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Review Article

Research Progress on Humidity-Sensing Properties of Cu-Based Humidity Sensors: A Review

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Novel humidity sensors based on semiconducting metal oxides with good humidity-sensing properties have attracted extensive attention, which due to their high sensitivity at room temperature, high safety, low hysteresis, and long-term stability. As a typical p-type semiconductor metal oxide, CuO is considered to be a high-performance moisture-sensitive material; however, with the development of production, the complex working environment has put forward higher requirements for its humidity sensitivity, especially sensitivity and stability. In this regard, workers around the world are working to improve the moisture-sensing properties of sensing elements. In this review, the humidity-sensing properties of CuO-based moisture-sensitive materials are comprehensively summarized, focusing on effective measures to improve the moisture-sensing properties of CuO-based moisture-sensitive materials, including surface modification and nanocomposites. The future research of semiconducting metal oxide humidity-sensitive materials is also prospected.

1. Introduction

As the source of life, water plays an important role that cannot be ignored in the production process of human daily life. It is also one of several basic substances that constitute the human body. Among the vast majority of substances used by human beings, water exists [1], and even low levels can affect the properties of the material. Therefore, before conducting the experimental operation, we need to measure the water content in the operating environment to avoid its influence on the experimental results. Importantly, the word "humidity" is usually expressed as the amount of water vapor in the atmosphere [2].

Humidity sensor is used to measure ambient humidity and is an important device widely used in our production and experimental process [3]. It can effectively monitor ambient humidity to improve human comfort. In addition, humidity sensors can also be used in medical, construction, biological, environmental monitoring, and other fields [4–7]. In order to prevent humidity from interfering with the measurement results, the humidity value of the experimental environment should be carefully measured and controlled by a humidity sensor [8].

The performance of the humidity sensor determines that only those materials with high sensitivity, rapid response, nontoxicity, and easy processing have the potential to become humidity-sensitive materials. Different types of humidity sensors have been developed using a variety of materials with good humidity sensitivity, among which the most distinctive ones are semiconductor metal oxides [9] and organic polymer materials [10], in addition, carbon-based materials, and it has also gradually become a research hotspot in humidity-sensitive materials [11]. And their composite materials [12] even show better humidity-sensitive properties than individual materials in some aspects. The new humidity sensor based on semiconductor metal oxide not only has high sensitivity but also can effectively detect humidity value in a wide range of humidity. With these advantages, the humidity sensor based on semiconductor metal oxide has gradually become the most popular in the field of humidity sensing [13, 14]. For this type of humidity sensor, the sensing mechanism is explained as the change in the resistance of the sensing element, which is now accepted by most people, and it is believed that when the humidity-sensitive material is exposed to the atmosphere, the surface of the material is exposed to water vapor. A physicochemical reaction causes the impedance of the material to change.

Among many semiconducting metal oxides, CuO has many unique physical and chemical properties, and it is nontoxic and easy to prepare, relatively stable in properties, and low in production cost [15]. For applications in humidity sensing, CuO is also the most popular material among several copper-based metal oxides [16]. It is worth mentioning that, compared with copper oxide, the two materials, Cu_2O and Cu_2O_3, are less stable and difficult to prepare, so they have great limitations in the application of humidity-sensitive materials. As a typical p-type metal oxide, CuO has a monoclinic structure with a narrow bandgap of only 1.2 eV [17, 18]. These properties make CuO widely concerned and applied in photothermal [19] and photoconductive fields [20]. In addition, studies have shown that copper oxides exposed to different gas atmospheres remain stable and exhibit relatively low changes in base resistivity, indicating that the application of copper oxides can effectively reduce the material cost in humidity-sensing elements [21].

Cuprous oxide (Cu_2O) is also one of the typical p-type semiconductor metal oxide materials. Although both are copper oxides [22], there are still many differences between Cu_2O and CuO, especially in terms of structure and performance. First, copper oxide is a black metal, but cuprous oxide is red; secondly, the structure of copper oxide is more complex, which is a monoclinic crystal structure. In this regard, the structure of cuprous oxide is much simpler, which is a typical cubic structure; in addition, cuprous oxide has a complete Cu 3d shell, and its direct bandgap is higher than that of copper oxide, which is 2.17 eV [23, 24]. In contrast, copper oxide has a very narrow bandgap (1.2 eV), which is fully capable of absorbing near-infrared light [25] . Recent reports claim that cuprous oxide has inferior electrical conductivity compared to cupric oxide but occupies a certain advantage in carrier mobility [26]. However, based on the principle of semiconductor metal oxide humidity sensor, it is clear that copper oxide with higher conductivity is more suitable as a humidity-sensitive material.

Although CuO and Cu_2O, two copper-based semiconductor metal oxides, have great differences in properties, they also have similarities in performance. For example, both of them have relatively low bandgap energy and excellent activation and catalytic performance. Both materials are nontoxic and easy-to-produce safe materials [27–30], which are widely used in optoelectronics, humidity sensing, and batteries and various in the catalytic process. In recent years, the synthesis and preparation of CuO and Cu_2O and the optimization and improvement of their nanostructured surface morphology have been extensively studied, and tremendous progress has been made [27, 28, 31–33]. However, copper oxide has gained greater attention and more in-depth research in the field of humidity sensing due to its better stability.

CuO is a typical chemical resistance sensing material, and its humidity sensing is mainly controlled by the change in the resistance of the humidity-sensing material itself when water and water derivatives (water vapor) contact and react with its surface [35]. In a humid atmosphere, water molecules in the environment will be adsorbed to the surface of the CuO material. Adsorption can be divided into physical adsorption and chemical adsorption [36]. When the relative humidity is low, the surface of CuO is lightly covered by water vapor molecules, chemical adsorption occurs, and the charge transfer is ensured by the hopping of protons (hydrogen ions) between the hydroxyl groups adsorbed in the chemical adsorption layer. The chemical adsorption layer that has been formed will continue to adsorb water molecules and then form physical adsorption. The water molecules form a physical layer on the hydroxyl group through hydrogen bonds (Figure 1), and a large number of water molecules are ionized into hydronium ions (H_3O^+). According to Grotthuss's Transport mechanism, it is between hydronium ions and water molecules. When the relative humidity is high, hydrogen ion exchange is a process in which protons (hydrogen ions) hop between adjacent water molecules, creating conduction, increasing ionic conductance, and reducing impedance values [37]. Therefore, it is due to the change in sensor resistance that humidity detection is achieved. There is no doubt that the adsorption of water vapor occurs on the surface of the copper oxide humidity sensor, so any factor that affects the apparent morphology of the material will significantly affect the impedance of the material. At present, the research of humidity sensor based on copper oxide has made great progress, and its humidity-sensitive performance shows outstanding advantages in response speed, selectivity [34, 38], etc. In particular, the selectivity of copper oxide to humidity is better than that of the commonly used metal oxide SnO_2. Under high humidity conditions, copper oxide shows high sensitivity to humidity [39]. The influence of other interfering gases in the ambient atmosphere on the copper oxide-based humidity sensor is basically negligible, and under low humidity conditions, gases such as H_2S will react with oxygen on the surface of the material, releasing electrons to reduce the resistance of the material [40]. Therefore, copper oxide-based humidity sensors can detect NH_3 and H_2S at low humidity levels [41, 42].

In the past ten years, more than 900 papers have been published on the humidity-sensing performance of copper oxide, and the number of papers has been increasing year by year (Figure 2). In the preparation of copper oxide humidity-sensitive materials, in addition to the traditional hydrothermal method and chemical deposition method [43], some new methods such as biosynthesis and microwave-assisted chemical solution synthesis have gradually attracted the attention of researchers [16, 44]. However, only a few reports describe the introduction of synthetic strategies for CuO nanostructures and their related applications [28, 31, 33]. Quite a few of these papers focus only on the production and fabrication of one-dimensional copper oxide nanostructures [27, 28, 31]. However, with the continuous development of production and processing technology and the increasingly complex production and experimental environment, the demand for the performance of humidity

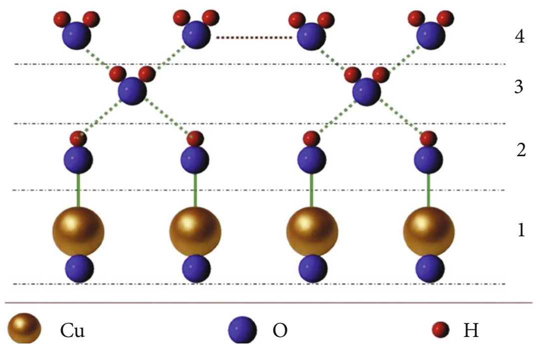


Figure 1: Schematic diagram of the humidity-sensing mechanism of CuO [34].

sensors is gradually increasing. The existing copper oxide humidity sensor urgently needs to be further improved and improved in some humidity-sensitive properties, especially the sensitivity and stability of humidity sensing [45, 46].

As far as we know, the performance of the humidity sensor depends to some extent on the surface topography of the humidity-sensitive material, including the size, the number of defects, and the specific surface area [47]. In addition, the working temperature is also an important factor. This temperature affects the electron migration rate inside the humidity-sensitive material and controls the electrical conductivity of the material [48]. The optimal operating temperature of traditional copper oxide-based humidity sensors is usually between 120 and 150 degrees Celsius [49]. But such humidity sensors also have good humidity sensitivity at room temperature. Operating in a high temperature environment limits the wide application of such humidity sensors, because high temperature operation means energy loss and waste, which is seriously inconsistent with the concept of energy conservation and emission reduction in today's society. High temperature environments can also affect the stability of the humidity sensor, resulting in deviations in the measurement results. In addition, the copper oxide-based humidity sensor that operates at room temperature does not require an additional heating device, which reduces power consumption, and also makes the sensor smaller and easier to carry. Therefore, according to the current development trend, copper oxide-based humidity sensors with good humidity sensitivity at room temperature are more in line with the needs of production and life in today's society [50].

In addition to the working ambient temperature, other gases in the atmosphere are also one of the main reasons that affect the performance of the humidity sensor [51], especially gases like NH_3 and H_2S. They can be adsorbed on the surface of the copper oxide humidity-sensitive material and react with the molecular sites of oxygen to limit the normal adsorption of water vapor [52]. Therefore, when studying the humidity-sensitive properties of materials at room temperature, the interference of other gases needs to be considered, which requires the material to have good selectivity to humidity [53]. Fortunately, copper oxide-based humidity-sensing materials have good selectivity to humidity. Under high humidity conditions, the effect of interfering gases on the sensor is basically negligible. Under low humidity conditions, most organic volatile gases do not affect the measurement of humidity by copper oxide-based sensors [34]. In short, the biggest challenge for the further development of the current copper oxide-based humidity sensor is how to improve its sensitivity and response speed.

Although many articles have reported improving the sensitivity and response speed of copper oxide-based humidity sensors to a certain extent so far, this has not fully met the needs of the work. Perillo et al. [54] synthesized copper oxide nanofilms on silicon wafers by the continuous ionic layer adsorption reaction method (SILAR), and the fabricated sensors exhibited good response and recovery time at room temperature. Hsu et al. [55] synthesized high-density CuO/Cu_2O composite nanowires by heating oxidation method, which effectively improved the sensitivity of the sensor to humidity. Much work has been done to improve the humidity sensitivity of the sensor, including surface modification based on copper oxide nanomaterials and doping of various additives with different properties, and the enhancement mechanisms of these two technologies are different, which will be explained in detail in Sections 2 and 3 below.

But to the best of our knowledge, substantial progress has been made in extensive research on CuO-based humidity sensors, and reviews on this related topic are lacking. In this paper, the humidity-sensing properties of copper oxide-based humidity sensors are summarized, and the effective strategies and mechanisms to improve the humidity-sensing performance of copper oxide-based sensing elements are discussed. We hope to provide some inspiration for future research on semiconductor-based metal oxide humidity sensors.

