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## Electrodeposited polyaniline films decorated with nano-islands: Characterization and application as anode buffer layers in solar cells

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### ABSTRACT

Polyaniline (PANI) thin films studded with nano-islands on their surface are electrochemically synthesized. The surface morphology of these films can be adjusted by controlling the deposition time during the synthesis. The PANI films decorated with nano-islands are used as the buffer layer in the organic solar cells based on a blend of poly[2-methoxy-5-(3',7'-dimethyloxy)-1,4-phenylenevinylene] (MDMO-PPV) and [6,6]-phenyl-C61 butyric acid methyl ester (PCBM). The investigation on the characteristics of the solar cells demonstrates that the nano-islands on the PANI buffer surface are helpful in improving the solar cell performance.

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### 1. Introduction

Organic semiconductor solar cells are the third generation of photovoltaic devices, and they have attracted much attention because of their flexibility, low-cost and lightweight [1–3]. After decades of active exploration, the conversion efficiency of polymer solar cells (PSCs) based on a poly(thiophene) derivative has been improved up to 6.77% [4], which is a big step towards commercial application. In fact, many efforts have been already put on the manufacture of PSCs from the laboratory level to an industrial level. Based on the research of solar cell fabrication under non-vacuum conditions [5] and small area cells with a roll-to-roll method [6], Krebs et al. first publicly demonstrated stabilized large area PSCs fabricated with a commonly available screen-printing method under industrial condition [7]. Further efforts made it possible to prepare and upscale large PSCs using full roll-to-roll process [8]. In addition, feasibility of stabilizing the performance of PSCs using a standard barrier technology was demonstrated, with relatively small degradation over 4 months [9]. More interestingly, PSCs can even be fabricated and integrated as a source in a lightweight lamp [10], from which rural environment illumination can be benefit.

On the way to be commercially applicable, further optimization of polymer solar cells is still necessary. Actually, a trend is

that not the optimization but relatively novel studies, usually deriving from the standard approach, may advance the development of PSCs [11]. Herein, we devote to the fabrication of an appropriate anode buffer layer for the solar cells. To the anode buffer layers in PSCs, besides some specific properties such as being chemically stable, highly electrically conductive, and thin enough in thickness to insure light transparency, an anode buffer layer with an array of outstretched building blocks on its surface should be more suitable to the cells. In such a topology, the hole-collection panels in an anode extend into the photoactive layers, which is to reduce both the transportation time of holes from the photoactive layer to the anode and their recombination with electrons in the active layer (AL) compared with a planar anode buffer surface. This motivation is based on the observation that a vertically aligned nanostructure (nano-wires, nanorods, nanotubes or branched nanostructures) can provide increased surface areas and convenient electron transport channels, which is good for the performance of solar cells [12,13].

In this work, polyaniline is chosen as the anode buffer layer because of its low-cost and easy processing properties comparing with the commonly used PEDOT:PSS. Furthermore, it has a large band gap with its work function to be 0.1 eV higher than that of ITO [14], making it suitable for transporting holes between the ITO anode and the photoactive polymer [15]. However, the commonly used spin-coating method generates a planar surface, which is less applicable to the solar cells. Besides the spin-coating method, the electrochemistry method has also been used in order to produce a PANI film [16,17], and these efforts resulted in a

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network of PANI nano-wires. Herein, we fabricate the PANI film by using the electrochemical deposition method in a simple water solution with aniline as the monomer and perchloric acid as the doping. In order to obtain a PANI film with the topology more suitable for the fabrication of the cell, the deposition time of PANI material is precisely controlled during the electrochemical deposition. We obtain the PANI film whose surface is studded with nanoscale islands. The optical and electrical characteristics of the nano-particles decorated PANI film as obtained are investigated and used as anode buffer layer in organic solar cells. The performance of solar cells can be tuned through the nano-islands density on the buffer layer surface by adjusting the deposition time, with the largest density giving the best photovoltaic performance.

## 2. Experimental

### 2.1. Synthesis of PANI thin films

A computer-controlled three-electrode electrochemical cell is used to synthesize the perchloric acid doped PANI film on an indium tin oxide (ITO) coated glass. The ITO-coated glass serves as the working electrode, the platinum electrode serves as the counter, and Ag/AgCl serves as the reference electrode. The electropolymerization of a PANI film is carried out at a constant voltage of 0.7 V in the aqueous solution with 0.08 M aniline and 1.2 M perchloric acid. In order to obtain various surface morphologies of the films, the deposition time,  $t_{dep}$ , is varied in the range of 15–120 s. The PANI films, green in color, as obtained are cleaned by deionized water and dried at 70 °C in air before being physically characterized and used as the anode buffer layer in organic solar cells. In order to investigate the reason for the formation of PANI film morphology, similar experiments are carried out by exchanging the glass/ITO substrate for glass/Au substrate and introducing aminobenzenesulphonic acid into the reaction mixture, respectively.

