Elevated Temperature Anodized Nb$_2$O$_5$: A Photoanode Material with Exceptionally Large Photoconversion Efficiencies

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O rdered titanium dioxide (TiO$_2$) nanotube arrays in dye-sensitized solar cells (DSSCs), which can potentially increase the electron diffusion length, have shown enhancements in the efficiencies of both charge collection and light harvesting.$^{1-3}$ However, similar to other alternative approaches,$^{4-7}$ the power conversion efficiency of the TiO$_2$ nanotube arrays still remains lower than that of nanoparticle films.$^{8-10}$ It has been suggested that this is due to their reduced available surface sites for dye loading and the possible existence of exciton-like trap states.$^{11}$ In searching for a better solution for developing highly efficient DSSCs, niobium pentoxide (Nb$_2$O$_5$) could be a more suitable candidate than TiO$_2$ and other semiconductors$^{12-14}$ in view of its wider band gap and higher conduction band edge (presented in Figure 1),$^{15,16}$ comparable electron injection efficiency,$^{17,18}$ as well as better chemical stability.$^{19}$ While Nb$_2$O$_5$ nanoparticles,$^{16}$ nanobelts,$^{20}$ and nanofiber networks$^{15}$ have been studied for the development of DSSCs, their photocurrents and photoconversion efficiencies have not reached those of TiO$_2$-based DSSCs due to the reduction in their dye-loading sites.$^{15,16,20}$ It has been suggested that the large unit cell dimension of orthorhombic Nb$_2$O$_5$, in comparison to anatase TiO$_2$, makes it a challenging task to obtain the optimum Nb$_2$O$_5$ morphology for DSSC applications.$^{19}$ The original discovery of a vertically positioned Nb$_2$O$_5$ nanoporous layer gave hope for solving this problem, but the limited thickness of the layer (<500 nm) made it unrealistic as a candidate for DSSCs.$^{21,22}$ Here, we report a critical breakthrough with the synthesis of Nb$_2$O$_5$ crisscross nanoporous networks with thicknesses of up to ~4 μm via a novel electrochemical anodization method carried out at elevated temperatures. The elevated temperature condition was applied based on

**KEYWORDS:** dye-sensitized solar cell · Nb$_2$O$_5$ · nanoporous network · TiO$_2$ · anodization

ABSTRACT

Here, we demonstrate that niobium pentoxide (Nb$_2$O$_5$) is an ideal candidate for increasing the efficiencies of dye-sensitized solar cells (DSSCs). The key lies in developing a Nb$_2$O$_5$ crisscross nanoporous network, using our unique elevated temperature anodization process. For the same thicknesses of ~4 μm, the DSSC based on the Nb$_2$O$_5$ layer has a significantly higher efficiency (~4.1%) when compared to that which incorporates a titanium dioxide nanotubular layer (~2.7%). This is the highest efficiency among all of the reported photoanodes for such a thickness when utilizing back-side illumination. We ascribe this to a combination of reduced electron scattering, greater surface area, wider band gap, and higher conduction band edge, as well as longer effective electron lifetimes.

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the hypothesis that it increases the ion diffusion rate during the anodization process, hence increasing the anodized film thickness. DSSCs with photoanodes based on these structures have been fabricated and demonstrate superior performances in comparison to their TiO$_2$ counterparts.

RESULTS AND DISCUSSION

In the anodization process of niobium (Nb), two factors have been suggested to be the main causes for preventing the formation of porous layers thicker than 500 nm. The first is the high chemical dissolution rate of the porous layer caused by fluorine ions in the electrolytes. The second is the formation of a thick barrier layer on the bottom of the pores, which inhibits further ion diffusion and growth of the porous layer. In order to increase the layer thickness to several micrometers, we first utilized ethylene glycol instead of water as the solvent, which helps reduce the chemical dissolution effect on the porous layer. Second, we increased the electrolyte temperature to 50 °C to enhance the diffusion rate of the ions, thereby enhancing the growth rate of the porous layer. The selection of electrolyte temperature is another important parameter that requires optimization. In this study, we found that the chemical dissolution effect on the porous layer is greatly increased even in the presence of ethylene glycol for temperatures above 50 °C, while the growth rate of the porous layer drops rapidly at temperatures below 50 °C. A detailed description of the anodization process is provided in the Methods section.

