High-sensitivity detection of H₂S by In₂O₃/C composite prepared by inert-ambient sealed-tube pyrolysis

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Abstract

Indium acetylacetonate, a β -diketonate complex, was pyrolyzed at 700 °C in inert ambient in a sealed quartz tube, to yield a powder composite of nanocrystalline In₂O₃ and elemental carbon (In₂O₃/C), as deduced from characterization by powder X-ray diffraction and Raman spectroscopy. Scanning electron microscopy shows that the metal oxide is embedded in micrometer-sized spherical structures, composed largely of carbon. The spherical entities are likely formed when the metal complex melts, decomposes, and vaporizes during pyrolysis, with the vapour condensing into spherical “droplets” as the sealed tube cools gradually to room temperature. The In₂O₃/C composite was tested (in pellet form) as a gas sensor, specifically the conductometric sensing of H₂S. At 5 ppm of H₂S, the composite shows a high response of 225% at 250 °C, with the response and recovery being swift (~5 s and ~15 s, respectively). At 250 °C, the detection limit is found to be of 500 ppb of H₂S, with selectivity over NH₃, NO₂, CH₄, and SO₂ being considerable. The In₂O₃/C sensor also displays good cyclability. When carbon in the composite is removed by annealing it in air (550 °C, 60 min), the resulting In₂O₃ powder (in pellet form) shows a much poorer response to H₂S at 250 °C (25% to 5 ppm), illustrating that the elemental carbon in In₂O₃/C enhances sensitivity to H₂S. The advantages of a simple fabrication process and low power consumption make the carbonaceous composite sensor potentially useful.

Keywords Metal oxide/carbon composite · In₂O₃/C · Sealed tube pyrolysis · H₂S sensor · Low ppm detection · High selectivity

1 Introduction

Hydrogen sulfide (H₂S) is a very toxic gas with a characteristic foul odour. It is a strong neurotoxin, capable of causing severe damage to humans even at low concentration [1, 2]. It is also a naturally occurring gas in mines and is often present in industrial processing areas [3]. H₂S is flammable and highly corrosive and is easily absorbed by the human body at relatively low concentrations [4]. Therefore, the detection of hydrogen sulfide with high sensitivity is attracting significant effort worldwide [5]. Various

H₂S-sensing elements and methods have been studied, such as optical sensors [6, 7], electrochemical sensors [8, 9], and metal-oxide conductometric sensors [10–13]. Sensors reported to date are usually expensive, show poor stability and unreliable long-term performance [14].

Metal oxide gas sensors are frequently considered attractive for the fabrication of portable devices, owing to their high sensitivity towards target gases, simple device structure, and low power consumption [15]. However, a few major challenges need to be addressed to make metal oxide-based gas sensors more useful. In general,

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metal oxide sensors react not only with the analyte (target) gas but also with the surrounding atmosphere [16]. Consequently, in conductometric sensors, response and recovery times, and resistance of the sensor in the ambient, deteriorate significantly over time due to presence of water vapor and other trace gases in the ambient. Selectivity of the gas sensor, which refers to the ability of a sensor to respond selectively to a specific analyte, must be high and is essential for reliable analysis.

Indium oxide, In_2O_3 , is among the binary oxides studied for sensing H_2S . The strong chemical interaction between In_2O_3 and H_2S and the conversion of In_2O_3 into In_2S_3 upon exposure to H_2S is considered the basis for sensing. Recent investigations have shown that In_2O_3 is a promising candidate for gas-sensor applications. Though indium oxide (In_2O_3) has been studied as sensor material for NO_2 , CO, and O_3 [17–20], there are only a few published investigations of In_2O_3 and In_2O_3 -based materials as the conductometric sensor for H_2S . Two others depend on transistors fabricated with In_2O_3 as the sensor [21, 22]. Tu et al. [23] have reported detecting 2 ppm H_2S at 150 °C with Pt-doped In_2O_3 , whereas Kapse et al. [24] have shown detection of 50 ppm H_2S at 100 °C by Pd/Au-impregnated, 5% La-doped In_2O_3 nanoparticles. Xu et al. [10] have reported sensing 50 ppm at 270 °C by nanocrystalline In_2O_3 prepared by hydrothermal synthesis. Bari et al. have reported detecting 500 ppm H_2S at 25–150 °C by spray-pyrolysed films of nano- In_2O_3 [25–30]. To date, there is no report in the literature of conductometric sensing of H_2S at sub-ppm concentrations by an In_2O_3 -based sensor.

