

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COMMUNICATION

Polymethylmethacrylate Coating on Aligned Carbon Nanotube-Silicon Solar Cells for Performance Improvement

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Polymethylmethacrylate (PMMA) coating has been spin-coated onto aligned carbon nanotube-silicon (CNT-Si) solar cells with the efficiency increased from 7.1% to 11.5%, and further increased to 13.1% when doped with nitric acid (HNO_3) under air mass (AM 1.5) condition. The antireflection of PMMA coating and the decreased resistance at the CNT-Si interface during PMMA drying process together contributed to the performance improvement.

Over the past several decades, schottky junction solar cells have been extensively studied due to their simple fabrication procedure and high efficiency.[1-3] However, oxidation of metal electrode and costly high vacuum deposition method has become a major issue for schottky junction cell application. As alternatives to metal electrode, carbon nanotube (CNT) and graphene with tuneable transparency, high conductivity and good chemical stability have been developed recently.[4-6] Wei *et al*. first reported the CNT-Si solar cell with an efficiency of 1.3%.[7] Jia *et al*. further increased the cell efficiency to 7.4% by using double-walled CNT.[8] So far, major efforts have been devoted to modify CNT films with higher conductivity and better junction contacts for cell performance improvement. For example, Jia *et al.* obtained an efficiency of 13.8% using dilute nitric acid infiltration.[9] Jung *et al.* achieved the 11% efficiency through combination of single-walled carbon nanotube and $HAuCl_4$ doping.[10, 11] However, only minor efforts have been made on CNT-Si solar cells to understand the effect of light trap on device performance,[12] even as Si surface has a high reflectance of 36%.[13] Recently, nanostructures such as pyramid,[14] nanocone,[15] nanowire[16] and random texture[17] have been widely developed for Si based solar cells, presents prominent light trap effect and obvious performance improvement. Moreover, deposition of uniform thin films on Si solar cell surface such as TiO_2,[18] Si_3N_4[19] and Ta_2O_5[20] also can facilitate light trap through destructive interference. Very recently, Shi *et al.* reported a recorded efficiency of 15% for the CNT-Si solar cells via a TiO_2 antireflection film,[21] implying a large room for light trap on the CNT-Si solar cells. The above mentioned antireflection nanostructure and thin film deposition are effective for light trap. However, photolithography and high vacuum method hinder their applications in a simple and low-cost process.

Spin-coating has been widely used as a simple and low-cost method in different fields to form uniform thin films. Herein, we presented spin-coating of PMMA layer onto the aligned CNT-Si solar cells could improve the performance from 7.1% to 11.5% under 100mW • cm^2 illumination, and further increased to 13.1% when doped with HNO_3. The aligned CNT structure was formed by drawing a transparent CNT film from a double-walled spinnable CNT array.[22] Compare to pristine CNT-Si solar cells, the optimized PMMA coating showed about 40% increase in short-current density, exhibited obvious light trap effect. In addition, decreased resistance at the CNT-Si interface during PMMA drying process also accounted for the performance improvement.

Commercially available n-type, 4-inch diameter, 400 µm thick Si wafers with 300 nm-thick oxide and a bulk resistivity of 0.05-0.2 Ω·cm were used for the device fabrication, rectangle windows (1×0.13 cm^2) were made onto the Si substrates by etching off the exposed SiO_2 before devices fabrication (Fig. 1a). Then, a double-walled spinnable CNT array (about 1.5 cm in width) was drawn into a transparent CNT film (Fig. 1b). The CNT-Si solar cells were fabricated by directly transferring the CNT film onto the n-type Si substrate. The film transfer was readily achieved by placing Si substrate under the CNT film. After that, ethanol vapour was applied onto the CNT film to enhance the contacts between CNTs and Si substrates. At the front, micrometre-thick silver (Ag) paste was applied around the rectangle windows to enclose a nearly square window as the device area, and back contact was made by applying liquid-state gallium-indium eutectic (E-GaIn) onto the back side of Si substrates. Different PMMA solution was spin-coated onto the device surface at 6000-7000 rpm for 30 s, forming an antireflection layer with a thickness of 80-240 nm. Finally, the device was doped with HNO_3 vapour 15-20 s before test.

