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Methanol and ethanol vapor sensitivity of MWCNT/SnO_2/Ru nanocomposite structures

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Abstract:

Multi-walled carbon nanotubes (MWCNTs) were successfully coated with tin-dioxide (SnO_2) nanoparticles using both hydrothermal process and sol-gel technique under different solvent conditions. The obtained MWCNTs/SnO_2 nanocomposites had the mass ratio of the components 1:4, 1:8 and 1:50, respectively. The as-prepared nanocomposites were characterized in detail using scanning electron microscopy (SEM) and X-ray powder diffraction (XRD) technique. On the base of these materials gas-sensor structures are developed. The high sensitivity to methanol and ethanol vapour as well as i-butane gas at 200°C operation temperature have been revealed for the functionalized with Ru nanocomposite thick-film sensor structures having the ratio of the components 1:8 and 1:50. The structures with 1:4 ratio of the components are characterized by the best selectivity towards influence of methanol and ethanol vapor.

Key words: SnO_2-MWCNTs nanocomposite, gas sensor, Ru, ethanol, methanol, i-butane

1. Introduction

The hybrid materials made of semiconductor metal oxides mainly SnO_2 as the most prospective and widely used gas-sensitive material and carbon nanotubes (CNTs) have been given much attention in recent years for their various applications. The special geometries and properties of such materials facilitate their great potential applications as high-performance gas sensors [1-3]. Previous research works have demonstrated that the hybrid materials gas sensors, for example SnO_2/CNTs have a better performance in comparison with the sensors based on the separated same materials. One of the reasons responsible for the enhancement of the sensing performance of the sensors based on CNTs/SnO_2 nanocomposite is attributed with their very large specific surface area and the advent of additional nanochannel in the form of hollow CNTs for gas diffusion. Surface modification of the hybrid gas sensors and sensors based on the nanocomposites components with noble metals promotes increasing in sensitivity and improvement of the gas sensors selectivity [1, 3].

In this work we prepared and studied thick-film gas-sensor structures using various precursors for wet chemical processes. The choice of corresponding treating conditions and regimes for CNTs functionalization were focused on obtaining sensitivity to such target gases as hydrogen, ethanol, methanol and i-butane. We obtained and studied hybrid MWCNTs/SnO_2 surface-modified with Ru thick films. Results of these investigations we present here.

2. Experimental

We studied 2 groups of samples with gas-sensitive layers consisting of SnO_2 nanoparticles and carbon nanotubes: a) thick-film structures based on MWCNTs and SnO_2 mixed nanopowders without any noble metal or metal-oxide catalysts, and the same thick-films but sensitized with Ru catalyst.

MWCNTs membranes made in EPFL (Lausanne, Switzerland) were used for preparation of nanocrystalline MWCNTs/SnO_2 powder by wet chemical methods. Millimeter long MWCNTs grown by CVD were used to prepare membranes by vacuum filtration form a suspension in isopropanol. MWCNTs from the

membranes were transferred in slurry in HNO_3/H_2SO_4 acid mixture for one hour having for an object the functionalization of nanotube walls with oxygen-containing functional groups such as hydroxyl (OH), carbonyl (C=O), and carboxylic (COOH) ones. After rinsing with distilled water and drying at 80°C MWCNTs were mixed with deionized water and treated in ultrasonic bath for 5 min. Then, $SnCl_4 \cdot 5H_2O$ was added to obtained suspension in the ratio of 1:7 with thorough mixing followed by sonication for 5 min. After that, the solution was left in drying oven for 5 hours at 140°C to evaporate aqueous content. 77 mg of the resulting precipitate was added to 346 ml of $SnCl_4 \cdot 5H_2O$ 0.5M solution and sonicated during 5 min. Ammonium was used for keeping pH of the solution at the level of 8.3. Mixed suspension was left overnight at 80°C whereupon MWCNTs/SnO_2 composite powder was rinsed, dried, grinded and annealed in air at 400°C for 1 hour (ECS series powder).

The paste for thick film deposition was obtained by addition of 40µl distilled water to 100mg ECS powder and mixing with α-terpineol ("Sigma Aldrich"). Obtained in such a way slurry was printed over the ready-made Pt interdigitated electrodes by means of home-made screen-printer. Thin-film heater was formed on the backside of the substrate.

