

Stabilizing inorganic photoelectrodes for efficient solar-to-chemical energy conversion†

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An efficient, inexpensive and stable photosynthetic material system that absorbs sunlight and uses the absorbed energy to electrochemically produce chemical and fuel products including hydrogen requires photoelectrode assemblies that are stable in electrolytes. Here we report a photoelectrochemical/ photosynthetic cell based on inorganic semiconductor photoelectrodes that shows the long-term operational stability necessary for the production of solar fuels and chemicals. The cell's stability is achieved by forming an active device using an inexpensive spin casted (20 nm) transparent conducting polymer coating (poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)). PEDOT:PSS protects the photoelectrodes from photoelectrochemical corrosion and functionally serve as either a Schottky contact or as an efficient hole transport layer depending upon the choice and design of the underlying semiconductor heterostructure. Coated semiconductors were assessed both as photoelectrochemical and as freestanding, "autonomous" photosynthetic units and found to be stable for over 12 hours (for wired configuration) in corrosive electrolytes. The solar-to-chemical conversion efficiencies match or exceed devices with more expensive metal-based coatings. Furthermore, the PEDOT:PSS was found to have high electrocatalytic activity, thus no additional electrocatalyst was required. The results suggest a pathway to large scale, inexpensive, hybrid organic-inorganic solar-to-chemical energy conversion systems.

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Broader context

Artificial photosynthesis and photoelectrocatalysis has been considered since the early 1900's as a means of harnessing the sun's energy. Enormous effort has been spent by a variety of researchers exploring many possible approaches; however, all attempts have been hindered by several factors: (1) lack of inexpensive material systems with a high efficiency for solar spectrum light absorbance and conversion, and/or (2) photocorrosion of active photoelectrodes. For example, TiO₂ has been investigated more than any other material for photoelectrocatalysis. It is a wide bandgap semiconductor and absorbs only ultraviolet light efficiently; even with modifications the best overall solar-to-chemical efficiencies have been less than 1–2%. Highly efficient (>10%) photoelectrochemical systems based on narrow-band gap semiconductors have been made, however; these device structures operate only for short periods of time or rely on exotic processes to protect them for stable operation. We show in this paper that PEDOT:PSS, a solution processable, inexpensive, transparent conducting polymer can be effectively used as a stable coating material for high-efficiency semiconducting light absorbers. The results may provide a platform for the development of a new group of inexpensive, earth abundant, stable coating materials and functional heterostructures for cost effective artificial solar photosynthesis.

1 Introduction

Photoelectrochemical (PEC) conversion using sunlight to drive redox reactions for the production of fuels and chemicals has been investigated for decades.^{1–10} In the solar PEC process sunlight is absorbed and excites electron-hole pairs, which are separated and their electrochemical potential used to perform reduction and oxidation reactions at cathodic and anodic interfaces with electrolytes. One of the most studied

PEC reactions has been "water splitting" using inorganic semiconductors as absorbers to convert sunlight into charge carriers with sufficient electrochemical potential to electrolyze water and evolve molecular hydrogen at a cathode and molecular oxygen at an anode. Frequently, the semiconducting absorber is a distinct material that transfers electrons to a hydrogen evolution electrocatalyst and holes to an oxygen evolution electrocatalyst to maximize efficiency by reducing the overpotential for the respective reactions. Alternative hydrogen evolving PEC reactions oxidize alternative species such as hydrocarbons or hydrogen halides instead of water and evolved hydrogen by reducing water or hydrogen ions.¹¹

In the laboratory, cells that approach theoretical limiting conversion efficiencies have been produced; however, they are

