

Silicon Nanowire/Polymer Hybrid Solar Cell-Supercapacitor: A Self-Charging Power Unit with a Total Efficiency of 10.5%

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Supporting Information

ABSTRACT: An integrated self-charging power unit, combining a hybrid silicon nanowire/polymer heterojunction solar cell with a polypyrrole-based supercapacitor, has been demonstrated to simultaneously harvest solar energy and store it. By efficiency enhancement of the hybrid nanowire solar cells and a dual-functional titanium film serving as conjunct electrode of the solar cell and supercapacitor, the integrated system is able to yield a total photoelectric conversion to storage efficiency of 10.5%, which is the record value in all the integrated solar energy conversion and storage system. This system may not only serve as a buffer that diminishes the solar power fluctuations from light intensity, but also pave its way toward



cost-effective high efficiency self-charging power unit. Finally, an integrated device based on ultrathin Si substrate is demonstrated to expand its feasibility and potential application in flexible energy conversion and storage devices.

KEYWORDS: Silicon nanowires, organic/inorganic hybrid solar cells, supercapacitors, integrated self-charging power unit

he rapid developments of modern electronics raise the demand for sustainable technologies by integrating multiple functions in one device. Compared with the intensive research on improving the power conversion efficiency (PCE) of various kinds of solar cells or energy storage devices, integrated systems combing energy conversion and storage functions are still far to be well investigated. Electrochemical systems including batteries and electrochemical supercapacitors designed for energy storage are specially favored since they are more sustainable and environmentally friendly.¹ Supercapacitors are outstanding due to their high power density, low weight, quick response to potential changes, high cycle life, and long-term stability that can easily exceed one million operation cycles.^{2–4} Self-charging power unit consists of solar cells for energy conversion with supercapacitors for energy storage have attracted more attention than lithium-ion batteries (Table S1).^{5–18} In this case, the supercapacitors can not only store the energy but also balance the solar electricity fluctuations by acting as both energy storage and output regulator. The current attempts are focusing on the dye-sensitized solar cells (DSSC) or organic solar cells (OSC) as the energy source part in either planar structure or fiber shape, which have shown their ability as self-charging units. However, the overall total efficiencies of the reported system are still $\sim 10\%$ despite of the efforts put into the optimization of the integrated device structure and the usage of expensive materials, which are mainly restricted by the relatively low efficiency of the solar energy capturing part and the energy loss caused by the external electrical interconnections in the energy storage process. Since achieving a PCE of over 10% for a single DSSC or OSC is still challenging and even lower in a fiber shape, $^{19-21}$ the efficiency of the integrated system is even lower. Pint's group has pioneered the work using a porous silicon (Si) electrode energy storage system integrated with a DSSC to realize multifunctional platform, and a total efficiency of 2.1% was achieved.¹⁸ Alternatively, an integrated system combining a fiber DSSC and a wire supercapacitor is a good design to achieve multifunctional system; however, the best reported overall energy conversion efficiency remains near ~2.1%.¹³ Wang and co-workers reported a power pack combing a new emerging perovskite solar cell with a polypyrrole-based supercapacitor for the first time with a high total efficiency of 10%.²² The perovskite showed a highest PCE

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Figure 1. (a) Schematic of the integrated hybrid device containing a SiNW based heterojunction solar cell and a polypyrrole based supercapacitor. (b) SEM image of as-fabricated SiNW. (c) SEM image of SiNW after 2 h PCl₅ treatment. (d) TEM image of a single as-fabricated Si nanowire. (e) TEM image of a single Si nanowire after 10 min methylation treatment. The scale bars are 500 nm in the insets of (b) and (c).

of 13.6%, which was the origin for the superior performance of the power pack. However, both devices were connected in series by two external wires, resulting in additional resistance and low integration level.⁹

