



Structural Effects of Tungsten Oxide Electro-Catalyst Towards High Stable CO Tolerance Mechanism

K. KATHIRESAN¹, P. ELANGOVA² and M.S.S. SARAVANAKUMAAR^{3,*}

¹Department of Physics, PSNA College of Engineering & Technology, Dindigul-624 622, India

²PG & Research Department of Physics, Pachaiyappa's College, Chennai-600 030, India

³Department of Physics, Saraswathi Narayanan College (Autonomous), Madurai-625 022, India

*Corresponding author: E-mail: 2ssaravanakumar@gmail.com

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In this work, a cost effective, facile and rational synthesis of two different nanostructures including nanosphere shaped and nanorod sized tungsten oxide nanomaterials. The prepared nanoparticles were characterized by powder X-ray diffraction, scanning and transmission electron microscopic analyses, energy dispersive spectroscopy and Raman spectroscopy. The XRD result confirms that the nanoparticles have a polycrystalline nature with well-developed monoclinic crystalline structure. The microscopic images evidently confirm the nanosphere shaped and nanorods sized WO₃ samples. Further the purity and stoichiometry amount of chemical compositions were confirmed by the EDS spectra. The modes of vibrations of the WO₃ nanoparticles were identified by Raman spectroscopy. From these structural investigations, it is evidently showing that the morphologies of the final products can be tuned *via* synthesis process. In addition, the WO₃ nanosphere exhibited excellent long-term durability and CO tolerance against the high quality Pt/C catalyst. To our best of knowledge, this is the first report of the use of WO₃ nanocrystals that act as CO₂ tolerance catalysts with high stability. The enhanced activity of the WO₃ nanosphere is due mainly to the higher structural openness in WO₃ and this makes the WO₃ nanosphere a good candidate for high-performance non-precious metal-based electrocatalysts with low cost and high efficiency for electrochemical energy conversion.

Keywords: Tungsten oxide, Fuel cell catalysts, Nanosphere, Nanorods, Carbon monoxide.

INTRODUCTION

The continuing increase in both global population and energy needs threatens society with a depletion of fossil energy resources and environmental concerns, such as global warming and CO₂ emissions. In specific, solar cells [1,2], metal-air batteries [3], solar water splitting [4,5] and fuel cells and hydrogen energy [6-9] are requisite for upcoming energy conversion and storage applications. In this concern, the development of facile, cost effective, naturally abundant, environmentally benign and highly active catalysts for energy conversion and storage is of ultimate significance and is an essential topic in renewable energy research. Owing to the unique properties of tungsten oxide nanomaterials have been received considerable attention in various device applications such as supercapacitors [10], gas sensors [11], electrochromic coatings [12] solar cells, quantum dot LEDs [13,14], photoelectrocatalysis and water splitting photocatalyst as main catalyst [15] and acetone selective detection [16] *etc.*, WO₃ has also been used as smart windows [17] for energy-efficient buildings. Also, tungsten oxide shows

high functional response to various gases, such as H₂ [18], H₂S, NO_x, trimethylamine *etc.* [18,19]. Tungsten oxide (WO₃) is well known n-type semiconductor and the band gap is about 2.6-2.8 eV. The inherent conductivity improves from its non-stoichiometric arrangement giving rise to a donor level made by the defect of lattice oxygen vacancy. Typically, the tungsten has several oxidation states, *i.e.*, 2, 3, 4, 5 and 6, the tungsten compound can exist in various forms. Recently, the tungsten oxides were prepared by various methods like electrochemical route [20], solution-based colloidal technique [21], bio-ligation method [22,23] and chemical vapour deposition [24,25]. It is reported that oriented WO₃ nanowires and other nano structures were tuned by hydrothermal treatment [26-33]. In this article, we report on a facile, low temperature hydrothermal process to synthesize two different types of WO₃ nanoparticles including sphere and nanorod structured electrocatalysts towards CO tolerance mechanism. By using this simple synthesis method, it is possible to produce the large quantities of resultant nanoparticles without costlier equipment, which is essential for industries.

EXPERIMENTAL

The tungsten oxide nanoparticles were synthesized using low temperature hydrothermal method. During synthesis, 40 mL of hydrochloric acid were added drop-wise to a 150 mL 20 mM sodium tungstate solution ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$) while the precursor solution was kept at 60 °C. Finally the yellow coloured solution was centrifuged and washed many times and dried for 5 h at 200 °C in an oven. In the case of rod like structures, additionally, the 15 mL of acetic acid was added drop wise to the precursor solutions.