The composition of the electrochemically deposited films is determined by the Fourier transform infrared microscopy (FTIR, Varian, Excalibur-3100) characterization to give a perchloric acid doped PANI material (not given here). The surface morphology of the PANI films is measured by using scanning electron microscopy (SEM, Hitachi, S-4800) and atom force microscopy (AFM, Solver P47 SPM, probe tip with resonant frequency 205 kHz, force constant 5.5–22.5 N/m). To the AFM characterization, semi-contact mode, FB in MAG, FB Gain 1.5 and Set Point 9.884 nA is used. Ultraviolet–visible (UV–vis, Varian, U-3000) absorption spectra in the form of photon energy are recorded on a U-3000 model spectrophotometer. Cyclic voltammetry (CV) measurement is carried out on an electrochemical workstation (CHI 660D).

### 2.2. Fabrication of organic solar cells with the PANI films as the buffer layers

For the fabrication of the cells, a chlorobenzene solution containing the hybrid composed of MDMO-PPV and PCBM (5:20 in weight ratio) is firstly spin-coated on the PANI film with its rotation at 1500 rpm for 30 s, which is the best fabrication parameter for the solar cell with traditionally used PEDOT:PSS as the anode buffer layer. Then, onto the hybrid film, a 20-nm ZnO buffer layer is spin-coated at 5000 rpm in the ZnO methanol solution (30 mg ml<sup>-1</sup>) synthesized according to Ref. [18]. The cell fabrication was finished by depositing a 100-nm Al film on the ZnO surface in the Al vapor of  $4 \times 10^{-3}$  Pa in pressure. The effective area of the solar cell is about 0.07 cm<sup>2</sup> determined by a

covered membrane. For comparison, solar cell with PEDOT:PSS as the buffer layer is also fabricated and tested under the same condition. Further, solar cells with different MDMO-PPV/PCBM layer thickness are given by varying the spin coating speed from 800 to 5000 rpm. The current–voltage ( $I$ - $V$ , Keithley 2400 source) measurement on the PSCs is performed in forward bias mode under 100 mW cm<sup>-2</sup> illumination. The quantum efficiency (QE) testing is performed on a DH1720A-1 250 W Bromine Tungsten arc source and a Digikröm DK240 monochromator. The side-view cross-section morphology of the device without Al electrode is obtained from Hitachi S-4800 high resolution scanning electron microscopy (HRSEM).

## 3. Results and discussion

### 3.1. Surface morphology and physical property of PANI films

Fig. 1(a–e) is the SEM images of the surfaces of the PANI films, as obtained with  $t_{dep}$  being in the range 15–120 s. These figures show that the surface morphology of a PANI film is a function of the deposition time. As shown in Fig. 2(a), with  $t_{dep}$  = 15 s, the film surface is almost planar. With  $t_{dep}$  increasing to 45 s (Fig. 2(b)), nano-islands begin to appear on the surface; at  $t_{dep}$  = 60 s (Fig. 2(c)), the number density of these nano-islands reaches maximum (about  $6 \times 10^8$  cm<sup>-2</sup>); with  $t_{dep}$  further increasing, the number density decreases. At  $t_{dep}$  = 120 s, the number density further drops down. Fig. 1(f) is the AFM image of the PANI film having the maximum density of nano-islands with  $t_{dep}$  = 60 s. This figure demonstrates clearly the nano-islands decorated on the PANI film surface from a three-dimensional perspective. Such nano-islands are seldom observed on the surface of the PANI film.

With regard to the formation of PANI film with this kind of surface morphology, one supposition is that the acid condition may cause corrosion to the ITO substrate, which can induce preferential nucleation and growth of PANI particles through chemical bond coupling between the aniline monomer and the ITO. This supposition can be confirmed through introducing a more stable glass/Au substrate. Another reason may be a mechanism as plat film formation firstly, followed by as-formed nano-particle's deposition. If this, water-soluble aniline may inhibit the formation of suspended nano-particles in solution. Thus, aminobenzenesulphonic acid was introduced into the mixture in another experiment. The results obtained from the two parallel experiments are shown in Fig. 3(a) and (b). However, films studded with nano-particles on surface still exist. It seems a process irrelevant with the substrate and reaction monomer. The formation is probably dominated by preferential nucleation-growth of particles on the flat film that is also growing simultaneously. This can be depicted in Fig. 3(c). During the growing process of PANI film, preferential nucleation happens at some point of polymerized PANI film surface. The as-formed nuclei play the role of seeds that catalyze the following linear growth of PANI, standing upright on the surface of flat PANI films. Meanwhile, PANI film grows faster and faster among the linear PANI particles, which may be covered by the following long time growth of PANI, showing a decreasing density of particles on the surface. During film formation, loosely bonded PANI particles may drop off the base film, which may interpret the existing of nano-sized holes on the film surface due to the detachment of the weakly bonded nano-particles.

In order to determine the energy level of the PANI films, their redox properties are measured by using cyclic voltammetry (CV) [19]. As shown in Fig. 4, the CV curve with four cycles apparently demonstrates that the onset oxidation potential  $\Phi_p$  is about 0.40 V, from which the highest occupied molecular orbit (HOMO)

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