

Facile Hydrogen Evolution Reaction on WO₃ Nanorods

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Abstract Tungsten trioxide nanorods have been generated by the thermal decomposition (450 °C) of tetrabutylammonium decatungstate. The synthesized tungsten trioxide (WO₃) nanorods have been characterized by XRD, Raman, SEM, TEM, HRTEM and cyclic voltammetry. High resolution transmission electron microscopy and X-ray diffraction analysis showed that the synthesized WO₃ nanorods are crystalline in nature with monoclinic structure. The electrochemical experiments showed that they constitute a better electrocatalytic system for hydrogen evolution reaction in acid medium compared to their bulk counterpart.

Keywords Tungsten trioxides · Thermal decomposition · Nanorods · Hydrogen evolution reaction · Electrocatalyst

Introduction

One-dimensional (1D) nanostructures such as nanorods, nanowires and nanotubes have attracted attention due to their novel physical and chemical properties as well as their potential use in a wide range of advanced applications in the past decade [1, 2]. As a consequence, many synthetic methods have been developed to prepare various 1D nanostructures [3–6]. Of particular interest is the preparation of 1D nanostructure of tungsten trioxides (WO₃) and its suboxides (WO_{3-x}). WO₃ is used extensively as

materials for electrochromic devices [7–10], gas sensors [11, 12], catalysts [13, 14] and secondary batteries [15]. Several synthetic approaches including electrochemical techniques, sonochemical approach, template mediated synthesis, bioligation, hydrothermal, wet organic and inorganic routes and thermal methods have been reported to fabricate WO₃ nanorods [16–51]. A method for the synthesis of tungsten oxide nanorods with planar defects or textured structure has been introduced by Zhang et al. and this method involves growth of WO_{3-x} nanorods on the tips of electrochemically etched tungsten filament [16]. However, synthesis of such structure has been possible only in the presence of H₂ atmosphere. The nanorods of WO₃ have also been obtained by sonochemical method wherein Koltypin et al. have synthesized a mixture of WO₂–WO₃ nanorods by ultrasound irradiation of W(CO)₆ in diphenylmethane [17]. Tungsten oxide nanorods could also be obtained from templated route by using CNTs and colloidal gas aphanes as templates [18–20]. Therese et al. have adopted an organic amine assisted low temperature hydrothermal route for the synthesis of hexagonal WO₃ nanorods [23]. Inorganic compounds such as Na₂SO₄, Rb₂SO₄ and K₂SO₄ have been demonstrated as structure directing agents for the hydrothermal synthesis of 1-D WO₃ nanorods by Gu et al., Lu et al. and Xiao et al. [24–26]. Srivastava et al. have reported sol–gel followed by dip coating to produce WO₃ nanorods [28]. By altering the composition and concentration of solvent, it was shown that different morphologies and phases of WO₃ nanorods can be achieved [29]. However, all of these reported efforts involve multistep processes and limited to the use of directing agents such as CNTs and M₂SO₄ (M = Na, Rb and K). Hence, the synthesis would be tedious and requires careful removal of the structure directing agents to avoid contaminants. Moreover, sol–gel and hydrothermal

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methods proceed with a low yield. In order to overcome the difficulties mentioned, thermal method has been employed widely for the large scale synthesis of tungsten oxide nanorods/nanowires as they are simple, easy and free from catalysts and contaminants. Heat treatment of tungsten metal, such as, tungsten foil or tungsten filament heated at 800–1,600 °C [40–42], tungsten powder heated at 950 °C under the Ar gas flow on ITO glass/tungsten substrate at 900–1,100 °C [44], thermal evaporation of tungsten powder [45] and tungsten hexacarbonyl heated at 700 °C [39] have yielded 1-D WO₃ nanorods. All the above thermal methods related to 1-D tungsten oxide formation from the gaseous phase (vapor deposition) or thermal evaporation techniques are technically complex, require high temperature, harsh growth conditions, expensive experimental setup and complicated control processes. Recently, the single source molecular precursor route has opened a useful way for the synthesis of WO₃ nanorods/nanowires by thermal decomposition method [49–51]. It offers the distinct advantage of simplified fabrication procedure and equipment as compared with the thermal evaporation or vapor deposition methods. However, multiple steps for the synthesis of both precursor and 1-D WO₃, longer reaction time for precursor (6 days or 10 h) and relatively higher pyrolysis temperature (750 °C) were required. In this report, a facile synthesis of WO₃ nanorods based on the thermal decomposition of tetrabutylammonium decatungstate has been described. The method has several unique advantages. Firstly, it has been possible to obtain high yields of WO₃ nanorods at a relatively low temperature (450 °C) and short reaction time as compared to previously reported methods involving high temperature (≥700 °C). Secondly, different morphologies of the material (nanosheets and nanorods) can be achieved by altering the pyrolysis time. Moreover, the method followed for the synthesis of precursor is a simple precipitation which does not require any tedious experimental set up or does not consume much time when compared to the other methods. Finally, it is a generic method which can be applied for synthesis of other metal oxides such as MoO_x and V₂O₅ by suitably altering the metal in the precursor.

