Highly Porous NiO Nanoflower-based Humidity Sensor Grown on Seedless Glass Substrate via One-Step Simplistic Immersion Method

N. Parimon, M. H. Mamat, M. K. Ahmad, I. B. Shameem Banu, M. Rusop

Abstract*: A highly porous nickel oxide (NiO) nanoflower was deposited directly onto glass substrates by the simplistic immersion method. The nanostructural property of the NiO was studied by X-ray diffraction pattern and obtained high crystal quality after annealing at 500 °C with an average crystallite size of 15.5 nm. The optical characterization was measured by ultraviolet-visible spectroscopy, with an average transmittance of 58 %. The value of 3.63 eV was estimated and confirmed as NiO bandgap energy. The current-voltage measurement result indicates that the NiO nanoflower has good electrical properties with resistance, resistivity, and conductivity value of 2.31 MΩ, 2.12 Ω.cm, and 4.71 × 10^{-1} S.cm^{-1}, respectively. The NiO is capable of performing satisfactorily as humidity sensor with a sensitivity of 138 with the response and recovery time were estimated at 389 s and 172 s, respectively. Besides, this sensor has stability at a humidity level of 40 - 90% relative humidity.

***Keywords*: Highly porous, NiO nanoflower, Glass substrate, Immersion method, Humidity sensor.**

I. INTRODUCTION

The humidity sensors based on metal oxide semiconductors such as TiO_2 [1], SnO_2 [2], WO_3 [3], Fe_2O_3 [4], ZnO [5], and NiO play an important role, most notably in the field of semiconductor, food processing, automotive, medical and health, and weather telemetry works. It can measure relative humidity (RH) and became an intermediary for monitoring and detecting both the moisture content as well as the air temperature.

In the family of metal oxides, NiO is rarely been used and investigated in the detection of humidity. More precisely, it is arguable that there is no comprehensive study on single NiO compound for humidity sensing applications that have been reported. The NiO is well known as the vital p-type metal oxide semiconductor that has captivating substance for its wide applications in sensors. This is due to its excellent chemical and thermal stabilities, as well as a large number of chemisorbed oxygen present in NiO compared with other metal oxides [6]. With certain and controllable synthesis techniques, the different dimensions, specific, and unique morphological NiO nanostructures can be produced, since the properties of the substance are potently dependent on it [6]. It is also crucial as it can determine the specific application in nanodevices.

Among the nanostructures-based NiO that have been synthesized using various methods, the three-dimensional (3-D) nanoflower structures were frequently reported for multiple applications. To date, the formation of 3-D NiO nanoflowers has attracted a great deal of their excellent in good physicochemical properties [7]. The unique and porous nanostructures also received a lot of consideration because of their high surface-to-volume ratio as well as the wide exposure area, which contribute to adequate dissemination path and improved reactive regions [8]. Some researches that have been conducted on NiO nanoflower-based sensing applications is by Wang et al. [8]. They have synthesized three hierarchical NiO nanoflowers with diverse petal thicknesses for ethanol gas sensors. Similarly, Miao et al. have reported NiO nanoflowers assisted with CTAB and SDS for their ethanol gas sensing performances [7]. Besides, Khorshidi et al. have successfully prepared an undoped, W-doped, and Pd-doped NiO nanoflowers for o-xylene detection [9].

Although many studies have been conducted into the synthesis of NiO nanoflowers-based gas sensing applications, it is still infrequent to be carried out the research for humidity detection. Starting from our previous research regarding nanocarnation-like NiO which is grown on indium tin oxide (ITO)-coated glass substrate [10], it is motivated to continue research and develop the application to the humidity sensor in the ambient temperature. However, on this work, a highly porous NiO hierarchical nanoflower was synthesized via one-step facile immersion method directly onto the glass substrate without any seed layer.

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NiO nanoflower is then annealed at an annealing temperature of 500 °C. Furthermore, the studies on structural, optical, and electrical that affecting sensitivity to humidity sensing were carried out.

II. FABRICATION METHODOLOGY

A. Experimental Procedure

Before the growth process of the NiO nanoflower, the glass substrate was cleaned for 15 minutes each with ethanol, acetone, and de-ionized (DI) water in the ultrasonic bath (Hwashin Technology PowerSonic 405, 40 kHz). Then, the glass substrate was blown using nitrogen gas for drying. The highly porous NiO nanoflower was then grown directly on the glass substrate using a mixture of three materials which involved one-step simplistic sol-gel immersion method. The precursor, stabilizer, and solvent used are nickel (II) nitrate hexahydrate, hexamethylenetetramine, and DI water respectively were mixed as the solution. The solution then went through a sonication process using an ultrasonic bath for 30 minutes. After that, the solution was stirred for 45 minutes at a constant speed of 300 rpm. Then, the sample was dried for 15 minutes at 150 ºC followed by annealing process at a temperature of 500 ºC for 1 hour in a furnace.

