Ultra-fast $\alpha$-MoO$_3$ nanorod-based Humidity sensor

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Abstract One-dimensional nanostructure metal oxide nanomaterials shows high potential for applications in sensor. The molybdenum oxide is widely used in various applications from electronics to energy storage. We have synthesized molybdenum trioxide (MoO$_3$) nanorods by simple hydrothermal method and characterized by X-ray diffraction, Raman spectroscopy, UV-visible spectroscopy, photoluminescence spectroscopy, scanning electron microscopy, and transmission electron microscopy (TEM). The TEM confirmed the formation of highly crystalline MoO$_3$ nanorods with a length of 5–10 μm. The MoO$_3$ nanorods were used for the humidity sensing in the range of 11–97% relative humidity. The synthesized MoO$_3$ nanorods sensor device was exposed to different humidity levels which show the fast response and recovery time. This indicates that the MoO$_3$ nanorod-based humidity sensor has potential for industrial applications.

Keywords Humidity sensor, $\alpha$-MoO$_3$, Nanorods

Introduction

One-dimensional (1D) nanostructure materials have significant advantages for improving the sensing properties and applications in sensors such as semiconducting carbon nanotubes,$^{1,2}$ polymers, and metal oxides.$^{3-7}$ A metal oxide nanomaterial possesses interesting range of properties such as optical, magnetic, chemical, and electronic properties.$^{8,9}$ There are number of applications of humidity sensor device such as monitoring of industrial product, climatology, agriculture, and also for instrumentation application.$^{10}$ Metal oxide semiconducting materials have low-cost, high sensitive, and good compatibility. One-dimensional nanostructure materials have high surface to volume ratio suitable for humidity sensors. Stability of materials and sensitivity are the major challenges for making high-performance sensor devices. Since the first report on field effect transistors based on single-layer graphene has appeared almost a decade back, the study of 1D and two dimensional (2D) nanomaterials such as metal dichalcogenides, WS$_2$,$^{11,12}$ MoS$_2$,$^{13}$ MoSe$_2$,$^{14}$ WSe$_2$,$^{15-19}$ layered materials,$^{20-24}$ metal oxide (V$_2$O$_5$, SnO$_2$)$^{25,26}$ has become one of the active areas of material science research. 1D and 2D materials can be prepared synthesized by various methods such as micromechanical exfoliation of bulk crystal using scotch tape,$^{27}$ chemical vapor deposition,$^{28,29}$ liquid exfoliation,$^{30}$ pulsed laser deposition,$^{31}$ and other chemical methods like hydrothermal, solvothermal methods.$^{29}$ We were interested in 1D nanostructure humidity sensor due to easy charge carrier properties of analyte molecules.$^{32}$ The MoO$_3$ is present in nature as a single-valance compound. MoO$_3$ is n-type semiconducting material with wide band gap (~3.2 eV) responsible for reactions of hydrogen and oxygen molecule.$^{33}$ Metal oxide adsorbs water molecule to form hydroxyl molecule that helps to increase the conductivity of n-type semiconducting molecules.$^{34}$ The MoO$_3$ nanomaterials has unique properties such as high chemical stability and various applications in sensors.$^{35,36}$ Catalysis,$^{37,38}$ lithium-ion battery,$^{39,40}$ and photodetector.$^{41}$ In present investigation, we have synthesized MoO$_3$ nanorods using hydrothermal method with high aspect ratio for application in humidity sensing. This technique is very simple and widely accepted for synthesis of nanostructure materials including metal oxide and metal...
dichalcogenides nanostructure materials. Also, this method has number of advantages such as low cost, fast reaction time and easily scales up and controlled morphology with high-purity product.

Experimental section
Sensor device fabrication

The device fabrication was done using Tin doped indium oxide (ITO) substrate. The scratch was formed using glass cutter on the conductive surface of ITO to separate the drain and source. The humidity sensing device was ~1 x 1 cm² with channel length 1 cm and ~width ~600 μm. The two-probe device was connected with GPIB 488A interface cable which attached to the computer-controlled system. The MoO₃ nanorods powder was dispersed in ethanol which was sonicated and then drop casted in between the drain and source electrode. The device was then dried by keeping in vacuum oven at 100 °C.

Chemicals
All the chemicals purchased of analytical grade and used without any further purification. Commercially available ammonium heptamolybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O) (Merck 99%) and nitric acid (HNO₃) (Chemlabs 67–71%) were used for the synthesis of MoO₃ nanorods. The salts required for humidity sensing measurements were purchased from the Chemlabs (99%) chemicals Bangaluru, Karnataka (India).