There has been a continuous interest in studying the dimensionality-dependent properties of WO₃ and ultimately to fabricate nanodevices. Wang et al. have shown high Li intercalation capacity (1.12 Li per formula unit) for WO₃ nanorods than its bulk counterpart (0.78 Li per formula unit) [31]. The enhanced electrochemical performance has been attributed to the unique rod-like structure combined with increased edge and corner effects. Non stoichiometric WO_{2.72} nanorods are found to function as sensors with extraordinary sensing ability and the activity has been attributed to the very small grain size and high surface to volume ratios associated with the nanorods

[43]. Liu et al. have exhibited low turn on field for electronic emission by WO_{2.9} nanorods [46]. Photoluminescent emission spectrum of tungsten oxide nanorods was found to show an additional blue emission peak at 437 nm than its bulk system [30]. All these results show the unique properties of WO₃ nanorods in comparison to their bulk counterpart. Similar enhanced activity can be expected for WO₃ nanorods in hydrogen evolution reaction. The aim of the current study is to verify such a supposition experimentally which is significant in the development of electrodes for electrochemical hydrogen production.

In recent years, hydrogen, in combination with fuel cells, has been proposed as a major alternative energy source. It provides energy at less environmental damage, with greater efficiency and acceptable cost compared to the conventional fossil fuels. Electrochemical production is one of the possible methods for hydrogen production. Materials such as Raney Ni, Ni–Mo and noble metals such as Pt, Pd and Ru have been employed for this purpose [52–55]. In spite of their high catalytic activity for hydrogen evolution reaction, the process involving Pt and Pd are not commercialized due to their high cost and low abundance. This has led to the investigation of newer materials or reduction of the loading of noble metals. Savadogo et al. have shown the HER using nickel electrodes with phosphotungstic acid. It has been demonstrated that the presence of W in the form of WO₃ in the polyoxometalates enhanced the electrocatalytic activity for hydrogen evolution [56, 57]. Baruffladi et al. have shown electrodeposited composites of non-stoichiometric tungsten oxides and either RuO₂ or IrO₂ to catalyze the hydrogen evolution in acid medium [58]. Platinum when supported on tungsten trioxide showed electrocatalytic activity for HER due to the synergism towards reactions in acid involving hydrogen atoms [59]. All these results show the significance of WO₃ in hydrogen evolution reaction.

In this article, we report a surfactant directed large scale synthesis of monoclinic WO₃ nanorods. This has been achieved by a simple pyrolysis of a single source precursor which consists of surfactant encapsulated tungsten oxide clusters. The employed route is template free, contaminant free, easy, economical and requires a low temperature for the fabrication of WO₃ nanorods. The morphology, chemical composition and structure were characterized by Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), High resolution transmission electron microscopy (HRTEM) and X-ray diffraction (XRD). The as-synthesized tungsten trioxide nanorods have been employed as an electrocatalyst for hydrogen evolution reaction (HER). The electrocatalytic activity of the material for HER was investigated by cyclic voltammetry, linear sweep voltammetry and Tafel plots. The activity was compared with that of commercially obtained

bulk tungsten trioxide. Enhanced catalytic activity has been observed for WO_3 nanorods compared to bulk WO_3 as an electrocatalyst for HER.

Experimental

Materials

The commercial tungsten trioxide was purchased from Alfa Aesar. All other chemicals were purchased from Sisco Research Laboratories Pvt. Ltd and used as received.

