

High-Performance Photoelectrochemical Cells from Ionic Liquid Electrolyte in Methyl-Terminated Silicon Nanowire Arrays

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In high-efficient silicon solar cells, in order to ensure collection of the photo-generated charge carriers before recombination, minority-carrier diffusion length needs to be compatible with the ultralong absorption optical depth (up to 200 μm) which is associated with the indirect band gap semiconductor properties.¹

Highly purified crystalline as well as thick absorption sheet is required to provide the basis for this high-efficiency planar silicon solar cell.² Silicon nanowire arrays (SiNWs) are an attractive alternative to this planar one due to their unique properties.^{3–10} First, SiNWs can provide a long optical path for efficient light harvesting along the axial direction, and photogenerated carriers only need diffuse short distance along the radial direction to be collected, decreasing the charge recombination velocity.^{11–13} Second, SiNWs have advantageous optical properties for light harvesting, including extended near-infrared absorption and enhanced light-trap capability. Compared with planar-sheet absorbers, SiNWs have effective optical concentration over a wide range of incident angles.^{14–18} In that case, SiNWs fabricated from low-purity silicon, with a short minority-carrier length associated with thin-sheet absorber, could achieve a high-performance solar cell. They afford new opportunities to improve the solar power conversion efficiency (PCE) and to reduce their costs.¹⁹ Indeed, in principle, the mathematical model has predicted that the radial-junction geometry solar cell could achieve PCE greater than 10% even when

ABSTRACT Photoelectrochemical (PEC) cells based on silicon nanowire arrays (SiNWs) have, to date, exhibited modest power conversion efficiency (PCE) and suffered serious degradation, though they exhibit advantageous properties of charge-transfer/transport properties at the radial-junction and strong light-trap capabilities. The main challenge for this low-cost PEC cell is the surface photooxidation and photocorrosion of the silicon surface when contacting with the electrolyte. In this report, SiNWs derivatized with covalently attached methyl groups, prepared *via* a two-step chlorination/methylation procedure, demonstrate excellent stability even in the presence of water. Furthermore, SiNWs PEC cells utilizing a room temperature ion liquid (IL) acting as an electrolyte solvent display neglectable surface oxidation. A PEC cell based on a platinum (Pt) nanodots decorated and methylated ($-\text{CH}_3$) SiNWs electrode in combination with an IL electrolyte yields a PCE of 6.0% and shows excellent stability under simulated air mass (AM) 1.5 solar spectrum irradiation, while the PCE of a PEC cell based on planar silicon only exhibits 0.003%. The inherent performance of these structures indicates that a $-\text{CH}_3$ (Pt) SiNWs electrode in combination with an IL is a new approach to develop a high-performance and low-cost solar cell.

KEYWORDS: silicon nanowire arrays · ionic liquid electrolyte · photoelectrochemical cell · surface derivation

using silicon with a minority-carrier length less than 10 μm .¹

High-density and large-area wafer-scale SiNWs are generally fabricated by use of potentially inexpensive techniques, such as metal-assisted electroless etching.^{20,21} To date, the performances of the low-cost photoelectrochemical (PEC) cells based on SiNWs are generally modest. The highest efficiency of a PEC cell with the PCE of 8.1% can be achieved from a SiNWs electrode in which hydrogen bromide (HBr)/bromine (Br_2) in aqueous solution act as the redox pair.²² It has been demonstrated that SiNWs are rather photoactive, affording a high potential for inexpensive cells. However, the aqueous concentrated HBr/ Br_2 electrolyte is toxic, corrosive, and volatile, and water

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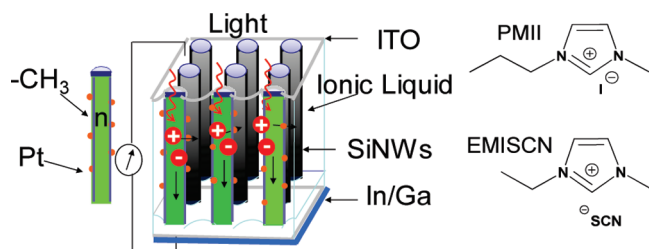


Figure 1. Schematic drawing of the PEC cell structure using SiNWs as electrode. The vertical SiNWs surface is covalently attached by methyl groups and decorated with Pt nanodots. The space between SiNWs is filled with electrolyte. Light passes through the top transparent electrode (ITO-coated glass) and is absorbed along wire path. The produced minority-carrier holes can diffuse readily to the silicon/IL interface. The molecular structures of ILs utilized for PEC cell are shown in the right side.