2. Surface Modification

At present, the materials of humidity sensors are mostly nanomaterials, because the size of nanomaterials is smaller, which is conducive to the current research direction of miniaturization of humidity sensors. In addition, nanomaterials have more prominent physical and chemical properties than ordinary bulk materials. Usually, nanomaterials have a large specific surface area, which makes a considerable part of atoms located on the surface of the material [56–58], fully in contact with the outside atmosphere, and the specific surface area of nanomaterials is closely related to its size.

Obviously, the nanostructured copper oxide is smaller in size, which makes its specific surface area much higher than that of ordinary copper oxide bulk material. In addition, the surface of copper oxide nanomaterials has more active centers, which fully shows the great advantages as humidity-sensitive materials. It has been found that the grain size of copper oxide nanostructures is an important factor affecting its moisture-sensing properties [34]. In recent years, how to reduce the grain size of copper oxide nanostructures has become the goal of many scientific

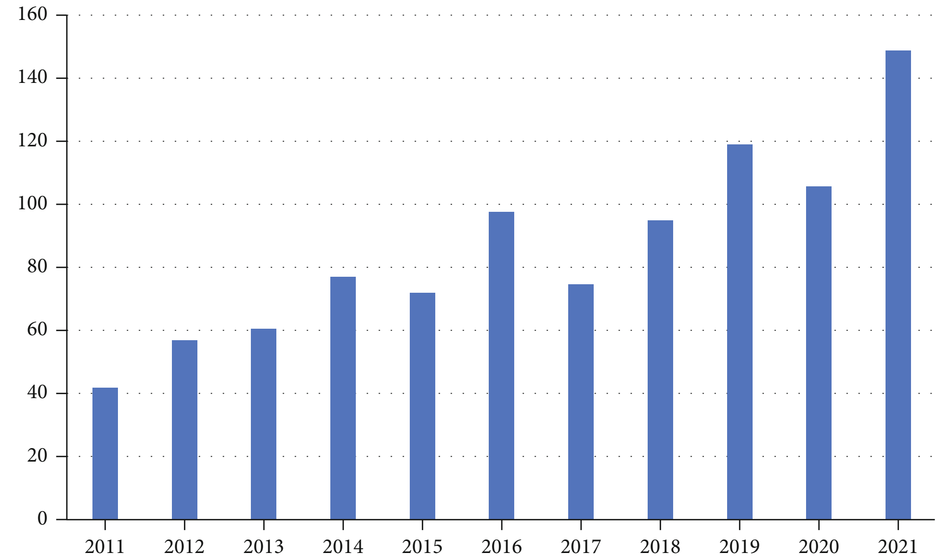


Figure 2: Number of papers on CuO-based humidity sensing.

experiments. But it is worth mentioning that the grain size cannot be reduced indefinitely; van der Waals force is an important factor to promote particle aggregation, and its size is inversely proportional to the grain size [59]. This means that if the particle size is blindly reduced, although the size and specific surface area of the material are effectively improved, the thermal stability of the material will be seriously reduced, and the resistance of the gas diffusion process between particles will also increase, which will affect the material's moisture-sensitive properties [60]. In addition to the size of the grains, the surface morphology of the copper oxide nanostructures also affects the humidity-sensing properties of the sensing element. In reality, there are always some defects and pores on the surface of nanomaterials. The morphology and structure of these regions are different, and the diffusion ability of water vapor molecules in these regions is also different. Different copper oxide nanostructures have large differences in their spatial structure and surface area, and these properties will lead to different diffusion capabilities of water vapor during the adsorption and desorption processes on the surface of copper oxide.

In general, the nucleation and growth process of copper oxide nanostructures are controlled by adjusting the parameters of material preparation and synthesis [61], which in turn affects the surface morphology of nanostructures, such as increasing the surface porosity and increasing the grain size [62], so as to obtain copper oxide nanostructured materials with good moisture-sensitive properties. In particular, some complex structural materials are composed of basic one-dimensional nanostructures, such as nanorods and nanofibers. Its complex layered structure can effectively improve the electron mobility of the material, thereby effectively reducing the impedance of the humidity sensor [28, 63, 64].

So far, researchers around the world have designed and synthesized CuO nanostructures with various morphologies through various methods to realize CuO-based humidity sensors.

Malook et al. [34] reported that CuO nanoparticles were prepared by decomposing basic copper carbonate (BCC) at high temperature (Figure 3), which has a large specific surface area (56.25 m2/g). Its average pore size is 32-37 nm. At 293 K, the RC response of the humidity-sensitive material varies with frequency and relative humidity as shown in Figure 4(a). Expose the sensor to moisture and notice a sudden drop in resistance. A graphical representation of the resistive and capacitive responses of moisture-sensitive materials as a function of applied frequency was also investigated (Figure 4(b)). It was found that the effect of frequency on the resistance and capacitance response dominates at low humidity levels. However, at higher humidity, the effect of frequency on the moisture-sensitive materials' resistive response is negligible. The humidity sensor has a good response/recovery speed, which indicates that the sensitivity of the humidity sensor with mesoporous copper oxide particles is better (Figure 4(c)). Even after 30 days of alternating exposure to a higher humidity environment (90%RH) and an indoor humidity environment, the sensor still maintained a good sensing behavior with little change in the dynamic response curve (Figure 4(d)). In addition, the authors also studied the humidity selectivity of copper oxide nanoparticles. By detecting the response of the sensor to different interfering gases (H_2S and NH_3) in different humidity environments, it was found that under high humidity conditions, interfering gases have little effect on the sensor, and it shows that this material has good selectivity to humidity.

Rupashree and colleagues [65] selected green tea extract as the raw material and synthesized a new type of moisture-sensitive material by sintering(Figures 5(a) and 5(b)) with a particle size of 64.5 nm, and CuO NPs achieved an optimal 99% (7–97% relative humidity). It may be due to the increase in grain size, which leads to the change of the surface

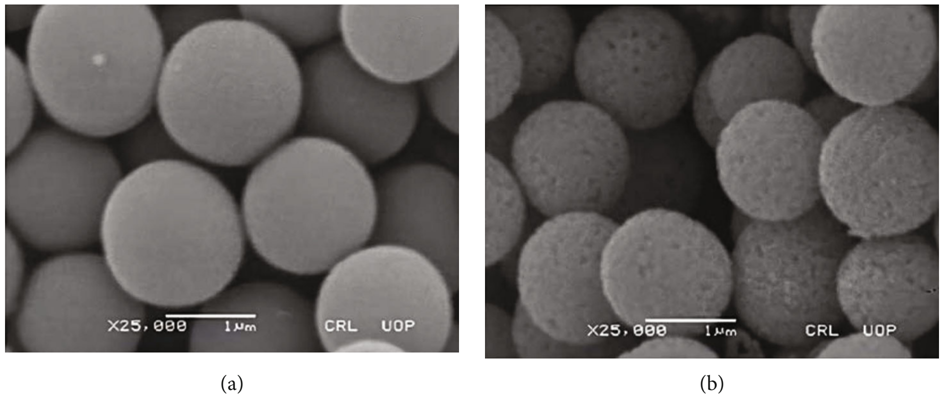


Figure 3: SEM micrograph of (a) basic copper carbonate and (b) calcined CuO [34].

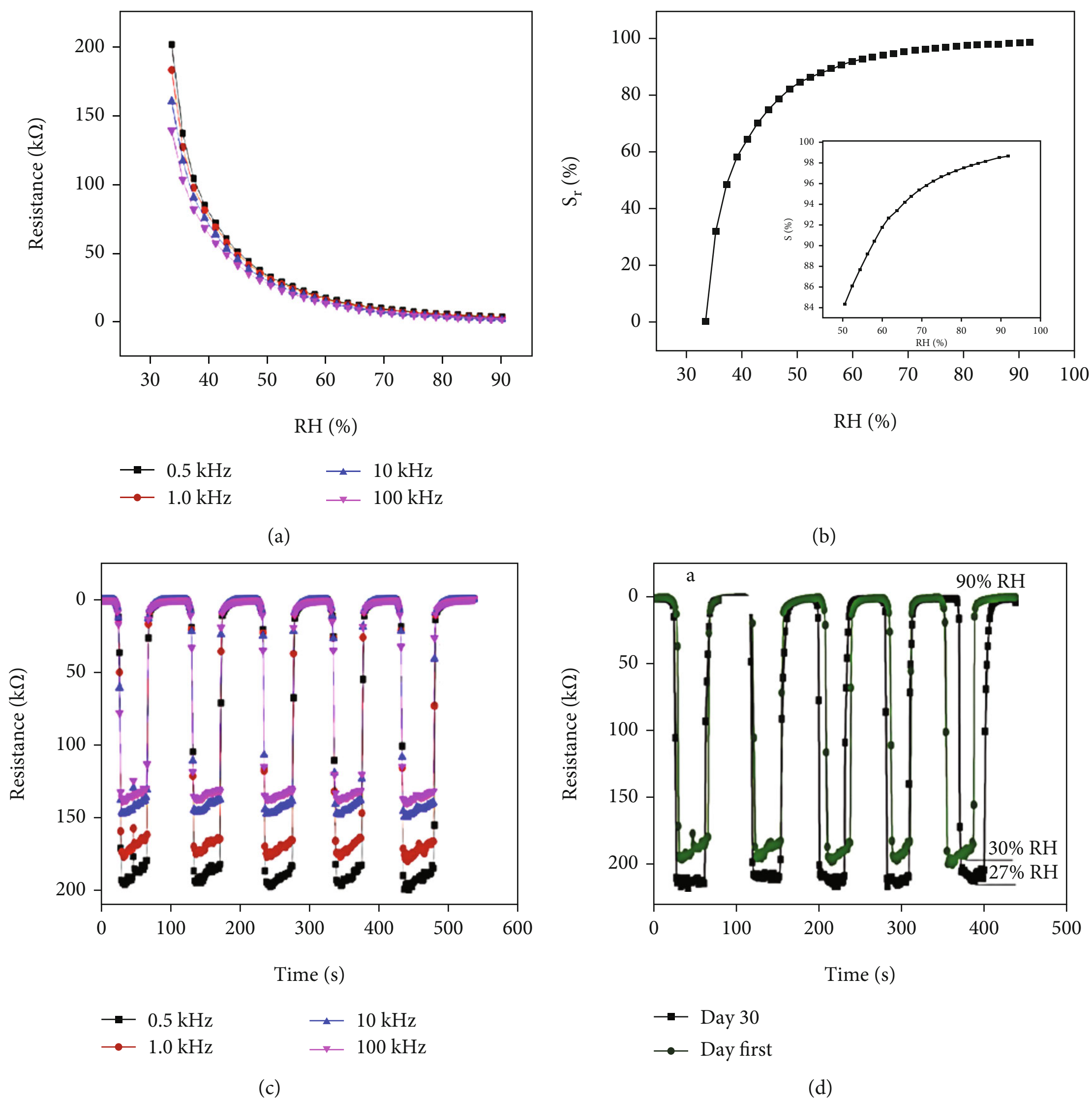


Figure 4: (a) Graph of the change of resistance with humidity at different frequencies (CuO-based sensor). (b) Copper oxide-based humidity sensor resistance sensitivity change graph with humidity (18-22°C). (c) Resistive dynamic response to humidity under a CuO-based humidity sensor (18-22°C). (d) Comparative resistive dynamic response of CuO-based sensor towards humidity on day first and after 30 days [34].