Instrumental analysis: The crystalline nature was identified by powder X-ray diffraction (Rigaku XRD; Cu- K_α radiation). The surface morphologies were identified by Field emission scanning electron microscopy (FESEM; JSM 6500F) and transmission electron microscopy (TEM; JEOL JEM 2100F). The vibrational, rotational and other low frequency modes in the sample were analyzed by Raman spectroscopy (Thermo Scientific DXR). The electrochemical measurements were carried out in 1.0 M KOH at room temperature by BioLogic, SP-50 cyclic voltammetry with a rotating disk electrode (RDE, 3 mm in diameter, RRDE-3A, ALS Co., Japan). The three-electrode cell consisted of an Ag/AgCl electrode as the reference electrode, Pt as the counter-electrode and a glassy carbon electrode (GC)/rotating disk electrode (RDE) loaded with the various catalysts as the working electrode. As the working electrode, the electroactive materials in ethanol (1 mg mL^{-1}) and 10 mL of Nafion solution (0.5 wt % in isopropanol) as a binder were mixed by sonication. Subsequently, catalysts with the same loading of about 0.10 mg cm^{-2} were coated on glassy-carbon RDEs and dried in air for the electrochemical characterization. Finally, the measured potential vs. Ag/AgCl was altered to the reversible hydrogen electrode (RHE) scale using the Nernst equation.

RESULTS AND DISCUSSION

The sharper peaks and higher number of reflections were observed in the XRD patterns of the WO_3 (Fig. 1), indicating the higher degree of crystalline nature of the nanoparticles. The patterns are well matched with monoclinic structure of WO_3 using the standard data (JCPDS No. 83-0950). The stable monoclinic WO_3 can have a ReO_3 -type structure. Here, no other impurity peaks were identified in the XRD patterns, which show the purity of the nanoparticles formation. These results suggested that the prepared nanoparticles have a polycrystalline spherical and rods structure with well-developed crystallinity. It is reported that spherical shaped nanoparticles turn an oval nature into a rod-like structure when the partial pressure during synthesis is changed. The defects in the lattice may have a substantial influence on the structures of the WO_3 nanoparticles [34-38].

The microscopic images (Fig. 2) evidently showing the sphere shaped tungsten oxide nanoparticles with an average diameter of 20-50 nm. As shown in Fig. 3 FE-SEM and TEM, tungsten oxide nanorods are very straight. The long length nanorods have the length about 3-4 μm and the thickness of about 0.1-0.2 μm . Usually the vapour-liquid-solid (VLS) growth mechanism is favour for this type of rod like structures

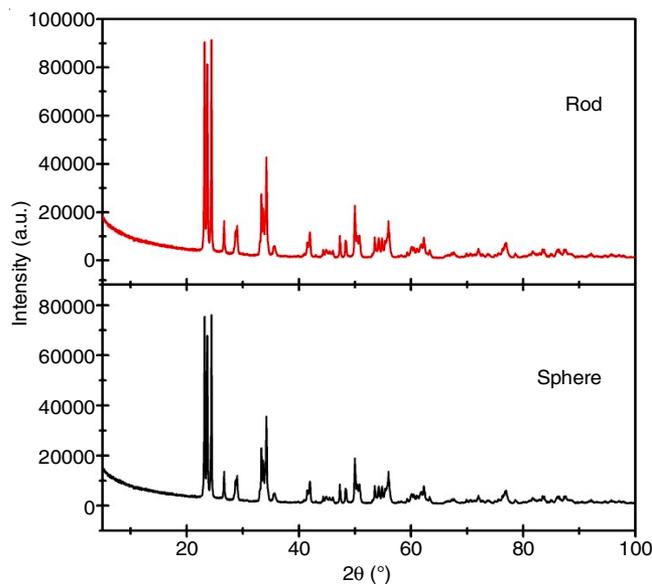


Fig. 1. X-ray diffraction pattern of sphere shaped and nanorod shaped WO_3 nanomaterial