Nanostructures are specially favored for their superior properties beyond their bulk counterparts. The nearly ideal light harvesting ability of Si nanowire array (SiNW) makes it a good candidate for low cost and high efficiency solar cells. Vertically aligned SiNW solar cells gain several advantages over the predominant commercial planar crystalline ones by reducing the material volume fraction, eliminating the need for vacuum-deposited antireflection coatings and lowering the purity request. Nowadays, solar cells based on p-n junction architectures composed of vertical SiNWs have been widely explored and demonstrated significant light absorption enhancement.^{23–25} However, the conventional p-n junction formation process of the Si solar cells normally involves complicated and expensive ion implantation, annealing, or dopant diffusion processes of which high temperatures (>800 °C) are required. Furthermore, high dopant concentrations bring about doping effects in the emitter such as Auger recombination, which leads to carrier losses especially for nanostructures with high surface to volume intrinsic property.² Heterojunctions formed between Si and other carrier-selective materials such as organic films by solution process or transition metal oxides through vacuum deposition has been demonstrated and shown great potential for the dopant-free configuration of Si-based high efficiency photovoltaic devices.²⁷⁻³⁰ Heterojucation solar cells composed of inorganic SiNWs as light absorption medium and low temperature solution processed organic poly(3,4-ethylenedioxythiophene)/ poly(styrenesulfonate) (PEDOT:PSS) as hole-selective and antireflection layer have achieved efficiencies of over 13% and emerged as a promising alternative.³¹⁻³³

In this letter, a new self-charging power unit is fabricated via integrating a high performance SiNW/PEDOT:PSS hybrid solar cell with a polypyrrole supercapacitor. We demonstrate a 13% efficiency hybrid solar cell by precise control of the nanowire parameters via metal-assisted chemical etching with nanosphere lithography and modification of the wire surface by a solution-based passivation process. The hybrid solar cell shows an efficiency enhancement after the surface modification of SiNWs. A dual-functional titanium (Ti) film is employed as a conjunct electrode to connect the energy conversion and storage parts. With simple solution process and device structure, the integrated system is able to yield a total energy conversion efficiency of 10.5%. Based on our best knowledge, it is the record value for solar cell based functional self-charging power system so far. The high efficiency originates from the excellent performance of solar cells and the supercapacitors as well as the conjunct connecting electrode without any external interconnections. Finally, an integrated device based on ultrathin Si substrate is demonstrated to expand its feasibility and potential application in flexible energy conversion and storage.

Figure 1a schematically illustrates the configuration of the integrated self-charging power unit, where the top part is a hybrid solar cell as the energy conversion section, and the bottom part is a polypyrrole supercapacitor as the energy storage part. This integrated device was realized by a thermally deposited Ti films on the back side of the Si substrate acting both as the rear electrode of the hybrid solar cell and one of the electrodes of the supercapacitor. For the solar cell part, PEDOT:PSS was spin-coated onto the SiNWs to form a Si/ polymer heterojunction. The polypyrrole films were electrochemically deposited on Ti to form a symmetric supercapacitor, where porous polyethylene (PE) membrane was used as a separator, H_3PO_4/PVA (poly(vinyl alcohol)) gel as the electrolyte.

Figure 1b shows a scanning electron microscopy (SEM) image of the as-fabricated highly ordered SiNWs with controlled diameters of ~250 nm and a period of ~360 nm (the center to center distance of two adjacent nanowires). Although ordered SiNWs assembled well on the Si substrate with hexagonal distribution, the nanowire surface somehow became rougher after the metal-assisted chemical etching, which inherited from the plasma induced irregular etching of the nanospheres (inset of Figure 1b, also see Figure S1 for the fabrication process). As shown in Figure 1c, diameters of the SiNWs decreased after 2 h chemical methylation etching process (for more details also see Figure S2), where PCl₅ solution was used as Si chemical etching agent. The surface of the SiNWs became smoother, and the cross-section shape turned from rounded to quasi-square, which resulted from the anisotropic etching of PCl₅ solution. According to our previous study, this process not only resulted in a methylate passivated nanowire surface but also decreased the roughness of the SiNWs.³¹ In addition, the edge to edge distances of the adjacent wires were enlarged, which eventually benefited the polymer penetration at the bottom part. To further confirm this, Figure 1d,e compares transmission electron microscopy (TEM) images of two single nanowires before and after the PCl₅



Figure 2. J-V curves of the hybrid solar cells (a) under 1 sun illumination at 100 mW/cm² and (b) in the dark. (c) Reflectance spectra of different samples without and with PEDOT:PSS coating. (d) EQE spectra of the devices based on planar Si and SiNWs without and with surface treatment.

treatment. As clearly displayed in Figure 1d, the surface of the chemically etched nanowire was much rougher than the methylation processed one even when the etching time was as short as 10 min (Figure 1e). Figure S3 shows the optical images of a SiNW hybrid solar cell taken at different viewing angles of incidence from 30° to 55° . The color of the device surface gradually changed with the light incident angles, which was caused by the white light scattering with the periodic nanowire array, indicating the excellent uniformity of the nanowire structures.