Optical image in Fig. 1c shows the CNT-Si solar cell without PMMA coating shows a bright colour, while presents a deep blue colour with PMMA coating. Atom force image (AFM) image reveals the average thickness of CNT film is 50 nm with a

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roughness of 13.1 nm (Fig. S1), and the film is so thin with the transparency nearly 90% in the visible wavelength range (Fig. S2). The colour variation with and without PMMA coating obviously shows the light trap effect induced by PMMA coating. Fig. 1d and Fig. 1e show the detailed characterization of the CNT-Si solar cells by optical microscope and scanning electron microscope (SEM) with and without PMMA coating, respectively. The detailed SEM (Fig. 1d) study reveals that the CNTs attached onto Si surface were loosely packed and aligned in different sized CNT bundles along the drawing direction, with different spacing distance within each other. Moreover, "*cross bundle*" can also be distinguished, indicating the loosely packed CNT film structure. When coated with PMMA layer, small CNT bundles are encapsulated while large ones can still be distinguished (Fig. 1e).

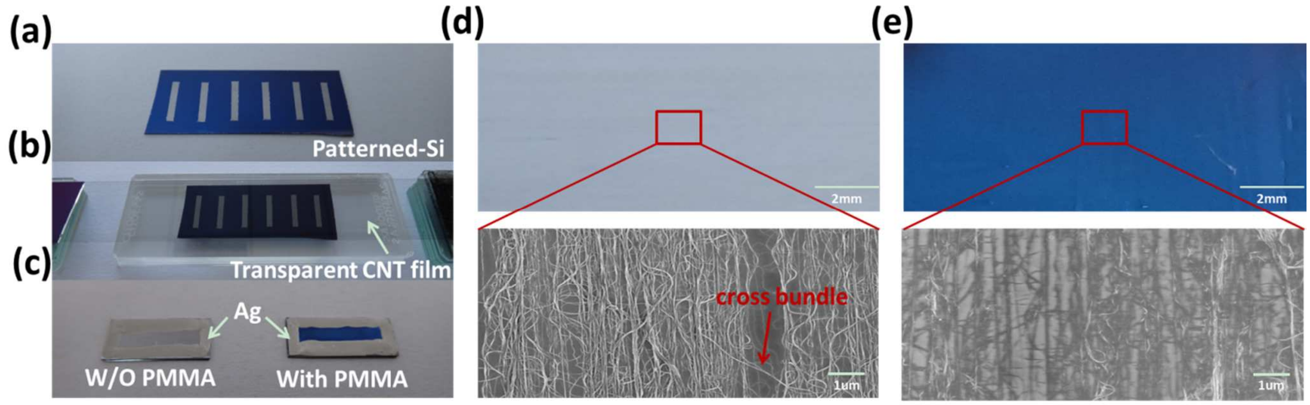

Fig.1 (a) A patterned Si substrate with pre-etched area in bright color; (b) Typical fabrication process for a batch of CNT-Si solar cell; (c)The different reflective effect of a CNT-Si cell with and without PMMA coating; (d) Optical and SEM characterization of an uncoated CNT-Si solar cell, showing an obvious light reflection effect and non-uniform CNT morphology on surface; (e) Optical and SEM images of a PMMA coated CNT-Si solar cell, revealing a light trapping effect and the resultant embedded CNT bundles.

