Solution-processed rapid synthesis strategy of Co₃O₄ for the sensitive and selective detection of H₂S

S. T. Navale^{a,b}, Chenshitao Liu^a, P. S. Gaikar^c, V. B. Patil^d, R. U. R. Sagar^{a,b},
Bing Du^a, R. S. Mane^e and F. J. Stadler^{a,*}

^aCollege of Materials Science and Engineering, Shenzhen Key Laboratory of Polymer Science and Technology, Guangdong Research Center for Interfacial Engineering of Functional Materials, Nanshan District Key Lab for Biopolymers and Safety Evaluation, Shenzhen University, Shenzhen 518060, P. R. China. (*E-mail: fjstadler@szu.edu.cn)

^bKey Laboratory of Optoelectronic Devices and Systems of Ministry of Education and Guangdong Province, College of Optoelectronic Engineering, Shenzhen University, Shenzhen, 518060, P. R. China.

^cDepartment of Physics, Institute of Science, Nagpur, 440008, MS, India, ^dSchool of Physical Sciences, Solapur University, Solapur-413255, (MS), India.

^eCenter for Nanomaterials & Energy Devices, Swami Ramanand Teerth Marathwada University, Dnyanteerth, Vishnupuri, Nanded, 431606, India.

Abstract

A simple, rapid, and inexpensive solution-processed synthesis strategy for mass production of cobalt oxide (Co₃O₄) *micro*-dandelions has been applied and reported. As-synthesized Co₃O₄ *micro*-dandelions are initially characterized for their structure and morphology **confirmations and subsequently** utilized for the fabrication of low-cost high-performance hydrogen sulfide (H₂S) gas sensor. Structural analysis is in accordance with the formation of polycrystalline **face-centered** cubic Co₃O₄. Several aggregated Co₃O₄ *micro*-dandelions, composed of number of individual *nano*-needles, with substantial porosity are evidenced from the surface morphological analysis. Gas sensing results demonstrate that the Co₃O₄ *micro*-dandelions reveal higher selectivity to H₂S gas at the operating temperature **of 200 °C**. Maximum response of 481% is corroborated **to 200 ppm of H₂S at 200 °C**. In addition, Co₃O₄ *micro*-dandelions detect H₂S at levels as low as 5 ppm with enhanced response of 68%, rapid response time of 5 s and recovery time of 30 s, demonstrating its potential as a sensing material in the development of H₂S related sensors.

Keywords: Metal oxides; **CBD**; Co₃O₄; **Gas sensing properties**; H₂S sensor

1. Introduction

Today's civilization requires quite a few lushness items, however, with them series of problems such as pollution of air and emission of toxic and hazardous gases through auto and industrial exhausts have also been initiated. In order to control and monitor these toxic and hazardous gases, one must know the kind of gases present in the atmosphere. Thus, the development of highly efficient devices for the recognition of toxic and hazardous gases using different materials, including carbonaceous compounds, metal oxides, chalcogenides, nitrides etc., and technologies has an important challenge in the gas sensor field [1-3]. Among other pollutant gases, hydrogen sulfide (H_2S) is a highly toxic and flammable gas with a distinct smell of rotten eggs, which is responsible for the number of diseases such as eye irritation, fatigue, nausea, headaches, and pulmonary edema [4]. Furthermore, it's long term low-level exposure affect on the human's nervous system causes people to lose consciousness [4]. As a result development of simple and cost-effective efficient chemical sensor systems, in order to detect toxic H_2S at the low concentration level, is crucial for both human health and environmental safety purposes [1, 4]. Traditional metal oxide semiconductors, such as cobalt oxide (Co_3O_4), nickel oxide (NiO), iron oxide (Fe_2O_3), indium oxide (In_2O_3), titanium oxide (TiO_2), zinc oxide (ZnO), tungsten oxide (WO_3), and tin oxide (SnO_2) etc., have so far been considered as one of the extensively studied group of chemiresistive gas sensors in the past decades because of their easy fabrication process, low-costs, non-toxic nature, simplicity in use, power consumption, and flexibility in detecting broad range of toxic and hazardous oxidizing and reducing gases under diverse conditions [1, 3-7]. Among various traditional metal oxide semiconductors, Co_3O_4 , one of the eco-friendly *p*-type transitional metal oxide materials, which has attracted more attention of researchers because of its wide range of applications such as gas sensors, supercapacitors, Li-ion batteries, magnetic materials, and heterogeneous catalysts [8-12]. So far, successful attempts have been made for the synthesis of Co_3O_4 by different techniques such as sol-gel method [13], chemical spray pyrolysis [14], pulsed laser deposition [15], thermal deposition [16], chemical vapor deposition [17], and combustion method [18]. All of these methods require comparatively high processing temperatures and sophisticated instruments. Till today, facile and inexpensive fabrication routes for the synthesis of Co_3O_4 structures with well-defined morphologies at ambient temperatures are limited. Considering this fact, we have developed a facile and eco-friendly chemical bath deposition (CBD) route for the formation of dandelion flower-like Co_3O_4 .