We report on the synthesis of a novel carbonaceous composite of In_2O_3 nanocrystals with high surface-to-volume ratio by the simple, one-step process of sealed-tube pyrolysis (STP) of the acetylacetonate complex of indium in an inert ambient. We demonstrate the ability of the carbonaceous composite to sense even sub-ppm concentrations of H_2S at a modest sensing temperature, and the high selectivity of the sensor over several other hazardous gases like NH_3 , NO_2 , and SO_2 . We show that, when the carbon in the composite is removed, the oxide alone has a much lower sensitivity to H_2S .

2 Experimental

2.1 Preparation of indium acetylacetonate, $\text{In}(\text{acac})_3$

The metal complex, denoted by $\text{In}(\text{acac})_3$, was prepared using indium nitrate. All reagents used were of analytical grade. A calculated amount of the nitrate dissolved in water and 10% of methanol was stirred for 20 min to achieve homogeneity. Next, 2.4 ml of acetylacetone

(20 mmol) was added to 2.5 ml of methanol and mixed well, following which this acetylacetonate solution was added to the metal nitrate solution and stirred until the solution became clear. The reaction mixture was neutralized by 30% ammonia solution added dropwise until a pH of 7 was attained. The resulting pearl-white solution was stirred for 1 h at room temperature. The solid precipitate thus obtained was separated through vacuum filtration, dried, and crystallized at 4 °C using a mixture of 10% methanol in acetone as the solvent. This resulted in the formation of the desired complex as a white powder. The average yield of the reaction was 92%. The formation of the complex was verified by various means, such as powder XRD and FTIR spectroscopy (ESI).

Pyrolysis of the indium complex, $\text{In}(\text{acac})_3$, was carried out in a quartz tube 1.5 cm in diameter and ~ 15 cm in length. The middle part of each tube was thinned to form a small neck, which could be easily cut and sealed. The tube was evacuated and backfilled with ultra-high purity (UHP) nitrogen. About 0.5 g of $\text{In}(\text{acac})_3$ powder was introduced into the tube, followed by evacuation and backfilling with UHP nitrogen. The tube was cut in the middle and sealed so that the indium complex could be pyrolyzed in the inert ambient of the sealed tube.

The sealed-tube was heated to 700 °C and held at that temperature for 24 h, after which the tube was allowed to cool naturally to room temperature. After cooling to room temperature, the tube appeared completely black. (The seal had to be broken with care, as high pressure had developed inside the tube because of decomposition taking place at elevated temperatures, forming different vaporous species.) The inner wall of the tube was found to be coated with a black reaction product. So, the inner wall of the broken tube was scraped carefully to collect the powdered product of the STP process.

2.2 Characterization

The crystallized powder of the metal acetylacetonate complex was characterized Fourier transform infrared (FTIR, Perkin Elmer Model BX) spectroscopy to verify the presence of metal–oxygen bonds, viz., In–O bonds (ESI). Powder XRD data on the STP sample were collected using Cu-K_α radiation (Panalytical, Model MPD). The morphology of the STP product was examined by field emission scanning electron microscopy (FESEM, Zeiss Ultra 55). Transmission electron microscopy (TEM, TECNAI F-30) was used to analyze the finer details of the morphology and the crystallinity of the powder product of the STP process. Raman spectra were obtained for the STP product (514 nm argon ion laser, Horiba Jobin–Yvon LabRAM HR 100 spectrometer). Further, H_2S sensing by the carbonaceous product, taken in pellet form, was carried out at

various ppm concentrations of the H_2S diluted with nitrogen. During sensing, gas flow and H_2S concentration were regulated with electronic mass flow controllers (Alicat). A source-measure unit (Keithley Model 2450) was used for recording the resistance of the sample in the presence and absence of H_2S .

3 Results and discussion

Indium acetylacetonate in powder form could be obtained at high yield. It was found by X-ray powder diffraction to be crystalline in the as-prepared and recrystallised forms. The FTIR spectra [SI] show the presence of In–O bond in the complex, providing preliminary evidence that the metal complex had been formed.