could attack the silicon surface, leading to its oxidation. An alternative less-volatile electrolyte, such as an aqueous methyl viologen^{2+/+} electrolyte, is developed but only a very limited PCE of 3% can be observed.⁷ For planar silicon PEC cells, ferrocene^{0/+} and their derivatives in methanol, acetonitrile and water have been exploited to achieve a promising PCE.^{23–26} However, all these devices suffer from serious stability issues. The device performances decay very quickly under light illumination because the hydrogen terminated (–H) silicon surface is susceptible to be photocorrosive and photooxidized when contacting with the electrolyte, leading to a very short lifetime of the device. In addition, electrolytes containing acetonitrile and methanol are volatile and flammable in the PEC cell vessel, which are not easily operated in a practical application.

Room temperature ionic liquid (IL) is an organic salt presenting liquid status at or near room temperature, showing many attractive properties, such as good chemical and thermal stability, negligible vapor pressure, nonflammability, high conductivity, and a wide electrochemical window.²⁷ Since the discovery of air-stable IL, various ILs have been explored for applications, such as solvents for green synthesis, lubricants, and catalysts. The physical and chemical properties of ILs could be tuned *via* varying the nature of cations and anions. They have been employed as benign alternative electrolytes/solvents for dye sensitized PEC cells, and over 8% PCE is attained.²⁸ This offers a practical advantage, for example, in realizing devices using IL elec-

trolytes instead of volatile molecular solvents which would permeate across the cell walls or would even cause an explosion.

In 1980s, the n-GaAs PEC cell with molten salt aluminum chloride–butylpyridinium chloride as an electrolyte typically showed a PCE of ~1% under illumination with a tungsten lamp at 40 mW cm⁻².²⁹ Based on our best knowledge, there is no further report on this non-aqueous electrolyte IL used in a semiconductor PEC cell, except the widely investigated mesoscopic dye-sensitized solar cells.²⁸

In this report, this ‘green solvent’ IL combined with SiNWs as a photoelectrode is explored in order to evaluate the possibility of achieving a stable and efficient solar cell. Methyl (–CH₃) groups are anchored onto the SiNWs surface in order to passivate dangling silicon bonds so as to suppress the photocorrosion and photooxidation. Platinum (Pt) nanodots, acting as an effective catalyst for interfacial carrier transfer, are decorated on the SiNWs surface. The PEC cell based on –CH₃ terminated as well as Pt nanodots decorated (–CH₃ (Pt)) SiNWs in combination an IL mixture acting as an electrolyte solvent has achieved a PCE of 6.0% under simulated air mass (AM) 1.5 solar spectrum illumination (see Figure 1). These explored results point toward a new avenue that could be utilized profitably in the area of energy conversion.

RESULTS AND DISCUSSION

Characterization of SiNWs. Large-scale and high-density oriented SiNWs are fabricated on a silicon wafer through electroless etching, followed from a previous method.^{20,21} The SiNWs demonstrate strong light-trapping properties in comparison with the planar one, as shown in Figure 2s of Supporting Information. The reflectivity light ratio is dramatically suppressed in this SiNWs structure, which is consistent with the performance of SiNWs fabricated by an alternative method, such as a vapor–liquid–solid growth process.³⁰ The top-view and cross-section scanning electron microscopy (SEM) images of SiNWs are shown in Figure 2. The diameter distribution of SiNWs is in the range of 50 nm to 1 μm, and the length is about 18 μm. Light can be absorbed along the long axis path, whereas the minority carrier only needs to diffuse a short distance

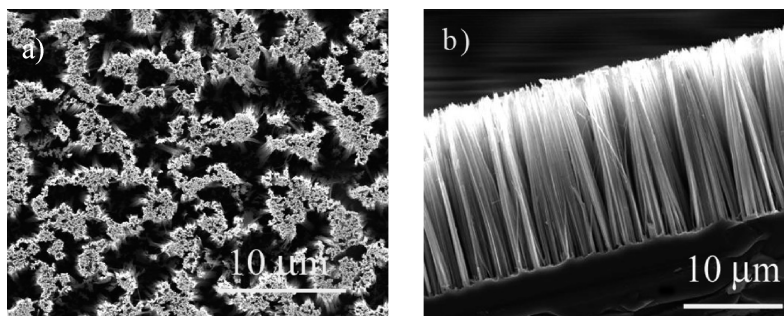


Figure 2. Scanning electron microscope images showing the top- (a) and cross- (b) view of SiNWs.

