ZnO nanoparticles doped with cobalt and indium mechano-chemically for methane gas sensing application

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Abstract. Mechano-chemical technique was utilised to synthesise the undoped ZnO, 5% cobalt and indium single doped and Co-In double doped ZnO nanoparticles. The kenosistec station equipment was employed to probe the prepared samples for gas sensing application. Methane (CH_4) gas is being investigated in the present work. Current versus time curves show good response and recovery at 200 °C. Sensitivity against concentration curves reflect good sensitivity of (Co-In)-ZnO nanoparticles at 200 °C and good sensitivity of Co-ZnO nanoparticles at 350 °C. The Co-ZnO nanoparticles show great sensitivity to methane gas at the concentration of 40 ppm. In-ZnO nanoparticles have the fastest response and recovery times for the methane gas.

1. Introduction

Methane (CH_4) gas is a naturally occurring hydrocarbon, which forms whenever plant and animal matter decays. It is extremely flammable and dangerous because it is lighter than air, odorless, colorless, and tasteless, which makes it difficult to sense [1]. This gas has been reported to have a significantly higher global warming potentials than carbon dioxide [2, 3]. In so speaking, there is a great need for monitoring concentrations of CH_4 gas in the atmosphere. Hence, some techniques such as the infrared absorptions spectroscopy, optical interferometry, catalytic combustion, and semiconductor based modus are used to detect methane (CH_4) gas in the atmosphere [4, 5]. In this article semiconductor metal oxide based gas sensor applications are being discussed. This is because such gas sensors have been found to be cost effective and easy to develop as compared to the other form of sensors. CH_4 is also a useful gas for domestic purposes; it is used for cooking and heating. In industry, methane is used to refine petrochemicals and in power stations to drive turbines for generating electricity. Food processors and other companies that work with clay, stone and glass, make use of the energy released during extraction of CH_4 gas [6, 7]. This helps in maintaining healthy working and living environment, to avoid risk of accidental explosion and public safety in general [4]. It is in this regard that the development of pocket size, portable CH_4 and related gases detector is of crucial importance for human and environmental safety.

Various literature studies confirm that metal oxides have been identified as good candidates for gas sensors due to their ability to react with various elements [8]. To be precise, the development of these oxides at nanoscale level seem to be the ideal breaker for the optimum performance of gas sensors. Further on, one and two dimensional nanostructures pave the way in the design and development of high performing gas sensors [9]. In this article, ZnO doped nanoparticles are being discussed. Specifically, single against dual doped ZnO nanoparticles are being explored for the detection of CH_4 gas. ZnO

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nanoparticles are n-type semiconducting, non-toxic, physically and chemically stable with rich defect chemistry [10 -12] . Schmidt-Mende et. al [10] further reported that the ZnO nanostructures have high surface area and their electronic processes are strongly influenced by surface morphology. The crystal defects of ZnO nanostructure surface such as oxygen vacancies [13], or shallow donors [14] play a major role as absorption sites for gas molecules. This feature assist in determining the gas sensing property of the nanostructures. Thus, ZnO nanostructures have a high sensitivity to a variety of chemical environments. To enhance their sensitivity and selectivity more, introduction of transition metal dopants into the ZnO matrix has been considered [15]. The In-doped ZnO nanofibers show high sensitivity to acetone than ethanol at 275 ^{o}C with minimum concentraton of 37.5 ppm [16]. Moosavi et al. [17] further reported good performance of Co-doped ZnO thin films to volatile organic compounds depsite a notable increase in the crystallite size. In order to overcome the increasing crystallite size with some dopants but not compromising the sensitiviyy and selectivity of the system, a dual doping with indium (In) and cobalt (Co) is proposed. Studies by Shah et al. [18] suggested that double doping ZnO nanostructures by Al and Cr enhance its properties. Even Wang et al. [12] in 2010 illustrated that the gas sensing performance significantly increases with the decreasing crystallite size. In this approach, synthesis of nanoparticles by varying their morphology as well as reducing their crystallite sizes anticipates improving sensing towards CH_4 and other gases.

