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.

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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 (TiO2), 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 the TCO substrate is responsible for more than 40% of the total device cost, In-doped SnO2 (ITO) or F-doped SnO2 (FTO). Since the TCO glasses commonly used in the expensive fabrication process. The TCO glasses commonly used in DSSCs that use TCO-free counter electrodes are of great interest for reducing 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].

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 the electrodes are In-doped SnO2 (ITO) or F-doped SnO2 (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 reducing 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].
Many transition metal nitrides such as MoN, Ni₃N, TiN, and W₂N 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.

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 (H₂SO₄) or nitric acid (HNO₃). 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% H₂ 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 TiO₂ film with an active area of 0.2 cm² was prepared by depositing a viscous TiO₂ paste (Ti-Nanoxide D/SP, Solaronix Co., Switzerland) onto the FTO-coated glass (FTO glass; 8 Ω cm⁻², Pilkington TEC glass™, USA). The TiO₂ electrode was immersed in 0.5 mM N719 dye (Ru[LL0-(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 TiO₂ 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.
2.3. Characterization and photoelectrochemical measurements

The thickness and morphology of the nitrided Ni foam were confirmed by field emission-scanning electron microscopy (FE-SEM; SUPRA 55VP, Carl Zeiss, Germany) at an acceleration voltage of 2 kV. Atomic force microscopy (AFM; Innova SPM, Veeco, USA) in tapping mode was also used to examine the surface morphology of the nitrided Ni foam. An X-ray photoelectron spectrometer (XPS; Thermo VG Scientific, USA) was used to determine the chemical composition of the Ni nitride film after 300 s of etching using an Al Kα source. The results were calibrated by referencing C1s at 285 eV and fitted using Avantage Software. The phase and structural changes in the films were examined by X-ray diffraction (XRD; D-MAX2500-PC, Rigaku, Japan) with Cu-Kα radiation (λ = 1.54178 Å).

Electrochemical tests, including three-electrode cyclic voltammetry (CV) and a dummy cell test, were performed using a potentiostat/galvanostat (PGSTAT30, AUTOLAB PGSTAT30, The Netherlands) with an electrolyte of dissolved iodide redox couple in acetonitrile solution of 10 mM LiI, 1 mM I₂, and 0.1 M LiClO₄ at a scan rate of 50 mV s⁻¹. The in-situ optical transmittance change during the CV measurement was observed using a He–Ne laser (λ = 633 nm) to identify and compare the electrochromic properties of the nitrided Ni foam samples with and without etching. The photocurrent density-voltage (j–V) characteristics of the assembled DSSCs and current transient measurement were evaluated using a 500-W xenon isotope lamp (XIL; model 05A50KS source units, SERIC Ltd., Japan) with a light intensity of 1 sun (100 mW cm⁻²), which was adjusted using a Si reference solar-cell fabricated at the National Institute of Advanced Industrial Science and Technology (AIST) in Japan. The j–V characteristic test was carried out under front and rear illuminations. The incident photon-to-current efficiency (IPCE; the QEX10 solar cell quantum efficiency measurement system, PV Measurements Inc., USA) was measured from 300 to 800 nm under short-circuit conditions. The electrical impedance spectra (EIS) were measured using an impedance analyzer (IM6, ZAHNER-Elektrik GmbH & Co. KG, Germany) at a frequency ranging from 0.5 to 10⁵ Hz. The Nyquist plot of EIS was analyzed using an equivalent circuit model presented in the literature [11,35].

3. Results and discussion

A comparison of field-emission scanning electron microscopy (FE-SEM) images of the nitrided Ni foam and foil is shown in Fig. 4. The thicknesses of the nitrided Ni foil and foam are 117 and 458 μm, respectively. While the nitrided Ni foil has the typical dense structure with smooth surface, the Ni foam has a three-dimensional porous structure. In particular, the Ni foam shows interconnected structures consisting of small and large open pores with a compact and uniform surface [35]. In addition, a triangle-shaped hollow space is observed inside the interconnected structures, with ca. 10 μm wall thickness, as depicted in FE-SEM images of Fig. 3(a). The interconnected porous structure consists of small Ni struts, as shown in the magnified FE-SEM surface images of Fig. 3(b). The density of the Ni foam was measured by physical measurement, which was obtained as the ratio of the mass to volume of a rectangular cuboid specimen. The Ni foam has a density of 1.09 g cm⁻³, indicating a porous structure with 12.3 ± 0.6% relative density compared to the theoretical density of Ni foil (8.83 g cm⁻³), which was calculated by X-ray diffraction (XRD, PDF #01-089-7128). This suggests that the Ni foam has a highly porous structure with...
87.7% porosity, which is expected to enhance direct contact with the electrolyte and improve mass transport in the electrode [36–38].