B. Characterization

The highly porous NiO nanoflower was identified the morphological studies by using field emission scanning electron microscopy (FESEM) (model: JEOL JSM-7600F). The crystallinity of the sample was investigated using X-ray diffraction (XRD) measurement (model: PANalytical X'Pert PRO). The optical property of the grown NiO was characterized using ultraviolet-visible (UV-vis) spectrophotometer (model: Varian Cary 5000). The electrical characteristic of the sample was analyzed using a two-probe current-voltage (I-V) measurement system (model: Advantest R6243). Lastly, the humidity sensing analysis was measured in a chamber (model: ESPEC-SH261) equipped with I-V versus time measurement system (model: Keithley 2400).

III. RESULT AND DISCUSSION

A. Surface Morphological Observation

Fig. 1 displays the morphological characteristic of the highly porous NiO nanoflower with observation at different magnifications by FESEM. It can be clearly seen from the image of Fig. 1 (a), the 500 °C-annealed NiO consists of hierarchical flower-like spheres with good dissemination. As shown in Fig. 2 (b) and (c), each of the clearer flower blooms are observed as pretty thin and congregated by a number of two-dimensional curving of highly porous nanosheets. Each nanosheet petal has an average thickness of about 20 nm thick, while the average diameter of individual NiO nanoflower is about 1.9 µm. The diameter size is approximate with reported by Liu et al. [11] which is about 2 µm, but it is much smaller when compared to reported by Wang et al. [6] which is about 4.7 µm. Meanwhile, a morphological image at a larger magnification of 75,000 × is shown in Fig. 1 (d). We can see from the picture each petal on the flower is formed from the chain of fine holes that are joined to each other. Overall, this nanoflower morphology is closely related and its shape looks almost identical to the nanocarnation-like NiO which grown on the ITO-coated glass substrate [10].

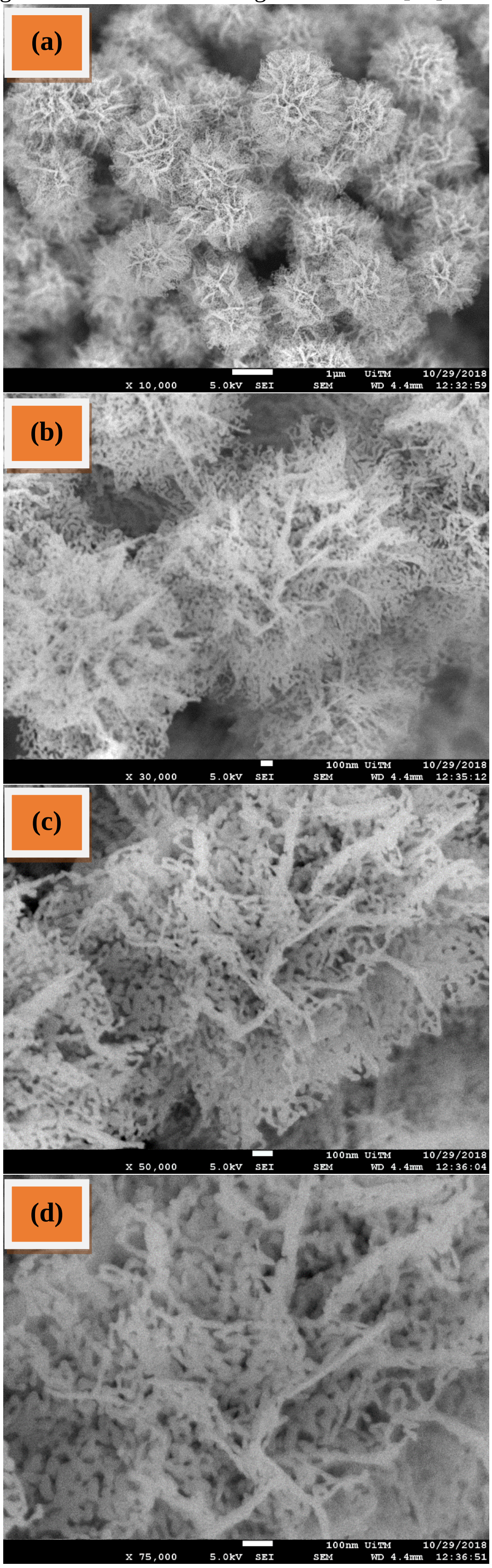

Fig. 1. FESEM images of the highly porous NiO nanoflower at different magnifications with (a) 10,000×, (b) 30,000×, (c) 50,000×, and (d) 75,000×.