Preparation of Tungsten Trioxide Nanorods

Tungsten trioxide nanorods have been synthesized by using tetrabutylammonium decatungstate as the precursor material. The starting material was prepared according to the work described elsewhere [60]. The typical procedure involved the precipitation of tetrabutylammonium decatungstate by adding an aqueous tetrabutyl ammonium bromide solution to a clear yellow solution of tungstic acid preformed using sodium tungstate and concentrated hydrochloric acid. The white precipitate was washed with boiling water and ethanol, filtered, dried and then recrystallized in hot dimethyl formamide to give yellow crystals. The thermogravimetric analysis revealed that the tetrabutylammonium cation content in the compound is 29.0% (theoretical value: 29.2%) and the decomposition temperature is around 450 °C as reported [60]. The synthesis of tungsten trioxide (WO_3) nanorods from tetrabutylammonium decatungstate ($(\text{C}_4\text{H}_9)_4\text{N}_4\text{W}_{10}\text{O}_{32}$) is carried out as follows: The precursor compound (1 g) was taken in an alumina or quartz boat and loaded inside a tubular furnace and heated at 450 °C at a heating rate of 25 °C per min under Ar atmosphere for 3 h. This was followed by gradual cooling to room temperature to obtain a blue powder of WO_3 nanorods. The total yield of the obtained material was 71% by weight (relative to the starting material). To further investigate the role of tetrabutylammonium (TBA) group on the morphology of WO_3 , an experiment has been carried out in the absence of tetrabutylammonium ion. To achieve this, $(\text{NH}_4)_{10}\text{H}_2\text{W}_{12}\text{O}_{42} \cdot \text{XH}_2\text{O}$ has been taken as the precursor and pyrolysed under similar experimental

conditions that were employed for the formation of WO_3 nanorods.

Structural Characterization

X-Ray Diffraction (XRD) patterns were obtained by a powder diffractometer (XRD - SHIMADZU XD-D1) using a Ni-filtered $\text{CuK}\alpha$ X-ray radiation source. CRM 200 Raman spectrometer was employed, using the 514.5 nm line of an Ar ion laser as the excitation source. The morphology of the WO_3 nanorods was investigated by a scanning electron microscopy (SEM) (FEI, Model: Quanta 200). Transmission electron microscopy (TEM), Electron diffraction and Energy Dispersive X-ray Analysis (EDAX) were performed on a Philips CM12/STEM instrument. High-resolution Transmission Electron Microscopy (HRTEM) was carried out on a JEOL 3010.

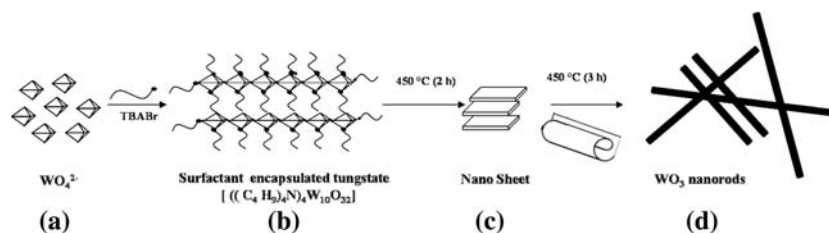
Electrochemical Characterization

A three electrode cell consisting of the glassy carbon as working electrode (0.07 cm^2), Pt wire and Ag/AgCl (satd. KCl) electrodes as counter and reference electrodes respectively were used. All electrochemical measurements were performed using a CHI660A potentiostat/galvanostat. The working electrodes for electrochemical measurements were fabricated by dispersing 5 mg of the catalyst in 100 μL of deionized water by ultrasonication for 20 min. From this dispersion 10 μL has been taken and placed on a glassy carbon electrode. The solvent was slowly evaporated by placing the electrode in an oven at 70 °C. Five microliter of nafion solution has been coated on the electrode as a binder and dried at room temperature. One molar H_2SO_4 was used as the electrolyte. The electrolyte solution was deaerated with high purity N_2 (99.99%) for 30 min before the electrochemical measurements.

Results and Discussion

A schematic representation of the formation of WO_3 nanorods is shown in Fig. 1. It shows the possible mechanism of tungsten trioxide nanorods formation. The

Fig. 1 Scheme for the formation of WO_3 nanorods



precursor material is composed of the cationic surfactant group (tetrabutyl ammonium ion) and the anionic decatungstate ion, represented as octahedral units [60]. Formation of the precursor can be understood as follows: The TBA⁺ cations react with the tungsten oxide octahedra (Fig 1a) and forms lamellar aggregates (also supported from the SEM image Fig 3a) of the ((C₄H₉)₄N)₄W₁₀O₃₂ in which the tungstate anions are encapsulated in the array of TBA groups. The TBA groups are suggested to behave as glue that holds the WO₆ octahedra together with spacing between different lamellar layers (Fig 1b). In the crystallization process, surfactant molecules may serve as a growth controller, as well as an agglomeration inhibitor, by forming an encapsulated layer. When heated at 450 °C for 2 h, the structure directing, tetrabutylammonium group decomposes resulting in the formation of lamellar sheets of WO₃ (Fig 1c). On gradual increase of the pyrolysis duration to 3 h these lamellar sheets were rolled onto themselves to form WO₃ nanorods (Fig. 1d). The presence of tetrabutylammonium group in the precursor plays a vital role in the formation of nanorods. The hydrophilic head group of the surfactant binds to the W₁₀O₃₂⁴⁻ anions. During this process the hydrophobic tail groups form a shield outside the anionic octahedra which prevents their agglomeration. The presence of the surfactant coating is of key importance not only for hydrophilic stabilization of the octahedra, but also for controlling long range self-assembly in concentrated dispersions.

