Three-dimensional porous vanadium nitride nanoribbon aerogels as Pt-free counter
electrode for high-performance dye-sensitized solar cells

Guiqiang Wang ^{a*}, Shuo Hou ^a, Chao Yan ^a, Yuan Lin ^b, Shaomin Liu ^c

^a School of New Energy, Bohai University, Jinzhou 121013, China

^b Institute of Chemistry, Chinese Academy of Science, Beijing 100190, China

^c Department of Chemical Engineering, Curtin University, WA 6845, Australia

* Corresponding author, email: wgqiang@bhu.edu.cn (G. Wang),

Abstract: Three-dimensional (3D) porous vanadium nitride nanoribbon aerogels (PVNNRAs) are prepared by hydrothermal synthesis and subsequent nitridation in ammonia/argon atmosphere and investigated as Pt-free counter electrode in dye-sensitized solar cells (DSCs). 3D porous nanoribbon aerogel can simultaneously offer more electrocatalytic active sites, a fast electron-transport pathway, and a favorable electrolyte diffusion channel, which endows the PVNNRA electrode with high electrocatalytic activity for the reduction of I_3^- . Under full-sun illumination (AM 1.5, 100 mW cm⁻²), the DSC fabricated with PVNNRA counter electrode achieves a conversion efficiency of 7.05%, which is comparable to that of DSCs fabricated with Pt counter electrode. In addition, the PVNNRA electrode exhibits good stability in I^-/I_3^- redox electrolyte. Thus, 3D PVNNRAs can be considered as a cost-effective alternative to Pt as the counter electrode of DSCs.

Keywords: porous vanadium nitride nanoribbon; electrocatalytic activity; aerogels; counter electrode; dye-sensitized solar cells

1 Introduction

Owing to their low cost, relatively high conversion efficiency, and simple fabrication process, dye-sensitized solar cells (DSCs) have attracted extensive attention and been considered as one of the most prospective alternatives to traditional Si solar cells [1-4]. A typical DSC holds a sandwich structure with a dye-sensitized nanocrystalline photoanode, an electrolyte containing I^-/I_3^- reox couple, and a catalytic counter electrode. As one of the main components of DSCs, the counter electrode plays a significant role in regulating the photovoltaic performance of the cell by collecting the electron from external circuit and catalyzing the I_3^- reduction at the electrolyte/counter electrode interface. Thus, an ideal counter electrode should exhibit good electrocatalytic activity and electrical conductivity. So far, Pt is still the preferred counter electrode material in DSCs due to its excellent electrocatalytic activity, high conductivity, and good stability [5-9]. However, the limited reserves and associated high cost of Pt severely restrict its large-scale application in DSCs. Therefore, considerable efforts have been made to replace Pt counter electrode with cheaper materials, such as carbonaceous materials [10-17], conducting polymer [18,19], transition metal compounds [20-26], and metal alloy [27-29].

Recently, our works as well as others reports demonstrated that some transition metal nitrides exhibited Pt-like electrocatalytic activity due to the similarity of the electronic structure of transition metal nitrides to that of the noble metals [30-34]. Therefore, it is reasonably expected that a certain transition metal nitride can be the low-cost substitute for Pt in fabricating the counter electrodes of DSCs. Vanadium nitride (VN) is a low cost inorganic material, which is attracting increasing attention

in the field of energy conversion and storage due to its high electrical conductivity and electrochemical activity [35-37]. Wu et al. employed VN nanoparticles as the counter electrode material to replace the expensive Pt in DSCs [33]. However, the VN counter electrodes cannot yet be as effective as the Pt counter electrode in the I^-/I_3^- redox electrolyte. Previous studies indicate that the electrochemical property of the electrode materials could be greatly improved by their nanostructuring [38]. Various nanostructured counter electrodes, such as nanorods [39], nanotubes [40], nanosheets [41], and nanospindles [42], have been prepared to enhance their electrocatalytic performance.