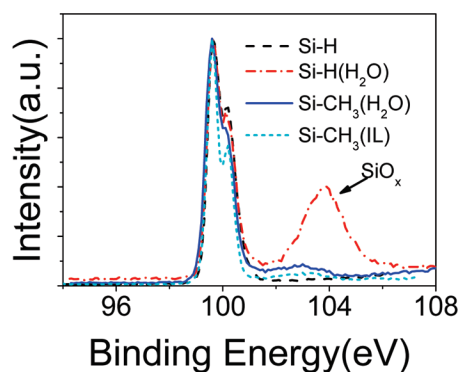


Figure 3. XPS measurements (in eV) of freshly prepared $-H$ SiNWs (dash line), $-H$ SiNWs immersing in water for 24 h (dash-dot line), $-CH_3$ SiNWs immersed in water for 24 h (solid line), and $-CH_3$ SiNWs immersing in a mixed IL (PMII: EMISCN = 13:7) for 24 h (dot line).

along the radial direction to be collected. Thus, in principle, low-purity SiNWs with a minority-carrier distance as short as 10 μm can achieve high efficient solar cells.¹ However, in previous studies, PEC cells based on SiNWs only provide limited PCE and exhibit poor device stability.^{7,22} The reason is that silicon photoelectrodes are susceptible to be oxidized into insulating SiO_x when contacting with water.³¹ Different SiO_x layers will give different barrier heights at the silicon surface, which leads to dramatic variation of the charge-transfer/transport properties. Meanwhile, a large number of dangling silicon bonds could also act as charge recombination centers at the surface.³² In that, in order to investigate silicon-molecule electronics, we need reproducible, high-yield preparations of device systems that allow reliable and reproducible data collection.³³ Only in this way can we investigate how the molecule/silicon interface affects or even dictates charge-transfer and -transport in the PEC cell. Therefore, surface modification plays a crucial role to evaluate the possibility of utilizing IL in SiNWs PEC cell.

Silicon Surface Decoration. Perfect surface passivation of dangling silicon bonds can be obtained by hydrogen termination.³¹ However, it only exhibits rather limited chemical stability. After hydrogen termination, the silicon electrode could still react with water and form insulating SiO_x in the electrolyte, which not only contributes to increase the series resistance by exhibiting a tunneling barrier to the interfacial charge transfer but also generally yields surface states that increase the charge recombination velocity, both leading to a decrease in the photovoltage of the silicon/electrolyte device.³⁴ As shown in Figure 3, no detectable SiO_x is observed in the freshly prepared $-H$ SiNWs by X-ray photoelectron spectroscopy (XPS) measurement. Once the $-H$ SiNWs are dipped into water, a strong SiO_x signal is obtained. In previous studies, electrolytes using water as a solvent were involved in serious photocorrosion, thus leading to permanent device degradation.²³

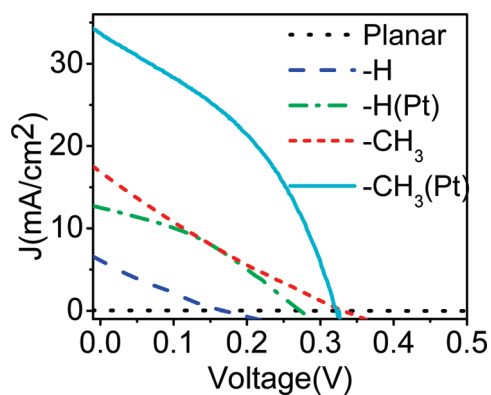


Figure 4. Current density versus voltage responses under simulated AM 1.5 solar spectrum irradiation at 100 mW cm^{-2} for cells with various electrodes: planar silicon (dot line), $-H$ SiNWs (dash line), $-H$ (Pt) SiNWs (dash-dot line), $-CH_3$ SiNWs (short dashed line), and $-CH_3$ (Pt) SiNWs (solid line).

Surface-grafted molecules can provide full saturation of silicon dangling bonds associated with stable chemical properties. Direct Si-C bonding is expected to provide excellent stability. The methyl group is one of few groups whose small size in principle allows mostly passivation of dangling bonds.^{34,35} Here methyl groups are anchored onto SiNWs surface *via* a two-step chlorination/alkylation route in Grignard reagent. In XPS measurement, the SiO_x signal for $-CH_3$ SiNWs dramatically decreases in comparison with $-H$ ones when contacting with water, as shown in Figure 3. It indicates that methyl groups can prevent water from attacking the silicon surface. However, water is still not advisable as an electrolyte solvent since it still can cause instability of the silicon surface after a period of time. Nonaqueous ILs thus may be excellent alternative candidates to act as electrolyte solvents for SiNWs PEC cells. As it is expected, the SiO_x formation is dramatically suppressed when SiNWs are contacting with IL, confirmed by XPS measurement, as shown in Figure 3.