The scanning electron microscopy (SEM) image in Figure 2a depicts the surface morphology of the as-anodized niobium oxide layer. A highly organized pore distribution is observed with nanosized pores ranging from 30 to 50 nm. The side walls are around 10 to 20 nm thick. The bottom of the anodized layer (Figure 2c) consists of uniform and packed pseudo-semispheres with a diameter of approximately 50 nm, which is close to that of the pore dimensions. Similar to the anodization of Ti and Al, the formation of these pseudo-semispheres could result from the mechanical stress induced by the effect of the niobium oxide volume expansion. Figure 2d depicts a ~4 μm thick porous layer which is formed after 2 h of anodization with a stratified structure consisting of couple different regions. By zooming in on the cross-sectional image, a ~100–200 nm thick porous layer can be seen on top (Figure 2b). The top morphologies of both upper and underneath layers are almost similar, except that the side walls of the upper layer are thinner and the pores are less ordered, probably due to the chemical dissolution effect (Figure 2a). This upper layer, with similar morphology and thickness to previously reported anodized niobium oxide structures, could be the initial porous layer formed at the beginning of the anodization process. The absence of a barrier layer underneath this initial layer provides further evidence for an enhancement of the rate of ion diffusion created by our unique anodization method at an elevated temperature. The main thick (underneath) layer appears to be made of continuous and highly packed vein-like nanostructured networks (more cross-sectional SEM

![Figure 1](image1.png)

**Figure 1.** Energy state diagram of Nb$_2$O$_5$ and TiO$_2$-based DSSCs featuring their operation principle, in which CS, CE, CB, VB, VAC, and NHE stand for conductive substrate, counter electrode, conduction band, valence band, vacuum, and normal hydrogen electrode, respectively.

![Figure 2](image2.png)

**Figure 2.** SEM images of a Nb$_2$O$_5$ nanoporous network. (a) Top view of the nanoporous network. (b) Cross-sectional view of the top of the nanoporous network. (c) Bottom view of the nanoporous network. (d) Cross-sectional view of the whole nanoporous network. (e) Higher magnification SEM images of cross-sectional view of the nanoporous network. (f) Three-dimensional schematic of the cross-sectional view of the nanoporous network.
images are provided in Figure S1 in the Supporting Information). There are also occasional lateral openings interconnecting them (Figure S1b,f). The “nanoveins” have internal diameters ranging from 30 to 60 nm, while the diameters of the “nanovein valves” are typically reduced by up to 80% of the veins’ original internal diameters (Figure 2e,f). The valves are possibly the residual growths from the internal walls due to the chemical dissolution caused by fluorine ions in the electrolytes. However, two possible chemical dissolution processes, which are field-assisted and localized (random) dissolutions, are generally suggested to contribute to the metal oxide anodized nanoporous structure formation. In order to find out the dominant mechanism for the formation of these Nb2O5 nanoveins, we weakened the electrical field by reducing the anodic voltage from 10 to 5 V during the anodization process, while keeping the fluoride concentration and the rest of the process conditions the same. From the SEM images shown in Figure S2, it can be observed that the density of nanoveins was dramatically reduced. We hence conclude that the formation of these nanoveins is mainly due to the field-assisted chemical dissolution.

From the cross-sectional transmission electron microscopy (TEM) image shown in Figure S3, this criss-cross nanoporous network can provide excellent directional and continuous pathways for electron transfer in addition to enhanced surface area. This potentially reduces the electron scattering that has commonly been seen in a system made of only nanoparticles, hence fulfilling the prerequisites for developing highly efficient DSSCs.

The growth of the nanoporous network is very efficient with a growth rate of ~2 μm/h for the first 2 h (Figures S4 and S5). However, the organized porous surface is partially destroyed, due to excessive chemical dissolution when the anodization duration exceeds 2 h. In addition, saturation occurs and the thickness does not increase further after 3 h of anodization. The surface morphology and thickness of the nanoporous

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Figure 3. Crystal structure of a niobium oxide nanoporous network before and after annealing. (a) Dashed blue line is the XRD pattern of an as-anodized niobium oxide nanoporous network under the same fabrication conditions as Figure 2, and the red line is the XRD pattern of the network after annealing at 440 °C in air for 20 min. Orthorhombic Nb2O5 (ICDD 27-1003) is indicated with *, while Nb metal (ICDD 35-0789) is indicated with ▲. (b) Corresponding Raman spectra of the as-anodized (dashed blue line) and post-annealed network (red line). (c) HRTEM image of one of the nanoporous areas for Nb2O5 nanoporous networks after annealing. The 0.39 nm spacings with no cross-hatches indicate that the orthorhombic phase is present. (d) Corresponding selected area diffraction pattern indexed to the Nb2O5 orthorhombic phase.
network can also be controlled by varying the fluoride content, the applied voltage, the water content, and the temperature. Details are provided in the Supporting Information.

