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TiO_2-Coated Carbon Nanotube-Silicon Solar Cells with Efficiency of 15%

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Combining carbon nanotubes (CNTs), graphene or conducting polymers with conventional silicon wafers leads to promising solar cell architectures with rapidly improved power conversion efficiency until recently. Here, we report CNT-Si junction solar cells with efficiencies reaching 15% by coating a TiO_2 antireflection layer and doping CNTs with oxidative chemicals, under air mass (AM 1.5) illumination at a calibrated intensity of 100 mW/cm^2 and an active device area of 15 mm^2. The TiO_2 layer significantly inhibits light reflectance from the Si surface, resulting in much enhanced short-circuit current (by 30%) and external quantum efficiency. Our method is simple, well-controlled, and very effective in boosting the performance of CNT-Si solar cells.

There have been intensive efforts in exploring innovated solar cell structures with high performance and cost-effective manufacturing methods[1,2]. Emerging competitive technologies include solar cells based on organic molecules (with efficiencies of 7%)[3,4], colloidal quantum dots (efficiencies reaching 6%)[5,6], and dye-sensitized solar cells (efficiencies up to 12%)[7–9]. An alternative approach is to combine inexpensive materials with well-established semiconductors (e.g. silicon) to create new architectures that have the potential of simplifying fabrication processes and lowering cost. To this end, researchers have explored various candidates, particularly transparent conductive films of carbon nanotubes (CNTs), graphene and semiconducting polymers that can be conveniently deposited on commercial Si wafers to make efficient solar cells[10–18]. During the past years, considerable progresses have been achieved in this area and power conversion efficiencies have been steadily enhanced to about 8% for graphene-Si[17] and 13.8% for acid-doped CNT-Si cells[13]. At this high level, even 1% increase of efficiency is critical for pushing forward practical applications and sometimes requires substantial modification or improvement of current cell structures.

The light-to-electricity conversion in a solar cell involves several key steps, including light absorption, charge separation and carrier collection. The light absorption step determines how much fraction of incident photons can be absorbed by the semiconductor and the excitation of charge carriers, therefore directly influences the external quantum efficiency and cell efficiency. For planar substrates such as polished Si, light reflection from their surface could be as high as 36%, resulting in substantial energy loss in the light absorption stage[19]. Antireflection structures such as vertical semiconducting nanowire arrays grown on or etched from a Si substrate[20], nanodome-like amorphous Si films[21], and patterned Si nanocones[18] with suitable aspect ratios have been reported recently, and showed effective light trapping and reflection reduction for the devices. Those approaches generally created a rough surface on top of the Si substrate and involved complex photolithography techniques to make patterns. In addition, the non-smooth Si surface may prevent conformal transfer of nanotube or graphene films and bring additional charge recombination sites, for example, on the surface of patterned nanowires and nanocones.

Recently, several groups and our team have particularly studied CNT-silicon solar cells that were fabricated by transferring a semi-transparent CNT film onto a n-type single-crystalline Si wafer to form Schottky junctions and heterojunctions[10–15,22]. By applying a series of doping and gating methods such as $SOCl_2$ treatment[22], ionic liquid electrolyte infiltration and electronic gating[14,15] as well as nitric acid doping[13], the power conversion efficiencies of these CNT-Si cells have been continuously pushed from initially about 1.3% to 13.8% (a ten-fold increase) during the past several years, indicating a very promising architecture with reduced manufacturing cost and also the potential of achieving high performance.

Here, we report an improved device structure, a TiO_2-coated CNT-Si (TiO_2-CNT-Si) solar cell, with measured power conversion efficiencies reaching above 15% under air mass (AM 1.5) global illumination conditions after chemical doping. The main original idea is to introduce a TiO_2 colloidal antireflection layer on the top to boost the cell efficiency to a higher level. The spin-coating process was very simple and layer thickness well controlled. Mechanism study revealed that the TiO_2 coating reduced light reflection from the cell surface to less than 10%, enhanced the short-circuit current by 30% and external quantum efficiency to nearly 90% in the visible region.