As compared to various traditional synthesis methods used for decades, CBD is an easy and cheap method used for the deposition of various kinds of materials on the preferred conducting, non-conducting substrates as thin films or powers as bulk. Additionally, it offers the opportunity to researchers of preparing high quality uniform films on a large area substrate at lower temperatures [19], thus, also allowing for deposition on temperature sensitive (e.g. polymeric) substrates.

Herein, CBD route has been employed for the formation of Co_3O_4 films composed of *micro*-dandelions at lower temperature, which further is envisaged for high performance H_2S gas sensing application. This CBD approach offers a one-step, common, uncomplicated, and low-price method for the development of the Co_3O_4 *micro*-dandelions. The structural, morphological, and gas sensing properties towards various oxidizing and reducing gases at various operating temperatures of Co_3O_4 films composed of *micro*-dandelions are carried out and described in-detail. Gas sensing results demonstrate that the Co_3O_4 films exhibit high selectivity and rapid response to a very low concentration (5 ppm) of H_2S at 200 °C operating temperature. To the best of our knowledge, this is the first ever report of the H_2S sensing properties of Co_3O_4 films synthesized by CBD.

2. Experimental details

2.1 Chemicals

Cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), urea ($\text{CO}(\text{NH}_2)_2$), and ammonium fluoride (NH_4F) are used as received. These chemicals were of analytical grade and used without further purification. All syntheses were carried out in distilled water.

2.2 Synthesis of Co_3O_4 films

The Co_3O_4 films were synthesized directly onto glass substrate using CBD method with the subsequent process using cobalt nitrate as a source material. 0.1 M of the $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ salt, 0.2 M NH_4F , and 0.5M $\text{CO}(\text{NH}_2)_2$ were dissolved in 50 ml distilled water. The desired mixture was stirred for 20 min leading to the formation of pink colored solution and then transferred into falcon tube of 50 ml capacity. Cleaned glass substrates were immersed within the tube and the tube was kept inside the water bath at 90° C for 11 h. After finishing the reaction, pinkish colored cobalt hydroxide films (*supporting fig. 1(a)*) were obtained, which were washed with distilled water and dried in air for 1 h. Finally, obtained films were annealed at 400 °C under atmospheric conditions in a muffle furnace for 1 h and used for further studies. In the

present work, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was used as a reducing agent and NH_4F were used as an additive, supporting growth to enhance the density of the morphology. The synthesis scheme of the formation of Co_3O_4 *micro*-dandelions by solution-processed synthesis strategy is presented in Fig.1. The reactions responsible for the formation of Co_3O_4 are given in [Supporting Information \(SI\)](#).

2.3 Characterization tools and gas sensing measurements

Structural information of *as*-synthesized films was carried out using X-ray diffraction technique [XRD, Rigaku X-ray diffractometer, CuK_α source ($\lambda=0.15418$ nm)] in the 2θ range of 10 - 90° with the step width of 0.2° . Fourier transform infrared (FTIR) and Raman studies were carried out with the help of Perkin-Elmer 100 spectrophotometer and Hololab series 5000 Raman spectroscopy, respectively. Surface morphology was **confirmed with the scanning** electron microscopy (SEM, Model: JEOL-6300F) and transmission electron microscopy (TEM, Model: FEI TECNAI G2 S-TWIN **instruments**) **digital photoimages**. Surface area was analyzed using Brunauer-Emmett-Teller technique (BET, Model: Belsorp II, BEL Japan Inc.). X-ray photoelectron spectroscopy (XPS) was used to determine the bonding states of the elements present in the sample was performed using XPS, VG, Multilab 2000, Thermo VG, Scientific, UK.