The XRD pattern of the black powder product of STP is shown in Fig. 1. The material is clearly well crystallized, and the peaks can be indexed to indium oxide, In_2O_3 , of the cubic bixbyite structure (JCPDS card number-06-0416). The average crystallite size is estimated to be 50 nm (Scherrer formula). In addition to the peaks due to In_2O_3 , two peaks are observed and are labeled in blue. These two peaks, centred around $2\theta = 43^\circ$ and 54° , may be indexed respectively to the (101) and (004) planes of the graphite (elemental carbon) in the powder composite [31].

The Raman spectrum of the powder product of STP shows very clearly the presence of elemental carbon (Fig. 2), confirming the preliminary inference based on its black colour. The first-order Raman spectrum consists of an envelope of peaks centered at G (1596 cm^{-1}) and D (1352 cm^{-1}), typical of amorphous graphitic carbon. The second-order feature D' is present at 2489 cm^{-1} . Thus, the STP process results in carbon with structural disorder, as confirmed by Raman-active vibrational modes that are

Fig. 1 XRD of powder from the STP of $\text{In}(\text{acac})_3$ at 700°C , 24 h

Fig. 2 Raman spectrum of the STP product of $\text{In}(\text{acac})_3$ (700°C , 24 h), evidencing the presence of elemental carbon

forbidden in the case of graphite [32]. Based on the XRD and Raman data, therefore, the STP product may be designated $\text{In}_2\text{O}_3/\text{C}$, denoting a carbonaceous composite.

XPS spectra (Krotos Axis instrument, Al-K_α radiation) collected on the STP powder sample exhibit characteristic peaks for indium and oxygen (Figs. 3a, b and 4), in good agreement with data in the literature for In_2O_3 [31]. In order to acquire a more accurate chemical composition of the as-prepared $\text{In}_2\text{O}_3/\text{C}$, the XPS spectra were obtained. The XPS spectra of the samples confirm the presence of In, O, and C atoms in the STP product. The $\text{O}1s$ XPS spectrum of $\text{In}_2\text{O}_3/\text{C}$ samples may be deconvoluted into two peaks, with the binding energies at $\sim 530.3\text{ eV}$ and 531.9 eV assignable to oxygen and the adsorbed oxygen species, respectively [31]. The main $\text{O}1s$ XPS peak at 529.4 eV corresponds to lattice oxygen in crystalline In_2O_3 . The binding energies corresponding to $\text{In}3d_{5/2}$ and $\text{In}3d_{3/2}$ are at 444.1 and 452.7 eV , respectively [32].

Figure 4 shows the $\text{C}1s$ spectrum which may be deconvoluted into peaks at 284.6 , 285.2 , and 286.4 eV , which are associated with carbon in the states of C-H , O=C-H , and C=O , respectively. Quantitative analysis of the XPS data spectrum shows that the percentage of sp^3 carbon (81.3%) is higher than that of sp^2 carbon (19.6%), evidencing the presence of the carbon.

The SEM micrograph of the STP product, $\text{In}_2\text{O}_3/\text{C}$, is shown in Fig. 5a. The sample consists of numerous highly spherical entities ranging in diameter from ~ 1 to $\sim 6\text{ }\mu\text{m}$, together with non-spherical entities several microns in diameter, often agglomerated with the spheres (Fig. 5a, b). Elemental analysis shows that the spheres are made of carbon. TEM analysis of the STP products shows (Fig. 6a,

Fig. 3 **a, b** XPS spectrum of the STP product, $\text{In}_2\text{O}_3/\text{C}$, confirms the formation of In_2O_3 as shown by the In and O spectra

Fig. 4 XPS spectrum of the STP product, confirming the presence of elemental carbon

b) nanocrystalline In_2O_3 present in a carbon-rich matrix. Individual units of unique morphology could be observed (Fig. 6a), which comprise In_2O_3 crystallites embedded in amorphous carbon. These data corroborate the Raman analysis, and confirm that inert-ambient STP of $\text{In}(\text{acac})_3$ results in a composite of carbon and crystalline In_2O_3 .

