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# Hydrothermally synthesized tungsten trioxide nanorods as $NO_2$ gas sensors

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**Abstract**

One-dimensional single-crystalline h-$WO_3$ nanorods have been synthesized by using a facile hydrothermal technique. Crystal structure, morphology evolution and thermal stability of the products are characterized by using X-ray Diffraction pattern, Scanning Electron Micrographs, Photoluminescence reflectance spectrum; UV–vis diffused reflectance spectral analysis and Raman techniques. The evolution and distribution of $WO_3$ nanorods strongly depend on hydrothermal reaction temperature and time of reaction. Hydrothermal reaction temperature of 170 °C for 48 h ensures the formation of well-defined agglomerated $WO_3$ nanorods. Gas response measurements reveal that $WO_3$ sensor operating at 250 °C exhibits highest sensitivity towards $NO_2$ with low cross sensitivity towards LPG, acetone and ammonia gas, which makes this material a competitive candidate for $NO_2$ sensing applications. A possible adsorption and reaction model is proposed to illustrate formation of one dimensional nanostructure and gas sensing mechanism.


*Keywords:* Tungsten oxide; Hydrothermal synthesis; Nanorods; $NO_2$ sensor

## 1. Introduction

With increasing concerns of air pollution on human health and safety, the need of highly sensitive gas sensors has been heightened. For the purpose of effective detection of toxic and hazardous gases, significant effort has been made on exploring new materials with enhanced gas-sensing performance. Recently, transition metal oxide nanostructures including nanoparticles, nanosheets, nanowires and nanorods, have been intensively studied for gas-sensing applications [1–4]. The enhanced performance of the nanostructured sensor is mainly ascribed to the dramatically increased surface area, great level of crystallinity and possible complete depletion of carriers within the nanostructure on exposure towards the target gases [2,5–8]. Generally, the working mechanism of semiconductor gas sensors lies in change of the sensor resistance resulting from surface effects. $WO_3$ has exhibited excellent catalytic and adsorption properties [9–12]. A high degree of crystallinity and atomic sharp terminations make $WO_3$nanorods a promising material for high performance gas sensors [4,7]. Ponzoni et al. reported the effect of thermal annealing on the stability of morphological and gas-sensing performance of the $WO_3$ nanorod films [13]. Yan et al. reported synthesis, formation and ammonia response of $WO_3$ nanowire assembled spheres [14]. Although there are a few reports on the gas sensing properties of $WO_3$ nanorods, most of the studies focused on gas sensors made up of $WO_3$ films. Therefore, it is interesting to obtain well defined $WO_3$ nanorods, study their structures and associate them to the gas-sensing properties.

Up to now, several methods have been reported for the synthesis of one-dimensional (1D) $WO_3$ nanostructures, including chemical vapour deposition (CVD) [15], flame synthesis [16], thermal evaporation [17], hydrothermal reaction [18,19], electro spinning [20], spray pyrolysis [21], microemulsion based

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solution synthesis [22] and electron-beam annealing [23]. Hydrothermal treatment can provide a cost-effective and morphology controllable route to obtain 1-D nanostructures, and hence has become an advantageous method. Among the existing hydrothermal methods, $WO_3$ nanorods are usually synthesized at a reaction temperature higher than 180 °C. Salmaoui et al. have reported synthesis of $WO_3$nanorods by using a hydrothermal method at a temperature of 180 °C for 72 h by using aniline and sodium sulfate together as structure-directing templates [24]. Qin et al. reported preparation of $W_{18}O_{49}$ nanorods at 200 °C by using tungsten hexachloride ($WCl_6$) as a tungsten precursor and cyclohexanol as a reaction solvent [25]. To the best of our knowledge, the controlled synthesis of $WO_3$ nanorods at a temperature below 180 °C has rarely been demonstrated to date [26].

