Fabrication of p-type semiconducting NiCo$_2$O$_4$ thin films using hydroxide nanoplatelet precursors and their application to N749-sensitized photocathodes

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NiCo$_2$O$_4$ is promising as one of the p-type oxide semiconductors for practical applications in optoelectronic devices. In this study, we have elaborated NiCo$_2$O$_4$ hexagonal nanoplatelet films and examined their photovoltaic properties. The film fabrication was actually achieved by four steps: the synthesis of hexagonal nanoplatelets of a Ni$_{1/3}$Co$_{2/3}$(OH)$_2$ precursor, the dispersion of the nanoplatelets in liquid media, the self-assembly of the nanoplatelets on dipped substrates, and the topological conversion of the hydroxide to the oxide by the heat treatment. The resultant NiCo$_2$O$_4$ thin films had structural features such as the crystallographic (111) orientation, the high specific surface area, and the high light-scattering ability. As a result, the NiCo$_2$O$_4$ thin films loaded with an N749 dye could work effectively as photocathodes in the configuration of dye-sensitized solar cells.

Key-words : Semiconductors, Hydroxides, Thin films, Self-assembly, Micropores, Mesopores, Dye-sensitized solar cells

1. Introduction

Dye-sensitized solar cells (DSSCs) and perovskite solar cells are photovoltaic devices that can be chemically processed at low temperatures. Since their pioneering works,$^{1,2}$ they have been attracting much attention due to practically high light-to-electricity power conversion efficiencies as well as relatively low processing costs. These kinds of photovoltaic cells consist generally of charge separation materials and charge transport materials. In particular, the development of hole transport materials (HTMs) is highly required because they have been shown to influence or govern the overall performance of the photovoltaic devices.$^{3-6}$

HTMs are roughly classified into organic and inorganic semiconductors. For organic semiconductors, poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) and 2,2’,7,7’-tetraakis(N,N-di-p-methoxyphenylamino)-9,9’-spirobifluorene (spiro-MeOTAD) are widely used in the photovoltaic devices. While these organic HTMs have excellent electrical conductivities, their long-term use is limited due to their environmental instability.$^7$ On the other hand, inorganic semiconductors have been proven to be thermally and chemically stable, and are expected for realizing highly efficient, long-life devices. Nickel oxide (NiO) is one of the well-known p-type oxide semiconductors$^8$ and has been intensively studied as the candidate of inorganic HTMs.$^1,9,10$ However, it is difficult to control precisely the electronic properties of NiO because of their sensitivity to processing conditions and microstructural characteristics. Furthermore, the low hole mobility of NiO is a major factor of limiting its performance when applied to the photovoltaic devices.

Nickel cobaltite (NiCo$_2$O$_4$) has the inverse spinel structure where Ni occupies the octahedral sites and Co is distributed over both the octahedral and the tetrahedral sites. NiCo$_2$O$_4$ is fundamentally a p-type semiconductor and its electrical conductivity is reported to be on the order of $10^1$ to $10^2$ S cm$^{-1}$,$^{12-15}$ ensuring the rapid transport of charge carriers. NiCo$_2$O$_4$ is also a multifunctional material that can be applied to a supercapacitor,$^{16,17}$ a photodetector,$^{16}$ Na-ion or Li-ion batteries,$^{17,18}$ and electrolyzer.$^{19}$ Several low-cost and simple wet chemical processing methods of NiCo$_2$O$_4$ have been reported so far: the sol–gel method,$^{20}$ the hydrothermal synthesis method,$^{19}$ and the homogeneous precipitation.$^{12}$ The morphological control of NiCo$_2$O$_4$ has also been successful for producing nanoparticles,$^{20}$ nanowires,$^{4}$ nanosheets,$^{21}$ and so on. The pyrolytic conversion of metal hydroxides to metal oxides is another interesting approach to obtain shape-controlled materials.$^{22}$ In particular, layered hydroxide compounds
based on divalent and/or trivalent transition metal ions, namely, Co(OH)$_2$ and Co–Ni layered double hydroxides, can be synthesized by the homogeneous precipitation using a hydrolysis reaction.$^{23,24}$ These hydroxides are well-oriented and converted into pertinent oxides with atomic relative positions remaining almost unchanged.

In the present study, NiCo$_2$O$_4$ thin films were fabricated by using a hydroxide precursor with a nominal Ni$_{1/3}$Co$_{2/3}$ (OH)$_2$ composition. The precursor having a hexagonal platelet morphology was synthesized first by the homogeneous coprecipitation method. The platelets were then placed on a substrate surface using the self-assembly technique$^{16,25}$ through two different fabrication procedures. The resulting hydroxide films were converted into NiCo$_2$O$_4$ by the heat treatment. The films were then applied to photocathodes with an N749 dye. A relationship between the film microstructure and the photovoltaic performance was discussed based on all the experimental results.

