CHAPTER 3

FACILE SYNTHESIS OF TUNGSTEN CARBIDE NANORODS AND ITS APPLICATION AS COUNTER ELECTRODE IN DYE SENSITIZED SOLAR CELLS

3.1 INTRODUCTION

TM-Carbides are considered as a potential substitute for Pt because of their low cost, high catalytic activity, selectivity and good thermal stability under rigorous conditions (Chen et al. 1994). WC is a versatile material exhibiting good hardness, a high melting point, durability and conductivity. Lee et al. also prepared tungsten carbide polymer-derived WC (PD) and microwave-assisted WC (MW) by different synthesis methods. The reported energy conversion efficiency was 6.61% and 7.01% respectively (Jang et al. 2010). The aim of this work is to synthesize WCNRs and to apply for DSSC as novel WCNRs based CE catalysts for the regeneration of the Iodolyte redox electrolyte. The WCNRs based CEs were prepared and performance of binder free based DSSC, was compared with the performance of binder based DSSC. Binder based DSSC shows better efficiency.

3.2 MATERIALS AND SYNTHESIS

Sodium tungstate dihydrate ((Na₂WO₄.2H₂O), ACS Reagent, ≥99%), ammonium sulfate ((NH₄)₂SO₄, Bioxtra, ≥99%) and zirconium (IV) oxide (99%, 5µm) powders were purchased from Sigma Aldrich. Glucose (C₆H₁₂O₆, 99%) was purchased from Alfa Aesar. TiO₂ (Degussa P25) was
received from System. N719 Ruthenizer 535-bisTBA and Iodolyte Z-100 were bought from Solaronix. Indium doped tin oxide (ITO) conducting glass slides (7 Ω/sq.cm) were purchased from Xin Yan Technology Limited, China.

3.2.1 Synthesis of WCNRs

3.2.1.1 Synthesis of W$_3$O$_8$ nanorods

The schematic representation for the synthesis of WCNRs is shown in Figure 3.1.

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**Figure 3.1 Schematic representation for the preparation of WCNRs**

$W_3O_8$ nanorods were synthesized by hydrothermal method using $(NH_4)_2SO_4$ as a capping agent as follows. $Na_2WO_4.2H_2O$ and $(NH_4)_2SO_4$ were taken in the 1:2 molar ratio, dissolved in deionized water (15 mL) and then HCl (3 M) aqueous solution was added to adjust the pH value to 2. The
obtained solution was transferred into a Teflon lined stainless autoclave where the reaction was maintained at 180 °C for 8 h. Then the precipitate was isolated by filtration and then washed sequentially with water and ethanol for three times. Finally the solution was centrifuged and resultant precipitate was dried at 60 °C.

3.2.1.2 Synthesis of WC nanorods

In a typical synthesis procedure of WCNRs, suitable amounts of as-prepared W₃O₈NRs and glucose (molar ratio W/C=1:12.8) were dissolved in deionized water (15 mL) and vigorously stirred for 20 min. The mixture was hydrothermally treated in a sealed Teflon lined stainless steel autoclave at 180 °C for 8 h to form carbon coated W₃O₈ nanorods. The as-prepared precursors were calcinated at 900 °C under a flow of H₂/Ar (V_H₂/V_Ar = 1:3, 300 mL min⁻¹) for 3 h and finally WCNRs were obtained.

3.3 CELL FABRICATION

3.3.1 Preparation of WCNRs CE

200 mg of WCNRs powder was finely ground in mortar and then mixed into the 8 mL of ethanol and vigorously stirred overnight until homogeneous suspension was obtained. The resultant homogeneous WCNRs suspension was coated onto the conducting side of ITO glass substrate by spin coating method. The WCNRs coated films were dried at room temperature and heated at 450 °C for 1 h.

A mixture of 200 mg WCNRs material and 4 g zirconium dioxide pearl were dispersed in 8 mL of isopropanol. The mixture was then milled for 4 h using mortar and pestle. Finally the prepared material was ultrasonically dispersed for 48 min (6 segments) and 50 mg of TiO₂ was prepared by the same method. The WCNRs with the mixture of TiO₂ and ZrO₂ binder coated films were dried at room temperature and the product was heated at 450 °C for 1 h.
3.3.2 Fabrication of DSSC

The TiO$_2$ modified photoanode (prepared by doctor blade technique (Pandikumar et al. 2013)) was immersed into the ethanolic solution of 0.3 mM N719 (Ruthenizer 535-bisTBA) dye for 24 h at room temperature. The dye-adsorbed photoanode was withdrawn from the solution and immediately cleaned with ethanol. A WCNRs (with binder and binder free) modified ITO plate was placed on dye-absorbed photoanode and then clamped firmly together. The redox electrolyte (Iodolyte Z-100) solution was introduced into the cell assembly by capillary action. An active area of 0.5 cm×0.5 cm was used to measure the cell performance. A 150 W Xenon arc lamp (Newport, Model 69907) containing simulated AM 1.5G filter with a manual shutter was used as a light source for the experiments.