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all either extraordinarily expensive or unstable and operate for only short periods of time.^{12–14} All of the previously reported high efficiency cells were based on high quality semiconductors such as sulfides, arsenides and phosphides that are not stable in most electrolytes. In addition, an upper ceiling of an overall system cost of 150 per m² exists (assuming a sustainable 10% efficient solar-to-hydrogen conversion) due to the basic technoeconomics of H₂ as a product.¹⁵ As a result no commercial chemical/fuel producing PEC system has so far been reported despite the appearance of increasingly efficient and cost-effective photovoltaics based on semiconductors such as Si, Cu₂S, CdSe, CdTe, and Cu₂ZnSnS₄. A major challenge is inexpensively stabilizing these high efficiency materials against photocorrosion when operating in the electrochemical environment of a PEC cell. A particular challenge is on the anode side where photogenerated holes produce highly oxidizing species such as peroxides, O₂, Br₂, I₂, and Cl₂.^{9,16–19} Until recently efforts were focused on finding photoanodes which were themselves stable in the electrolyte, limiting the choices to a few wide bandgap oxide semiconductors such as TiO₂, WO₃, and CeO₂, *etc.* which cannot have sufficient efficiency for cost effective solar energy conversion systems.^{20–23}

Another alternative is to protect high efficiency semiconductors such as silicon, gallium arsenide, sulfides, and phosphides with transparent and electrocatalytically active materials. Several investigators have attempted to protect photoelectrodes using coatings of electrocatalytically active metal thin films, covalent electroactive molecular species, dark photoactive conducting polymers such as polypyrrole, polyaniline, polyacetylene, *etc.*, or by use of less corrosive non-aqueous electrolytes.^{24–34} To date these efforts have not been wholly satisfactory. With coatings of electroactive metal thin films such as platinum, iridium, *etc.* the light absorption at the semiconductor surface is compromised. Furthermore, in addition to their relatively high cost such coatings suffer from poor mechanical adhesion and the challenge of forming the required continuous conformal barrier over complex surface morphologies. Covalent functionalization with stable molecular species can be applied on large scales cost effectively including the methyl termination of Si surfaces and coating semiconductors with electrically conducting dark polymers. However, methyl terminated Si anodes have been shown to be stable for only brief periods of operation under corrosive aqueous environments such as HBr³⁴ and the conducting polymers used thus far suffer from delamination and require further incorporation of expensive electroactive metals for improved stability and efficiency. Dark polymer coatings also reduce light absorption by the underlying semiconductors.

Recently, greater success has been achieved with transparent thin conformal coatings applied on semiconductor electrode surfaces using atomic layer deposition (ALD) of wide band gap oxides.^{35,36} These coatings on silicon and copper oxide films showed sustained PEC operation in aqueous environment under applied bias for long durations. Although ALD is a successful commercial process, it is expensive and difficult to apply over large surface areas. Furthermore, it still requires the

additional step of depositing often-expensive fuel forming catalysts such as iridium and platinum over the ALD coating for efficient operation since the wide gap conducting oxides do not typically function as efficient electrocatalysts.

PEDOT:PSS (poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)) is an inexpensive and easily synthesized and processed optically transparent conducting polymer made of two ionomers. PEDOT:PSS is used as an efficient hole transport layer in organic solar cells and has been investigated recently as transparent Schottky contacts for many semiconductor electrodes.^{37–39} Along with its high chemical stability and high electrical conductivity, the ease of solution processing makes PEDOT:PSS an attractive candidate for large scale conformal coating applications.

Here, we report our efforts to stabilize high efficiency semiconductor photoelectrodes with a conformal coating of PEDOT:PSS. We demonstrate the stabilization of Si and GaAs coated with a ~20 nm PEDOT:PSS film in electrolytes containing bromine and iodine. In addition, PEDOT:PSS exhibits high electrocatalytic activity for production of Br₂ and I₃[–] eliminating the need for otherwise expensive electrocatalysts such as Pt, Ru, Ir, *etc.*

2 Results and discussions

For assessment of the PEDOT:PSS coating, two types of cells were fabricated. The first was a Schottky junction photoelectrolytic cell, where simulated sunlight was used to drive the photoelectrolysis at the n-Si/PEDOT:PSS surface. The photoanode was connected to a dark Pt counter electrode (wired) through an ammeter. The second was fabricated to mimic natural photosynthesis as a free-standing, autonomous, photosynthetically active heterostructure. The light absorption occurs in the photovoltaic structure (p–n GaAs junction) which creates and separates charge carriers for oxidation on the PEDOT:PSS surface and reduction on the Pt surface with no external wires.