Results

Our fabrication of TiO_2-CNT-Si solar cells involved the following steps, as illustrated in Fig. 1 (see Experimental for details). The single-walled nanotube films were synthesized by chemical vapor deposition (CVD) with controlled optical transparency and sheet resistance, as described in our previous reports[23]. We started from a n-type Si wafer with 400 nm oxide, and transferred a CNT film onto the oxide surface to form smooth contact. Micrometer-thick Ag paste was applied around to enclose a nearly square-shaped window and define the active device area (about 15 mm^2). The surrounding Ag paste was thick enough to prevent light penetration to the underlying Si from outside of the window, thus ensure precise calculation of the current density (output current divided by device area). Inside the window, the SiO_2 was removed by HF vapor etching, resulting in direct CNT-Si contact and junction formation. After that, a TiO_2 nanoparticle colloid synthesized by sol-gel method[24] was spin-coated at an appropriate thickness (50–80 nm) onto the CNT film. Characterization of the TiO_2 colloid and solid layer by transmission electron microscopy (TEM), UV-Visible absorption and Raman spectrum revealed aggregations of crystalline nanoparticles with diameters of several nanometers and an absorption range at 350 nm (corresponding to a bandgap of ~4 eV) (Supplementary Information, Fig. S1). Before solar cell measurements, the device was sequentially exposed to nitric acid and hydrogen peroxide vapors for a few seconds for doping CNTs. Here, the TiO_2 coating and chemical doping are two critical steps in order to obtain maximum efficiency, in which the TiO_2 layer mainly increases the current density and the latter improves fill factor (discussed later).

We have characterized the morphology of CNT-Si cells and the TiO_2 layer by optical and scanning electron microscope (SEM). Our typical device area (~15 mm^2) allows spin-coating of a uniform TiO_2 layer on top of the CNT film. Before coating, the CNT-Si cell surface appears to be bright because the CNT film is so thin and the planar Si substrate is reflective (Fig. 2a). In contrast, the cell coated by TiO_2 shows a dark blue-to-violet color, indicating effective reduction of light reflection (Fig. 2b). SEM image of the bare cell shows the spiderweb-like CNT film consisting of interconnected nanotube bundles with diameters of several to tens of nanometers. After spin-coating, the nanotube features can not be distinguished easily. Instead, we observe a uniform film of aggregated TiO_2 nanoparticles. The TiO_2 colloid covers not only the top of every nanotube bundle but also the porous area among the CNT network, therefore could form good adhesion to the Si substrate and ensure uniform thickness across the CNT film (Fig. 2c, 2d). Before and after HNO_3/H_2O_2 doping, the TiO_2 layer shows similar morphology by SEM characterization (Fig. S2), indicating that the chemical vapors could penetrate through the layer to affect the underlying device. Cross-sectional view obtained by breaking the cell at the middle reveals the layer thickness of about 70 nm (ranging from 50 to 80 nm for different samples with slight fluctuation), and the CNTs are embedded within the bottom part of TiO_2 layer yet still maintain contact to Si (Fig. 2e, 2f). Many CNT bundles hang down on the fractured cross-section of Si wafer, indicating good strength and interconnection. There are also some tiny (nanoscale) protrusions present on the TiO_2 layer, which could help light trapping like nanocones. The TiO_2 layer thickness is controlled by the rotation speed during spin-coating, and most of areas in the middle of the solar cell have uniform thickness except for the edge portion where the layer meets Ag paste resulting in increased thickness (Fig. S3).

We have measured the current density-voltage (J-V) characteristics in the dark and light conditions under AM 1.5 at calibrated intensities of 70 to 100 mW/cm^2. The TiO_2-CNT-Si cell shows a short-circuit current density (J_{sc}) of 32 mA/cm^2, an open-circuit voltage (V_{oc}) of 0.61 V, a fill factor (FF) of 77%, resulting in an efficiency of 15.1% at 100 mW/cm^2 (Fig. 3a). The J_{sc} decreases

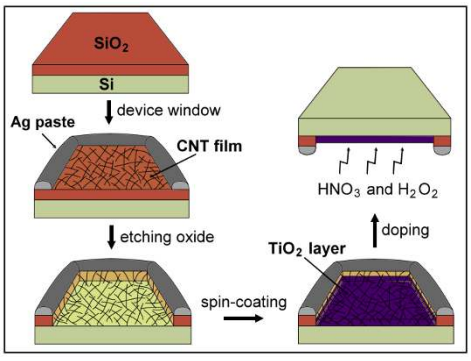

Figure 1 | Illustration of the fabrication process of a TiO_2-CNT-Si solar cell involving the following steps: 1) creating a cell device window by transferring a CNT film on a Si wafer (with 400 nm oxide) and applying Ag paste around the film, 2) etching away the oxide layer to form direct CNT-Si contact and junction, 3) spin-coating a thin TiO_2 colloid on top of the CNT film as antireflection layer, and 4) chemical doping of the cell by vapor of HNO_3 and H_2O_2.