Figure 2a shows the XRD recorded for WO₃ nanorods synthesized by a single step pyrolysis of tetrabutylammonium decatungstate. All the peaks can be undisputedly indexed to monoclinic WO₃ (JCPDS: 75–2072). There are no peaks detected for other phases, indicating that single phase of WO₃ with high purity has been prepared. No peaks of impurities were detected from this pattern. The average crystallite sizes of the nanorods was calculated by using Scherrer's formula

$$L = 0.89 \lambda / \beta \cos \theta,$$

where, L is the average crystallite size, $\lambda = 0.15418$ nm for CuK α , β is the half maximum peak width and θ is the diffraction angle in degrees. The average crystallite sizes calculated by the Scherrer's formula along the (001), (020), (200), (021) and (220) have values of about 36, 27, 34, 39 and 33 nm, respectively. The Raman spectrum (Fig. 2b) for the material shows characteristic O–W–O bending (260 and 334 cm⁻¹) and stretching modes (703 and 813 cm⁻¹) of WO₃. The typical morphology of the precursor compound, tetrabutylammonium decatungstate, ((C₄H₉)₄N)₄W₁₀O₃₂ and the as synthesized WO₃ are presented in the SEM images (Fig. 3a, b, respectively). Figure 3a displays the side view of the precursor

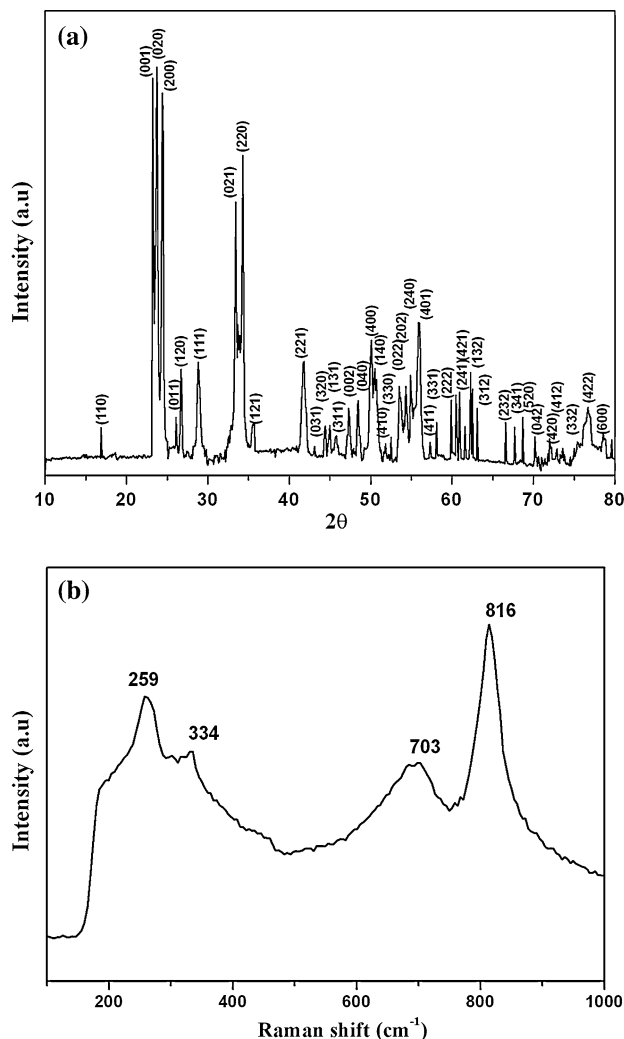
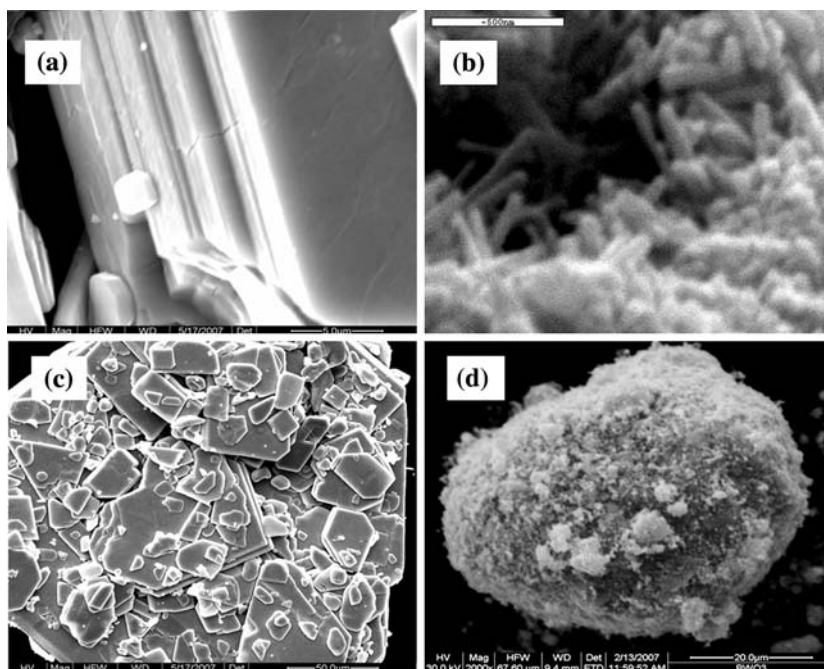