In this work, we report a hydrothermal synthesis of $WO_3$ nanorods at a reaction temperature of 170 °C. By adjusting the amount of oxalic acid, the control of precipitation between $WO_4^{-2}$ and $H^+$ is achieved, which ensures the formation of small, uniform crystal seeds in a strongly acidic solution. The obtained h-$WO_3$ nanorods are considered as a capable sensing material. They exhibit highest sensitivity and selectivity towards 20 ppm level of $NO_2$, which makes them a reasonable candidate for application in $NO_2$ sensors.

## 2. Experimental

$WO_3$ nanostructures were synthesized by using an aged-hydrothermal route. A saturated aqueous solution of ammonium metatungstate [$(NH_4)_{10}W_{12}O_{41}xH_2O$] (0.15 mol of W) was prepared and acidified with $HNO_3$ (2.2 N) to produce ~5 pH. The product was kept in a hermetically sealed Teflon container with stirring for one week at 60 °C. Then 5 ml of aged solution was transferred into a Teflon-lined stainless steel autoclave and heated at 170 °C for 48 h. The material obtained was filtered, washed with deionized water and dried in air at room temperature and finally calcined at 400 °C.

### 2.1. Characterization technique

The structural characterization was conducted using X-ray diffraction (Bruker D2 phasor X-ray diffractometer with CuKα radiation $\lambda =$ 1.5456 Å). The morphology of powder was studied by SEM (JEOL 6360). The structure of samples was investigated further by TEM and HRTEM (Techni $2G^2$ 20U Twin-FEI Netherlands). The Raman spectroscopy was studied by Nd:YAG laser source (Bruker Multi-RAM Germany Make) with an excitation wavelength of 1064 nm and resolution 4 $cm^{-1}$ at 336 mW laser power. PL properties were analyzed by using Flurolog (Horiba Joinyvon) spectrometer. Diffuse reflectance electronic spectra (DRS) were measured with a Perkin-Elmer UV WinLab spectrophotometer equipped with R Beam Att, SBeamAtt, multipurpose optical bench Hitachi integrating sphere accessory.

### 2.2. Thick film preparation

Thick films of nanostructure $h$-$WO_3$ were prepared by using an screen printing technique. In the present process, thixotropic paste was formulated by mixing the synthesized $h$-$WO_3$ powder with ethyl cellulose (as a temporary binder) in a mixture of butyl carbitol acetate and turpineol organic solvents. The ratio of $h$-$WO_3$ to ethyl cellulose was kept at 95:05. The ratio of inorganic to organic part was kept as 75:25 in formulating the pastes. The thixotropic pastes were screen printed on a glass substrate in the desired patterns. The as-prepared films were fired at 400 °C for 2 h. The prepared thick films were called as pure h-$WO_3$ thick films.

### 2.3. Gas sensing characterization

The gas sensing studies were carried out in a static gas chamber to sense test gas in air ambience. The h-$WO_3$ thick films were used as sensing elements. The sensing element was directly kept on a heater in a gas chamber and the temperature of the sensing element was monitored by chromel-alumel thermocouple placed in contact with the sensing element. Known volume of $NO_2$ was introduced into the gas chamber prefilled with air. The electrical resistance of the sensing element was measured by a simple two-probe configuration before and after exposure to $NO_2$ vapor using digital electrometer (Keithley – 6514).

The sensitivity ($S\%$) of the sensing element is defined as,

For n-type semiconductor the response ($S$) in case of reducing gases were calculated using the formula

$$S(\%) = \frac{(R_a - R_g)}{R_a} \times 100 \quad (1)$$

For n-type semiconductor the response ($S$) in the case of oxidizing gases were calculated using the formula,

$$S(\%) = \frac{(R_g - R_a)}{R_g} \times 100 \quad (2)$$

where, $R_a$ is the resistance in air and $R_g$ is the resistance in presence of test gas at a given temperature.

## 3. Results and discussion

Therese et al. [27] reported synthesis of $WO_3$ nanostructures using additives. The main difference between Therese et al. method and ours is that we did not use additives to form the nanostructures. Owing to the structure of ammonium tungstate to convert $W_{12}O_{41}^{10-}$ anions to neutral $W_{12}O_{36}$ the excess divalent oxygen anions must be removed during the aging of the precursor solution and hydrothermal treating. Stoichiometrically