In this work, we proposed a novel strategy to fabricate high-efficiency Pt-free counter electrode materials. Three-dimensional (3D) porous VN nanoribbon aerogels (PVNNRAs) were prepared by a simple hydrothermal process and subsequent annealing in an ammonia/argon atmosphere, and investigated as the counter electrode for DSCs. 3D PVNNRAs have a wealth of optimized properties: 1. high porosity and few grain boundaries are beneficial to the electron transport and electrolyte diffusion; 2. large accessible surface area is advantageous in increasing the electrolyte/electrode contact area and electrocatalytic active sites. The DSC based on the PVNNRA counter electrode achieves a conversion efficiency of 7.05%, which is very close to that of the cells with conventional Pt counter electrode.

2 Experimental

3D PVNNRAs were prepared by a hydrothermal process using NH_4VO_3 as the precursors, followed by annealing in an ammonia/argon atmosphere. Briefly, 0.3 g

NH_4VO_3 was dispersed in 80 mL mixed solution of water and ethanol with volume ratio of 9:1. Then, HCl was dropped into the above solution to adjust pH value to 3. The mixture was stirred at room temperature for 30 min and then transferred to a 100 mL Teflon-lined autoclave. The autoclave was heated at 180°C for 20 h, and then cooled down to room temperature. The obtained sample was washed with distilled water for several times and freeze-dried for 48 h. 3D PVNNRAs were obtained by annealing the freeze-dried sample at 550°C for 3 h under a mixed gas of ammonia and argon ($\text{NH}_3:\text{Ar}=40\text{ sccm}:40\text{ sccm}$).

PVNNRA counter electrodes were prepared by spraying PVNNRA dispersion onto pre-cleaned F-doped tin oxide (FTO) glass with an air brush and sintered at 400°C for 15 min under a nitrogen atmosphere. To obtain PVNNRA dispersion, 150 mg of the as-prepared PVNNRAs were mixed with 10 μL tetrabutyl titanate and 10 mL isopropanol by sonication.

TiO_2 colloidal paste was prepared according to the procedures reported previously [43]. The TiO_2 electrodes with 9 μm -thick TiO_2 film were prepared by coating TiO_2 colloidal paste on FTO glass using doctor-blade method, followed by thermal treatment at 450°C for 30 min. After that, the as-prepared TiO_2 electrodes were immersed into the ethanol solution of N719 dye (0.5 mM) at room temperature for 16 h. The dye-sensitized TiO_2 electrodes were rinsed with absolute ethanol and dried in air. DSCs were fabricated by assembling the dye-sensitized TiO_2 electrodes, the electrolyte, and the counter electrodes in a sandwich structure. The electrolyte was composed of 0.5 M 1-hexyl-3-methylimidazolium iodide, 0.2 M LiI, 0.05M I_2 , and

0.4 M 4-tert-butylpyridine with 3-methoxypropionitrile as the solvent.

Scanning electron microscopy (SEM, Hitachi S-4800) and transmission electron microscopy (TEM, JEM-2100F) were employed to investigate the morphologies of as-prepared samples. X-ray diffraction (XRD) patterns were recorded with a Bruker D8 diffractometer using Cu K α radiation. Electrochemical impedance spectroscopy (EIS) measurements were performed on a Solartron 1287/1255 electrochemical system in the frequency range of 0.1-10⁵ Hz at zero bias. Tafel-polarization measurements were carried out in a symmetric dummy cell with a scan rate of 20 mV s⁻¹. Cyclic voltammetry (CV) measurements were carried out in the three-electrode system using a Pt sheet as the counter electrode and an Ag/Ag⁺ electrode as the reference electrode at a scan rate of 30 mV s⁻¹. The acetonitrile solution of 1 mM I₂, 10 mM LiI, and 0.1 M LiClO₄ was used as the electrolyte. Photovoltaic performance of DSCs was tested with a Keithley 2400 Source Meter under the solar simulator (AM 1.5) illumination at the light intensity of 100 mW cm⁻². The light intensity was calibrated by a standard Si solar cell. A black mask with an aperture area of about 0.2 cm² was applied on the surface of DSCs. The fill factor (*FF*) and the conversion efficiency (η) for a solar cell were calculated according to following equations:

$$\eta = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}} \quad (1)$$

$$FF = \frac{P_{max}}{J_{sc} \times V_{oc}} \quad (2)$$

where J_{sc} is the short-circuit current density (mA cm⁻²), V_{oc} is the open-circuit voltage (V), P_{in} is the incident light power, and P_{max} is the maximum power of the solar cell

per unit area.