To investigate the effects of methylation process, hybrid solar cells based on planar, SiNW without further process (hydrogen terminated Si, SiNW-H) and SiNW with methylation (SiNW-CH₃) configurations were fabricated. Figure 2a depicts the current density-voltage (I-V) curves of the fabricated devices tested under air mass (AM) 1.5 G (100 mW/cm²) illumination. The electrical output characteristics are summarized in Table S2. The SiNW-H based device exhibited an open circuit voltage $(V_{\rm oc})$ of 0.51 V and a lower fill factor (FF) of 0.64. While the SiNW-CH₃ one showed an improved V_{oc} of 0.59 V and a FF of 0.72, which benefited from a better surface passivation and junction contact. The planar device showed a slightly higher $V_{\rm oc}$ of 0.62 V and an improved FF of 0.75 due to the superior junction quality of polished surface with PEDOT:PSS, which was a typical behavior in most of the solar cells and has been indicated in the lower dark saturation current density, as shown in Figure 2b. However, the final PCE of a solar cell was determined by the trade-off among V_{oc} , the short current density (J_{sc}) and the FF. The main shortage of planar Si was the high reflectance over 30% in the whole spectra (Figure 2c), thus resulting in a relatively lower J_{sc} . Although the transparent conducting polymer PEDOT:PSS exhibited a refractive index of \sim 1.6 and could somehow act as an antireflection layer on

planar Si substrate, reducing the average reflectance to ~25.34%, the $J_{\rm sc}$ of the device based on that was only 26.20 mA/cm^2 . Benefiting from the enhanced light trapping ability of nanostructures with further antireflection coating of the polymer (Figure 2c), the devices based on SiNWs produced much improved J_{sc} compared with the planar counterpart. The average reflectance of the three samples among 380-1100 nm decreased from 41.29% to 25.34% (Planar), 10.48% to 6.66% (SiNW-H), and 11.31% to 6.03% (SiNW-CH₃) after deposited with ~70 nm-thick PEDOT:PSS, respectively. The reflectance of the SiNW-CH₃ sample with PEDOT:PSS in 500-920 nm was lower than the SiNW-H one, with a red-shift, as a result of antireflection effect of the polymer and the light coupling effect among the nanostructures. The PCE of planar device was 12.18%, higher than the SiNW-H based one, 9.54%, which suffered from severe recombination loss in the rough junction area. The SiNW-H based device showed an improved J_{sc} of 29.23 mA/cm² due to the low reflectance of the nanowire array-polymer surface, while with similar reflectance, the SiNW-CH₃ based one exhibited higher J_{sc} of 31.38 mA/cm², which was ascribed to passivation effect from the methyl group anchoring on Si. The enhanced $J_{\rm sc}$ was confirmed by the external quantum efficiency (EQE) spectra in Figure 2d, with an integrated photocurrent of 32.04 mA/cm², which was close to the J_{sc} value extracted from J-V measurements. On one hand, surface passivation played a key role on the front surface especially for the nanostructures, leading to higher EQE values in short wavelength region. On the other hand, since the rear side of the SiNW-CH₃ device also benefited from the passivation effect, it was reasonable to observe the EQE value in this region larger than SiNW-H one in 500-1100 nm. The SiNW-CH₃ based device yielded a superior PCE of 13.39%



Figure 3. (a–d) SEM images of Si/PEDOT:PSS samples with planar Si, SiNW-H, SiNW-CH₃, and Ag electrode on SiNW-CH₃/PEDOT:PSS. (e–g) Minority carrier lifetime mapping of three corresponding samples to (a–e). The bottom values are the corresponding average minority carrier lifetime extract from mapping data. All sample sizes are 1 cm \times 1 cm.



