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Solution-Processed Co_3O_4 Nanoarchitectures as High Performance Chemiresistors

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Abstract:
A simple, rapid, and inexpensive solution-processed synthesis strategy for mass production of various Co_3O_4 nanostructures has been successfully applied and reported herein. *Nano-platelets, nano-needles, nano-grass*, and *micro-dandelion-type* of Co_3O_4 morphologies are corroborated from morphological observations. Gas sensing results demonstrate that the nano-needles-type of Co_3O_4 reveal higher selectivity (Response = ~1200% to 300 ppm) to C_2H_5OH @200 ℃ along with rapid response/recovery kinetics.

Key words: Metal oxides, Solution synthesis, Co_3O_4, Nanoarchitectures, Gas sensing properties

Introduction

In recent years, various metal oxide nanostructures such as ZnO, TiO_2, Fe_2O_3, Co_3O_4, WO_3, etc., have been successfully synthesized through different synthesis methods and further utilized as potential sensing materials for the detection of variety of target gases at different operating temperatures [1]. Amongst them, Co_3O_4 is assumed as one of the widely studied promising materials in variety of fields, including supercapacitors, magnetic materials, catalysts, and chemiresistive sensors, wherein their performances are strongly reliant on their structure, shape, size, and morphology [2]. In case of nanomaterials morphological control, different parameters, such as size, shape, surface structure, crystal orientation, and aspect ratios, have essential significance. As a result, number of attempts has been centered on the controlled synthesis of Co_3O_4 nanomaterials by variety of synthesis routes along with different architectures. In literature, various attempts have been undertaken for the successful synthesis of Co_3O_4 nanostructures through different methods such as thermal deposition, pulsed laser deposition, sol–gel method, chemical spray pyrolysis, chemical vapor deposition, and combustion method [1-3]. All these methods require sophisticated tools in addition to relatively higher processing temperatures. Until now, the simple, economical, and large scale synthesis methods for the growth of Co_3O_4 nanostructures along with controlled morphologies at lower temperature are very limited. Considering this fact, we report a facile solution-processed approach, which offers homogeneous films onto the large substrate area, for the development of different Co_3O_4 architectures using different cobalt precursors at lower temperature. The effect of deposition time on the structural, morphological and gas sensing properties of Co_3O_4 films were systematically studied and reported.

In typical experiments, appropriate amount of cobalt salts and $CO(NH_2)_2$ were mixed together in DI water and stirred for 20 min. Afterwards, NH_4F was added gradually inside the desired mixture and the preferred mixture was transferred into falcon tubes, wherein pre-cleaned substrates were immersed vertically, and were kept in the water bath.

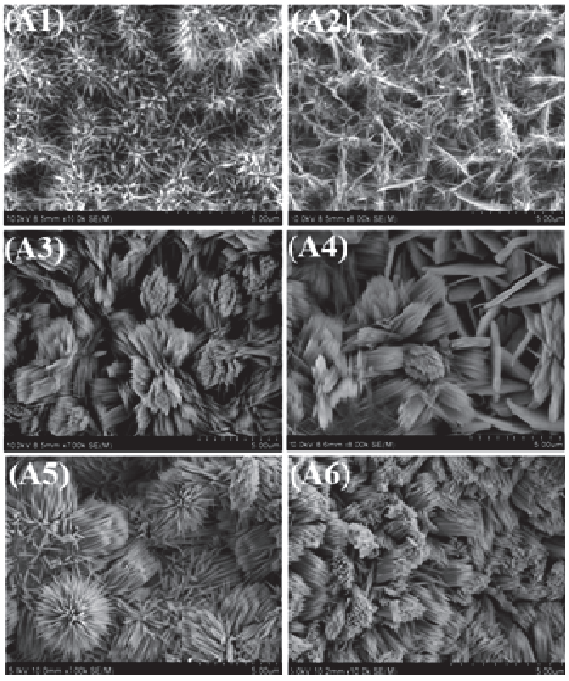

Fig. 1.SEM images of Co_3O_4 nanoarchitectures

The deposition for each cobalt precursor was carried out at 9 hr and 11 hr. After the deposition, obtained films were washed with DI water and dried in air. Finally, obtained samples were air annealed at 400 ℃ in furnace for 1 h. The samples prepared with $Co(CH_3COO)_2{\cdot}4H_2O$ precursor at 9 hr and 11 hr are designated as A1 and A2. Correspondingly, the samples prepared with $CoCl_2{\cdot}6H_2O$ and $Co(NO_3)_2.6H_2O$ precursor at 9 hr and 11 hr are assigned as A3, A4, A5, and A6, respectively.