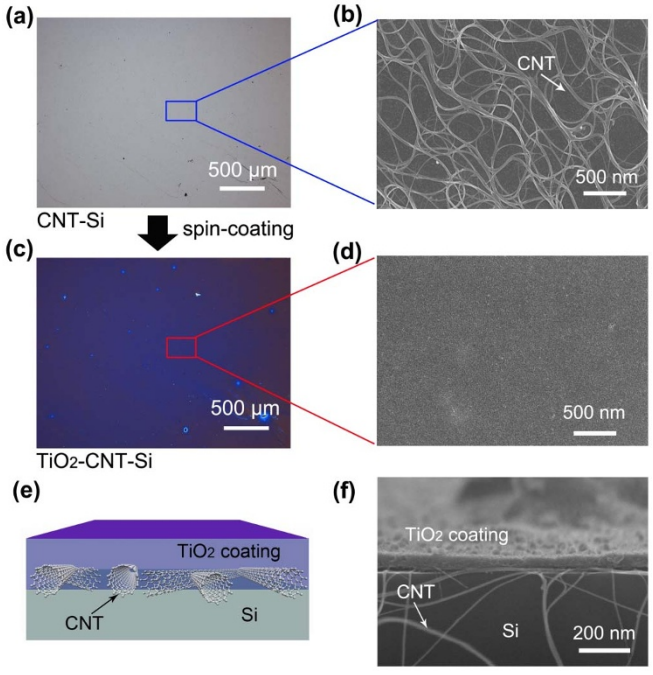

Figure 2 | Characterization of TiO_2-CNT-Si solar cells. (a) Optical image of a CNT-Si cell without coating. (b) SEM image of the CNT film transferred to the Si wafer. (c) Optical image of this cell after spin-coating a TiO_2 layer, showing change of color appearance. (d) SEM image on the cell surface showing a uniform layer of TiO_2 covered on top of the CNTs. (e) Illustrated solar cell structure consisting of a Si substrate, a CNT film and a TiO_2 layer. (f) Cross-sectional SEM image of the cell after coating.

consistently under reduced illumination intensity, and the cell efficiency is 15.3% for an intensity of 90 mW/cm^2, about 14.8% for 80 and 70 mW/cm^2. The high efficiency (15%) is attributed to a combination of good parameters including very high *FF* (77%) and reasonable J_{sc} and V_{oc} values. Previously, there were several relevant Si-based hybrid cells using different strategies to obtain good performance. Among those, patterned CNT grid lines filled with ionic electrolyte at a gate voltage (−0.75 V) showed a comparable J_{sc} (29.8 mA/cm^2) and efficiency of 12%[15]. A CNT-Si cell with nitric acid infiltration into the CNT network showed higher J_{sc} (36.3 mA/cm^2) but lower V_{oc} (0.53 V) and *FF* (72%), with an efficiency of 13.8%[13]. A conjugated polymer-Si nanocone cell (antireflection structure) with top Au grid had a similar J_{sc} (31 mA/cm^2) but lower V_{oc} (0.50 V) and *FF* (63%), with an efficiency of 11%[18]. Compared with those structures, our TiO_2-CNT-Si cells are free from liquids and do not use metal contacts on top of the active junction area.

We found that the TiO_2 coating and subsequent chemical doping are responsible for improving the current density and fill factor, respectively. To study these effects, *J-V* curves of solar cells after each step were recorded and plotted together (Fig. 3b). An original bare CNT-Si cell without treatments had an efficiency of about 8%, and after coating TiO_2, the J_{sc} increased from 24.4 to 32.2 mA/cm^2. The enhancement of J_{sc} by more than 30% indicates that the TiO_2 layer is very effective in increasing the current density (due to antireflection). However, it does not influence the values of V_{oc} and *FF*. The second step was done by exposing the TiO_2-CNT-Si cell to H_2O_2 and HNO_3 vapors sequentially for 5 to 15 seconds, which caused the *FF* to increase from 65% to 74% while the J_{sc} remained unchanged. The combined effects yielded much enhanced cell efficiency of 14.5%. For the three parameters that determine the final cell efficiency, J_{sc}, V_{oc} and *FF*, TiO_2 mainly improves J_{sc} while exposure to H_2O_2/HNO_3 mainly improves *FF*. Our previous work has demonstrated that HNO_3 doping can improve solar cell efficiency by reducing the sheet resistance of CNT films and possibly forming oxide on Si surface[12]. Here, we found that the maximum *FF* was obtained by combining HNO_3 with H_2O_2 vapor treatments, likely because that oxygen bubbles generated from H_2O_2 could produce tiny pores or cracks in the TiO_2 layer similar to previous reports on TiO_2 and other oxides[25,26], making it easier for HNO_3 vapor to penetrate through TiO_2 and reach the CNT film.