PEC Cells Based on Silicon Substrate. The photovoltaic characteristics of different silicon electrodes contacting with IL are investigated. A mixed IL electrolyte is utilized in order to obtain the lowest viscosity of the electrolyte as well as the excellent solubility of the redox I^-/I_3^- pair.²⁸ There are two crucial roles of the ILs in the charge-transfer process. First, ILs act as an excellent solvent media for the I^-/I_3^- pair in order to realize the redox pair physical diffusion. Meanwhile, IL PMII also can afford partial I^- ions for the redox pair. Figure 4 shows the current density (J) – applied potential (V) behaviors of planar silicon and SiNWs with different surface modification, in contact with the IL electrolyte under the simulated AM 1.5 solar spectrum irradiation at 100 mW cm^{-2} , and the photovoltaic parameters are summarized in Table 1. For the planar silicon sheet, with low surface/volume ratio, the electrode yields a low short-circuit current densities (J_{sc}) of 0.042 mA cm^{-2} , open-circuit voltage (V_{oc}) of 0.281 V , fill factor (FF) of 0.27 , and PCE of 0.003% . In comparison to the planar ones, the

TABLE 1. J - V Properties of Planar $-H$ Si, $-H$ SiNWs, $-CH_3$ SiNWs, $-H$ (Pt) SiNWs, and $-CH_3$ (Pt) SiNWs in Contact with IL Electrolyte under Simulated AM 1.5 Solar Spectrum Irradiation at 100 mW cm^{-2}

electrodes	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)
planar Si $-H$	0.282	0.042	0.27	0.003
Si NW $-H$	0.167	6.09	0.23	0.22
Si NW $-CH_3$	0.330	16.8	0.22	1.2
Si NW (Pt)	0.272	12.5	0.35	1.2
Si NW $-CH_3$ (Pt)	0.322	33.7	0.40	4.3

surface area could increase by a factor of at least approximately 40 for SiNWs (diameter = $\sim 1 \mu\text{m}$ and length = $\sim 18 \mu\text{m}$) electrodes. Under the same conditions, $-H$ SiNWs electrode exhibits $J_{sc} = 6.09 \text{ mA cm}^{-2}$, $V_{oc} = 0.167 \text{ V}$, FF = 0.33, and PCE = 0.22%. The performance of $-H$ SiNWs electrode is much better than that of the planar one. This observation is quite different from the previous reports on silicon PEC cells based on methanol or water used as electrolyte.^{22,36} The difference could be explained by the diffusion process. In previous systems, both planar silicon and SiNWs can exhibit comparable PCE when the electrolyte is quickly stirred in a large reaction cell. Quickly stirring the solution can guarantee a sufficient chemical diffusion velocity which offers efficient mass transport of redox species, while in our system, the electrolyte is not stirred. In addition, methanol and water display a lower viscosity than that of the present IL electrolyte, which also enhance the charge transport. Further investigation is under way to verify this process. However, the previous PEC cells obviously face serious challenges to practical application. In our system, the thin IL layer between two electrodes (approximately $10 \mu\text{m}$) compensates the disadvantages of viscosity and volatility issues as well as avoiding stirring solution.

Compared with planar electrodes, $-H$ SiNWs electrodes provide a larger interface area for charge transfer and exhibit a lower V_{oc} . The decrease of V_{oc} versus the increase of interface area could be explained by the fact that the electrode with high junction area per unit will produce a lower charge-carrier flux from a fixed intensity light illumination source³⁶ and that V_{oc} can be affected by the quasi-Fermi level, which is set by position of the steady-state charge-carrier concentrations, while the steady-state charge-carrier concentrations are in turn determined by photocarriers per junction area. Because the minority carriers are capable of being transferred across all of the exposed radial junction area, for a large interface junction area, the quasi-Fermi level becomes negative (for n-type silicon) due to the lower photocarriers concentration, then V_{oc} is reduced. In contrast, the J_{sc} dramatically increases for $-H$ SiNWs electrode.

