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Counter electrodes from polymorphic platinum-nickel hollow alloys for high-efficiency dye-sensitized solar cells

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HIGHLIGHTS

- Polymorphic hollow PtNi alloy CEs are synthesized with ZnO templates.
- The resultant PtNi alloy CE has superior electrocatalytic activity to redox electrolyte.
- A promising cell efficiency of 8.43% is determined on the optimal DSSC.
- The dissolution-resistance of PtNi alloy electrode is markedly enhanced.

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ABSTRACT

Precious platinum counter electrode (CE) has been an economic burden for future commercialization of dye-sensitized solar cells (DSSCs). Low-platinum alloy CE catalysts are promising in bringing down the solar cell cost without reducing photovoltaic performances. We present here a facile strategy of fabricating ZnO nanorods assisted platinum-nickel (PtNi) alloy microtube CEs for liquid-junction DSSCs. By adjusting the concentration of zinc precursors, the ZnO nanostructures and therefore PtNi alloys are optimized to maximize the electrocatalytic behaviors toward triiodide reduction reaction. The maximal power conversion efficiency is determined as high as 8.43% for liquid-junction DSSC device with alloyed PtNi microtube CE synthesized at 75 mM $Zn(NO_3)_2$ aqueous solution, yielding a 32.8% enhancement in cell efficiency in comparison with the solar cell from pristine platinum electrode. Moreover, the dissolution resistance and charge-transfer ability toward redox couples have also been markedly enhanced due to competitive dissolution reactions and alloyed effects.

1. Introduction

Dye-sensitized solar cell (DSSC) is a cost-effective and high-efficiency photoelectrochemical device by converting solar energy into electricity [1,2]. Among three crucial components including photoanode, redox electrolyte, and counter electrode (CE), CE pumps electrons from external circuit and catalyzes the reduction of oxidized species of redox electrolyte such as triiodide (I_3^-) ions. Therefore, a golden rule in selecting robust CE catalysts is highlighted on their catalytic behaviors toward I_3^- reduction reaction at CE/electrolyte interface, charge-transfer ability arising from the energy difference between redox potential of I^-/I_3^- couples and work function of CE, and anticorrosion by liquid electrolyte. Precious platinum (Pt) is the state-of-the-art CE catalyst in a DSSC device [3–5], while its high cost has been an economic burden for commercial application of DSSCs. To address this issue, various earth-abundant elements have been considered as alternative CE materials [6,7] to enhance the photovoltaic performances of DSSC devices [8–12]. In a typical DSSC, the photogenerated electrons from photosensitive dye molecules will transport through percolating TiO_2 pathways to external circuit and subsequent CE for reducing I_3^- ions [13,14]. In this fashion, CE is crucial in circuiting the electrochemical processes for persistent electricity generation. Additionally, the chemical dissolution of Pt species in I^-/I_3^- liquid electrolyte is inescapable according to negative thermodynamical Gibbs free energy ($\Delta_r G_m$) calculated by Van't hoff isothermal formula [15]. Therefore, a promising route is to explore cost-effective, robust and stable CE materials to replace expensive Pt electrode.

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According to our previous report, binary PtNi alloy is considered as a kind of promising alternative CE materials for DSSCs. The cyclic voltammetry (CV) method is a simple in preparing PtNi alloy [16–21], yielding nanoparticles structure and a power conversion efficiencies as high as 8.77% for optimal $PtNi_{0.1}$ CE based DSSC [19]. Moreover, PtNi alloy CEs can also be realized by a simple hydrothermal method, demonstrating polymorphic structures such as nanowires [22], networks [23], and urchin-like structure [24]. The maximal power conversion efficiency is determined up to 9.08% for liquid-junction DSSC device with alloyed PtNi CE with urchin-like shaped structures [24]. The experimental results reveal that the enhanced charge-transfer ability at CE/electrolyte interface arises from alloying effects including electron deviation form Ni to Pt, creation of gigantic active sites, matching work function to redox potential of I^-/I_3^- couples. Moreover, the chemical dissolution of Pt in I^-/I_3^- liquid electrolyte is also markedly enhanced due to competitive dissolution reactions. Notably, the assignability of polymorphic PtNi alloy CEs benefits to provide extraordinary charge transfer pathways and specific surface area for electrolyte adsorption in comparison with planar Pt electrode [25].

Aligned one-dimensional (1D) CE catalysts can maximize the electron transfer and therefore I_3^- reduction rate. In this fashion, the optimization of CE topographies may enhance solar cell performances by increasing the specific surface area for electrolyte adsorption. Nonetheless, it is still a challenge to fabricate aligned 1 D alloy CE architecture by a one-step method. We present here an easy preparation method using polymorphous ZnO nanostructures as templates, which are prepared with a common hydrothermal method [26–30] by adjusting $Zn(NO_3)_2$ and hexamethylenetetramine (HTMA) concentrations. Ni layer in nanometer thickness is electrochemically deposited on outward ZnO surface, partial Ni species are subsequently displaced by H_2PtCl_6 to form ZnO supported PtNi electrodes. After dissolving ZnO core by acidic solution, hollow PtNi alloy CEs can be successfully realized for DSSC applications. The highlight of the current work is placed on the dependences of CE performances as well as photovoltaic performances in their corresponding devices on concentrations of $Zn(NO_3)_2$ and HTMA precursors. The preliminary results show that a power conversion efficiency as high as 8.43% can be determined in optimized hollow PtNi based solar cell in comparison with 6.36% for DSSC with planar Pt electrode, yielding a 32.8% enhancement in cell efficiency. Moreover, the long-term stability of PtNi alloy electrode is also markedly enhanced, arising from competitive dissolution reactions.

