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Implication of potassium trimolybdate nanowires as highly sensitive and selective ammonia sensor at room temperature

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Abstract

Potassium trimolybdate nanowires are demonstrated as unique and highly selective NH_3 sensing materials at room temperature. The nanowires were synthesized by using chemical route under normal ambient conditions and subsequently characterized by scanning electron microscopy (SEM) and x-ray diffraction (XRD). Gas sensors based on nanowires were fabricated by isolating and aligning nanowires between microspaced electrodes using dielectrophoresis. Room temperature gas sensing studies for different vapors indicated excellent selectivity for NH_3 and capability to detect NH_3 at concentrations down to ppb level. The sensors exhibited higher sensitivity for concentration range much below toxic limit of NH3 from 500 ppb up to 25 ppm. Since nanowires are isolated and aligned, the gas sensing reaction is rapid, and the availability of abundant oxide and hydroxyl surface groups on nanowires surface makes the reaction significantly prominent and selective with highly reducing nature of NH_3.

Introduction

Chemiresistive gas sensors form the backbone of majority gas sensor devices owing to its ease of operation, accuracy and facile design. It involves detection of a target gas by two or three terminal devices. Chemiresistive sensors have captured considerable attention with key features towards the advancement of low-cost, portable, low power, ultrasensitive and selective applications in chemical, biological and physical monitoring [1]. It outlines the necessity of resistive devices in fabrication of gas sensors.

Eventually, major focus has been given to development of metal oxide based gas sensors that exhibits high sensitivity and selectivity with a fast response recovery profile at a certain operating temperature. Most commonly reported gas sensing oxide materials include SnO_2, ZnO, Fe_2O_3, WO_3, In_2O_3 and TiO2 which exhibit good sensing characteristics due to the abundant microstructural defects that are beneficial for the formation of absorbed oxygen ions [2].

Ammonia is one of the most key ingredient amongst many industry applications, like in Agriculture industry for fertilizers, livestock feed products; semiconductor industries during growth process of GaN/Si_3N4; several areas of waste water treatment and also in petroleum industries. Nevertheless, ammonia belongs to series of hazardous and toxic gases that needs monitoring under specific level. According to United States Occupational Safety and Health Administration (OSHA), the specified short term exposure limit of ammonia is 35 ppm whereas the threshold limit is 25 ppm. Superfluous level of ammonia causes major damage to respiratory systems, eyes and skin and the long term exposure may lead to permanent defects in any of these systems. This necessitates the development of ultrasensitive ammonia sensor operable under ambient conditions. Recently, many of the reports are available on NH_3 sensors based on metal oxides as well as organic semiconductors and composites. Nanomaterials in diverse morphologies like nanoparticles, nanofibers have proved to be efficient in gas sensing applications. These 1D nanostructures show very high surface-to-volume ratios and great surface activities, which could translate to better gas response and selectivity properties in terms of chemical sensing. Furthermore, these 1D nanostructures can be integrated with conventional devices and device fabrication

techniques and could potentially be massively multiplexed in nanosized devices. Liu *et al* reported Pt nanoparticles activated SnO_2 nanoclusters based NH_3 sensors operating at 115 °C with sensitivity of 200 for 500 ppm [3]; polyaniline-TiO2 based NH_3 sensors reported by Gong *et al* detecting NH_3 at ppt levels [4]. Amidst all these conventional metal oxide materials a new element of polyoxymetalates has captured certain amount of interest, it is built by combining transition metals from group V and VI with shared oxide ions. It has been of prime attention due to its unique optical, magnetic, biological properties that makes them suitable for application in photocatalytic oxidation of organic compounds, H_2 production and photo electrochemical production of electricity [5–8]. Potassium trimolybdate belongs to family of polyoxymetalates and is considered among variety of polymolybdates subgroup. It has been reported as efficient catalyst in high quality single crystals [9, 10]. In our previous work we have used Potassium molybdate nanowires for as templates in fluidics application [11].