The XRD patterns of the Ni foil, Ni foam, and their nitrided counterparts are shown in Fig. 5. All of the diffraction peaks of the Ni foil and Ni foam after nitridation can be indexed to face-centered-cubic (f.c.c.) Ni (PDF #00-004-0850). A preferential orientation of Ni (200) at a 2θ of 52° is obtained in the Ni foil and nitrided Ni foil, whereas a strong peak at a 2θ of 44° is observed in the Ni foam and nitrided Ni foam. Although the XRD patterns of the Ni foams are different from those of the Ni foil, they are similar to those of Ni particles [25]. The Ni foam comprises interconnected Ni struts well-oriented to the (1 1 1) plane, despite the Ni foil showing orientation to the (2 0 0) plane. This orientation of the electrode in XRD patterns is maintained after the nitridation process. On the other hand, very small peaks around 2θ values of 42° and 52° corresponding to the peaks of NiO were detected in the nitrided Ni foam, which suggests that a small amount of oxidation of the Ni foil and foam also occurred during nitridation at 450 °C in an ammonia atmosphere. Although a rather porous NiO oxide layer generally develops on the surface of pure Ni, the amount of NiO formed at a relatively low temperature of 450 °C for such a short time of 2 h in an ammonia atmosphere is expected to be minimum, and hence, it is not seen in the images in Fig. 4 [39].

The nitridation and oxidation that occurred in the Ni foil and foam were analyzed by X-ray photoelectron spectroscopy (XPS) with Ar ion sputtering, as demonstrated in Fig. 6(c). The binding energy of the oxidized Ni state, NiO, on the surface is observed at 855.0 or 854.3 eV, which gradually disappears with increasing Ar ion sputtering time. As shown in the XPS spectrum of the surface (Fig. 6), a larger amount of Ni nitride or metallic Ni is detected on the surface of the nitrided Ni foam, but a relatively smaller amount is observed on the surface of the nitrided Ni foil. In contrast, the oxidized Ni, NiO, is mainly observed in the nitrided Ni foil electrode. This suggests that the Ni foam was able to be nitrided on a very fine scale because of its porous structure and large surface area [25]. As shown in the XPS depth profiles in Fig. 6(a) and (b), the relative oxygen and nitrogen atomic concentrations are dramatically

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**Fig. 4.** Comparison of FE-SEM images: the surface images of (a) the nitrided Ni foil and (b) nitrided Ni foam; cross-sectional images of (c) the nitrided Ni foil and (d) nitrided Ni foam.

**Fig. 5.** Comparison of XRD patterns of the Ni foil, nitrided Ni foil, Ni foam, and nitrided Ni foam.
decreased, and the metallic Ni state is clearly increased in both of the nitrided Ni electrodes with increasing Ar ion sputtering time. The binding energy of 853.6 eV indicates the presence of Ni nitride in the bulk of the nitrided Ni foam, that of 852.3 eV indicates the presence of metallic Ni, and that of 853.8 eV indicates the presence of Ni nitride in the bulk of the nitrided Ni foil [40].

The electrical resistance of the film plays a significant role in the performance of the electrode, which can also be affected by its bulk state. Indeed, the resistances of the nitrided electrodes differ. For example, the four-point probe measurement reveals a value of 3.3 mΩ cm² for the nitrided Ni foam electrode, which is only slightly larger than that of the Ni foil without nitridation (2.9 mΩ cm²); therefore, the metallic Ni in the bulk state is believed to provide good electron transfer ability to the surface-nitrided Ni foam, which makes it a promising alternative to the TCO substrate.