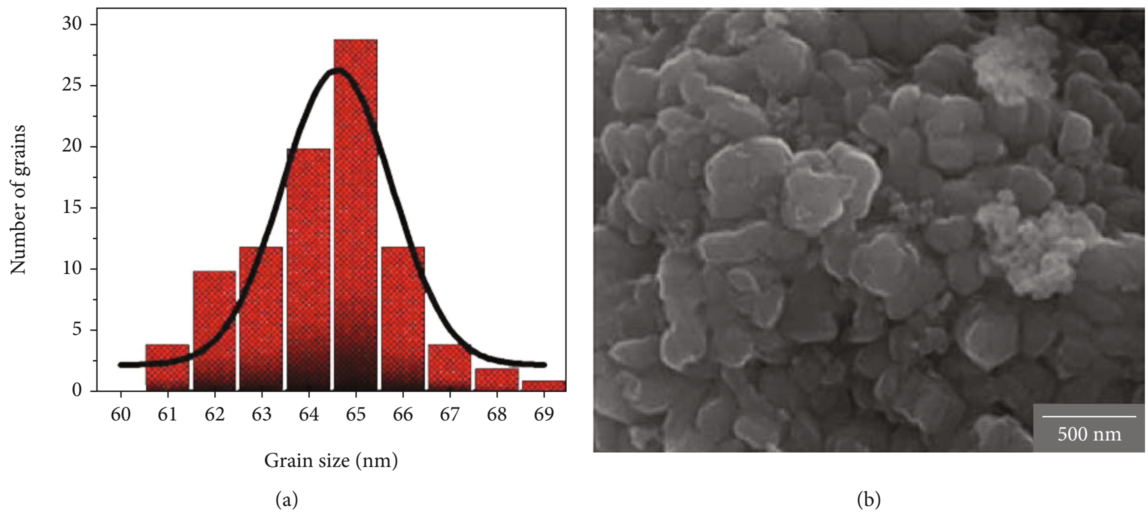


Figure 5: (a) Histograms for grain size. (b) SEM image of CuO NPs [65].

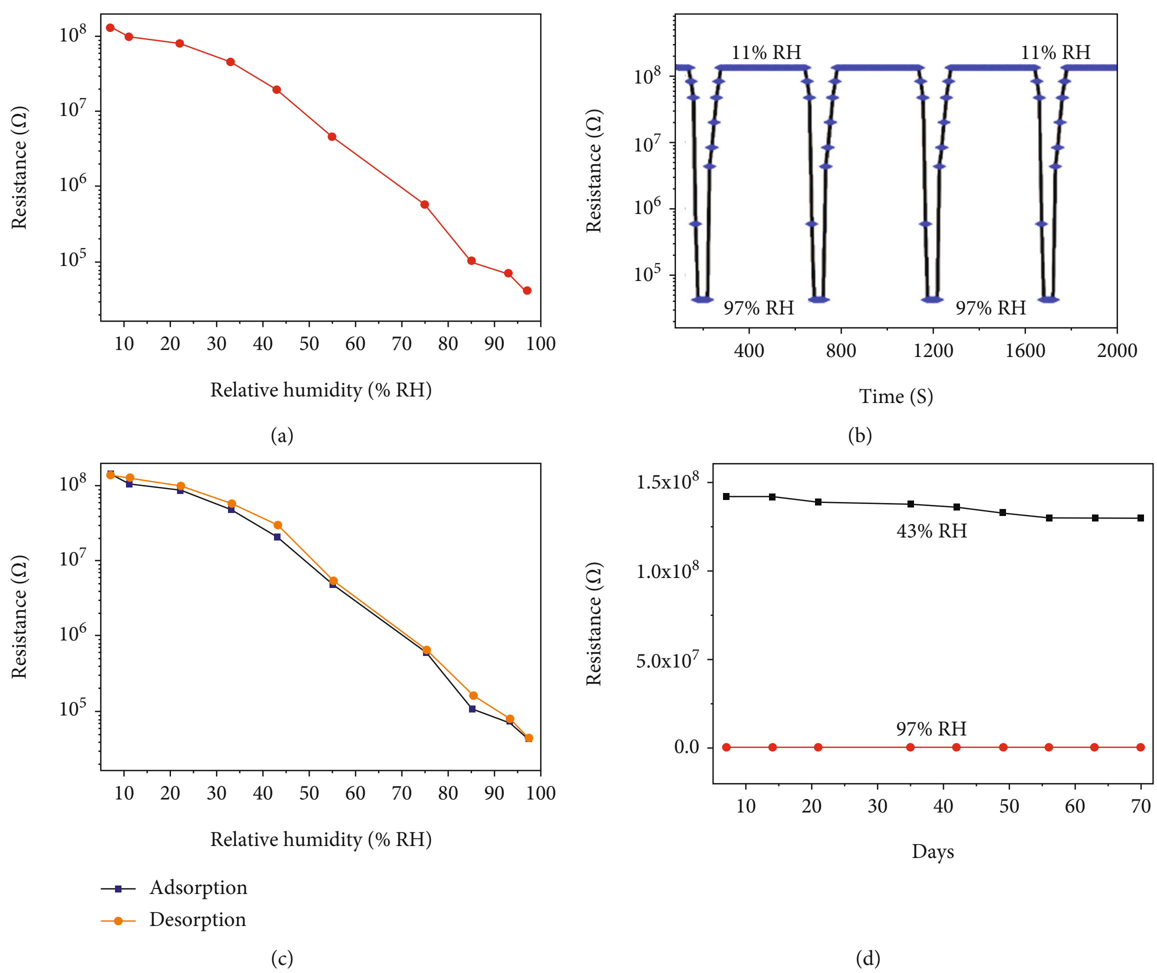


Figure 6: (a) Graph of resistance-humidity function (CuO NPs). (b) The timing behavior of the CuO NPs. (c) The humidity hysteresis of CuO NPs. (d) The humidity stability of the CuO NPs [65].

morphology of the moisture-sensitive material, allows more water vapor to adsorb on the surface of the moisture-sensitive material and condense in the capillary pores, and enhances the electrical conductivity of moisture-sensitive materials. Its response time was 22 seconds, and recovery time was 31 seconds (Figure 6(b)). Over a two-month period, CuO NPs showed minimal hysteresis and good stability (Figures 6(c) and 6(d)), and the moisture-sensitive

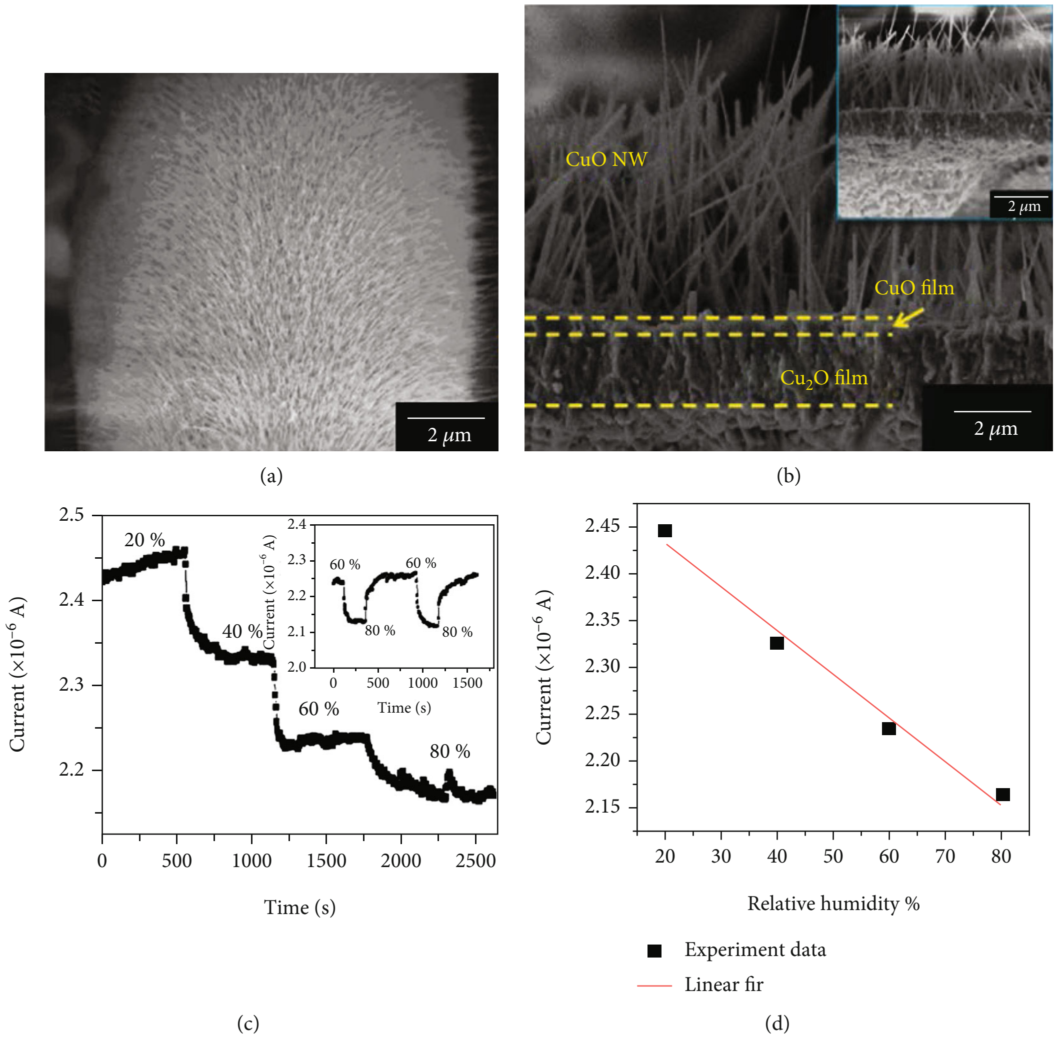


Figure 7: (a) Top-view. (b) Cross-sectional FESEM images of the thermally treated sample. (c) Graph of current versus time and inset the reproducible sensing response. (d) Measured current as a function of RH [8].

materials based on green synthetic copper oxide nanoparticles are more stable and more sensitive at lower humidity.

Wang et al. [8] reported that Cu wires can be transformed by thermal annealing into $CuO/Cu_2O/Cu$ core-shell trilayers covered with high-density CuO nanowires (Figures 7(a) and 7(b)), average length is 2-5 μm, and average diameter is 50 nm. During the high temperature treatment, Cu atoms diffuse into the outer layer of the material and oxidize to form a Cu_2O layer and then further oxidized to CuO, forming a $CuO/Cu_2O/Cu$ core-shell three-layer structure. By studying the growth mechanism of copper oxide nanowires, it is found that the shape of copper oxide nanowires is affected by experimental parameters, including temperature and time, which similarly affects their sensing performance. The currents of the humidity-sensing materials measured in different humidity environments are shown in Figure 7(d). In addition, the sensing characteristics of the fabricated device are not only stable but also reproducible (Figure 7(c)), which has the potential for application in humidity-sensing devices.