The effect of TiO_2 coating can also be seen from the incident photon to current efficiency (IPCE) results, a measurement of external quantum efficiency (EQE) (Fig. 3c). The same original CNT-Si cell as in Fig. 3b showed a flat IPCE of about 60% from 400 to 1000 nm corresponding to the wavelength absorption range of Si (1.12 eV), indicating that the Si substrate is responsible for photon absorption and carrier generation. After coating TiO_2, there was a pronounced increase of IPCE in the same region, which reached nearly 90% from 600 to 800 nm. The current density values calculated from the accumulating area under each curve were 23.8 and 31.7 mA/cm^2 before and after coating, respectively, very close to the J_{sc} values in the *J-V* curves in Fig. 3b (24.4 and 32.2 mA/cm^2). In comparison, the EQE of the graphene-Si model with cell efficiency of 8.6% was between 60% to 70%[17], similar to our un-coated cell with efficiency of 8.25% and IPCE of 60%. Another work on polymer-Si nanocone cells reported an EQE of 70% to 90% (with or without top Au grid) and cell efficiency of 11% owing to the antireflection device structure[18]. Therefore the process of TiO_2 coating could improve

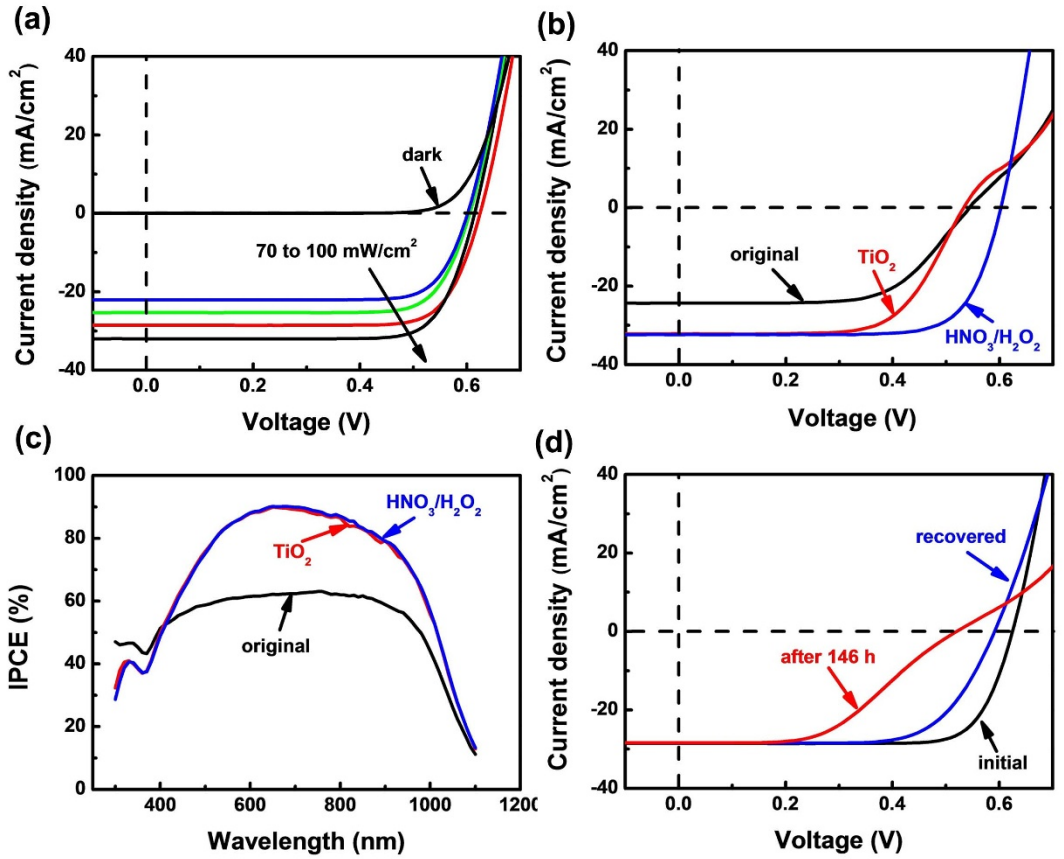

Figure 3 | Solar cell characteristics. (a) *J-V* curves of a TiO_2-CNT-Si cell measured in the dark and light conditions (from 70 to 100 mW/cm^2). (b) *J-V* curves of a CNT-Si cell recorded in original state (without coating), with a TiO_2 antireflection layer, and after HNO_3/H_2O_2 treatment, respectively. (c) IPCE data of the same cell in original state, with a TiO_2 layer, and after doping, respectively. (d) *J-V* curves of a TiO_2-CNT-Si cell measured in initial state (maximum efficiency), after storing 146 hours in air without encapsulation, and recovered by chemical doping again (light intensity: 90 mW/cm^2).

IPCE significantly, which was directly related to the 30% increase of J_{sc} observed in *J-V* curves (Fig. 3b). Another consistent result was that the HNO_3/H_2O_2 treatment did not increase IPCE at all (Fig. 3c), and in the corresponding *J-V* curves we can see that only *FF* was affected by such chemical doping while J_{sc} remained constant (Fig. 3b).

Since our process involved chemical doping, it is necessary to investigate the device stability during storage. We found that the effect of HNO_3/H_2O_2 treatment could last for several hours, in which the *FF* maintained a high value (larger than 70%). For long time storage in air without using additional encapsulation techniques, the *FF* dropped from 77% to 48.5% after 146 hours exposure to air although the J_{sc} remained unchanged (Fig. 3d). However, a HNO_3/H_2O_2 treatment again could recover the *FF* to 68.6% immediately and the *J-V* curve also shifted toward the