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Large Area Platinum and Fluorine-doped Tin Oxide-free Dye sensitized Solar Cells with Silver-Nanoplate Embedded Poly(3,4-Ethylenedioxythiophene) Counter Electrode

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ABSTRACT

Low-temperature, cheap, highly conductive triangular silver-nanoplates (Ag-NPs) embedded in poly (3, 4-ethylenedioxythiophene) (PEDOT) films were prepared on bare glass substrates via spin coating and chemical polymerization. The films acted as a very good alternative to conventional platinum (Pt) and fluorine-doped tin oxide (FTO) counter electrodes (CEs) in dye-sensitized solar cells (DSSCs). The effect of the Ag-NPs in the PEDOT CE was evaluated by adding different weight ratios of Ag-NPs (0.06, 0.60, and 1.20 wt%) to the PEDOT solution before producing the film, and the catalytic and conductive properties were compared against those of pristine PEDOT films for use in DSSCs. The catalytic properties of all CEs in the DSSCs were characterized via cyclic voltammetry (*CV*), current-voltage (*I-V*) measurements, and electrochemical impedance spectroscopy (EIS). The PEDOT CE with embedded Ag-NPs functioned as excellent electrocatalysts for tri-iodide reduction, as compared to pristine PEDOT CEs. DSSCs (cell area: 1 cm^2) with the 0.60 wt% samples exhibited a power conversion efficiency of 6.0% under 1 sun illumination (100 mW cm^{-2}), which is higher than that of DSSCs with pristine PEDOT CE (5.5%). The Ag-NPs embedded PEDOT CE has very good catalytic activity and conductivity, which is more suitable for large area Pt and FTO less DSSC. In addition, no noticeable efficiency decay was observed after adding Ag-NPs in PEDOT CEs.

1. Introduction

Dye-sensitized solar cells (DSSCs) are a promising alternative to capture solar energy for both commercial and scientific purposes due to their low-cost, ease of fabrication, non-vacuum process and capability of operating with different colors and transparencies [1–4]. In general, DSSCs are composed of a ruthenium dye-sensitized TiO_2 photoanode (PE) deposited on an FTO glass substrate, platinum (Pt)-coated FTO glass substrate as a counter electrode (CE), and iodide based redox electrolytes that fill the space between the PE and CE. Pt is an important material for two purposes: it is used to quickly carry the electron to the external circuit and to simultaneously generate the electrocatalytic activity for the tri-iodide reduction [4].

One of the biggest hurdles to develop DSSCs is to find suitable, stable material as an alternative for both FTO and Pt. Although both materials have very good properties that could be of use in DSSCs, these also have disadvantages in that they form rigid, brittle glass that requires a high cost of production through a high temperature process. In addition, the low abundance of these materials inhibits the large-scale application of Pt and FTO in DSSCs [4–6]. In recent years, a number of studies have shown the successful use of FTO- and Pt-free CEs in DSSCs, and the photovoltaic performance of these is close to that of FTO and Pt CEs [7–12]. To replace Pt, several materials have been proposed for use in the CEs of DSSCs, including carbon-based materials, conducting polymers, sulfides, oxides and carbides [4,5,7–15]. Most importantly, all of these materials have yielded efficiencies comparable to those of Pt-based DSSCs.

A number of conducting polymers have attracted much interest for use as alternatives to FTO- and Pt-based CE materials, and these polymers have several promising properties, such as a favorable electrical conductivity, good catalytic activity, high chemical stability and ease of synthesis [8–10]. Notably, poly (3,4-ethylenedioxythiophene) (PEDOT) polymer with thin films (100-200 nm) can achieve very good catalytic and conductive

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behavior to successfully replace Pt and FTO while such is not possible for other CE and conducting materials [8,10]. So far, few studies on FTO- and Pt-free CEs have reported a performance comparable to that of Pt- and FTO-based devices [7–10]. More importantly, Pt and FTO-free CEs using pure PEDOT polymer could not achieve high efficiency in large area DSSCs because of the poor electrical conductivity of PEDOT compared to the FTO substrate.

Here we have developed promising large area DSSCs with thin 2D Ag-nanoplates (NPs) embedded in the PEDOT CEs. We can control the conductivity and surface area of the CEs by adjusting the Ag-NP weight ratios in the PEDOT solution. As a result of their superior conductivity and larger active surface area, the Ag-NPs embedded in the PEDOT CEs showed a higher efficiency than the pristine PEDOT CEs. More importantly, efficiency decay of DSSCs as increasing cell area was greatly retarded with the help of Ag-NP.

2. Experimental section

2.1. Synthesis of the silver nanoplates

3.6 g of polyvinylpyrrolidone (PVP) (Mw ≈ 29 kDa) were dissolved in 16 mL N-Methyl-2-pyrrolidone (NMP). Then, 6 mL of the NMP solution containing $AgNO_3$ (188 mM) were injected into the vial. The mixture solution was kept for 12 h under heat at 100 °C with stirring. The synthesized particles were collected via centrifugation and were washed with DI water several times to remove the NMP and PVP. During the washing process, the suspension was centrifuged at 14[thin space (1/6-em)]000 rpm for 10 min. Finally, the precipitate was re-dispersed in butanol for further use.