Figure 1 The growth mechanism of MoO₃ nanorods formation

Figure 2 MoO₃ nanorods: a XRD pattern, b Raman Spectra, c UV–visible spectra, and d PL spectra
Synthesis methods
The MoO₃ nanorods have been synthesized by hydrothermal method. In typical synthesis, 0.88 mmol (NH₄)₆Mo₇O₂₄·4H₂O and 30 ml deionized water were sonicated for 30 min, the turbid solution was formed, after that concentrated HNO₃ (~2–3 ml) was added to above reaction mixture. The transparent solution formed was stirred for 30 min at room temperature. Then the reaction mixture was transferred to Teflon-containing stainless steel autoclave, having 50 ml capacity, for hydrothermal treatment at 180 °C for 24 h. After completing the reaction the autoclave was cooled to room temperature naturally and product was separated by centrifugation. The product was washed with distilled water and ethanol and then finally dried at 60 °C under vacuum for 12 h.

Material characterizations
The synthesized MoO₃ nanorods were characterized with Raman spectroscopy (HR-800 Raman spectrometer, Horiba Jobin Yvon, France) using 632.8-nm red laser (NRS1500W). X-ray diffraction (XRD) spectrum was recorded by X-ray diffractometer (XPERT-PRO) equipped with Cu Kα (λ=1.5406 Å). Photoluminescence spectroscopy (PL) spectrum was done using exciting wavelength at 325 nm (Horiba Jobin Yvon fluorolog 3 spectrophotometer having 450W Xenon lamp). Scanning electron microscopy (SEM) images were captured using FEI, QUANTA 200 3D SEM with tungsten filament as electron source. Transmission electron microscopy (TEM) images were recorded with FEI TECNAI TF-30 (FEG instrument).

Shimadzu UV-3600 plus UV-vis-NIR spectrophotometer was used for recording UV-visible spectra.

Humidity sensing
All electrical measurements were carried out using Keithley 2612A system source meter attached to computer through GPIB 488A interface. The sensing device response was monitored at different relative humidity levels using saturated solutions in closed vessel.

Results and discussion
The proposed growth mechanism for forming MoO₃ nanorods is shown in Fig. 1. Initially, the seed nucleation takes place by reaction of (NH₄)₆Mo₇O₂₄·4H₂O with conc. HNO₃. When reaction temperature is increased the oxidation process occurs which give rise to Mo species that reacts with oxygen and forms octahedral MoO₆. The anisotropic growth of octahedral MoO₆ crystals occur along with a preferential direction by Ostwald ripening mechanism and leads to self-assembled 1D behavior growth of MoO₃ nanorods. The typical XRD pattern of MoO₃ shown in Fig. 2a has a well-defined spectrum along with more enhanced peaks with (0 4 0) and (0 2 0) direction. The crystal structure and phase composition of MoO₃ nanocrystalline materials were shown in XRD pattern. The XRD pattern matches with standard JCPDS No. 35–0609 and peaks corresponding to facet (0 2 0), (1 1 0), (0 4 0), (0 2 1), (1 1 1), (0 6 0), (0 8 1), and (0 6 2) are of orthorhombic α-MoO₃. Figure 2b shows typical Raman spectra of MoO₃. The Raman spectrum

Figure 3  a–d SEM images of MoO₃ nanorods
of MoO$_3$ shows various low-order and high-order vibration modes which appear due to the stretching and deformation in MoO$_3$. The strong peak at 995 and 817 cm$^{-1}$ appeared due to antisymmetric ν (Mo = O) stretching ($A_g$) and symmetric stretching mode ($A_g$) ν (Mo–O–Mo), respectively. The weak peak appeared at 664 and 470 cm$^{-1}$ are due to antisymmetric stretching ($B_{2g}$) and bending ($A_g$) ν (Mo–O–Mo). The peaks at 380, 337 cm$^{-1}$ corresponds to scissoring modes ($B_{1u}$) of δ (Mo=O=Mo) and the peaks at 244, 215 cm$^{-1}$ corresponding to δ (Mo–O–Mo) ($B_{2g}$ and $A_g$) modes. The peak at 389 cm$^{-1}$ appeared due to wagging mode δ (Mo=O=Mo).47,48 Figure 2c shows the UV–visible spectra of MoO$_3$ nanorods. The more intense with maximum absorption peak appeared at 212 nm in UV-C region.49 The PL shown in Fig. 2d was recorded with an excitation wavelength of 325 nm at room temperature. The PL spectra of MoO$_3$ shows strong emission band at 363 nm.50 Figure 3a–d shows the typical SEM images of MoO$_3$ nanorods clearly indicating the rods like morphology with length between 5 and 10 μm. Figure 4a–c) depicted the low magnification TEM images of MoO$_3$ nanorods. The TEM confirmed the MoO$_3$ nanorods with length and width as 5–10 μm and 100–200 nm, respectively. The high-resolution TEM images in Fig. 4d with lattice fringes measured the lattice spacing 0.336 nm corresponds to plane (0 2 1). The inset of Fig. 4d shows the selective area electron diffraction pattern, which clearly indicates the highly crystalline nature of orthorhombic MoO$_3$ nanorods.