Figure 4. Analysis of the supercapacitor performance. (a) Electrochemical impedance spectroscopy curves at open circuit voltage. The inset shows capacitance as a function of frequency in the range of 0.01-10 kHz. (b) Cyclic voltammetry curves at 10, 25, and 50 mV/s scan rates. (c) Galvanostatic charge–discharge curves taken at different current densities. (d) Area-specific capacitance under different discharge current densities.

contributing good light trapping ability, improved surface passivation, and better junction contact.

To probe the effects of surface modification on recombination, a microwave photoconductance decay technique was applied to conduct the spatial mapping of minority carrier lifetime. Minority carrier lifetime is the time that it takes for the photoinduced holes and electrons to recombine, where higher lifetime usually indicates higher PCE for a solar cell. Since the measured lifetime is determined by both the lifetime in the bulk and recombination at the wafer surfaces, it will reflect the front surface recombination rate for the same samples with different front surface treatments. The higher carrier lifetime reflects the better surface passivation. Figure 3 shows the SEM images of Si/PEDOT:PSS samples with different Si surface morphologies and their corresponding minority carrier lifetime mapping. The averaged minority carrier lifetimes for the samples of planar, SiNW-H, and SiNW-CH₃ surface were ~40, ~24, and ~35 μ s, respectively. As shown in Figure 3a, ~80 nm-thick PEDOT:PSS film could fully cover the whole planar Si substrate. For the SiNW-H sample, only the top part of



Figure 5. Performance of the integrated device. (a) Voltage-time (black line) and the corresponding photocurrent-time profiles for photocharging of an integrated system charged to 0.55 V using the hybrid solar cell. (b) Photocharging curve under AM 1.5 G illumination and the discharging curves in the dark at constant current densities of 3, 5, 7, and 10 mA/cm². (c) System capacitance under different discharge current densities. (d) Self-discharging of the power unit without load.

nanowire was covered by the polymer, leaving their bottom space difficult for the polymer to penetrate. The poorer contacts and rougher nanowire surface consequently led to severe recombination problem. In contrast, the SiNW-CH₃ sample possessed much uniform polymer film coverage and junction contacts as depicted in Figure 3c. Figure 3d also clearly shows the morphology of Ag electrode deposited on the SiNW-CH₃/PEDOT:PSS surface, which further confirms the good contacts of nanowire/polymer–metal.

Electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV), and the galvanostatic discharging method were used to characterize the electrochemical properties of the supercapacitor, as shown in Figure 4. Figure 4a shows the EIS curve at open circuit voltage condition. The imaginary part of the resistance at low frequencies was almost vertical to the real part, indicating a superior capacitive behavior. The capacitance as a function of frequency presented a stable high capacitance plateau at the low frequencies area, which was 220 mF at 10 mHz, indicating a fast charging/discharging ability (inset of Figure 4a). Figure 4b shows the CV curves of the symmetric supercapacitors performed in a window range from 0 to 0.6 V. The CV curve was consistent with the $V_{\rm oc}$ of the hybrid solar cell. The rectangular shape like curves scanning at 10, 25, and 50 mV/s indicated the good electrochemical capacitance of the supercapacitor. Galvanostatic charge-discharge curves measurements were performed at different current from 3 to 10 mA/cm^2 . As shown in Figure 4c, the curves exhibited typical symmetric features with nearly perfect triangular shapes,

indicating a good capacitive performance. An area specific capacitance (C_s) of 234 mF/cm² was obtained at a low discharge current density of 3 mA/cm². C_s was defined by $C_s = It/V$, where I, t, and V correspond to the discharge current density (mA/cm²), discharge time (s), and the potential window (V), and it only decreased to 200 mF/cm² when the discharge current density increased to 10 mA/cm², which was maintained 85.47% compared with the value at 3 mA/cm² (Figure 4d).

