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# Ozone sensing properties of nickel phthalocyanine:ZnO nanorod heterostructures

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***Abstract*— We report on the chemiresistive gas sensing characteristics of ZnO nanorods (NRs) modified by a thin layer of nickel phthalocyanine (NiPc). Ozone detection was carried out through electrical measurements with an optimized performance at 250ºC, good reproducibility and suitable concentration range (from 80 to 890 ppb) for technological applications. The hybrid NiPc:ZnO films had superior performance to pure ZnO nanorods in terms of response time and sensitivity. The response times were 22 s and 26 s, respectively, whereas the ratio of resistances under ozone and air was 3.27 for NiPc:ZnO films and 2.56 for the pure ZnO NRs. The improvement in response time is attributed to the large surface area generated with the coating of the ZnO nanorods with the NiPc layer. Significantly, images taken with field-emission scanning electron microscopy (FE-SEM) indicated that the ZnO nanorods were fully covered with NiPc. X-ray diffraction measurements (XRD) revealed a preferential growth of the nanorod-like structures along the [100] direction. In summary, a successful approach has been developed to functionalize ZnO nanorods, which is promising for detection of ppb levels of ozone gas.**

***Keywords*— *Hydrothermal technique; heterostructures; Ozone; Gas sensing***

## I. INTRODUCTION

Ozone ($O_3$) is an oxidizing gas used in numerous practical applications, including drinking-water treatment and microelectronic cleaning processes [1-2]. However, over exposure of ozone ($O_3$) can bring risk to the environment and to public health, causing damage to the respiratory system by affecting the lung function, with inflammation of airways and pain [3-5]. Due to the negative role of ozone in the atmosphere, its monitoring in the environment is crucial. As per the European Guidelines (2002/3/EG), exposure to ozone levels above 120 ppb is not recommendable [6]. Sensing toxic or non-toxic gases has been done successfully with nanostructured semiconducting oxides serving as resistive sensors [7]. These sensors, however, exhibit limitations with regard to the required high operation temperatures and lack of selectivity for different gases. Organic semiconductors have therefore been used to overcome such limitations [8], as they are advantageous due to room temperature operation, short response and recovery times, facile fabrication and high sensitivity. Among the organic semiconductors used for gas sensing are included metal phthalocyanines (MPcs), porphyrins, pentacene, etc. MPcs, in particular, are of most technological importance owing to their excellent environmental stability, and possible tailoring of physical and chemical properties. The disadvantage of MPcs, though, is in their slow response at room temperature. To improve the response kinetics and overcome these drawbacks, metals such as platinum, gold and silver are incorporated with organic semiconductors because of their catalytic effect [7]. In addition, incorporation of metal oxides, e.g. ZnO and $SnO_2$, into organic semiconductors can also improve response kinetics [9]. For similar reasons, hybrid structures containing metal phthalocyanines and metal oxides are exploited in solar cells and diodes [10].

In this study, we report on chemisresitive gas sensing properties of ZnO nanorods with nickel phthalocyanine thin films. We demonstrate that these hybrid films not only improve sensitivity toward ozone but also decrease the response time.

## II. EXPERIMENTAL SECTION

### A. Synthesis of Nickel Phthalocyanine:ZnO nanorods heterostructure

The synthesis of ZnO nanorods was accomplished using the hydrothermal method, with all reagents purchased from Aldrich. Firstly, ZnO nanoparticles (NPs) were prepared by dissolving zinc acetate dehydrate (30mM) in methanol (250mL) under vigorous stirring at 60°C.