2.1 Hybrid photoelectrolytic cell (wired configuration)

As received n-Si wafers were used as photoelectrodes. To achieve conformal coating, ethylene glycol modified PEDOT:PSS (EG-PEDOT:PSS) was spin coated on the polished side of the wafer (see Methods for more details). Apart from its excellent stability and solution processability, the main advantage of EG-PEDOT:PSS is its optical transparency in its conducting state. Fig. 1a shows the number of photons reaching the surface of earth for air mass 1.5 global (AM 1.5G) reference solar spectrum,⁴⁰ the normalized transmission spectra of EG-PEDOT:PSS and silicon. The silicon has a broad absorption range with the red absorption edge of 1200 nm and extending over the entire visible–ultraviolet portion of the spectrum. By contrast, the absorbance of EG-PEDOT:PSS (thickness of 20 nm) is negligible throughout the UV/visible range, transmitting more than 75% of light over the entire solar spectrum. An EG-PEDOT:PSS thickness of only 20 nm was found to be sufficient to stabilize the Si anode.

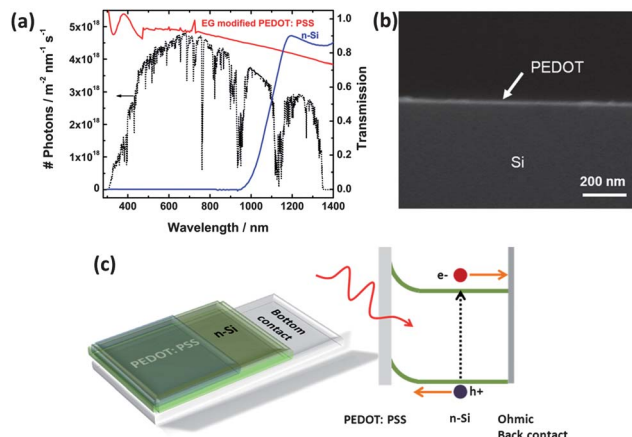


Fig. 1 (a) The photon flux reaching the surface of the earth (black dotted line) calculated from the data for air mass 1.5 solar spectrum obtained from National Renewable Energy Laboratory⁴⁰ with superimposed normalized transmission spectra of EG-PEDOT:PSS (red trace) and of crystalline n-Si wafer (blue trace). (b) Cross-sectional scanning electron microscopic image of an n-Si photoanode with 20 nm thin EG-PEDOT:PSS coating on the top. (c) Schematic of the optimized photoanode device with its corresponding band diagram.

The cross-sectional scanning electron micrograph (SEM) image in Fig. 1b shows the thin EG-PEDOT:PSS polymer coating on the surface of the photoelectrode. No additional electrocatalysts were required for PEC operation hence not compromising the transmission of sunlight to the Si substrate. The PEC properties of the EG-PEDOT:PSS coated Si photoanode were measured using a two electrode configuration. A schematic representation of the PEC photoanode with a corresponding band diagram is shown in Fig. 1c.

Ideally, the protective coating should form a Schottky contact or a staggered type-II band offset with the photoelectrode for efficient extraction of photogenerated carriers. To assess the interfacial contact between the n-Si and EG-PEDOT:PSS, solid state photovoltaic (PV) devices were fabricated. Fig. 2a demonstrates the characteristic J - V performance for n-Si devices with spin coated EG-PEDOT:PSS under air mass 1.5G illumination of 60 mW cm⁻². The n-Si/EG-PEDOT:PSS devices exhibited an open circuit voltage (V_{oc}) of 380 mV, a short circuit photocurrent density (J_{sc}) of 11.5 mA cm⁻², and a fill factor (FF) of 0.63, yielding overall photon conversion efficiency (PCE) of 4.58%. The device-to-device variability was observed to be less than 3% and the data presented here represents the performance of the best devices. It is worth mentioning that, n-Si/EG-PEDOT:PSS devices exhibited superior performance when compared to PV devices made from n-Si substrates with gold or platinum as the Schottky contact (blue trace). This is due to the Fermi level pinning between Pt and n-Si lowering the open circuit voltage considerably, a common drawback for all metal-semiconductor Schottky barrier solar cells.⁴¹