Fig. 2 (a) Powder X-ray diffraction pattern and (b) Raman spectrum of WO₃ nanorods

compound revealing a lamellar aggregations. Figure 3b presents the image of the as synthesized WO₃ showing the formation of nanorods. The rods are polydispersed with few hundred nanometers (100–500 nm) of length and 20–60 nm of width. Thus the findings indicate that the pyrolysis products are obtained from the ((C₄H₉)₄N)₄W₁₀O₃₂ microsheets and the synthesized material constitutes nanosized one dimensional tungsten oxide materials. Figure 3c displays the SEM image of the WO₃ obtained from the pyrolysis of ammonium paratungstate, (NH₄)₁₀H₂W₁₂O₄₂ · XH₂O. It can be seen that the material is composed of irregular particles of varying size with plate like morphology. From the SEM analysis, it is revealed that rod like morphology can be obtained only when tetrabutylammonium group is present in the precursor compound. SEM has also been employed to observe the morphology of the commercially obtained WO₃ (Fig 3d). It shows agglomerated microparticles with

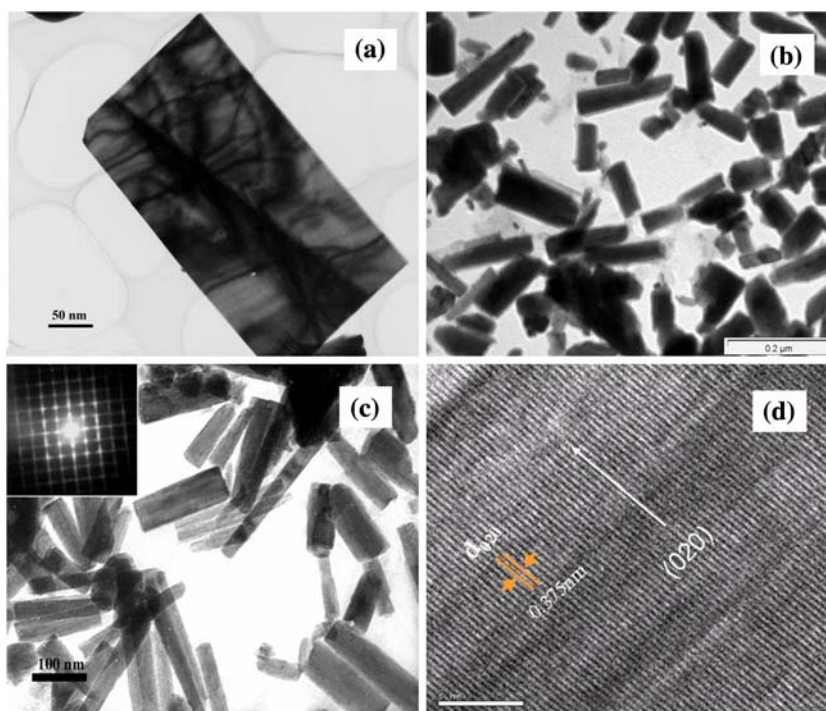
Fig. 3 (a) SEM images of tetrabutylammonium decatungstate, (b) WO_3 nanorods obtained from the pyrolysis of tetrabutylammonium decatungstate, (c) WO_3 obtained from the pyrolysis of ammonium paratungstate and (d) commercially obtained WO_3



