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Nickel-nitride-coated nickel foam as a counter electrode for dye-sensitized solar cells

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ABSTRACT

This study employs for the first time surface-nitrided Ni foam as a counter-electrode free of Pt and transparent conducting oxides (TCOs) to realize a cost-effective counter electrode for dye-sensitized solar cells (DSSCs). This electrode simultaneously features high catalytic activity for triiodide reduction and high conductivity in a single layer. The nitrided Ni foam is synthesized by nitridation treatment of open-cell Ni foam in an ammonia atmosphere. This electrode presents high catalytic activity on the nitrided surface and easy electron transport ability in the three-dimensional, interconnected metallic structure. This study provides a preliminary design concept for utilizing the nitrided Ni foam as a promising cost-effective counter electrode that does not require expensive Pt and TCO.

1. Introduction

Solar cells have been drawing attention as advanced alternative energy devices to generate energy without the emission of carbon dioxide [1]. Dye-sensitized solar cells (DSSCs) have received great interest from both academia and industry, because they are reported to have photovoltaic efficiencies above 12% [2–4]. DSSCs usually consist of dye-adsorbed, mesoporous titanium dioxide (TiO_2), an electrolyte containing redox couples, and a counter electrode [5]. The typically used counter-electrode consists of platinum (Pt) catalyst deposited on glass coated with transparent conducting oxide (TCO), which performs two critical functions: it transfers electrons from an external circuit to triiodide and reduces triiodide ions in the electrolyte [6–8]. Many recent studies have focused on finding inexpensive alternative materials with high electrocatalytic activity as a replacement for Pt, because Pt electrodes in DSSCs have several problems such as high material cost (more than ~8% of the total device cost [9]) and poor stability in corrosive electrolytes despite Pt's exceptionally good catalytic activity [7,10]. Various carbon-based materials have received much attention as promising alternatives to Pt and many research groups have reported high photovoltaic performance of 6.6–9.7% efficiency by using various carbon materials such as graphite, active carbon, and carbon nanotubes [8,11,12]. Conducting polymers have also been used effectively as counter electrodes in various redox electrolytes [13–15]. In addition, other approaches involving applying new inorganic materials such as metal carbide, metal sulfide, and metal nitride in counter electrodes have shown good photovoltaic performance (2.7–8.3%) [16–18].

Glass coated with TCO (TCO-coated glass or TCO glass) that is used as a substrate for counter electrodes also has a drawback of cost, owing to the expensive fabrication process. The TCO glasses commonly used in electrodes are In-doped SnO_2 (ITO) or F-doped SnO_2 (FTO). Since the TCO substrate is responsible for more than 40% of the total device cost, DSSCs that use TCO-free counter electrodes are of great interest for reduction in the production cost [19]. Pt-like active material coated onto metal foil, such as Ti or stainless steel foil, is one of the most widely investigated TCO-free electrodes because of its low cost, superior conductivity, and facile synthesis [20,21]. Several attempts have been made to construct cost-effective DSSCs using Pt- and TCO-free counter electrodes. For example, DSSCs with submicron-graphite counter electrodes have achieved 6% cell efficiency [19]. Metal carbide film with conductive carbon has shown 6.6% efficiency [22]. The research groups of Park and Sung utilized poly(3,4-ethylenedioxythiophene) (PEDOT) and camphorsulfonic-acid-doped polyaniline (CSA-doped PANI) film as a TCO- and Pt-free counter electrode for DSSCs, respectively, and demonstrated comparable photovoltaic performance to DSSCs with a platinized TCO counter electrode [23,24].

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Many transition metal nitrides such as MoN, Ni_3N, TiN, and W_2N have been reported previously as highly efficient counter electrodes for DSSCs [17,25–28]. Despite an earlier work by Jiang et al., who applied the surface-nitrided Ni particle film (approximately 200 nm Ni particles onto the surface of the metallic Ni film 200 μm in thickness) as a Pt- and TCO-free counter electrode [25], this paper reports the first usage of nitrided nickel foam as a three-dimensional porous Pt- and TCO-free counter electrode for DSSCs. The Ni foam used in this study is a more advanced three-dimensional porous structure than a structure of particles, because it is comprised of three-dimensionally interconnected metallic struts with pores. As such, it exhibits comparable conductivity to that of a metal foil, allowing metal foam to act as a good electron-transporting substrate from an external circuit to the redox electrolyte when compared to TCO. More importantly, the regularly-spaced open-pore structures in the metal foam can provide a high specific surface area to redox couples in the electrolyte and reduce mass transport limitations of the electrolyte in the electrode. To obtain a bi-functional structured electrode that features good electrocatalytic activity and electrical conductivity, nitrided Ni foam was prepared through nitridation treatment in an ammonia atmosphere. The resulting nitrided Ni foam was observed to have high conductivity in the bulk Ni foam and great catalytic activity on the nitrided surface. The transition metal nitrides in the nitrided surface were able to show high electrocatalytic activity because of their noble-metal-like electronic structures to confirm that the nitrided Ni foam can be used as a new effective counter-electrode without employing expensive Pt and TCO (Fig. 1).