Figure 5a shows the typical current–voltage (I–V) plot of MoO$_3$ nanorod-based humidity sensor device at various relative humidity in which the current increases with increasing in relative humidity. The typical I–V measurement shows the linear nature of slope with increasing relative humidity. The typical resistance and sensitivity vs. relative humidity plots for MoO$_3$ nanorods are shown in Fig. 5b. The resistance of MoO$_3$ nanorods was found to be decreasing with the increasing relative humidity. The sensitivity increases with increasing relative humidity. The maximum sensitivity of device for relative humidity at 97.3% is 229%. The sensitivity ($S$) for the sensor was calculated using the following equation.51

$$S = \frac{R_L - R_H}{R_H}$$

where $R_H$ is the resistance of device at higher humidity level and $R_L$ is the resistance of device at lower humidity level (11.3%). The water molecule acts as an electron donor, i.e. n-type doping so that Fermi level of MoO$_3$ shifted toward the conduction band by decreasing the resistance of MoO$_3$ sensor with adsorption of water molecule, i.e. positive sensitivity was observed. Figure 5c shows the current–time (I–t) plot related to different relative humidity level. The stability
Table 1 shows the comparative data for various kinds of metal oxide nanostructure materials with different morphology in terms of response and recovery time with the performance of our humidity sensor device. Water protonation and protonic conduction mechanism of adsorbed water molecule on the surface of material helps for increasing electrical conductivity. In our sensor device, the recovery time was found to be very fast because the adsorbed water molecule get desorbed very fast when device get shifted from higher humidity level to lower humidity level.

Figure 5a shows the I–V characteristics for various relative humidities, Figure 5b shows the typical plot of resistance and sensitivity vs. relative humidity, Figure 5c shows the typical response of sensor device with relative humidity switching between 11.3 and 97.3% for repeated cycles, and Figure 5d shows the typical response of the humidity sensor device with relative humidity switching between 11.3 and 97.3% after three months showing good stability of the sensor device.
Conclusions

We have synthesized MoO₃ nanorods by simple hydrothermal method. The synthesized MoO₃ nanorods were used for humidity sensing in the range of 11–97% relative humidity. We found the good and long-term cyclic stability and reproducibility of the results even after three months. The MoO₃ nanorod-based humidity sensor showed very fast response ~118 s and recovery time within ~5 s along with high sensitivity of ~229% indicating that MoO₃ nanorod-based humidity sensor has potentials for industrial and a wide range of other applications.

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Disclosure statement

The authors declare no competing financial interest.

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Table 1 The comparative data of various kinds of metal oxide nanomaterial with MoO₃ nanorods related to response/recovery time are shown in table

| Sr. no. | Metal oxide nanomaterials | Morphology | Response time (sec) | Recovery time (sec) | References |
|--------|---------------------------|------------|---------------------|---------------------|------------|
| 1.     | SnO₂ Nanowire             | 120–170    | 20–60               |                     | [52]       |
| 2.     | V₂O₅ Nanosheets           | ~240       | ~300                |                     | [53]       |
| 3.     | CuO Nanowire              | ~120       | ~120                |                     | [54]       |
| 4.     | ZnO Nanosheets            | ~600       | ~3                  |                     | [55]       |
| 5.     | Al₂O₃ Thin film           | ~1080      | ~1320               |                     | [56]       |
| 6.     | TiO₂ Nanotube             | ~100       | ~190                |                     | [57]       |
| 7.     | MoO₃ Nanorods             | ~118       | ~5                  | Present work        |            |

Figure 6 a Humidity sensing response at room temperature with different relative humidities, b Typical I–t plot for MoO₃ nanorod-based humidity sensor device, c Typical sensor device of MoO₃ nanorods for humidity measurements.
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