2. Experimental procedure

2.1 The first film-fabrication procedure

0.5 mmol of Ni(NO$_3$)$_2$·6H$_2$O (98.0 %, FUJIFILM Wako Pure Chemical Corporation), 1.0 mmol of Co(NO$_3$)$_2$·6H$_2$O (98.0 %, Wako), and 9.0 mmol of hexamethylenetetramine (HMT, 99.0 %, Wako) were dissolved in 200 mL of deionized water. The resultant aqueous solution was magnetically stirred for 1 h at room temperature and then heated at 100 °C for 5 h under reflux in flowing N$_2$ atmosphere. Precipitates after the reaction were collected by suction filtration, washed with deionized water and methylated alcohol several times, and dried at 60 °C using a vacuum dryer to obtain hydroxide nanoplatelets (designated as NP1) with a nominal Ni$_{1/3}$Co$_{2/3}$ (OH)$_2$ composition as a precursor.

Slide glass substrates (Matsunami Glass) or fluorsilicon-doped tin oxide (FTO)-coated conducting glass substrates (Touki) 26 mm × 10 mm in size were washed by acetone under ultrasonication for 15 min and underwent an ultraviolet (UV)/O$_2$ treatment (ASM401N, Asumi Giken) for 5 min. A 0.02-g portion of the NP1 precursor was dispersed in 5 mL of ethanol (95 %, Imazu Chemical) several times, and dried at 60 °C using a vacuum dryer to obtain hydroxide nanoplatelets (designated as NP1) with a nominal Ni$_{1/3}$Co$_{2/3}$ (OH)$_2$ composition as a precursor.

Photocathodes were prepared by immersing the F1-350, F1-550, or F2-550 films in a 0.3 mM ethanol solution of [RuL’(NCS)$_3$]$_2$TBA (L’ = 2,2’:6’,2”-terpyridyl-4,4’,4”-tricarboxylic acid; N749, Solaronix) at 60 °C for 15 min.
The N749/\(\text{NiCo}_2\text{O}_4\) photocathodes were then assembled into a sandwich-type open cell using a flat platinum plate as a counter electrode. The photocathode and the counter electrode were spaced by a polyester film 50\(\mu\)m in thickness and pressed by clamps. An electrolyte solution, which was composed of 0.6 M LiI (97.0\%, Wako), 0.3 M I\(_2\) (99.8\%, Kanto), and 3-methoxypropionitrile (99.0\%, Wako), was introduced into the clamped electrodes by the capillary action. Photocurrent density (\(J\)) and photovoltage (\(V\)) of the cells were measured with an active area of 0.25 cm\(^2\) under the AM 1.5 illumination at 100 mW cm\(^{-2}\) (1 sun). An AM 1.5 filter, a water filter, and an infrared cut filter were placed in the light path to regulate light in the wavelength range of 300–800 nm and reduce the mismatch between the simulated sunlight and AM 1.5.

3. Results and discussion

3.1 Structure and morphology of precursors and films

Figure 1 summarizes results of the basic characterization of the NP1 precursor. The morphology of NP1 is observed to be hexagonal platelets 1.72 \(\pm\) 0.50 \(\mu\)m in average size in an FESEM image of Fig. 1(a). The platelets are piled up in layers as a result of the final drying process. XRD peaks of NP1 in Fig. 1(b) can be indexed to a hydroxide phase which is isosctructural with \(\beta\)-Co(OH)\(_2\) and \(\beta\)-Ni(OH)\(_2\) having the brucite-type hexagonal structure.\(^{24,26,27}\) The (001) peak is strongest in the NP1 precursor, which is due to its well-developed platelet morphology. As seen in Fig. 1(c), an abrupt weight loss is observed at temperatures around 220 °C in TG–DTA curves of NP1. The gradual weight loss then continues at temperatures up to 400 °C. At this point the conversion of the hydroxides to the oxides should be almost completed. An overall reaction of this conversion would be expressed as follows:\(^{28}\)

\[
3\text{Ni}_{1/3}\text{Co}_{2/3}(\text{OH})_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{NiCo}_2\text{O}_4 + 3\text{H}_2\text{O}
\]

A part of the \(\text{Co}^{2+}\) ions in the hydroxides needs to be oxidized to \(\text{Co}^{3+}\) in the spinel oxide phase. The heat-treatment temperature of the F1 film derived from the NP1 precursor was selected as 350 or 550 °C according to the above thermal analysis.

