Research Article

Electrochemical Response for Spherical and Rod Shaped WO_3 Nanoparticles

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A rapid and new technique describes synthesis technique of spherical and rod shaped tungsten trioxide (WO_3) nanoparticles with similar band gap at visible wavelength. Acid catalyzed exothermic reaction and structure directing reagent follows the formation of two different morphologies and monoclinic WO_3 phase. Rod shaped WO_3 nanoparticle coated ITO glass electrode exhibits high current density at identical low voltage and scan rate due to its better adherence and coating uniformity in comparison with spherical nanoparticles. WO_3 -ITO electrode alters to blue tungsten bronze in color at low voltage, and further the color restores after removing the same applied voltage.

1. Introduction

In recent years, different morphology nanostructured materials have stimulated great interest due to their importance in basic scientific research and technological applications [1, 2]. Tungsten trioxide (WO_3), an important n-type semiconductor, has received much attention in the past few decades for its potential application in fabricating the miniature electrochromic and photochromic devices, gas sensors, and solar energy devices and also its usage as photoanode to generate hydrogen by photocatalytic splitting of water [3, 4]. The importance demands control over the dimension, size, and crystal structure of this class of particles for higher technology applications. Apart from being a promising electrochromic material, a great deal of effort has been made for improving the performance of WO_3 films by several researchers. Thus, it is essential to control the morphology and also the surface coating over transparent coating oxide glass substrate [5]. Mostly, fabrication of WO_3 films has been prepared by dip or spun coating of peroxopolytungstic acid on the Indium doped Tin Oxide (ITO) glass substrate and subsequent firing at optimum temperature [6, 7]. Leftheriotis et al. prepared sol-gel derived highly porous thick and opaque WO_3 films. These films exhibited a similar reversible electrochromic property for 1st and 1000th cycle of cyclic

voltammograms in 1 M LiClO_4 with 0.2 mA/cm^2 as current density [8]. Comparison of the electrochromic performance for orthorhombic rod and platelet type hydrated WO_3 was investigated by Wei and Shen. Poly vinyl alcohol (PVA-124) and glacial acetic acid were used as structure directing agent and stabilizer for the preparation of single crystalline $\text{WO}_3 \cdot \text{H}_2\text{O}$ nanorods, which exhibited highest current density of 40 mA/cm^2 with fast response time and improved redox performance [5]. Peroxotungstic acid was used for the deposition of $\text{WO}_3 \cdot n\text{H}_2\text{O}$ film on conducting (F-doped SnO_2 coated) glass substrate by dip technique. A dark blue coloration was observed upon intercalation of Li^+ from 0.5 M LiClO_4 solution [9]. A crystal seed assisted hydrothermal method was employed for assembling plate and brick like nanostructured $3\text{WO}_3 \cdot \text{H}_2\text{O}$ films on FTO glass substrate through Na_2SO_4 as the capping agent. Nanoplate exhibited higher current density of 0.2 mA/cm^2 than nanobrick films for both intercalation/deintercalation processes over the same time period [10]. Several strategies have been considered to synthesize such WO_3 nanostructures through hot wall chemical vapor deposition, thermal evaporation, hydrothermal method, sol-gel precipitation, and various others [11, 12]. In this backdrop, we have developed a new and rapid technique to synthesize two different morphologies of WO_3 nanoparticles, optimized their crystallite sizes and band gap energies.

The influence of morphology on the electrochemical activity of WO_3 coated ITO has also been reported.

2. Materials and Methods

2.1. Preparation of WO_3 Nanopowders. Synthesis of spherical WO_3 nanopowders (SW) was carried out through solution reaction within tungstic acid (H_2WO_4) and hydrogen peroxide solution. The analytical grade H_2WO_4 powder was initially heated to 90°C in a dry glass vessel attached to Pt-sensor. Hydrogen peroxide (30% v/v) solution was added to dry tungstic acid powder. Following this, concentrated nitric acid was added to maintain pH~1 of the reaction. The exothermic nature of the reaction favored the direct dehydroxylation of tungstic acid to tungsten oxide amorphous nanopowders. The light greenish precipitate was washed twice through centrifuge at 14000 rpm and freeze dried at -52°C for 20 torr. The dried powder was flash calcined at 500°C for 5 minutes [13]. A minimum batch size of 100 gm spherical WO_3 nanoparticles was prepared without degradation of the quality. The crystallization temperature was confirmed by a dynamic thermal analysis prior to flash heating of as-synthesized amorphous nanoparticles. On the other hand, addition of structure directing agent CTAB (Cetyltrimethylammoniumbromide, $\text{C}_{19}\text{H}_{42}\text{BrN}$) to base precursor $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ produced rod shaped WO_3 nanopowders on acidification at pH~3. Starting precursors and the solution pH were found prime factors to make such different morphologies.

