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Au-NPs/ZnO single nanowire nanosensors for health care applications

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***Abstract*— Herein, the room temperature gas sensing properties of a device fabricatedbased on an individual gold nanoparticles (AuNPs)-functionalized zinc oxide nanowire (ZnO NW) is reported. The Au-NPs/ZnO nanowires were depositedusing theelectrochemical approachin a classical three-electrode electrochemical cell. The dual beam focused ion beam/scanning electron microscopy (FIB/SEM) was usedto integrate the singlenanostructuresinto gas sensing nanodevices.The results are promising for futureapplications in monitoring H2gas for health care applications and clinical breath analysis.**

Keywords—nanosensors; hydrogen gas sensor; ZnO nanowire; gold nanoparticles

I. INTRODUCTION (*HEADING 1*)

Hydrogen is the lightest and most abundant chemical element in the universe. H_2 gas is odorless, colorless, highly reactive and highly flammable with a wide flammable range (5–75%) [1, 2]. Currently, the two largest uses of hydrogen are fossil fuel processing, ammonia production for fertilizer and as clean energy source, being by 3-times more energy dense by mass than gasoline (143 MJ/kg vs 46.9 MJ/kg) [3]. Since the 2007 discovery that molecular hydrogen has selective antioxidant properties, multiple studies have shown that H_2 has beneficial effects in diverse animal models and human disease, and can be also used as a preventive and therapeutic medical gas for various diseases [4]. H_2 have several advantages over current pharmacological therapies: (i) high diffusivity which allows to reach subcellular compartments; (ii) selective reduction of detrimental hydroxyl radicals and peroxynitrite, without decrease of the steady-state levels of nitric oxide; (iii) hydrogen treatment did not eliminate O_2^- or H_2O_2 when tested in vitro [3, 5]. In gaseous phase the H_2 can be easily inhaled using a ventilator circuit, face-mask or nasal cannula [3].

Since 2007 the number of publications on the biologically or medically beneficial effects of H_2 is still growing and are mainly focused on tissue dysfunctions, reproductive, urinary, respiratory, digestive, cardiovascular and central nervous systems, metabolic syndrome, etc. [4]. Along with the therapeutic applications, the measurement of breath hydrogen has also attracted a great attention in recent years [6]. Hydrogen in the human body is eliminated through three pathways: flatus, respiratory excretion after absorption into the systemic circulation and metabolism by colonic microbiota (through three metabolic methods) [3].

Despite the fact that the potential of clinical breath analysis has been recognized for centuries, it still remains in its infancy [7]. Breath analysis can be used to detect disease, monitor disease progression, or monitor therapy [7]. The main advantages of breath analysis are: (i) method is noninvasive; (ii) sampling procedure is safe and fast; (iii) does not require any additional apparatus and the subjects are only requested to deeply breathe into the collecting system [8].

In the case of preventive and therapeutic medical applications the safety is a primary concern with respect to H_2 transportation, storage, and administration [4]. Therefore, due to the dangerous character of H_2 gas and because it cannot be detected by human beings it is important to elaborate the devices for rapid and accurate H_2 gas detection even to small concentrations (in range of ppm) [2].

In this context, metal oxide structures are ideal candidates for gas sensing applications due to their advantages such as: (i) low cost; (ii) detection of a wide range of reducing and oxidizing gases and VOCs vapors; (iii) high sensitivity; (iv) possibility to fabricate portable devices [9-11]. For example, recently the highly selective room temperature hydrogen gas sensor was elaborated based on ZnO columnar films doped with Pd and decorated with PdO_2/PdO nanoparticles [12]. Among all types of structures, the quasi-one-dimensional (1-D) structures, such as nanowires, nanobelts, nanorods, etc., have attracted a great attention due their high surface-to-volume ratio, which makes them highly sensitive to surface reactions

[1]. Exhaled breath contains thousands of endogenous VOC in low concentration ranging from ppb to ppm [13]. A recent review identified 1764 human related VOC, 874 of which are found in exhaled breath [14]. Therefore, it is very important to develop the highly selective H_2 gas sensors with no cross-sensitivity to VOCs vapors.