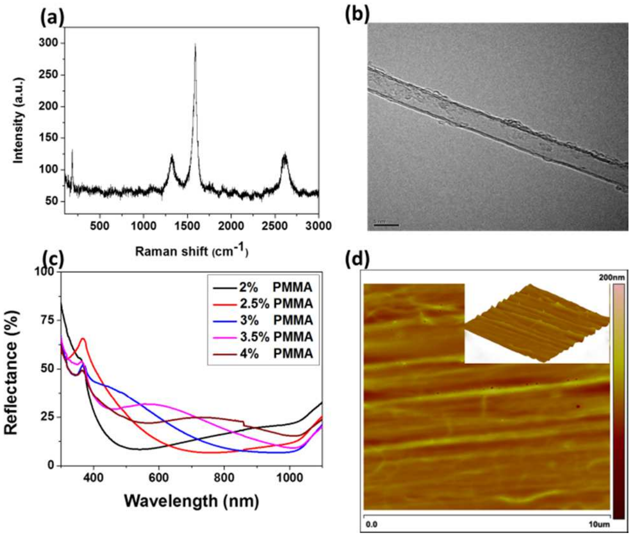

Fig. 2 (a) Raman spectrum of the pristine CNT array; (b) HRTEM image of a single CNT shows double-walled and diameter (4.7nm); (c) Reflectance of PMMA coating spin-coated onto Si surface from different PMMA concentration; (d) AFM image of PMMA-CNT coating with a roughness of 6.32 nm, inserted correspond to the3D surface images.

The quality of the pristine CNT array was surveyed by using raman spectrum analysis (Fig. 2a). The G/D intensity ratio of 3.5 reveals the moderate quality of the pristine CNT. High resolution TEM (HRTEM) image shows the CNTs are double-walled with average diameter at 4.7 nm (Fig. 2b). According to theory calculation and experimental data, as the double-walled CNT diameter exceed 4 nm, it is liable to collapse under external force.[23] To optimize antireflection effect, different concentration of PMMA solution was used to roughly control the PMMA film thickness (Fig. 2c), and the corresponding thickness fitted from ellipsometer data was shown in Table S1. As PMMA thickness increases, the wavelength of lowest reflectance increases correspondingly (Fig 2c). Considering Si solar cell has maximum spectra response in the wavelength range of 600-800 nm, then 2.5 wt. % was chosen as the optimized PMMA concentration. Fig. 2d shows the surface AFM image of CNT-Si solar cell fabricated with optimized PMMA concentration, inserted is the three dimensional (3D) surface image, the 6.32 nm roughness of the PMMA-CNT surface is too small compared to the wavelength of visible light (400-900 nm), thus we assume the PMMA-CNT surface can be treated as plane antireflection surface.

Fig. 3a shows the effect of optimized PMMA coating on the performance of the CNT-Si solar cells tested under 100mW·cm^{-2} condition, the corresponding characterization data was listed in Table 1. Without PMMA coating, the original CNT-Si solar cell shows a J_{sc} of 24.3 $mA{\cdot}cm^{-2}$, an open-circuit voltage (V_{oc}) of 0.56 V, a fill factor (FF) of 52.5%, resulted in power conversion efficiency (PCE) of 7.1%. Compared to literature work, the relatively low FF could be ascribed to the moderate quality of pristine CNT array.[21] In contrast, the cell performance was improved remarkably when coated with PMMA, which mainly originated from the 40% increase of the J_{sc}. The J_{sc}, V_{oc}, FF of PMMA-CNT-Si cells were increased to 35.6 $mA{\cdot}cm^{-2}$, 0.6 V and 53.7%, respectively, resulted in a PCE at 11.5%. The obvious increase of J_{sc} by PMMA coating reveals the effective role in light reflection reduction on Si surface. As the CNT conductivity is very sensitive to absorbed gas molecular,[24] the cells were intentionally doped with nitric acid vapour (HNO_3) to reduce resistance,[25] the FF was further increased to 61.5%, resulted in a PCE of 13.1%, confirmed HNO_3 treatment could largely reduce the sheet resistance and increase the FF^{25}.

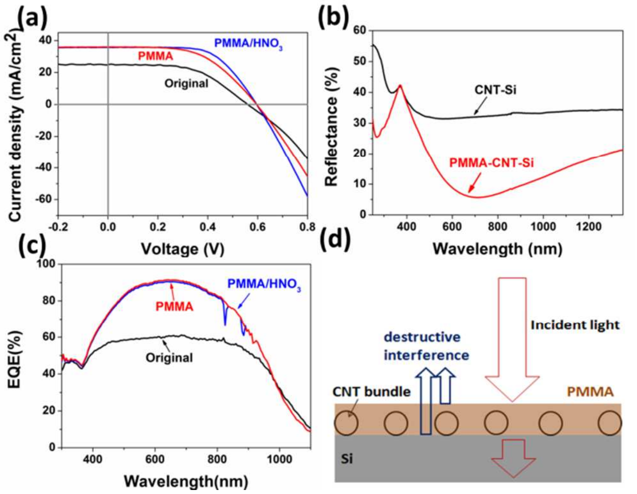

Fig.3 Performance and light trap characterization results. (a) *J-V* curves of the CNT-Si solar cells with different treatments including original, coated with PMMA noted as PMMA, treated with PMMA coating and nitric acid vapor, noted as PMMA/HNO$_3$, respectively; (b) Light reflectance of a CNT-Si cell before and after coating with PMMA; (c) EQE data corresponding to Fig. 3a; (d) Illustration of the light reduction induced by the PMMA coating.