Methylation provides a convenient way for surface passivation of dangling silicon bonds, it not only suppresses charge recombination at the interface but also

decreases the leakage current due to the insulating properties of methyl groups. Under the simulated AM 1.5 solar spectrum irradiation at 100 mW cm^{-2} , the $-CH_3$ SiNWs electrode displays $J_{sc} = 16.8 \text{ mA cm}^{-2}$, $V_{oc} = 0.330 \text{ V}$, FF = 0.22, and PCE = 1.21%. The performance of the cell is improved. This result is consistent with the result of PEC cell based on methylated n-Si in aqueous solution consisted of $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$, where the alkyl-terminated silicon surfaces consistently showed excellent current density potential characteristics.³⁴ However, it is in contrast to the result of Nakato *et al.* who report rather poor performance with methylated n-Si in an aqueous HBr/Br₂ electrolyte.³⁷ In their report, they claim that the difference with and without methylation passivation might arise from the fact that the oxidation of $[\text{Fe}(\text{CN})_6]^{4-}$ in water at the silicon surface is caused by a simple electron-transfer process. In contrast, this simple electron transfer does not fit for the PEC cell based on the silicon electrode employing the HBr/Br₂ pair. They believe that the methyl groups hinder the absorption of Br⁻ in aqueous solution, which is essential for the oxidation thus leading to a dramatic decrease in the oxidation efficiency. However, it is still unclear in our case since IL is a novel electrolyte for silicon PEC cells. We surmise that the main role of the methyl groups anchored onto the surface is to suppress the charge recombination in this system, which is consistent with the previous reported chemical model that strong chemical bonds at the semiconductor solid/liquid interface can prevent gap states from involving charge recombination.^{38,39} This idea is also verified in a nonaqueous silicon/electrolyte system, where an ultrathin SiO_x layer formation can be rather effective on n-Si/methanol interface.⁴⁰ The chemical passivation provides ideal junctions for silicon solar cells which are limited only by bulk-diffusion recombination inherent to silicon itself.

It is worth mentioning that PEC cells based on $-CH_3$ SiNWs electrodes display a higher V_{oc} than that of their undecorated counterparts, which is caused by formation of the barrier height resulting from the surface modified with methyl groups. As measured by XPS in previous works, the electron affinity of $-H$ Si surface changed from 4.04 eV ⁴¹ to 3.67 eV of $-CH_3$ surface.⁴² The barrier height changed by $\sim 0.5 \text{ V}$ for methylated n-Si (111) surface, relative to $-H$ Si(111) surface. The maximum output potential is proportional to this barrier height, which leads to V_{oc} enhancement in PEC cells based on $-CH_3$ SiNWs. This observation of the V_{oc} increase after methyl termination is consistent with the results that output potential enhances for mercury contacting with short-chain terminated silicon surface.⁴²

Ultrafine Pt nanodots have been explored to enhance planar silicon PEC cells *via* its 'catalyst effect' as well as SiNWs ones.^{22,37,43,44} Under the same condition, Pt nanodot decorated $-H$ ($-H$ (Pt)) SiNWs electrode provides $J_{sc} = 12.5 \text{ mA cm}^{-2}$, $V_{oc} = 0.272 \text{ V}$, FF = 0.35,

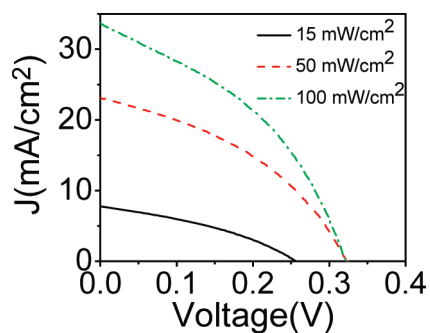


Figure 5. Current density versus voltage responses for a device using $-\text{CH}_3$ (Pt) SiNWs as an electrode under simulated AM 1.5 solar spectrum irradiation with different light intensity: 15 (solid line), 50 (dash line), and 100 mW cm^{-2} (dash-dot line).