In this work, the individual Au-NPs/ZnO nanowires were integrated into gas sensing devices using a dual beam FIB/SEM system. The room temperature investigations of gas sensing properties demonstrated high sensitivity and the excellent selectivity to H_2 gas compared to VOCs vapors, such as ethanol, acetone, *n*-butanol and 2-propanol, as well as CO_2 and NH_3 gases. The presented results are of high interest for monitoring of H_2 gas level in different applications, including health care applications and clinical breath analysis.

II. Experimental part

The Au-NPs/ZnO NW arrays were grown on glass sheet substrates coated with polycrystalline F-doped SnO_2 (FTO, resistance of 10 Ω/□) by electrochemical deposition in a classical three-electrode electrochemical cell [15-17]. In this study, only the samples grown using 0.3 μM of $HAuCl_4$ (Sigma-Aldrich, > 99.9%) in an electrochemical bath were used for nanosensor fabrication. More details on synthesis of AuNPs/ZnO NW arrays are presented in previous works [15-17]. The detailed morphological, structural, optical and chemical characterization of AuNPs/ZnO NW arrays are presented in previous work [15].

The devices based on individual ZnO:Au NWs were fabricated in a dual beam FIB/SEM scientific instrument, using the method developed by Lupan *et al.* [1, 18]. The gas sensing measurements were performed at room temperature (RT, ~ 25 °C) in normal ambient air (relative humidity of 30 – 40 %). The gas response (*S*) was measured as ratio of device current under exposure to tested gases and VOCs (I_{gas}) and under exposure to ambient air (I_{air}). The response (t_r) and recovery (t_d) times were defined as necessary time to reach and recover 90% of full response. The electrical measurements were continuously monitored using a computer-controlled Keithley 2400 source meter using LabView software (National Instruments).

III. Results

Figure 1 shows SEM images at different magnifications of AuNPs/ZnO nanowire arrays grown using 0.3 μM of $HAuCl_4$ in the electrolyte solution. From **Figure 1a** can be observed that samples are composed of fairly uniformly distributed nanowires on the substrate, which are oriented upward with respect to the FTO film underlying glass substrate. The NWs diameters vary in the range of 100 – 200 nm (see **Figure 1b,c**). It was observed that NWs are tilted from the vertical direction with increased surface texture. From **Figure 1b** and **1c** it can be clearly observed that on the surface of ZnO NWs the nanoparticles with different diameters (10 – 30 nm) are attached. The origin of these nanoparticles was investigated in previous work using transmission electron microscopy, selected area electron diffractions patterns and energy-dispersive X-ray (EDX) spectroscopy [15], and was demonstrated that these NPs are composed of *fcc* gold, with *d*(1 1 1) = 0.231 nm, *d*(0 0 2) = 0.201 nm and with Fm-3m space group. The deposition of Au NPs on the surface of ZnO NWs can be described by the following equation [15]:

$$AuCl_4^- + 3e^- \leftrightarrow Au^0 + 4Cl^- \quad (1)$$

No evidence of ZnO NWs doping with Au was observed, which can be a result of low solubility of Au in ZnO [15]. The performed high resolution X-ray photoelectron spectroscopy measurements of Au-4d core level demonstrated that Au is present in metallic form and no oxidation was observed.

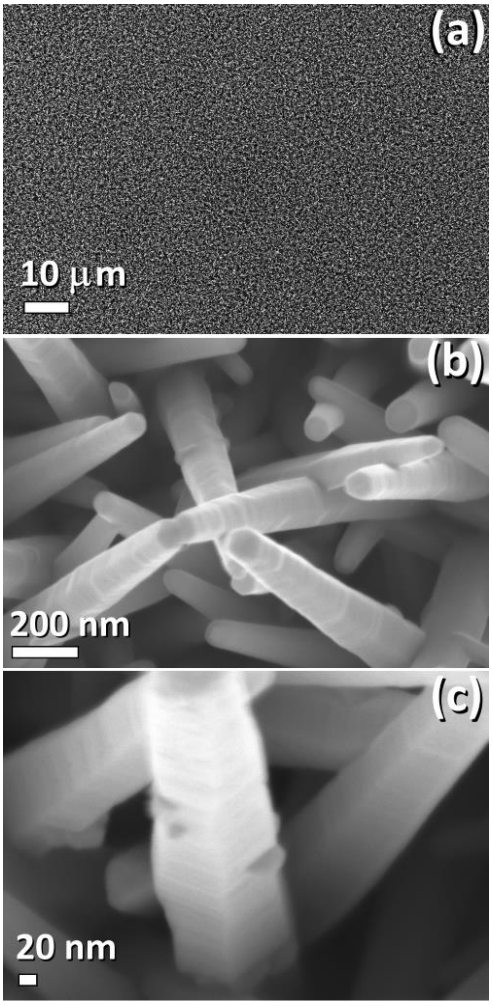

Fig. 1. SEM images of Au-NPs/ZnO nanowire arrays at different magnifications: (a) low; (b) medium; (c) high.