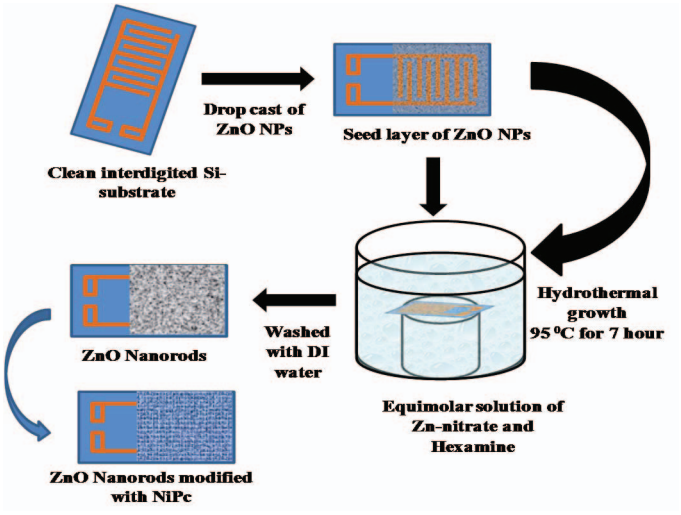


Fig. 1: Schematic showing the modification of ZnO nanorods by NiPc

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Subsequently, a 15mM solution of NaOH in methanol (250mL) was added dropwise and the reaction mixture was stirred for 100 min. at 60°C. The ZnO suspension was then dropped by covering the contact pad onto a $SiO_2$/Si substrate containing 100 nm thick Pt interdigitated electrodes separated by a distance of 50 µm. The sample was heat-treated for 10 min at 60°C to evaporate the remaining solvent. ZnO nanoparticles coated interdigited Si-substrates were kept upside down over a solution containing an aqueous equimolar (25 mM) concentration of zinc nitrate and hexamethylenetetramine. The growth of the nanorods was carried out at 95°C for 7 h, and the substrates were then thoroughly washed with de-ionized water and dried with argon flow. In the following step, the substrates with the nanorods were functionalized by dipping them in a nickel phthalocyanine-tetrasulfonic acid tetrasodium salt (NiPc) solution (0.5mg/mL) for 1 h. Fig. 1 schematically shows the different steps involved in the fabrication process.

### *B. Material Characterization*

The structural characterization of the samples was carried out by using X-ray diffraction (XRD) with a Rigaku Rotaflex RU-200B diffractometer. The morphology of the samples was studied with a field emission scanning electron microscope (FE-SEM, Zeiss Sigma).

### *C. Gas sensing measurements*

Gas sensing measurements were performed in a dynamic mode using the two-probe method [11]. The sensing unit was inserted into a test chamber with controlled temperature and under different ozone concentrations. Ozone was formed by oxidation of oxygen molecules of dry air (8.3 $cm^3$ $s^{-1}$) with a calibrated pen-ray UV lamp (UVP, model P/N 90-0004-01) that provided different ozone concentrations. The dry air containing ozone was blown directly onto the sensor placed on a heated holder. The DC voltage applied was 1 V while the electrical resistance was measured with a Keithley (model 6514) electrometer. The sensor response (S) was defined as $S = R_{ozone}/R_{air}$, where $R_{ozone}$ and $R_{air}$ are the electric resistances of the sensor exposed to ozone gas and dry air, respectively. The response time was defined as the time required for a change in the sample's electrical resistance to reach 90% of the initial value when exposed to the gas. Similarly, the recovery time was defined as the time required for the electrical resistance of the sensor to return to 90% of the initial value after the gas source had been turned off.

## III. RESULTS AND DISCUSSION

Fig. 2 shows typical scanning electron microscope images of pure and hybrid NiPc:ZnO NRs thin films. The NRs resulting from the hydrothermal method have diameter between 300 and 500 nm and length < 5 µm, according to Fig. 2(a). The modification with NiPc causes uniform coating of the NRs as observed in Fig. 2(b). Morphology is known to play an important role in governing the sensor response kinetics. Indeed, the surface area to volume ratio, porosity, surface roughness and film thickness are crucial parameters for the gas sensing properties of a material. Fig. 3 displays XRD patterns with an enlarge view of diffraction peak at 2Θ = 31.5 which attributed to diffraction from the (100) plane assigned to the hexagonal wurtzite phase of pure ZnO NRs. This diffraction peak (100) systematically shifts to higher 2Θ values when the ZnO NRs are modified with NiPc, which indicates that higher compressive strain is generated in ZnO close to NiPc:ZnO [12].