In this article, we report highly sensitivity and selective NH_3 sensors based on potassium trimolybdate nanowires operable at room temperature. In this potassium trimolybdate nanowires are synthesized using simple chemical route under normal ambient conditions. Nanowires based gas sensors are fabricated by aligning the nanowires between microspaced electrodes using dielectrophoresis technique. The nanowire based sensors demonstrate excellent sensitivity with few orders change in conductivity after exposures to NH_3 vapor much below its toxic limit with rapid response recovery profile at room temperature. To the best of author's knowledge this is first of its kind of application of potassium trimolybdate nanowires in gas sensing. Moreover these sensors are highly specific towards NH_3 against other volatile compounds.

Methods

Synthesis of $K_2Mo_3O_{10}.4H_2O$ nanowires

Nanowires of K2Mo3O10.4H2O were synthesized using aqueous precursors $(NH4)_6Mo_7O_{24}.4H2O$ and KCl using a previously reported protocol [11]. Powders of pure $(NH_4)_6Mo_7O_{24}.4H_2O$ and KCl were dissolved separately in DI water, and further mixed together in 3:1 mass ratio [11]. This ratio of precursors was considered as it produced best quality nanowires in terms of uniformity and purity in phase. The reaction was conducted at room temperature under normal atmospheric conditions. Nanowires were obtained as white floccule like precipitates in reaction vials in 15 min The products were cleaned by repeated cycles of centrifuging and rinsing by deionized water. The morphology and composition of nanowires was characterized using scanning electron microscope (SEM) and x-ray diffraction (XRD).

Preparation of microspaced electrodes

In our proposed scheme microspaced electrodes were prepared by standard physical vapor deposition method having premasked glass substrates. The substrates were then placed in evaporation chamber and aluminum was evaporated. Wires were attached on aluminum electrodes using silver paste for making contacts. The nanowires were aligned between micro gap by DEP process. The detail process parameters are given supporting information (SI).

Gas sensing studies

In order to measure the gas response, the resistance of the films was measured in air ambient and in gas atmosphere. For monitoring the response of the films to various gases, the films were mounted in 1 liter air tight container and the known vapor of particular concentration was injected through a syringe. The sensor response was measured by voltage divider method. In this, a standard resistance was added in series with sensor and potential drop across the fixed resistance was measured using 3½ digit multimeter. The sensor resistance values were subsequently estimated using appropriate procedure. All the gas sensitivity measurements were carried out at room temperature. The sensitivity is defined as ratio of resistance in air to resistance in gas, $S = R_g/R_a$; where Ra : Resistance of device in air, Rg: Resistance of device in presence of desired gas.

Results and discussion

Nanowires of $K_2Mo_3O_{10}.4H_2O$ were synthesized at room temperature as reported earlier [12]. Optical microscope (Nikon-MM 40) (Biotech labs) with a resolution of ~2 μm was used initially to observe products obtained. The precipitate obtained in reaction revealed formation of clusters of nanowires. The detailed morphology was examined under SEM using a dispersed sample on glass substrate. The typical SEM images of nanowire are given in figure 1. The dimensions of nanowires grown were ~300 nm (figures 1(a) and (b)) in diameter and length ranging from 10–30 μm. The elemental analysis is added in supp info (figure S1).