Figure 2a shows SEM image of the integrated individual AuNPs/ZnO nanowire, which was contacted to Au/Cr pads on the chip using Pt complex. The chip represents a SiO_2-coated Si substrate (10 mm × 10 mm) with preliminary deposited Au/Cr contacts as external electrodes. More information on chip can be found in our previous work [16]. On one chip can be integrated a maximum of 8 individual nanowires, which is very important for further developments of multi-sensor systems, such as "electronic nose" in order to discriminate complex mixtures of gases and VOCs. In our case, the diameter

of AuNPs/ZnO nanowire is ~ 150 nm, while the length between Pt contacts is ~ 2 μm. The current – voltage characteristic of device, measured at room temperature in a relatively wide range of – 5 V to + 5 V is presented in **Figure 2b**, showing the formation of double-Schottky contacts due to higher work function of Pt compared to electron affinity of ZnO [1].

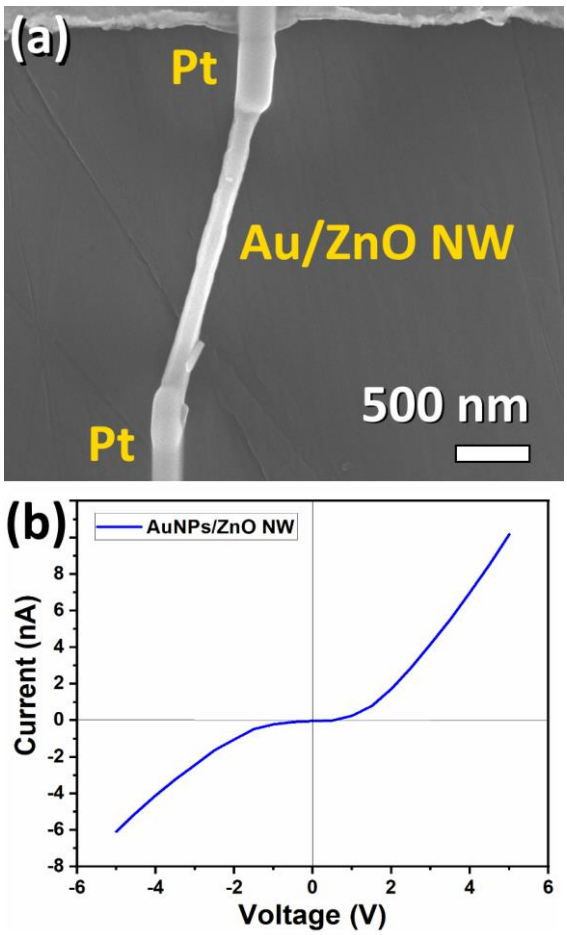

Fig. 2. (b) SEM image of device based on individual AuNPs/ZnO nanowire. (b) Current – voltage characteristic of device.

The schematic illustration of H_2 gas detection in exhaled breath using an individual Au-NPs/ZnO NW is presented in **Figure 3**. According to this method, the elaborated device need to selectively detect the H_2 gas among other types of gases such as CO_2, CO and NH_3 and a big variety of VOCs vapors, such as ethanol, acetone, 2-propanol and n-butanol, which are also present in exhaled breath. The direct measurement of exhaled breath cannot be used due to contamination from ambient air and interference from other molecules [7]. Therefore, the exhaled breath needs to be collected in a special sealed container where is placed the sensor unit, for a better accuracy of measurements.

