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One-dimensional hollow metal-complex as catalytic electrode for dye-sensitized solar cells

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ABSTRACT

We report the application of *N,N′*-Ethylene-bis(salicylideneiminato)-nickel (II) complex (Ni(salen)) and platinum (Pt) functionalized Ni(salen) complex as neoteric catalytic electrode (CE) for dye-sensitized solar cells (DSSC). Crystalline, one-dimensional (1D) hollow Ni(salen) complex was prepared via low-temperature chemical processes and used as a CE in DSSCs. 1D hollow Ni(salen) complex-based device exhibited low photo and dark-current density, due to the poor electron conduction and catalytic activity. Further improving the electrical and catalytic property of Ni(salen) complex, the complex functionalized with Pt on/in surface via sol-gel method at ambient condition; thereby enhance electron conduction and catalytic activity, increasing the photocurrent density (Jsc) from 9.05 to 14.40 mA·cm^{-2} and efficiency (η) 1.02 to 2.76%, respectively. The cyclic voltammetry data revealed that the Pt functionalized Ni(salen) complex electrode better electrocatalytic activity for I_3^-/I^- redox reaction relative to that of Ni(salen) electrode. The Pt functionalized Ni(salen) complex electrodes open-up a neoteric catalytic material for designing high–performance optoelectronic devices.

1. Introduction

Dye-sensitized solar cell (DSSC) converts sunlight into electricity based on photovoltaic effect, reported a power conversion efficiency of 13.0% and proved a better alternate candidate for silicon solar cells (Mathew et al., 2014). In the present growing photovoltaic technologies, DSSC is suitable for integrating to the houses and smart-electronic device applications and grabbed great attention by (Wang et al., 2014) the researchers due to their low-cost, easy fabrication procedures, also have several-options to boost efficiency (Yoon et al., 2011; Carlo and Brown, 2008; Guo et al., 2012). The DSSCs consist of a sensitized metal-oxide and catalytic electrode (CE) with an electrolyte slot-in between them (O'Regan and Grätzel, 1991). CE is a key material for DSSCs; that serves in charge carrier transport from external circuit to I_3^-/I^- in redox electrolyte at interface of CE-electrolyte which has a significant influence on the photovoltaic performance and long-term stability (Chen et al., 2017). At Present scenario, Pt-coated transparent conducting oxide/flexible substrates are extensively used as a CE in DSSCs but restricts the large-scale application because of limitations and high price. In this regard, a great effort has been made to develop novel CE materials; alternative to platinum (Pt) (Wang et al., 2013; Batmunkh et al., 2015; Veerender et al., 2014; Soo Kang et al., 2015; Wei et al., 2016; Chen et al., 2015). Recently, several attempts have been made to replace Pt electrode with carbonaceous materials, inorganic compounds, conductive polymers; these materials are chemical inertness, modest electron transfer kinetics with I_3^-/I^- redox electrolyte and low-temperature processing methods (Wang et al., 2013). Graphene (Wang et al., 2013), nickel nitride (NiN) (Soo Kang et al., 2015), and $CoNi_2S_4$ (Chen et al., 2015) showed conversion efficiency of 7.01%, 3.75% and 7.03%, respectively. However, the energy conversion efficiency of these CEs has always less than the Pt electrodes (Zhang et al., 2014). Later, researches developed a composite CE, the composite electrode based solar cells shows superior performance than Pt electrode (Cheng et al., 2013; Lan et al., 2016). These findings have inspired us to carry-out extensive studies on developing neoteric catalytic materials for DSSCs (Thuy et al., 2016). Herein; we demonstrate *N,N′*-Ethylene-bis(salicylideneiminato)-nickel (II) complex (Ni(salen))and Pt functionalized Ni(salen) complex are alternative to the Pt and carbon materials. The 1D hollow Ni(salen) complex was prepared by green low-temperature chemical process. In addition, 1D hollow structured Ni (salen) complex can easily functionalized with Pt for enhancing electrical and catalytic property. Finally, we present our views on the

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current challenges and future development of Ni(salen) complex and Pt functionalized Ni(salen) complex as a catalytic material for DSSCs. Also, their morphological and photovoltaic properties were characterized by SEM, TEM and I–V measurements, respectively. The device performance of Ni(salen) and Pt functionalized Ni(salen) complex have lower than Pt-based device due to the weak adhesion, lower catalytic-activity and conductivity. Therefore, our studies are still going on to overcome this issue.

2. Experimental details

2.1. Materials

The salicylaldehyde (99.8%, Sigma-Aldrich), ethylenediamine (98.5%, Sigma-Aldrich), Nickel acetate tetrahydrate (Ni $(OCOCH_3)_2{\cdot}4H_2O$) (95%, Sigma-Aldrich), dichloromethane (Fisher Scientific), diethyl ether (Fisher Scientific), Methanol (Fisher Scientific) and ethanol (Fisher Scientific) were purchased and used as received. Solvents were dried according to published procedures and distilled under argon prior to use.

2.2. Synthesis of ligand (L)

0.025 mol of salicylaldehyde dissolved in 30 mL of ethanol in a round bottom flask and heat the solution to ~70 °C, the 0.0125 mol ethylenediamine solution which dissolved in 5 mL of ethanol and reflux the mixture for 1 h. After completion the reaction, the solvent was removed using the rotary evaporator at low-temperature and high vacuum (Mohammadikish, 2014). Subsequently, washed with cold methanol to remove excess starting materials. Isolated compound was recrystallized from methanol and dry under vacuum pump at room temperature. Calculate the percent yield was 60% and analyzed by various spectroscopic tools.