2.2. Characterization of WO_3 Nanopowders. X-ray diffraction (XRD) pattern for all powders was obtained by using Philips X-Ray diffractometer with Ni filtered CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$). The morphology of WO_3 nanopowders was estimated by transmission electron microscopy (JEOL JEM-2100, TEM). The Raman measurements were carried out in backscattering geometry with a triple-grating spectrometer equipped with a cooled charge coupled device detector. For excitation, the 488 nm line of an Ar+/Kr+ mixed-gas laser was used. Diffuse reflectance measurement was done through Shimadzu spectrophotometer (UV-2450) to evaluate band gap energy for all WO_3 nanopowders. Room temperature diffuse reflection percentage was measured in the wavelength region 200–700 nm. Barium sulphate was considered as reference to characterize this spectroscopic analysis.

2.3. Preparation and Electrochemical Measurements of WO_3 Coated ITO. Spherical and rod shaped WO_3 nanoparticle suspension was prepared by dispersion of 0.1 gm of each WO_3 nanopowders in 2 mL ethanol followed by ultrasonication. Homogenous suspension was then coated on commercial grade conducting Sn-doped Indium oxide (ITO) coated glass substrate having 84% transparency. Conductive ITO glass substrate was cleaned by ultrasonication through successive immersion in distilled water, ethanol, and acetone prior to WO_3 coating. A simple droplet technique was adopted to make WO_3 /ITO electrode, where $0.3 \mu\text{L}$ WO_3 suspension was dropped on ITO substrate, dried at 60°C for 20 min,

FIGURE 1: XRD patterns for spherical and rod shaped WO_3 nanoparticles.

and repeated twice the same cycle [14]. The electrochemical property for both spherical and rod shaped WO_3 /ITO film was determined by cyclic voltammetry (CV) using a three electrode cell configuration in 0.5 M aqueous solution of sulphuric acid as the electrolyte as shown in experimental set-up. Spherical and rod shaped WO_3 nanoparticle coated ITO electrodes were designated as SWI and RWI, respectively. The cell consisted of a WO_3 coated ITO substrate as working electrode, Pt, rod as counter electrode and Ag/AgCl as reference electrode, respectively. The three electrode based CV experiment was conducted near to 10 min.

3. Results and Discussion

3.1. Phase and Morphology Analysis of WO_3 Nanopowders. The phase analysis of flash calcined nanopowders was carried to understand the purity and crystallinity. Figure 1 represented the XRD pattern of the spherical (SW) and rod shaped (RW) WO_3 nanopowders. The obtained XRD pattern confirmed the formation of pure monoclinic WO_3 crystalline phase as per JCPDS file no. 43-1035 [15]. The intensities of both the powders depicted more crystallinity for rod shaped WO_3 than spherical WO_3 nanopowders. The crystallite sizes of both the SW and RW powder were determined using the Scherrer's equation: $D = 0.9\lambda / B \cos \theta$, where D is the crystallite size (nm), λ is the wavelength of the X-ray radiation, θ is the Bragg's angle, and B is the full width half maximum (FWHM). The crystallite size for SW and RW was found to be 42 nm and 55 nm, respectively. Figure 2 represented the TEM micrographs with inset HRTEM images for both SW and RW nanopowders. Near to spherical WO_3 nanoparticles with an average particle size of nearly 50 nm and agglomerated secondary particles were observed in Figure 2(a). An average particle length 140 nm and width 40 nm were found for rod shaped WO_3 nanoparticles. Lattice fringes in HRTEM indicated the crystallinity difference between both the particles having d -spacing value of 0.33 nm.

FIGURE 2: TEM images for spherical (a) and rod shaped (b) WO_3 nanoparticles.TABLE 1: Raman spectral frequencies of WO_3 nanoparticles.

Raman spectral peaks (cm^{-1})	Assigned Raman groups ν = stretching vibration and δ = bending vibration
132	—
187	ν (W-W)
268	ν (O-W-O)
327	δ (O-W-O)
716	ν (W-O-W)
808	δ (W-O-W) and O-W-O deformation mode

3.2. Bond Characteristics of WO_3 Nanopowders. Table 1 represented the Raman spectral peaks of both the spherical and rod shaped WO_3 nanopowders with their corresponding bond characteristics. Similar wavenumbers were observed for both the powders in the lower and higher spectral zone. Raman peaks at 716 cm^{-1} were related to O-W-O vibration and deformation mode, whereas 808 cm^{-1} was associated with crystalline WO_3 stretching vibration of the bridging oxygen of W-O-W. These two peaks attributed to the formation of crystalline WO_3 monoclinic phase. The variation in the intensity was also observed due to difference in crystallinity. The O-W-O stretching and bending vibrations were evaluated in the lower spectral zone with peak positions at 327 cm^{-1} and 268 cm^{-1} . The W-W bond was recognized near to 187 cm^{-1} wave number [16].