no specific morphology. TEM was also employed to provide further insight into structure and morphology of the as synthesized material. The morphologies of the products obtained after 2 h and 3 h were confirmed by the TEM images to be nanosheet (Fig. 4a) and nanorod (Fig. 4b, c), respectively. The sheet has a dimension of about 350 nm and 190 nm lateral size and thickness, respectively. The dimensions of the nanorods vary in

ranges 130–480 nm and 18–56 nm of length and width, respectively. The high resolution TEM image of a nanorod is illustrated in Fig. 4d. The lattice fringes are explicitly clear with d spacing of 0.375 nm for the (020) plane. There has been a strong correlation on the d value obtained from the HRTEM and XRD. The electron diffraction shown in the inset of Fig. 4c indicates the crystallinity of the material. The EDAX (Fig. 5) results

Fig. 4 TEM images of WO_3 obtained from tetrabutylammonium decatungstate at various pyrolysis time. (a) 2 h and (b, c) 3 h, (d) HRTEM image of a WO_3 nanorods. Inset of Fig. 4c Electron diffraction pattern of WO_3 nanorods



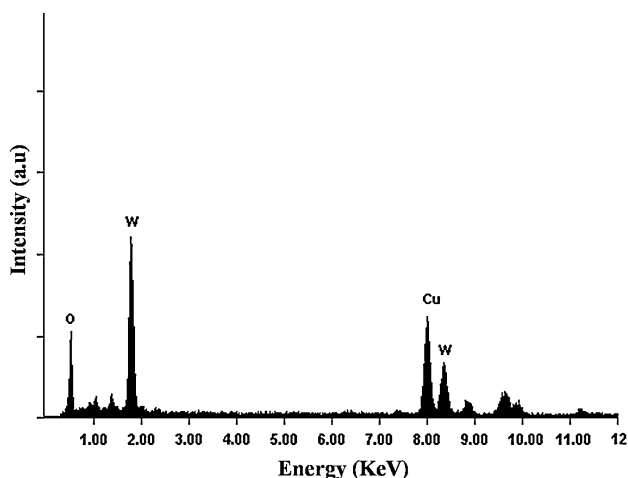


Fig. 5 EDX spectrum of WO_3 nanorods

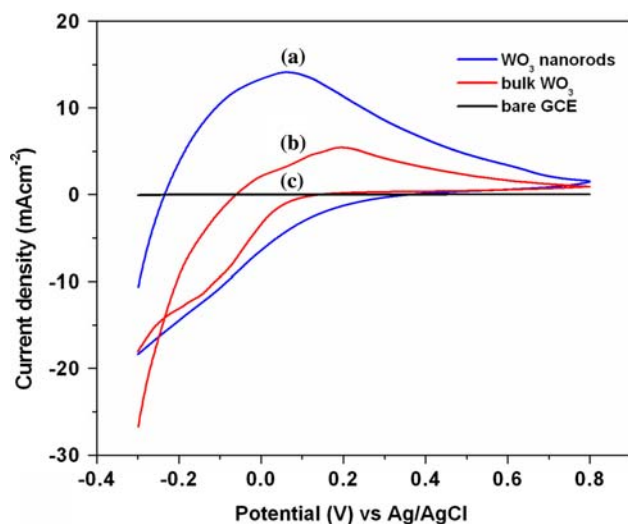
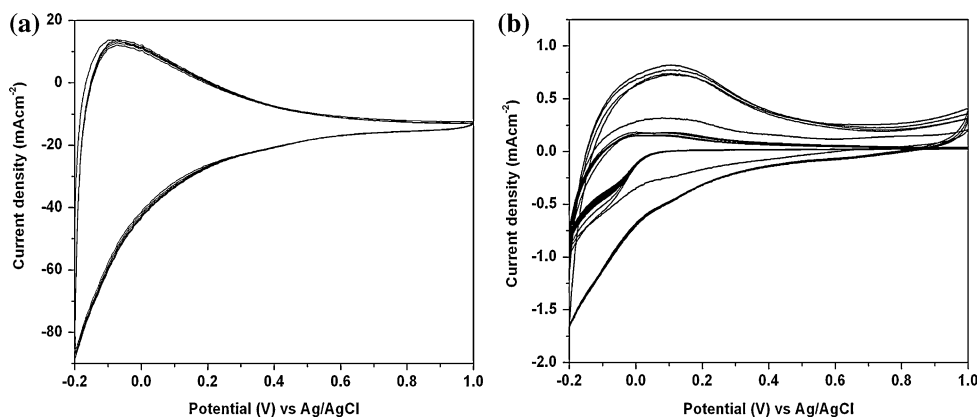


Fig. 6 Cyclic voltammograms of (a) WO_3 nanorods, (b) bulk WO_3 and (c) bare glassy carbon electrode in 1 M H_2SO_4 at a scan rate of 25 mV s^{-1}

confirmed the presence of respective constituent elements in WO_3 nanorods. The copper signals originate from a copper supporting microgrid.