Hsueh et al. [3] fabricated CuO nanowires (NWs) on glass substrates (Figures 8(a) and 8(b)), and it was found that with the increase of the initial thickness of the copper film after oxidation, the length of the copper oxide nanowires also increased, respectively (Figure 8(c)), and the resistance of the samples (80°C) when we increased the RH from 20% to 90% increased from 0.55×10^6 to $0.62 \times 10^6\,\Omega$ (Figures 9(a) and 9(b)), which mainly because the adsorbed oxygen ions take away the electrons on the surface of the humidity-sensitive material, leading to the accumulation of holes on the surface of CuO. And the trapped electrons would follow the mechanism leaving holes, oxygen ions react with hydrogen ions generated by water vapor dissociation to form hydroxyl groups [66, 67], this liberates the electrons previously taken away by oxygen ions, and this part of the electrons will neutralize the vacancies on the surface of the moisture-sensitive material, thereby reducing the number of surface vacancies, thereby increased the resistance of the CuO NW surface layer [68]. The authors fabricated a humidity sensor based on CuO NWs, and during the measurement process, the low hysteresis

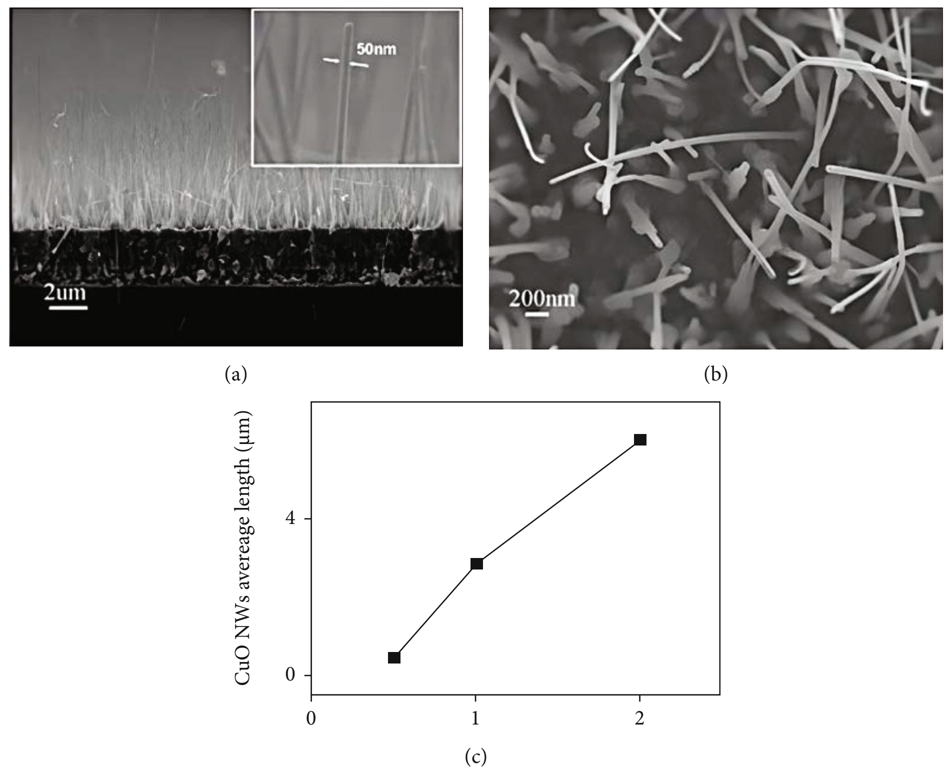


FIGURE 8: (a) Cross-sectional and (b) top-view SEM images of the thermally treated sample. (c) Average length of CuO NWs as a function of initial copper film thickness [3].

(Figure 9(c)) and stability (Figure 9(d)) of the humidity sensor were confirmed.

Xu et al. [69] prepared copper oxide nanomaterials with special structures by a two-step electrochemical deposition method (Figures 10(a)–10(d)). Scanning electron microscopy images found that the CuO honeycombs consisted of well-oriented nanowires with high surface volume ratio. This material has a honeycomb-like structure, and its unique surface structure and high porosity can improve the adsorption of water vapor molecules on the surface of the material. The authors and collaborators prepared $Cu(OH)_2$ in KOH solution and further heated to synthesize the target material. The prepared CuO honeycomb was peeled off the substrate by a rapid annealing process, and a CuO humidity sensor was prepared. From 12 to 97% humidity, the sensor impedance changes significantly with increasing humidity, the sensitivity factor $Sf = 130$ and the resistance at 12% and 97% relative humidity are $3 \times 10^6\ \Omega$ and $2.3 \times 10^4\ \Omega$, respectively (Figure 10(e)), and the sensor resistance remained stable during the measurement lasting one week (Figure 10(f)).

Gu and coworkers [70] reported the preparation of CuO nanosheets of different sizes using different concentrations of NaOH solutions(Figures 11(a)–11(c)). In the performance test, it was found that the copper oxide nanosheet with the smallest size has the highest sensitivity in the humidity range of 11.3-97.3% (Figures 12(a) and 12(b)), has the best low humidity hysteresis characteristics (Figure 12(c)), and has the fastest response time (32 s), but the recovery time was longer (22 s) (Figure 12(d)).

The authors attribute the excellent humidity-sensing performance of CuO nanosheets with a length of 1 μm to their largest specific surface area, which enables a larger area of the sensor-sensing interface and higher activity, both for chemisorption at low humidity levels, or physical adsorption behind. Small-sized copper oxide nanosheets have larger specific surface area, and their adsorption capacity is stronger. So the sensitivity of the humidity sensor will increase with the decrease of the copper oxide nanosheets, but at the same time, the stronger the adsorption capacity of the surface of the material, the tighter the binding with water molecules, which will cause the water molecules to suffer greater resistance during the desorption process and seriously affect the recovery time of the moisture-sensitive material.

We summarize some reports on the humidity-sensing properties of pure CuO with different morphologies, including nanoparticles, nanowires, and nanosheets, and details are shown in Table 1. The increased specific surface area of the copper oxide nanostructures enhances the adsorption capacity of water vapor in the outer layer of the material, thereby improving the sensitivity of the humidity sensor. We found that the surface modification of pure copper oxide increases the defect density on the surface of the material, and changing its nanostructure can improve the sensitivity and response speed of the copper oxide-based humidity sensor to a certain extent, and the working stability of the product has also been proved. However, in general, copper oxides with different nanostructures show poor room temperature sensitivity; in other words, only surface modification of pure

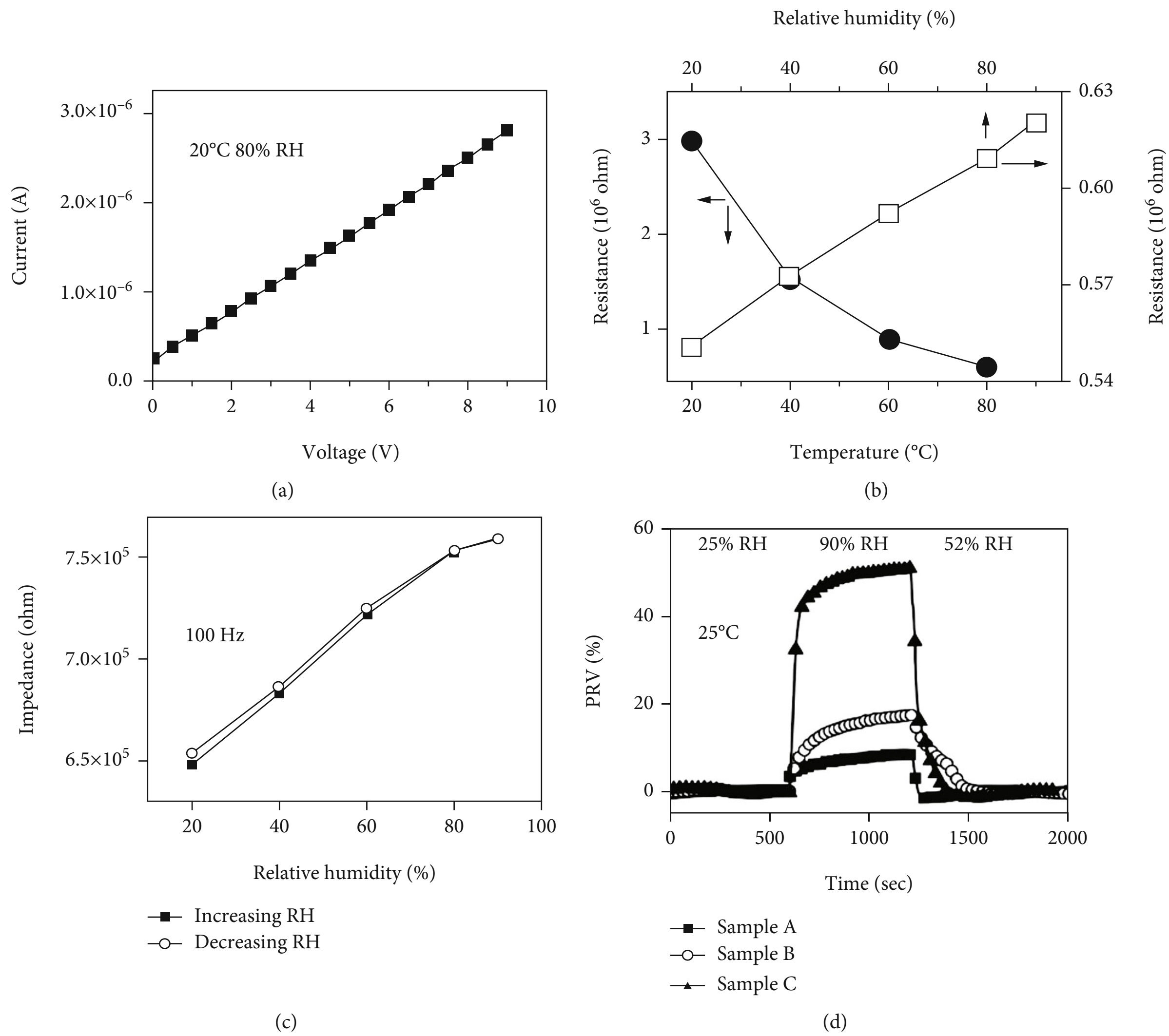


FIGURE 9: (a) I–V characteristics of sample C measured at 25°C, 80%RH. (b) Sample impedance as a function of time, temperature with 5 V applied bias. (c) Hysteresis of CuO NW samples (1 V applied bias and 80°C). (d) Dynamic response of three humidity sensors at room temperature (5 V applied bias) [3].

copper oxide materials can only improve their humidity-sensitive properties to a certain extent, and we need to find more suitable method to further improve the sensitivity and response speed of the sensor.

3. Additive Doping

At present, the attention of many researchers has been attracted by the field of nanometers. Many materials based on nanometer size will have special properties [74]. The further improvement of the physicochemical properties of nanomaterials depends on the synthesis of nanoparticles with different structures and properties and the ability to obtain the desired performance [75]. Nanocomposites are a new topic in the field of materials. By compounding different or the same type of nanoparticles to obtain expected properties [8, 76], it is also possible to dope pure copper oxide nanostructures by doping additives (mainly organic polymers, metal oxides, and carbon-based materials) as secondary components to improve the moisture-sensing properties of copper oxide, as Table 2.

3.1. Organic Polymer Doping. Organic polymers include polypyrrole (PPy) [88], polyvinylpyrrolidone (PVP) [89], polyethylene oxide (PEO) [90], polyvinyl alcohol (PVA) [91], polyaniline (PANI) [92], cellulose acetate (CA) [93], and polyethyleneimine (PEI) [94]. As sensing materials, they have low cost, high sensitivity, small hysteresis, and low response short time and easy to prepare and process [95], and they can also operate at room temperature, and the advantages of using polymeric materials as humidity sensors have been widely reported [96, 97].