Thick films were also made by similar technique using MWCNTs/SnO_2 powder obtained in the weight ratio of the components 1:4 and 1:8, respectively (further, marked as KCS1 and KCS2 samples). For preparation of these samples hydrothermal synthesis was used. In both cases $SnCl_2 \cdot 2H_2O$ was chosen as a precursor material. Both water and ethanol were used as solvents. Hydrothermal synthesis was carried out at 150°C during one day and at 60°C for 4 hours, respectively. The following heat treatments were fulfilled at 450°C for 3 hours.

After annealing and cooling the MWCNTs/SnO_2 thick films were surface-ruthenated by dipping them into 0.01M and 0.03M $RuOHCl_3$ aqueous solutions for 20 min whereupon dried at 150°C for 30 min followed by calcination treatment at 400°C for 2 hours. The cooling of the samples after all the abovementioned heat treatments occurs along with furnace cooling down.

3. Results and discussions

3.1. Materials characterization

The morphologies of the prepared SnO_2/MWCNT nanocomposite different powders were studied by Hitachi S-4700 Type II FE-SEM equipped with a cold field emission gun operating in the range of 5-15 kV. XRD analysis was carried out using Rigaku Miniflex II diffractometer.

SEM image of MWCNTs/SnO_2 powder obtained with components ratio 1:50, respectively, is presented in Fig. 1a. It can be seen that in this case CNTs are well embedded in tin oxide matrix in contrast with MWCNTs/SnO_2 hybrid materials having proportions of the components 1:8 and 1:4, respectively (for example, only Fig. 1b presents for the material with 1:8 ratio of the components). The micrograph shows that covered with spherical tin oxide nanoparticles CNTs are well dispersed and separated from each other.

Corresponding XRD patterns (not presented here) show that the crystallization of the MWCNTs/SnO_2 composite samples having components ratio of 1:4 and 1:8 takes place adequately. Relatively broad peaks in the XRD pattern indicate that the SnO_2 nanoparticles are very small.

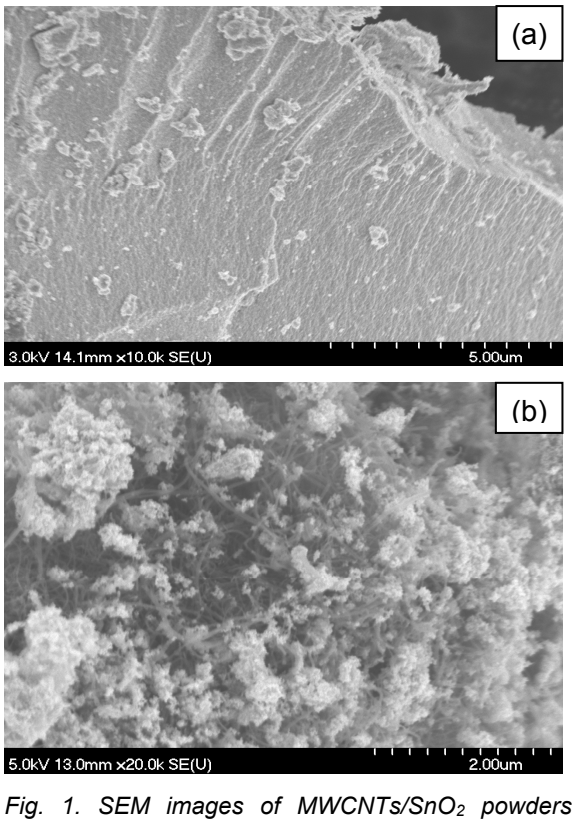

Fig. 1. SEM images of MWCNTs/SnO_2 powders obtained with components ratios: 1:50 (a); and 1:8 (b).

3.2. Gas-sensing characteristics

Testing and studying of the sensors performance was carried out on the basis of software controlled automated gas sensor parameters measurement setup. The sensor response for a given test gas is calculated as R_{air}/R_{gas}, where R_{air} and R_{gas} are the electrical

resistances of the sensor in air and in ambient containing test gas, respectively.