For efficient operation of PEC cells, the stable coating should act as an efficient carrier mediator layer transferring the extracted carriers from the photovoltaic site to the electrochemical reaction site. We benchmarked the electronic transfer kinetics of the EG-PEDOT:PSS films on an ITO electrode using a solution of 10 mM potassium ferricyanide ($K_3[Fe(CN)_6]$) in 1 M

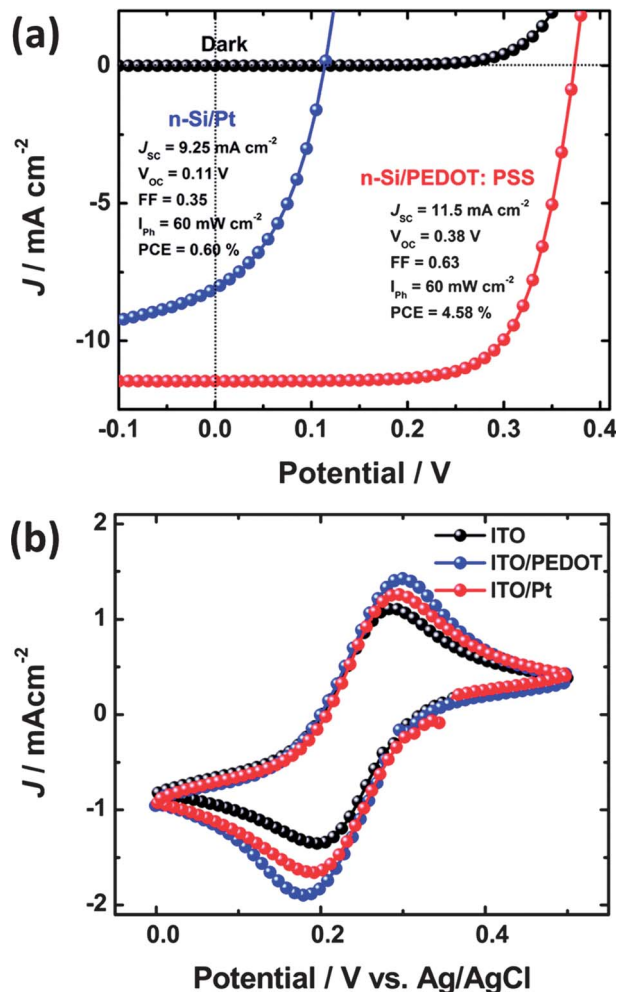


Fig. 2 (a) Comparison of current-voltage curves for n-Si Schottky barrier solar cell with platinum (blue trace) and EG-PEDOT:PSS (red trace) as corresponding Schottky contacts. Aluminum e-beam evaporated at the back served as the Ohmic contact. (b) Cyclic voltammograms (CVs) obtained for different electrodes ITO (black trace), ITO/EG-PEDOT:PSS (blue trace) and ITO/Pt (red trace) at 50 mV s⁻¹ in 0.5 M KCl/10 mM $K_3[Fe(CN)_6]$ solution.

KCl solution (Fig. 2b). The electron transfer kinetics, as measured by the one electron redox couple of $K_3[Fe(CN)_6]$ ($Fe(CN)_6^{3-} + e^- \leftrightarrow Fe(CN)_6^{4-}$) provides a suitable technique to examine the electrochemical activity and is widely used as an electrochemical probe to investigate the characteristics of films on electrode surfaces.