original state. Certainly, the stability issues caused by chemical doping need be addressed in the future, for example, by selecting more stable doping agents. Here, one of the advantages in our cells is that the TiO_2 coating not only serves as the antireflection layer, but also protects the underlying CNT-Si junction and ensures a stable J_{sc} over long time (previously TiO_2 film was deposited onto organic solar cells to improve stability[27]).

Discussion

The main effect of the TiO_2 layer in our solar cells was antireflection, as proved by light reflection measurements and other control experiments. Without coating, a bare CNT-Si cell showed a reflectance of 30% to 40%. With a 70 nm TiO_2 layer, the light reflectance dropped substantially in the visible region, especially to a minimum value (<5%) at around 600 nm (Fig. 4a). The overall reflectance was inhibited to less than 10% to 20% across the spectrum. Recall that the maximum IPCE (nearly 90%) of a TiO_2-coated cell also occurred at the position of 600 to 800 nm (Fig. 3c). If we assume a refractive index of 1 for air, the condition for a coating to generate destructive interference at the air-coating interface can be expressed by $d_{TiO2} = \frac{\lambda}{4n_{TiO2}}$, where λ is incident light wavelength, d_{TiO2} is the layer thickness and n_{TiO2} is the refractive index for TiO_2 nanoparticles (~2.2)[19] (as illustrated in Fig. 4b). Given an incident wavelength of λ=600 nm (where maximum antireflection occurs), the calculated optimal layer thickness is 68 nm which is well within the thickness range of our spin-coated TiO_2 layers (50–80 nm). While other structures such as periodic nanodome and nanocone arrays can re-direct the route of light transport for light scattering and trapping, here we used a thin TiO_2 layer to serve as an interference antireflection coating.

Because TiO_2 nanoparticles were directly deposited on CNTs, electronic interaction might exist between TiO_2 and CNTs as revealed in some semiconducting nanoparticle-CNT hybrid systems[28]. To study this, a CNT film was put on an insulating silica sheet and TiO_2 colloid was spin-coated on top of CNTs. We configured a two-probe device by contacting the two sides of the TiO_2-covered CNT film and scanning the voltage from −1 to 1 V (inset of Fig. 4c). If electron transfer from the TiO_2 nanoparticles to CNTs occurs under light excitation, the current flow through the device should change accordingly. However, under illumination (90 mW/cm^2) the current-voltage curve almost did not change (Fig. 4c). Combining with the IPCE results where no peaks corresponding to the TiO_2 bandgap appear, we think that the TiO_2 coating only serves as the antireflection layer and does not provide appreciable charge carriers for the solar cell.