Gas sensing properties of CBD-inspired Co_3O_4 films were measured in the presence of an air atmosphere and various target gases. In present study, different kind of oxidizing [nitrogen dioxide (NO_2), chlorine (Cl_2)] and reducing [H_2S , ammonia (NH_3), methanol (CH_3OH), and ethanol ($\text{C}_2\text{H}_5\text{OH}$)] gases were used as target gases. These gases were commercially procured in the form of canisters with each 1000 ppm concentration. Changes in electrical resistance values of the Co_3O_4 sensor films as a function of time upon interaction of different target gases **were recorded with a 6-digit Keithley 6514E System Electrometer coupled to a computer**. Two silver electrodes (0.1 mm thick and 10 mm separated from each other) **were developed, with the help** of paint brush, on the Co_3O_4 film surface for better and continuous electrical contacts and the sensor film was mounted in leak tight chamber (volume = 250 cm^3). A preferred concentration of target gases in the chamber was attained by inserting a known quantity of gas by a syringe. Digital temperature controller of the sensing unit, which can be heated from room temperature (**30°C to 500°C , was used to control** the temperature of sensor films. Recovery of the developed sensors

was achieved by exposing the sensors to fresh air, which was achieved by opening the outlet of chamber.

3. Results and discussion

3.1 Structural elucidation

The XRD pattern of *as*-synthesized Co_3O_4 (shown in Fig. 2(a)) demonstrates the number of sharp diffraction peaks at various 2θ values of 19.15° , 31.40° , 36.90° , 38.58° , 44.70° , 55.70° , 59.65° , 65.80° , and 77.38° , which are assigned to the scattering from (111), (220), (311), (222) (400), (422), (511), (440), and (533) planes, respectively; suggesting the polycrystalline behavior of *as*-synthesized Co_3O_4 . All observed diffraction peaks are perfectly indexed to the face-centered cubic structure of Co_3O_4 (JCPDS card no. 43-1003). No other noticeable diffraction peaks, of either other phase or impurity levels, are seen in the XRD pattern of Co_3O_4 , indicating stoichiometric phase purity of the synthesized product with the entire decomposition of precursors to Co_3O_4 after annealing at 400°C . For testing the purity of the material, elemental composition present in the *as*-synthesized Co_3O_4 films was detected by energy dispersive X-ray spectroscopy (EDX) and displayed in Fig. 2(b). Presence of cobalt (Co) and oxygen (O) elements, without any impurity, is clearly noticed from the EDX spectrum of Co_3O_4 , which also shows that the percentages of oxygen (60.18 at% vs. 57.1 % from stoichiometry) and cobalt (39.82 at% vs. 42.8 % from stoichiometry) are very close to the expected values, thus proving the formation of Co_3O_4 . In the FTIR spectrum of Co_3O_4 (see supporting fig. 1(b)), the peaks located at 568 and 662 cm^{-1} are due to the ν (Co-O) modes, indicating formation of Co_3O_4 [17]. While the broad peak at 3458 cm^{-1} is due to the O–H stretching mode of water. Five distinct Raman active modes are seen in the Raman spectrum of Co_3O_4 (Fig. 2(c)). The Raman band located at 192 cm^{-1} is ascribed to the feature of the tetrahedral site (CoO_4), which is assigned to F_{2g} phonon mode [17]. Moreover, Raman bands at 478 and 520 cm^{-1} are due to the E_g and F_{2g} phonon mode, respectively. The weak peak positioned at 608 cm^{-1} is accounted for F_{2g} phonon mode. The sharp Raman band positioned at 686 cm^{-1} is nothing but the characteristic of octahedral site (CoO_6) which follows the A_{1g} phonon mode. All observed Raman active bands are identical with those reported in literature for Co_3O_4 [17].

