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Effects of solvent and copper-doping on polyaniline conducting polymer and its application as a counter electrode for efficient and cost-effective dye-sensitized solar cells

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ABSTRACT

In this study, the synthesis of Copper-doped polyaniline (NPANI-Cu-X) was performed in the following solvents: H_2O, DMF, DO, THF, ACTN and ACN, and then the solvent effects on the formation of NPANI-Cu-X (X represents the dopants, I^- and BF_4^-) were investigated. NPANI-Cu-X was characterized using scanning electron microscopy (SEM), X-ray diffractions (XRD), energy-dispersive X-ray analysis (EDAX), Fourier transform infrared spectrometry (FTIR), Atomic Absorption spectrometer (AAS), Ultraviolet–visible spectrophotometers (UV–vis), thermal analysis (TGA, DTA) and electrical conductivity measurements. The results show that the solvent is effective in the formation of NPANI-Cu-X. This effect was observed in the polymer structures, conductivities, copper contents and crystalline structures. The NPANI-Cu-X polymers synthesized with the various solvents were notably different from each other because some of the solvents create a copper-solvent complex with the copper. To understand the influence of solvent type and Cu inclusion on photoelectric performance, the obtained PANI were employed as counter electrode in a DSSC configuration. The highest double layer capacitance (24.1 μF), low charge transfer resistance (5.13 Ω) together with series resistance (14.62 Ω), and good photovoltaic performance with conversion efficiency (6.37%) for counter electrodes are obtained the NPANI-Cu-X in ACN solvent media which is higher than that fabricated with N-PANI in same solvent media (1.36%). These results represent a promising route for developing new counter electrodes of Pt-free DSSCs by Cu doping and choosing an appropriate solvent.

1. Introduction

The discovery of electronically conducting polymers suggests many new applications for polymeric materials. Conducting polymers have been intensively investigated for the last two decades due to their fundamental physical properties, electrical behaviors and potential applications in various electronic devices, such as chemical sensors, light emitting diodes, organic field-effect transistors, electromagnetic interference shielding, antistatic materials, sensing materials, secondary batteries and solar cells [1–7].

Polyaniline (PANI) has been one of the most studied conducting polymers during the last few decades due to its easy synthesis, low cost, environmental stability, simple doping/dedoping process, high conductivity, eminent catalyst activity and high pseudocapacitance [8–11]. It has been widely applied in many fields, including supercapacitors [12–14], electrochromic-materials [15], hydrogen-photoproduction [16], gas sensors [17], environmental remediation [18,19], photodiodes, lightweight batteries, electrochemical capacitors, corrosion capacitors, corrosion inhibitors, drug delivery, electromagnetic interference shielding and especially in dye-sensitized solar cells (DSSCs) [20–24].

Over the years, DSSCs have been intensively investigated due to their low cost compared with silicon-based solar cells, simple fabrication process, and relatively high efficiency of converting solar energy into electricity [25,26]. A typical DSSC consists of three main components: a dye-sensitized mesoporous semiconductor photo-anode (working electrode), a counter electrode (CE), and an electrolyte usually containing a I^-/I_3^- redox couple between the photo-anode and the CE. The CE is indispensable as it possesses the electrocatalytic activity for the I^-/I_3^- redox reaction in DSSCs. The most commonly employed CE in DSSCs is prepared by

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deposition of platinum (Pt) on a transparent conducting oxide (TCO) substrate, such as a floruin-doped tin oxide (FTO) glass substrate [27]. Although noble Pt exhibits excellent catalytic activity for I_3^- reduction and high conductivity, its high cost (the cost of a platinum CE is more than 40% of the cost of the whole photovoltaic cell), limited reserve and potential for corrosion by the iodide solution restrict its use in large-scale manufacture [28]. Therefore, to fabricate a low cost DSSC with a long life, many efforts have been devoted to develop a CE with high chemical stability, low cost, high conductivity and efficient electrocatalytic activity. It has been proposed that various carbon materials could replace Pt [29–31], but the photovoltaic conversion efficiency (PCE) of a DSSC based on the use of these carbon materials as the CE was relatively low due to their poor catalytic activity. Conducting polymers such as PANI are promising candidates for use as CE materials in DSSCs due to their low cost, high-conductivity and excellent catalytic activity for I_3^- reduction [32–34]. For example, Tang et al. reported the fabrication of DSSCs based on chemically and electrochemically deposited PANI CEs. While the PCE of DSSCs based on chemically deposited PANI CE was 3.92%, the PCE reached 6.92 for DSSCs based on electrochemically deposited PANI [35]. In another study, Tai et al. proposed the application of an in situ-prepared transparent PANI electrode in bifacial DSSCs. The PCEs of DSSCs with a Pt CE and PANI CE were 6.54 and 6.69%, respectively [36]. However, the commercial application of PANI has been limited by its restricted processability. Therefore, research on conductive polymers continues to search for new materials that are stable, possess excellent electronic properties and are easily machinable. Previous studies have reported the preparation of different polyaniline composites by using various transition metal salts and metal oxides and their subsequent characterization [37–44].

