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Synthesis of mesoporous K_2O-In_2O_3 nanowires and NO_x gas sensitive performance study in room temperature

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ABSTRACT

In this work, highly crystalline mesoporous In_2O_3 nanowires (NWs) doped with K_2O, $ZnCl_2$ or $CaCl_2$ were synthesized by template-calcined method using SBA-16 as template. The mesoporous K_2O-In_2O_3NWs (INW-K2), which was synthesized by mixing 0.2 mol L^{-1} $In(NO_3)_3$ solution with 0.02 g KNO_3 so that $In(NO_3)_3$ and KNO_3 mass ratio was 30:1, has high density of chemisorbed oxygen. Its diameter is about 4 −8 nm and pore size is 3−5 nm. For INW-K2, K_2O doped on its surfaces serves as alkaline center and benefits the adsorption and diffusion of acidic NO_x. Meanwhile, the INW-K2 provides large number of active centers for gaseous reactions on the surface of the nanowires. Therefore, the gas sensing property of INW-K2 is significantly improved, the response of NO_x to 97 ppm is about 151.78 and response time is only 12 s, the detection limitation decreased to 48.5 ppb at room temperature (RT). The highly crystalline mesoporous K_2O-In_2O_3 nanowires might offer a new opportunity for synthesizing multifunctional sensing materials in future.

1. Introduction

One dimensional nanostructural materials have shown excellent performance as chemical sensors. As gas-sensing material research gradually progresses, people become more and more aware of the practical applications of semiconductor materials especially in gas sensing. In order to improve the performance of gas sensitive materials, semiconductors with high catalytic activities are pleasing to prepare as they show enhanced gas sensitivities and prolong the life time as sensors. Many researchers around the world tried to dope pure semiconductors with different elements to increase the sensitivity of the catalyst, decrease its response time and prolong stability. Although theseresearchersdeveloped easy methods of preparation using low cost synthesizing materials, yet performance of the existing catalysts is still debatable [1–11].

In the last few decades, main focus has been given to precious metals, such as platinum, palladium, ruthenium. Although the catalysts doped with these precious metalshave improved the material properties, yet high cost of the raw materials still hinders large scale production of these catalysts [12–14]. Therefore, precious metals doped catalysts could not receive much popularity in achieving the required properties [15–17]. Up to now, many composites materials such as SnO_2-ZnO [18], SnO_2/α-Fe_2O_3 [19], TiO_2-SnO_2 [20], and In_2O_3-CeO_2 [21] nanotubes have been reported to be very promising gas sensing materials. Recent research have proved that both In_2O_3 and SnO_2 are important materials for sensing different gases [22–25] and their composites (In_2O_3-SnO_2) [15,26] have shown remarkable properties in this field. Recent report shows that In_2O_3-SnO_2 composites are excellent sensors for ethanol [27]. In our previous works, pure mesoporous In_2O_3 nanowires (PMINWs) were prepared using SBA-16 as template, and exhibited excellent sensing performance to NO_x [28]. However, the as prepared pure mesoporous In_2O_3 nanowires (PMINWs) have increased resistance noise and the response time was relatively slow. Elemental doping have effectively improved the sensitivity of In_2O_3 nanomaterial toward target gases and efficiently reduced the response time. Although different elemental doping has been reported to improve the quality of In_2O_3 gas sensor, yet there are very few reports on K_2O promoter to manipulate In_2O_3 gas sensor. Therefore, it is quite challenging to develop mesoporous K_2O-In_2O_3 nanowire sensors with a high and fast response.

In present work, we used SBA-16 as template material and $In(NO_3)_3$ solution as precursor solution to synthesize K_2O ($CaCl_2$ or $ZnCl_2$) - In_2O_3 nanowires (NWs) with significantly improved gas

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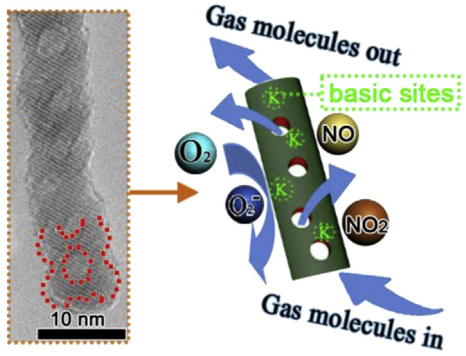
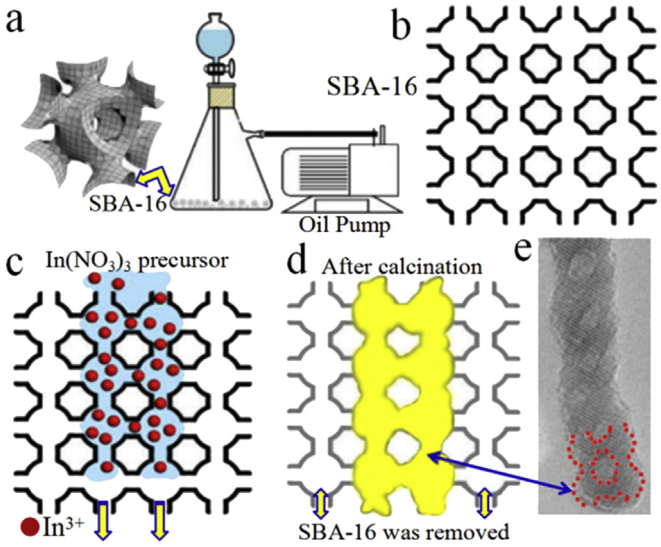


Scheme 1. The designed synthesis of mesoporous K_2O-In_3O_3NWs and gas sensing.