Finally, we studied the effect of TiO_2 layer thickness on solar cell characteristics. With increasing layer thickness from about 60 to

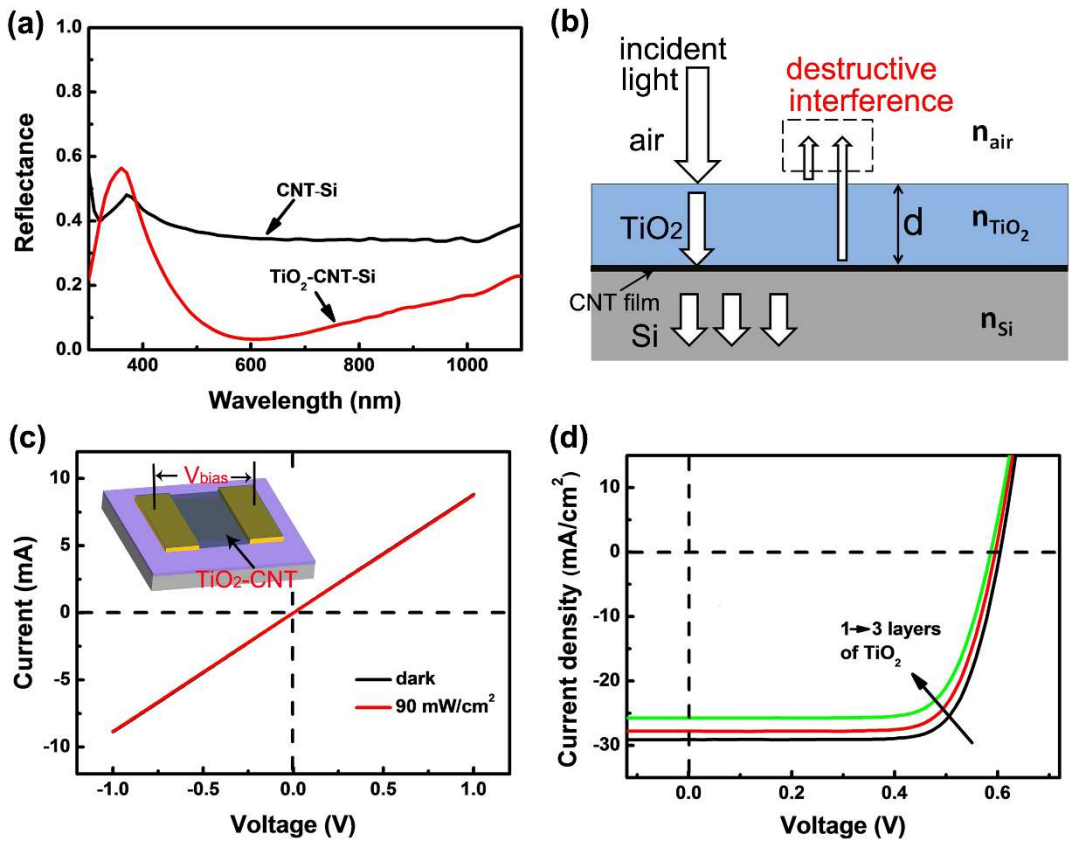

Figure 4 | Mechanism study. (a) Light reflectance of a CNT-Si cell before and after TiO_2 coating. (b) Illustration of the reflection reduction effect by the TiO_2 layer. Destructive interference occurs at the layer surface when the layer thickness (*d*) is appropriate. (c) Current-voltage curves of a TiO_2-coated CNT film under a bias of 1 V in the dark and light (90 mW/cm^2), respectively. Inset shows the device setup (on an insulating substrate). (d) *J-V* curves of a CNT-Si cell with 1 to 3 coated TiO_2 layers (thickness from 60 to 180 nm) under 90 mW/cm^2.

180 nm, the current densities produced under the same illumination intensity dropped slightly from 29.1 to 25.8 mA/cm^2 and the cell efficiency decreased from 14.6% to 12.3% (Fig. 4d). There are two factors underlying this phenomenon. First, an optimum layer thickness of about 60–80 nm exists in our solar cells for maximum inhibition of light reflection in the visible range, determined by the 1/4 wavelength relationship (Fig. 4b). Second, although TiO_2 is almost transparent to visible light, a thick layer consisting of aggregated nanoparticles may produce light scattering and reduce incident light to Si. A previous report has used a slightly thinner TiO_2 layer (48 nm in thickness) to reduce light reflection in p-n junction Si solar cells[19].

