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# Bifunctional polyaniline electrode tailored hybridized solar cells for energy harvesting from sun and rain

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## ABSTRACT

Pursuit of energy-harvesting or -storage materials to realize outstanding electricity output from nature has been regarded as a promising strategy to resolve the energy-lack issue in the future. Among them, the solar cell as a solar-to-electrical conversion device has been attracted enormous interest to improve the efficiency. However, the ability to generate electricity is highly dependent on the weather conditions, in other words, there is nearly zero power output in dark-light conditions, such as rainy, cloudy, and night, lowering the monolithic power generation capacity. Here, we present a bifunctional polyaniline film via chemical bath deposition, which can harvest energy from the rain, yielding an induced current of 2.57  $\mu\text{A}$  and voltage of 65.5  $\mu\text{V}$  under the stimulus of real raindrop. When incorporating the functional PANi film into the traditional dye sensitized solar cell as a counter electrode, the hybridized photovoltaic can experimentally realize the enhanced output power via harvesting energy from rainy and sunny days. The current work may show a new path for development of advanced solar cells in the future.

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## 1. Introduction

Advanced construction design for nano-scale energy-harvesting devices, such as supercapacitor [1], solar cells [2,3] and nanogenerators [4,5] has shown a major roadmap for energy conversion from nature to electricity in the future. Among them, solar cells present great potential along with the maximal power conversion efficiencies of 11%/14% for quantum dots/dye sensitized solar cell [6,7], 11% for polymer solar cell [8] and 22.1% for perovskite solar cell [9]. Unfortunately, the power output of as-developed solar cells are highly dependent on the weather, in other words, there is no electricity generation with no solar irradiation (such as night, foggy, cloudy, rainy), restricting the overall power output. In order to address the climate-limited issue, hybridized solar cells which can capture various energies from nature proposed in recent study have been committed to a promising strategy to break this impasse. For this, several research efforts integrating nanogenerators into solar cells to capture mechanical energy and solar energy simultaneously have been reported previously [10,11]. However, the rational design of the multi-functional devices possessing the ability to produce electricity from rain water still remains a challenge. Following this line of thought, graphene and Pt-alloys tailored dye-

sensitized solar cells (DSSCs) with sensitivity to sunlight and simulative rainwater have been created [12,13], realizing electricity generation beyond sunny days.

The general operation principle of graphene or Pt-alloys film tailored electric signal outputs when dropping rainwater is mainly based on interfacial charge interactions, arising from enriched electrons from the functional films and cations in rainwater such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{H}^+$ ,  $\text{Ca}^{2+}$  and  $\text{NH}_4^+$ . According to previous reports [12,13], there is a fact that electrical double-layer (EDL) pseudocapacitors could be formed between electron-rich film and ionic-rich rainwater because cations can be absorbed by surface electrons and therefore yield periodical electricity during expanding/shrinking processes of rain droplets over the films [14]. According to above-mentioned mechanism under the stimulus of raindrops, a "classic" conductive polymer including polyaniline (PANi), poly(3,4-ethylenedioxythiophene) (PEDOT) and polypyrrole (PPy) are also feasible to harvest energy from rain owing to their unique graphene-like electron distribution features [15–17]. It is well known that the conjugated structure between benzene ring and the nitrogen in PANi can introduce  $\pi$ -electron system along whole molecular chain, resulting in excellent conductivity [18]. We demonstrate here the experimental realization of persistent energy harvesting by PANi tailored DSSCs from sun and rain according to solar cell architecture in Fig. 1, yielding a photoelectric conversion efficiency of 6.5% under AM1.5 illumination as well as average

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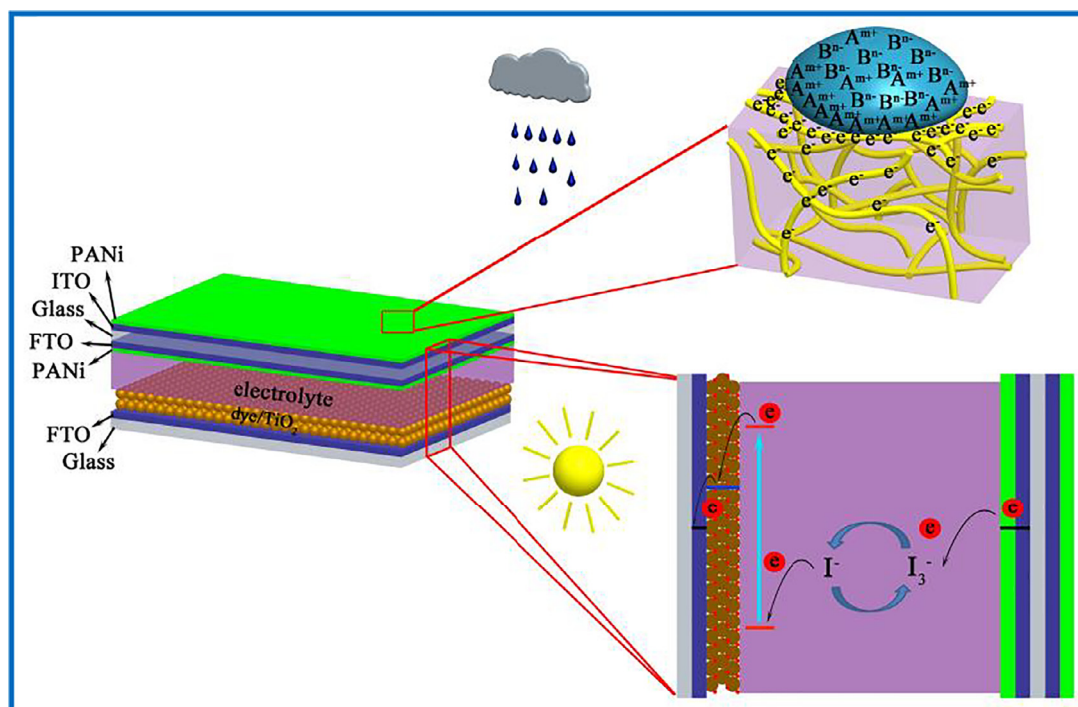