3 Results and discussion

As shown in Scheme 1, 3D PVNNRAs were prepared by a two-step process consisting of the hydrothermalization and subsequent nitridation. Vanadium oxide nanoribbon aerogels were prepared through the hydrothermal decomposition of NH_4VO_3 at 180°C . The freeze-dried vanadium oxide nanoribbon transformed into the black porous VN nanoribbon by annealing in an ammonia/argon atmosphere. Fig. 1 shows the XRD curves of the hydrothermal product and NH_3 -annealing sample. Seven diffraction peaks at 2θ of 16.6° , 25.5° , 34.2° , 42.9° , 46.7° , 49.8° , and 61.2° were observed in the XRD curve of hydrothermal product, assigning to (200), (201), (310), (202), (600), (112), and (321) lattice planes of V_2O_5 , respectively. The ammonia-annealed sample exhibits four peaks at 38.1° , 44.3° , 64.3° , and 76.8° , which can be indexed to (111), (200), (220), and (311) crystal planes of cubic VN (JCPDS Card no.73-0528), respectively. These results demonstrate that vanadium oxide nanoribbons were successfully transformed into VN nanoribbons.

Fig. 2 displays the SEM images of the as-prepared vanadium oxide and VN samples. From Fig. 2a, it can be seen that the as-prepared vanadium oxide has a nanoribbons-like morphology with a smooth surface. Fig. 2b shows an aerogel-like structure consisting of interwoven porous VN nanoribbons. The width of VN nanoribbons are between 100 and 500 nm, while the lengths are up to tens of micrometers. Fig. 2b and 2c exhibit that the covered VN nanoribbons can be clearly seen through the upper VN nanoribbons, indicating that the as-prepared VN

nanoribbons are very thin. From the above analysis, it can be concluded that the nitridation process did not destroy the overall shape and size of the nanoribbons, while the interior of nanoribbons become porous. The TEM image shown in Fig. 3a further verifies the porous structure of the VN nanoribbons. The high resolution SEM (Fig. 2c) and TEM (Fig. 3a) images of VN nanoribbons reveal that the pores of nanoribbons have irregular shapes with an average pore size of about 20 nm. The porous structure can increase the surface area of VN nanoribbon. The Brunauer-Emmet-Teller (BET) surface area of 3D porous VN nanoribbon aerogels measured by N₂ adsorption at 77 K is 66.7 m² g⁻¹. The high surface area can provide more electrocatalytic sites, and then is beneficial for enhancing the electrocatalytic performance. The inset in Fig. 3a shows the selected area electron diffraction pattern of porous VN nanoribbon, which confirms that as-prepared porous VN nanoribbon is a single crystal. The high-resolution TEM image shown in Fig. 3b suggests that the inter-planar spacing is 0.24 nm, which corresponds to (111) crystal plane of cubic VN. The energy-dispersive X-ray elemental mappings of nitrogen and vanadium shown in Fig. 3c further confirm the formation of porous VN nanoribbons.