2.2. Fabrication of Silver Nanoplate embedded PEDOT counter electrode

Bare glass substrates were used to prepare both the pristine and the silver nanoplate (Ag-NPs)-embedded PEDOT counter electrodes (CE). First, two types of solutions were prepared to make pristine PEDOT CEs. A monomer solution was formed by dissolving 0.2 g of 3,4-ethylenedioxythiophene (EDOT), 0.02 g of poly(vinyl pyrrol-idone) as a matrix polymer and 0.1 g of pyridine as a retardant in 2 mL of butanol. An oxidant solution was then formed by dissolving 2.38 g of ferric p-toluene sulfonate (FTS) in ethanol (45 vol%). The monomer and oxidant solutions were mixed together, followed by pre-polymerization at 70 °C for 20 min. Ag-NPs were added at different weight ratios (0.06, 0.60, and 1.20 wt%) to the above solution to prepare the Ag-NPs PEDOT film CE. Each of the Ag-NPs were of 400-500 nm in size. Pre-polymerized PEDOT solution with and without Ag-NPs was

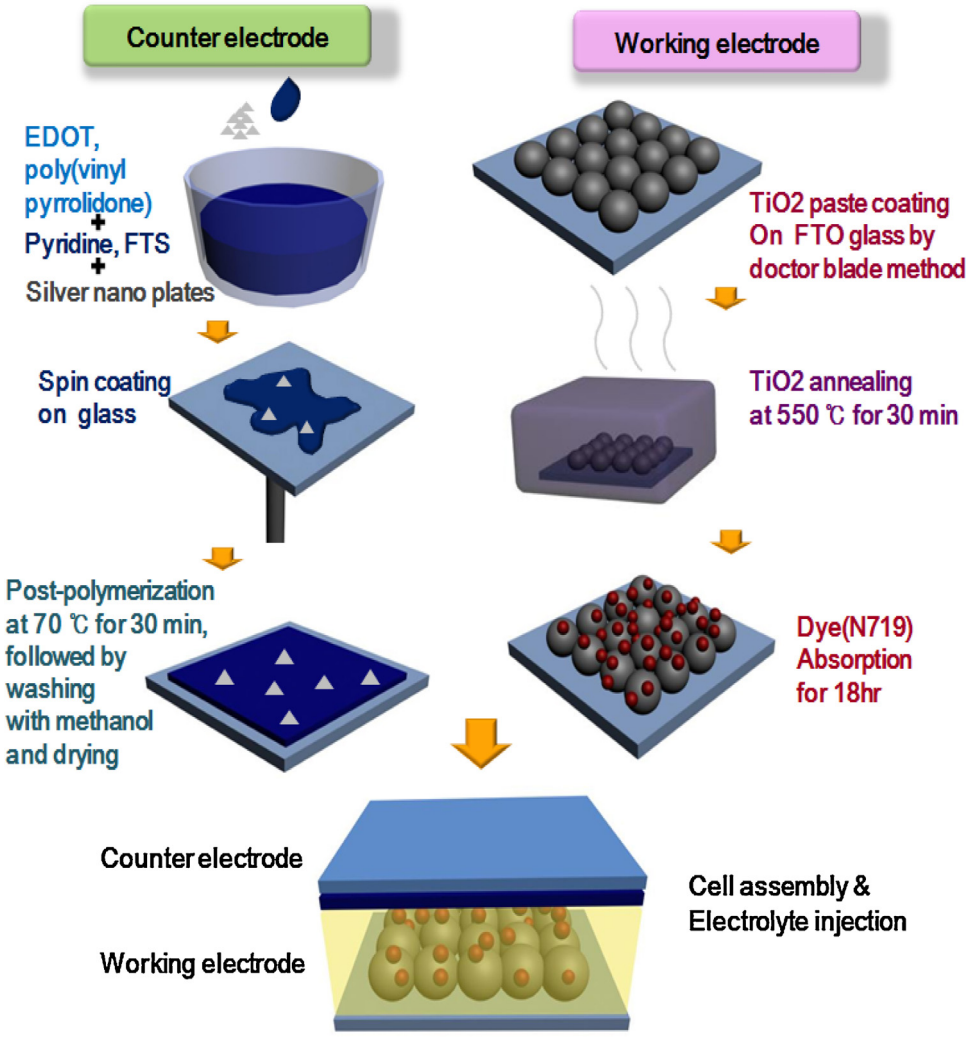

Fig. 1. Schematic of the DSSCs assembly with a counter electrode using silver nanoplate (Ag-NPs)-embedded PEDOT (conducting polymer) film instead of FTO glass and platinum.