In this paper, the undoped ZnO, (Co or In) single and (Co, In) dual doped ZnO nanoparticles are subjected to CH_4 gas to check their sensitivity and selectivity. The gas sensing ability of the nanostructures towards CH_4 gas are analysed with reference to their response to ammonia (NH_3) [19] gas. The operating temperature has an effect on how the nanostucture react with the CH_4 gas molecules for an appropriate selectivity and response. The results obtained suggest that the undoped and dual doped ZnO nanoparticles exhibits good sensitivity and response at a temperatue of 200 °C.

2. Procedure

The mechano-chemical technique was utilised to prepare the undoped ZnO nanoparticles, 5wt.% Co-ZnO, In-ZnO and (Co-In)-ZnO nanoparticles samples. The KENOSISTEC station equipment was used to characterise the prepared samples for CH_4 gas sensing at various temperatures (200-350^{o}C) and concentrations (5-100 ppm). In the process, all the samples which were in powder form were sonicated in ethanol for 5 minutes before being coated on the surface of the aluminium substrate. The latter was placed between two Pt electrodes and a heater. The substrates coated with undoped ZnO, Co, In and Co-In double doped ZnO nanoparticles were inserted in a chamber within the KENOSISTEC station machine. All the samples were subjected to concentrations of 5, 10, 20, 40, 60, 100 ppm of CH_4 gas. The station was maintained at constant voltage of 5 V. The gas flow in and out of the station was maintained at 5 minutes intervals.

3. Results and discussion

3.1 Gas sensing applications

The undoped, Co and In single doped and (Co-In) double doped ZnO nanoparticles samples were all examined in the CH_4 gas environment for gas sensing application. In resemblance to the earlier ammonia (NH_3) gas testing [19], four distinct temperatures: 200, 250, 300 and 350 ^{o}C, were adopted for CH_4 gas testing. The response curves in CH_4 gas environment are plotted for the said temperatures as shown in figure 1. All in all, it can be observed that a good response occurs at 200 ^{o}C. When the temperature is elevated to 250 ^{o}C and above, a poor response even with low CH_4 gas concentrations is observed. The indication is that the various ZnO nanoparticles samples operate very well at lower temperatures for CH_4 gas. Stolper et al. [20] reported that the thermogenic gases get produced in the temperature range of 157° to 221 °C. This further suggest that the nanoparticles reported in this paper could only sense methane gas at 200 °C.

In figure 2, the undoped ZnO nanoparticles shows poor sensitivity to CH_4 gas throughout all the tested temperatures. The double doped ZnO nanoparticles also reflect an ascending order in sensitivity as the concentration is increasing in the operating temperature of 200 ^{o}C. At 350 ^{o}C, all the single doped

samples reflect enhanced sensitivity in all the concentrations. On the other hand, Co doped ZnO nanoparticles sensitivity to CH_4 gas reflects an ascending order with increasing concentration in the 250 and 300 ^oC operating temperatures. In the same manner, the opposite is observed for the sensitivity of Co doped ZnO nanoparticles to NH_3 gas between 200 – 300 ^oC [19]. The In doped ZnO nanoparticles sensitivity is typically low at 250 and 300 ^oC operating temperatures with a maximum sensitivity of 5 at 350 ^oC in all the gas concentrations except 5 ppm. An overall observation is that Co-ZnO nanoparticles is the most sensitive to CH_4 gas at concentrations greater than 40 ppm and high temperatures [21]. Motaung et al. [21] also observed similar results for ZnO nanostructures which were exposed to CH_4 gas of different concentrations at 300 ^oC for 24 hours. In table 1**,** the double doped ZnO nanoparticles show constant response and recovery time to methane gas, while In-ZnO nanoparticles have the fastest response time. The undoped ZnO nanoparticles demonstrate the fastest recovery time.

