

NO<sub>2</sub> GAS SENSING PROPERTIES OF MWCNTs/NiO NANOCOMPOSITENAHIDA MUSAYEVA<sup>A</sup>, HADIYA KHALILOVA<sup>A</sup>, SEVINJ GULUZADE<sup>B</sup>,  
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This study explores the influence of nickel oxide (NiO) nanoparticles on the nitrogen dioxide (NO<sub>2</sub>) gas-sensing properties of multi-walled carbon nanotubes (MWCNTs). Initially, MWCNTs functionalized with oxygen-containing groups exhibited modest sensitivity to NO<sub>2</sub> gas, and insignificant change in resistance was observed when exposed to other oxidizing and reducing gases. Following the decoration of functionalized MWCNTs (f-MWCNTs) with NiO nanoparticles, significant enhancement in NO<sub>2</sub> sensing responses was achieved at room temperature. The study highlights improved selectivity and elucidates the catalytic role of NiO nanoparticles in the gas-sensing mechanisms of these structures. It was found that although the sensitivity to NO<sub>2</sub> gas increases with increasing NiO nanoparticle concentration, the mechanism of sensitivity does not change.

**Keywords:** nickel oxide, f-MWCNTs/NiO, sensor, NO<sub>2</sub> gas, catalytic.**PACS:** 62.23Pq; 74.25nd; 81.05 U; 81.07 -b

## 1. INTRODUCTION

In recent years, the development of sensor systems for detecting gaseous pollutants has become increasingly important due to the concerns for environmental protection and public safety. This has promoted significant research efforts toward synthesizing novel materials for sensor applications, particularly to address challenges posed by hazardous gases in air pollution [1,2]. Carbon nanotubes (CNTs) have emerged as promising candidates for gas sensing due to their unique properties, such as large surface area and chemical reactivity. The functionalization of CNTs enhances their adsorption properties, expanding their potential for sensor applications. Sensitivity is a crucial parameter in gas sensing that depends on sensor materials' surface characteristics and morphology [3-6]. Functionalized CNTs and graphene have shown sensitivity to various gases and vapors, facilitated by strategies like covalent or non-covalent attachment of functional groups [7-9]. Decorating CNTs with metal and metal oxide nanoparticles offers improved sensitivity and selectivity. [10]. Considering all the mentioned, this paper discusses the synthesis and sensing properties of multi-walled carbon nanotubes (MWCNTs) decorated with NiO nanoparticles, providing comparative analyses of their performance in detecting gases like NO<sub>2</sub>, NH<sub>3</sub>, ethanol, methanol, and water vapors at room temperature.

## 2. MATERIALS AND METHODS

To obtain the f-MWCNTs/NiO nanocomposite, ultrasonic waves are applied to f-MWCNT dispersed in ethylene and nano-sized NiO powder at concentrations of 2:1 and 4:1.

**NiO nanosized powder synthesis**-0.1 M NiCl<sub>2</sub> ·6H<sub>2</sub>O was dissolved in 100 ml deionized (DI) water (solution 1) and 2) 0.8 M NaOH was dissolved in 80 ml DI water (solution 2). Then solution 1 was stirred at 90°C

for 30 minutes at 1500 rate/min, then solution 2 was added to it by drop casting method. The reaction between the two solutions continued for 2 hours. The greenish precipitate produced because of the reaction was then washed several times with DI water dried in the oven at 100 °C and calcined at 300 °C for 30 minutes.

**Functionalization of MWCNTs** - The MWCNTs were functionalized with oxygen-containing groups and analyzed as previous works [13].

**Preparation of f-MWCNTs/NiO nanocomposite**- The ultrasonic method was used for mixing NiO powder and f-MWCNTs in 95% ethanol for 1 hour and two different concentrations (1:4 and 1:2 ratios) were prepared using f-MWCNTs as base material. The obtained mixture was dried at 80 °C for 2 hours.

**Fabrication of Ag- f-MWCNTs/NiO-Ag structure** - f-MWCNTs/NiO were dispersed on a dielectric (pyro ceramic) substrate. To obtain a thin f-MWCNT/NiO network layer, a colloid was prepared by uniformly dispersing 0.01 mg f-MWCNT in 50 ml pure ethanol. Ag-f-MWCNTs/NiO-Ag were prepared with Ag contacts to study the sensor properties. The stability of their initial resistance was tested, and the I-V characteristics were studied to control metal contact ohmicity.

X-ray diffraction and Raman scattering measurements were conducted using a D2- Phaser X-ray diffractometer by CuK radiation (1.5406 Å) and EnSpectr R532 spectrometer with 532 nm excitation laser with maximum power 60 Wt, respectively.