Copper oxide and organic polymers are doped together to form hybrid nanocomposites; this mechanism of enhanced sensing performance can be attributed to the heterojunction of organic polymers forming vacancy-electron depletion layers on the surface of copper oxide materials, electrons, and vacancies in copper oxide materials and organic polymers will migrate. This process will cause the energy band to bend,

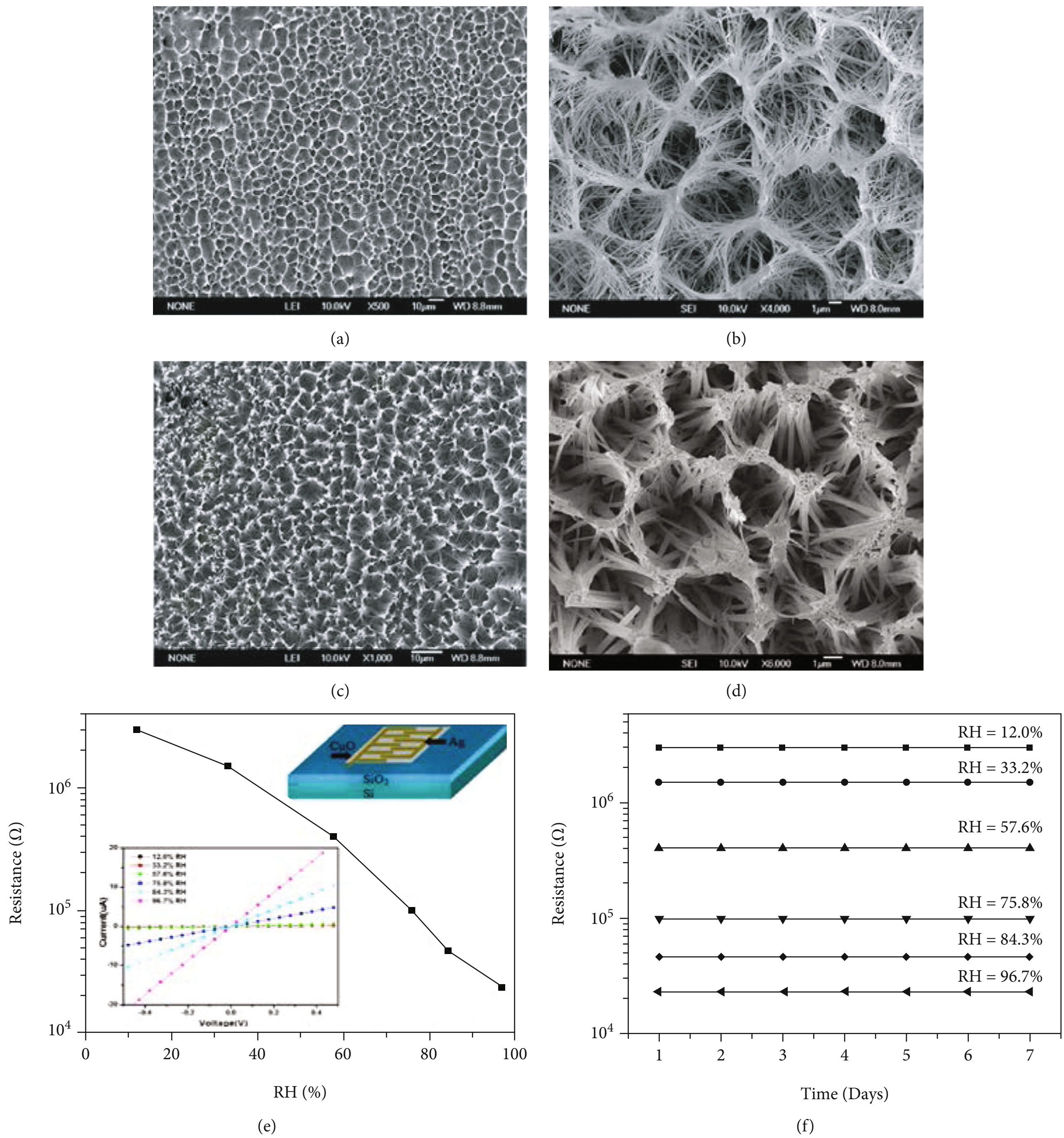


Figure 10: SEM images of CuO honeycombs via two-step electrochemical deposition at different voltage for 4 h: (a, b) $E = 3$ V and (c, d) $E = 5$ V. (e) The impedance versus humidity plot of CuO honeycombs (25°C). The insets show schematic illustration (upper-right) and the corresponding I–V curves (lower-left) of a CuO honeycomb-based humidity sensor. (f) Resistance variations with time for the CuO sample at various RH levels [69].

and eventually, the Fermi level will reach a new equilibrium state, thereby forming a heterojunction at the interface where the copper oxide and the polymer come into contact. the current across the heterojunction barrier is known to be exponentially related to the junction barrier height [15]. Therefore, the conductivity of the heterojunction is very sensitive to small changes in the junction barrier height. When the moisture-sensitive material is in contact with water vapor in the atmosphere, the water vapor will be adsorbed on the surface of the material, and the width of the depletion layer will change, resulting in a change in the height of the potential barrier [96]. The conductivity of the material is unusually sensitive to the barrier height, so this approach would be effective in increasing the sensor's moderate sensitivity.

Polyvinylpyrrolidone (PVP) is a hydrophilic polymer with good sensing properties. It is a conjugated polymer that

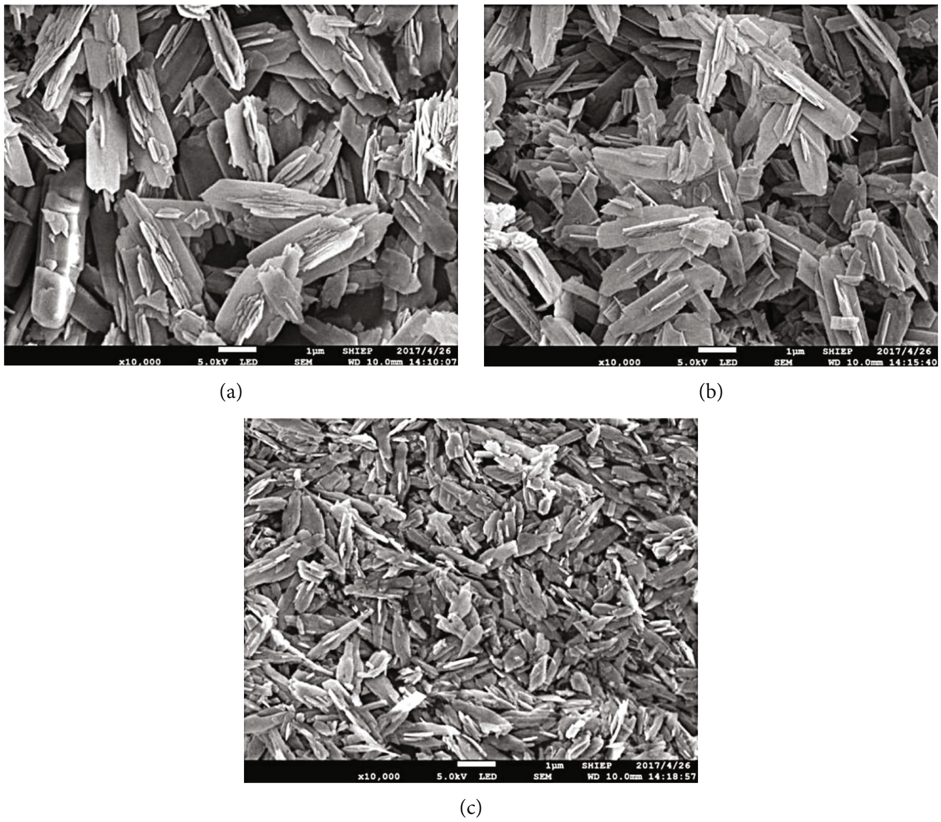


Figure 11: SEM micrographs of CuO nanosheets prepared with different concentrations of NaOH: (a) 0.5 mol/l (sample 1), (b) 0.125 mol/l (sample 2), and (c) 0.05 mol/l (sample 3) [70].

is soluble in water and still maintains relatively good properties at high temperatures [89]. Therefore, polyvinylpyrrolidone is suitable as a hydrophilic polymer to be doped into copper oxide to prepare nanocomposites to improve the humidity-sensitive properties of pure copper oxide, and its thermal stability can effectively reduce the operating temperature of copper oxide sensors. Conductivity can also be complementary to copper oxide. Khan et al. [15] reported the preparation of polyvinylpyrrolidone (PVP)/CuO composites with a dense structure by polymerization (Figure 13(a)). The authors found that the SEM micrographs showed that the copper oxide particles distorted and destroyed the PVP. The smooth structure makes the PVP surface rough, and the rough surface makes it easier for the water vapor in the environment to adsorb on the surface of the composite material, thus enhancing the sensing performance of the thin film. The authors fabricated PVP/CuO nanocomposite by a simple drop method the humidity sensor of the material, and it is observed that the PVP/CuO composite material has superior resistance response in the humidity range of 25-95%RH (Figure 13(b)), and the sensitivity is high. The response/recovery times at room temperature are 35 seconds and 12 seconds, respectively. The response-recovery behavior is better than that of the pure copper oxide sensor, with a hysteresis of only 2.1% (Figure 13(c)), while showing good stability over 60 days of repeated detection (Figure 13(d)).

In another experiment, Ahmad and coworkers [77] successfully prepared nanomaterials composed of polyethylene oxide (PEO), oxidized multiwalled carbon nanotubes (MWCNT), and copper oxide (CuO) by electrospinning. The composite nanofibers composed of particles (Figures 14(a) and 14(b)), copper oxide, and carbon nanotubes were filled into polyethylene oxide as fillers (PEO–CuO–MWCNT: 1% and PEO–CuO–MWCNT: 3%). A digital LCR meter was used to measure the capacitance and resistance of the material at different relative humidity levels, and the moisture sensing properties of the composite nanomaterials were investigated. Scanning electron micrographs showed that the composites exhibited fine fibers with smooth surfaces, which indicated that the fillers in the polymer matrix were uniformly dispersed. Experiments show that PEO–CuO–MWCNT: 1% and PEO–CuO–MWCNT: 3% exhibit high sensitivity to humidity in the humidity range of 30–90% at 25°C (Figures 14(c) and 14(d)). Both materials exhibit fast response and recovery rates (Figures 14(e) and 14(f)).

Similar to polyethylene oxide (PEO), polyvinyl alcohol (PVA) also has good hydrophilicity, no harm, and excellent thermal stability [98], which makes it suitable for use in biotechnology and sensing field as promising candidates [99]. Hashim et al. [78] synthesized a nanocomposite film of polyvinyl alcohol-polyethylene oxide and copper oxide (PVA–PEO–CuO) nanoparticles by a casting method. The study found that the PVA–PEO–CuO nanocomposite film showed good sensitivity in the humidity range of 30-70%. The authors believe that in environments with low relative