The cyclic voltammetry (CV) of $K_3[Fe(CN)_6]$ at the bare ITO electrode is shown in the black trace of Fig. 2b. The data show the expected reversible electrochemical response for $K_3[Fe(CN)_6]$ with peak separation (the potential difference between the oxidation peak potential and the reduction peak potential) of 85 mV at 100 mV s⁻¹. Coating the ITO electrode with 20 nm layer of PEDOT:PSS polymer film did not compromise the electronic communication between the substrate and the electrolyte. We observed nearly reversible CVs of $K_3[Fe(CN)_6]$ (Fig. 2b, blue trace), and larger peak current and peak separation (115 mV) matching closely that obtained for the bare ITO electrode. Similar responses were obtained for a Pt

catalyzed electrode formed by depositing a 20 nm Pt onto the ITO layer (Fig. 2b, red trace). The increase in peak separation from ITO to ITO/Pt to ITO/EG-PEDOT:PSS is likely due to the contact resistance between ITO and Pt and ITO and spin casted EG-PEDOT:PSS.

Fig. 3 shows bias voltage dependence of the photocurrent of an n-Si/EG-PEDOT:PSS/acidified HI (\sim pH 2)/Pt cell and of an n-Si/EG-PEDOT:PSS/8.4 M HBr/Pt cell. All measurements were made with electrodes maintaining similar surface areas (\sim 0.3 cm²). The current-voltage curves in dark and under simulated illumination of 35 mW cm⁻² show that the electrode performs well in different solutions without a separate catalyst. For aqueous I⁻/I₃⁻, the planar n-Si electrode with no coating exhibits very low short circuit current density (J_{sc} , 0.2 mA cm⁻²), V_{oc} (0.11 V), FF (0.2), and PCE (0.012%). In comparison, the n-Si electrode with EG-PEDOT:PSS coating exhibited much better performance with a high short circuit current density (6.82 mA cm⁻²), V_{oc} (0.29 V), FF (0.45), and PCE of 2.54%. It is worth emphasizing that the above results were obtained for as received n-Si wafers without the additional surface texturing or anti-reflection coating which is typical in commercial photovoltaics to improve efficiency. However, texturing can readily be done on the EG-PEDOT:PSS coated devices if desired. The 2 \times increase in open circuit voltage observed for the EG-PEDOT:PSS coated n-Si electrode compared to the uncoated electrode is due to the formation of a Schottky barrier between the conducting EG-PEDOT:PSS polymer and n-Si electrode. Furthermore, high fill factors observed for the EG-PEDOT:PSS coated Si anode demonstrates its role as an efficient charge carrier. These anodes were active in toxic, corrosive and volatile HBr solution.

The n-Si/EG-PEDOT:PSS/8.4 M HBr/Pt cell at light intensity of 35 mW cm⁻² and operating at bias voltages >0.4 V showed evolution of H₂ bubbles at the Pt cathode and bromine evolution (red liquid) at n-Si/EG-PEDOT:PSS photoanode.

Stability tests for six hours (Fig. 4a) in aqueous electrolyte containing I⁻/I₃⁻ pair (red trace) under continuous

illumination of 35 mW cm⁻² showed no deterioration in short-circuit currents.

The EG-PEDOT:PSS coated Si anodes also displayed remarkable stability in the highly corrosive and toxic HBr solution. Although previous reports of HBr electrolysis have shown high performance of Si electrodes using precious metal coated films, the performance of Si electrodes with non-precious metals such as -CH₃ terminations are unstable indicating the need for expensive metal catalysts for HBr electrolysis.³⁴

The organic EG-PEDOT:PSS polymer coating on n-Si photoanodes demonstrates stable performance for HBr electrolysis in 8.4 M HBr. Fig. 4a, blue trace shows the photocurrent obtained on EG-PEDOT:PSS/n-Si as a function of time over a period of 6 h while being held at a constant potential of 0.6 V *versus* the platinum electrode. Fig. 4b shows the measured potential required for a constant current of 10 mA cm⁻² at the photoanode in HBr solution under illumination with and without the