PVNNRAs were deposited on FTO glass by spray coating method. Four electrodes with various thickness of PVNNRA layer were prepared, which were designated as PVNNRA1, PVNNRA2, PVNNRA3, and PVNNRA4, corresponding to the PVNNRA layer thicknesses of 1.1, 2.1, 3, and 4.2 μm, respectively. Fig. 4 shows the top-view and cross-sectional SEM images of the as-prepared PVNNRA3 electrode. The top-view SEM image (Fig. 4a) shows a uniform film consisting of porous VN

nanoribbons. The cross-sectional SEM image of PVNNRA3 electrode (Fig. 4b) reveals that the aerogel-like structure was well maintained throughout the entire porous VN nanoribbons layer on the FTO glass. The electrocatalytic performance of PVNNRA electrodes was characterized by EIS measurements using a symmetric thin-layer cell, which can avoid possible effects from TiO_2 photoanode. For comparison, Pt electrode was also prepared by thermal decomposition of H_2PtCl_6 on FTO glass at 390°C for 15 min, with Pt loading of about $10 \mu\text{g cm}^{-2}$. Fig. 5a compares Nyquist plots of Pt and PVNNRA electrodes. Nyquist plots of all electrodes show two semicircles, which are assigned to the Nernst diffusion impedance of I^-/I_3^- redox couple within the electrolyte and the charge-transfer process at the electrolyte/electrode interface in the order of increasing frequency. The equivalent circuit fitting the EIS spectra is shown in the inset in Fig. 5a, where R_s is the ohmic serial resistance, R_{ct} and CPE is the charge-transfer resistance and the constant phase element at the electrolyte/electrode interface, Z_N is Nernst diffusion impedance in the electrolyte. In previous works, it was reported that the Nernst diffusion impedance of the electrolyte in the small-size pores of the electrode ($Z_{N,pore}$) should be taken into account for the electrodes made from porous materials in contact with I^-/I_3^- electrolyte, especially for those having large catalyst layer thicknesses [13, 44]. The $Z_{N,pore}$ can usually be omitted for the Pt/FTO electrode because the electrocatalytic reaction occurs on the nonporous surface. For as-prepared PVNNRA electrode, the large-size pores of VN nanoribbon and the aerogel-like structure form a favorable 3D channel for the electrolyte diffusion, which can greatly enhance the electrolyte transport

within VN nanoribbon layer and thus render the $Z_{N,pore}$ negligible for the PVNNRA electrode in our case. The EIS parameters were determined by fitting Nyquist plots with the equivalent circuit and summarized in Table 1. CPE increases gradually with the thickness of PVNNRA layer as expected due to the increase in the surface area. The R_s is dominated mainly by the ohmic resistance of FTO substrate and does not vary significantly with the thickness of PVNNRA layer. The R_{ct} value is often used to evaluate the electrocatalytic activity of counter electrode materials in DSCs. A smaller R_{ct} value reflects a higher electrocatalytic activity. From Table 1, it can be seen that the R_{ct} value decreases with the increase in the thickness of the PVNNRA layer. The optimal R_{ct} value of PVNNRA electrode is $1.36 \Omega \text{ cm}^2$ at a PVNNRA thickness of $3 \mu\text{m}$ (PVNNRA3). Clearly, the R_{ct} value of PVNNRA3 electrode is comparable to that of the Pt electrode ($1.06 \Omega \text{ cm}^2$). This demonstrates that the PVNNRA3 electrode can catalyze the I_3^- reduction as effectively as the Pt electrode. The high electrocatalytic activity of PVNNRA3 electrode can be attributed to its unique 3D aerogel architecture consisting of porous nanoribbon. The porous nanoribbons with high surface area can provide more electrocatalytic active sites and fast electron-transport pathway. The aerogel-like structure can provide a 3D electrolyte diffusion channel, in which the diffusion of I^-/I_3^- redox couple is favorable with small hindrance. The combined effect of porous nanoribbon and 3D aerogel-like structure endows the PVNNRA electrode with an excellent electrocatalytic performance. The R_s and Z_N values of PVNNRA3 are slightly higher than those of the Pt electrode. This result demonstrates that the 3D aerogel structure formed by porous nanoribbons hardly suppress the electrolyte

diffusion and has a high electrical conductivity.