Specific surface area and pore-size distribution of *as*-synthesized Co_3O_4 powder, scratched from the film, was investigated by using the BET and Barrett–Joyner–Halenda (BJH) measurement techniques, respectively. The nitrogen (N_2) adsorption/desorption isotherms of

solution processed Co_3O_4 are shown in *supporting fig. 1(c)*, indicating presence of *type-IV* isotherm with a comparable *H1-type* hysteresis loop. The obtained specific surface area for Co_3O_4 product powder is $34.12 \text{ m}^2/\text{g}$. The pore-size distribution plot of Co_3O_4 product is shown in the inset of *supporting fig. 1(c)*, where the average pore-diameter of $\sim 24 \text{ nm}$ is evidenced, supporting the mesoporous structure of *as-synthesized* Co_3O_4 . The EDX mapping images of *solution-processed* Co_3O_4 film are shown in *supporting fig. 2*, which evidently demonstrate that *as-synthesized* product is composed of Co and O elements. The XPS measurement on Co_3O_4 film was performed and the equivalent results are presented in Fig. 3. Core level spectrum of Co-2p (shown in Fig. 3(a)) exhibits two major peaks at the binding energies of 780.26 and 795.63 eV, with difference of 15.37 eV between the peaks, which are due to the Co-2p_{3/2} and Co-2p_{1/2} doublets of Co_3O_4 phase, respectively. The O-1s core level spectrum of Co_3O_4 is shown in Fig. 3(b). The O-1s core level spectrum shows two peaks at the binding energies of 529.62 and 531.42 eV, which are due to the typical surface lattice oxygen and adsorbed oxygen species on the sample surface, respectively. The observed core levels, with equivalent binding energies, are in accordance with those of reported in literature [26, 27], supporting the formation of pure Co_3O_4 .

3.2 Morphological evolution study

The SEM micrographs, recorded at different magnifications, of CBD mediated Co_3O_4 films are shown in Fig. 4(a-d). High magnification SEM images [Fig. 4(a, b)] demonstrate that a large number of aggregated Co_3O_4 *micro-dandelions* are homogeneously distributed over the substrate surface. The observed Co_3O_4 *micro-dandelions* are found to be interconnected to each other with high porosity. Low magnification view of single Co_3O_4 dandelion, as shown in Fig. 4(c), is confirming $\sim 20 \text{ }\mu\text{m}$ average diameter of the single Co_3O_4 dandelion. A closer view of a single Co_3O_4 dandelion [Fig. 4(d) and *supporting information fig. 3(a)*] has revealed that these flowers are composed of a large number of individual *nano*-needles clustered together so that they can form the aforementioned Co_3O_4 *micro-dandelions*. Such kind of interconnected network of Co_3O_4 *micro-dandelions* offers more porosity followed pathways than a dense type surface morphology, as it has a higher surface area to volume ratio, making it more appropriate for gas sensing applications, as higher surface areas maximizes the surface reactions and, consequently, increases the sensor response values [5, 21]. In addition, the fluffy nature of the system, having large open spaces existing between the individual *nano*-needles, permits effortless diffusion of

gas molecules into the inner region of the *micro*-dandelions. TEM measurements [Fig. 4(e) and *supporting information fig. 3(b)*] were also carried out in order to provide further insight into the inner structure of the hierarchical *micro*-dandelions. In concurrence with SEM analysis, uniform *nano*-needle type architecture, **with a tip diameter of ~15 nm is obtained**. Furthermore, TEM image **also reveals** that the *nano*-needle type architecture is composed of a large number of well-**connected crystallites of ~5-6 nm diameters**. Ordered lattice fringes **are clearly seen** from the high resolution TEM image of Co₃O₄ film (*supporting information fig. 3(c)*), which confirms the polycrystalline nature of Co₃O₄ *micro*-dandelions. Selected area electron diffraction (SAED) pattern of Co₃O₄ [Fig. 4(f)] clearly demonstrates **an existence** of the several concentric diffraction rings, which indicates once again the polycrystalline nature of *as*-deposited Co₃O₄. Hence, the *micro*-dandelions can be considered to be a hierarchically ordered, mesoporous structure. The BET-surface area of 34.12 m²/g is only a fraction of the surface area that could be expected for round nanoparticles of 5-6 nm diameters (ca. 160-200 m²/g). Thus, the *micro*-dandelions pores only allow accessing a rather small part of the surface area of the individual nanoparticles, corresponding to very small to diminishing gaps between them. While this leads to a decrease of the accessible surface area, it also means that the individual nanoparticles are better connected and, thus, mechanically more stable. It can be speculated that the rather fragile looking *micro*-dandelion structure can only be created and preserved through all processing steps because of the rather tightly packed *nano*-crystals, which do not fall apart too easily.