To increase the surface roughness of the Ni metal foam electrode, the Ni foam was chemically etched with nitric acid or sulfuric acid because they are both effective pickling reagents and strong oxidizers [41]. Etching the nitrided Ni foams with HNO₃ and H₂SO₄ created a rougher surface compared to the nitrided Ni foam electrode [35–41]. A roughness comparison of the nitrided Ni foam and two etched nitrided Ni foams, Ni foam (H₂SO₄) and Ni foam (HNO₃), is shown in the atomic force microscope (AFM) images of Fig. 7(a)–(c) in comparison with roughness of the Ni foil (Fig. 7(d)). The root mean square (RMS) roughnesses of the Ni foam, Ni foam (H₂SO₄), and Ni foam (HNO₃) are respectively 20.1, 45.7, 43.9 nm, all of which are significantly higher than that of the Ni foil (9.6 nm). The increased surface area is expected to influence the electrocatalytic activity of the triiodide redox reaction and increase the current density in solar-cell devices [41–43]. In addition, the wall thicknesses of the Ni foams were decreased with chemical etching because the acids could dissolve the Ni metal easily. Although the thickness of the Ni foam strut decreased by acid treatment from ~19 μm to ~14 μm as shown in Fig. 8, the triangle-shaped hollow space and the total thickness of the Ni foam electrode remained unchanged.

As shown in Fig. 9(a), the XRD patterns of the Ni foams were not changed after etched with acids. In particular, the preferential orientation of Ni (111) at a 2θ of 44° was also observed in the nitrided Ni foam regardless of acid treatment. The binding energy of the nitrided Ni foam electrode was slightly shifted to a higher value in the XPS analysis of Fig. 9(b). As shown in the XPS spectrum of Ni₂p, the binding energy for metallic Ni was 852.7 eV and the Ni nitride peak also appeared for the nitrided Ni foam without acid treatment. In addition, the nitrided Ni foams treated with sulfuric acid and nitric acid had binding energies at 853.06 eV and 853.02 eV, respectively, which is attributed to the Ni foam being finely nitrided and oxidized owing to the increased surface area from chemical etching [25].

A comparison of electrocatalytic activity for triiodide reduction is shown in the j–V curves for the I⁻/I₃⁻ redox of the three different nitrided Ni foams in Fig. 10(a). According to the j–V curves in Fig. 10(a), the
Nitrided Ni foam electrodes exhibit only cathodic peaks, whereas the Pt electrode generally exhibits both a cathodic peak and an anodic peak [44]. Furthermore, the acid treatment in the Ni foam greatly influenced the electrochemical activity of the iodide reduction. The reduction-peak current densities of the Ni foam (HNO₃) (−2.52 mA cm⁻²) and Ni foam (H₂SO₄) (−2.45 mA cm⁻²) are significantly higher than that of the Ni foam (−1.6 mA cm⁻²). Fig. 10(b) shows the linear relationship between the scan rate and cathodic peak current. The adsorption of the iodide species was slightly affected by the redox reaction on the electrode surface and the major rate-determining step of the reaction was the diffusion process [10,45]. In addition, the lower slope of the nitrided Ni foam owing to the faster redox reaction was altered by the acid treatment; in particular, the Ni foam (HNO₃) electrode showed the highest slope among them [45]. The nitrided Ni foam (HNO₃) thus has superior electrocatalytic activity for triiodide reduction.

The stability of the nitrided Ni foam electrode was measured by cyclic voltammetry (CV) cycling tests. Iodine typically reacts with metal during corrosion, which causes iodine depletion in the electrolyte [10]. Although the loss of iodine by metal corrosion typically changes the color of the electrolyte from yellow to transparent, the electrolyte remained yellow throughout the CV cycling measurements; furthermore, the absorbance also did not show any change in color after 100 CV cycles [23,46–48]. Only a peak at 360 nm, contributed by the iodide anion, was observed in the UV–vis absorbance spectra of Fig. 11(a), which suggests that the nitrided Ni foams were not degraded by any corrosion of the metal substrate in the iodide electrolyte because the nitrided Ni layer on the surface functioned as a protective layer for the metallic Ni foam [23]. As shown in Fig. 11(b), the cathodic current density only slightly changed after 100 CV cycles from −0.8 V to +0.5 V (vs. Ag/AgCl (sat. KCl)), which implies that the redox reaction of iodine was well maintained in the nitrided Ni foam electrode after long electrochemical tests. Therefore, the nitrided Ni foam demonstrated good reversibility and stability as an electrode in the iodide redox couple.

Fig. 12 shows a comparison of DSSC performance of the counter electrodes with Pt-coated ITO glass, nitrided Ni foil, and nitrided Ni foam. Table 1 also lists the performance of DSSCs with these counter electrodes. The conventional DSSC system consisting of a photoanode, N719 dye-adsorbed 10 μm anatase TiO₂ film on the FTO substrate, and
gel-type iodide redox couple, was tested under 1-sun front-illumination conditions. The nitrided Ni foil counter-electrode shows a poor conversion efficiency of 1.20% owing to its low electrocatalytic activity for the reduction of triiodide. These low conversion efficiency and fill factor (FF) are attributed to the nonporous texture and hence, low density of active surface area. On the other hand, the photovoltaic performance of the nitrided Ni foam counter-electrode is clearly enhanced, because of its much higher active surface area from its three-dimensionally

Fig. 9. Comparisons of (a) XRD patterns, and (b) Ni2p XPS spectra of the nitrided Ni foam, nitrided Ni foam etched with H2SO4 (20 min) and nitrided Ni foam etched with HNO3 (20 min).

