



Regular article

Mesoporous nickel cobalt hydroxide/oxide as an excellent room temperature ammonia sensor



Alfa Sharma^a, Prateek Bhojane^a, Amit Kumar Rana^b, Yogendra Kumar^a, Parasharam M. Shirage^{a,b,*}

^a Discipline of Metallurgy Engineering & Material Science, Indian Institute of Technology Indore, Simrol Campus, Khandwa Road, Indore 453552, India

^b Discipline of Physics, Indian Institute of Technology Indore, Simrol Campus, Khandwa Road, Indore 453552, India

ARTICLE INFO

Article history:

Received 2 August 2016

Received in revised form 29 September 2016

Accepted 4 October 2016

Available online xxx

Keywords:

RT ammonia sensor

Mesoporous

SEM

BET

Ni-Co hydroxide/oxide

ABSTRACT

We report an excellent room temperature NH₃ gas sensing performance using highly mesoporous nanoflakes of Ni-Co hydroxide/Oxide synthesised by facile and economical wet chemical method. The dynamic sensing of NiCo₂(OH)₆(NCH) and NiCo₂O₄ (NCO) shows nearly 3 and 2 fold increase in sensitivity by varying NH₃ concentrations demonstrating excellent sensitivity which is in accordance to Freundlich equation. The interesting behaviour of NCO being *p*-type material spectacles *n*-type gas sensing behaviour towards low ammonia concentration at RT. The anomalous sensing response is ascribed to transition of majority charge carriers due to surface reaction of chemisorbed oxygen ions and ammonia gas vapours.

© 2016 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

It is very well understood fact that exposure ~50 ppm of NH₃ gas in air causes acute poisoning or life threatening situations, such as permanent blindness, lung disease, respiratory disease, skin disease, and so on. Therefore, it is an extremely essential to design and fabricate a long-term-reliable, highly-sensitive, miniaturized and room-temperature-efficient ammonia gas sensor, which can detect and monitor NH₃ concentration in real time in the surrounding atmosphere [1–5]. In this context complex oxides comprising spinel oxides has attracted remarkable interest with the opportunity to optimize physical and chemical properties of gas sensor [6–8]. The fundamental sensing mechanism of metal oxide semiconductor gas sensors is that they generally operate at elevated temperatures i.e. above 150 °C [9]. The major issue is that the recovery performance of sensors is very poor at room temperature because the desorption of gas molecules adsorbed on the sensor takes a long time [1]. Till now approaches like noble metal decoration (Pd, Pt) [10–13], CNT-based combined structures [14,15], self-powered gas sensing system [16–19], metal elemental doping and UV light activation [20,21] has been explored. Nanostructured materials such as nanorods [22–25], nanowires, nanotubes, nanoflowers [26], nanoparticles and like nanoflakes [27] are promising because of their high surface area, high surface-to-volume ratio, small size, low energy consumption, and

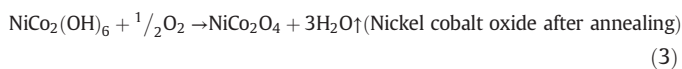
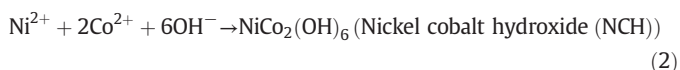
unique electronic properties [28–31]. It has been known that the cobalt-containing spinel oxides i.e. MCo₂O₄ (*M* = Ni, Cu, Zn, Mg, Mn, Cd etc.) have many applications in the areas like chemical sensors, electrode materials for supercapacitor and Li-ion batteries, electro-catalysts and as pigment [32]. Here we present the economical wet chemical synthesis method of mesoporous spinel Nickel Cobalt Hydroxide/oxide nanoflakes and investigate low concentration ammonia gas sensing properties of fabricated sensing elements. The results demonstrate that these materials have excellent sensitivity and selectivity towards detection of toxic ammonia gas at room temperature.