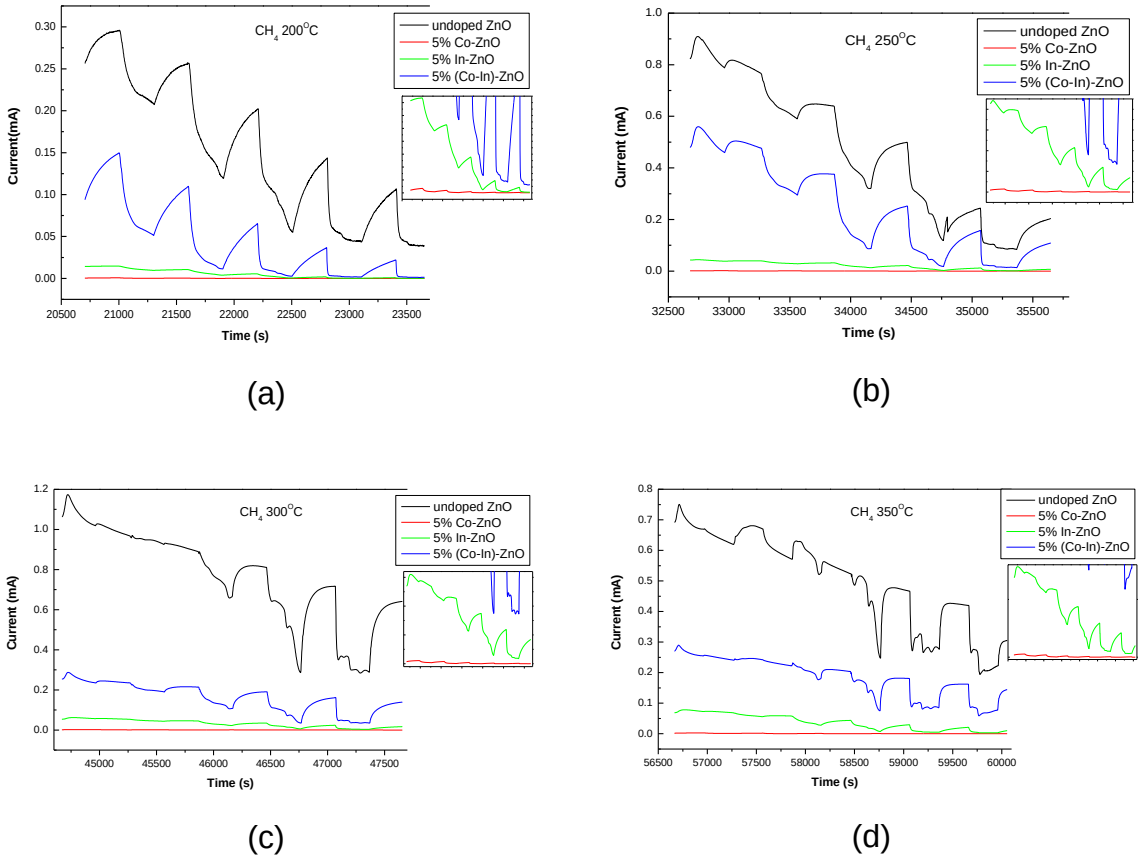

Figure 1: The graphs of current against time for the doped and undoped ZnO nanoparticles at various temperatures for concentrations range 5-100 ppm.