4. Gas sensing properties

In the present study, for the gas sensing measurement of Co₃O₄ films obtained from CBD method, different oxidizing (Cl₂, NO₂; *electron accepting*) and reducing (H₂S, NH₃, CH₃OH, and C₂H₅OH; *electron donating*) compounds were used as target gases. **The schematic of gas sensing measurement setup is shown in *supporting fig. 4***. For the sensor response measurement, **changes in electrical resistance values of Co₃O₄ film upon exposure to different target gases as a function of time were recorded**. **The response (S) of Co₃O₄ sensor films** was calculated using subsequent relation:

$$S (\%) = \frac{(R_g - R_a)}{R_a} \times 100 \quad (1)$$

where, R_a and R_g are the resistances of the Co₃O₄ sensor films in presence of air ambient and target gas, respectively.

Selectivity towards target gas and the operating temperature are considered as crucial parameters in the gas sensing study. Therefore, primarily the selectivity study of Co_3O_4 sensor film was studied towards various target gases (each with 100 ppm concentration @200 °C) and the corresponding results are depicted in fig. 5(a). Before exposing the sensor to the target gases, resistance of Co_3O_4 sensor film was stabilized (*see supporting information fig. 5(a)*) inside the gas chamber with respect to operating temperatures for ~1 h. It was noticed that, in presence of oxidizing gases the resistance value of Co_3O_4 sensor film is decreased and in case of reducing gases it is increased, which supports for the *p*-type behavior of *as*- synthesized Co_3O_4 , which is in good agreement with previous reports [22]. The selectivity bar chart clearly shows that the Co_3O_4 sensor films are found to quite sensitive and selective towards H_2S gas as compared to other target gases. The response values, calculated using eqn. (1), of Co_3O_4 sensor films to 100 ppm exposure of NO_2 , Cl_2 , H_2S , NH_3 , CH_3OH , and $\text{C}_2\text{H}_5\text{OH}$ are found to be 16, 22, 340, 46, 25, and 18%, respectively. Selectivity coefficient (*K*) of H_2S gas over other target gases was calculated using the relation, $K = S_{\text{H}_2\text{S}}/S_x$ (where, $S_{\text{H}_2\text{S}}$ and S_x are the response of sensor in presence of H_2S and other (*X*) gases) and calculated ‘*K*’ values for NO_2 , Cl_2 , NH_3 , CH_3OH , and $\text{C}_2\text{H}_5\text{OH}$ gases are 21.25, 15.45, 7.39, 13.6, and 18.88, respectively. The higher value of ‘*K*’ indicated the developed sensor has a superior capability to differentiate target gas (herein H_2S) between the mixtures of gases [23, 24]. Based on the selectivity results it is concluded that the Co_3O_4 film composed of *micro*-dandelions has demonstrated superior selectivity to H_2S gas. As a result, for the further study H_2S was used as the optimized target gas. Temperature dependent response of Co_3O_4 sensor film, towards fixed 100 ppm concentration of H_2S , is shown in Fig. 5 (b). It is observed that the response of the Co_3O_4 sensor towards 100 ppm H_2S increases with rising temperature (response = 44% at 140 °C) to 200°C (340%) and higher temperatures (from 200-260 °C) it decreases again. The observed correlation between the sensor response value and the operating temperatures for Co_3O_4 sensor follows an “increase-maximum-decay” trend [25, 26]. It is well-known that, the chemical interactions among the sensor element (herein Co_3O_4 film) and the target gas (herein H_2S) play an important character in the response value of the sensor and the intensity of these reactions are mainly influenced by the operating temperatures of the sensing elements, which influences the physical-chemical balance of the reversible reactions of the target gas with the surface of the sensor material [25]. The lower response value obtained for Co_3O_4 sensor at lower temperatures (below 200 °C) is mainly due to the H_2S gas molecules

that are not possessing sufficient thermal energies for the interaction with adsorbed oxygen species. On the other hand, higher temperatures (above 200 °C) hinder the adsorption of gas; as a result reduces the exploitation rate of the sensing material and, thus, lowers the response value. At 200 °C, these two competing processes are in an optimum level. On the one hand, the H₂S gas molecules possess sufficient thermal energies to interact with adsorption oxygen species and on the other hand the prevention or the immediate desorption due to excessive thermal energy, thus, sensor reaches to its best response value [5, 25, 26]. The temperature dependent response study has revealed that the Co₃O₄ films exhibit its maximum response value to H₂S @200 °C, therefore 200 °C is considered as an optimized working temperature of the sensor and the same was applied for further studies.