In conclusion, a CNT-Si solar cell with efficiency of 15% was reported. Our results indicate one step further for constructing alternative high performance Si-based photovoltaics with advantages in cost reduction and process simplification. This efficiency is also important for practical applications and commercialization of this type of solar cells in the future. The TiO_2 antireflection layer represents an effective strategy to improve the efficiency of CNT-Si solar cells and possibly other similar models such as the graphene-Si structures.

Methods

Synthesis of CNT films and TiO_2 nanoparticles. Single-walled CNT films were grown by CVD using a source solution of ferrocene (0.045 g/mL) and sulfur (0.001 g/mL) dissolved in xylene. The solution was injected into the upstream side (200∼250°C) at rates of 3∼5 μL/min by a syringe pump, and the vapor was carried to the reaction zone by a mixture of argon and hydrogen (volume ratio of Ar/H_2 is equal to 0.85:0.15) flowing at 1500 standard cubic centimeters per minute (sccm). Growth temperature was set at 1160°C and typical reaction time was 30 minutes. Spiderweb-like CNT films were floating to the downstream end and collected by substrates. For synthesis of TiO_2 colloid, about 5 mL $Ti(OBu)_4$, 23 mL ethanol and 0.5 mL ethyl acetate were mixed in a flask as precursors. Then a hydrolysate solution containing 1.5 mL HNO_3 (0.1 mol/L), 1.5 mL de-ionized water and 12 mL ethanol was added by droplets into the precursor solution at a rate of 0.5∼1 mL/min. The mixture was stirred continuously for 12 hours at 800 rpm (revolutions per minute) and then aged for 12 hours at room temperature.

Fabrication of TiO_2-CNT-Si solar cells. Commercially available n-type, 4 inch-diameter, 400 μm-thick Si wafers with 400 nm-thick oxide and bulk resistivities of 0.05∼0.2 Ω·cm were cut into pieces and used as substrates. As-synthesized CNT films were immersed in H_2O_2 and HCl to remove amorphous carbon and wash away residue catalyst. A purified expanded film was transferred onto the surface of Si (oxide) to make a conformal contact. At the front, micrometer-thick Ag paste was applied around the film to enclose a nearly square window as the device area. Back contact was made by applying liquid-state gallium-indium eutectic (E-GaIn) onto the back side of Si wafer. The SiO_2 inside the window was removed by exposing the device (CNT side) to HF vapor for 2–3 minutes resulting in direct CNT-Si contact. The device was placed in ethanol vapor for a few hours to clean the surface. After that, a TiO_2 nanoparticle colloid was spin-coated onto the device surface at 5000–6000 rpm for 1 minute, making a uniform antireflection layer with a thickness of 50–80 nm. The spin-coating process was repeated at the same parameters for coating multiple TiO_2 layers. Chemical doping was done by placing the cell downward on the vapor of concentrated HNO_3 and H_2O_2 (30% in water) sequentially for15 seconds each.

Characterization and electrical measurements. The structure and morphology of CNT films, TiO_2 layer and solar cells were characterized by optical microscope (Olympus BX51M), Raman Spectrometer (Renishaw inVia plus), SEM (Hitachi S4800) and TEM (FEI Tecnai G2 T20). Solar cell characteristics were tested by a source meter (Keithley 2635A) and a solar simulator (Newport Thermo Oriel 91195A-1000) under AM 1.5G condition at an illumination intensity of 70–100 mW/cm^2, calibrated by a standard Si solar cell (91150V). IPCE and optical reflectance were measured by solar cell QE/IPCE measurement system (Zolix solar cell scan100) across a wavelength range of 300–1100 nm.

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Author contributions

E.S. designed experiments and performed solar cell fabrication, characterization and tests. L.Z., Z.L. and Y.S. synthesized TiO_2 colloids and CNT films. P.L. and Y.J. participated in device fabrication and optimization. S.Z. performed optical reflection measurements. D.W. and A.C. designed experiments. E.S. and A.C. wrote the paper. All authors contributed to discussion, analysis of results and preparation of manuscript.

Additional information

Supplementary information accompanies this paper at http://www.nature.com/scientificreports

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