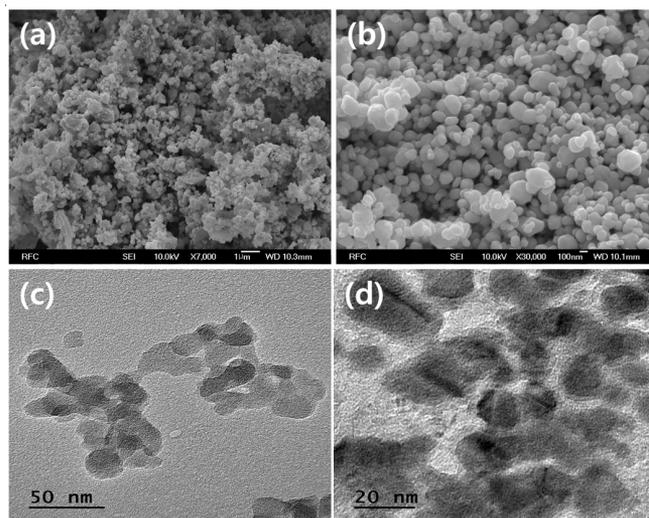


Fig. 2. (a-b) FE-SEM and (c-d) TEM images of sphere shaped WO_3 nanomaterial

during hydrothermal method. The formation of WO_3 and its chemical compositions are confirmed from energy dispersive X-ray spectroscopy analysis was performed. The EDS spectra (Fig. 4) show that two main elements W and O are existed in the prepared samples, which confirms that prepared WO_3 nanoparticles with high purity. From the Fig. 4, it evidently showing that the tungsten element is found in large that is reliable with the concentration of XRD patterns and SEM micrographs.

From the Fig. 5, the Raman spectra of WO_3 nanomaterials exhibited the six predominant vibrational bands within 99-1200 cm^{-1} [35-37]. The major vibrational modes of WO_3 are located at 805 cm^{-1} for W=O stretching mode, 714 cm^{-1} for W=O bending mode and 272 cm^{-1} for W-O-W deformation mode, respectively. The 324 cm^{-1} peak was correlated to W=O bending vibrations, other than these, the peaks at 131.41 and 184.69 cm^{-1} could be attributed to low temperature phonons.