3.4 CHARACTERIZATION TECHNIQUES

The same instruments were used to analyse the WCNRs as discussed in chapter 2, section 2.4 of this thesis. EIS measurements were carried out using an Ametek VERSASTAT 3-200 Potentiostat. The AC signal had amplitude of 10 mV in the frequency range from 0.1 to $10^5$ Hz at ~0.7 V ($\sim V_{oc}$) DC bias voltage under dark condition.

3.5 RESULTS AND DISCUSSION

3.5.1 Powder X- Ray Diffraction Analysis

PXRD analysis was used to determine the phases of the samples. Figure 3.2 (a, b) indicates W$_3$O$_8$ formed which is identified by the peaks at the 2θ of 23.8°, 27.9°, 28.5°, 34.3°, 37.7°, 47.9°, 50.2°, 56.1°, 56.2°, 58.3°, 63.4° and 71.4°. Those Peaks are corresponding to the (001), (200), (130), (040), (131), (002), (330), (331), (202), (061), (401) and (332) facets of W$_3$O$_8$, in good agreement with the Orthorhombic W$_3$O$_8$NRs (JCPDS card no.: 81-2262; a=6.386 Å, b=10.43 Å c=3.800 Å, SG: C222). The peaks at the 2θ of 31.5°, 35.6°, 48.2°, 65.7°, 73.1° and 75.2° are corresponding to the (001), (100), (101), (002), (111) and (200) facets of WCNRs, in good agreement with the hexagonal WCNRs (JCPDS card no.: 51-0939; a =2.906 Å, c =2.837 Å, SG:
The formation of WC is known to depend on the amounts of carbon sources, heating rate and especially, temperature (Oyama 1992). The main phase observed is WC, although significant amounts of W$_2$C were seen after synthesis from precursor W$_3$O$_8$/Glucose (W/C) (Rees et al. 2008). The diffraction peaks at the 2θ of 34.4º, 39.5º, 52.2º, 61.6º, and 69.4º are corresponding to the (002), (102), (221), (132) and (321) facets of Orthorhombic W$_2$C. These peaks matched with JCPDS card no: 89-2371(a=4.728 Å, b=6.009 Å c=5.193 Å, SG: Pbcn).

![Figure 3.2 PXRD patterns of as prepared (a) W$_3$O$_8$NRs and (b) WC NRs](image-url)
3.5.2 SEM and EDS Analysis

Carbon-coated W$_3$O$_8$NRs were used as the precursors for WCNRs synthesis. This way of introducing carbon within nanorod-structured W$_3$O$_8$ facilitates the reaction by ensuring a uniform distribution of carbon onto W$_3$O$_8$NRs and improving their contact. Figure 3.3 (a) shows the FESEM image of as prepared W$_3$O$_8$NRs. The W$_3$O$_8$NRs have rod like morphology with the length of 300-400 nm and diameter 33 nm.

![Figure 3.3 FESEM images of as prepared (a) W$_3$O$_8$NRs and (b) WCNRs](image)

Figure 3.3 FESEM images of as prepared (a) W$_3$O$_8$NRs and (b) WCNRs
Figure 3.4 EDS images of as prepared (a) $W_3O_8$NRs and (b) WCNRs

The nanorods show no alignment and majority of nanorods is similar in size. The WCNRs show well defined morphology (Figure 3.3 (b)) with 350-400 nm length and 94 nm diameter. WCNRs have been obtained due to the gradual chemical conversion of $W_3O_8$NRs, beginning at the exterior surface and diffusing inward through solid-state carburization towards the nanorod center. From the perspective of the pseudomorphic transformation, solid-state carburization is preferred for the morphological retention of the $W_3O_8$NRs rather than carburization by carbonaceous gases, which had relatively high rates of nucleation. Besides, the excess surface carbon is also likely to be responsible for increased retention of the WCNRs (Yan et al. 2012). The nanorods may act as one-dimensional conductors and thus the nanorods are expected to be
efficient in electron transfer to the electrolyte. The EDS analysis of W\textsubscript{5}O\textsubscript{8}NRs and WCNRs is shown in Figure 3.4 (a, b). The emission peaks corresponding to the elements O and W were observed at 0.57 (O), 1.4, 1.8, 7.4, 8.4, 9.6, 11.3 (W) respectively. The EDS analysis of WCNRs showed the emission peaks corresponding to the elements C and W at 0.3 (C), 1.4, 1.8, 2, 7.4, 8.5, 9.7, 10 (W), respectively (Figure 3.4 (b)).