B. XRD Analysis

The typical XRD pattern of the NiO nanoflower grown on a seedless glass substrate is shown in Fig. 2. By referring to the standard spectrum of NiO (JCPDS No. 01-075-0197), the diffraction peaks at the angle of 2θ can be indexed to the cubic type of β-NiO and display a polycrystalline structure. The diffraction patterns with high intensity revealed peaks at approximately 36.7 ° and 42.8 ° which can be indexed as (111) and (200), respectively. However, crystal planes of (220), (311), and (222) showed weak intensities at approximately 62.5 °, 75.1 °, and 79.0 °, respectively. The NiO was highly uncontaminated as there is no other peak was detected as impurities. The XRD peaks also show that no other diffraction peaks corresponding to nickel hydroxide, $Ni(OH)_2$. This result confirmed that it was completely converted into NiO at an annealing temperature of 500 °C same as reported by Parimon et al. [10]. In addition, the average crystallite size (D) of the NiO can be calculated according to the Scherrer formula (1):

$$D = (0.94\ \lambda)/(\beta \cos \theta) \quad (1)$$

where λ is the X-ray wavelength (λ = 1.54 Å), β is the full width at half maximum (FWHM, in rad) intensity of the peak, and θ is the diffraction angle of the peak. The values of β and θ were acquired from (200) plane orientation. Thereby, the calculated D of the NiO nanoflower is about 15.5 nm.

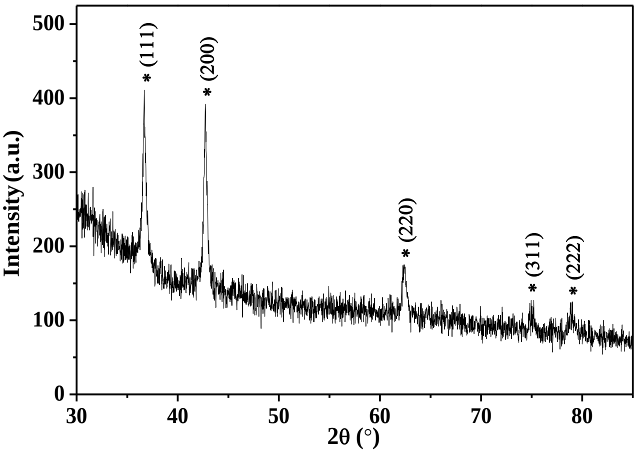

Fig. 2. The XRD pattern of NiO nanoflower.

C. Ultraviolet-visible Spectroscopy

The study of the optical properties from UV-vis spectroscopy enables us to obtain some important parameters such as optical transmittance and energy bandgap (E_g) for this highly porous NiO nanoflower. Fig. 3 demonstrates the optical transmittance of the NiO nanoflower where the measurement has been performed in wavelength ranges from 300 to 800 nm. From the graph, we can observe clearly that the transmittance of NiO nanoflower shows modest transparency. The average transmittance value of the NiO nanoflower in the visible region which is between 400 to 800 nm was estimated to be approximately 58 %. This may be due to the density of a bunch of nanoflowers and also their hierarchical structure causing the thickness to be high and thus blocks the absorption of ultraviolet light into the glass substrate.

To determine the E_g, the Tauc plot was generated and depicted in Fig. 4. The E_g of NiO nanoflower was determined from the intercept of the tangent to $(\alpha h\nu)^2$ versus photon energy ($h\nu$) with an estimated value of 3.63 eV with the thickness of the 500 °C-annealed NiO is approximately 727 nm. From the obtained value, it shows the E_g is within the range of wide bandgap (3.6 to 4.0 eV) [10] of NiO. The width of the E_g of the NiO nanoflower can be determined from the following relation:

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (2)$$

where E_g, α, A, and $h\nu$ is the optical bandgap, absorption coefficient, constant, and photon energy, respectively.