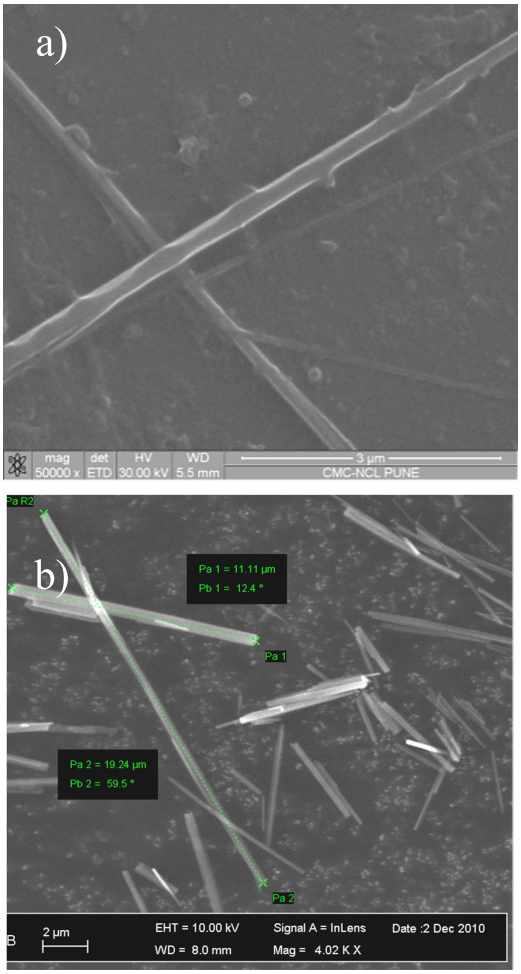

Figure 1. SEM micrograph of $K_2Mo_3O_{10}.4H_2O$ nanowires synthesized at room temperature. (a) bunch of nanowires (b) Nanowires with measured scale.

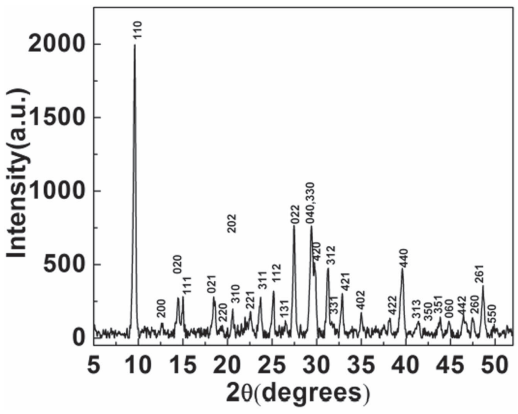

Figure 2. XRD data for nanowires sample (JCPDS-051-1628).

Crystal structure of nanowires was characterized using XRD technique. The powder diffractogram shown in figure 2 was found to match with previously reported data [12, 13]. Various planes associated with standard structure of NWs were identified and observed peak values were found to be identical to standard data (JCPDS 051-1628). The results indicate pure orthorhombic phase of $K_2Mo_3O_{10}.4H_2O$ nanowires.

Optical microscopy imaging for microspaced electrodes was performed. The total spacing between electrodes was of the order of 30 μm. DEP process was used to isolate and align nanowire across the

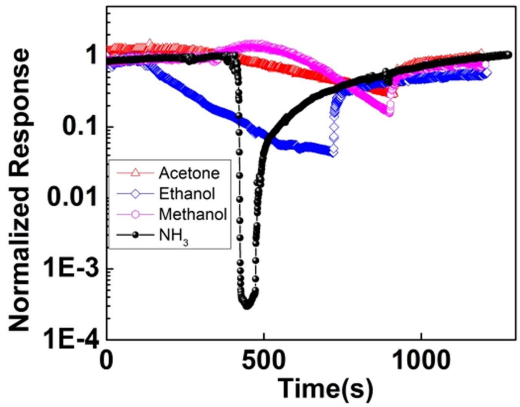

Figure 3. Gas response curve for 12.5 ppm NH_3, Acetone, Ethanol, Methanol. Inset shows sensor response to other vapors.

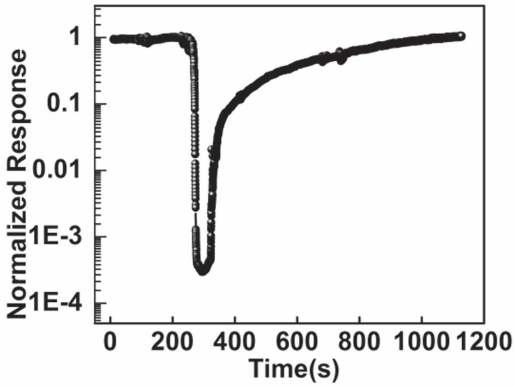

Figure 4. Gas response curve for 12.5 ppm NH_3.

microelectrodes. Optical microscope images of electrodes after DEP revealed deposition of nanowires isolated and aligned between two electrodes and middle segment was suspended as seen in figure S2.