Scheme 2. The formation mechanism of mesoporous In_2O_3NWs using SBA-16 template. (a)vacuum assistance diagram; (b) SBA-16 template; (c) $In(NO_3)_3$ precursor in SBA-16 by vacuum assistance; (d) calcination and removal SBA-16 template; (e) the single mesoporous In_2O_3NW.

sensing properties. The K_2O-In_2O_3 nanowires (NWs), in particularly INW-K2 sample synthesized by the addition of 0.02 g KNO_3 to 0.2 mol·$L^{-1}$$In(NO_3)_3$ precursor solution have nanowires net-like scattered structure with pores size of 3–5 nm on their surfaces. This would not only offer many basic centers and channels for gas adsorption/electronic transmission, but also provide rich active sites for gas sensing, thus improve the sensing properties towards NO_x gas (see Scheme 1).

2. Experimental section

All chemicals used in these experiments were of analytical grade and used without further purification. Deionized water was used throughout the experiment. An appropriate amount (0.02 g) of KNO_3, $CaCl_2$ and $ZnCl_2$ was added to 10 mL of 0.2 mol·$L^{-1}$$In(NO_3)_3$ solution to obtain the mass ratio of $In(NO_3)_3$ to KNO_3,$CaCl_2$ and $ZnCl_2$ as 30:1. 0.3 g of SBA-16 powder was taken in a 500 mL filtration flask and mouth of the flask was closed tightly with a rubber stopper. It was then connected with a long neck drop funnel, shut down valve, use rotary vane vacuum pump for 30 min to reduce SBA-16 channels of air resistance (see Scheme 2). The prepared precursor solution was transferred to a dropping funnel with a long neck and the valve was opened so that the solution added drop wise into the suction flask sufficiently impregnate SBA-16 powder. The mixture was then placed in an ultrasonic cleaning bath (sonicated for 30 min), then dried, and calcined at 550 °C for 4 h at a heating rate of 1 °C per minute.

The resulting yellow solid powder was transferred to a flask containing 5 mol L^{-1} NaOH solution, heated and stirred for 72 h. The obtained product was washed several times with deionized water and centrifuged. Finally the yellow sample collected was dried overnight in the oven.

2.1. Preparation of K_2O-In_2O_3 nanowires

First 10 mL of 0.2 mol L^{-1} $In(NO_3)_3$ solution was taken and 0.02 g, 0.04 g and 0.06 g of $KNO_3$was added to it so that $In(NO_3)_3$ and KNO_3 mass ratio was 30:1, 15:1 and 10:1 respectively. 0.3 g of SBA-16 powder was taken in a 500 mL filtration flask. The flask was evacuated for 30 min and then the mixture of $In(NO_3)_3$ and KNO_3 was added drop wise to it. After drying, the mixture was ultrasonicated for 30 min and then calcined in a muffle furnace at 550 °C for 4 h at a heating rate of 1 °C·min^{-1}. The as prepared samples were cooled to room temperature, washed multiple times with distilled water. The obtained In_2O_3 NWs with 0.02 g $CaCl_2$, 0.02 g $ZnCl_2$, or 0.02 g, 0.04 g and 0.06 g of KNO_3were labeled as INW-C2, INW-Z2, INW-K2, INW-K4 and INW-K6, respectively. And the In_2O_3 NWs synthesized with 0.2 mol L^{-1} $In(NO_3)_3$ solution was labeled as INW-2.

2.2. Characterization

The morphology of the samples were observed by transmission electron microscopy (TEM, JEOL-2100). The crystalline structure of

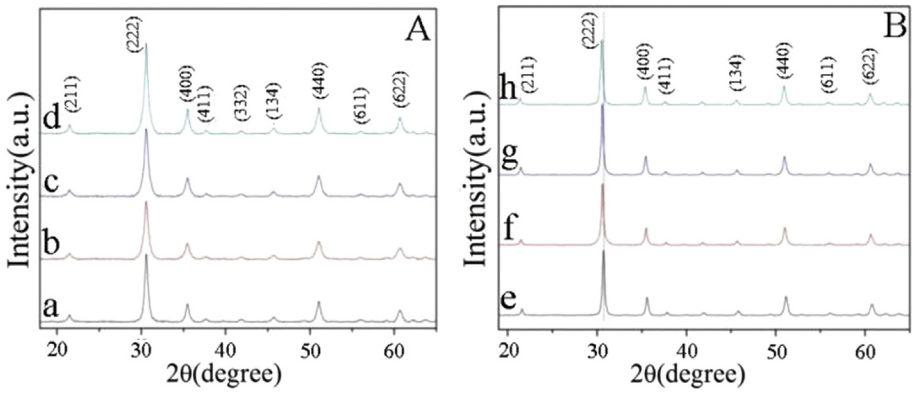


Fig. 1. The XRD diffraction patterns of samples (a) INW-2, (b) INW-K2 (c), NW-Z2(d) INW-C2, (e)INW-2, (f) INW-K2, (g) INW-K4, (h) INW-K6.