3.5.3 BET Surface Area Analysis

For studying the pore structures of W\textsubscript{5}O\textsubscript{8}NRs and WCNRs samples and understanding their influence on the catalytic performance, the BET surface area and porosity were analyzed in detail. Figure 3.5 (a) and (b) shows Nitrogen adsorption-desorption isotherm of the W\textsubscript{5}O\textsubscript{8}NRs and WCNRs. The pore size distribution curve of the W\textsubscript{5}O\textsubscript{8}NRs and WCNRs is inserted in Figure 3.5 (a) and (b). Based on these measurements, the specific surface area and the average pore diameter calculated by the BET method and by the BJH method are about 56.86 ± 0.5 m\textsuperscript{2}/g and 401.0302 ± 1.3208 m\textsuperscript{2}/g and 1.986 Å and 7.249 Å, respectively. The total pore volume was about 0.282 cm\textsuperscript{3}/g and 0.238 cm\textsuperscript{3}/g. W\textsubscript{5}O\textsubscript{8}NRs and WCNRs exhibit representative type I and type II isotherms with H3 and H2 hysteresis loop, as shown in Figure 3.5 (a) and (b) respectively. The surface of the W\textsubscript{5}O\textsubscript{8}NRs is composed of mesopores. W\textsubscript{5}O\textsubscript{8}NRs compared to WCNRs has very low surface area. Increased surface area plays crucial role for CE in DSSC applications (Sebastián et al. 2014). The synthesized WCNRs have a highly porous structure and large specific surface area, which may be the key factor to enhance the performance for DSSC. In addition, the mesoporous structure can be considered as an effective electron transport network that facilitates the collection and transfer of electrons from the external circuit and subsequent regeneration of the redox couple. Further, the network is also favorable for the mass transport of the redox couple (Wu et al. 2012).
Figure 3.5  (a) N$_2$ adsorption/desorption isotherm of W$_3$O$_8$NRs and the inset indicates pore-size distribution obtained by the BJH method; (b) N$_2$ adsorption/desorption isotherm of WCNRs and the inset indicates pore-size distribution obtained by the BJH method
3.5.4 Photovoltaic Performance of DSSC with WCNRs CE

The DSSC was fabricated using the WCNRs CE and its photovoltaic performance was evaluated under simulated AM 1.5G solar irradiation of 100 mW cm\(^{-2}\). The working mechanism of the fabricated DSSC is shown in Figure 3.6. During light illumination, the dye molecules are excited which simultaneously inject photogenerated electrons into the conduction band of TiO\(_2\). Then, the electrons move through the TiO\(_2\) surface towards the ITO conducting glass and reach the load via external circuit. At the same time the photogenerated holes reach the WCNRs CE with the aid of I\(^-\)/I\(_3^-\) redox couple in the electrolyte.

![Schematic representation of WCNRs modified CE based DSSC configuration](image)

**Figure 3.6  Schematic representation of WCNRs modified CE based DSSC configuration**

The better performance of the WCNRs CE can be explained as follows: the CE consists of irregular arrangement of WCNRs (Figure 3.6), which exhibits the probability of directed electron pathway along the long axis of the nanorods. These 1D nanorods facilitate rapid transport of photogenerated holes to the conducting glass through straight conduction pathway along the direction parallel to the axis of the nanorods that leads directly to the electron collecting electrode. The highest electrochemical
activity for regeneration of the $\Gamma^{}/I_3^{-}$ redox couple due to the 1D nanofeatures, provided good electron transport (Wu & Ma 2012; Wang et al. 2010). The J-V characteristics of the fabricated DSSC are shown in Figure 3.7 (a). The photovoltaic parameters, such as short circuit $J_{sc}$, $V_{oc}$, FF and $\eta$ of the DSSC with binder free WCNRs based solar cell were found to be 5.44 mA/cm$^2$, 370 mV, 0.29 and 0.59 % respectively. But in the case of mixture of TiO$_2$ and ZrO$_2$ binder based solar cell, the value of $J_{sc}$, $V_{oc}$, FF and $\eta$ were found to be 5.92 mA/cm$^2$, 807 mV, 0.40 and 1.92% respectively.