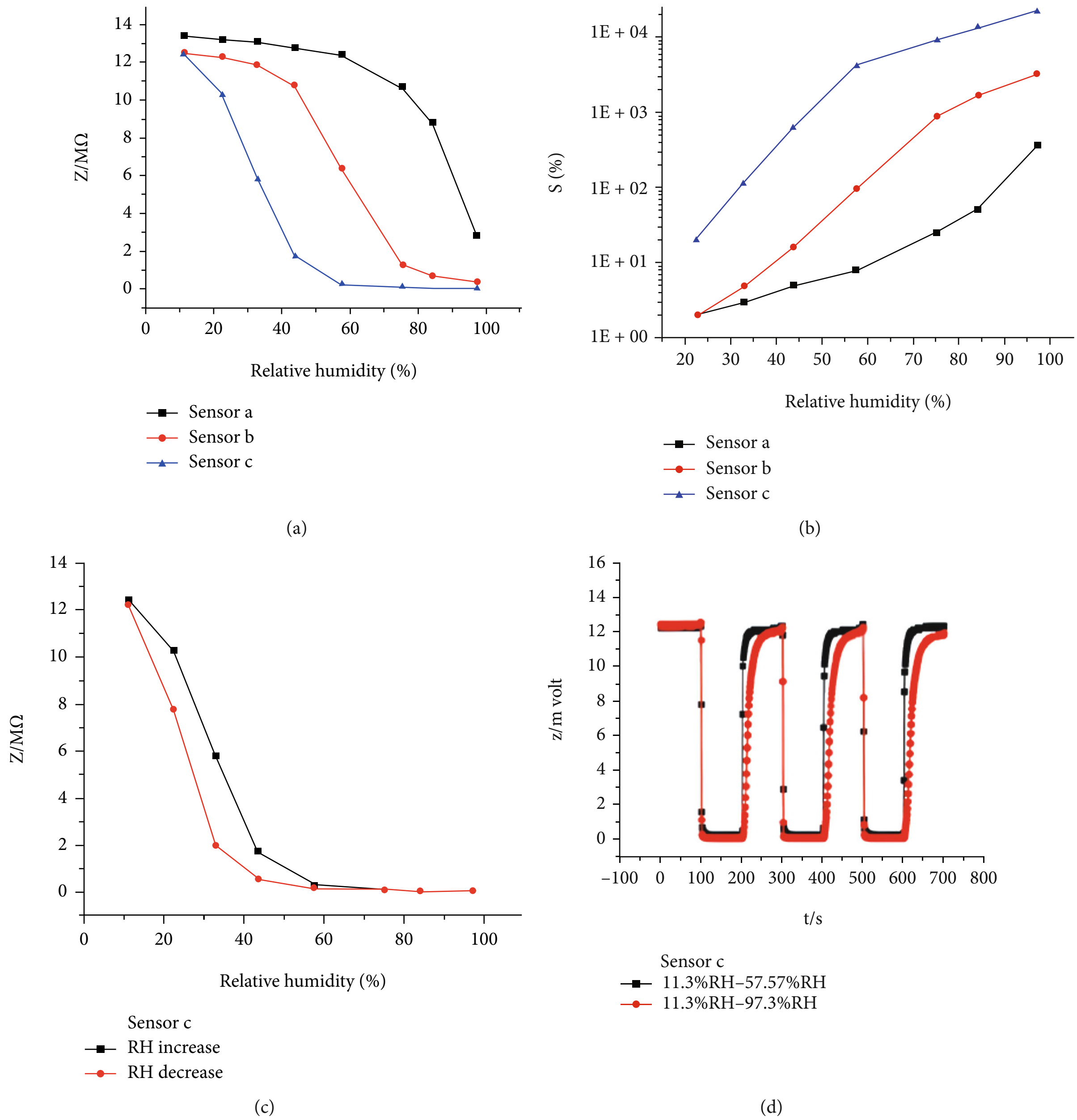


Figure 12: (a) Impedance changes of CuO nanosheets of different sizes with humidity. (b) Sensitivity of CuO nanosheets of different sizes varies with humidity. (c) Hysteresis characteristic of CuO sensors at different RH (1 μm). (d) The response/recovery behavior and repeatability of CuO sensors (1 μm) [70].

humidity, polymer chains curl and the migration of copper oxide particles is restricted. As the humidity increases, the material absorbs the water molecules to unfold and align, reducing the hopping resistance of charge carriers, thereby enhancing the sensing response of the composite.

Hashim et al. [78] chose polyaniline (PANI) with good electrical conductivity as the doped polymer material. Polyaniline itself is relatively stable, low cost, and easy to produce [100, 101]. At the same time, the combination of copper oxide and polyaniline also optimized the adsorption performance of polyaniline [102] and can also effectively address the limitations of poor processability and insufficient mechanical properties of PANI. The authors and colleagues [79] reported the synthesis of polyaniline-copper oxide nanocomposites (CuO/PANI) using ammonium persulfate as the polymerization agent by a chemical oxidative polymerization route (Figure 15(a)). According to the experiments, the electrical resistance of the composite changes significantly with increasing humidity (Figure 15(b)). This shows that the CuO/PANI composite has a good response to humidity changes and further explains the sensing mechanism (Figure 15(c)). The material exhibits regular repeatability at room temperature with a response and recovery time of 40 and 55 seconds, respectively (Figure 15(d)), while the material also has a good response intensity (Figure 15(e)) and showed sufficient stability in the six-month test.

Table 1: Moisture-sensitive properties of copper oxide nanostructures with different morphologies.

Morphology	Synthesis method	T_{opt} (°C)	Humidity range	Humidity-sensitive properties Response time (s)	Recovery time (s)	Hysteresis	Response	Ref.
Mesoporous particles	Thermal decomposition	25	33-90%RH	~1	11	NA	NA	[34]
Nanoparticles	Biosynthesis	25	7-97%RH	22	31	NA	99%	[65]
	Microwave-assisted chemical solution	25	25–95%RH	NA	NA	NA	99%	[71]
Nanowire	Thermal annealing	25	20-80%RH	~98	~98	NA	NA	[8]
	Deposition	25	20-90%RH	NA	NA	<1.5%	NA	[3]
	Two-step electrochemical deposition	25	12-97%RH	NA	NA	NA	130	[32]
Nanosheets	Hydrothermal	25	11.3-97.3%RH	32	22	NA	NA	[70]
	Spin-spray	25	20-90%RH	2.1	2.8	4%	170%	[72]
Nanorods	Hydrothermal	25	30-85%	NA	NA	NA	82.03%	[73]
Nanofilm	SILAR	25	20-80%	130	320	5%	NA	[54]

Note: T_{opt}: operating temperature; NA: not available.

Table 2: Humidity-sensing properties of dopants/CuO.

Dopant	Synthesis method	T_{opt} (°C)	Humidity range	Humidity-sensitive properties Response time (s)	Recovery time (s)	Hysteresis	Sensitivity	Ref.
PVP	Polymerization	26.85	25-95 RH	35	12	2.1%	NA	[15]
PEO	Electrospinning	25	30-90%RH	20	11	NA	53837.6%	[77]
PVA	Casting	25	30-70%RH	NA	NA	NA	NA	[78]
PANI	Chemical oxidative polymerization	25	10-95%RH	40	55	NA	70%	[79]
CA	Instrument-less novel technology	25	0-90%RH	13	17	NA	3.8 MΩ/%RH	[80]
Chitosan	Magnetic stirrer	25	20-95%RH	20	50	NA	−0.72to −2.1%RH	[81]
O-B-EG-B	Organic surfactant template	30	5–83.8%RH	180	160	NA	1.25%-7.9%	[82]
ZnO	Solid-state reaction	25	10-95%RH	NA	NA	±4%	29.95 MΩ/%RH	[83]
	Hydrothermal	25	30-90%RH	6	7	21%	6045 ± 731	[84]
TiO_2	Microwave-assisted synthesis	25	10-98%RH	162	428	NA	3.4%	[85]
Cu_2O	Heated oxidation	25	35-98%RH	NA	NA	NA	-10.0%	[55]
rGO	Microwave-assisted hydrothermal	25	11-98%RH	2	17	NA	NA	[86]
MWCNT	Electrospinning	25	30-90%RH	3	22	NA	3798.2%	[77]
KCl	WEE	25	11-95%RH	40	50	4%RH	NA	[87]

Note: T_{opt}: operating temperature; NA: not available.

Chani and colleagues [80] first introduced a new instrument-free technique to fabricate a smart humidity sensor based on cellulose acetate-copper oxide (CA-CuO) nanocomposites. The SEM images were compared (Figures 16(a) and 16(b)). The authors found that thin-film composites have higher porosity than granular composites, and the porosity is favorable for the adsorption of water vapor, which in turn improves the moisture-sensing performance. For granular materials, the surface porosity is low. The reason given by the authors is related to the manufacturing pressure of granular material processing. The humidity sensor based on the CA-CuO nanocomposite film has obvious changes in its capacitance and resistance between 0 and 90%RH (Figure 16(c)) and shows very little lag in experiments (Figure 16(d)). It is possibly due to higher porosity and smaller thickness of the material, which

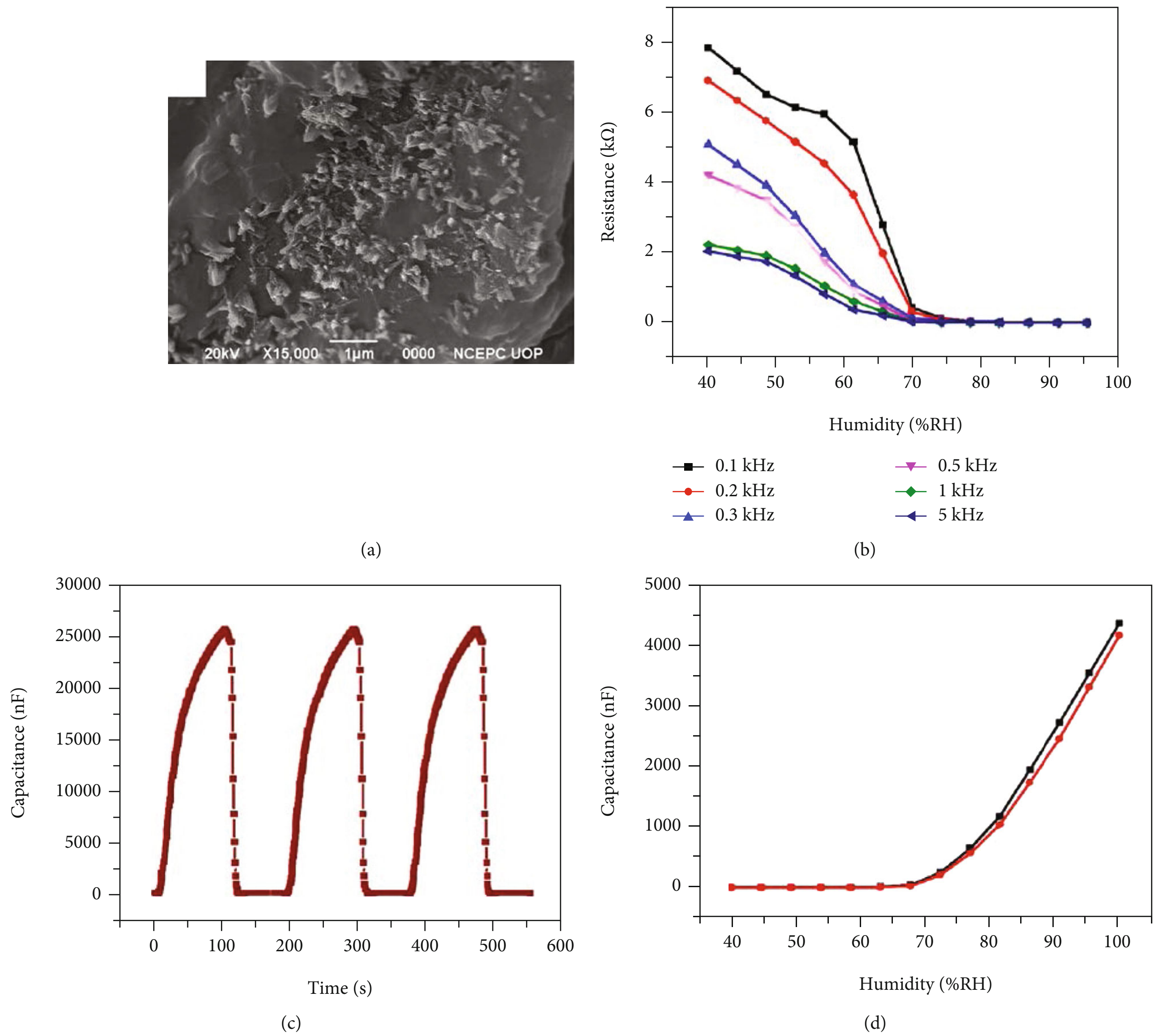


Figure 13: (a) SEM micrograph of PVP/CuO nanocomposite. (b) Resistance variation with different %RH at different frequencies of PVP/CuO nanocomposite. (c) Response and recovery curve of PVP/CuO nanocomposite sensors. (d) Hysteresis curve of PVP/CuO nanocomposite sensors at 100 Hz [15].

illustrates that the problem of large hysteresis in hydrophobic polymer-based sensors is further improved.