2.3. Synthesis of metal complexes

0.01 mol of ligand (L) dissolved in 70 mL of ethanol and heated at 70 °C for 10 min. After heating this solution 0.0112 mol of Nickel acetate tetra hydrate hot solutions were added and refluxed for an hour. After completion of reaction time, the reaction mixture was cooled at room temperature (Mohammadikish, 2014; Siegler and Lutz, 2009). Then, as formed precipitate was filtered and washed with the methanol, to remove excess un-reacted ligand. Subsequently, an additive dripping technique using dichloromethane and diethyl ether for tuning Ni(salen) crystallization for obtained in significant yields.

2.4. Pt functionalized Ni(salen) complexes

The Ni(salen) complex was dispersed in dichloromethane (DCM) (1 mg/ml) and separately 0.25 mg/ml of hexachloroplatinic(IV) acid in ethanol at room temperature. Drop wise Pt solution added into the Ni (salen) complex at 50 °C for 10 min. After that, Ni(salen) and Pt-Ni (salen) solution was deposited on FTO substrates via spin coating (4000 rpm/20 s) and dried at 200 °C for 10 min. The Pt functionalization confirmed using the transmission electron microscopy and device performance. Still Pt is a dominant catalyst electrode and highly electron conductive in dye-sensitized solar cells, due to the Ni(salen) complex were functionalized with Pt. After functionalization catalytic activity was enhanced and we discussed briefly in Section 3. The chemical state Pt in solution form (IV) $(H_2PtCl_6{\cdot}XH_2O)$; after Pt functionalization on Ni(salen) complex, chemical state of Pt changes from (IV) to (II). The Pt(II) nanoparticles (111 phase) based electrode highly chemically and thermal stable. The Pt(II) nanoparticles based films have more electrical and catalytic property as compare to the Pt(IV) (Chen et al., 2017).

2.5. Device fabrication

The mesoporous TiO_2 layer was deposited on FTO glass substrate (sheet resistance 12 Ω/cm^2) by following similar our previously reported process and annealed at 500 °C for 30 min, then immersed in a 3×10^4 mM solution of N719 dye (Solaronix) in the mixture of acetonitrile/*tert*-butanol for 12 h (Islavath et al., 2015). Dye soaked TiO_2 electrode rinsed in anhydrous ethanol and assembled with Pt, Ni(salen) complex and Pt functionalized Ni(salen) complex. Polymer surlyn of thickness (60 μm) used as a sealant of photo and CEs. The liquid electrolyte of 0.05 M iodine, 0.1 M guanidine thiocyanate, 0.5 M 1-butyl-3-methylimidazolium iodide and 0.5 M 4-*tert*-butyl pyridine in acetonitrile was injected into the device by vacuum back filling technique through a hole on CE side. Finally, the hole was sealed with surlyn sheet and microscope cover glass. Subsequently, junction property and performance of device measured under dark and illumination of 100 mW cm^{-2} (Islavath et al., 2015, 2017a).

2.6. Characterization

The morphology of Ni(salen) molecular crystal complex was characterized by using scanning (Nova SEM 450) and transmission electron microscopy (Tecnai-T 30). Current-voltage (I-V) characterization of DSSCs was measured in the dark and under simulated solar light conditions (Oriel Sol3A, 1600 W). The output power is calibrated to 1 sun condition (AM 1.5G) using NREL certified silicon reference cell. All the mentioned solar cell performance values are average of 6 cells. The electrochemical activity of Pt, Ni(salen) molecular crystal and functionalization of Pt on Ni(salen) complex were analyzed using cyclic voltammetry (CH instruments, CH-620E). Uv–visible absorption spectra recorded using Shimadzu spectrophotometer (Uv-3600).

3. Results and discussion

The *N,N′*-Ethylene-bis(salicylideneiminato)-nickel (II) complex (Ni (salen)) was synthesized by the low-temperature chemical process, and it consumes less time with a tunable nanostructure besides exhibiting high reproducibility. After the completion of reaction, the formed product washed with methanol, dried in an oven overnight. Here, we found that the polar solvent (methanol) washing and ageing is the most prominent process for increasing crystallization of Ni(salen) complex, and it aids to grow large-sized crystals with a smoother surface. The chemical structure of ligand and Ni(salen) complex is characterized by using the ^{1}H NMR spectra as shown in Fig. S1. Fig. 1(a) shows the synthetic scheme of Ni(salen) complex. Color changes slowly during the following 2 h from vivid brown to dark-brown and forms several crystals, size of the crystal is around 4 mm, hexagonal shaped as depicted in Fig. 1(b and c). Ni(salen) complex dispersed in polar solvents (1 mg/ml) and deposited on FTO substrate via spin-coating process (4000 rpm/20 s) and annealing at 200 °C for 10 min, to remove the impurity from the electrode. The digital photographs of Ni(salen) film, displays a vivid yellow color with layered crystals on the scale of micrometers (Fig. 1(d)). Single cycle coated Ni(salen) films exhibit good adhesion when compared with the number of coating-cycles.

The FE-SEM image of Ni(salen) complex, showed in Fig. 2(a), and as grown Ni(salen) complex exhibits one-dimensional (1D) rod like morphology with a smooth surface and observed rods are in hollow nature. These rods are in micron length and a diameter ranging from 50 to 150 nm (Mohammadikish, 2014; Siegler and Lutz, 2009). TEM was used to further confirm the hollow nature of the rod is shown in Fig. 2(b). The partly broken hollow rod can be more clearly seen from the high-magnification TEM image (inset Fig. 2(b) right side of the image), and the outer surfaces of this rod are perfectly smooth (Mohammadikish, 2014). It is worthy to note here that before and after adding platinum into the Ni(salen) solution and film, no difference was observed as shown in Fig. 2.