Conjugated polymers containing transition metal complexes have been identified as the most attractive systems by material scientists [45]. Copper is known as a better doping material and can be doped on PANI and polypyrrole in both the elemental and salt form. A literature survey reveals evidence of a strong interaction between Cu^{2+} and PANI chains [46,47]. Water has also been used as the solvent in these studies. Water and certain other solvents have ligand properties as amino group and form complexes with transition metals [48].

In this study, the solvent effects were investigated by the addition of Cu^{2+} to neutral polyaniline (NPANI). NPANI-Cu-X polymer has been synthesized and characterized using SEM, FTIR, XRD, UV–vis, AAS techniques and dry conductivity measurements. Moreover, synthesized PANI, NPANI in acetonitrile solvent and NPANI-Cu-X synthesized in various solvents were employed as a catalyst instead of Pt in a conventional DSSC configuration. The fabricated DSSCs were characterized by $I-V$ and electrochemical impedance spectroscopy measurements to understand the influence of the chosen solvents with Cu^{2+} additive on the electrochemical and photovoltaic performances of DSSCs. To our knowledge, this is the first report of the synthesis of NPANI-Cu-X in different solutions and its characterization.

2. Experimental procedure

2.1. Equipment

Aniline (97%, Aldrich) was distilled before use. Deionized water, dimethylformamide (99.8%, Sigma–Aldrich), 1,4-dioxane (99.8%, Merck), tetrahydrofuran (99%, Fluka), acetone (99.5%, Merck), acetonitrile (99.8%, Aldrich), H_5IO_6 (99%, Sigma–Aldrich) and $Cu(NO_3)_2$ (Sigma–Aldrich) were used without purification. The UV–vis spectra of the polymers were performed in the range of 200–600 nm using a PerkinElmer Lambda-35 UV–vis spectrophotometer. The infrared spectra of the polymers were recorded in the range of 2000–400 cm^{-1} using a Jasco FTIR-430 Fourier transform infrared spectrometer. The X-ray diffractions of the powdered polymer samples were analyzed by a Rigaku D/MAX-2200 diffractometer using CuKα radiation from 2 to 50° (2θ) at a scanning rate of 4 min^{-1}. For the SEM/EDS measurements, the polymer samples were subjected to a thin gold coating by using a Quanta 400 FEG model SEM fine coater. The thermal analysis curves (TGA and DTG) were obtained using a PerkinElmer diamond thermal analyzer with a sample size of 5–10 mg and a heating rate of 10 °C min^{-1} under nitrogen atmosphere. A PerkinElmer Analyst 700 (PerkinElmer Company, Norwalk, CT, USA) atomic absorption spectrometer with a deuterium background corrector was used for the analyte determinations in an air/acetylene flame using hollow cathode lamps. Before DC conductivity measurements, the dry pellets were prepared from powder polymer material under a pressure of 5 t cm^{-2}. The dry conductivity of the polymers was measured by using a four-probe electrical conductivity measuring device (Entek Electronic) at room temperature. Gold-plate probes were used to avoid any errors caused by ohmic contacts. The resistivity of the samples was measured at five different positions, and at least two pellets were measured for each sample, providing an average of 10 readings for the conductivity calculations. The photocurrent–voltage ($I-V$) curves of the fabricated cells were obtained by using a Keithley 4200 semiconductor characterization system and a standard solar irradiation of 30 mW cm^{-2} (Xe lamp with AM 1.5 filter) as the light source. Furthermore, the electrochemical impedance spectroscopy (EIS) measurements were conducted by Ivium compactStat in a dark media.

2.2. Synthesis of polymers

2.2.1. Synthesis of PANI

The aniline–solvent mixtures were prepared for each solvent, and the solution containing the oxidizing agent (H_5IO_6) was added to the mixtures drop wise. All of the resulting black polymers were filtered and washed with the solvents used in the polymerizations and dried under vacuum.

2.2.2. Synthesis of neutral polyaniline (NPANI)

The aniline-solvent-oxidant (H_5IO_6) mixtures were prepared for the different solvents and kept for 24 h to complete the polymerization reaction. The resulting black polymers were then filtered. Each PANI polymer sample was subjected to multiple rinsing procedures with the polymerization solvent used to remove any residual monomers, oxidants and HBF_4. Tetrabutylammonium hydroxide solution was added to the colloidal PANI (H^+PANI) polymer and kept for 24 h to complete the deprotonation of PANI. After 24 h, the polymer was filtered and washed.

2.2.3. Synthesis of copper-doped polyaniline (NPANI-Cu-X)

The solvent was added to the washed NPANI. The solution, including Cu^{2+} and dopant (BF_4^-), was added to the NPANI-solvent mixtures, and after 24 h, the polymer was filtered, washed and dried under vacuum. Iodine also participated in the polymer as a dopant because the oxidizing agents used (H_5IO_6) contains iodine.

2.3. Fabrication of cell assembly

2.3.1. Preparation of counter electrodes

The obtained dried Cu-doped N-PANI in various solvents were dissolved in formic acid at the same concentration and then stirred with a magnetic stirrer for 2 h. Before deposition, the FTO glasses (Asahi Glass, fluorine-doped SnO_2; sheet resistance: 15 sq^{-1}) were cleaned in a detergent solution in an ultrasonic bath for 15 min,