Fig. 7 Cyclic voltammograms of (a) WO_3 nanorods and (b) bulk WO_3 for 50 cycles in 1 M H_2SO_4 at a scan rate of 25 mV s^{-1}



Tungsten trioxides in sulfuric acid medium form tungsten bronzes which are highly electron and proton conducting [61–63]. The redox processes involved in acid medium can be represented as follows: During the forward process represented in Eq. 1, H_xWO_3 (tungsten bronze) is formed and in the reverse process (Eq. 2), hydrogen is evolved.

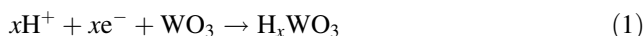


Figure 6a and b shows the cyclic voltammograms of WO_3 nanorods (as synthesized) and bulk WO_3 (commercial) respectively on glassy carbon electrode in 1 M H_2SO_4 at a scan rate of 25 mV s^{-1} . The bare glassy carbon electrode (GCE) shows no activity towards hydrogen evolution (Fig. 6c). WO_3 nanorods show a broad anodic peak at potential 0.1 V whereas the peak has shifted towards positive potential (0.2 V) for bulk WO_3 . The anodic peak current density of WO_3 nanorods and bulk WO_3 are 14 mA cm^{-2} and 5 mA cm^{-2} , respectively, at a scan rate of 25 mV s^{-1} . The current density for WO_3 nanorods is enhanced by 2.8 times to that of the bulk WO_3 . The lower anodic peak potential and higher current density for WO_3 nanorods reveal the facile formation of tungsten bronzes in nanorods compared to the bulk material.

The stability of electrode in working electrolyte is one of the important properties when it is applied in industrial production [64]. CV is employed to investigate the stability of the electrode. Figure 7a and b shows the cyclic voltammograms of WO_3 nanorods and bulk WO_3 respectively in 1 M H_2SO_4 at a scan rate of 25 mV s^{-1} for 50 consecutive cycles. For the WO_3 nanorods almost no activity variation was observed even after several cycles indicating its stability in sulfuric acid medium. Whereas for the bulk WO_3 , the peak current was observed to decrease as the cycle number increases. This shows the poor stability of bulk WO_3 in acid medium. This result is in agreement with

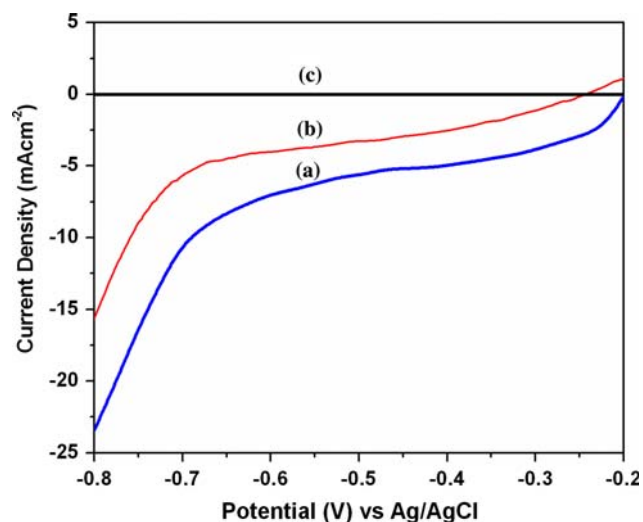


Fig. 8 Linear sweep voltammograms of (a) WO_3 nanorods and (b) bulk WO_3 and (c) bare glassy carbon electrode in 1 M H_2SO_4 at a scan rate of 5 mV s^{-1}

the stability of the nanostructures of WO_3 described by Lee et al. [65] and Ganesan et al. [66]. It has been demonstrated that the nanoparticles of WO_3 and WO_3 microspheres exhibit excellent cycling stability in 1 M H_2SO_4 compared to the amorphous WO_3 films. The linear sweep voltammograms of WO_3 nanorods and bulk WO_3 carried out in 1 M H_2SO_4 at a scan rate of 5 mV s^{-1} in the potential range -0.2 to -0.8 V are shown in Fig. 8a and b, respectively. The bare glassy carbon electrode showed no activity towards hydrogen evolution as evident from the Fig. 8c. At -0.8 V , the current densities of HER on WO_3 nanorods (23 mA cm^{-2}) is higher than that of bulk WO_3 (15 mA cm^{-2}) indicating the enhanced electrocatalytic activity of WO_3