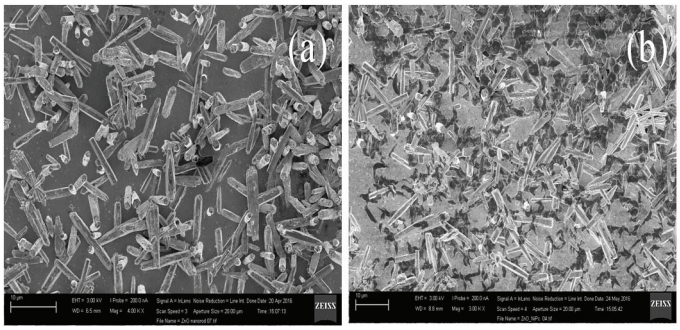


Fig. 2 SEM images of pure ZnO NRs and ZnO NRs modified with NiPc.

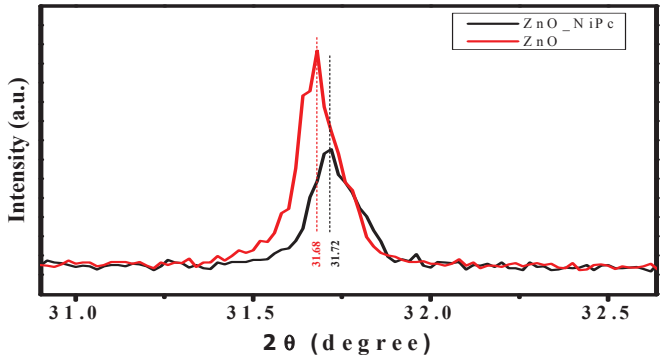


Fig. 3. X-ray diffraction data for NiPc grown film on ZnO NRs.

The electrical response of the heterostructure NiPc:ZnO film was investigated at a fixed operating temperature of 250˚C under the exposure of 80 ppb of ozone gas at different times (5 to 30 s). Fig. 4(a) shows that NiPc:ZnO is sensitive to ozone gas even for the shortest exposure time, with no evidence of saturation upon increasing the time. Fig. 4(b) shows that the best sensor response was obtained at 250°C for pure ZnO NRs, which is close to traditional gas sensors [12].

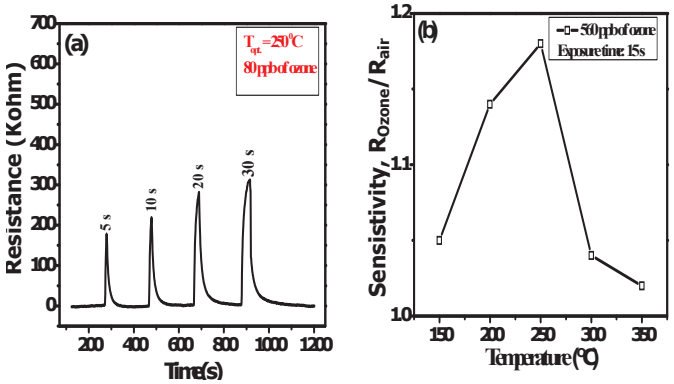


Fig. 4(a). Gas sensing response of the hybrid NiPc:ZnO film exposed for different times to 80 ppb $O_3$ at 250 °C. (b) Gas sensing response of ZnO NRs exposed to 560 ppb $O_3$ at different operating temperatures.

Additionally, we emphasize that the NiPc:ZnO films also detected the same amount of ozone gas, i.e. 80 ppb, at lower temperatures, even at room temperature. However, the recovery time was too long or could even not be reached.

