PbS Nanocrystals Synthesis And Preparation For Room Temperature Methane Sensing

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Abstract—PbS colloidal nanocrystals have been synthesized and their methane gas sensing properties have been studied. PbS nanoparticles have been synthesized during an all-chemical process and its XRD pattern has been analyzed to verify the quality and estimate the particle size of produced nano-powder. Size estimation by XRD analysis confirm production of approximately 40 nm PbS nanoparticles. The sensor was fabricated by drop casting method on interdigitated electrodes and tested at different temperatures. The best achieved sensitivity was 47.6% for 5% methane concentration at room temperature. A comprehensive discussion on sensing mechanism, temperature dependency and sensor's benefits is also provided in the article. The sensor has the benefit of room temperature detection and being highly sensitive. Moreover the sensor's detection range is 1-5% which is an important and applicable range for air quality monitoring and safety control systems in industrial environments.

Keywords-component; Colloidal nanocrystals, PbS, Methane Gas Sensor, Room Temperature

I. INTRODUCTION

Methane is a colorless and odorless gas which is produced in airless environments like the gust of some animals, landfills and even during the carbohydrates breakdown in the colon of human[1], [2]. Although it is neither toxic nor harmful in the case of being inhaled, methane can cause suffocation as its molecules replace oxygen in respiratory system. There is also the risk of explosion when methane is mixed with air at concentrations more than 5%. Concentration of methane is allowed to be lower than 1% in ambient air. Therefore it is essential to detect methane in environment and alarm when its concentration is reaching to 5% [3]–[5]. Thus methane gas sensing has a special importance from the immunity point of view. Besides, determining the concentration of methane in exhalation has applications in medical diagnostic tests[6].

Among different types of methane sensors, semiconducting gas sensors have been widely employed for methane detection because of their ease of application and inexpensive fabrication process. Metal oxides such as SnO_2 and ZnO [7]–[9] having the advantages of low cost and good sensitivity are probably the most attractive materials to be employed as sensing materials in methane gas sensors. However, they suffer from the limitation of being well sensitive only at elevated temperatures[10]. Simply formulated metal complexes like PbS, have shown good response to some gas targets at room temperature especially in their nanostructure forms such as nanowires and quantum dots[11]–[16]. Implementation of materials in their nanostructure forms is one of the most efficient ways to improve their gas sensing properties. On the other hand, low cost and simplicity of fabrication process play an essential role in commercial manufacturing. Therefore facile and economic production process of Colloidal nano-products (Quantum dots and nanocrystals) makes them appropriate candidates to be chosen as a nanostructure sensing material. In this approach large surface-to-volume ratio is reached without the difficulty and expense of CVD- based methods. Although PbS CQDs have been extensively used as light detectors and emitters, but there are few reports of their application as gas sensing material. Response of PbS Colloidal Quantum Dots (CQDs) based sensors to NH_3 , NO_2, SO_2 , H_2S and NO have been studied[17]–[19]. To date there is not any report on fabrication of a methane sensor using PbS CQDs. Here we present a chemical method to synthesize PbS CQDs and a simple fabrication process using a Printed Circuit Board (PCB) interdigitated electrode to fabricate a low cost, room temperature and highly sensitive methane sensor. Experimental details including synthesis process, sensor fabrication method, and test setup configuration are described in section II. In section III structural analysis and sensing properties are presented and sensing mechanism has been discussed. We have provided Conclusion in section IV.

II. EXPERIMENTAL DETAILS

A. *Preparation of PbS CQDs*

In this study we used a room temperature and simple chemical reaction to synthesize lead sulfide colloidal nanoparticles. To this end, Sodium sulfide was used as a sulfur source, lead (II) nitrate as a lead source and 2-mercaptoethanol as the capping agent. All chemicals such as sodium sulfide, lead (II) nitrate and 2-mercaptoethanol were purchased from Merck Company and used without any purification. All chemical reaction stages were done at room temperature and deionized water was used for the process.

Pb(NO3)2was dissolved in deionized water to prepare 100 ml of solution with 0.1 M concentration. Solution of Na2S with the same concentration and volume was also prepared. Triple-neck round-bottom flask was used as reaction media. To prevent products oxidation, pure nitrogen was used in all stages of experiment.