SEM images of Co_3O_4 films synthesized using different cobalt precursors are shown in Fig. 1. The SEM images of Co_3O_4 films synthesized using $Co(CH_3COO)_2{\cdot}4H_2O$ as precursor at 9 hr and 11 hr are shown in Fig. 1(A1) and Fig. 1(A2), correspondingly. These SEM images display brush–like morphology, along with several pores are available therein, of Co_3O_4. The brush-like morphology is found to be composed of numerous nano-needles. The SEM images of Co_3O_4 films synthesized using $CoCl_2{\cdot}6H_2O$ as precursor at 9 hr and 11 hr are shown in Fig. 1(A3) and Fig. 1(A4), respectively. From Fig. 1(A3), bunch of nano-needles were obviously seen. Whereas, clusters of nano-needles along with nano-platelets-type of Co_3O_4 morphology is clearly noticed from Fig. 1(A4). For deposition time of 9 hr, in case of $Co(NO_3)_2.6H_2O$ as a precursor, dandelion flower-type Co_3O_4 morphology was observed (Fig. 1(A5)). These dandelion flowers found to be made up of number of nano-needles. Fig. 1(A6) shows the SEM image of Co_3O_4 film synthesized using $Co(NO_3)_2.6H_2O$ as cobalt precursor at 11 hrs. Fig. 1(A6) demonstrating nano-grass-type of morphology, composed of Observed Co_3O_4 nanostructures offers higher surface area to volume ratio and more porosity followed pathways than a dense type of surface morphology, making these materials more appropriate candidates for energy storage and gas sensing applications [1-3].

Gas sensing properties of as-deposited Co_3O_4 nanostructured films were carried out towards variety of oxidizing and reducing target gases. For the gas sensing measurements, CH_2COCH_3, NO_2, C_2H_5OH, NH_3, SO_2, and H_2S were used as target gases. Change in electrical resistance of Co_3O_4 sensor films upon the interaction of target gases were recorded and plotted as a function of time. Response (S) of sensor was calculated using the formula, $S = |R_a-R_g|/R_a * 100$, where, R_a and R_g are the resistances of Co_3O_4 samples in presence of fresh air and target gas, respectively. Selectivity study of Co_3O_4 sensor films, synthesized using different cobalt precursors at various deposition times, towards variety of target gases (100 ppm each) at 200 ℃ is shown in Fig. 2. All Co_3O_4 samples show their maximum response to C_2H_5OH when compared to other target gases, demonstrating highest selectivity of as-deposited Co_3O_4 nanostructures towards C_2H_5OH. Among several developed nanostructures, Co_3O_4 prepared using $Co(CH_3COO)_2{\cdot}4H_2O$ as precursor at the deposition time of 11 hr exhibit maximum response of ~1200% to C_2H_5OH. The observed superior sensing performance towards C_2H_5OH is mainly due to the porous hierarchical Co_3O_4 nanostructures, where offers higher surface area to volume ratio. As a result, the higher the interactions between sensor surface and C_2H_5OH gas molecules [1-3].

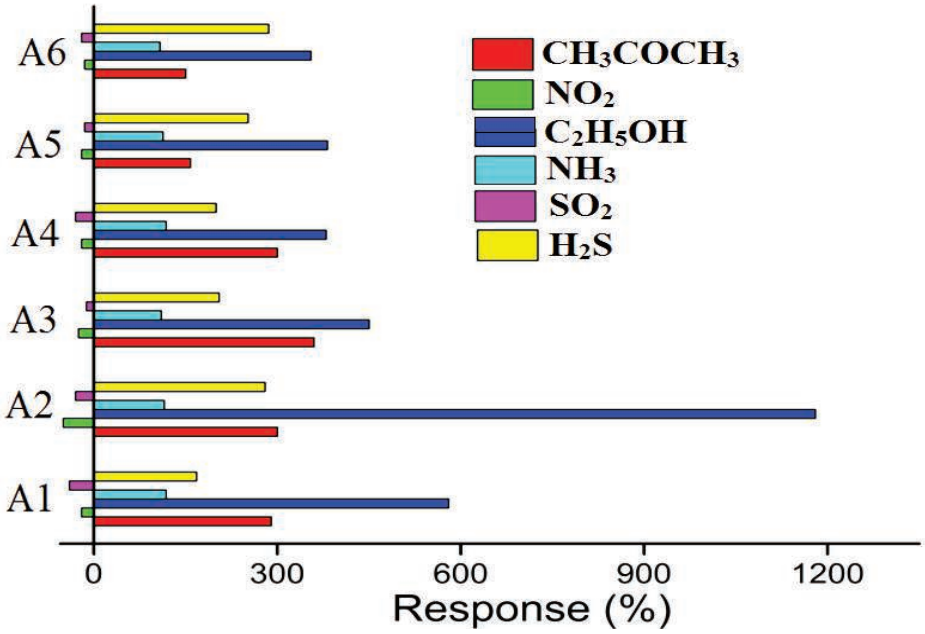

Fig.2.Selectivity study of Co_3O_4 sensor towards various target gases

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