From the XRD patterns (Figure 3a), the as-anodized nanoporous network appears to be amorphous and only niobium peaks are present in the diffractogram. Annealing of the porous network results in crystallization into a Nb$_2$O$_5$ orthorhombic structure (ICDD 27-1003, $a = 6.168$, $b = 29.312$, and $c = 3.936 \text{ Å}$) with diffraction peaks at 28.3, 49.7, 55.1, 58, and 63.1° (more detailed analysis of XRD patterns are provided in the Supporting Information). The Raman spectra (Figure 3b) confirm the results obtained from the XRD measurements. For the as-anodized layer, a broad peak at 242 cm$^{-1}$ can be assigned to bending modes of Nb–O–Nb linkages. The Raman peaks become more prominent after annealing. In addition, there is a peak shift from 650 to 690 cm$^{-1}$, and a new peak appears at 303 cm$^{-1}$, both indicative of the orthorhombic nature of the annealed nanoporous network. According to theory, the orthorhombic and hexagonal (some literature states it as “pseudo-hexagonal”) Nb$_2$O$_5$ structures both have very similar atomic structures. High-resolution transmission electron microscopy (HRTEM) was utilized to further identify the crystal structure of this nanoporous network. Figure 3c shows the HRTEM image of the Nb$_2$O$_5$ nanoporous network in which parallel lattice fringes with spacings of 0.39 nm have been observed. This spacing has been seen previously by Weissman et al., who characterized Nb$_2$O$_5$ structures through a thorough TEM and ab initio investigation and observed this spacing to be indicative of the orthorhombic phase. Figure 3d shows a selected area diffraction (SAD) pattern of the Nb$_2$O$_5$ structure, which has been indexed to the orthorhombic phase.

The DSSCs based on ~2 and ~4 μm thick crystalline Nb$_2$O$_5$ nanoporous networks were assembled using a conventional configuration (Figure 4a). The incident photon-to-electron conversion efficiency (IPCE) spectra of these DSSCs are shown in Figure 4b (pictures of samples after dye loading are provided in the Supporting Information) in comparison to anatase TiO$_2$ nanotube arrays with similar thicknesses as a benchmark (fabrication details are found in the Supporting Information).
Information). The IPCE spectrum of the dye-loaded 4 μm thick Nb2O5 nanoporous network indicates two broad peaks in a wide wavelength range (400–750 nm). The center of the first peak is at 450 nm with a peak magnitude of 52.4%, while the other is at 575 nm with a 61.1% conversion efficiency. Significant conversion efficiencies can also be observed for wavelengths up to 750 nm. These impressive results are far superior to any other reported Nb2O5-based DSSCs that we are aware of and approximately 20% higher than that of TiO2 nanotube arrays with a similar thickness. This enhancement becomes even more obvious for the 2 and 4 μm thick Nb2O5 nanoporous networks when compared to the equivalent TiO2 nanotube array when both thicknesses are reduced to ~2 μm. Note that the presence of a higher open circuit voltage VOC for Nb2O5 when compared to TiO2 is a commonly reported characteristic.15,16,20 This is mainly due to wider band gap (~0.29 eV wider) and higher conduction band edge energy (as shown in Figure 1) of Nb2O5, as VOC is proportional to the difference between the Fermi level of the Nb2O5 or TiO2 electrode and the electrochemical potential of the redox couple.33

In addition to the increase in open circuit voltage, the significant improvement in the short circuit photocurrent density JSC may be due to a larger amount of loaded dye and also possibly less dye agglomerates formed on the oxide surfaces due to the better
chemical stability of Nb$_2$O$_5$.\textsuperscript{18} However, it is widely known that the major drawbacks for utilizing nanoarchitectures, especially those that are based on nanoparticles, are the increase in the random diffusion of electrons (which leads to a higher likelihood of electron entrapment) and the increase in grain boundary density (which gives rise to defect states in the band gap that perform as trap centers for the free electrons).\textsuperscript{19,29} Hence, these effects can largely degrade the electron transport and recombination kinetics. Although TiO$_2$ nanotube arrays have been suggested to offset these drawbacks, recent research reveals that the possible fluoride and nitrogen impurities in TiO$_2$ nanotubes, mainly embedded during anodization, can create additional trap states, which is implied to be the cause for lower electron mobility and shorter electron lifetime.\textsuperscript{11} Here our Nb$_2$O$_5$ nanoporous networks can provide continuous and directional electron transfer pathways, which to a high degree, perform similar to those of TiO$_2$ nanotube arrays. More importantly, they have much better chemical stabilities, hence minimizing the fluoride and nitrogen doping effect. We find no impurities within these nanoporous networks by utilizing various surface characterization techniques, including XRD, Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS) (detailed XPS spectra of both Nb$_2$O$_5$ nanoporous networks and TiO$_2$ nanotube arrays are provided in Figure S13).