Fig. 10. Comparison of redox performances of the three different nitrided Ni foams under iodide redox electrolyte: (a) j−V curves at 50 mV s⁻¹ and (b) relationship between (scan rate)⁻¹/² (v⁻¹/²) and cathodic peak current density (jpc).

Fig. 11. Comparison of redox performances of the three different nitrided Ni foams under iodide redox electrolyte: (a) comparison of UV–vis spectra of electrolyte before and after CV measurement and (b) changes in the cathodic peak current density (jpc) during 100 CV cycles.
interconnected structure of Ni struts [25]. The short-circuit current density ($j_{sc}$) of the DSSCs indeed changed from 3.3 mA cm$^{-2}$ to 9.6 mA cm$^{-2}$ and the $FF$ slightly increased from 0.59 to 0.60. The nitrided Ni foam counter-electrode also exhibited higher catalytic activity in the electrochemical impedance spectroscopy (EIS) curves (Fig. 12(c)) compared to that of the nitrided Ni foil counter-electrode. The semicircle in the higher frequency region represents the charge-transfer process of the electrolyte/electrode interface, whereas that in the lower frequency region represents the Nernst diffusion impedance of $I^-/I_3^-$ redox species within a thin layer in the electrolyte [25]. The nitrided Ni foam counter-electrode showed lower charge transfer resistance ($R_{ct}$) in the range of high frequency in the EIS. On the other hand, the surface charge-transfer resistance of the nitride Ni foil electrode was higher, indicating the poorer electrocatalytic activity. The diffusion resistance ($W_s$) values appear to decrease in the nitrided Ni foam counter-electrode due to the three-dimensionally interconnected porous structures. Higher catalytic activity and easy electrolyte diffusion were demonstrated when the Ni foam electrode was used as a DSSC counter-electrode. Furthermore, mass transport limitations of the electrolyte were influenced considering that both the nitrided Ni foam and foil were used in the same form of thick film. As shown in the current transient test (Fig. 12(b)), the thick dimension of the nitrided Ni foil caused a dramatic decrease in initial photocurrent density generated in the cell, whereas the nitrided Ni foam could sustain the initial photocurrent density because the diffusion limitation of the photocurrent was reduced owing to its three-dimensionally interconnected porous morphology [49].

In an attempt to further improve the DSSC performance, the nitrided Ni foam counter-electrode was chemically etched and also used as a counter electrode, as illustrated in Fig. 13 and Table 2. The short-circuit current density of the DSSCs was particularly increased with chemical etching of the Ni foam electrode, from 9.6 (unetched nitrided Ni foam) to 10.7 (nitrided Ni foam etched with HNO$_3$) and 11.3 (nitrided Ni foam etched with H$_2$SO$_4$) mA cm$^{-2}$. This is attributed to the rougher surface created by chemical etching, which provides a larger specific surface area to the iodide redox couple in the electrolyte. The decline in $R_{ct}$ in EIS of Fig. 13(b) also indicates the improvement in iodide reduction owing to the surface roughened by chemical etching. In addition, the sum of all resistances of the DSSC with the nitrided Ni foam was lower than that of the DSSC with Pt-coated FTO glass because of the inherently lower resistance of the metallic Ni foam electrode; therefore, this low resistance benefited the $FF$ and cell conversion efficiency of the DSSC device with the nitrided Ni foam.