Lead nitrate solution was poured into triple-neck round-bottom flask. Then 2-mercaptoethanol with 0.1M concentration was slowly added to this solution via separatory funnel under vigorous stirring. Finally 100ml of 0.1M aqueous solution of Na2S was slowly added into above mixture via separatory funnel under vigorous stirring (about 100rpm). The mixture was stirring for a long period of time until color of final transparent colloidal suspensions gets black. Lead sulfide was produced through below chemical reaction:

$$Pb(NO_3)_2 + Na_2S \longrightarrow PbS + 2NaNO_3 \qquad (1)$$

To removeNaNO3 from products and obtain pure PbS, the products were washed by deionized water for several times. Then it was centrifuged to remove PbS from aqueous media. The resulted PbS was heated in the oven under 50 °c for several hours.

B. Sensor fabrication

A pre-patterned Interdigitated Electrode (IDE) - consisting of 37 combs, each one having 300 µm width with 150 µm spacing - was created on a PCB using the circuit printing board technique (Fig. 1). 12mg of PbS nano-powder was then ultra-sonicated in 12mL acetone for 70 minutes. To avoid evaporation of acetone, container had to be held in ice-water mixture. The dispersed liquid was drop-casted on the electrode using a micropipette in several steps, each following by few minutes intervals letting the active area to be dried by air flow. Totally 200µL was poured on the electrode. The prepared sensor was then simply mounted on the test setup circuit using conventional alligator leads.

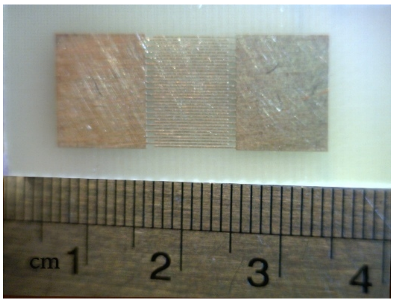

Fig. 1: Photograph of implemented PCB Interdigitated Electrode

C. Sensor characterization

A DC test-setup was configured as depicted schematically in (Fig. 2) to extract I-V characteristics of fabricated sensor in both clean air and at exposure to methane. The applied voltage was supplied and controlled using a digital power supply obtaining a bias voltage up to 63 volts and flowing current was measured with a digital microampere meter (Hioki 3801-50 Digital HiTESTER). The points of I-V characteristics of the sensor were plotted in an I-V plane and fitted to a linear curve to obtain the corresponding resistance. This procedure was done at each individual testing situation in order to calculate the sensor's resistance. The sensor's sensitivity was defined as the percentage of the resistance deviation at gas exposure (R_g) from the resistance in clean air (R_a):

$$S\% = \frac{R_g - R_a}{R_a} \times 100\% \qquad (2)$$

Sensor was put in a glass chamber having 2 L volume and its I-V characteristics extracted without gas injection to determine R_a. Then a controlled volume of gas was injected in the chamber in order to evaluate R_g by means of the new I-V characteristics of the sensor after gas exposure.

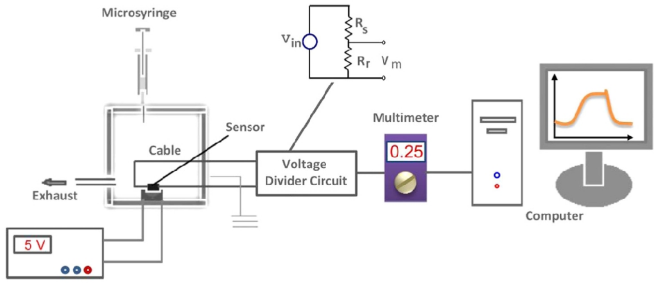

Fig. 2: Utilized test-setup schematic

III. Results & Discussions

A. Structural studies

To investigate the purity and estimate particle size of synthesized PbS CQD nano powder, X-ray diffraction (XRD) analysis was done. XRD pattern was recorded by powder diffraction using a D8 ADVANCE type (BRUKER-Germany) with a Cu-Kα source (λ= Cu-Kα 0.1542 nm). Fig. 3 shows XRD pattern of sample nano-powder which agrees well with the standard XRD pattern for PbS (*ICDD PDF-4 card No. 00-005-0592*).