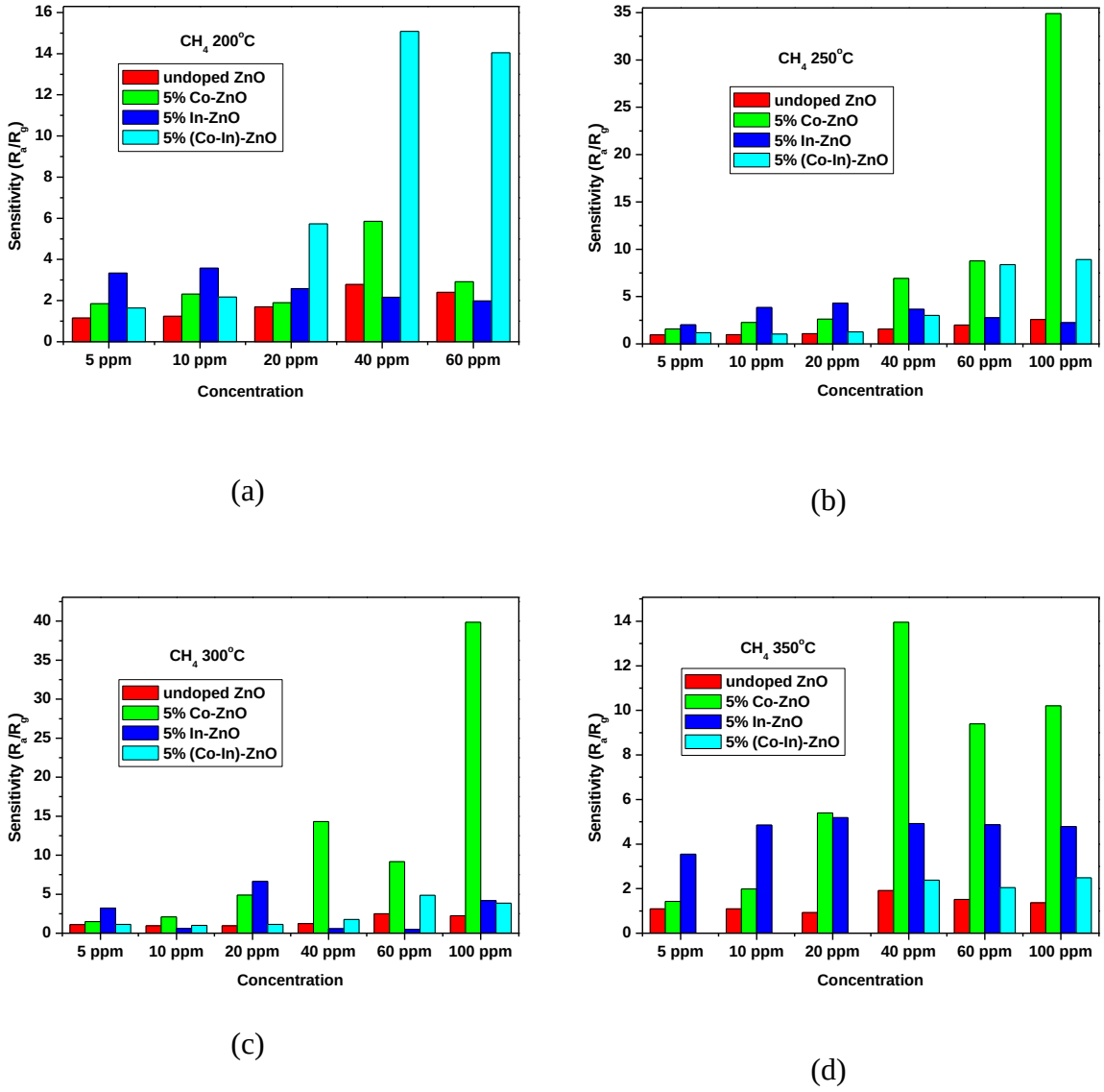

Figure 2: The sensitivity versus CH_4 gas concentration plot for the doped and undoped ZnO nanoparticles at various temperatures.

Table 1: The CH_4 gas response and recovery for the doped and undoped ZnO nanoparticles at 10 ppm.

Sample	Response time (s)	Recovery time (s)
Undoped ZnO	300	289
Co-ZnO	299	300
In-ZnO	298	297
(Co-In)-ZnO	299	299

4. Summary

The doped and undoped ZnO nanoparticles were successfully synthesised mechano-chemically. The current versus time curves show good response and recovery for undoped and double doped samples at 200 °C. The undoped and (Co-In) doped ZnO nanoparticles are more favoured compared to the Co and In single doped ZnO nanoparticles samples. The sensitivity of the Co doped ZnO nanoparticles is more dominant at 350 ºC. On the contrary, the (Co-In) doped ZnO nanoparticles is only sensitive at 200 ºC. The Co-ZnO nanoparticles reflect an ascending response magnitude with increasing concentration of CH_4 gas at all temperatures. The undoped ZnO nanoparticles reflect poor sensitivity in all operating temperatures. The In doped ZnO nanoparticles possess the shortest response time.

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