To assess the ability of the self-charging power unit, a hybrid solar cell and a supercapacitor were integrated according to Figure 1a. By connecting the front electrode of the hybrid solar cell with the bottom electrode of the supercapacitor, voltage of the storage component increased quickly to about 0.55 V after 20 s of photocharging under AM 1.5 G illumination (Figure 5a). Meanwhile, the photocurrent in the system rapidly decreased during the first few seconds of light illumination, which meant that most of the energy was well stored within this range. This was attributed to the decline of real power output of the solar cell when the operation voltage approached the $V_{\rm oc}$.^{15,18} The cutoff voltage of the integrated charging system was thus set at 0.5 V, and the device was subsequently galvanostatically discharged at current densities of 3, 5, 7, and 10 mA/cm² in dark (Figure 5b,c). From the 3 mA/cm² discharge curve in Figure 5b, an areal specific capacitance of 252 mF/cm^2 was achieved with a discharge time of 42 s. The energy density (E_s) in the supercapacitor during the discharge process was then calculated to be 8.75 \times 10^{-6} Wh/cm^2

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Figure 6. Flexible self-charging power unit. (a) Photograph of a 4-in. wafer-sized flexible Si wafer. (b) A digital photograph of organic-Si device integrated with a supercapacitor. (c) Electrical output performance of hybrid devices based on Si substrates with different thicknesses under AM 1.5 G illumination. (d) Curves of the flexible integrated device charged under AM 1.5 G illumination and then discharging at 5 mA/cm² without/with a solar cell.

according to the equation of $E_s = 0.5C_sV^2/3600 = C_sV^2/7200$, where C_s (252 mF/cm²) and V (0.5 V) were the area specific capacitance and operation voltage, respectively. A maximum total photoelectric conversion and storage efficiency (η_t) of the integrated system was calculated to be about 10.5% based on η_t = $E_{\text{output}}/E_{\text{input}} = E_s S_1/(P_{\text{input}}tS_2)$, where η_t was the total energy conversion and storage of the integrated device, E_{output} was the energy output of the supercapacitor, $E_{\rm input}$ was the total incident light energy, S_1 was the surface area of the supercapacitor (1 cm²), P_{input} was the illuminated light density (100 mW/cm²), t was the photocharging time (6 s according to Figure 5b), and S_2 was the active area of hybrid solar cell (0.5 cm²).¹⁷ Based on our best knowledge, this $\eta_{\rm t}$ value is the record one for all the solar cell based integrated energy conversion and storage system. To evaluate the storage property of the power unit, the self-discharging measurement was performed without load. The voltage of the power unit could be over 0.25 V after discharging for 40000 s, showing the good storage stability of the device (Figure 5d).

A flexible integrated device was subsequently fabricated based on ultrathin Si substrates. The thickness of the ultrathin Si could be controlled by the etching time and the substrate became flexible when the thickness went down to dozens of micrometers. As shown in Figure 6a, a 4-inch wafer-sized flexible Si wafer was demonstrated, indicating the good feasibility of the method and the potential to make a large area device. For the flexible integrated device fabrication, ultrathin Si substrate with thickness of ~25 μ m (Figure S4) was applied to fabricate the hybrid solar cell by following the same process as the conventional thick wafer. Figure 6b shows a

photograph of the three-electrode device with a sandwich structure. Figure 6c shows the performance of hybrid solar cells based on Si substrates with different thicknesses, in the range from ~23 to ~300 μ m. With the increase of the substrate thickness, the $J_{\rm sc}$ grew gradually due to the improved light absorption. Therefore, the PCE of the solar cell part increased from 7.29% (~23 μ m) to 13.39% (~300 μ m) accordingly. Benefiting from a higher PCE with increasing Si substrate thickness, the corresponding total efficiency was also enhanced from 5.68% to 10.5% (Table S2).

The flexible hybrid solar cell (with a Si substrate thickness of ~23 μ m) showed lower performance due to the increased transparency and unoptimized device structure. However, here we just tended to demonstrate the flexibility of the integrated power system. It is expected that the efficiency of the ultrathin Si substrate based solar cell could be further improved after proper device optimization. The flexible integrated device was able to charge a supercapacitor (680 mF) to 0.52 V in 78 s (Figure 6d); the longer charging time was due to the lower performance of the ultrathin solar cell and the large capacity of the supercapacitor (depends on the thickness of polypyrrole). As a result, the total conversion and storage efficiency was calculated to be 5.68% due to the relatively lower performance of the solar part (7.29%), and it remained at a stable voltage of about 0.40 V when discharged at 5 mA/cm² with the solar cell under sustainably light illumination, which showed the ability of the flexible integrated system as a continuous stable output power source.