and PCE = 1.20%. The lost voltage of Pt nanodots decorated electrode may be attributed to the higher overpotential which results from a higher increase in photocurrent density at the electrode. Significantly, decoration of Pt nanodots also enhances FF. Notably, the electrode with Pt nanodots decoration in combination with methyl termination shows the largest PCE. Under simulated AM 1.5 solar spectrum irradiation at 100 mW cm^{-2} , $-\text{CH}_3$ (Pt) SiNWs electrode provides $J_{sc} = 33.7 \text{ mA cm}^{-2}$, $V_{oc} = 0.322 \text{ V}$, FF = 0.40, and PCE = 4.3% in a nonoptimized PEC cell. The Pt nanodots decorated onto SiNWs surface are confirmed by transmission electron microscopy (TEM) image, as shown in Figure 3s of Supporting Information. The size of Pt nanodots is in the range of 3–7 nm, which is consistent with the previous reports where Pt nanodots with a size of approximately 10 nm have demonstrated high photocatalyst performance.^{43,44} Figure 5 displays J – V behaviors of a $-\text{CH}_3$ (Pt) SiNWs device under AM 1.5 illumination with a different light intensity. Under a light intensity of 50 mW cm^{-2} , $-\text{CH}_3$ (Pt) SiNWs electrode yields $J_{sc} = 23.2 \text{ mA cm}^{-2}$, $V_{oc} = 0.322 \text{ V}$, FF = 0.40, and PCE = 6.0%, which is ascribed to several unique advantages of SiNWs geometry associated with strong suppression of light reflection in the range of 300–1100 nm.³ First, the SiNWs electrode, yielding large interface area, is beneficial to charge transfer since photogenerated minority carriers only need to travel a shorter distance to be collected, thus leading to a higher carrier-collection efficiency. Second, methyl groups provide dangling silicon bond passivation associated with an IL electrolyte so as to suppress charge recombination. Third, the Pt nanodots would act as a catalyst on the SiNWs surfaces, enhancing the photocurrent. However, the PCE drops with light intensity increasing to 100 mW cm^{-2} , the highest PCE is derived from the condition of 50 mW cm^{-2} light intensity illumination, as shown in Table 2. The decrease of J_{sc} attributes to the PCE drop with 100 mW cm^{-2} light intensity illumination. For a liquid electrolyte PEC cell, the J_{sc} is generally limited by mass transport of the redox species. Under illuminating, the photogenerated hole immediately receives an electron

TABLE 2. J – V Properties of $-\text{CH}_3$ (Pt) SiNWs in Contact with IL Electrolyte Under AM 1.5 Solar Spectrum Irradiation with Different Light Intensities of 15, 50, and 100 mW cm^{-2}

light Intensity (mW cm^{-2})	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)
15	0.257	7.8	0.36	4.7
50	0.322	23.2	0.40	6.0
100	0.322	33.7	0.40	4.3

from an I^- ion, turning the I^- ion to an I_3^- ion, followed by the I_3^- ion diffusing to the counter electrode. Nevertheless, when the saturated stage appears, due to the limited conductivity and the higher viscosity of the electrolyte, keeping the improvement of the light intensity, the electrolyte cannot efficiently afford the electron to the photogenerated hole and cannot promptly transfer charges to the counter electrode. In addition, the modest value of FF leads to the lower PCE at a higher light intensity, which may be ascribed to the fact that IL does not totally fill up the space of the SiNWs, leading to a partial silicon/liquid contacting problem. Although IL is higher in viscosity than those of widely used solvents, such as water and methanol, the J_{sc} of the cell exhibits a rather promising value, higher than that of the PEC cell based on water or methanol as an electrolyte.^{7,22} Now, the PCE of the present $-\text{CH}_3$ (Pt) SiNWs electrode is limited by poor V_{oc} and modest FF, however, the decrease in V_{oc} with increasing radial-junction area could be solved by proper selection of redox systems. A larger V_{oc} of 0.6–0.7 V could be possible if redox pairs are optimized, which could presently achieve a three-fold efficiency up to 10–15%. In addition, a complete IL fill-up of the SiNWs space through density control could dramatically improve FF *via* playing the fill fraction ratio of SiNWs. It is worth mentioning that the PEC cell based on $-\text{CH}_3$ planar silicon decorated with Pt nanodots and employing an IL electrolyte only displays poor performance (PCE of 0.5%), as shown in Figure 4s of Supporting Information, which indicates that a nanowire array plays an important role on PEC cells.