Figure 2 shows a top-view FESEM image and an XRD pattern of the F1 film, which was formed on the slide glass substrate, together with its optical image. The platelets of the NP1 precursor could be transferred from the dispersion liquid and are laid on the substrate surface. The resulting F1 film is \(c\)-axis oriented as seen in its XRD pattern. The film appears almost transparent and is tinged with pale pink, thereby suggesting that it has quite a small thickness.

Influence of the heat treatment of the F1 film was examined next. Figure 3 shows FESEM images and XRD patterns of the heat-treated F1-350 and F1-550 films. The top-view FESEM images reveal that the hexagonal platelets still remain on the substrate although they macroscopically

![Fig. 1](image1.png)

Fig. 1. (a) An FESEM image, (b) an XRD pattern, and (c) TG–DTA curves of the NP1 precursor. Diffraction data of \(\beta\)-Co(OH)\(_2\) (ICDD 30-0443) are also included in (b).

![Fig. 2](image2.png)

Fig. 2. (a) An FESEM image and (b) an XRD pattern of the F1 film together with its optical image, in which the platelets are assembled on the left side of the substrate indicated by a red dotted line.
cracked after heating at both temperatures. The oblique-view images indicate that a few platelets are curled up, which may be due to the volume shrinkage after the heat treatment. The cross-sectional images suggest that the film thickness corresponds to one layer of the platelets. The thickness is apparently decreased at the higher heating temperature. The XRD pattern of the F1-550 film can be assigned to the NiCo$_2$O$_4$ phase with prominent (111) and (222) peaks. The (111) peak is slightly stronger than the (222) peak in the original ICDD powder pattern. An apparently enhanced (111)/(222) peak ratio for the F1-550 film may be due to the measurement inaccuracy, judging from the thinness of the film as well as the noisy background of the pattern. The color of the film is changed to black, supporting the formation of the oxide phase.

Comparing Fig. 2(b) with Fig. 3(g), the NiCo$_2$O$_4$ phase can be formed through the topotactic decomposition of the hydroxide precursor, as depicted in Fig. 3(h). The crystallinity is enhanced and the porous structure is developed in the F1-550 and F2-550 films, as shown in Figs. 5(d)-5(f), through the heat treatment at the higher temperature. The pore size appears to be increased from F1-350 to F1-550 and F2-550. The FFT patterns in Figs. 5(g)-5(i) also indicate the crystallization of the NiCo$_2$O$_4$ phase liquid. The reproducibility of the film fabrication could be confirmed after keeping the dispersion liquid for 1 month.

The morphology of the NP2 precursor was confirmed to be the hexagonal platelets and their size was 1.30 ± 0.22 μm in average, which was slightly smaller than that of the NP1 precursor. The F2 film obtained from the NP2 precursor was also c-axis oriented. Figure 4 shows FESEM images of the F2-550 film. The top-view image indicates that the platelets are more closely packed on the substrate surface than those of the F1-550 film in Fig. 3(d). This also seems to prevent the platelets from being curled up as seen in the oblique-view image. The thickness of the film shown in the cross-sectional image is on the same order as that of the F1-550 film.

### 3.2 Microstructure of films

Figure 5 shows FETEM images and fast Fourier transform (FFT) patterns of the platelets constituting the F1-350, F1-550, and F2-550 films. As seen in Figs. 5(a)-5(c), the formation of the cracks is considerably suppressed in the F2-550 film, which is due to the improved heat treatment where the smaller heating rate of 0.5 °C min$^{-1}$ was adopted in the temperature range between 200 and 350 °C. The crystallinity is enhanced and the porous structure is developed in the F1-550 and F2-550 films, as shown in Figs. 5(d)-5(f), through the heat treatment at the higher temperature. The pore size appears to be increased from F1-350 to F1-550 and F2-550. The FFT patterns in Figs. 5(g)-5(i) also indicate the crystallization of the NiCo$_2$O$_4$ phase.
through the above-mentioned topotactic decomposition without destroying the basic atomic arrangement. Figure 6 compares the N₂ adsorption/desorption isotherm and the pore size distribution of the platelets of the three films. The fitting analysis based on the BET equation revealed that specific surface areas of the platelets were 77.7, 28.8, and 11.9 m² g⁻¹ for F1-350, F1-550, and F2-550, respectively. The isotherm of the F1-350 film in Fig. 6(a) exhibits an initial rise at the low relative pressure and an adsorption/desorption hysteresis in the middle relative pressure range, indicating that the platelets have both micropores and mesopores. According to the IUPAC classification, the observed isotherm is assigned to the type IV and the hysteresis corresponds to the type H2(b), suggesting the presence of pore networks with a wide size distribution of neck widths. The isotherms of the F1-550 and F2-550 films are shifted to the higher relative pressure as compared to that of the F1-350 film, although they still keep the type IV shape with the type H2(b) hysteresis. This can be explained by the pore size distribution shown in Figs. 6(b) and 6(c). While the F1-350 film has a large volume of micro- and mesopores with a narrow size distribution up to 10 nm, the F1-550 and F2-550 films have only a small volume of mesopores with much wider size distributions. The isotherm of the F2-550 film shifts to the higher relative pressure because the pore size is mostly larger than 20 nm. The results of the adsorption/desorption analysis are in agreement with the above FETEM observation, and it is clear now that the heat-treatment condition is of prime significance to control the microstructure of the NiCo₂O₄ films fabricated from the hydroxide precursor.
3.3 Photovoltaic performance

