

Integration of polyelectrolyte based electrochromic material in printable photovoltaic electrochromic module

Lee-May Huang^{a,*}, Chih-Wei Hu^b, Cheng-Yu Peng^a, Chuang-Heng Su^a, Kuo-Chuan Ho^b

^a Green Energy & Environment Research Laboratories, Industrial Technology Research Institute, Chutung, Hsinchu 31040, Taiwan

^b Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan

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ABSTRACT

Compared to traditional electrochromic technology, photovoltaic electrochromic (PV-EC) module can achieve color change in electrochromic layers without additional power source. In this work, an innovative printable PV-EC module is provided. The device includes a plurality of planarly distributed silicon thin film solar cells (Si-TFSCs) configured in superstrate structure, covered with a layer of polyelectrolyte based electrochromic thin film (ECTF). The Si-TFSC consists of one anode (with a portion of area exposed from the Si-TFSC), a photoelectric conversion layer, and one cathode. The ECTF is prepared from nano-size polyelectrolyte based electrochromic material, which is composed of polyaniline (PANI) and polyanion poly(sodium 4-styrenesulfonate) (PSS) nanospheres mixture. When the printable PV-EC module is irradiated by sunlight, the PANI/PSS ECTF on the surface of the transparent anode layer exhibits anodic color changing, and transforms from pale green (emeraldine salt state) to light blue (emeraldine blue state).

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1. Introduction

Electrochromism is a reversible color change phenomenon displayed by some materials due to the generation of different absorption bands in the visible spectrum. Electrochromic devices provide switchable variable-tint window that preserves view out while modulating transmitted light, glare, and solar heat gains [1–3]. Other applications of electrochromic device such as anti-glare rearview mirrors, sunglasses, and displays [4] have also been proposed. Various types of materials can be used to construct the electrochromic device depending on the specific applications.

Much research has been recently directed towards designing solid-state electrochromic device due to the ease of assembling the device and no possibility of electrolyte leakage. A typical solid type electrochromic device includes two transparent substrates that sandwiched five electroactive layers such as: a transparent conductive layer, an electrochromic layer, a solid electrolyte, an ion storage layer, and another transparent conductive layer deposited in-between the two substrates to constitute a battery-like structure [5]. The electrolyte must be ionically conductive, but electronically insulating.

Nanostructured electrochromic materials with large specific areas are expected to facilitate the ion intercalation/de-intercalation

process during electrochromic redox reaction, and to enhance the properties of electrochromic materials and device performance. Some interesting nanostructures, including nanorod, nanospheres, nanowires, nanospheres, or nanotubes have been prepared from various electrochromic materials, such as transition metal oxides, and conducting polymers [6–8].

Polyaniline (PANI) has been receiving much attention owing to its broad range of tunable properties derived from its structure flexibility. This conjugated polymer exists in four different oxidation states, and can be switched between oxidation states by chemistry or by electrochemistry. The redox process involves anions insertion and extraction, which is associated with different structures of the PANI. In its fully reduced leucoemeraldine state, PANI is yellow. Upon chemical and electrochemical doping, PANI shows reversible transitions to its intermediate oxidized form of green, conducting emeraldine salt (ES) state or blue emeraldine base form (EB), while further oxidation to pernigraniline state renders the material purple [9,10].

Recent breakthroughs in the synthesis of conducting polymers with nano-dimensional control have managed to overcome the issue of poor processability of PANI. The nanosphere mixture of PANI with poly(sodium 4-styrenesulfonate) (PSS) is highly dispersed in aqueous solution as the emeraldine salt. The electrostatic interaction between PANI and the surfactant makes this nano-dispersion stable [11–14]. Nano-sized PANI has potential advantages in electrochromic

* Corresponding author. Tel.: +886 3 5912252; fax: +886 3 5834389.

E-mail address: lmhuang@itri.org.tw (L.-M. Huang).

application due to higher conductivity and rapid electrochemical switching.

The integration of photovoltaic and electrochromic device provides better efficiency in terms of energy saving, the photo-voltaic electrochromic (PV-EC) device can achieve color change in EC layers according to the intensity of sunlight converted electrical power. Until recently, there are several types of solar powered electrochromic devices available: tandem structure silicon (Si) based PV-EC device [15–18], dye-sensitized solar cell (DSSC) based photoelectrochromic (PEC) device [19,20], and planar structure Si based PV-EC device [21,22].

In our previous studies, both solution type and solid type PV-EC devices have been constructed based on the integration of planar structured silicon thin film solar cells (Si-TFSCs) with electrochromic solution [21], and with successively deposited EC layers [22]. The cathode of the Si-TFSCs is arranged in stripes, and the area outside the cathode blocks contains anode which is composed only of transparent conductive oxide (TCO).

In this paper, a novel printable PV-EC module with a superstrate structure is introduced. The structure of the PV-EC module includes a plurality of planarly distributed semi-transparent Si based TFSCs with exposed transparent anodes in-between the cathodes, and a layer of polyelectrolyte based electrochromic thin film (ECTF) covers both the cathodes and the anodes, as shown in Fig. 1. The electrodes of the Si-TFSCs also serve as the cathodes and anodes of the electrochromic system. The ECTF is prepared from nano-size polyelectrolyte based electrochromic material, which is composed of PANI and polyanionic PSS nanospheres mixture.