The fabricated device was measured to 100 ppm of H_2 gas and a much higher concentration of 1000 ppm for other gases and VOCs vapors. The obtained results are presented in **Figure 4a**, which demonstrates the high selectivity of Au-NPs/ZnO NW to H_2 gas. No response to CO_2, CO, NH_3, ethanol, acetone, 2-propanol and n-butanol with much higher concentration was observed. The gas response to 100 ppm of H_2 gas at room temperature is ~ 3. The dynamic response of the device is presented in **Figure 4b**. As can be observed, even at room temperature operation the response is reversible. The calculated response and recovery times are ~ 50 s and ~ 700 s, respectively.

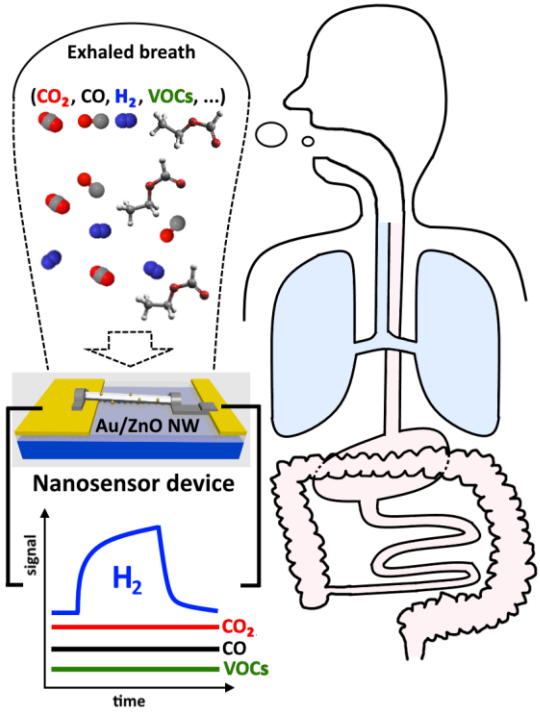

Fig. 3. Schematic illustration of H_2 gas detection in exhaled breath using a individual AuNPs/ZnO.

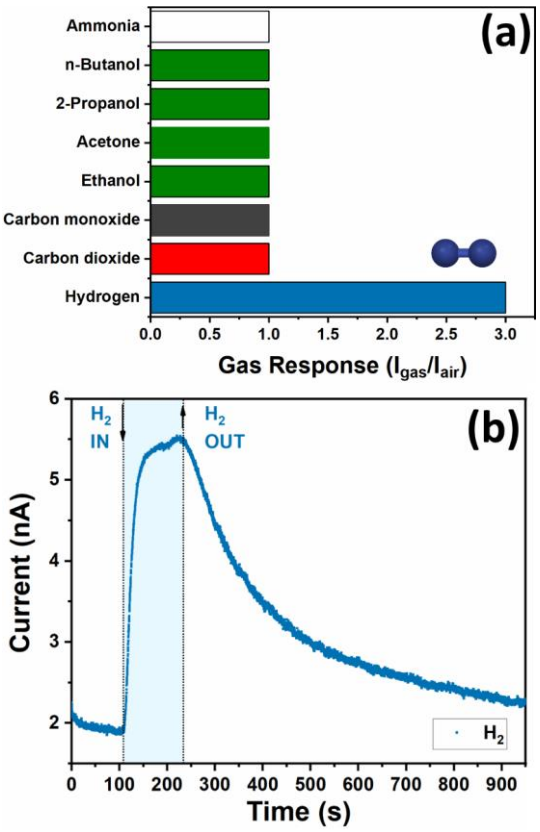

Fig. 4. (a) Gas response of the Au-NPs/ZnO NW to different gases and VOCs vapors. (b) Dynamic gas response to 100 ppm of H_2.

IV. Conclusions

In this study, the nanosensor based on a singleAu-NPs/ZnO NW with a diameter of ~ 150 nm and length of ~ 2 μm was successfully fabricated using FIB/SEM equipment. The investigation of gas sensingproperties, measuredat room temperature showed the high response and selectivity ofthe device to 100 ppm of hydrogen gas compared to other widely exhaled gases and VOCs vapors, such as carbon monoxide, carbon dioxide, ammonia, ethanol, n-butanol, 2-propanol and acetone. The obtained nanosensor can be further implemented into different devices for ambient monitoring of H2, H_2 level monitoring in medical systems for health care applications, as well as in clinical breath analysis for early detection of different diseases.

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