The investigation of TiO$_2$ bonding with FTO glass had been carried out by Ito et al (Ito et al. 2007). On the surface of TiO$_2$ and FTO/ITO glass, there are many hydroxyl groups (-OH). In the sintering process, an ether bond is formed, and the TiO$_2$ particles adhere to the FTO/ITO glass substrate firmly. Mixed oxides have been investigated as potential electrochemical capacitor or supercapacitor materials (Salari et al. 2011; Yang et al. 2011). We added TiO$_2$+ZrO$_2$ to WCNRs to improve the bonding strength with the FTO glass substrate and we obtained improved results which have been included. Structural, morphological, surface area, electrochemical and photovoltaic studies of the binder material (TiO$_2$+ZrO$_2$) will be reported along with several other binder materials in our future work.

Recently, the efficiency of 2.19% was achieved (Lim et al. 2014) for sputtered Pt CE. However, WCNRS CE based DSSC shows less efficiency than Pt based DSSC. But low cost WCNRS will have the prominent role in production of DSSC modules. The applicability of the WCNRs as CE in DSSC indicates the efficient regeneration of the electrolyte through pinholes and nanopores present in the 1D nanostructure. The stability and sustainability of DSSC with binder free WCNRs CE was studied and the results are shown in Figure 3.7 (b). The observed photocurrent-time profile of DSSC is in good agreement with their J-V characteristics. As soon as the light is turned ‘on’, the photocurrent rises quickly to a maximum value and showed steady-state current as well. When the light is turned ‘off’, sudden fall in the
photocurrent appears and no current in the dark. The steady-state photocurrent-maximum remains same after several ‘on-off’ cycles which revealed that cell has good stability.

Figure 3.7 (Continued)
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Figure 3.7  (a) Photocurrent density vs. voltage curve obtained for WC NRs (binder free, with binder) CE based DSSC under simulated AM 1.5G sunlight (100 mW/cm$^2$) irradiation. (b) Photocurrent vs. time profiles obtained for the WCNRs CE based DSSC under illumination on-off condition. (c) Nyquist plot, (d) Bode phase plot and (e) Bode amplitude plot obtained for the DSSC with WCNRs CE

EIS measurement was conducted at scanning frequencies from 0.01 to 100,000 Hz to analyze the electrochemical characteristics of the DSSC with binder free WCNRs CE. The Nyquist plot (Figure 3.7 (c)) showed several regions from the high frequency regions to the low frequency regions which correspond to different kinds of resistances: (a) Ohmic series resistance ($R_s$) due to the outside circuit resistance (between the substrates resistance and lead connections); (b) charge-transfer resistance ($R_{ct}$) originates from the electron transfer ability at the electrode/electrolyte interface; (c) electrical double-layer capacitance ($C_{dl}$); and (d) diffusion impedance ($Z_w$) of the triiodide/iodide redox couple in the electrolyte (Peng et al. 2011; Wu et al. 2011; Cho & Ouyang 2011). The Bode phase plot (plot of phase shift ($\theta$)
against frequency (Hz)) for the DSSC with WCNRs CE showed increased phase angle value in the lower frequency and decreased phase angle value at higher frequency (Figure 3.7 (d)) which suggests that the prepared WCNRs show higher conductivity and it could be suitable candidate for DSSC application. Further, an increase in the value of \(|Z|\) ohms at the lower frequencies region (\(10^{-1}\) and \(10^{2}\) Hz) in the Bode amplitude plot (plot of log impedance (\(|Z|\)) against frequency (Hz)) (Figure 3.7 (e)) suggests the enhanced catalytic activity of the WCNRs CE.

3.6 CONCLUSION

In this study, the tungsten carbide nanorods were synthesized by pseudomorphic transformation of chemically synthesized \(W_3O_8\)NRs. The synthesized WCNRs were characterized by PXRD, FESEM, EDS and BET surface area analysis. The electrochemical properties were studied with Nyquist plot, Bode phase plot and Bode amplitude plot using EIS measurements. Large surface area WCNRs was found to be good catalytic material. The WCNRs (with binder and binder free) based DSSC showed the overall conversion efficiency of 1.92 % and 0.59 %, respectively. The cell performance can be attributed to the WCNRs network, catalytic activity and 1D efficient charge-transfer network. Such WCNRs as CE provides a potential feasibility for CE in DSSC applications.