Open circuit voltage decay (OCVD) measurements were performed to estimate effective electron lifetime and verify the above assumptions. According to Figure 5c,d, electrons in these Nb$_2$O$_5$ nanoporous networks exhibit much longer effective lifetimes in comparison to those in TiO$_2$ nanotube arrays, indicating a combined effect of higher energy level of conduction band of Nb$_2$O$_5$ and fewer recombination centers in the nanoporous networks.\textsuperscript{15,29,34} We further analyzed the electron transport and recombination properties in the photoanodes of Nb$_2$O$_5$ nanoporous networks and TiO$_2$ nanotube arrays by utilizing electrochemical impedance spectroscopy (EIS). EIS is regarded as a powerful technique to characterize the transport and recombination in DSSCs, and appropriate physical models have been developed to interpret the results.\textsuperscript{35–37} EIS spectra of Nb$_2$O$_5$ and TiO$_2$ were measured in the dark under the bias voltage of $-0.67$ and $-0.60$ V, respectively. A well-developed equivalent circuit by Juan et al.\textsuperscript{35} was employed to fit the experimental data of impedance spectra for extracting parameters of DSSCs related to electron transport and recombination, using the electrochemical workstation in-built simulation software. Among several key parameters involved in this equivalent circuit, three fitted parameters, which are electron
transport resistance ($R_w$) in the oxide layer, charge
transfer resistance of the charge recombination be-
 tween electrons in the oxide and $I_3^-$ ions in the
electrolyte ($R_a$), and chemical capacitance of the oxide
layer ($C_m$), could be used in order to determine the
parameters for the evaluation of cell performance,
such as the electron transport time ($\tau_d$), effective
electron lifetime ($\tau_{e,ff}$), and effective diffusion length
($L_{eff}$). 16–39

According to the Nyquist plots of the impedance
spectra in Figure 6a,b, it is seen that the radiiuses of
the semicircles of the Nb$_2$O$_5$ nanoporous networks are
almost 10-fold larger than those of TiO$_2$ nanotube
arrays of similar thicknesses, which implies that
Nb$_2$O$_5$ films have much larger charge transfer resis-
tances and, therefore, greatly enhanced electron life-
times. This conclusion is also supported by both the
Bode phase plot displayed in Figure 6c, in which the
left frequency peaks of Nb$_2$O$_5$ films (centered at
around ~0.8 Hz) are more left-shifted as compared to
those of TiO$_2$, as well as the OCVD results shown in
Figure 5d. The fitted parameters shown in Figure 6d
indicate that the $\tau_{e,ff}$ values of 2 and 4 $\mu$m Nb$_2$O$_5$
nanoporous networks are 8.31 and 5.71 s, respectively,
which are approximately 13- and 11-fold longer than
those of TiO$_2$ nanoporous arrays with similar thicknesses.
However, their $\tau_d$ values are almost 4 times longer than
their TiO$_2$ counterparts, hence leading to smaller elec-
tron diffusion rates. This could be possibly due to the
lower natural conductivity of Nb$_2$O$_5$ itself. Fortunately,
their superiorly enhanced effective electron lifetimes
compensate the shortfall of smaller electron diffusion
rates in the photoanodes, which results in enhanced
$L_{eff}$ in comparison to those of TiO$_2$ nanotube arrays.
Additionally, we have conducted complementary tran-
sient absorption spectroscopy for electron recombina-
tion investigations of our Nb$_2$O$_5$ nanoporous network
in comparison to TiO$_2$ nanotube arrays of similar
thicknesses. However, no conclusive differences were
observed, and the results are not presented in this paper.