Figure 3 shows normalized response for 12.5 ppm concentration of different vapors like NH_3, acetone, methanol, and ethanol. It is observed that for NH_3, total change is 3 orders of magnitude that is adequately higher than other vapors. This implies exceptional selectivity of nanowire sensor to NH_3 vapors.

In order to estimate complete sensor parameters response recovery study for specific concentration of NH_3 vapor was performed. Figure 4 shows static response of sensor after exposure to 12.5 ppm NH_3 vapor. The response time, defined as time taken to reach 90% of saturation value is of order of 40 s and recovery time that is time required to reach 10% of saturation value is 10 min The fast response recovery of sensor indicates suitability of potassium trimolybdate nanowires as NH_3 sensors.

Further the sensor was exposed to various concentrations of NH_3 below its toxic limit; figure 5 shows sensitivity of sensor for concentrations ranging from 0.5 ppm–12.5 ppm. It was observed that sensitivity varies almost linearly with concentrations and even a lower concentration of 0.5 ppm can be detected with adequate sensitivity value (~15). The curve shows two regions of linear change between 0.5–10 ppm. Moreover the sensors were highly reproducible. The sensitivity for different sensor devices was significantly reproducible with ±10% error. The details are given in figure S3.

In order to study the influence of aligned nanowires, other samples were prepared using dilutely dispersed nanowires as well as thick mat type films of nanowires deposited over microspaced electrodes. Gas response studies for dispersed sample showed response recovery time of few minutes with lower sensitivity value ~180 (figure not shown) whereas for thick films the response was more than an hour to reach the saturation indicative of sluggish response towards NH_3. This signifies the characteristics of isolated nanowire sensors in detecting lowest concentrations of NH_3 which is of prime importance.

In the following we discuss the plausible sensing mechanism for potassium trimolybdate nanowire sensors.

In the previous research, it is stated that polyoxymetalates are anionic clusters that are formed by transition metals (Group V & VI) linked by shared oxide ions. In general, polyoxometalates (POM) can be considered as

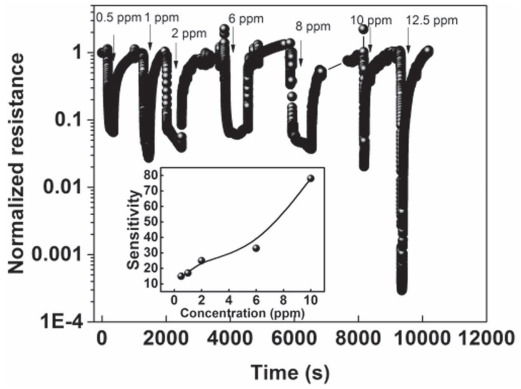

Figure 5. Sensor response as a function of NH_3 concentration. Inset shows gas response for lower concentrations.

class of compounds based upon metal oxide building blocks with a general formula {MOx}n, where M = Mo, W,V,and sometimes Nb and x = 4–7. Overall, POM clusters are normally anionic and thus can be complexed with additional cations as linkers [14]. Metal cations as counterions are also used in constructing the POM clusters, in such cases ionic crystal structures with different alkali metal ions can be formed. The potassium trimolybdate ($K_2Mo_3O_{10}$. $3H_2O$) is one of similar type of such POM clusters. The crystal structure consists of several Mo_xO_y based chains. The anion $(Mo_3O_{10})^{2-}$ is combined with a combined cation K^+ which exhibits catalytic effect in crystal growth applications [8, 9, 12] and another useful properties in nanofluidics. In POM clusters with metal counterion (i.e.potassium trimolybdate) the cavity volumes of the ionic crystals formed by desorption of solvated water vary with the nature of the alkali metal ions included. Such porous materials can be used for the selective sorption and successful separation of mixtures of alcohols, nitriles, esters,and water [15]. Effectively, this material has influential potential in gas sensor applications.