Stability Issue of PEC cells. Stability is an important issue for SiNWs PEC cells in future practical applications. A perennial problem in the efficient semiconductor PEC cell is the semiconductor electrode corrosion, particularly the cell employing aqueous electrolyte. Various strategies have been adopted to tackle this challenge, and most investigations have been focused on the semiconductor surface modification.^{34,37} The majority disadvantage of the efficient semiconductor PEC cells is that they involve the aqueous electrolyte, and there is always a possibility for water penetrating to the semiconductor layer across the thin decoration layer (<10 nm). The use of a nonaqueous electrolyte in replace of an aqueous one is a more profitable approach to deal with this problem. The nonaqueous solvent electrolyte, *i.e.*, ace-

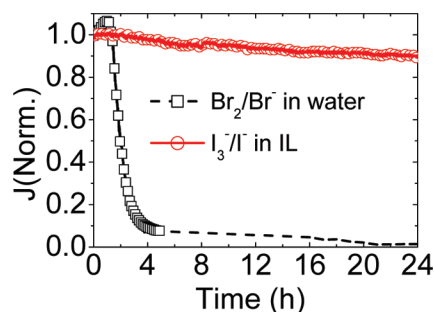


Figure 6. Normalized J_{sc} versus time responses of $-CH_3$ SiNWs electrode under simulated AM 1.5 solar spectrum irradiation at 100 mW cm^{-2} using different electrolytes: I_3^-/I^- in IL liquid (solid line) and Br_2/Br^- in water (dash line).

tonitrile²⁴ and methanol,^{25,45} has been demonstrated for the feasibility of converting sunlight to electricity. However, these volatile organic solvents could also face great challenges for their flammability and possible permeation across the device seal wall.²⁸ In contrast, as being verified in a dye-sensitized solar cell,²⁸ solvent free IL, which is thermally and chemically stable, with negligible vapor pressure, should be an excellent electrolyte solution used as in semiconductor PEC cell. Figure 6 displays the normalized J_{sc} responses of I_3^-/I^- in IL liquid (solid line) and Br_2/Br^- in water (dash line) versus time under a simulated AM 1.5 solar spectrum irradiation at 100 mW cm^{-2} irradiation. As consistent with the previous report, the SiNWs electrode yields very poor stability performance when an aqueous electrolyte is utilized even for the $-CH_3$ terminated electrode. It may be ascribed to a deleterious corrosion reaction undergone by the silicon electrode once in contact with an

aqueous electrolyte, as verified by our XPS measurement, where SiO_x is formed as $-CH_3$ silicon dipping into water for 24 h. Another reason may be the volatilization of the electrolyte consisting of Br_2/Br^- . In contrast, if IL is used for the electrolyte solvent, then the methylated electrode yields a much more stable behavior. The depicted stability clearly attests that $-CH_3$ silicon combined with IL improves the resistance to photocorrosion and photooxidation.

CONCLUSION

The combination of ion liquid (IL) electrolyte and $-CH_3$ termination as well as Pt nanodots decoration onto a silicon nanowire arrays (SiNWs) electrode provides a convenient system for evaluating the advantageous properties of ordered SiNWs utilized in PEC cells. The above data clearly illustrate that the two-step chlorination/methylation procedure can passivate dangling bonds, which not only prevents the formation of a substantially thick insulating oxide layer but also decreases the charge recombination velocity at the interface. ILs, acting as electrolyte solvents, afford solar cell functionalizing as well as allow SiNWs to preserve advantageous stability. In addition, Pt nanodots could offer high charge-transfer properties at the interface. Introduction of an IL electrolyte into the cell of the $-CH_3$ SiNWs, followed by Pt nanodots decoration, the PCE of the PEC cell attains 6.0%, while the PCE of a planar silicon PEC cell is only 0.003%. The combination techniques thus open a new avenue to achieve high-performance SiNWs solar cell based on the low-purity silicon wafer.

METHODS

Materials. Hydrofluoric acid (HF), hydrogen bromide (HBr), tetrahydrofuran (THF), and phosphorus pentachloride (PCl_5) are purchased from Sinopharm Chemical Reagent Co., Ltd. Deionized (DI) water with the resistivity of $18 \text{ M}\Omega \cdot \text{cm}^{-1}$ is supplied by a Nanopure Diamond system. Methyl magnesium chloride ($MgCH_2Cl$) in THF, lithium iodide (LiI), iodine, and bromine liquid are purchased from Alfa Aesar and used as received. Hexachloroplatinic (IV) acid (H_2PtCl_6) is provided by Aldrich. The 1-propyl-3-methylimidazolium iodide (PMII) and the 1-ethyl-3-methylimidazolium thiocyanate (EMISCN) are purchased from Shanghai Chengjie Chemical Co., Ltd. and carefully dehydrated. All the organic solvents are anhydrous. Indium tin oxide (ITO)-coated glass and fluorine-doped tin oxide overlayer (FTO) glass are commercially available with a sheet resistance $\sim 10 \Omega/\text{sq}$.