To obtain efficient light harvesting in DSSC devices, the use of scattering layers has been attempted previously [50,51]. Since the counter-electrode substrate can act as a back reflector, the Ni metal substrate might also increase the light harvesting in a DSSC due to its high reflectance property [23,50]. As shown in Fig. 13(d), the reflectance of

<table>
<thead>
<tr>
<th>Material</th>
<th>$V_{oc}$/V</th>
<th>$j_{sc}$/mA cm$^{-2}$</th>
<th>$FF$</th>
<th>$\eta$/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrided Ni foam</td>
<td>0.67</td>
<td>9.62</td>
<td>0.60</td>
<td>3.88</td>
</tr>
<tr>
<td>Nitrided Ni foil</td>
<td>0.62</td>
<td>3.25</td>
<td>0.59</td>
<td>1.20</td>
</tr>
<tr>
<td>Pt</td>
<td>0.74</td>
<td>11.11</td>
<td>0.67</td>
<td>5.27</td>
</tr>
</tbody>
</table>

The dimension of the TiO$_2$ electrode was 0.20 cm$^2$.
the Ni foam is indeed larger than that of the Pt-coated TCO electrode, although the reflectance was decreased by nitridation treatment owing to the formation of Ni nitride on the surface. After nitridation under an ammonia atmosphere, both the color and %R spectra of the Ni foam were changed by acid treatment; additionally, the two different types of chemically-etched nitrided Ni foam, Ni foam (H2SO4) and Ni foam (HNO3), showed different %R spectra. While the Ni foam electrode etched with H2SO4 exhibited a maximum reflectance at the wavelength of ~550 nm, the Ni foam electrode etched with HNO3 showed the lowest reflectance at ~500 nm. Given that the wavelength of 510–550 nm is the typical range for the maximum absorption value of the Ru dye used as a sensitizer of DSSCs, the Ni foam counter electrode etched with H2SO4 appears to have achieved the enhanced light harvesting in the DSSC due to the high reflectance at ~550 nm, which is also in agreement with the tendency observed in the IPCE spectra of Fig. 13(c) [15].

Among the three different Ni foam counter-electrodes used in this study, the nitrided Ni foam etched with HNO3 shows the best DSSC electrode performance by achieving a jsc, Voc, FF, and cell efficiency of 10.7 mA cm−2, 0.69 V, 0.64, and 4.73%, respectively. Taking into account the reference DSSC cell with a Pt-coated TCO electrode displaying a cell efficiency of 5.57%, the 4.73% cell efficiency of the nitrided Ni foam counter-electrode is considered excellent, particularly because this was accomplished by using a foam pore structure far from being optimized and by not using the costly Pt and TCO materials in the counter electrode. This first investigation on the DSSC cell assembled with the nitrided Ni foam counter-electrode indeed has a plenty of room for further improvement such as using Ni foams with a much finer pore size distribution. This study can be regarded as a preliminary framework for designing advanced DSSCs utilizing threedimensionally structured metallic-foam-based counter-electrode with further modifications. Based on this observation, further improved nitrided Ni foams can be considered promising for cost-effective Pt- and TCO-free DSSC counter-electrodes.

### 4. Conclusions

The nitrided Ni foam electrode was applied as a Pt- and TCO-free counter electrode to realize a new cost-effective counter electrode for DSSCs. The nitrided layer on the Ni foam demonstrated good electrocatalytic activity in the iodide redox electrolyte, due to its noble-metal-like electronic structures. Since this nitrided Ni foam consists of three-dimensionally interconnected metallic struts, it can provide good electron transfer paths. In addition, the open-cell porous structures in the Ni foams can provide larger specific surface areas to redox couples and reduce mass transport limitations of the electrolyte in contact with the electrode as compared to the common Ni foil. With further improvement, nitrided Ni foams with their inherent three-dimensionally-connected structure can be considered a promising solution to a cost-effective Pt- and TCO-free DSSC counter-electrode.

### Acknowledgments

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**Table 2**

Summary of the j–V characteristics of the dye-sensitized solar cells (DSSCs) with the three different nitried Ni foam and Pt counter electrodes.

<table>
<thead>
<tr>
<th>Material</th>
<th>Voc/V</th>
<th>jsc/mA cm−2</th>
<th>FF</th>
<th>η/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni foam</td>
<td>0.67</td>
<td>9.62</td>
<td>0.60</td>
<td>3.88</td>
</tr>
<tr>
<td>Ni foam (H2SO4)</td>
<td>0.66</td>
<td>11.3</td>
<td>0.59</td>
<td>4.45</td>
</tr>
<tr>
<td>Ni foam (HNO3)</td>
<td>0.69</td>
<td>10.7</td>
<td>0.64</td>
<td>4.73</td>
</tr>
<tr>
<td>Pt</td>
<td>0.74</td>
<td>11.1</td>
<td>0.67</td>
<td>5.57</td>
</tr>
</tbody>
</table>

The dimension of the TiO2 electrode was 0.20 cm2.
References

    3795–3799.
    F145–F149.
    4009–4014.
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