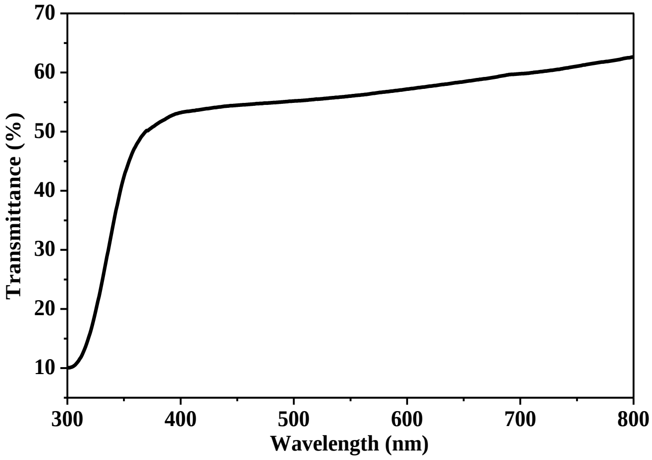

Fig. 3. Transmittance properties of NiO nanoflower.

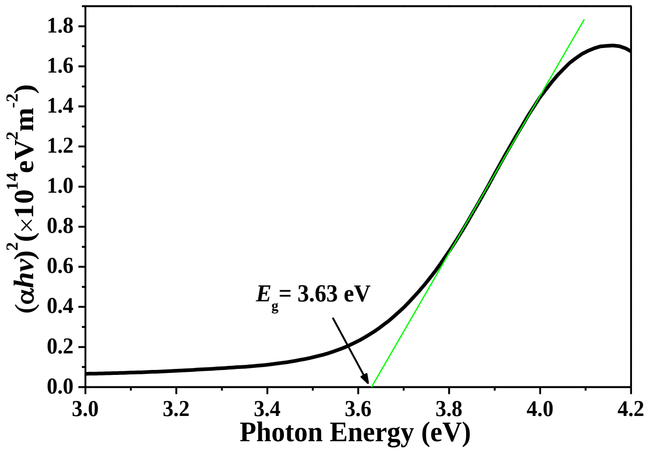

Fig. 4. The Tauc plot for an optical bandgap (E_g) estimation.

D. Electrical Properties

The I-V measurement plots using Pt electrode in the voltage range between −5 to 5 V at room temperature is depicted in Fig. 5. According to the obtained I-V characteristic, NiO nanoflower reveals an ohmic behaviour with a linear plot that complies Ohm's law. As mentioned by Mamat et al. [12], the current through a substance from one point to another is directly proportional to the voltage between those two points. The value of resistance (R), resistivity (ρ), and conductivity (σ) of the highly porous NiO nanoflower are further investigated and shown in Table I.

The resistivity of the NiO was calculated from the gradient of the I-V measurement plots using (3), while the conductivity as stated in (4) is vice versa from the resistivity value. As we can see from the calculated result, this NiO nanoflower has good electrical conductivity.

$$\rho = (V/I).(A/t) \quad (3)$$

$$\sigma = 1/\rho \quad (4)$$

where (V = voltage, I = current, A = the surface area of the electrode, and t = thickness).

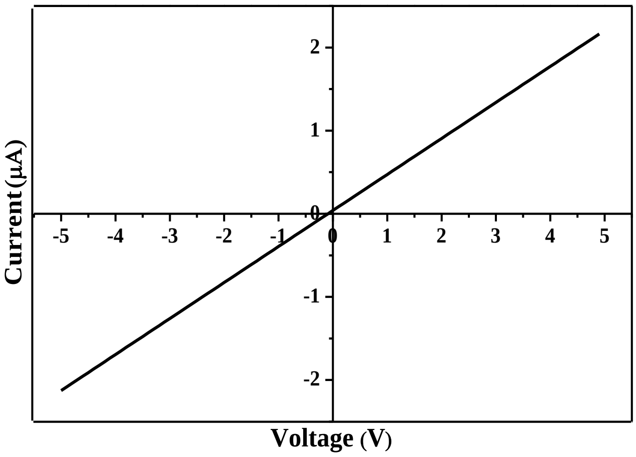

Fig. 5. I-V response of NiO nanoflower.

Table I: The resistance, resistivity, and conductivity values of NiO nanoflower

Resistance, R (MΩ)	Resistivity, ρ (Ω.cm)	Conductivity, σ ($S.cm^{-1}$)
2.31	2.12	4.71×10^{-1}

