Ultra-sensitive behaviour of ruthenium-doped nickel ferrite thin film humidity sensor

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ABSTRACT
Chemical sensors of homogenous particles, act as active centres, are envisaged for adsorption/desorption of water molecules. The adsorption/desorption of water molecules are lined up with surface of the sensor device. The sensor material was prepared via efficient chemical co-precipitation method. The ruthenium-doped nickel ferrite sensor endows ultra-sensitivity for humidity i.e. 4.04 and 4.37 MΩ/% relative humidity at low- and mid-range, respectively with rapid response/recovery time of 35/148 s.

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1. Introduction

Humidity is a root cause of decomposition, condensation, structural damage, health issues and corrosion, etc. [1]. Among these, corrosion accelerates the decrease of production efficiency followed quality from the industrial application perspectives [2]. Condensation of water molecules over metal surfaces takes place owing to relative humidity (RH). Higher condensation of water molecules legitimates ionic conduction that eventually accelerates corrosion phenomena which is common in machineries, precision parts and electronic devices which finally and gradually turns into debris (rust) [3]. In industry, the critical humidity level is close to 45% for clear and polluted air. The scales of humidity level are 10–20%, 20–70% and 70–95% [4,5]. From the classification of humidity, 20–70% humidity is the optimum humidity level to skip the corrosion. In this regard, the industries should develop ultra-sensitive sensors. Some of the sensors demonstrate high sensitivity towards 10–30% RH, below 30%RH, above 60%RH and elevated temperatures [6]. Ferrite-based sensors are efficient, non-toxic and economical candidates for humidity sensing applications and also used for broad scope of technological development [7–17]. Nickel ferrite, with inverse spinel structure, demonstrates a better electrical resistivity...
Ruthenium occupies octahedral and tetrahedral sites at partially or fully according to site preference which establishes normal or inverse spinel structure with lack off homogenous structure. Thus, coupling of different elements leads to promote the sensing performance of humidity sensor under investigation. Ruthenium has frequently been used for surface modification in literature to enhance the electrical conductivity of humidity sensor materials due to its precise electronic storage ability and fine electrical conductivity which produces high sensitivity at any one of the humidity level discussed above. The doping of impurity atoms can be adjusted over surface of the sensor material that can engineer adsorption/desorption of water molecules [21]. Resistive-type sensor increased detection level of RH in past few years [22]. On other hand, the repeatability of the sensor reaffirms reliability and long-term stability [23]. Nanostructured material can be prepared through chemical co-precipitation method and this method has some distinct features such as high yield, good purity, easily reproducible and low cost [24–28]. In addition, the prepared material may be called as nanocomposites and it have some advantages such as high surface to volume ratio, enhanced optical behaviour, better mechanical strength and electrical conductivity [29–32].

In this work, we report on %RH sensing application of ruthenium-doped nickel ferrite sensors at three different ranges. Ru-doped nickel ferrite sensor is outperformed in first two range of RH. Also, the sensor yields highest sensitivity and fast response cum recovery times. The sensor demonstrates ultra-sensitive for 10–20 and 20–70%RH levels. The sensitivity is significantly down at high %RH. This sensitivity is compared to earlier data and given in Table 1, claiming a bright future for reusability of the present humidity sensor. Ageing test elucidates that sensor has negligible ageing effect. Also, the sensor reproduces 96.4% performance after the few weeks, suggesting moderate chemical stability and mechanical robustness.

2. Experimental details

Ruthenium chloride, nickel chloride and ferric chloride were used for preparing required product. Those materials were disintegrated separately using double distilled water. Disintegrated solutions were stirred and then assorted to ferric solution. Subsequently, the sodium hydroxide appended to assorted solution whose pH was adjusted to 11 by liquid ammonium hydroxide solution. Assorted solution was rinsed using glass-rod and then impurities were spread on the top of the water surface where impurity content and precipitate were separated after few hours of rinsing. The extraction of the impurities from precipitate was obtained after one month which was dried and grinded. The powder was coated on borosilicate substrate and then annealed. Structural elucidation and morphology confirmation were obtained using scattering technique of X-ray diffraction (XRD) and
scanning and transmission electron microscopy (SEM and TEM) digital images, respectively. %RH sensing operations were performed using LCR meter.

3. Results and discussion

Figure 1 displays XRD pattern of the Ru-doped NiFe$_2$O$_4$ thin film sensor. The XRD pattern was taken during slow scanning process with step size of 0.02 degree. The Ru-doped NiFe$_2$O$_4$ sensor acquired (111), (220), (311), (222), (400), (422), (511), (440) and (622) reflection planes. Out of these reflection planes, the (311) reflection plane revealed high intensity which, in accordance with JCPDS card (74-2081), assures the formation of ferrites. An intended average particles size is $\approx 33$ nm.

Figure 2a–c displays surface appearance of Ru-doped nickel ferrite under different magnifications along with elemental mapping analysis. Figure 2a shows SEM images where homogeneously distributed ice-cube-like crystallites are clearly identified. These crystalline shapes of nanoparticles are ice cube structure of nanoparticles was discovered at 100 nm magnification as depicted in Figure 2b. The surfaces of these crystallites were well-polished. Perfectly ice cube structure corresponds to smooth surface which implies elements are homogeneously disseminated on the surface of the sensor. The elemental mapping spectrum obtained through EDX analysis reveals the presence of constituent elements of O, Fe, Ni and Ru, confirming successful doping of Ru in nickel ferrite.