Table 1 Photovoltaic properties of solar cells fabricated extracted from Fig. 3a

Sample	$J_{sc}/mA\cdot cm^{-2}$	V_{oc}/V	FF/%	PCE/%
Original	24.3	0.56	52.5	7.1
PMMA	35.6	0.60	53.7	11.5
PMMA/HNO$_3$	35.6	0.60	61.5	13.1

To elucidate the role of PMMA coating in performance improvement, ultraviolet-visible-near infrared spectrum (UV-Vis-NIR), external quantum efficiency (EQE) and dark *J-V* characterization were conducted on the controlled CNT-Si solar cells. UV-Vis-IR (Fig. 3b) shows the bare Si surface reflects more than 30% incident light. In contrast, when coated with PMMA, the reflectance can be largely reduced to less than 10% in the wavelength range of 600-1000 nm, even to 5% at 710 nm, indicating obvious antireflection effect. The EQE analysis confirms the antireflection effect (Fig. 3c). The uncoated CNT-Si solar cell shows a flat EQE of 60% in the wavelength range of 400-900 nm, corresponding to the wavelength absorption range of Si (1.12 eV), implying that the Si substrate is responsible for photon absorption and carrier generation. When the cell was spin-coated with PMMA layer, the EQE was increased to more than 80% in the wavelength range of 500-800 nm, nearly 90% at about 710 nm, which is consistent with the UV-Vis-IR data in Fig. 3b. Moreover, after intentionally doped with HNO$_3$, almost no differences within the EQE and J_{sc} data could be observed, which again confirmed the HNO$_3$ doping only changed the resistance of CNTs and increased the FF.[25] As the roughness of the PMMA-CNT layer (Fig. 2d) is too small to scatter incident light (400-900 nm), the antireflection effect should come from the destructive interference, which would satisfy the express $d_{PMMA} = \lambda/4n_{PMMA}$, where λ is the wavelength of incident light, d_{PMMA} is the thickness of PMMA layer, n_{PMMA} (1.49) is the refractive index of PMMA coating, the destructive interference was illustrated in Fig. 3d. Due to the existed CNT film, spin-coating of 2.5 wt. % PMMA solution formed a thicker (126 nm, 112 nm without CNT film) PMMA film (Fig. S3). Given an incident light wavelength of 710 nm (where maximum antireflection occurs), the optimized thickness is 120 nm, which is consistence with the actual thickness 126 nm, which proved the plane assumption is correct within the small roughness PMMA-CNT film surface.

Since our process involves chemical doping, the stability should be evaluated during storage. The efficiency could only last several hours before decrease of FF (Fig. S4). In the future, more stable doping agent, such as I$_2$ should be selected[26]. Table S2 shows the average efficiency of our PMMA-CNT-Si solar cell is 12% with a variation of 0.78.

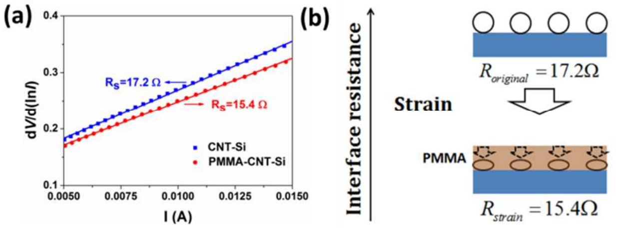

Fig.4 Mechanism study. (a) Series resistance (R_s) extracted from dark *J-V* curves of CNT-Si and PMMA-CNT-Si solar cell. (b) A schematic interface resistance decrease due to radial strain induced by PMMA layer.