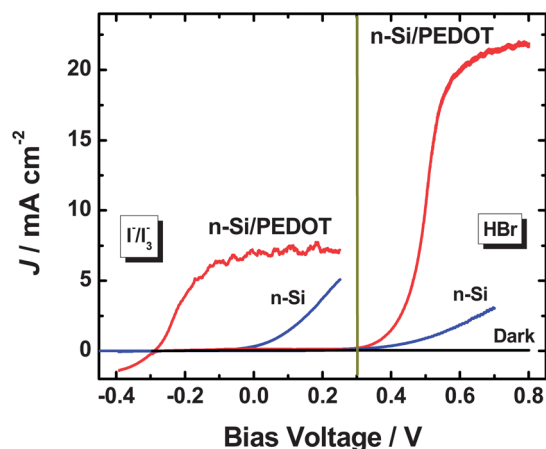


Fig. 3 Bias current-voltage characteristics of n-Si/EG-PEDOT:PSS/acidified HI (\sim pH 2)/Pt and n-Si/EG-PEDOT:PSS/8.4 M HBr/Pt in the dark (black trace) and under 0.35 sun illumination (red trace). Corresponding bias current-voltage curves for n-Si without the EG-PEDOT:PSS coating is shown in blue trace. For all the measurements the setup was a two-electrode system with n-Si as the photoelectrode and Pt foil as the second electrode.

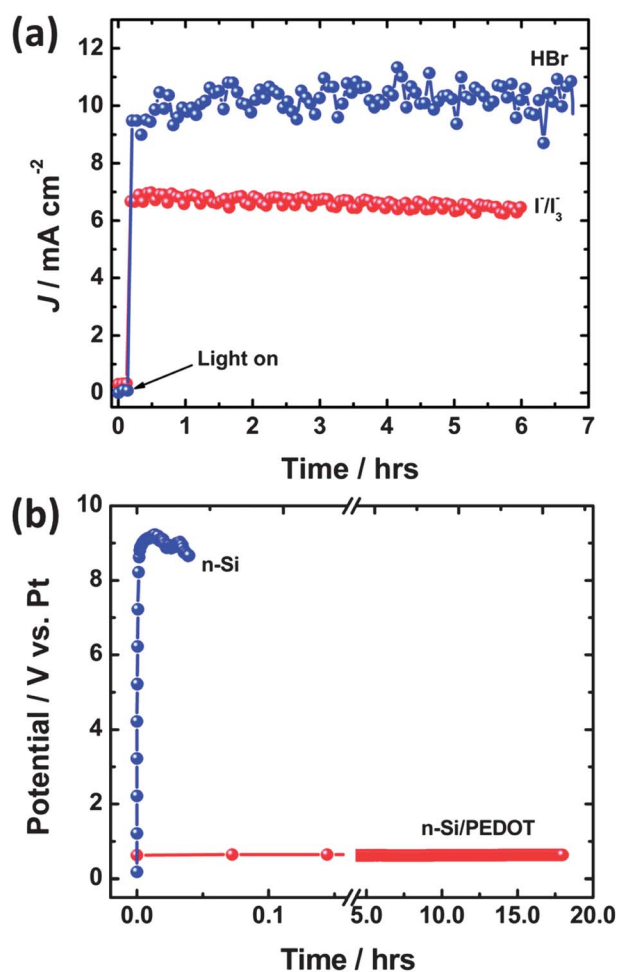


Fig. 4 (a) Photocurrent performance of EG-PEDOT:PSS coated n-Si anode illuminated at 35 mW cm⁻² in I⁻/I₃⁻ redox couple (red trace) and HBr (blue trace). No deterioration in short circuit photocurrents were observed in solution containing I⁻/I₃⁻ redox pair. HBr electrolysis was performed at a bias of 0.6 V with respect to platinum electrode. (b) Constant current stability test for the n-Si photoanode with and without the EG-PEDOT:PSS coating towards HBr under illumination. A constant current of 10 mA cm⁻² was applied for 18 hours.