3.3. Band Gap of WO_3 Nanopowders. Tauc plot determined the band gap energies for both the samples. The diffuse reflectance data obtained from UV-Vis spectroscopy was used to calculate the Kubelka-Munk unit of absorption from the following equation: $\text{KMU} = (1 - R)/2R$, (R = reflectance) [15, 17]. The square root of Kubelka-Munk function multiplied by the photon energy versus the function of photon

FIGURE 3: Cyclic voltammetry measurement for spherical and rod shaped WO_3 nanoparticles under identical voltage and scan rate.

energy ($E_{\text{photon}} = h\lambda$) gives the tauc plot. The comparative values of band gap energy along with their particle size and current density are given in Table 2. Near to similar band gap of 2.82 eV and 2.75 eV was observed for both SW and RW, respectively. From this result, it was evident that the band gap energy was not influenced by the similar range of crystallite size and morphology; however, contact geometry and adherence phenomena on conductive glass substrate altered the electrochemical response.

3.4. Electrochemical Property of Spherical and Rod Shaped WO_3/ITO Films. Optical transparency of spherical WO_3 nanopowders coated ITO (SWI) glass substrate was higher than the semitransparent rod shaped WO_3 nanopowders coated ITO (RWI) electrode. Cyclic voltammograms (CV) was influenced by the electrochemical response between the range of $+0.5$ and -0.5 voltage and scan rate of 50 mV/s as shown in Figure 3. RWI exhibited high current density

TABLE 2: Physical properties for spherical and rod shaped WO_3 nanoparticles.

Sample name	Morphology	Average particle size (nm)	Band gap energy (eV)	Current density (mA/cm^2)
SW	Spherical WO_3	50	2.82	0.14
RW	Rod shaped WO_3	Length = 140 Width = 40	2.75	1.8

FIGURE 4: FESEM images of the SWI and RWI films.

of $1.8 \text{ mA}/\text{cm}^2$ compared to $0.14 \text{ mA}/\text{cm}^2$ for SWI. It is interesting to note that both of the morphologies have near to equal crystallite size and band gap energy but a distinct difference in current density output under identical experimental conditions. Hence, the resultant current density difference was plausible to (1) adherence efficiency of WO_3 nanoparticles onto ITO surface due to contact geometry and (2) geometrical contact resistance between the film and electrolyte [15, 18]. The BET specific surface area for SW and RW was $9.91 \text{ m}^2/\text{g}$ and $5.61 \text{ m}^2/\text{g}$, respectively. Figures 4(a) and 4(b) represented the top view FESEM images of the SWI and RWI films prepared by drop coating technique to insight the texture and distribution of particles on the surface of ITO glass substrate, respectively. For both the coatings, the morphological texture indicated a rough surface topography. The particles on RWI film was relatively well distributed as compared to SWI film. Particles of SWI film formed islands on the surface due to high surface reactivity and their agglomeration tendency, whereas RWI film exhibited continuous structure. And hence the transparency and semitransparency of SWI and RWI film were quite evident from the images. Hence, the minimum coverage is expected by spherical particles on ITO substrate and at the same time the rod shaped particles favored more contact area and adherence to the substrate than spherical particles, which finally altered the charge transport phenomenon between the film and the electrolyte. Furthermore, the geometrical contact resistance, R_c , could be calculated from the slope of anodic and cathodic scans of the film in the electrolyte. Resistance

was calculated by applying the equation for $R_c(\text{SWI}) = (0.2 + 0.5)/(0.14 + 0.33) = 1489 \Omega \text{ cm}^2$ and similarly for $R_c(\text{RWI}) = (0.19 + 0.5)/(1.8 + 0.3) = 280 \Omega \text{ cm}^2$ [15]. The contact resistance for RWI was five times less than that of the transparent SWI which enhanced the current density. The incomplete RWI current density loop was due to the factors that extraction of hydrogen takes more time than insertion leading to incomplete reversible reactions. On the basis of this observation, the current density raised from initial lower set potential to higher set potential giving high current at saturation potential level [18]. Thus, results suggested that the contact resistance and morphological surface area of film were also important factors for getting fairly good electrochemical response. Figure 5 represented the bare ITO coated glass substrate, rod shaped WO_3 coated ITO (RWI), and electrochromic setup during CV measurement. The color of the RWI changed from pale yellow to dark blue which attributed to the change from WO_3 to blue tungsten bronze (H_xWO_3) as a result of reduction during the process of proton insertion in acidic medium [10].

Consider

The cathodic peak referred to the extraction of protons and anodic peak insertion of protons. The electrochemical reversibility of the films was observed to be good as its voltammograms were nearly overlapping with each other for repetitive cycles.

FIGURE 5: Electrochemical setup showing electrochromism during the cyclic voltammetry measurement.

4. Conclusion

High dispersible spherical (50 nm) and rod shaped (140 nm/40 nm—length/width) WO_3 nanoparticles are developed through combined wet chemical and flash heating technique. The band gap energy for spherical and rod shaped WO_3 nanoparticles is 2.8 and 2.75 eV, respectively. A distinct high current density of 1.8 mA/cm^2 is found for rod shaped WO_3 nanoparticles coated ITO glass compared to 0.14 mA/cm^2 current density for spherical particles under +0.5 to -0.5 V and 50 mV/s scan rate. Elongated rod shaped nanoparticle preferentially favors more electrochromic response from counterpart spherical particles.

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