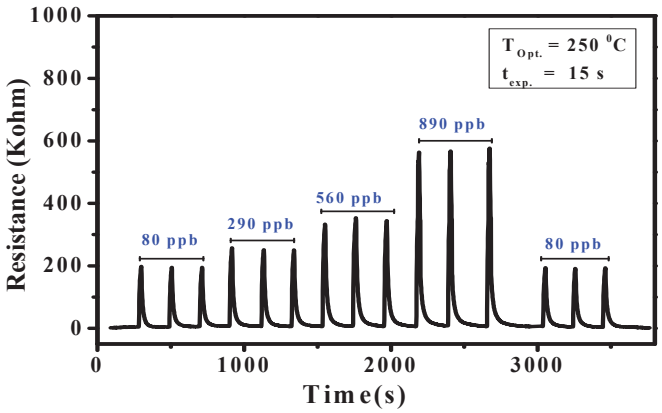


Fig. 5. Ozone gas sensing response for ZnO: NiPc heterostructure film as a function of the gas level at an operating temperature of 250°C.

For the remaining experiments, we used the optimized temperature of 250˚C. Fig. 5 displays the response curves for the NiPc:ZnO films, with good sensor response in the range 80 – 890 ppb, total reversibility, as well as good reproducibility for different ozone levels. The resistance of the sample increased upon exposure to the oxidizing gas, indicating the n-type semiconductor behavior.

Fig. 6 exhibits the response curve for ZnO and NiPc:ZnO heterostructure film at 80 ppb ozone for 30 s exposure time. It is clear that one layer of NiPc enhanced the sensitivity of ozone compared to pure ZnO NRs. The change is relatively small but if we increase the thickness of NiPc, the sensitivity increased [12]. In addition, the film shows a faster response (~ 22 s) and recovery (~33 sec) than pure ZnO nanorods (~26 s) and (~72 s) at 80 ppb. This hybrid film has also higher sensitivity, with 3.27 for the ratio between the resistances under ozone gas and dry air, compared to 2.56 for pure ZnO nanorods. The improvement in response time is ascribed to the large surface area of the NiPc layer grown over ZnO nanorods.

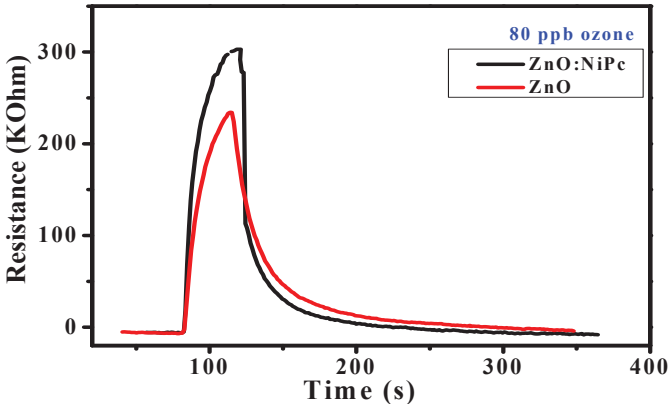


Fig. 6. Response curves for ZnO and ZnO:NiPc films for 80 ppb of ozone gas at an operating temperature of 250°C.

## Conclusion

A novel ozone sensor based on NiPc:ZnO heterostructures has been demonstrated. ZnO nanorods were synthesized using the hydrothermal method and a thin layer of nickel phthalocyanine was deposited on NRs by the layer-by-layer (LbL) technique. The heterostructure film exhibited an enhanced sensor response towards ozone at 250°C. The ratio between resistances is 3.27 for 80 ppb with the NiPc:ZnO heterostructures, to be compared with 2.56 for pure ZnO nanorods. Additionally, the heterostructured films show a faster response (~ 22 s) than the pure ZnO nanorods (~26 s) at lower ppb levels. Our results clearly indicate that NiPc modified ZnO NRs could effectively be used for practical ozone sensing applications.

## Acknowledgment

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