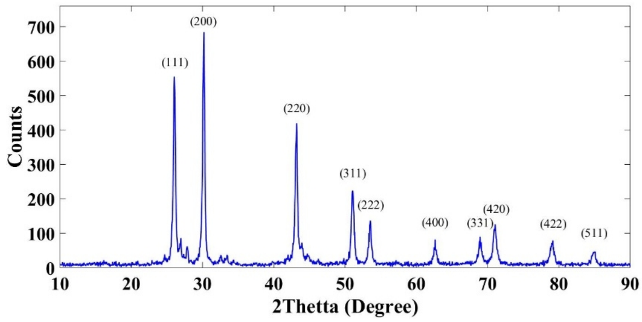

Fig. 3: XRD pattern of the synthesized PbS nanopowder. Related crystal orientation is demonstrated on each peak.

Also, average particle size of the powder was calculated using the Maud software and estimated to be 40 nm using Rietveld approach.

B. Gas sensing properties

Results of I-V measurement of the device in ambient air, depicted in (Fig. 4) shows fabricated sensor has resistive behavior in applied biasing range. Also it must be considered that, reversing the voltage polarity of power supply did not influence on device current and this translates that the sensor is electrically symmetric. Sensor's resistance in ambient air (R_a) was determined by fitting a linear curve. Line fitted to experimental data in Fig. 4 is obtained by least square method with *fitting quality* of R^2=0.9958 and its slope (288.3MΩ) is assigned to sensor's resistance.

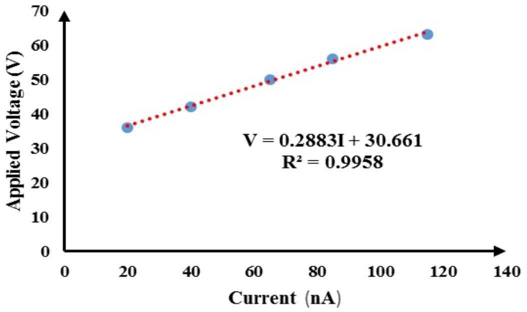

Fig. 4: Air resistance (R_a) extraction from experimental I-V curve of the sensor

To study the effect of temperature on sensor's performance, both I-V measurements in ambient air and sensing characterizations, were repeated at different temperatures between 20 and 80℃. Fig. 5 shows how R_a changes with temperature variation. It shows that the sensor's conductivity is strongly dependent on temperature and it increases with temperature increase. Fig. 6 shows the sensor's sensitivity to six different gas concentrations at room temperature. It reveals that the proposed sensor shows a good response at 1-5% (10000 to 50000 ppm).

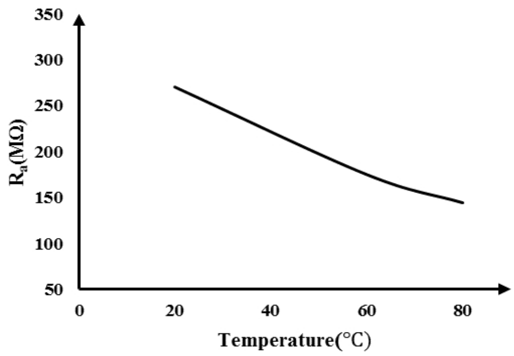

Fig. 5: Measured resistance at three different temperatures in air

Sensor's response to 1% methane was studied at three different temperatures between 20 and 80°C which is depicted inFig. 7. It is obvious that the sensor response is degraded at high temperatures.

C. Sensing mechanism

Klem *et., al* claimed that although PbS CQDs are originally an n-type semiconductor in synthesis conditions, but they show P-type semiconductor behavior in ambient air due to oxygen doping effect [20]. Regarding to this fact, methane sensing mechanism can be explained as follows: CH_4 - known to be a reducing gas- reacts with surface-absorbed oxygen molecules through below reaction:

$$CH_4 + 2O_2^- \rightarrow CO_2 + 2H_2O + 2e^- \qquad (3)$$

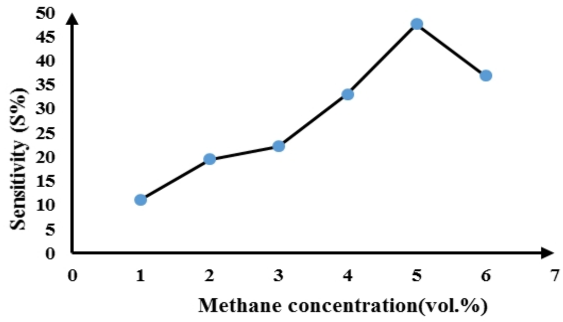

Fig. 6: sensor's response to different methane concentrations.