As a result of numerous testing of gas sensitivity of the samples carried out at various temperatures and target gas concentrations, the optimal operation temperatures were estimated for each type of the sensor. At that, we took into account both gas sensitivity and response and recovery times as well as achieved selectivity at certain operation temperature. The results of these investigations are summarized in the bar chart presented in Fig. 2.

The analysis of the results of testing the ECS7 and KCS series samples made without any catalysts revealed relatively high sensitivity to methanol and ethanol vapors. Therefore, in the view of improvement the alcohols sensitivity and selectivity of these sensors, we carried out the sensitization of these series of MWCNTs/SnO_2 nanocomposites with Ru catalyst. As can be seen from the bar chart, such sensitization leads to sharp rise in methanol and ethanol vapor sensitivity up to 10^3 and higher for the samples of both series. At that, the cross-sensitivity to other gases decreases or remains on the same level. The sensitivity to methanol and ethanol vapors appears at the operation temperature of 200°C and decreases exponentially with operation temperature rise up to 300°C. For example, the plot of ethanol sensitivity of the ECS7Ru sample versus operation temperature is shown in Fig. 3.

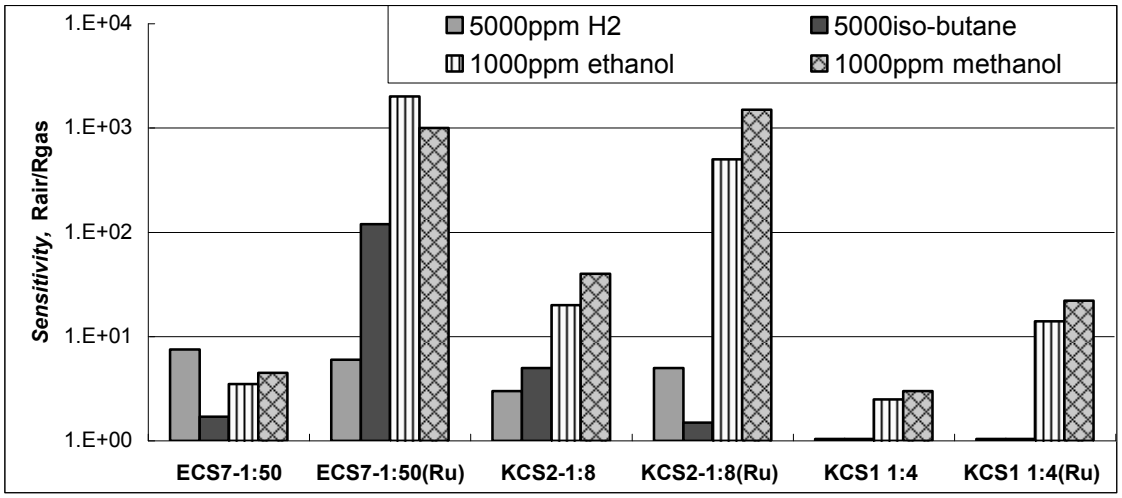

Fig. 2. Gas sensitivity column bar chart for all series of the studied structures Symbol Ru points to the test of same series of the samples but sensitized by ruthenium catalyst. The optimal operation temperature of 200°C is chosen for all test gases.

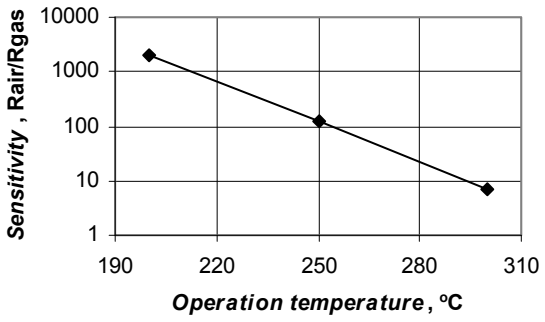

Fig. 3. Plot of ethanol sensitivity of the ECS7Ru sample versus operation temperature.