3.1 Possible mechanism of formation of the carbonaceous oxide

The presence of highly spherical, micron-sized entities (Fig. 5a, b) is indicative of the solidification of liquid droplets upon cooling. This can be understood by consulting the thermal analysis data for $\text{In}(\text{acac})_3$, which shows complete vapourisation of the complex at about 250 °C. During pyrolysis at an elevated temperature, the vapour fills the sealed tube, creating an elevated pressure in the tube as

Fig. 5 **a, b** Morphology of $\text{In}_2\text{O}_3/\text{C}$ obtained by STP (700 °C, 24 h)

Fig. 6 a, b TEM micrograph and SAED pattern of the STP product (700 °C, 24 h); the SAED pattern is that of nanocrystalline In_2O_3 , which is embedded in carbon; some nanocrystals of In_2O_3 feature apparently “exposed” surface, as seen in **a**

the temperature is raised during the STP process. At an unknown temperature above ~ 300 °C, the metal complex decomposes into various entities, presumably including carbonaceous ones.

Some of the vapours condense into spherical solid entities as the tube is cooled to room temperature. Decomposition of the complex also leads to the formation of oxide moieties, which form the “core” of the molecular structure of acetylacetonate complexes of metals. Given that the cooling is fairly rapid, the oxide crystallites formed are fairly small and are embedded in a carbon-rich matrix, thereby forming the observed carbonaceous oxide composite. The process is analogous to the formation of a similar composite during the inert-ambient STP of $\text{Fe}(\text{acac})_3$ [33–35].

3.2 H_2S -sensing studies

To examine the potential for the $\text{In}_2\text{O}_3/\text{C}$ composite to serve as a gas sensor, suitable structures based on $\text{In}_2\text{O}_3/\text{C}$ composites were fabricated, and their ability to sense H_2S was investigated. The carbonaceous indium oxide powder (formed by STP) was cold-pressed into pellets, to which electrical contacts were made with silver paste. The resistivity of the sensors was measured using the four-probe technique. The $\text{In}_2\text{O}_3/\text{C}$ pellets fabricated for use as sensors showed typical semiconducting behavior, where their resistivity decreased with increasing temperature (ESI). The resistance of the sensor elements was measured as a function of temperature in the presence and in the absence of the analyte, H_2S . Specifically, the sensor (pellet) was placed in a probe station provided with a heater and flow lines for supplying H_2S at the desired concentration in UHP nitrogen. Electronic mass flow controllers enabled the tuning of the analyte concentration precisely. The temperature of the sensor could be set precisely using a PID controller. In_2O_3 is a

p-type semiconducting oxide, in which the formation of a hole accumulation layer (HAL) is the operative mechanism for gas detection. H_2S is a reducing gas, which injects electrons into the surface of the hole-rich surface of the sensing oxide, altering the resistance of the sensor element. To quantify the sensitivity of $\text{In}_2\text{O}_3/\text{C}$ to H_2S , synthetic air (80% nitrogen and 20% oxygen) was used as the reference gas.

The response to the analyte H_2S is calculated using the equation:

$$\text{Response} = (I_g - I_a) / I_g \times 100\% \quad (1)$$

where I_a = current in $\text{In}_2\text{O}_3/\text{C}$ exposed to synthetic air and I_g = current in $\text{In}_2\text{O}_3/\text{C}$ in the presence of H_2S , at the same temperature. The response of the $\text{In}_2\text{O}_3/\text{C}$ sensor to H_2S is presented in Fig. 7. It is seen that not only does the sensor provide a rapid and significant response at a concentration as low as 500 ppb but that the response is effectively reproducible when the sensor is cycled thrice through a series of increasing H_2S concentrations. The apparent reduction in sensitivity from cycle 1 to cycle 3 is believed to be an artifact of the long interval (2 weeks) between successive measurements (due to limited availability of the measurement setup). The relevant statistics of the linear regression analysis of the data are given in the ESI.

The present sensor based on $\text{In}_2\text{O}_3/\text{C}$ composites shows a significantly greater response to H_2S than sensors based on In_2O_3 reported in the literature, as seen from Table 1 below.

Furthermore, the sensor based on $\text{In}_2\text{O}_3/\text{C}$ displays a strong, steady response to H_2S rather than to other gases. Specifically, the response to H_2S is much stronger than to other reducing gases, showing that the carbonaceous composite is selective to H_2S . It can be seen from Fig. 7 that the sensor response to H_2S increases significantly when operating temperature is raised to 250 °C.