## 3. EXPERIMENTAL RESULTS AND DISCUSSIONS

### X-ray analysis of NiO

The results of the X-ray diffraction analysis are shown in Fig 3. The peaks were recorded at 37.3<sup>0</sup>, 43.4<sup>0</sup>, 62.8<sup>0</sup>, 75.3<sup>0</sup> and 79.5<sup>0</sup>. According to these data,

the diffraction planes of NiO cubic phase crystallites correspond to [111], [200], [220], [311] and [222] Miller indices. There are two extra peaks observed in

the positions of  $31.65^\circ$  and  $45.5^\circ$ , which can be explained by the presence of some impurities.

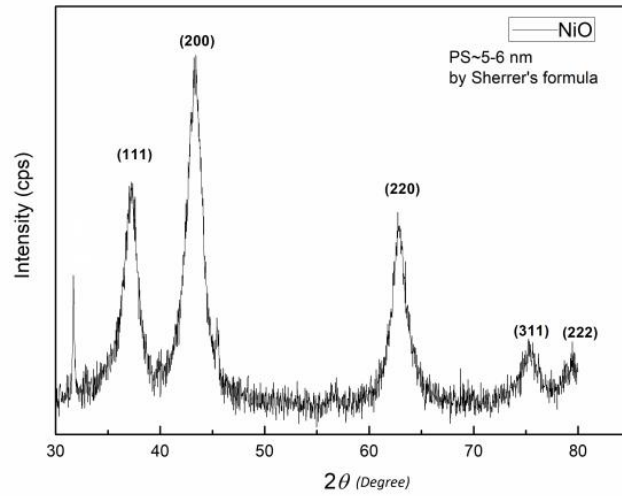


Fig. 1. X-ray diffraction of NiO.

Scherer's formula was used to calculate the particle size. The results of the calculation have shown that the average size of the NiO nanoparticles was around 5 nanometers (nm).

**Raman characterization**

The room temperature Raman spectrum of NiO NPs is shown in Fig. 2.

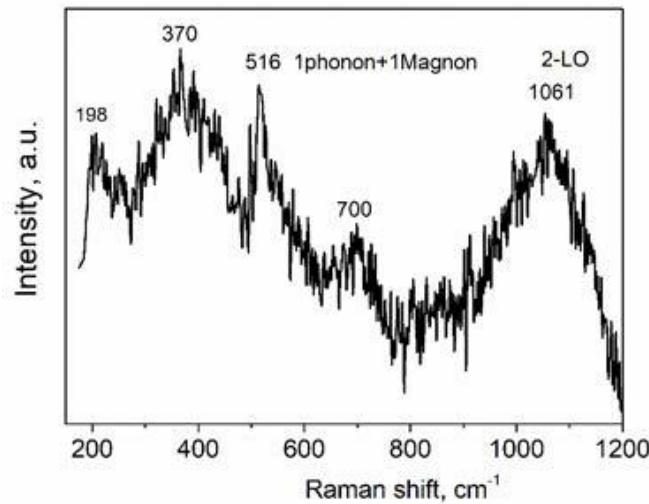


Fig. 2. Room temperature Raman spectrum of NiO NPs.

Two intense peaks observed at 370 and 1061  $\text{cm}^{-1}$  are attributed to transverse (TO) and longitudinal (2-LO) modes, respectively. The small peak at 700  $\text{cm}^{-1}$  is harmonic 2 phonon modes of a phonon TO mode (at 370  $\text{cm}^{-1}$ ), while the one-phonon mode (1P-LO) of the longitudinal 2-LO mode (at 1061  $\text{cm}^{-1}$ ) is not observed. The absence of the 1P-LO band, located at  $\sim 570 \text{ cm}^{-1}$  on the specter and disorder-induced, indicates the good quality of the single crystal. However, forbidden phonon mode is also observed at 198  $\text{cm}^{-1}$  on the specter, which indicates the lowered symmetry of the lattice due to the defects caused by the oxygen composition. The vibrational band at 513  $\text{cm}^{-1}$  shows the presence of strong phonon-magnon (1

phonon + 1 magnon) interaction at the particle surface [11,12].

**Sensing characteristics**

Fig.3 clearly shows that the resistance of the f-MWCNTs structure rises under the influence of all the tested gases and vapors, including  $\text{NO}_2$ , the only oxidizing gas among them. Weak response (about 1-4 % during 20 sec) of the f-MWCNTs structure to other gases and vapors was also observed.

These results give a reason to assume that a weak short-term interaction is happening between the f-MWCNTs surface and all the tested gases, i.e. the gas molecules are physically adsorbed by the hydroxyl

groups formed on the surface of carbon nanotubes during oxidation-reduction processes.

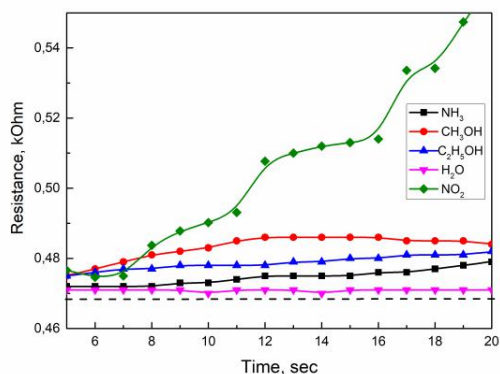


Fig. 3. The sensory response of f-MWCNTs to different gases and vapors.