The results show that by doping organic polymers into copper oxide to form a heterojunction, the sensitivity and response speed of the sensor to humidity can be effectively improved, and the product also has good stability at room temperature. It has the potential to further explore new moisture-sensitive materials.

3.2. Metal Oxide Doping. In addition to organic polymers, the coupling of semiconducting metal oxides ZnO [83, 84], TiO_2 [85], SnO_2 [103], In_2O_3 [104], and Fe_3O_4 and Cu_2O [81] into copper oxide can also significantly enhances its sensing performance. After careful summary investigations, we found that the resulting nanocomposites after coupling significantly improved the humidity-sensing behavior. More specifically, the effect of semiconducting metal oxides on the humidity-sensitive properties of CuO-based humidity sensors is mainly because of the formation of heterojunctions with vacancy-electron depletion layers between CuO and semiconducting metal oxides [105, 106]. As far as we know, CuO is a typical p-type material, and the metal oxide compound doped with it is usually an n-type semiconductor. Because of the carrier concentration gradient, the free electrons in the n-type metal oxide usually migrate to the p-type copper oxide with vacancies as the main carriers. At the same time, the vacancies in the copper oxide will gradually diffuse to the n-type copper oxide. In semiconducting metal oxides, the energy band bends and the Fermi level finally reaches a new equilibrium, thereby forming a heterojunction at the interface between the two. The tunneling current across the heterojunction barrier is exponentially related to the junction barrier height [107]. Therefore, the conductivity is very sensitive to the smile change of the

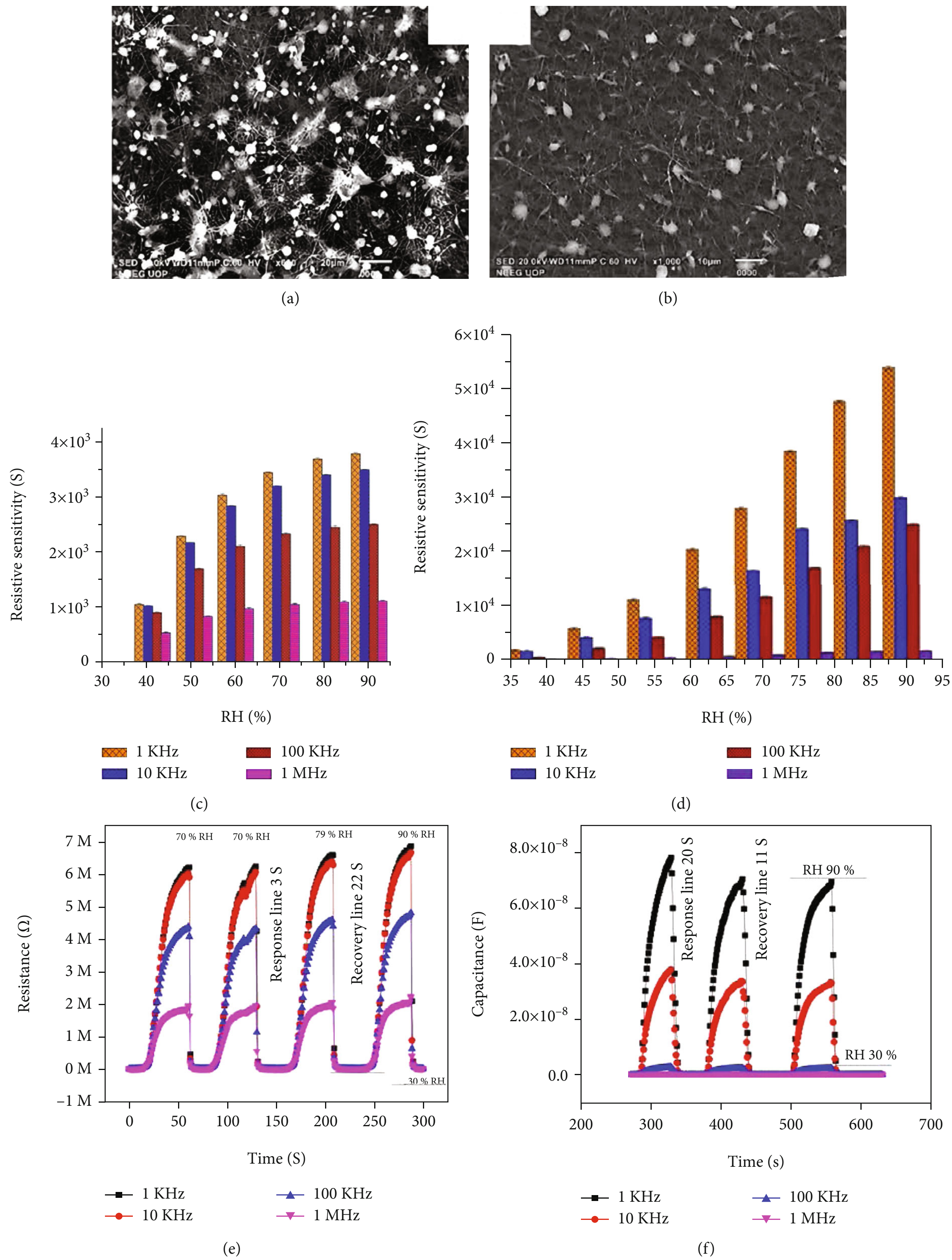


FIGURE 14: SEM micrographs of PEO–CuO–MWCNT: (a) 1% and (b) 3% nanofibers. Resistivity Sensitivity of PEO–CuO–MWCNT: (c) 1% and (d) 3% nanocomposite at different %RH. Resistivity response/recovery time for PEO–CuO–MWCNT: (e) 1% and (f) 3% nanocomposites [77].

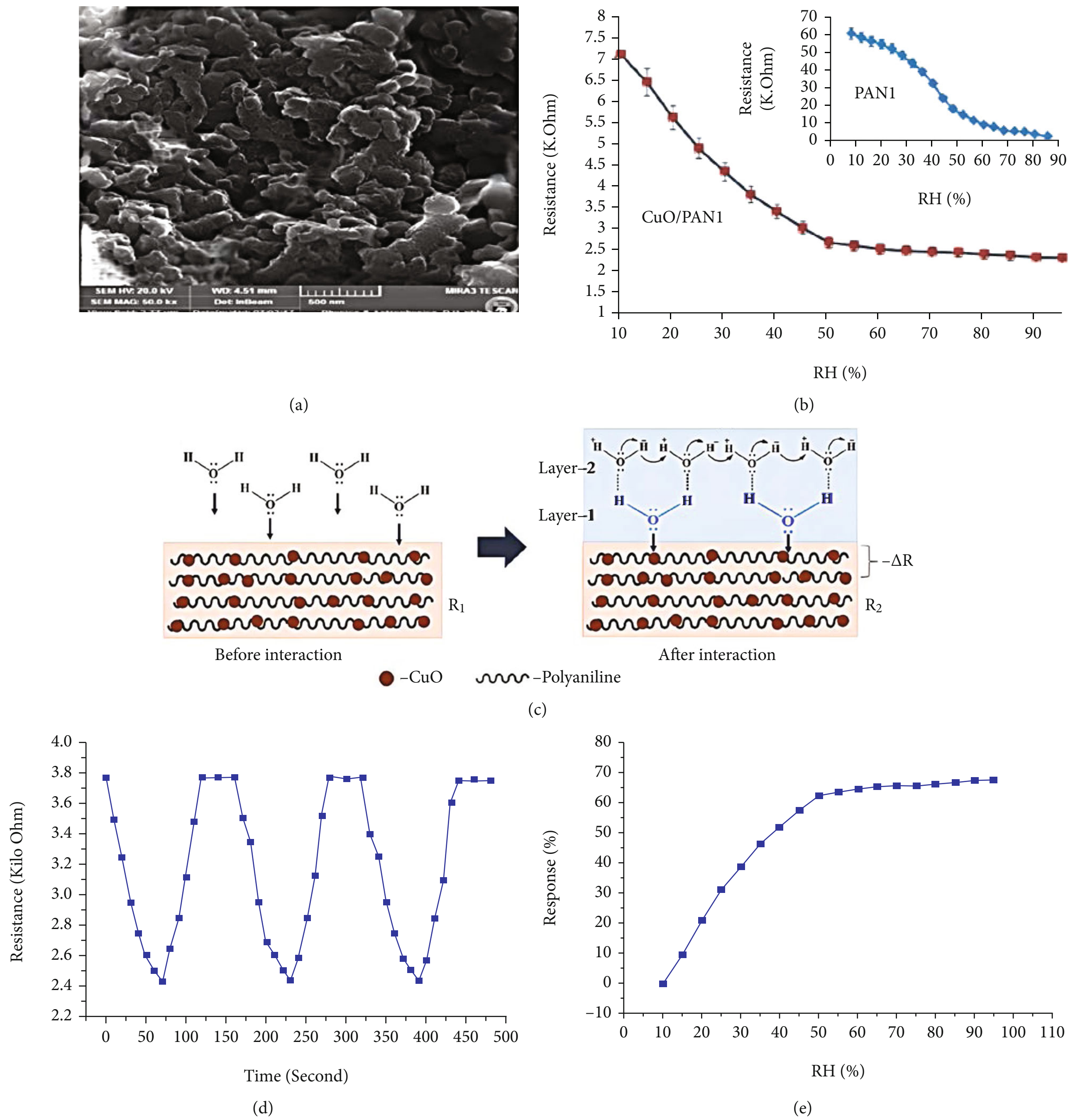


Figure 15: (a) SEM image of CuO/PANI. (b) CuO/PANI impedance as a function of humidity; the inset shows the variation trend of pure PANI impedance as a function of humidity. (c) Schematic illustration of sensing mechanism over CuO/PANI nanocomposite. (d) Change in resistance of CuO/PANI nanocomposite with time at 60%RH. (e) Percentage sensing response of CuO/PANI at different relative humidity [78].

junction barrier. Heterogeneous contacts of p-type and n-type semiconductors are humidity sensors acting through the contact interface [108–111], in such a sensor, and as the p-n junction is gradually exposed to the outside atmosphere, the water vapor in the environment gradually penetrates into the heterojunction interface, which also changes the electrical properties of the heterojunction [112].