Fig. 7 Typical response of **a** $\text{In}_2\text{O}_3/\text{C}$ pellet sensor to H_2S at 250°C . **b** Repeated response of $\text{In}_2\text{O}_3/\text{C}$ sensor to various concentrations of H_2S

Table 1 summarizes and compares published results on H_2S sensing by various metal oxide nanostructure-based sensors; R_a and R_g are the resistance of the sensor measured, respectively, in synthetic air and in the presence of H_2S gas at the respective optimum temperature

Material and morphology	Synthesis method	Concentration of H_2S (ppm)	Sensor response	Optimum temperature ($^\circ\text{C}$)	Response time (s)	References
Pt-doped mesoporous indium oxide	In situ Nano casting	2–300	NA	150	1500	[23]
La-doped In_2O_3	Hydrothermal decomposition	10–50	$R_a/R_g = 0.88\%$	100–150	NA	[24]
$\text{In}_2\text{O}_3\text{-ZnO}$	spray pyrolysis technique	1000	NA	250	NA	[38]
$\text{In}_2\text{O}_3\text{-SnO}_2$ nanorods	Co-precipitation method	10	$R_a/R_g = 4.98\%$	300	NA	[39]
Nanocrystalline In_2O_3 sensors	Carbothermal method	10	$R_a/R_g = 0.82\%$	RT	240	[40]
Flower like In_2O_3	Hydrothermal process	NA	$R_a/R_g = 98\%$	400	NA	[41]
$\text{In}_2\text{O}_3/\text{C}$ composite	Sealed tube pyrolysis	0.5	$I_g - I_a/I_g = 225\%$	250	4	Present work

As the sensitivity of gas sensors is influenced by temperature, the experiments were carried from 100 to 250°C to optimize the operating temperature of the material.

It is found that the response of the sensor to H_2S is strongest at 250°C . The detailed responses of H_2S sensor at elevated temperatures in the range $50\text{--}300^\circ\text{C}$ is listed in Table 2.

The response time of a sensor is defined as the time taken to reach 90% of the full (eventual) response of the sensor after it is exposed to the target gas, and the recovery time defined as the time taken for the response to decrease to 10% of the full response, after the flow of the target gas is terminated. It is to be noted that the response of the sensor is fast and nearly instantaneous when the analyte H_2S gas is introduced, reaching a steady state rapidly, within a few seconds.

As shown in Fig. 7a, the $\text{In}_2\text{O}_3/\text{C}$ composite sensor exhibits quite linear response from 500 ppb to 5 ppm of

Table 2 Response of the $\text{In}_2\text{O}_3/\text{C}$ sensor to H_2S at temperatures in the range $50\text{--}300^\circ\text{C}$

S. no.	Temperature ($^\circ\text{C}$)	Concentration (ppm)	Response (%)	Response time (s)
1	50	5	Nil	Nil
2	100	5	30	2000
3	150	5	47	1200
4	200	5	110	750
5	225	5	146	600
6	250	5	225	300
7	275	5	210	560
8	300	5	170	900

H_2S concentration. At 250°C , the response and recovery times are 5 s and 15 s, respectively. The detection limit of the sensor was determined to be 500 ppb on the basis of

reproducibility of sensing at 250 °C. Although H_2S could be detected at 200 ppb, the signal-to-noise ratio was not high enough.

At operating temperatures in the range 100–150 °C, the sensor exhibits lower sensitivity and slower recovery than at the more favorable operating temperatures in the range 225–300 °C, with 250 °C as the optimum (Table 2). This is due to the relatively slow kinetics of the sensing reactions at lower temperatures.

We believe that the unique spherical morphology provides “great numbers of carbon atoms on the surface”, facilitating the availability of many active sites for the adsorption and diffusion of H_2S molecules. As such, chemisorbed oxygen can participate in the oxidation–reduction reaction happening on the surface of the sensor, causing a large change in sensor resistance. It is clear that the observed high sensitivity to H_2S is closely associated with the unique morphology of $\text{In}_2\text{O}_3/\text{C}$.

To ascertain whether the carbon in the $\text{In}_2\text{O}_3/\text{C}$ composite plays a role in the sensing of H_2S , the composite powder material was annealed in air at 550 °C for 60 min to remove the carbon in the composite, yielding a powder of In_2O_3 . The oxide powder was made into a pellet and examined for its ability to sense H_2S gas, using the same protocols as described above.