2. Experimental

2.1. Preparation of ZnO nanostructures

1D ZnO nanorods were prepared through a typical hydrothermal method. The freshly prepared FTO conductive glass (12 Ω $square^{-1}$) was inserted into a container with equimolar solution ("growth solution") of zinc nitrate hexahydrate [$Zn(NO_3)_2 \cdot 6H_2O$, 99%] aqueous solution and hexamethylenetetramine [HTMA, $C_6H_{12}N_4$, 99%] aqueous solution. The concentrations of precursors were controlled at 10, 25, 50, 75, 100 or 125 mM. After being agitated for 10 min at room temperature, the reagent was sealed and placed in an oven at 95 °C for 12 h to obtain aligned ZnO nanorods.

2.2. Preparation of polymorphic PtNi alloy CEs

The polymorphic PtNi alloy CEs were synthesized by combining electrochemical deposition and displacing processes. The mixed solution for electrochemical deposition includes 0.05 M of nickel sulfate [$NiSO_4 \cdot 6H_2O$, 98%] and 0.02 M of ammonium chloride [NH_4Cl, 99.5%] aqueous solution. The electrochemical deposition were performed in a three-electrode cell in which a Pt plate was served as a CE, an FTO substrate supported with ZnO nanorods was served as a working electrode and a Ag/AgCl/KCl (3 M) electrode was a reference electrode. The current density was set at 0.25 mA cm^{-2} at air and the deposition time was set at 600 s. Subsequently, the attained substrates were immersed into 1 mM of chloroplatinic acid [$H_2PtCl_6 \cdot 6H_2O$, 37%] aqueous solution for 15 min for galvanic displacement of partial Ni atoms by $PtCl_6^{2-}$ ions. Finally, the resultant electrodes were immersed in 2 mM H_2SO_4 aqueous solution to remove ZnO species for obtaining hollow PtNi alloy CEs. It was known that ZnO nano/microstructures grew on FTO glass, therefore the removal of ZnO cores could not destroy the interfacial contact between PtNi alloys and FTO substrate. As a reference, the commercial Pt CE deposited by a magnetron sputtering method was purchased from Dalian HepatChroma SolarTech Co., Ltd.

2.3. Assembly of DSSCs

A TiO_2 colloid for mesoporous TiO_2 nanocrystal anode film was synthesized through a sol-hydrothermal method [31]. By controlling the active area of 0.25 cm^2 and the average thickness of 10 μm, the TiO_2 colloid film was calcined at 450 °C for 30 min, and subsequently sensitized by 0.25 mM N719 dye (purchased from DYESOL LTD) ethanol solution for 24 h. Finally, a DSSC device was fabricated consisting of dye-sensitized TiO_2 photoanode|redox electrolyte|CE architecture.

2.4. Electrochemical characterizations

The corresponding electrochemical performances were recorded on a conventional three-electrode CHI660E setup. The cyclic voltammetry (CV) curves were recorded with a three-electrode system comprising a Pt plate as a CE, an FTO substrate supported PtNi alloy CE as a working electrode, and a Ag/AgCl/KCl (3 M) electrode as a reference electrode in a supporting electrolyte. Electrochemical impedance spectroscopy (EIS) measurements were recorded on a frequency range of 1E-2 Hz ~ 1E5 Hz and an ac amplitude of 10 mV by assembling symmetric CE|electrolyte|CE dummy cells. Tafel polarization curves were also recorded on the same symmetric cells by scanning potential range of −1~1 V at a scan rate of 10 mV s^{-1}.

2.5. Photovoltaic measurements

The photovoltaic measurements of DSSCs were detected by recording the photocurrente-voltage (J-V) curves with an active area of 0.25 cm^2. The J-V curves were measured under irradiation of a simulated solar light (Xe Lamp Oriel Sol3A™Class AAA Solar Simulators 94023A, USA) from a 100 W xenon arc lamp in ambient atmosphere. To diminish the influence of experimental errors, each DSSC device was repeatedly measured at least twenty times.

2.6. Other characterizations

The top-view morphologies of the PtNi alloy CEs were detected using a scanning electron microscope (SEM, SU8020). X-ray photoelectron spectroscopy (XPS) was measured on an RBD upgraded PHI-5000C ESCA system (Perkin-Elmer) with Mg Kα radiation. The X-ray diffraction (XRD) data were collected in a scan mode with a scanning speed of 10° min^{-1} in the 2θ range of 10–70°. The Pt and Ni compositions in PtNi alloy electrodes were determined by ICP-AES measurement.