In order to devise the sensing mechanism, we need to consider the structure of sensor. It is composed of few nanowires isolated between micro spaced electrode. Hence most of the reactions involve contributions from nanowire surfaces since gas interaction is a typical case of physisorption on surface of nanomaterials. Since these materials exhibited excellent catalytic properties, there exists a typical delocalization within cluster structure itself as well as charge transfer reactions during electrochemical activities. That essentially produces specific redox states during electrochemical reactions. Similar mechanisms are extended towards interaction of nanowires with NH_3. When the sensor is exposed to NH_3 the resistance is decreasing and reaches saturation and then recovers back when exposed to air. The significant decrease in resistance can be correlated to typical surface reactions with different functional groups on nanowire surface. As mentioned earlier the POM structure consists of metal oxides group as well as alkali metal ions clustered together.Since the nanowires possess hydrate as well as oxide group at room temperature the resistance of wires are quite high since the adsorbed oxygen ions and oxide groups take electrons from bulk. NH_3 being an electron donating gas, when NH_3 is adsorbed on nanowire it reacts with oxide and hydroxyl groups as well as adsorbed oxygen ions on surface. Consequently after NH_3 interaction the captured electrons are given back to bulk of nanowires leading to increase in majority charge carrier concentration and thereby its conductance. Higher the concentration more change in conductance is observed since the charge carrier concentrations is increased significantly.

Since the sensor configuration is devised of isolated and aligned nanowires the response is rapid as only few nanowires are exposed and being a isolated nanowires it has a larger surface area available for NH_3 interaction. This results in a very fast response and recovery time which is unlikely in thick mat type films and dispersed network of nanowires.

Now we focus on mechanism behind high selectivity for NH_3 than other vapors. This is attributed to different interactions between sensing layer and adsorbed vapor and depends on characteristics of individual vapors. The difference in sensitivity can be ascribed to properties like higher electron affinity value of NH_3 (211 Kcal mol^{-1}) than other vapors (~185 Kcal mol^{-1}) [16, 17]; different adsorption kinetics of vapors in which NH_3 has an edge with adsorption capacity 6.4 mMol/g [18]and essentially higher electronegativity and work function. This validates higher selectivity for NH_3 over the other vapors.

We have compared our results with recent reports of different materials employed in ammonia sensing applications and given in table 1. It is observed that the sensor has better sensitivity at room temperature than other materials and comparable detection limit for NH_3.

Table 1 Comparison with Recent NH_3 Sensors.

Material	Sensitivity	Lowest detectable Concentration	Operating Temperature	Reference
PAni-DBSA	3.3	100 ppm	Room Temperature	[19]
V_2O_5 thin films	2%	80 ppb	350 °C	[20]
NiO nanocones-ZnO nanothorns	20%	15 ppm	Room Temperature	[21]
Cu-PANi	30%	5 ppm	Room Temperature	[22]
rGO-Ag nanowires	3%	15 ppm	Room Temperature	[23]
SnO_2-SnS_2 hybrids	1.2	10 ppm	Room Temperature	[24]
ZnO nanorods	2	20 ppm	Room Temperature	[25]
SWCNTs	4%	25 ppm	Room Temperature	[26]
Doped Graphene	1%	200 ppb	Room Temperature	[27]
Chemically reduced Graphene Oxide	5%	200 ppm	Room Temperature	[28]
$K_2Mo_3O_{10}.4H_2O$ Nanowires	**15**	**500 ppb**	**Room Temperature**	**Our work**

Conclusions

Chemiresistive gas sensors based on potassium trimolybdate nanowires were fabricated by simple dielectrophoresis technique. Potassium Trimolybdate nanowires have been validated as a novel material for room temperature operable NH_3 sensors with excellent sensitivity, selectivity and fast response recovery profile. The sensor has significant response for lower range of NH_3 concentrations much below its toxic limit. In addition to this the nanowires sensors have ability to detect NH_3 vapors down to ppb level. This indicates the potential of potassium molybdate nanowires in sufficiently suitable material for fabrication of NH_3 sensors.

Author contributions

The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

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