When the double-walled CNT film is transferred onto Si substrate, the CNT film is porous and loose, and tends to suffer a "*shrink force*" upon the spin-coating of PMMA solution. Particularly, when the double-walled CNT diameter is larger than 4 nm, the CNTs are liable to be collapsed or flattened under a small external pressure.[23] The possible flattening and shrinking effect may lead to radical strain on the CNTs, and therefore modify the CNT-Si interface resistance due to effective contact area variation. Actually, the FF of the same device was slightly increased after coated by PMMA coating (Fig. 3a and Table 1), and the increase would not originate from the bulk CNTs because PMMA has no doping effect and no conductivity, Fig. S5 ruled out the effect of PMMA coating on the CNT film, where no conductivity variation appears before and after PMMA coating. To further understand the PMMA coating role in CNT-Si interface, dark *J-V* measurements on the CNT-Si cells was conducted without HNO$_3$ treatment. The Series resistance (R_S) was extracted from Fig. 4a, which mainly consists of contact resistance between CNTs and Si, bulk resistance of the CNTs and bulk resistance of Si, where the bulk resistivity would not change under this specific condition. It is found the R_S decreased from 17.2 Ω to 15.4 Ω after PMMA coating within the same device. Here, we deduced that the decreased resistivity more likely arose from the contact improvement between CNTs and Si. During PMMA coating and solvent evaporation, the "*shrink force*" might press the CNTs in the film, thus the CNTs would suffer radical strain, resulted in a larger contact area between CNTs and Si, as illustrated in Fig. 4b.This assumption was confirmed by performance characterization shown in Fig. 3a and Table 1, the pristine CNT-Si solar cell shows a FF (relates to the series resistance of the cell) of 52.5%, and then increased to 53.7% after PMMA coating within the same device. Based on the antireflection and dark *J-V* analysis, we proposed in our specific large diameter double-walled CNT-Si solar cells, both the antireflection of PMMA and decreased resistance of CNT-Si interface together contributed to the performance improvement.

Conclusions

We demonstrate that surface engineering on aligned CNT-Si solar cell is a simple and promising strategy for the enhancement of cell performance. It's revealed that the surface coating of PMMA layer shows an obvious antireflection effect, leading to the increase of J_{sc}, V_{oc} and *PCE*. In addition, it is proved that the performance improvement mainly comes from the antireflection of PMMA coating and partly from the decreased interface resistance between CNTs and Si.

Acknowledgements

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Notes and references

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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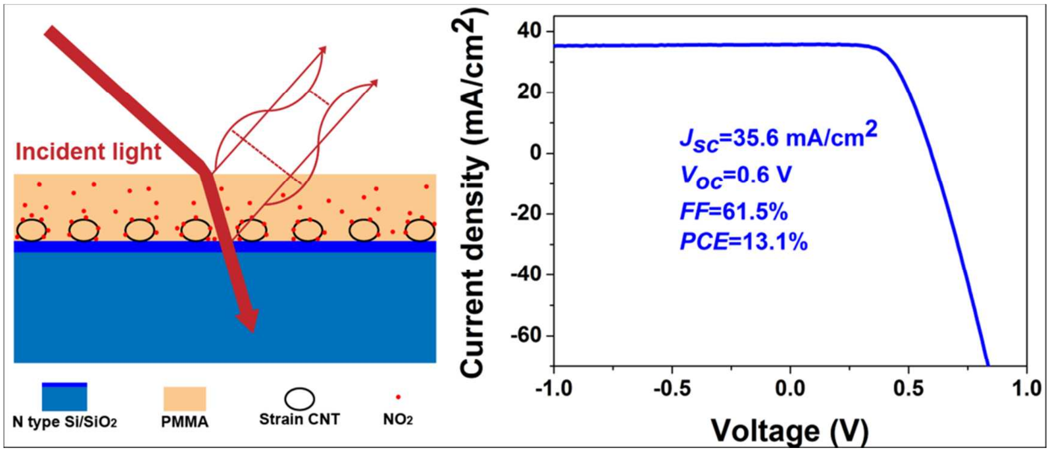

Text: PMMA coating on aligned CNT-Si solar cell with efficiency of 13% after doped by NO_2