SiNWs Growth. Silicon wafers (n-doped, 100) with a resistivity of $1-5 \Omega \cdot \text{cm}$ are ultrasonically degreased in acetone and ethanol in sequence, then successively immersed in a boiling solution of $H_2SO_4:H_2O_2$ (5:2) for 15 min. After each cleaning step, the substrates are rinsed with DI water. SiNWs are prepared by immersing the substrate in 5M HF/0.02M $AgNO_3$ solution, according to previous reports.^{20,21} In order to remove the silver dendrites from the nanowire surface, the prepared SiNWs should be immersed in a concentrated HNO_3 solution for at least one hour.

Silicon Surface Modification. The hydrogen terminated ($-H$) Si surface is obtained by dipping a silicon wafer in 5 M HF for 10 min, followed by immersing in DI water for 1 minute. A two-step process is employed to fabricate methyl terminated ($-CH_3$) silicon according to a previous method.^{32,46} The chemical scheme is

illustrated in Figure 1s of Supporting Information. First, the $-H$ SiNWs are immersed in a saturated chlorobenzene solution of PCl_5 at 100°C for 1 h, in which $Si-H$ bonds are transformed into metastable $Si-Cl$ ones. Second, the SiNWs are dipped into $MgCH_2Cl$ in THF solution at 80°C overnight, converting surface $Si-Cl$ bonds to $Si-C$ ones. The substrates are then washed with THF, acetone, and methanol subsequently. All of these processes are operated in a nitrogen-filled glovebox. In order to decorate platinum (Pt) nanodots, SiNWs are immersed in 2 mg/mL ethanol H_2PtCl_6 solution for one minute, dried with nitrogen flowing, and then annealed under nitrogen atmosphere at 200°C for 10 min.

The reflectivity light ratio of the substrates is measured by Perkin-Elmer Lambda 750 with integrating sphere. The morphology of SiNWs is carried out with a FEI Quanta 200 FEG high-resolution SEM. The FEI Tecnai G2 F20 STWIN TEM is used to characterize SiNWs decorated with Pt nanodots. XPS analysis is performed with a Shimadzu ESCA-1000 spectrometer and a KRATOS-AXIS-165 spectrometer using an Mg K-alpha line.

PEC Cell Measurements. The sandwiched two-electrode electrochemical cell for the photovoltaic measurement consists of silicon electrode, counter electrode, spacer, and liquid electrolyte. A schematic of cross-sectional view of the PEC cell is illustrated in Figure 1a. The transparent counter electrodes are prepared by chemically decorating Pt onto the cleaned ITO-coated glass slides via dipping into 2 mg/mL H_2PtCl_6 ethanol solution and then annealing at 300°C for 10 min. Insulating tapes ($10 \mu\text{m}$) are used as a spacer between the SiNWs electrode and the ITO-coated glass.

The electrolyte is composed of 0.05 M I₂ and 0.1 M LiI in a mixed IL (EMISCN:PMII = 7:13, V/V). The chemical structures of PMII and EMISCN are drawn in Figure 1. The conductivity and viscosity of the mixed IL is 1.07×10^{-3} S/cm and 115 cP at the room temperature. Once the electrolyte is loaded, two electrodes are encapsulated with acrylic acid adhesive. Ohmic contacts are obtained on the rear face of the silicon electrode with indium gallium alloy. With HBr/Br₂ used as the redox pair in the aqueous electrolyte, the counter electrode is Pt-decorated FTO-coated glass instead of ITO-coated one because of the high-corrosive properties of the electrolyte. The PEC cell with aqueous solution is fabricated by inserting both silicon and Pt-decorated FTO electrodes in a vessel filled with an electrolyte consisting of HBr/Br₂.

The PEC data is measured under illumination in simulated sunlight provided by a 500 W Oriol solar simulator fitted with an AM 1.5 global filter set as the light source. Light intensity is changed with meshes in front of the light source and measured with a Newport calibrated silicon solar cell 91150. The cell photocurrent density (*J*) vs applied potential (*V*) is measured using a Keithley 2612 digital source meter. The *J*–*V* characteristics of the cell under the light illumination and dark are determined by biasing the cell externally and measuring the generated current. This process is fully automated using Labview software.

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Supporting Information Available: Scheme of two-step methyl group termination of silicon surface, light reflection ratio versus wavelength, TEM image of Pt-decorated methyl terminated SiNWs, and current density versus applied potential of PEC cell based on –CH₃ planar silicon decorated with Pt nanodots and employing IL electrolyte. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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