CONCLUSION

In conclusion, we have fabricated Nb$_2$O$_5$ crisscross
nanoporous networks with a thickness up to ~4 $\mu$m by
using a unique electrochemical anodization method at
elevated temperatures that provides an efficient pro-
cess to obtain porous morphologies. This nanoporous
network offers superior dye-loading sites, excellent
continuous and directional pathways for electron transfer,
as well as enhanced effective electron life-
times. These advantages, together with the relatively
wider band gap and high conduction band edge of
Nb$_2$O$_5$, result in an ideal material for the creation of
photoanodes for highly efficient DSSC applications.
Demonstrated conversion efficiency of 4.1% from a
~4 $\mu$m thick Nb$_2$O$_5$ photoanode is >50% higher than
that of a TiO$_2$ nanotube array with a similar thickness.
The 4.1% efficiency achieved is lower than the 15%
value which justifies commercialization but creates real
research and development opportunities to enhance
performance by synthesizing thicker porous structures
as well as utilizing front-side illumination by realizing
these structures on transparent conductive substrates.

METHODS

Fabrication of Nanoporous Niobium Pentoxide. The starting ma-
terial was niobium foil (99.95% purity, Sigma Aldrich) with a
thickness of 0.25 mm. The surface of each specimen was
cleaned ultrasonically with acetone, then washed with isopro-
pyl alcohol and distilled water, and finally dried in a stream of
a general area detector diffraction system (GADDS) for X-ray
diffraction; and a Bruker D8 DISCOVER microdiffractometer fitted
with Al non-monochromated X-rays (20 kV, 15 mA)
instrument using Al non-monochromated X-rays (20 kV, 15 mA)
with the hemispherical energy analyzer set at a pass energy of
100 eV for the survey spectrum and 20 eV for the peak scans.

Solar Cell Fabrication. The Nb$_2$O$_5$ electrode was first immersed
in a 0.2 mM N3 dye (Solaronix) in a mixture of acetonitrile and
tert-butyl alcohol (volume ratio 1:1) and kept at room tempera-
ture for 24 h. The counter electrode was 30 nm thick platinum,
sputtered on a FTO substrate (Delta Technologies). The electro-
lyte was a solution of 0.6 M 1-butyl-3-methylimidazolium iodide
(Sigma Aldrich), 0.03 M I$_3$ (Sigma Aldrich), 0.10 M guanidinium
thiocyanate (Sigma Aldrich), and 0.5 M 4-tert-butyl pyridine
(Sigma Aldrich) in a mixture of acetonitrile and valeronitrile
(volume ratio, 85:15). The dye-adsorbed Nb$_2$O$_5$ photoanodes
and platinum counter electrodes were assembled into a sand-
wich-type cell and sealed with a hot-melt sealant with a
thickness of 25 $\mu$m (Solaronix). The Nb$_2$O$_5$ electrodes had
dimensions of 5 mm × 5 mm (i.e., 0.25 cm$^2$).

Solar Cell Characterization. Photovoltaic measurements were
performed using an AM 1.5 solar simulator (Photo Emission Tech.). The power of the simulated light was calibrated to
100 mW cm$^{-2}$ by using a reference silicon photodiode with a power
meter (1835-C, Newport) and a reference silicon solar cell to
reduce the mismatch between the simulated light and AM 1.5.
Current–voltage (I–V) curves were obtained by applying an external bias to the cell and measuring the generated photocurrent with a Keithley model 2400 digital source meter. The voltage step and delay time of photocurrent were 10 mV and 40 ms, respectively. OSCs fabricated with commercially available TiO2 nanoparticle-coated glass plates (Dyesol, Australia) were tested and compared with their factory specifications in order to standardize the cell fabrication and testing conditions. The IPCE values for the cells were determined using a system comprising a monochromator (Cornerstone 330), a 300 W xenon arc lamp, a calibrated silicon photodetector, and a power meter. To establish the dye loading of the sensitized Nb2O5 nanoporous networks and TiO2 nanotube arrays, samples sensitized with N3 were placed into a 10 mM solution of KOH to desorb the dye. Absorbance spectra of the desorbed dye were examined using a spectrophotometric system consisting of a Micropack DH-2000 spectrophotometer. EIS spectra were measured in the dark under different bias voltages using a CHI 700 electrochemical workstation with impedance analyzer in a two-electrode configuration.

**Conflict of Interest:** The authors declare no competing financial interest.

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**Supporting Information Available:** More SEM images of Nb2O5 nanoporous networks under different fabrication conditions, cross-sectional TEM image of Nb2O5 nanoporous networks, detailed analysis of XRD spectra of Nb2O5 porous layers before and after annealing, fabrication details of TiO2 nanotube arrays, digital images of Nb2O5 sample after dye loading and XPS spectra of both Nb2O5 and TiO2 samples. This material is available free of charge via the Internet at http://pubs.acs.org.

**REFERENCES AND NOTES**


