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Visible Light Activated Room Temperature Gas Sensors Based on CaFe_2O_4 Nanopowders [†]

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Abstract: Gas sensors based on CaFe_2O_4 nanopowders, which are *p*-type metal oxide semiconductor (MOX), have been fabricated and assessed for ethanol gas monitoring under visible light activation at room temperature. Regardless of their inferior sensitivity compared to thermally activated counterparts, the developed sensors have shown responsive sensing behavior towards ethanol vapors confirming the ability of using visible light for sensor activation. LEDs with different wavelengths (i.e., 465–590 nm) were employed. The highest sensitivity (3.7%) was reached using green LED activation that corresponds to the band gap of CaFe_2O_4 .

Keywords: CaFe_2O_4 nanopowders; gas sensors; *p*-type metal oxide semiconductor; visible light activated room temperature

1. Introduction

There are plenty of gas sensor types that have been developed with different materials and working principles. The conductometric gas sensors attract much attention due to several advantages such as simplicity in measurement setup and the ease of miniaturization for portable instruments. Typically, most conductometric gas sensors based on metal oxides (*n*- and *p*-type) need heat to reach the working temperature [1,2]. However, the heat-driven gas sensors have several disadvantages, such as high power consumption, extreme operation conditions and technical limitations in the detection of flammable or explosive analytes because of safety issues.

Many attempts have been made to decrease the operating temperature and to improve the sensitivity and stability of MOX gas sensors (e.g., noble metal doping [3], transition metal oxide incorporation [4], self-heated [5,6], and light irradiation [7,8]). Among these, irradiating light on the surface of metal oxides (e.g., ZnO [4] and TiO₂ [9]) is the most studied and promising method to achieve room temperature sensitivity. Light-activated sensors offer some advantages, such as the possibility to drastically reduce the power consumption by scaling down the light sources (LED platforms) or the possibility to use other technologies incompatible with heat driven sensors (i.e., functionalization). Also, most of the available conductometric sensing devices are based on wide band gap materials (e.g., ZnO and SnO₂), which is need UV light to activate the absorption and desorption processes occurring on the surface of the sensing material. The efficiency of UV LEDs is

however far from being competitive compared to visible LEDs. Therefore, materials with lower band gaps will be desirable for low power consumption gas sensor devices. In this work, we evaluated CaFe_2O_4 nanopowders for ethanol sensing under visible light exposure employing LEDs at room temperature. Since CaFe_2O_4 stands out as a potential candidate [1] because of its suitable band gap [1.9 eV] for visible light-driven sensors.

2. Experimental Details

Sol-gel auto-combustion method was used to synthesize CaFe_2O_4 nanopowders [1]. Gold-interdigitated electrodes (Au-IDE) on glass was (MicruX Technology, Asturias, Spain) used as electronic platform for measuring the electrical characteristics of the CaFe_2O_4 . The IDE size is (10 mm $\times$ 6 mm $\times$ 0.75 mm), with 90 pairs of electrodes having a separate distance of 10 μm and a width of 10 μm . CaFe_2O_4 nanopowders were deposited on the surface of the IDEs by drop casting process. 20 μL of CaFe_2O_4 was dropped on the IDE while keeping the temperature between 40–90 $^\circ\text{C}$. Afterwards, an annealing process at 450 $^\circ\text{C}$ for 1 h with a ramping level of 5 $^\circ\text{C}/\text{min}$ was applied in order to fix the material onto the substrate and obtain a good electrical contact with the Au-IDEs.

Gas sensing experiments were conducted in a customized chamber of 20 mL in volume. The gas flow was maintained stable at 200 mL/min during all the measurements. Reference gaseous atmospheres were provided by independent mass flow controllers blending synthetic air (SA) and ethanol (100 ppm in SA). To investigate CaFe_2O_4 optoelectronic properties, resistance measurements were conducted under synthetic air flow with different LED wavelengths (i.e., blue (465 nm), green (520 nm), and yellow (590 nm)). In order to determine the sensitivity of the CaFe_2O_4 sensors towards reducing gases, different concentrations of ethanol vapors (i.e., from 50 to 100 ppm with an interval of 10 ppm) were then applied to the chamber under LED illumination. The response was defined as $[(R_g - R_a)/R_a] \times 100\%$, where R_g and R_a are the electrical resistances of the sensor when it is exposed to ethanol and in the air, respectively. The response time and recovery time was defined as the time spent by a sensor to achieve 90% of the total resistance change during the adsorption and desorption process, respectively. All experiments were performed at room temperature.

3. Results and Discussion

The as-prepared sample powders are composed of amorphous-like anisotropically shaped and closely packed grains. Figure 1a shows an SEM image of the surface sensor on the Au-IDE after the annealing process. The porous structures of interconnected grains were observed, while the grains keep their anisotropic shape. The size of individual grains of smaller dimensions varies from 70 to 300 nm, while the length of anisotropic nanoparticles is up to 650 nm. Particles are very well interconnected and fused together, in which at the same time they maintain open structures for gas diffusion. Gas-accessible microstructures are preferred for a high gas response [1]. From the UV-vis diffuse reflectance spectra (DRS) of the sample indicate efficient visible light adsorption and the band gap energy of CaFe_2O_4 is ~ 1.9 eV [10], which was corroborated from the optoelectronic response to different LED wavelengths (Figure 1b). Band to band absorption was observed up to 590 nm (2.1 eV) wavelengths.