protective EG-PEDOT:PSS layer. The illuminated uncoated samples failed immediately with voltages reaching the maximum measurable voltage (9 V) to maintain the constant current; whereas the EG-PEDOT:PSS coated samples showed stable photo-voltages for 18 hours of continuous illumination. Raman spectroscopy and SEM were performed on n-Si/EG-PEDOT:PSS films to characterize the nature of the films after 18 hours of photoelectrochemical operation in fuming HBr. No apparent change in the electrode surface was observed by Raman spectra (Fig. S1†) and SEM (Fig. S2†) after this extended irradiation time. X-ray photoelectron spectroscopy (XPS) measurements on the underlying silicon surface (EG-PEDOT:PSS coating was mechanically removed by ultra-sonication) showed strong Si emission and a very small native SiO_x peak (Fig. S3†) indicating that EG-PEDOT:PSS coating can effectively prevent acidic electrolytes from attacking the silicon surface. Photoelectrochemical performance of EG-PEDOT:PSS *versus* untreated PEDOT:PSS coated n-Si anode in fuming HBr is shown in Fig. S4.† The EG-PEDOT:PSS showed superior stability potentially because of its higher reported electrical conductivity and decreased solubility in aqueous media.^{42–44}

2.2 Hybrid artificial photosynthetic cell (wireless configuration)

In order to test the universality of the coating on different semiconductor substrates, we also tested the PEC performance of PEDOT:PSS as transparent conducting coating/electrocatalyst on, highly efficient, single junction optimized p–n GaAs commercial solar cell wafers (Millennium Communication Co Ltd.). The open circuit voltages for these cells were 1 V, sufficient to perform a wireless demonstration of HBr electrolysis. The wireless PEC cell was fabricated by e-beam depositing platinum at the cathode side (n-side) and spin casting EG-PEDOT:PSS on the anode side (p-side). EG-PEDOT:PSS served as both transparent conducting hole transport layer and as an electrocatalyst for bromine evolution.

Upon illumination, clear visual observation of H₂ bubbles on the cathode and bromine evolution at the anode was obtained (Fig. 5a and Movie S1†). With no EG-PEDOT:PSS coating, the cells failed immediately in HBr (Movie S2†). The stability of the artificial photosynthetic unit was assessed by measuring the hydrogen production using a gas chromatograph (GC) column

(Hewlett Packard 5890 Series II) in a closed cell configuration (Fig. 5b). The cell was stable for 6 hours of continuous operation. Long term operation was determined by the stability of the Pt electrocatalyst which was e-beam deposited at the back of the cell for H₂ evolution. It is well known that Pt corrodes during HBr electrolysis. Approaches like using ruthenium sulfide or rhodium sulfide as opposed to Pt for H₂ evolution can be employed to improve the stability of the cells for HBr electrolysis.

3 Conclusions

We have demonstrated that EG-PEDOT:PSS functions as an efficient low-cost protective functional coating material for stabilizing high efficiency inorganic photoanodes against photochemical corrosion, thereby allowing such devices to operate without failure for extended periods of time. The EG-PEDOT:PSS can serve as both the charge extraction layer (Schottky contacts) and as the electrocatalytically active surface for sustained PEC cell operation in aqueous and corrosive solutions. The n-Si PEC device with transparent EG-PEDOT:PSS coating demonstrated a high *V*_{oc} of 0.3 V and a PCE of up to 2.5% with an I[−]/I₃[−] redox pair which is comparable to the reported values of Pt coated n-Si photoanodes. We also found that the PEDOT:PSS electrode exhibits excellent electron transfer kinetics similar to a Pt electrode supporting rapid charge separation/transfer of photogenerated carriers from the photovoltaic unit to the electrochemical reaction site. Significant enhancement of PEC performance is expected through optimization of the photoanode structure and anti-reflection measures (such as nanostructuring/texturing). This was evident when the EG-PEDOT:PSS was used as a coating/electrocatalyst on a highly efficient optimized commercial GaAs solar cell. The ability of the cell to drive the HBr electrolysis without external wiring for sustained periods opens up exciting possibilities for solar chemical and fuel production using inexpensive polymeric materials. This result points the way to large scale, inexpensive, hybrid organic–inorganic solar-to-chemical conversion systems.