Figure 3a shows a humidity sensing character of Ru-doped NiFe$_2$O$_4$ RH sensor device which is perceived from impedance versus relative humidity (%RH) where RH sensing is divided into three phase as discussed above. The impedance unveils linear decrease towards %RH which is common in all levels of test. The water molecule being highly polar attracts the metal part of the sensing element and to form the strong chemical bond between the metal and hydroxyl ion. The impedance of the sensor device decreases due to increase of the %RH suggesting an improvement in ionic conductivity of the sensor device. With the exposure of humidity, water molecules hit the sensor surface which corresponds to the impedance change. The adsorption/desorption of water molecules unveils nearly same nature as seen in Figure 3a. The sensitivity of the device was $4.04 \text{ M}\Omega/\%\text{RH}$.
Figure 2. (a) SEM, (b) TEM and (c) EDX images of Ru-doped NiFe$_2$O$_4$ nanomaterial.

Figure 3. Sensing performance of Ru–NiFe$_2$O$_4$ RH sensor with (a) sensing response, (b) reproducibility, (c) ageing effect and (d) response/recovery time measurements.
in 10–20%RH. In second phase, the sensitivity increased and set the value of 4.37 MΩ/
%RH which considerably declined in 70–100%RH. Average sensitivity of the device
was 3.20 MΩ/%RH. The fabricated sensor device could outperform in 10–20 and
20–70%RH which is one of the notable results in humidity sensor fabrication studies
reported till date. From this result, the as-developed Ru-doped nickel ferrite sensor
device endowed ultra-sensitive performance at low and mid-range levels of RH whilst
poor sensitivity at higher RH side. Figure 3b implies recycling test of the sensor device
at 10–100%RH. The figure implies adsorption of water molecules on the surface of the
sensor device. The recycling test confirms the repeatability where sensor device pro-
duced 96.4% repeatability. However, the adsorption curve presented same curve as
compared to principal experiment. The standard deviation figure demonstrated neither
repeatability nor reproducibility of the device. The low and mid-range of RH sensitiv-
ity unveiled maximum reproducibility whereas, high humidity presented poor repro-
ducibility. Reproducibility confirms reliability of the sensor device designed in the
laboratory.

Figure 3c confirms ageing test of the Ru-doped RH sensor device. Ageing test was per-
formed in two phases i.e. after one and two weeks. The impedance of the sensor device
demonstrated similar nature on merging one another, indicating insignificant ageing
effect. Figure 3d implies response/recovery time of the sensor device where the response
time was measured from adsorption whilst recovery time was confirmed while desorption
of water molecules. The response/recovery time of the sensor device was 35/148 s. The
capability of sensing device to humidity can be enhanced due to the doping of Ru and it
has good electrochemical sensing nature [39]. Also, ruthenium could occupy the sites for
more active centres for adsorption/desorption.

RH sensing mechanism of sensor device depends on impedance change. First, the
impedance of the sensor device decreased with increase of RH, suggesting n-type semi-
conductor behaviour of sensor material. The humidity could be transported to the device
and then adsorption might favour, facilitating chemisorption on the active sites of the
sensor device surface with additional two hydroxyl ions and protons formation. The
hydroxyl and protons were formed through dissociative mechanism for every water mol-
ecule [40]. This dissociation could afford more protons that plays role of charge hopping
to site over device surface [41]. Thereby, RH sensor device acquired high impedance and
sensitivity in 10–20%RH. In 20–70%RH, the impedance of device decreased whereas water
molecules increased which is a result of bonding of hydrogen to hydroxyl group which
could be ionized into hydronium ions with increase of ionic conductivity and decrease of
impedance[2]. Also, the device offered high sensitivity. In 70–100%RH, the impedance of
the device was severely reduced. Here, enormous amount of water molecules could adsorb
on forming continuous water layer through the process of physisorption. Additionally,
more water molecules could provide number of protons which on decomposing from
decreases impedance rapidly [42]. Simply, the water molecules that were transported to
the intermediate layer of the sensor device could decompose into hydroxyl and proton.
This decomposed proton combines with water molecule to form hydronium ion respon-
sible for ionic conduction [19]. Water layer thickness increased due to the high humidity
[6]. Here, continuous ion transportation was established and then hydrated hydronium
ions were easily transported to the device which elevates the ionic conductivity of the RH
sensor device [43]. In summary, the ionic conductivity of the sensor device was more pro-
nounced. The ruthenium-doped nickel ferrite RH sensor revealed ultra-sensitivity for
humidity below the critical level.
4. Conclusions

Efficient route of chemical co-precipitation is used to synthesize the mighty material of Ru doped NiFe$_2$O$_4$ sensor. The Ru-doped RH sensor demonstrates good sensing behaviour. In addition to this, the material reveals homogenous structure that benefits the chemisorption and physisorption. The fabricated sensor shows enhanced RH sensing capability and significant effects in sensitivity nature. The present sensor device is highly preferable to avoid corrosion. We demonstrated that ruthenium doping offered ultra-sensitive behaviour.

Disclosure statement

No potential conflict of interest was reported by the authors.

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