The new DSSC assembled using the nitrided Ni foam in this study exhibits a conversion efficiency approaching ~5%, which is comparable to that of the Pt-coated TCO electrode [29,30] and is considered an excellent efficiency, given that this was measured with gel electrolyte and the Ni metal foam used in this preliminary study was far from being optimized in terms of its pore size range, because the Ni foam used in this study had relatively large pores on the order of several hundred microns while smaller pores might provide better results. This study thus illustrates the great potential for efficient and low-cost Pt- and TCO-free DSSC counter-electrodes on the basis of an open-cell metal-foam-based configuration. In addition, this study can be considered as a framework for designing advanced DSSCs using an optimized metal-foam counter-electrode, because the experimental methods and insights gained here may also apply to other types of metallic-foam counter electrodes with further modified microstructural features, e.g., Ni or Ti foams with smaller pore sizes and larger specific surface area [31–34].

2. Material and methods

2.1. Preparation of nitrided Ni metal foam

The Ni foam (99.9% pure, Metal Foam Korea, Republic of Korea) with a thickness of 500 μm and Ni foil (99.9% pure, Sigma-Aldrich, USA) with a thickness of 125 μm were prepared and compared for use as DSSC's counter electrodes. The Ni foam with hollow strut walls was fabricated (Metal Foam Korea) through a Ni plating method with removable polymer foam as a precursor, which is schematically shown in Fig. 2. The precursor polymer foam was eventually removed thermally, leaving hollow strut structures in the final product of Ni foam (110 ppi, Fig. 3(a)). The Ni foam was immersed in a 0.1 M aqueous NaOH solution and dried to eliminate impurities from the foam surface. After the cleaning process, the Ni foam was chemically etched with sulfuric acid (H_2SO_4) or nitric acid (HNO_3). 10 wt.% sulfuric acid or nitric acid was dissolved in distilled water where the temperature was well maintained; nitric acid treatment was carried out at room temperature whereas sulfuric acid treatment was carried out at 60 °C. The cleaned Ni foam was then immersed in the prepared sulfuric or nitric solution for 20 min, which was stirred using a glass rod to remove bubbles from the foam surface. The prepared Ni foam was nitrided in a box furnace at 450 °C for 2 h, in a flowing pure ammonia atmosphere with a gas flow rate of 100 sccm. The nitrided Ni foam was then heated in a tubular furnace with an Ar/5% H_2 mixture gas at 230 °C for 24 h to reduce the constituent metal oxides. The prepared nitrided Ni foam electrode was finally attached to a TCO-free glass substrate using Surlyn (50 μm, Dupont, USA).

2.2. Electrode assembly for DSSCs

The microscale TiO_2 film with an active area of 0.2 cm^2 was prepared by depositing a viscous TiO_2 paste (Ti-Nanoxide D/SP, Solaronix Co., Switzerland) onto the FTO-coated glass (FTO glass; 8 Ω cm^{-2}, Pilkington TEC glass™, USA). The TiO_2 electrode was immersed in 0.5 mM N719 dye ($Ru[LL0\text{-}(NCS)_2]$, L = 2,20-bipyridyl-4,40-dicarboxylic acid, L′ = 2,2′-bipyridyl-4,40-ditetrabutylammonium carboxylate, Dyesol, Australia) for 24 h. This dye-adsorbed TiO_2 electrode was prepared for use as the working electrode and the nitrided Ni foam for use as the counter electrode. The two electrodes were assembled with electrolyte into a sandwich-type cell using thermal adhesive films (Surlyn: 50 μm, Dupont, USA). The gel-type electrolyte was obtained from Dyesol, Australia and was used as-received.

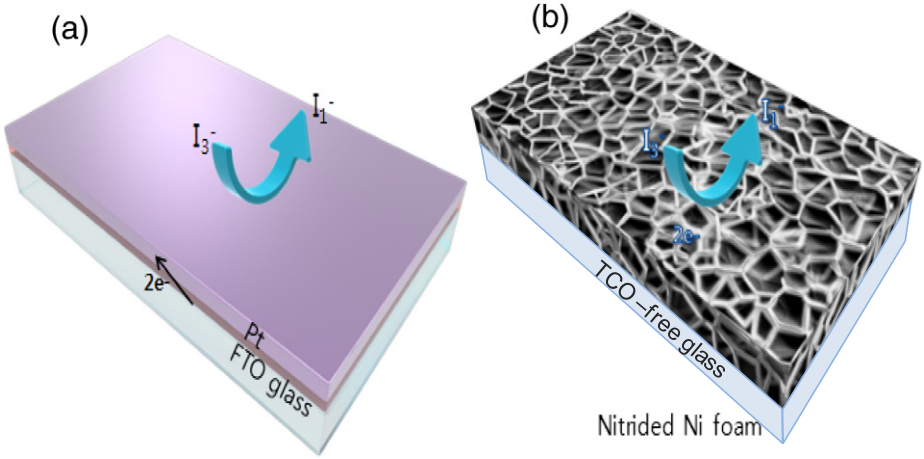

Fig. 1. Schematic diagrams of a DSSC: (a) DSSC with the typical counter-electrode (Pt and FTO glass) and (b) DSSC with the Pt- and TCO-free counter-electrode with nitrided Ni foam.