The results of the sensing measurement on In_2O_3 at 250 °C are shown in Fig. 8a. Comparing the sensing responses data in Figs. 7a and 8a, it is evident that, though In_2O_3 without carbon does sense H_2S , the sensitivity is significantly less than that of $\text{In}_2\text{O}_3/\text{C}$ (at 250 °C), and that the response and recovery times are poorer. The comparison of the results confirms that the carbonaceous composite of In_2O_3 is an excellent sensor for H_2S .

The carbon matrix plays a role in increasing sensitivity to H_2S significantly. Figure 9 compares the sensitivity of indium oxide to H_2S with and without carbon.

It is also seen that the rise time upon exposure to the analyte is noticeably longer than it is for the composite. The results imply, of course, that the oxide/carbon composite is more sensitive to the reducing gas than the oxide alone. Further investigation is needed to understand the role of carbon in enhancing sensitivity to H_2S .

Fig. 9 Comparison of responses of the $\text{In}_2\text{O}_3/\text{C}$ sensor and the In_2O_3 sensor to various concentrations of H_2S at 250 °C

Fig. 8 Response of **a** In_2O_3 pellet sensors to 5 ppm H_2S at 250 °C. **b** Response of In_2O_3 sensor to different concentrations of H_2S

3.3 Gas sensing mechanism

According to a generally accepted sensing mechanism, a reducing gas such as H_2S , upon interacting with the surface of the metal oxide through surface adsorbed oxygen, disturbs the carrier concentration, altering the resistance of the material.

Here the majority charge carriers are holes. When a p-type semiconductor material interacts with a reducing gas, it liberates electrons. These electrons combine with holes present in the material and neutralize it resulting an increase in resistance. A reverse effect is observed in the presence of oxidizing gas [36].

It is proposed that the sensing of H_2S gas sensing by $\text{In}_2\text{O}_3/\text{C}$ composites is related to surface-adsorbed oxygen species. When the sensors fabricated with the carbon-indium oxide composite are exposed to air, oxygen molecules readily easily adsorb on the surface of these composite and capture free electrons, giving rise to chemisorbed oxygen molecular ions (O_2^-). These chemisorbed oxygen species react with H_2S molecules on the surface, resulting in sensing action.

In overall reducing reaction between H_2S gas and chemisorbed oxygen species may be represented by the following equations [36, 37]

The above equation shows that the concentration of electrons increases as the H_2S gas interacts with the adsorbed oxygen molecules. These electrons neutralize the holes present in $\text{In}_2\text{O}_3/\text{C}$, thus reducing the majority charge carriers. This would result in increase of the resistance of the composite material, accounting for the sensitivity of the material to low concentrations to H_2S .

3.4 Selectivity

Metal-oxide gas sensors are generally sensitive to more than one target gas and normally show cross-sensitivity. Thus, selectivity is an important parameter which can be assessed by measuring cross-sensitivity. Figure 10 shows the sensitivity of $\text{In}_2\text{O}_3/\text{C}$ to H_2S relative to other reducing gases at the operating temperature of 250°C , demonstrating significant selective response of the sensor to H_2S .

Fig. 10 Selectivity of $\text{In}_2\text{O}_3/\text{C}$ towards H_2S vis-à-vis other gases (at 250°C)

4 Conclusion

Inert-ambient sealed-tube pyrolysis is a simple route to the synthesis of carbonaceous composites of metal oxides from the corresponding metal acetylacetonates (acac). Using $\text{In}(\text{acac})_3$, a composite of crystalline In_2O_3 and elemental carbon is obtained by pyrolyzing the complex at 700°C . A conductometric sensor made of a pellet of the $\text{In}_2\text{O}_3/\text{C}$ composite is found to sense H_2S at low concentrations as low as 500 ppb, at modest temperatures. The observed sensing action is better than that reported in the literature for conductometric sensors made of In_2O_3 nanoparticles and thin films when exposed to similar concentrations of H_2S . Measurements show that, when carbon in the composite is removed, sensing action is diminished significantly. Thus, the $\text{In}_2\text{O}_3/\text{C}$ composite obtained by sealed-tube pyrolysis is a good candidate for sensing H_2S at modest temperatures and in low concentrations.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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