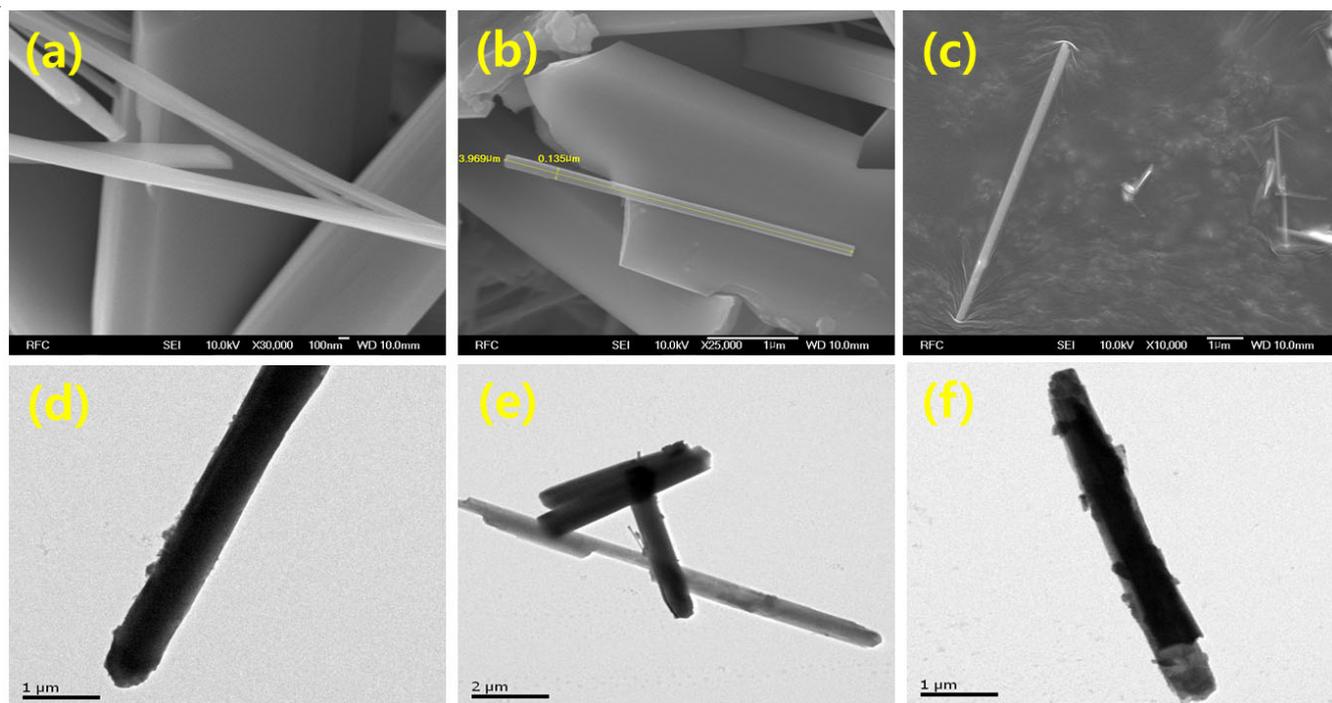


Fig. 3. (a-c) FE-SEM and (d-f) TEM images of nanorod shaped WO_3 nanomaterial

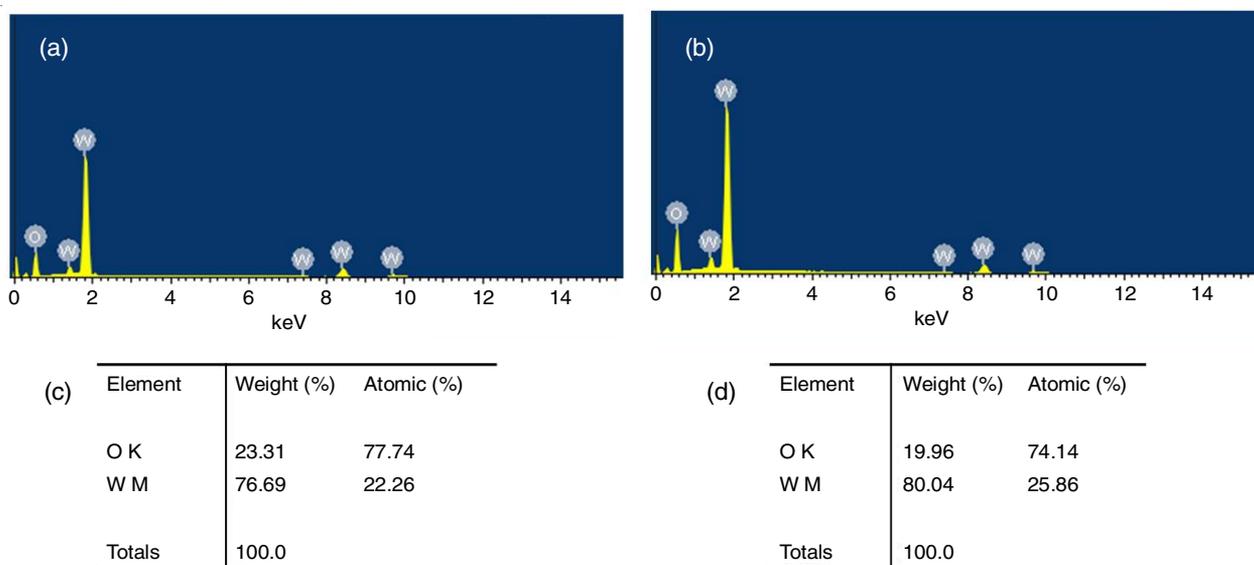


Fig. 4. (a and c) and (b and d) are the EDS analysis of the prepared nanosphere shaped and nanorod shaped WO_3 nanoparticles respectively

It is well known that, in alkaline electrolytes (for alkaline fuel cells), the Pt catalyst degrades gradually over time due to surface oxides, aggregation and particle dissolution. So, the long term durability is one of the most essential requirement for potentially active catalysts as electrocatalysts since they should needed to work for an extended time in a harsh environment. In this regard, the stability of nanosphere WO_3 , nanorod WO_3 and high quality commercial Pt/C was tested again using a glassy carbon electrode by continuously performing the CO_2 tolerance effect and durability test at 0.65 V vs. RHE in an oxygen saturated 1.0 M KOH solution at 1600 rpm (Fig. 6). It is reported that the long-term stability of other catalysts, such as Au, Pd, Ag and some bi-metallic nanocrystals, in alkaline solutions was better relative to Pt, but they still suffer from

deactivation and are below the target levels for energy storage device applications. Usually, carbon monoxide (CO) is one of the highest poisons of fuel cell catalysts since of their strong fascination to active metal surfaces, which reduces the rate of the catalytic reaction. Importantly, the present WO_3 nanoparticles exhibit superior CO tolerance to the Pt/C catalyst due to the injection of a 5.0 M methanol solution during the RDE experiment at a rotation of 1600 rpm. As shown in Fig. 6 a quick reduction in the normalized current was perceived for the Pt/C catalyst after methanol addition. In contrast, there was no change in the both nanosphere and nanorods shaped WO_3 catalysts, this indicates the excellent CO tolerance of the WO_3 nanostructured synthesized in this study. Fig. 6 clearly indicates that the nanosphere shaped WO_3 exhibited a superior CO