Fig. 1. Schematic illustration for PANi tailored hybridized solar cell as well as charge-transfer processes under stimulus of sun and rain.

current of 2.6  $\mu\text{A}$  and voltage of 65.5  $\mu\text{V}$  under the stimulus of real raindrops.

## 2. Experimental

### 2.1. Preparation of PANi electrode

The PANi electrode was prepared on a FTO/glass/ITO substrate. In details, quantified amount of indium nitrate was dissolved in diacetylmethane by adding diethanol amine into the solution as a stabilizer, and then refluxed at 60  $^{\circ}\text{C}$  for 3 h to form a homogeneous and stable sol. Subsequently, the stannic chloride (the molar ratio of In to Sn was 10:1) dissolved in ethanol was added into the above-mentioned mixture and stirred for 5–10 min to form a ITO (indium tin oxide) sol solution. Finally, the ITO sol was deposited onto the glass surface of FTO substrate and dried in air atmosphere, and then calcined at 550  $^{\circ}\text{C}$  for another 30 min. By repeating above processes for several times, the resultant FTO/glass/ITO substrate was obtained.

Next, 1.48 mL of aniline was dissolved in 50 mL of 1 M HCl aqueous solution to obtain a homogeneous mixture. A freshly cleaned FTO/glass/ITO substrate was immersed into the reaction vessel perpendicularly. Afterwards, 50 mL of 0.125 M ammonium peroxydisulfate aqueous solution was slowly dipped in the above mixture within 1 h. The polymerization reaction was carried out at 4  $^{\circ}\text{C}$  for 24 h. The resultant electrode was rinsed by 1 M HCl aqueous solution, and vacuum-dried at 60  $^{\circ}\text{C}$  for another 24 h, obtaining PANi/FTO/glass/ITO/PANi electrode.

### 2.2. Fabrication of all-weather solar cells

Generally,  $\text{TiO}_2$  film was coated onto the surface of FTO glass with 5 mm  $\times$  5 mm active area and 10  $\mu\text{m}$ -thickness by a doctor-blade method, following annealed at 450  $^{\circ}\text{C}$  for 30 min in air atmosphere. Then the substrate was immersed in ethanol solution of 0.50 mM N719 for 24 h, cleaned with ethanol and dried with  $\text{N}_2$  flow. For device fabrication, a dye-sensitized photoanode

(FTO/ $\text{TiO}_2$ /dye electrode) and a PANi/FTO/glass/ITO/PANi counter electrode were assembled into a sandwich-type construction along with injecting liquid electrolyte into the gap between two electrodes.

### 2.3. Device characterizations

The photocurrent density-voltage ( $J$ - $V$ ) plot of all-weather solar cell was recorded on a CHI600E electrochemical workstation (Shanghai Chenhua Device Company, China) under AM 1.5 G simulated solar illumination (100  $\text{mW cm}^{-2}$ , calibrated by a standard silicon solar cell). The introduced electrical signals generated from rainwater were also determined on a CHI600E electrochemical workstation. During characterization processes, the infusion rate was controlled by a medical syringe filled with realistic rainwater and 0.6 M aqueous solution of NaCl, KCl,  $\text{MgCl}_2$ ,  $\text{CaCl}_2$  along with the height of 8 cm between tip of syringe and ITO/PANi electrode. Meanwhile, the inclination angle of all weather solar cell was placed at 30 $^{\circ}$  for rainwater flowing. Herein, in order to analyze the data visually, we recorded the current and voltage signals employing baselines without raindrop as benchmarks.

### 2.4. Other characterizations

The surface morphology of PANi film was recorded via a SEM-4800-field-emission scanning electron microscope (SEM). X-ray diffraction (XRD) pattern spectrum was collected with a Ultima IV diffractometer using  $\text{Cu K}\alpha$  X-ray radiation. The Fourier transform infrared spectroscopy (FTIR) spectrum were recorded on a PerkinElmer spectrum 1760 FTIR spectrometer. The electrocatalytic parameters of PANi counter electrode was characterized on an electrochemical workstation comprising a working electrode of FTO glass supported PANi film, an Ag/AgCl reference electrode and a counter electrode of Pt sheet in a acetonitrile solution consisting of 50 mM LiI, 10 mM  $\text{I}_2$ , and 500 mM  $\text{LiClO}_4$ . The Nyquist and Tafel polarization curves were obtained from symmetric dummy cell, which was fabricated by assembling two counter electrodes and electrolyte together, indicating as PANi/electrolyte/PANi.

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