The formation of the surface-ruthenated MWCNTs/SnO_2 nanocomposite hybrid structure leads to high sensitivity to alcohols as well as increase in i-butane sensitivity at definite ratio of the nanocomposite components and decrease in operation temperature. As can be seen from the histogram (Fig. 2), different effects caused by the ratio of the components of nanocomposite are found. So, as it is mentioned above, the surface-ruthenated nanocomposite containing large amount of SnO_2 (1:50) nanocrystallites shows high sensitivity both to methanol and ethanol vapors. Simultaneously, relatively high i-butane sensitivity is also observed. Approximately the same sensitivity to alcohols (about 10^3) remains in case of the samples having 1:8 ratios of the nanocomposite components but the response to i-butane sharply decreases. The hydrogen and i-butane sensitivity disappears completely with the following decreasing of SnO_2 content in the nanocomposite (at 1:4 ratios of the components). At that, alcohols sensitivity also has a little fall. It should be noted that the functionalization of ECS7 series samples with Ru leads to significant increase in sensitivity to i-butane along with rise in sensitivity to ethanol and methanol vapor. The dependence of i-butane sensitivity vs gas concentration of ECS7 samples is presented in Fig. 4. As can be seen,

noticeable i-butane sensitivity is observed beginning from 50 ppm gas concentration.

The typical response and recovery times of the ECS7 series i-butane sensors measured on the 90% level of the signal amplitude and at operating temperature of 200°C are 5-7 s and about one minute, respectively. It is also interesting to note that increase in operating temperature to 250 °C leads to sharp decrease in both response and recovery times down to 2-3 s. At that, the sensitivity remains practically the same. With the following increase in operation temperature (≥300°C), adsorbed oxygen desorbs increasingly from the surface. As a result, i-butane sensitivity sharply decreases.

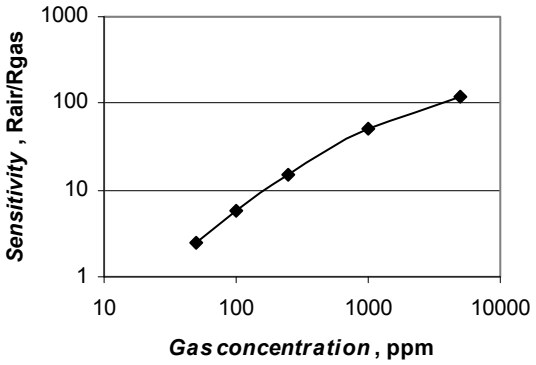

Fig. 4. Dependence of i-butane sensitivity vs gas concentration at 200°C operation temperature.

Due to the polar COOH groups attached onto the nanotubes sidewalls [1, 3, 4], the sensors give the stronger responses to methanol and ethanol vapors. It occurs because of absorption efficiency with these volatile organic molecules increases due to the dipole-dipole interactions between the COOH and the polar organic molecules. The Ru sites act as a catalyst for oxygenation and absorb oxygen [5] and, as a consequence, for increased adsorption of the target gas molecules which is also confirmed by the increased sensitivity of the ruthenated samples in comparison to that of the pure tin oxide as well as SnO_2/MWCNTs nanocomposite samples.

As is obvious from Fig. 3, the response to ethanol (that is typical also both for methanol vapors and for i-butane gas) decreases at higher temperatures. Apparently, with rise in operating temperature, the adsorbed oxygen ions increasingly desorb from the surface of the sensor. At that, progressively less number of oxygen ions present on the surface of the SnO_2 to react with the affecting gas, and therefore the response decreases at high operating temperatures.

4. Conclusion

As a result of investigation of thick-film MWCNTs/SnO_2 structures it was revealed that the functionalization by Ru leads to increase in gas sensitivity of studied structures, particularly the response signal to methanol and ethanol vapor rises sharply up to 10^3 and higher.

It was also established that from all concerned MWCNTs/SnO_2/Ru powders the powder with the ratio of MWCNTs to SnO_2 1:8 and 1:50 is the most interesting from the point of view of methanol and ethanol sensitivity at relatively low operation temperature. Moreover, surface-ruthenated ECS7 series samples exhibited the highest sensitivity to i-butane.

In addition to abovementioned properties, KCS series sensors exhibited also good selectivity to ethyl and methyl alcohols vapors.

Thus, by means of certain choice of the ratio of nanocomposite components as well as by using Ru catalyst, it is possible adjusting both the MWCNT/SnO_2/Ru nanocomposite based gas sensors sensitivity and selectivity.

Acknowledgements

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