E. Humidity Sensing Performance

The humidity sensing response at ambient temperature on the highly porous NiO nanoflower can be observed in Fig. 6. The measurement has been conducted using 5 V bias at a humidity level between 40 to 90%RH. We can see from the response that the NiO displayed a stable current at 40%RH. Afterward, the humidity level was increased to 90%RH parallel with the current signal until they reached the maximum value at the humidity level of 90%RH. Subsequently, the humidity level was reduced to 40% RH to complete the response curve. From the graph of the response, the sensitivity (S), as well as the response (T_r) and recovery (T_c) time were measured. It was compiled and can be seen in Table II. From the humidity sensing result, the sensitivity was calculated to be 138 by referring to (5). By using the same fabrication method, it can be said that this NiO nanoflower has a very high sensitivity value if compared with the ZnO-based humidity sensor produced by Ismail et al. [13]. It might be due to the availability of the large surface area that intensified the diffusion of water vapors as well as facilitates the adsorption of water molecules during the sensing activity [14].

$$S = I_{max} / I_{min} \quad (5)$$

where I_{max} and I_{min} are the current values at 90%RH (highest humidity level) and 40%RH (initial humidity level), respectively.

In general, the response-recovery times refer to the time taken for the sensor to reach 90% of current change during adsorption-desorption activity [5]. The response and recovery time found to be 389 s and 172 s, respectively. The recovery time that has been calculated shows an approximate two times faster than the response time.

Generally, the humidity sensing mechanism based on metal oxide material is due to the protonic conduction which is the chemical reaction leaves H^+ ions, which jump from one site to another to contribute to the flow of electricity. At the very beginning, the water molecules are adsorbed on the highly porous NiO nanoflower surface to form the chemisorbed layer. When the RH level increases, more water molecules are adsorbed on the NiO nanoflower surface and the physisorbed water layer is formed on top of chemisorbed water monolayer. The thickness of the physisorbed water layer increases together with the increases in the RH level. Therefore, more H^+ ions can be generated during the protonic conduction at high RH levels and cause the current signals also to be high.

To measure the stability under identical condition, this NiO nanoflower-based humidity sensor was evaluated the sensing response between 40% and 90%RH for five cycles. The repeatability behaviour of the humidity sensor is presented in Fig. 7. The sensor shows an almost similar result with the same height at each curve. For this reason, it was realistic to exploit it in high-performance p-type metal oxide-based humidity sensor device with a variety of optimized synthesis.

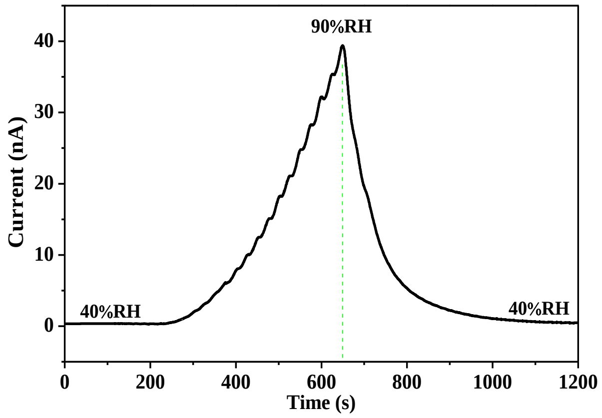

Fig. 6. Humidity sensor response with a bias voltage of 5 V.

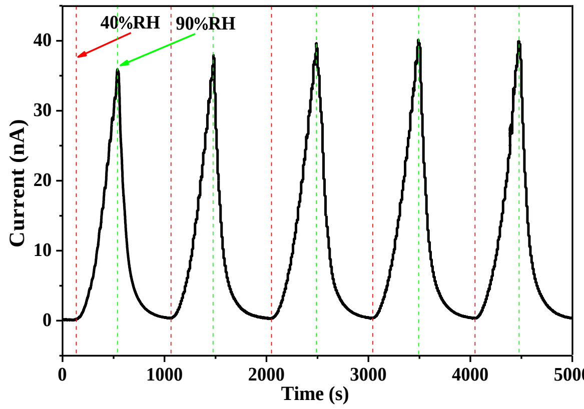

Fig. 7. Repeatability behaviour of humidity response for five cycles.

Table II: Response and recovery time along with the sensitivity of highly porous NiO nanoflower

Response Time, T_r (s)	Recovery Time, T_c (s)	Sensitivity, S
389	172	138

IV. CONCLUSION

We found that the highly porous NiO nanoflower with the high surface area can be fabricated using a direct synthesis onto the glass substrate without any seed layer. The NiO nanoflower can be said quite transparent and firmly attached to the substrate. The morphology with highly porous nanoflower and the hierarchical structure is added value since its high surface area and stability of the structure strongly help in detection of the humidity sensing. It has proven to perform well in the application of humidity sensor. In conclusion, the sensitivity value for the NiO nanoflower-based humidity sensor is 138, while the recovery time is approximately two times faster than the response time.

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