Table 1 EIS parameters of PVNNRA and Pt electrodes

Electrode	R_s ($\Omega \text{ cm}^2$)	R_{ct} ($\Omega \text{ cm}^2$)	CPE (μF)	Z_N ($\Omega \text{ cm}^2$)
PVNNRA1	16.5	5.12	18	3.7
PVNNRA2	16.6	2.71	26	4.1
PVNNRA3	16.8	1.36	36	2.8
PVNNRA4	16.9	1.86	42	3.9
Pt	16.6	1.06	13	2.3

The electrochemical stability of as-prepared PVNNRA electrode was tested by monitoring the variation of the R_{ct} value with time using a sealed symmetric thin-layer cell. As shown in Fig. 5b and 5c, Nyquist plot of the symmetric cell based on PVNNRA3 electrode exhibits no marked time-dependent changes of its shape, and the R_{ct} values are nearly identical within the experimental error. These results demonstrate that the as-prepared PVNNRA electrode possesses good electrochemical stability in the I^-/I_3^- redox electrolyte.

Fig. 6a shows CV curves of PVNNRA3 and Pt electrodes in the I^-/I_3^- electrolyte. All curves display the typical redox peaks corresponding to redox reaction of I^-/I_3^- . As shown in Fig. 6a, PVNNRA3 electrode exhibits similar anodic and cathodic peaks to Pt electrode, suggesting that PVNNRA3 electrode is effective in catalyzing the reduction of I_3^- to I^- . Fig. 6b shows consecutive CV curves of PVNNRA3 electrode in I^-/I_3^- electrolyte. With a 30 cycles test, the curves do not change significantly and show stable peak current density. This result indicates that as-prepared PVNNRA3

electrode has excellent electrochemical stability in I^-/I_3^- electrolyte.

The electrocatalytic performance of PVNNRA3 electrode was further investigated by Tafel-polarization measurements. Fig. 7 displays the Tafel polarization curves of dummy cells fabricated with PVNNRA3 and Pt electrodes. Tafel curve can be divided into the polarization zone at low potential, the Tafel zone at intermediate potential, and the diffusion zone at high potential. In the Tafel zone, the exchange current density (J_0), which is directly related to the electrocatalytic activity of an electrode, can be determined by the extrapolation of the cathodic branch to the zero potential line. Fig. 7 indicates that the J_0 value of PVNNRA3 electrode is 0.92 mA cm^{-2} , which is comparable to that of Pt electrode (1.01 mA cm^{-2}). This means that the PVNNRA3 electrode show a similar electrocatalytic activity to the Pt electrode. Therefore, the PVNNRA3 can be used as a highly efficient counter electrode material in DSCs.

Fig. 8a compares the photocurrent density-voltage curves of DSCs based on V_2O_5 , PVNNRA3, and Pt counter electrode under simulated AM 1.5 illumination (100 mW cm^{-2}). The corresponding photovoltaic parameters are listed in Table 2. From this Table, it can be seen that the DSC based on V_2O_5 counter electrode shows a poor conversion efficiency of 2.78%. The DSC based on PVNNRA3 counter electrode shows a V_{oc} of 0.70 V, a J_{sc} of 15.51 mA cm^{-2} , a FF of 0.65, and a η of 7.05%. The IPCE curve of DSC based on PVNNRA3 electrode shown in Fig. 8b is in accordance with the photocurrent density-voltage curve. The value of J_{sc} calculated from IPCE spectrum is 15.82 mA cm^{-2} , which is in good agreement with the measured J_{sc} value. The corresponding photovoltaic parameters (V_{oc} , J_{sc} , FF , and η) of the DSC based on

Pt counter electrode are 0.69V, 16.33 mA cm⁻², 0.66, and 7.43%, respectively. Obviously, the photovoltaic parameters of the DSC with PVNNRA3 counter electrode are very close to those of the cell with Pt counter electrode. This result is consistent with the EIS analysis performed on a symmetric thin-layer cell.