The mesoporous nanoflakes of NCH and NCO were grown using facile and economical wet chemical process from high purity nitrates of 50 mM concentration. An aqueous solution of Ni(NO₃)₂·6H₂O and Co(NO₃)₂·6H₂O (Alfa Aesar) was prepared (1:2 ratio, respectively) in deionized water and stirred for 30 min followed by ammonium hydroxide solution (Merck) was slowly added under constant stirring. The pH of the solution was maintained at ~12–13 in order to obtain desired mesoporous flake like structures [33]. Then the solution was heated at 80 °C on a hotplate until thick viscous dark greenish fluid was obtained. The obtained fluid was washed several times with DI water and ethanol and dried in air for overnight. For formation of the NCO, half the amount of as prepared sample (green powder) was annealed at 450 °C for 4 h which turns to black in colour in this process [34]. The plausible mechanisms are given as follows:



* Corresponding author at: Discipline of Metallurgy Engineering & Material Science, Indian Institute of Technology Indore, Simrol Campus, Khandwa Road, Indore 453552, India.

E-mail addresses: paras.shirage@gmail.com, pmsirage@iiti.ac.in (P.M. Shirage).



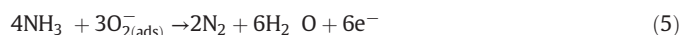
The gas sensing measurements were conducted in a home-built setup (please see Supporting information S1). The NCH and NCO pellets were prepared using hydraulic press under a load of 15 t and used as sensing element. In order to perform the electrical measurements as a function of temperature and ammonia concentration, the schematic of obtained sensor pellet is shown in Supporting information S2, where it is equipped with two parallel thin film silver electrodes separated by a gap of about 2 mm and width of each electrode was about 1 mm, height of 10 mm. The performance of the sensing element is presented in terms of gas response (S), which is defined as $S (\%) = (\Delta R / R_0) \times 100$ where $\Delta R = R - R_0$ i.e. R and R_0 are resistance value of sensing material with and without ammonia gas presence [35]. Response time is defined as the time required for the conductance to reach 90% of the equilibrium value after the test gas is injected and recovery time is taken as the time necessary for the sensor to attain a conductance 10% above the original value in air.

From XRD, (Supporting information S3) it has been observed that all the diffraction peaks are broad indicating nano-crystalline NCH, which can be indexed to the mixed phase of nickel hydroxide peaks (001), (006), (100) (JCPDS no: 00-001-1047) and cobalt hydroxide peaks (001), (102), (104) planes (JCPDS no: 00-051-1731). Fig. S3 (b) shows the XRD pattern of nickel cobalt oxide (JCPDS no: 00-002-1074) and its corresponding Reitveld refinement (Supporting information S3(c)). The lattice parameters obtained from Reitveld refinement for NCO are $a = b = c = 8.120 \pm 0.005 \text{ \AA}$ which is in good agreement with available literature [36]. Fig. 1 depicts the FESEM image of (a) NCH sample and the inset shows the high magnification image and (b) NCO sample and the inset shows the high magnification image indicating well interconnected, highly dense mesoporous flakes. The interconnected features of flakes were perfectly retained after thermal transformation indicating highly stable surface morphology. The flake-like morphologies are considered to provide high surface area for better adsorption of ions [37]. HRTEM image of the mesoporous NiCo_2O_4 (Supporting information S4) indicates inter-planar spacing of 0.135 nm for (440) plane (spacing between two consequent fringes). The (440) plane orientation of the NCO was confirmed by the *d*-spacing calculated from lattice fringes of HRTEM and XRD. The porous nature of NCH and NCO was studied by nitrogen adsorption-desorption isotherm measurements at 77 K. The adsorption-desorption isotherm can be categorized as type IV for NCH suggesting the monolayer-multilayer adsorption and capillary condensation, hence the complete pore filling takes place in this case. In case of NCO adsorption-desorption isotherm is categorized as type III suggests weak adsorptive-adsorbent interactions and

incomplete pore filling [38,39]. Brunauer-Emmett-Teller (BET) multipoint surface area of NCH and NCO measured that of $118.933 \text{ m}^2 \text{ g}^{-1}$ and $45.481 \text{ m}^2 \text{ g}^{-1}$, respectively. The corresponding Barrett-Joyner-Halenda (BJH) pore size distribution for NCH was between 2 nm to 4 nm (Fig. 2 (a)) and for NCO few of the pores lies in the between 2 and 5 nm whereas the majority of the pores lie in the region of 5–50 nm (Fig. 2 (b)). The high surface area with advantageous mesoporous structure promotes enhanced sensing properties as well as high selectivity for ammonia gas.