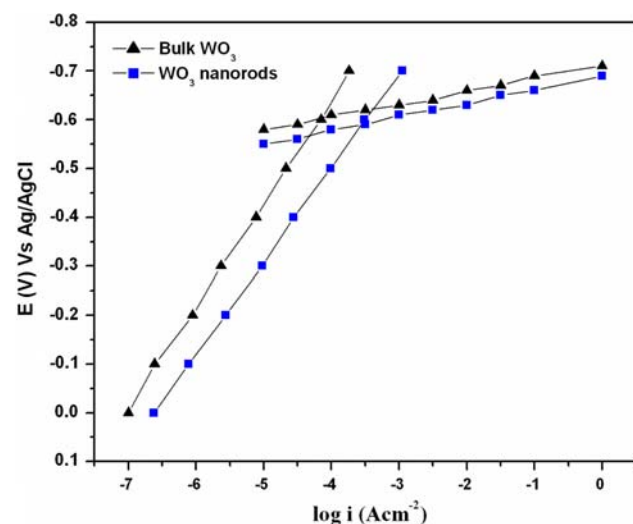


Fig. 9 Tafel plots for HER on WO_3 nanorods and bulk WO_3 in 1 M H_2SO_4 at a scan rate of 2 mV s^{-1}

Table 1 Electrochemical parameters of the HER obtained from the Tafel plots for different electrode materials

Electrode	Slope, b ($\text{V A}^{-1} \text{ cm}^2$)		i_0 (A cm^{-2})
	Region 1	Region 2	
Bulk WO_3	-213	-30	8.57×10^{-7}
WO_3 nanorods	-188	-25	2.75×10^{-6}

nanorods. The kinetic parameters of the electrodes were determined from the Tafel plot as shown in Fig. 9 and the data are summarized in Table 1. The Tafel plots show two well-defined linear regions for both bulk WO_3 as well as WO_3 nanorods. The slopes in the low current density region (region 1) for bulk WO_3 and WO_3 nanorods are -213 and $-188 \text{ mV A}^{-1} \text{ cm}^2$, respectively. The slopes are -30 and $-25 \text{ mV A}^{-1} \text{ cm}^2$ in the high current density region for bulk WO_3 and WO_3 nanorods respectively (region 2). The lower Tafel slope obtained for WO_3 nanorods in comparison to bulk WO_3 indicates the facile HER on WO_3 nanorods as the electrode. The exchange current densities calculated at -0.199 V (Ag/AgCl (Satd KCl)) for 1 M H_2SO_4 solution provides information on the catalytic activity of the electrode for HER. The higher exchange current density value of WO_3 nanorods ($2.75 \times 10^{-6} \text{ A cm}^{-2}$) when compared to bulk WO_3 ($8.57 \times 10^{-7} \text{ A cm}^{-2}$) shows the better catalytic performance of WO_3 nanorods towards HER. The results can be attributed to the unique electrochemical behavior of 1-D nanostructures. 1-D nanostructures provide large electrode-electrolyte interface for the reaction to take place in a facile manner. Moreover, it has also been reported that the nanorod and nanowire form of the material is considered to influence its physical properties, which depart from the properties of their bulk phases due to the quantum effects related to the shape and size [67]. Thus it is demonstrated that improved HER activity can be achieved by using WO_3 nanorods as an electrocatalyst.

Conclusions

In summary, we demonstrate a thermal decomposition method for the synthesis of 1-D WO_3 nanorods in high yield using a single source precursor. One of the important aspects of this method is the in situ formation of nanostructures due to the surfactant encapsulated metal oxide clusters. The advantage of this method is the tunability of the metal precursor and the surfactant group. This aspect of the method can be exploited for the synthesis of several other transition metal oxide nanorods. We have also synthesized nanorods of molybdenum oxide and mixed oxides of molybdenum and vanadium using similar strategy. The

as synthesized WO_3 nanorods perform well as an electrocatalyst with enhanced electrocatalytic activity for HER when compared to its bulk counterpart. The results show the possibility of minimizing the loading of noble metal electrocatalyst for HER by using WO_3 nanorods as catalyst support.

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