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# One-Dimensional $MoS_2$-Decorated $TiO_2$ nanotube gas sensors for efficient alcohol sensing

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ABSTRACT

One-Dimensional (1D) $MoS_2$-decorated $TiO_2$ nanotubes were synthesized by the anodization of $TiO_2$ nanotubes followed by a hydrothermal process for $MoS_2$-decoration. The structure, morphology and surface characteristics of the $MoS_2$-$TiO_2$ composites were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), and Brunauer–Emmett–Teller (BET). The results showed that $TiO_2$ nanotubes can be filled and covered by flake-like $MoS_2$ nanostructure. The numbers of the $MoS_2$ layers ranged from 1 to 3. The $TiO_2$ nanotube sensor shows a normal n-type response to reducing ethanol gas, whereas $MoS_2$-$TiO_2$ exhibits p-type response with excellent sensing performances. Specially, the sensitivity for the $MoS_2$-$TiO_2$ heterojunction increased almost 11 times than $TiO_2$ nanotubes. This conversion of sensing behavior can be explained by the formation of p-n heterojunction structures.



## 1. Introduction

Volatile organic compounds (VOCs) such as ammonia, acetone, methanol, formaldehyde, and ethanol are the basic sources of indoor air pollution and give rise to harmful influences on human health [1–4]. Therefore, a great deal of research has been focused on the development of functional materials for high-performance of VOCs sensing. Titanium oxide, n-type semiconductor with the band gap of ~3.2 eV, is one of the most promising candidates for gas sensor due to its low cost and environmental safety [5–8]. Specially, $TiO_2$ nanotubes were fabricated to improve gas sensing characteristics on a large scale, as nanotubes being one dimensional, nanostructure with uniform morphology and a large surface area with controllable less agglomeration have potential applications. But titanium oxide nanotubes has shortcoming of poor selectivity from a mixture of gas, long response and recovery time, and high operating temperature. Recently, many methods were investigated with the focus of improving the gas sensing performance of $TiO_2$ nanotubes. Doping with noble metals such as Au, Pt, Pb, and Ag is known to be effective, because active sites can be produced for particular gas species by doping [9–12]. However, these sensitive materials can be poisoned easily in some gas atmospheres, which can lead to reduction in sensitivity and stability. Nowadays, semiconducting 2D materials have recently attracted intensive attention, mainly due to the atomically thin-layered 2D structure and excellent electrical properties of graphene sheets [13–15]. Among the various inorganic 2D layered materials, molybdenum disulfide ($MoS_2$) has been investigated by a number of researchers due to its good electrical, mechanical, optical, magnetic and electrochemical properties [16,17]. Intrinsic $MoS_2$ is a kind of *n*-type semiconductors and its band gap is in the range of 1.2–1.9 eV determined by the layer numbers [18]. However, $MoS_2$ can exhibit either a *p*-or a *n*-type gas sensing response to reductive vapor [19] depending on their annealing temperature in air. Especially, it is reported that incorporating two or more semiconductors to form a heterojunction interface could enhance the gas sensor performance [20,21]. However, till date, to the best of our knowledge, no report has been published on the $MoS_2$-$TiO_2$ p-n junctions on gas/vapor sensing performance.

Accordingly, we reported a facile way to tune gas and vapor sensing performance by blending n-type $TiO_2$ nanotube with p-

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type $MoS_2$ (in present work) to form hybrid architectures. This novel features of this p-n heterojunction not only take the advantages of $TiO_2$ nanotubes that (i) fast electron transportation through vertical tube walls (ii) high effective surface area facilitating more number of adsorption sites, but also can potentially present localized highly reactive areas by $MoS_2$ modification and thus achieve unexpected characteristics for sensing applications. The sensing properties of $MoS_2$-$TiO_2$ composites were evaluated with $NO_2$, $NH_3$, $C_2H_5OH$, and other organics. The $MoS_2$-$TiO_2$ composites show excellent sensing performances towards ethanol vapors at low operating temperature. The mechanisms of the outstanding sensing performance for the $MoS_2$-$TiO_2$ heterojunction were also proposed. This undoubtedly opens up new possibilities for flexible and wearable devices for various environmental sensing applications.

## 2. Experiment

### 2.1. Synthesis of $MoS_2$-$TiO_2$ composites

Highly ordered $TiO_2$ nanotubes were fabricated via anodization of commercially available pure titanium foils, the detailed synthesis route is as follows [22]. Ti plate was anodized in water/ethylene glycol (1:100 Vol.%) mixtures containing 0.13 M $NH_4F$ in a 30 °C water bath with a platinum foil as a cathode, and Ti substrate as an anode. A constant anodization voltage of 60 V (time = 2 h) was applied. After anodization, the samples were rinsed in deionized water, and dried in air. Modification of the $TiO_2$ nanotubes with $MoS_2$ nanoflake was done by hydrothermal routes [23]. In a typical procedure, 0.137 g $MoCl_5$ was dissolved in 5 ml of distilled water, and then was dissolved in the mixture solution of ethanol, oleic acid, and water (15 ml: 4 ml: 5 ml). 0.3 g $Na_2S \cdot 9H_2O$ dissolved in 5 ml of distilled water as reducing agent was injected into the above solutions and stirred for 10 min. The final solution was transferred into a 60 ml Teflon-lined stainless steel autoclave and the Ti sheet with $TiO_2$ nanotubes was immersed in this solution. The autoclave was maintained at 180 °C for 12 h. After natural cooling, the Ti sheet with $TiO_2$ nanotubes was removed from the autoclave and washed multiple times with distilled water, and then dried in air. Subsequently, the as-synthesized Ti sheet was calcined at 400 °C in Ar atmosphere for 1 h.