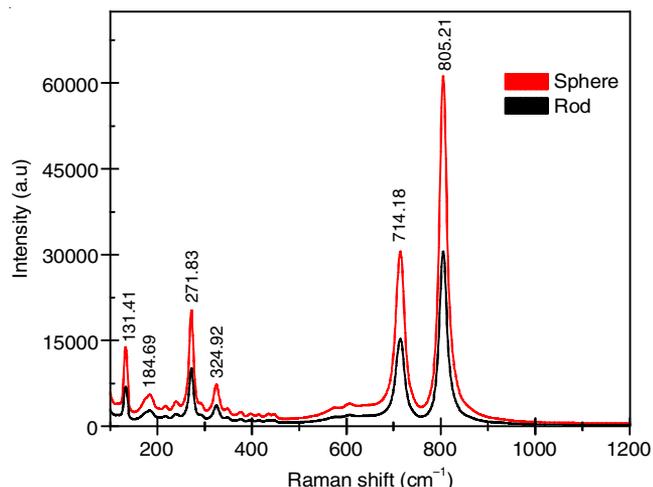


Fig. 5. Raman spectra of nanosphere shaped and nanorod shaped WO_3 nanomaterials

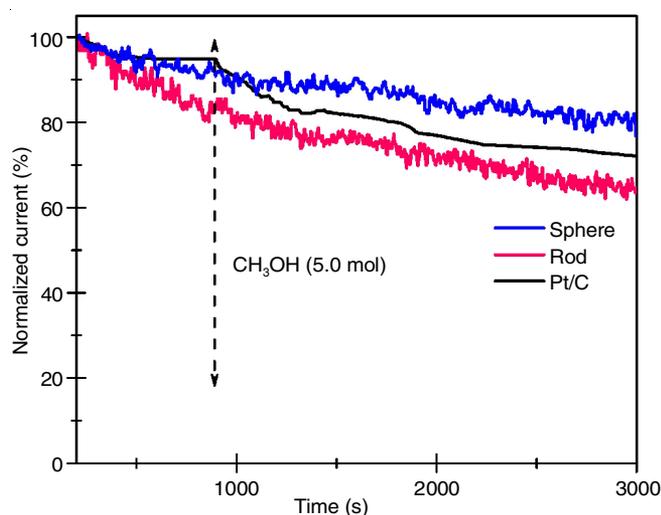


Fig. 6. Long term durability and CO tolerance effect by chronoamperometric responses of the sphere shaped and rod shaped tungsten oxide and commercial Pt/C catalysts kept at 0.65 V versus RHE in an O_2 -saturated 1.0 M KOH electrolyte at 1600 rpm

tolerance and highly stable (79.5 %) than the commercial Pt/C and WO_3 nanorod. The enhanced activity of the WO_3 nanosphere particles may result from the small particle size, high surface area, higher structure openness in the tunnel structure WO_3 during the synthesis process.

Conclusion

Two different morphologies including sphere shaped and nanorods shaped monoclinic tungsten oxide nanoparticles were prepared using the facile, cost effective low temperature hydrothermal treatment. The monoclinic crystalline nature was confirmed by X-ray diffraction. Nanosphere and nanorods shaped tungsten oxide nanoparticles were visibly identified by microscopic images. Additionally, the purity and chemical compositions of the WO_3 samples were confirmed by the energy dispersive X-ray spectroscopy. The modes of vibrations of the prepared samples were clearly documented by Raman spectroscopy. From these investigations, it is evidently showing that the structural morphologies of the nanoparticles can be tuned by the additions during the synthesis route (*e.g.*, the addition of acetic acid give rise to nanorods). This synthesis method is

simply scalable for industrial manufacturing applications and does not require any special instruments and/or vessels. Usually, the poor catalyst durability and CO tolerance effects are the main tasks for alkaline fuel cells. Hence, the outstanding stability of the WO_3 nanosphere makes it favourable for the fuel cells and further significant catalytic kinetic reactions in alkaline solutions.

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