The Co₃O₄ sensor response for different H₂S concentrations (5-200 ppm) @200 °C is shown in Fig. 5(c), suggesting the sensor response is increased with increasing H₂S concentration. The Co₃O₄ sensor film has exhibited a good response value of 68% for the very low H₂S concentration of 5 ppm, indicating a very low detection limit of Co₃O₄ *micro*-dandelions film. Maximum response of 481% is obtained to 200 ppm exposure of H₂S. With increase in the H₂S concentration from 5-200 ppm, more and more H₂S gas molecules may take part in the surface reactions and hence response value is increased accordingly. The sensor response within the low H₂S concentration range, from 5-100 ppm, is indicating that the Co₃O₄ *micro*-dandelions can be reliably used to monitor the H₂S gas in this range. The plot of variation of resistance value as a function of time to 100 ppm H₂S @200 °C is shown in Fig. 5(d). Sudden increase in resistance value, with high response of 340%, is observed after the interaction of H₂S gas with Co₃O₄ sensor film. From Fig. 5(d) it is obviously seen that the Co₃O₄ sensor film has responded extremely fast after the introduction of H₂S gas and has recovered instantly when it is exposed to fresh air. The response plot of Co₃O₄ *micro*-dandelions film to 40, 60 and 100 ppm levels of H₂S as a function of time is shown in Fig. 6(a). From the Fig. 6(a), rapid increase in response value with increasing concentration of H₂S is clearly noted. The observed response values for 40, 60, and 100 ppm H₂S are 160, 210, and 340 %, correspondingly. Response and recovery time values are also important in gas sensor study. From the viewpoint of practical application, response and recovery time values of the sensing materials should be fast. The time required for sensor to reach 90% of the maximum raise in resistance value upon exposure of target gas is represented as response time and the recovery time is the time taken by sensor to return to 90% of the

maximum resistance value, when exposed to air. The plot of variation of response vs. time to 5 ppm H₂S @200 °C is shown in Fig. 6(b). Fast response (5 s) and recovery (30 s) time values with enhanced response of 68% are documented for 5 ppm H₂S. Obtained fast response and recovery time value with superior response for lower 5 ppm H₂S itself indicates that the potentiality of *as*-synthesized Co₃O₄ *micro*-dandelions film in the fabrication of high performance H₂S sensors. Reproducibility study of Co₃O₄ sensor, towards fixed 100 ppm H₂S concentration @200 °C, was also carried out and the subsequent results are presented in Fig. 6(c). From Fig. 6(c), a reasonably equivalent response to all the measurements is evidently seen; indicating Co₃O₄ sensor possesses an excellent repeatability in response.

4.1 Gas sensing mechanism

In present study, rapid increase in resistance value after the interaction of H₂S with Co₃O₄ *micro*-dandelions film is observed, which is caused by the adsorption/desorption process of H₂S on the surface of Co₃O₄ film. It is well-known that the chemiresistive gas sensing mechanism of metal oxide semiconductors is mainly associated with the change in electrical resistance of the sensing material, which is predominantly initiated as a result of adsorption/desorption activities of variety of target gas molecules [5]. The interaction between Co₃O₄ sensor film and H₂S gas was described with the help of energy band diagram shown in Fig.7 [27-30]. As Co₃O₄ is a *p*-type semiconductor with holes as majority carriers [27, 22]. When the Co₃O₄ sensor film is exposed to air, oxygen molecules can be adsorbed on the surface of sensor by capturing electrons from Co₃O₄, giving rise to an electron depletion layer on the surface, which leads to the formation of adsorbed oxygen species (such as O⁻, O₂⁻, and O₂²⁻) [31]. Because of the adsorption of oxygen (by capturing the electrons from Co₃O₄) more holes are induced in Co₃O₄, leading to the decrease in resistance value. Oxygen adsorbs on metal oxide surface by the following reactions [27, 32]:

When H₂S gas molecules come in contact with adsorbed oxygen species on the Co₃O₄ sensor surface, they release the captured electrons because of the electron donating nature of H₂S gas, leading to an increase in thickness of the electron depletion layer (shown in Fig. 7) and,

consequently, higher resistance of the sensor is obtained. The possible reaction mechanism between adsorbed oxygen species and H₂S gas molecules can be described as follows [27]:

We compared the H₂S sensing performance of Co₃O₄ *micro*-dandelions with those of reports available in literature on Co₃O₄ for H₂S gas merely (comparison is tabulated in table 1) and it can be seen that the H₂S sensing performance of Co₃O₄ *micro*-dandelions is better than that of the formerly reported sensors. The Co₃O₄ *micro*-dandelions based H₂S sensor in our work, synthesized by easy and inexpensive CBD route, has a lower operating temperature (200 °C), high selectivity, and short response and recovery times. In addition, according to the literature survey we found that till today no single report is available where the H₂S sensing properties of CBD mediated Co₃O₄ films has been reported.

Taking into account the experimental and gas sensing results, it is concluded that the grown Co₃O₄ *micro*-dandelions, using solution processed synthesis route, have extremely promising features in fabricating low-cost high-performance H₂S gas sensors.

5. Conclusions

In summary, Co₃O₄ films composed of *micro*-dandelions have been successfully synthesized at lower temperature by a rapid solution-process method and further were utilized for the gas sensing application. Gas sensing results reveal that the Co₃O₄ films demonstrates an outstanding selectivity, high response, rapid response and recovery time values, and excellent repeatability in response to H₂S gas at lower operating temperature of 200 °C. Furthermore, Co₃O₄ is capable in detecting as low as 5 ppm H₂S concentration with reasonable response. The presented CBD method for the synthesis of metal oxide (herein Co₃O₄) for high performance gas sensors is rapid, robust, and efficient and can be extended to synthesize other metal oxides too with hierarchical morphologies, which is subject of continuing research.

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Figure captions

Fig. 1: Synthesis scheme of formation of Co_3O_4 films.

Fig. 2: (a) XRD, (b) EDX, and (c) Raman spectrum of Co_3O_4 .

Fig. 3: (a) Co-2p and (b) O-1s core level XPS spectrums of Co_3O_4 .

Fig. 4: (a-d) Low- and high-magnification SEM images of Co_3O_4 *micro*-dandelions, (e) TEM and (f) SAED pattern of Co_3O_4 .

Fig. 5: (a) Selectivity study of Co_3O_4 films towards different gases, (b) Plot of response study of Co_3O_4 films as a function of operating temperatures, (c) Plot of variation of Co_3O_4 response as a function of different H_2S concentration, and (d) Variation of resistance as a function of time to 100 ppm H_2S @200 °C.

Fig. 6: (a) Plot of response as a function of time to 40, 60, and 100 ppm H_2S @200 °C, (b) Plot of response as a function of time upon 5 ppm exposure of H_2S @ 200 °C, and (c) Reproducibility study of Co_3O_4 sensor films.

Fig. 7: Schematic of sensing mechanism, in presence of air and H_2S atmosphere, with energy band diagram of Co_3O_4 sample.

Table caption

Table 1: Comparison of H_2S sensing performances of Co_3O_4 *micro*-dandelions with other published Co_3O_4 related H_2S sensors.

Graphical abstract

Solution-processed rapid synthesis strategy of Co_3O_4 for the sensitive and selective detection of H_2S

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

Table:1

Composition	Synthesis method	Morphology	Sensor temp.	Res-t/ Rec-t	Rec	Res
Co ₃ O ₄ ^[27]	e ⁻ -beam deposition	Nano-crystalline	325° C	Several minutes	100%	≈45% (10 ppm)
Co ₃ O ₄ ^[33]	Sol-gel method	Nano-crystalline	200° C	n.a.	n.a.	≈1% (100 ppm)
Co ₃ O ₄ -SWCNT ^[34]	Arc-discharge method	Round nanoparticle attached to CNT	250° C	Several minutes	Only ca. 80%	≈100% (5 ppm)
Co ₃ O ₄ (this work)	CBD	Micro-dandelions	200° C	Several seconds	100%	≈91% (10 ppm)

Res-t – response time (vs. H₂S), Rec-t – recovery time (vs. H₂S), Res – response (to H₂S), Rec - recovery from H₂S (resistance before experiment vs. resistance after experiment),