### 2.2. Characterization

The surface morphology and structure of samples were characterized by field emission scanning electron microscopy (FE-SEM, Hitachi S-4800), X-ray diffraction (XRD, RIGAKU/DMAX), and transmission electron microscopy (TEM, PhilipsTecnai G2 F20). Surface chemical analysis of $MoS_2$-$TiO_2$ binary oxides were performed by X-ray photoelectron spectroscopy (XPS) using a PHL1600ESCA instrument equipped with a monochromatic Mg Ka X-ray source (E = 1253.6 eV) operating at 250 W. The nitrogen adsorption–desorption isotherms were measured at −196 °C with a Gemini VII surface area and porosity system. The specific surface area was estimated by the Brunauer–Emmett–Teller (BET) method.

### 2.3. Gas sensing measurement

The sensor tests were carried out by using a high-precision sensor testing system NS-4003 series (Zhong-Ke Micro-nano IOT (Internet of Things) Ltd, China) in a chamber with a volume of 10 L at a relative humidity (RH) of 45%. The fabrication process was illustrated as follows. Briefly, the sensor device was fabricated by dispersing the $MoS_2$-$TiO_2$ sample into an adhesive terpineol to form a paste and then coated onto the outside surface of an alumina tube. To purify the sensor and improve the electrical contact, the devices were annealed in 80 °C before measurements. In the analysis of the gas responses, the sensitivity ($S$), is defined as the ratio between the electrical resistance to a target gas ($Rg$) and the electrical resistance in air ($Ra$) for a given gas concentration if $Rg > Ra$ or vice versa if $Ra > Rg$. The sensitivity is defined as the slope of the output calibration curve, which is sensor response versus gas concentration.

## 3. Results and discussion

### 3.1. Structural characterization

SEM images of the surface morphology of the $TiO_2$ nanotubes and $MoS_2$-$TiO_2$ nanocomposite are shown in Fig. 1. The fabricated $TiO_2$ nanotubes are found to have an average pore diameter of approximately 120 nm with a wall thickness of 20 nm in Fig. 1(a). The regularly spaced rings at the smooth sidewalls of the nanotubes are observed in Fig. 1(b). After reaction in Mo/S precursors, the morphology of hybrid nanostructure is distinctly different from that for blank $TiO_2$ nanotubes, in which flake-like nanostructure were uniformly distributed on the framework of $TiO_2$ nanotubes. In addition, the wall thickness of nanotubes increases to 90 nm, and the surface of the tube wall becomes much rougher in Fig. 1(d). Moreover, it is noteworthy that the in situ produced $MoS_2$ phases can be intimately attached to the whole cross-sectional profile and internal tubes. The nanocomposite has a large surface area, which is beneficial for sensing performance. The phase and crystallinity of samples were examined by X-ray diffraction. Fig. 2(I) shows the XRD patterns of $TiO_2$ nanotubes before and after $MoS_2$ modification. Both of the two samples were annealed at 400 °C in Ar ambient. As can be seen in Fig. 2(I)a, the $TiO_2$ nanotubes exhibit two phases of anatase $TiO_2$ and Ti substrate. The diffraction peak situated at 25.3° is ascribed to anatase $TiO_2$ (1 0 1). Fig. 2(I)b shows the XRD patterns of $MoS_2$ decorated $TiO_2$ nanotubes. Obviously, a weak diffraction peak at $2\theta = 33.9°$ in the figure can be attributed to the (1 0 0) diffraction of the $MoS_2$ films. To investigate the specific surface area of the two samples, the nitrogen physisorption isotherms of the two samples were shown in Fig. 2(II). Both of the samples show a type II isotherm with type–H3 hysteresis as defined by IUPAC conventions. The BET surface area of $MoS_2$-$TiO_2$ composites is 47.4 $m^2/g$, which is much higher than those of $TiO_2$ nanotubes (with BET surface area of 26.8 $m^2/g$). The larger surface area could provide more active sites, which may be favorable to the improvement of gas response.

In order to further confirm the formation of $MoS_2$ nanostructure, TEM images of the resulting $MoS_2$-$TiO_2$ are shown in Fig. 3. Fig. 3(a) exhibits the low-resolution TEM images of a single $MoS_2$-$TiO_2$ heterojunction, which indicates that the $TiO_2$ tubes were filled by $MoS_2$ nanostructure. It can be observed in a higher magnification that a small amount of belt-like structure scattered in the surface of $TiO_2$ (marked by triangular symbols), exhibiting parallel lines corresponding to the different layers of $MoS_2$ sheets (number of layers ≈1–3). The $MoS_2$ sheets present an expanded interlayer distance of 0.8 nm (standard for 0.61 nm), indicating a significant lattice expansion [24]. The grain labeled by red circle shows the lattice fringes of 0.352 nm, which can be attributed to anatase $TiO_2$ (1 0 1) plane. The inset in Fig. 3(a) shows the elemental distribution along the horizontal direction of tube length. It can be seen that the concentrations of Ti and O in the two edges of nanotubes are lower than the middle region, while Mo and S exhibit a stable distribution along this direction. This further confirms that the $TiO_2$ nanotubes were well coated by $MoS_2$ structure. The Ti, O, Mo, and S elemental maps (in Fig. 3(c)–(f)) of the $MoS_2$-$TiO_2$ composite confirm homogeneous distribution of the four