Table 2 Photovoltaic parameters of DSCs based on Pt, PVNNRA3, and V₂O₅ counter electrodes

Electrode	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF	η (%)
Pt	0.69	16.33	0.66	7.43
PVNNRA3	0.70	15.51	0.65	7.05
V ₂ O ₅	0.59	12.09	0.39	2.78

VN particles with different morphologies were prepared and used as the catalyst for the counter electrode of DSCs in the literature [33]. The conversion efficiencies of 5.59%, 6.53%, and 7.29% were achieved for large VN cube, small VN cube, and VN pea, respectively. Although there is no perfect comparison of the DSC in this study with the cell in the literature because the experimental conditions were different, the high conversion efficiency in this study can demonstrate that as-prepared PVNNRA is a promising low-cost alternative to Pt for the counter electrode of DSCs. Additionally, the long-term stability of the DSC based on PVNNRA3 counter electrode was evaluated in a period of 21 days. The device was sealed using a Surlyn film and stored in the ambient air; the photovoltaic parameters were measured once per day. Fig. 9 exhibits the variation of the photovoltaic parameters with time. It can be seen that J_{sc} of the cell remains 92.4% of its initial value after 21 days, while V_{oc} and FF are nearly

unchanged, resulting in a slight decrease in the overall conversion efficiency. This result demonstrates the good stability of the DSC fabricated by PVNNRA3 counter electrode.

4 Conclusions

3D PVNNRAs were prepared by hydrothermal process and subsequent nitridation and successfully demonstrated as an efficient counter electrode material in DSCs. 3D porous nanoribbon aerogel can provide a fast electron transport pathway, more electrocatalytic active sites, and an interconnected channel for electrolyte diffusion. As a result, the PVNNRA electrode displayed a high electrocatalytic activity for the reduction of I_3^- . The DSC based on PVNNRA3 counter electrode achieved a conversion efficiency of 7.05%, which is comparable to that of the cell based on Pt counter electrode. These results showed that as-prepared 3D PVNNRA is a promising low-cost alternative to expensive Pt for application in the counter electrode of DSCs.

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Figure captions

Scheme 1 Schematic preparation procedure for PVNNRAs.

Fig. 1 XRD patterns of vanadium oxide nanoribbon areogels and PVNNRAs.

Fig. 2 SEM images of vanadium oxide nanoribbon areogels (a) and PVNNRAs (b and c). The inset in (b) is the photograph of 3D PVNNRAs.

Fig. 3 (a) TEM image of porous VN nanoribbon; (b) high-resolution TEM image of VN; (c) scanning TEM images porous VN nanoribbon and the corresponding elemental mapping for V and N.

Fig. 4 Top-view (a) and cross-sectional (b) SEM images of as-prepared PVNNRA3 electrode.

Fig. 5 Nyquist plots of the symmetric thin-layer cells based on Pt and PVNNRA electrodes, the symbols and lines correspond to the experimental and simulated data, respectively; (b) Nyquist plots of the freshly prepared cell and that after 20 days; (c) variation of the R_{ct} values of PVNNRA3 electrode with time.

Fig. 6 (a) CV curves for PVNNRA3 and Pt electrodes; (b) Consecutive 30 cycles CV curves for PVNNRA3 electrode at scan rate of 30 mV s^{-1} .

Fig. 7 Tafel polarization curves of dummy cells with Pt and PVNNRA3 electrodes.

Fig. 8 (a) Current density-voltage curves of DSCs based on V_2O_5 , PVNNRA3, and Pt counter electrodes; (b) IPCE spectrum of DSC with PVNNRA3 electrode.

Fig. 9 Variation of photovoltaic parameters of the DSC based on PVNNRA3 counter electrode with time.

Figure 1

Figure 2a

Figure 2b

Figure 2c

Figure 3a

Figure 3b

Figure 3c

Figure 4a

Figure 4b

Figure 5a

Figure 5b

Figure 5c

Figure 6a

Figure 6b

Figure 7

Figure 8a

Figure 8b

Figure 9