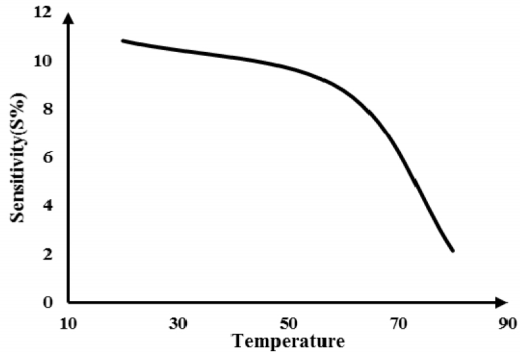

Fig. 7: Effect of temperature on sensor's response. Sensor is exposed to 1% methane in different temperatures.

As a result, oxygen anions are consumed during this reaction and their excess negative charges are released and returned into the semiconductor conduction band resulting in an increment in negative charge concentration. Increment in electron (minority carrier) concentration increases recombination rate and consequently majority carriers (holes) concentration decreases and therefore, the semiconductor's conductivity degrades. This is, however, in contrast with the N-type semiconductor behavior at exposure to methane. In that case, exposure to methane improves conduction, as in N-type semiconductors, electrons are majority carriers and excess electrons released from the methane reaction enhance the material's conductivity. Although this mechanism is popular for metal oxide gas sensors but, considering oxygen absorption on PbS surface and its doping effect as mentioned in [20] we can generalize this mechanism for PbS.

Our experimental results also show a strong dependency of sensor's behavior on temperature variations. Fig. 5 shows detraction in sensor's resistance at higher temperatures and Fig. 7 demonstrates response degradation of sensor due to temperature increase.

One scenario to explain this effect could be the dependency of charge mobility on temperature. This is generally known that carrier mobility decreases with temperature increase at temperatures higher than a specific threshold temperature for each semiconductor, but before that threshold, the mobility increases with temperature increase[21]. This completely explains resistance decrease according to temperature increase in our sensor. It can also explain the degradation of sensor's response in higher temperatures. In the situation of gas exposure total number of carriers involving in current flow is lower than the non-exposure situation and charge mobility is more sensitive to temperature variations when charge carrier density is less[21]. As a result, although both R_g and R_a decrease with temperature, but the decrease in R_g is more significant than the decrease in R_a. Consequently at higher temperatures the term (R_g-R_a) decreases which results in lower sensitivity.

D. Sensor Advantages

The sensor -as described before- is fabricated on a PCB. It aims sensor integration with related electronics circuits- either driving or readout- which are usually implemented on such PCBs. Besides, this type of substrate has a great electrical isolation to avoid current leakage which improves sensor reliability. The low cost of the substrate is another important benefit to be mentioned as each electrode costs less than 1$. The last but not the least important property of this sensor is its high sensitivity at room temperature (47.6%) and wide detection range of operation compared to recently published room temperature methane gas sensors. Table1 shows a comparison between this work and recently published room temperature methane sensors.

TABLE I. RECENT ROOM TEMPERATURE METHANE SENSORS

Sensing Material	***Best Sensitivity***	***Detection Range(ppm)***	***Year***
Graphene/PANI ([22])	5%	20-1600	2013
MWCNT/PANI ([23])	8%	5000-25000	2013
VO_2 ([24])	3.2%	100-500	2014
MWCNT ([25])	23.4%	20-140	2015
PbS CQDs (*This work*)	47.6%	10000-50000	2015

IV. CONCLUSION

We have reported the fabrication and characterization of PbS CQDs as methane gas sensor in this paper. PbS CQDs have been successfully synthesized during an all-chemical process and drop casted on an interdigitated electrode. Production of PbS nanoparticles was approved by XRD and TEM studies. The implemented IDE had been fabricated on a printed circuit board which has the advantages of low cost and good electrical isolation and the ability of being integrated with bias and readout electronics circuits. The sensor can detect methane in the range of 1-5% concentration having the best sensitivity of 47.6% at room temperature. The sensing mechanism is based on the reaction of CH_4 with surface-absorbed O_2 molecules and affecting charge carrier density in sensing material. Both conductivity enhancement at high temperatures and conductivity decrement at exposure to methane verify that the synthesized PbS acts as a P-type semiconductor.

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