In conclusion, we demonstrated a high performance selfcharging power unit based on a hybrid SiNW/polymer solar cell and a polypyrrole supercapacitor, which simultaneously achieved both photoelectric conversion and energy storage. A low temperature, chemical solution process was carried out to reduce the nanowire surface roughness thus suppressing the charge recombination at SiNW/polymer interface. As a result of better junction contact and lower surface recombination rate, the minority carrier lifetime of the as-treated devices was improved and an enhanced solar cell PCE of 13.39% was achieved. The total photoelectric conversion to storage efficiency of the self-powering unit was as high as 10.5%, which was a record value for solar cell-based integrated systems. A flexible device was also demonstrated to expand its potential application in energy conversion and storage field such as portable electronics. Further strategies toward the integrated self-charging power system should be focused on the optimization of the individual parts to harvest/store more energy as well as the connecting unit to reduce the energy loss during the storage process.

Experimental Section. SiNW Fabrication. The highly ordered vertically SiNW were fabricated via a simple and low cost process of nanosphere lithography combined with metalassisted chemical etching. Hexagonal close-packed monolayer polystyrene (PS) nanospheres (360 nm in diameter) were selfassembled on the surface of water and then loaded on a clean 300 μ m n-type Si(100) substrate with resistivity of 1–3 Ω ·cm. Then reactive ion etching (RIE) was applied to reduce the diameters of the PS nanosphere with 40 sccm flow rate oxygen (O_2) gas and the sphere diameters were well controlled by varying the etching time. Ti film (1 nm-thick) and gold (Au) film (20 nm-thick) were sequentially thermally deposited on the substrate by electronic beam evaporation. Here the ultrathin Ti film can strengthen the adhesion between the Si substrate and Au film without affecting the etching process. The PS nanospheres were then ultrasonically removed in chloroform, leaving a nonclose-packed honeycomb-pattern Au film. The metal-assisted chemical etching of SiNW arrays were obtained by immersing the Si substrate in an etchant solution containing 5 M hydrofluoric acid (HF) and 0.5 M hydrogen peroxide (H₂O₂) in room temperature for different time to control the desired length. During this process the nanowire diameter and length were under precise control, which was of vital importance to the light-trapping property of the SiNW and the contact with polymer. After the nanowire fabrication, excess aqua regia $(3:1, v/v, HCl to HNO_3)$ was used to remove the Au film thoroughly, and any metal residual on the nanowire surface would cause a severe recombination problem in the interface of the Schottky junction. The substrate was then sequentially ultrasonically cleaned in acetone, ethanol, and deionized (DI) water for 20 min and immersed in 5 M HF for 10 min to remove the native oxidation layer. After the HF cleaning by DI water and drying under nitrogen gas flow, the Si-H substrate was transferred immediately into the nitrogen atmosphere glovebox. The main processes including methylation were schematically depicted by scanning electron microscope (SEM) images in Figure S1.

Ultrathin Flexible Si Substrates Fabrication. The ultrathin flexible Si substrates were etched from single side polished Si wafers as mentioned above. A 4-inch wafer-sized Si substrate was dipped into KOH solution with a concentration of 50% at 120 °C for a certain time to be reduced to the desired thicknesses. The wafer became flexible when the thickness went down to dozens of micrometers.

Methylation Process. The method used to fabricate Si-CH₃ substrate was followed from a previous report.^{31,34,35} Briefly, the Si-H substrate was dipped into a saturated solution of phosphorus pentachloride (PCl₅) dissolved in chlorobenzene (CB) at 150 °C to get a chlorinated group (Si-Cl) on the surface. It should be noted that this process not only resulted in a Si-Cl surface but also etched the sidewalls of the Si-H nanowires thus leading to a smoother surface. The Si-Cl substrate was then dipped into a solution of 1 M methyl magnesium chloride (CH₃MgCl) in tetrahydrofuran (THF) for at least 8 h at 90 °C to form a Si-CH3 monolayer, which passivated the surface of SiNW. The as-processed samples were transferred out from the glovebox and immersed in concentrated HCl for 40 min to remove any residual CH₃MgCl, then rinsed sequentially with acetone, ethanol, and DI water.