For comparison, the sensitivities of f-MWCNTs/NiO-based sensor structures to the same gases and vapors were tested. The results of the tests are summarized in Fig.4. It was established, that the resistance of this sensor, like the f-MWCNTs-based sensor, increases under the influence of all the tested gases and vapors, except NO<sub>2</sub> gas.

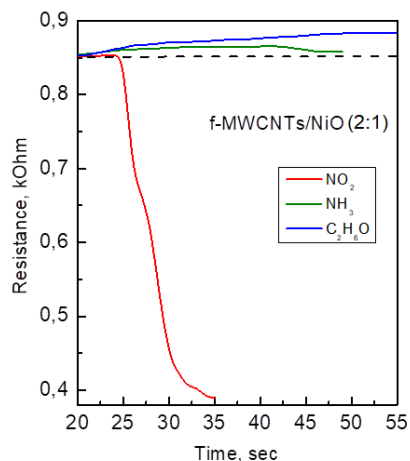


Fig. 4. The sensory response of f-MWCNTs/NiO to oxidized and reduced gas and vapors.

**NO<sub>2</sub> sensing characteristics**

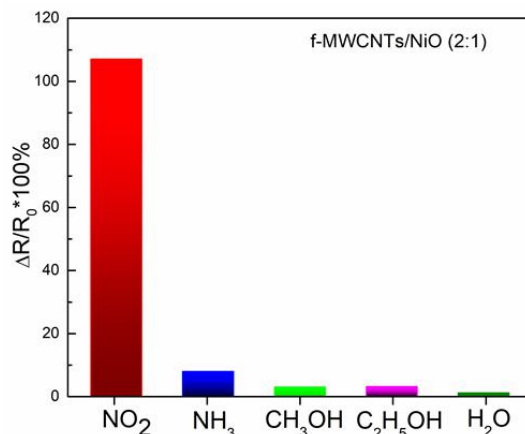


Fig. 6. Selectivity diagram of f-MWCNTs/NiO-based sensor structure.

The NO<sub>2</sub> gas response of the sensor structures is shown in Fig.5. Under the same condition, the f-MWCNTs/NiO-based sensor structure in the concentration of f-MWCNTs and NiO (in 4:1 ratio), shows 72 % response to NO<sub>2</sub> gas and f-MWCNTs/NiO based sensor structure in the concentration of f-MWCNTs and NiO (in 2:1 ratio) shows 107 % response to NO<sub>2</sub> gas within 7 sec. The experiments have shown that the sensitivity of the sensor increases when the amount of NiO increases. The sensors were tested for stability before starting experiments and the results have shown very good stability of the sensor structures. Fig.5 indicates the resistance values for 25 sec. before and after NO<sub>2</sub> passing to the system.

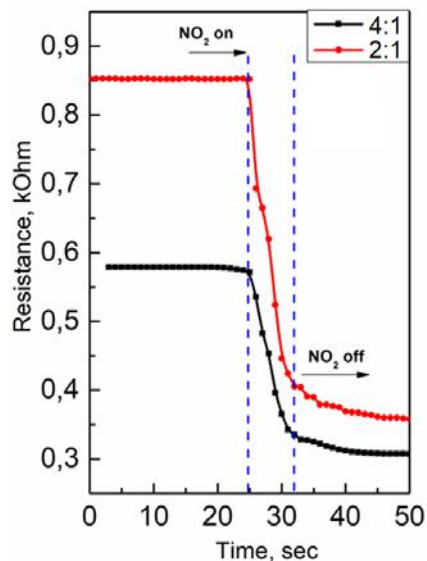


Fig. 5. NO<sub>2</sub> sensing graphs of f-MWCNTs/NiO based sensor structures: f-MWCNTs/NiO (4:1) and f-MWCNTs/NiO (2:1).

**Selectivity testing**

The selectivity of the f-MWCNTs/NiO-based sensor structure was also tested with both concentrations of NiO using increased amounts of NH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>OH, CH<sub>3</sub>OH, and H<sub>2</sub>O vapor compared to NO<sub>2</sub> concentration (Fig.6). It is evident from the illustration that despite the incoming gas concentration into the testing chamber being 150 (ppm), the sensor's responsiveness to the 10 ppm NO<sub>2</sub> registers at 107%.

#### 4. CONCLUSION

Efficient gas sensors were successfully synthesized by decorating f-MWCNTs with NiO nanoparticles to achieve increased sensitivity to NO<sub>2</sub> gas. The NiO-decorated f-MWCNTs have demonstrated over 10 times higher sensing capability compared to f-MWCNTs alone which can be

associated with the catalytic role of NiO. The f-MWCNTs/NiO structure exhibited superior performance characterized by high responsivity and short response time together with stability and selectivity, which make it promising for application in environmental monitoring and safety implementations.

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