It is important to know the spectroscopic properties of the semiconductor thin films for their use as photoelectrodes. Figure 7 shows transmittance spectra of the F1-350, F1-550, and F2-550 films, which were fabricated on the slide glass substrates, measured in the wavelength region between 200 and 800 nm. The decreased transmittance in the UV region below 320 nm is due to the absorption by the slide glass. The band gap of NiCo2O4 is reported to be 3.40 and 1.97 eV, corresponding to the electronic transition from the O 2p valence band to the Ni 3d-eg/Co 3d-eg and the Ni 3d-t2g/Co 3d-t2g conduction band, respectively. A slight decrease in the transmittance below 600 nm is then ascribed to the band-gap absorption by NiCo2O4. The highest transmittance of F2-550 among the three films is attributed to less light scattering by the platelets which could be attached better to the substrate as observed in Fig. 4. Adversely the lowest transmittance of F1-550 is caused by the enhanced light scattering by the cracking and/or peeling platelets.

Figure 8 shows J-V curves of the N749-sensitized NiCo2O4 photocathodes using the F1-350, F1-550, and F2-550 films. The bare NiCo2O4 photocathode without dye was also prepared for comparison using the F1-550 film. The N749 dye was chosen because of its higher absorbance in the longer wavelength region. Table 1 summarizes the characteristic cell parameters: the open-circuit voltage (Voc), the short-circuit photocurrent density (Jsc), the fill factor (ff), and the conversion efficiency (η). Because of the absorption and scattering of the visible light, the bare NiCo2O4 photocathode can work as the photovoltaic device although its performance is considerably low. The N749-sensitized NiCo2O4 device improves the cell performance by making all the cell parameters increase. This indicates that the highest occupied molecular orbital level of N749 lies below the valence band of NiCo2O4 and hence the photogenerated holes in N749 can be injected to NiCo2O4 effectively.

Comparing among the three N749-sensitized photocathodes, the highest Voc and ff are attained with the F2-
550 film. This is explained by the better charge transport at the interface between the NiCo2O4 platelets and the FTO glass substrate: the suppression of the charge recombination increases $V_{oc}$ and the smooth charge transport improves $J_{sc}$. In contrast, the highest $J_{sc}$ is observed for the F1-350 film. This may be associated with multiple effects of the enhanced light scattering and the higher specific surface area, which are both beneficial to improving the light harvesting efficiency.

Interestingly, the F1-350 film, which was proven to have the much lower crystallinity through the XRD and FETEM analyses, can also serve appreciably as the photocathode. In both the n-type and the p-type photoelectrodes of DSSCs, the carriers injected from dyes are transported through the nanocrystalline semiconductor layer, at least a few micrometers in thickness, to the conducting glass substrate. The number of the carrier-trapping defects should be minimized by improving the crystallinity of the semiconductor layer for enhancing the photovoltaic properties. In the present case, because of the relatively thin NiCo2O4 semiconductor layer, the carrier path is also as short as a few tens of nanometers and hence the defect trapping might be negligible. This is the possible reason for the F1-350 film working as the photocathode.

4. Conclusions

The p-type semiconducting NiCo2O4 thin films were fabricated through the self-assembly of the hydroxide nanoplatelet precursors and their application to N749-sensitized photocathodes. The sensitization of the NiCo2O4 films with the N749 dye led to the appreciable photovoltaic effect as the photocathodes in the DSSC configuration. Furthermore, the photovoltaic performance was shown to be dependent on the microstructure of the NiCo2O4 thin films. Our results demonstrate that the semiconductor layers a few tens of nanometers in thickness can work as the photoelectrode when their microstructure is controlled appropriately.

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