4 Experimental

4.1 Photoanode fabrication

As received phosphorous doped n-Si wafers (n-Si, P doped, 1.0 to 10.0 Ω cm, and 432–533 μm thickness) were used as photoelectrodes. The substrates were treated with buffered HF to remove native oxide layer before any further processing. To achieve conformal coating, PEDOT:PSS (Clevios PH500) in 5 v/v % dimethyl sulfoxide (DMSO) was spin coated on the polished side of the wafer, followed by annealing in air at 120 °C for 10 minutes to evaporate the water molecules in the polymer. Since the spin casted PEDOT:PSS film is water-soluble, the surface of the film needs to be further modified to prevent delamination effects during electrolysis. As a post synthesis processing step the spin casted PEDOT:PSS films were immersed in ethylene glycol (EG) for 3 minutes that renders the polymer film water-insoluble and has been reported to increase its electrical conductivity and electrochemical activity.^{42–44} The increase in

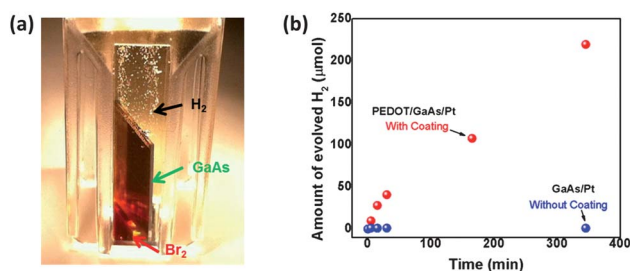


Fig. 5 (a) Digital photograph of a Pt/GaAs/PEDOT:PSS wireless cell under 2 sun illumination evolving H₂ bubbles at the cathode side (black arrow) and Br₂ liquid (red arrow) on the anode side. Green arrow indicates the GaAs solar cell wafer. (b) GC data for wireless PEDOT:PSS/GaAs/Pt cell under 0.7 sun illumination in 8.4 M HBr.

electrical conductivity with EG treatment was credited to the removal of insulating PSS chains from the surface of PEDOT and also due to increase in crystallinity.^{42–44} The samples were annealed in vacuum at 120 °C for 10–30 minutes to completely remove any traces of ethylene glycol. Aluminum was e-beam evaporated at the backside for Ohmic contacts. Raman spectroscopy was used to investigate the characteristics of untreated PEDOT:PSS films and ethylene glycol modified PEDOT:PSS films (Fig. S1†).

4.2 Device characterization

The solid state performance of the device was characterized in the dark and under illumination using a solar simulator with AM 1.5 global spectrum with 60 mW cm^{−2} illumination. The current–voltage data were recorded using a Keithley 2612 A source meter. For characterizing the electronic communication between the EG-PEDOT:PSS and the electrolyte, CVs were performed using Bio-Logic Model SP 150 potentiostat in 10 mM ferricyanide solution with 0.5 M potassium chloride as the supporting electrolyte. Saturated Ag/AgCl served as the reference and Pt mesh as the counter electrode.

4.3 Photoelectrochemical measurements

All photoelectrochemical measurements were performed in an open container with two electrode cell configuration. The working electrode was n-Si with and without EG-PEDOT:PSS coating. The counter electrode was a platinum mesh. All the photoelectrochemical measurements were conducted using a Bio-Logic Model SP 150 potentiostat. Two electrolytes were used, (1) 0.025 M KI with 0.002 M I₂ and (2) fuming HBr (8.4 M). For wireless PEC cell demonstration, a standalone single junction GaAs solar cell was employed with EG-PEDOT:PSS as protective anode coating and Pt as protective cathode coating. Fuming HBr was used as the electrolyte. For all measurements the cells were illuminated with a solar simulator with AM 1.5 global spectrum.

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