The operating temperature is important for the study of gas sensing properties because of its considerable influence on the surface state of materials on which the gas-detection process usually takes place [40]. Fig. 3 (a) & (b) shows the ammonia gas concentration dependent sensing property of NCH and NCO respectively. NCH shows a dynamic response and recovery plot of typical *p*-type. Upon purging with ambient air, the resistance drastically decreased to a minimum and forming a plateau, which can be explained by the saturation of reaction sites on the surface changing a minute or without affecting any actual variation of electrical resistance [41,42]. A 3 fold rise in response(S) of NCH (i.e. from 165% to 439%) with increase in NH_3 concentration from 2 to 10 ppm (Supporting information S5).

The sensing performance of semiconductor oxides is usually attributed to the plausible mechanism of adsorption and desorption of oxygen on the surface of the oxides. The NH_3 sensing process is based on the changes in the resistance of the NCH which is controlled by the ammonia species and the amount of the chemisorbed oxygen on the surface. It is known that the oxide surface of a *p*-type semiconductor is readily covered with chemisorbed oxygen, even at low oxygen partial pressure and even at temperatures from room temperature up to $500 \text{ }^\circ\text{C}$ [43,44]. When exposed to reducing gas like NH_3 , the gas molecules are chemi-adsorbed at the active sites on the NCH surface. The free electrons released via the interaction between the NH_3 molecules and the pre-adsorbed O_2^- neutralize the holes or the majority carrier in *p*-type sensing material. This compensation results in a decrease in the hole carriers in NCH and consequently, an increase in the resistance. Nguyen et al. discussed that generally lone pair of electrons of NH_3 provide strong electron acceptor behaviour. But in case of metal oxides or mixed metal oxides NH_3 acts as an electron donor to the oxide, when reacted with the adsorbed oxygen ions on the surface by reverting the trapped electrons. As it has been known that gas sensing is surface mediated phenomena hence the widely accepted mechanisms that generates free electrons accomplished by the number of oxygen ions reacted with NH_3 molecules. The equations are mentioned below: [45].



Secondly, here in this work we demonstrated in Fig. 3(b) the dynamic sensing behaviour of NCO which is obtained from NCH by heat

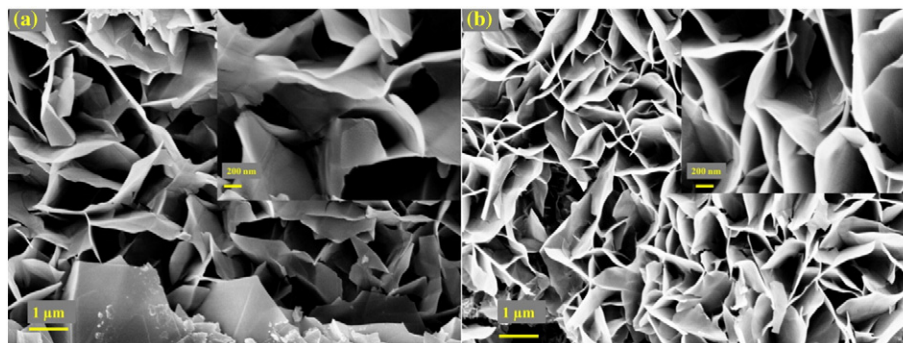


Fig. 1. FESEM images of (a) $\text{NiCo}_2(\text{OH})_6$ (NCH) & (b) NiCo_2O_4 (NCO).

Download English Version:

<https://daneshyari.com/en/article/5443767>

Download Persian Version:

<https://daneshyari.com/article/5443767>

[Daneshyari.com](https://daneshyari.com)