Under sunlight irradiation, electron–hole pairs are immediately generated by the Si-TFSCs, and redox reactions occur simultaneously within the PANI/PSS ECTF. The color change in the ECTF is achieved through the ion exchange mechanism provided by the polyanionic PSS. By the inclusion of one layer PANI/PSS ECTF, the printable PV-EC module has the benefit of simple device structure, which is only composed of a single layer of anodic electrochromic material mixed in polyelectrolyte. No extra electrolyte layer, ion storage layer or counter electrode layer is required (as needed for conventional electrochromic device) in order to achieve charges neutrality.

In addition to providing self-powered color changing, the series-integration of each Si-TFSC adds-up the photopotential of the printable PV-EC module, which can generate electrical power as a general Si-TFSC module does [23,24].

Although, studies of the integration of solar cell and electrochromic device in one single device still in their infancy and face huge challenges in the development. With the recent advances in the study of printable PV-EC module, we expect major breakthroughs in this dual functions PV-EC module development, which may provide an alternative solution to building integrated photovoltaic (BIPV) applications [25].

2. Experimental

2.1. Materials

Hydrochloric acid, ammonium persulfate, polysodium styrene sulfonate, lithium perchlorate, and propylene carbonate were

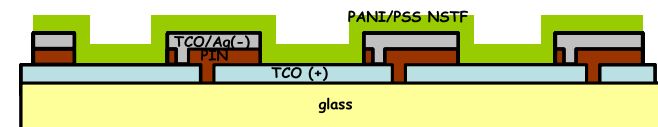


Fig. 1. A schematic cross-sectional view of PV-EC module with monolithically series connected Si-TFSCs structure, and a layer of ECTF covers the cathodes and the anodes simultaneously.

purchased from Aldrich. Aminobenzene (99.5%) was purchased from Merck. All reagents were used as received without further purification. All aqueous solutions were prepared using deionized water (DIW) with 18.2 M Ω cm resistivity.

2.2. Semi-transparent Si-TFSC fabrication

Details about fabrication of semi-transparent Si-TFSC were reported earlier in our published paper [22,26]. The structure of the Si-TFSC included a glass substrate, a ZnO:Al transparent conducting oxide layer which served as the anode, a double junction of amorphous and microcrystalline Silicon (a-Si:H/ μ c-Si:H) thin films which served as the photoelectric conversion layers, and a ZnO:Al layer and a back reflector metal layer together to constitute the cathode. A pulse laser of 532 nm was used to remove a portion of the silicon thin film to form the Si-TFSC in stripes. The ratio of anode and cathode blocks was 1:1. An area of an anode and a cathode of each stripe-shaped Si-TFSC was 3 cm \times 0.5 cm.

2.3. PANI/PSS nanosphere synthesis

The method of synthesizing the PANI nanospheres and the PSS polyelectrolyte was reported previously [11–13]. The PANI/PSS nanospheres (NS) were synthesized by chemical-oxidation polymerization in the presence of HCl and PSS. The water soluble PSS was introduced as a counter ion dopant during the polymerization. 0.6 mmol of aminobenzene monomer was added into 20 mL DIW containing 0.5 M HCl, and 1.0 g of PSS was added into 20 mL of DIW. 0.7 mmol of ammonium persulfate (APS) was then added into the mixture solution as an oxidant to obtain a dark green (emeraldine salt) water dispersible PANI/PSS NS solution.

2.4. Electrolyte solution

The electrolyte used was propylene carbonate containing 0.1 M LiClO₄ and dehydrated using molecular sieves before use.

2.5. Preparation of electrochromic thin films

2.5.1. Preparation of PANI/PSS NS on ITO glass

The PANI/PSS nanospheres thin films (NSTFs) were prepared by spin coating PANI/PSS NS on ITO glass with an active area of 2 \times 2 cm². Different thin film thicknesses were obtained through repeated coating cycle, in order to have sufficient color-bleach contrast of the PANI/PSS NSTFs. Three layers of PANI/PSS NS were successively spin coated on the ITO glass. Here, 1 mL of PANI/PSS-NS was deposited dropwise with a spin rate of 1500 rpm for 1 min.

2.5.2. Preparation of electropolymerized PANI on ITO glass

Anodic electropolymerization of aminobenzene on the ITO glass substrate (with an active area of 2 \times 2 cm²) was used to form PANI thin film. The bath solution was composed of 1.0 M aminobenzene, 2.0 M HCl, and deionized water [9]. The current density and deposition time were set at 0.8 V vs Ag/AgCl (3 M KCl) and 100 s, respectively. The average thickness of the PANI thin films was 260 nm.

2.6. Fabrication of printable PV-EC module

The printable PV-EC module was fabricated by repeatedly spin coating 3 layers of PANI/PSS NS on a semi-transparent Si-TFSC module with an active area of 3 \times 3 cm². The Si-TFSC module included three sets of Si-TFSCs connected in series. The area of an anode and a cathode of each of the cell was 3 cm \times 0.5 cm.

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