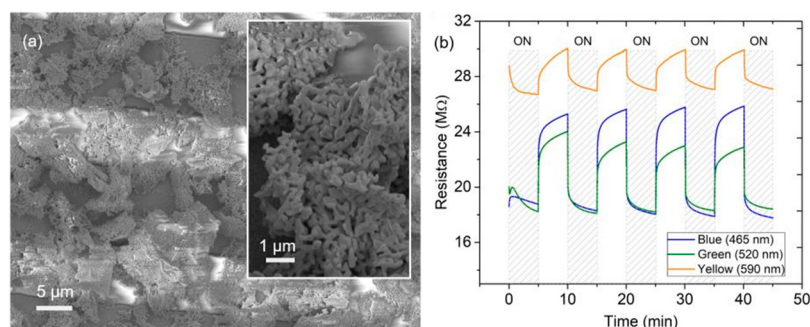
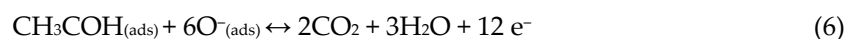
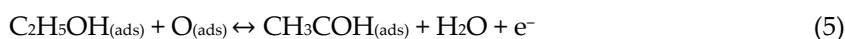


Figure 1. (a) SEM images of a gas sensor based on CaFe_2O_4 nanopowders and (b) their behaviors under exposures of visible light from LEDs with different wavelengths.

To investigate the sensitivity of the CaFe_2O_4 sensors towards reducing gases, different concentrations of ethanol vapors (i.e., from 50 to 100 ppm with an interval of 10 ppm) were then applied to the chamber under LED illumination. The first phenomenon to note was that the resistance increased in presence of ethanol (reducing gas), confirming that CaFe_2O_4 is a p -type material. When CaFe_2O_4 is exposed to air, oxygen molecules are adsorbed on the surface and the electrons are extracted from the conduction band (CB). The kinetic reaction can be explained in the following equations [2]:



When the sensor is exposed the ethanol vapors, the ethanol molecules are absorbed on the surface of the sensors and react with absorbed oxygen species to form water vapor (H_2O) and CO_2 .



On exposure to ethanol, the gas molecules will react with pre-absorbed oxygen. The reaction release free electrons, which naturalize the hole in the p -type of oxide semiconductor, thereby increasing the measured resistance.

Figure 2a–c show the dynamic response to different concentrations of ethanol under illumination of blue, green, and yellow LEDs. The maximum sensitivity of CaFe_2O_4 is 3.7% at 100 ppm for green LED (Figure 2d). This maximum response corresponds to the maximum absorption of CaFe_2O_4 (520 nm). In this case, the response and recovery times were ~22 min and ~49 min, respectively. Overall, the obtained results provide evidence that CaFe_2O_4 is a good candidate for visible light driven gas sensor because of its suitable band gap (i.e., energy of visible light spectra is 1.9–2.7 eV).

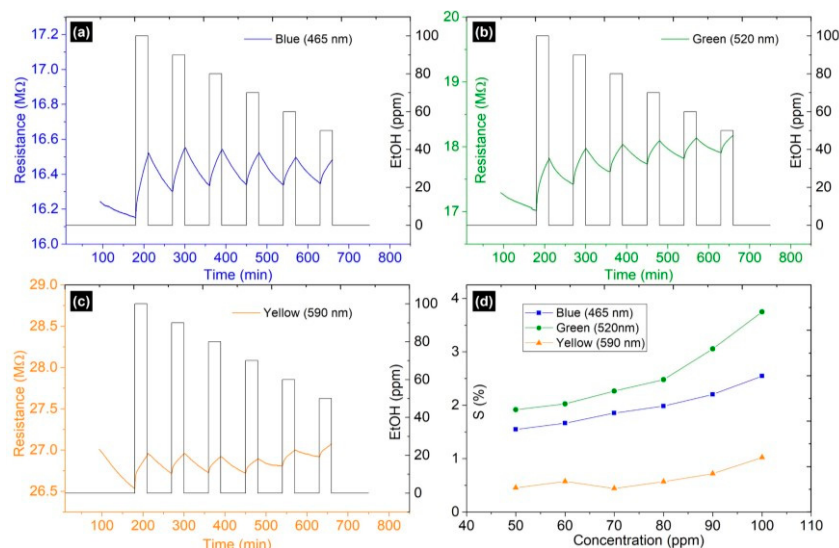


Figure 2. CaFe_2O_4 sensor responses in varied ethanol vapor concentrations (i.e., 50–100 ppm) under activation of (a) blue (465 nm), (b) green (520 nm), and (c) yellow (590 nm) LEDs. (d) Comparison of the sensor sensitivity under different light exposures.

4. Conclusions

Visible light activated at room temperature gas sensors based on metal oxide have been tested and validated. The maximum responses toward ethanol gas, response and recovery times were 3.7%

at 100 ppm, ~22 min, and ~49 min, respectively. The results indicate that CaFe_2O_4 nanopowders synthesized by sol-gel auto-combustion method had good stability with visible light activation capability at room temperature, which can then be a promising candidate for the next generation of narrow bandgap MOX-based gas sensors.

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Conflicts of Interest: The author declares no conflict of interest.

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