Solar Cell Fabrication. The as-prepared $1.2 \times 1.2 \text{ cm}^2$ samples with SiNW arrays were spin-coated with highly conductive PEDOT:PSS (Clevios PH1000) mixed with 5 wt % dimethyl sulfoxide (DMSO) and 1 wt % Triton X-100 (surfactant) at 3000 rpm for 1 min, and then annealed at 125 °C for 30 min at glovebox. It was important to wait for 1 min just after dropping the solution onto the nanowire surface to penetrate sufficiently into the spacing of the nanowires, which would benefit from the contact between Si and polymer. Finally, 200 nm-thick silver (Ag) finger grid with a shading ratio of ~10% was thermally evaporated on PEDOT:PSS film as front electrode and 200 nm-thick aluminum (Al) as the rear contact with a total active area of 0.5 cm².

Supercapacitor Device Fabrication. The supercapacitor was symmetrically fabricated by using two polypyrrole plates as electrodes and H₃PO₄/PVA (poly(vinyl alcohol)) gel as electrolyte. The polypyrrole was electrochemically synthesized on Ti sheet in the aqueous solution containing 0.3 M pyrrole, 0.1 M p-toluenesulfonic acid (TOSH), and 0.4 M sodium ptoluenesulfonic acid (TOSNa). The H₃PO₄/PVA gel electrolyte was prepared as follows: 5 g H₃PO₄ was added into 50 mL of deionized water and then 5 g of PVA powder. The mixture was heated to 85 °C under stirring until the solution became clear. The synthesized polypyrrole electrodes were immersed into PVA/H₃PO₄ solution for 10 min, with their two-end parts kept above the solution. After being taken out, every two electrodes were assembled face to face onto a Kapton film substrate, leaving aside the bare part as the electrode terminal. Then, they were fully covered by a piece of Kapton film on top.

Integrated Device Fabrication. One hundred nanometerthick Ti was deposited onto the rear side of the Si substrate before the solar cell fabrication, and the front side was protected by polydimethylsiloxane (PDMS). Polypyrrole was then synthesized on the Ti side by using the method mentioned above as one of the electrodes of the supercapacitor with an active area of 1 cm^2 , which acted as the rear side of the hybrid solar cell as well.

Characterization. The morphology of SiNW on the planar Si substrate was carried out with a FEI Quanta 200 FEG highresolution SEM. A FEI Tecnai G2F20 STWIN TEM was used to characterize the surface of SiNWs. Reflectance spectra were characterized by a PerkinElmer Lambda-750 using LAB-SPHERE reflectance integrating spheres. The photovoltaic characterization was conducted in an ambient environment. Newport 91160 solar simulator equipped with a 300 W xenon lamp, and an AM 1.5 filter was used to generate simulated AM 1.5 solar spectrum irradiation source. The irradiation intensity

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was 100 mW/cm², calibrated by a Newport standard Si solar cell 91150. Newport monochromator 74125 and power meter 1918 with Si detector 918D were used in the EQE measurements. All of the electrical data were recorded by a Keithley 2612 source meter. The electrochemical properties of the supercapacitors were characterized by an electrochemical workstation (Princeton Application Research).

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nano-lett.7b01154.

SEM images of Si NWs with different process conditions, optical photographs of SiNW hybrid solar cell taken at different light angle of incidence angle, cross-sectional SEM images of ultrathin Si, summary of reported integrated devices of solar-storage/conversion systems, and electrical output parameters of the hybrid devices under AM 1.5 G illumination (PDF)

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R.L. and J.W. contributed equally to this work. The manuscript was accomplished through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

PCE, power conversion efficiency; SiNW, Si nanowire array; PEDOT:PSS, poly(3,4-ethylenedioxythiophene)/poly-(styrenesulfonate); PE, polyethylene; EQE, external quantum efficiency; EIS, electrochemical impedance spectroscopy; CV, cyclic voltammetry

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