ZnO, a typical n-type semiconductor with a wide bandgap of 3.37 eV, is abundant in nature [113]. It has stable physical and chemical properties, low dielectric constant, nontoxic, and low cost [114]. Generally, the combination of narrow bandgap semiconductor and wide bandgap semiconductor will improve its sensing performance. Rajput et al. [83] reported the preparation of CuO–ZnO nanocomposites. It was found that between 10% and 95%RH, with the increase of copper oxide content, the resistance of the nanocomposite changed more significantly, and its humidity-sensitive performance and sensitivity were better

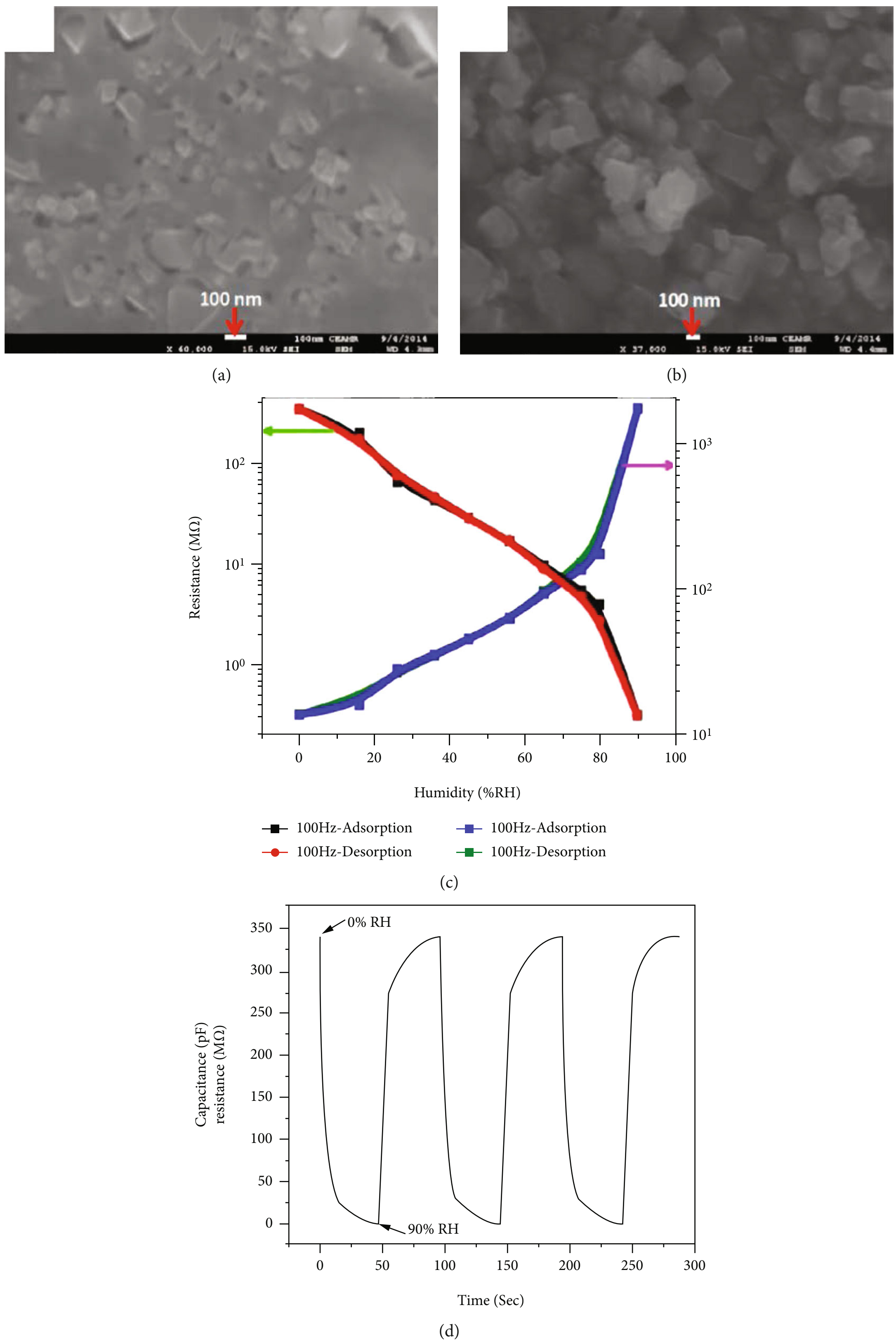
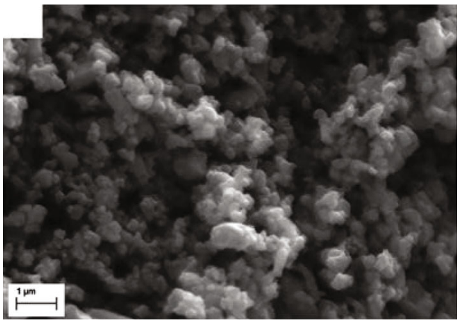
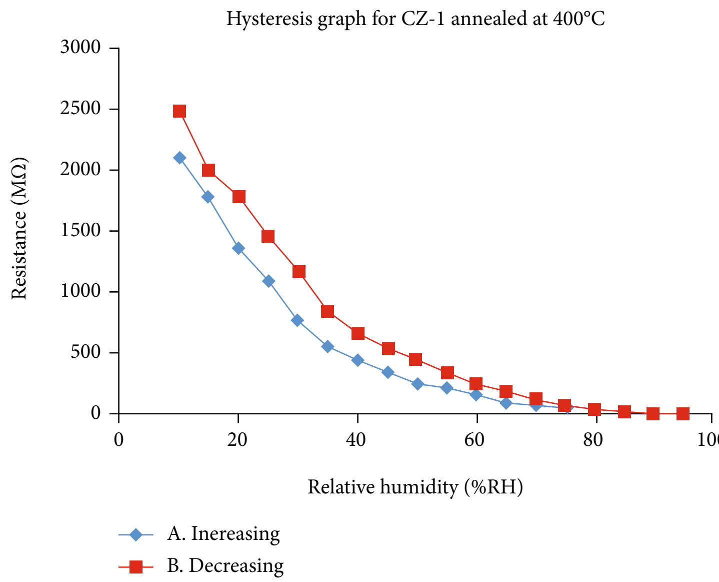


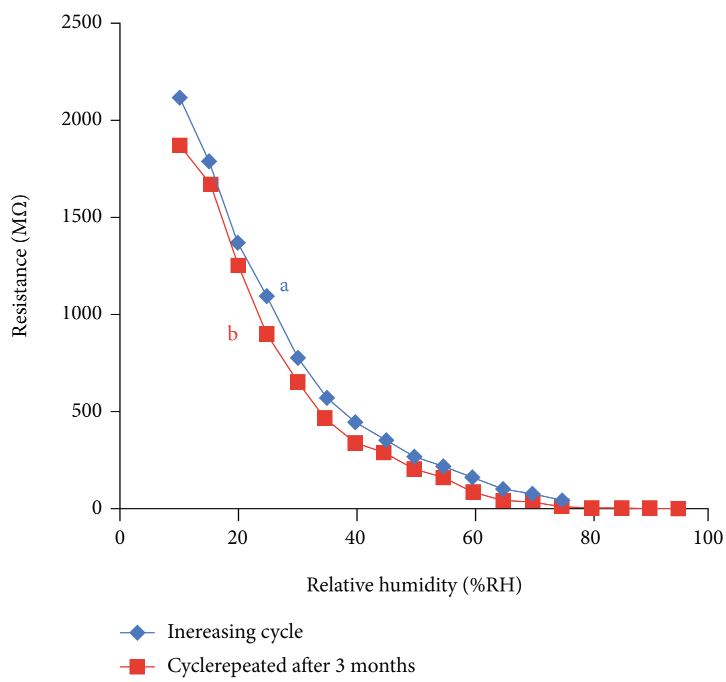
FIGURE 16: Surface morphologies of the (a) CA-CuO nanocomposite films and (b) pellets. (c) Capacitance and resistance-humidity relationships of CA-CuO humidity sensors. (d) Response-recovery behavior of the CA-CuO nanocomposite-based film sensors [80].



(a)

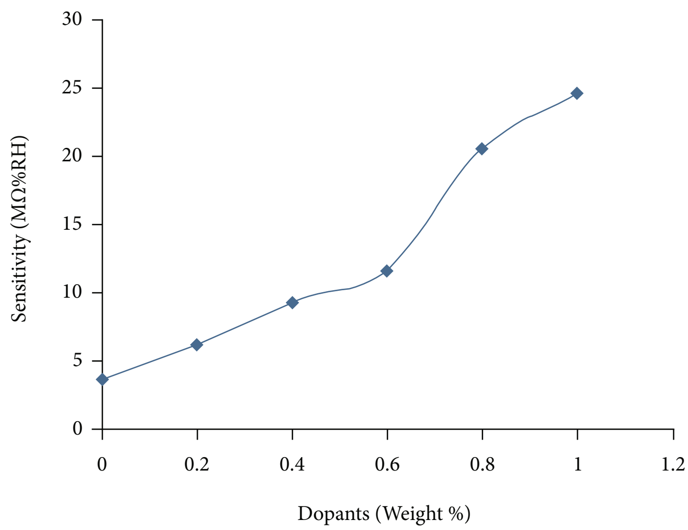


(b)



(c)

FIGURE 17: Continued.



(d)

Figure 17: (a) Scanning electron micrograph of sample CZ-1 (1.0% by weight of CuO in ZnO). (b) Variation in resistance with change in %RH for sample CZ-1: (A) increasing cycle and (B) decreasing cycle. (c) Variation in resistance with change in %RH for sample CZ-1 for annealing temperature 400°C: (A) increasing cycle and (B) repeated cycle after 3 months. (d) Variation in sensitivity with wt% of CuO in ZnO [83].

(Figure 17(d)). Figure 17(a) is a scanning electron microscope photograph of 1.0% by weight of CuO in ZnO. The calculated sample exhibits good hysteresis with a minimum hysteresis of ±4% (Figure 17(b)). The experimental results were reproducible across different operating cycles, with an aging of ±4% after three months (Figure 17(c)).

In another experiment, Zainelabdin and colleagues [84] reported the preparation of copper oxide nanomaterials with special morphologies on ZnO nanorods (NRs) by a hydrothermal method. During the hydrothermal treatment, the surface of the ZnO nanorods was eroded and hydroxylated, which promotes CuO nanostructure growth through directional attachment. After four hours of hydrothermal treatment, the surface of ZnO nanorods was completely covered by CuO nanostructures, and ZnO was completely chemically dissolved at this time (Figures 18(a)–18(c)). According to the experiments, the humidity sensor based on ZnO/CuO nanocoral shows good linearity and sensitivity between 30% and 90%RH (Figure 18(d)), and the sensitivity factor 32Sf (referred to as R30%/R90%) was found to be 6045 (±731). Using the same process to fabricate four different sensors, the measured standard deviation was 12%, which the authors attribute to the different densities of ZnO nanorods and/or CuO nanostructures. Importantly, the sensor exhibited a high hysteresis of 21%, indicating the presence of a reactive reaction that affects water desorption from nanocoral voids, which requires further experimental investigation.

Similar to zinc oxide, TiO_2 is also an n-type semiconductor material with a bandgap of 3.2 eV [115]. Ashok et al. [85] reported the synthesis of CuO/TiO_2 nanocomposites using EMISE (1-ethyl-3-methyl-imidazolium-ethylsulfate). It was found by scanning electron microscopy that the nanocomposites presented a nanotube-like structure, and with the increase of copper oxide content in the composites, the longer the nanotubes were, the longer the nanotubes were. When the mass percentage of copper oxide is 8%, the length of the resulting nanotubes is 36 nm (Figure 19(a)). Within the humidity range given in the experiment, it can be observed that the resistance of the CT-8 sample changes most significantly and has good sensitivity at 300 K (Figures 19(b) and 19(c)). The response and recovery time are measured as 162 and 428 seconds. The authors attribute the sensitivity of the sensing element to the nanocomposite tube structure of CuO/TiO_2, and it enhances the diffusion of water.

Besides cupric oxide, cuprous oxide is also one of the earliest typical p-type materials [116]. As mentioned in the first section, the crystal structure of cuprous oxide is cubic with a narrow direct bandgap (=2.1 eV), and although the conductivity is lower than that of copper oxide, it has higher carrier mobility. Hsu et al. [55] reported the preparation of Cu_2O/CuO nanomaterials on Cu through-silicon vias by thermal oxidation. It is observed that the RH response of the sensing element increases with increasing humidity, as explained by the authors when water molecules displace O^{2-} and liberate electrons from oxygen ions, which reduces the vacancy concentration in the outer layer of the nanowire, and the electrical conductivity declines.

3.3. Carbon-Based Material Doping. Some carbon-based materials with good properties and easy mass production, such as reduced graphene oxide (rGO) [86] and carbon nanotubes (CNT) [77], are doped as the second component to improve the humidity sensitivity of copper oxide characteristic.

Graphene is a unique two-dimensional carbon structure, and it not only has excellent electronic performance [117], but also has excellent stability [118]. In addition, graphene is nontoxic and rich in raw materials, making it a hot and

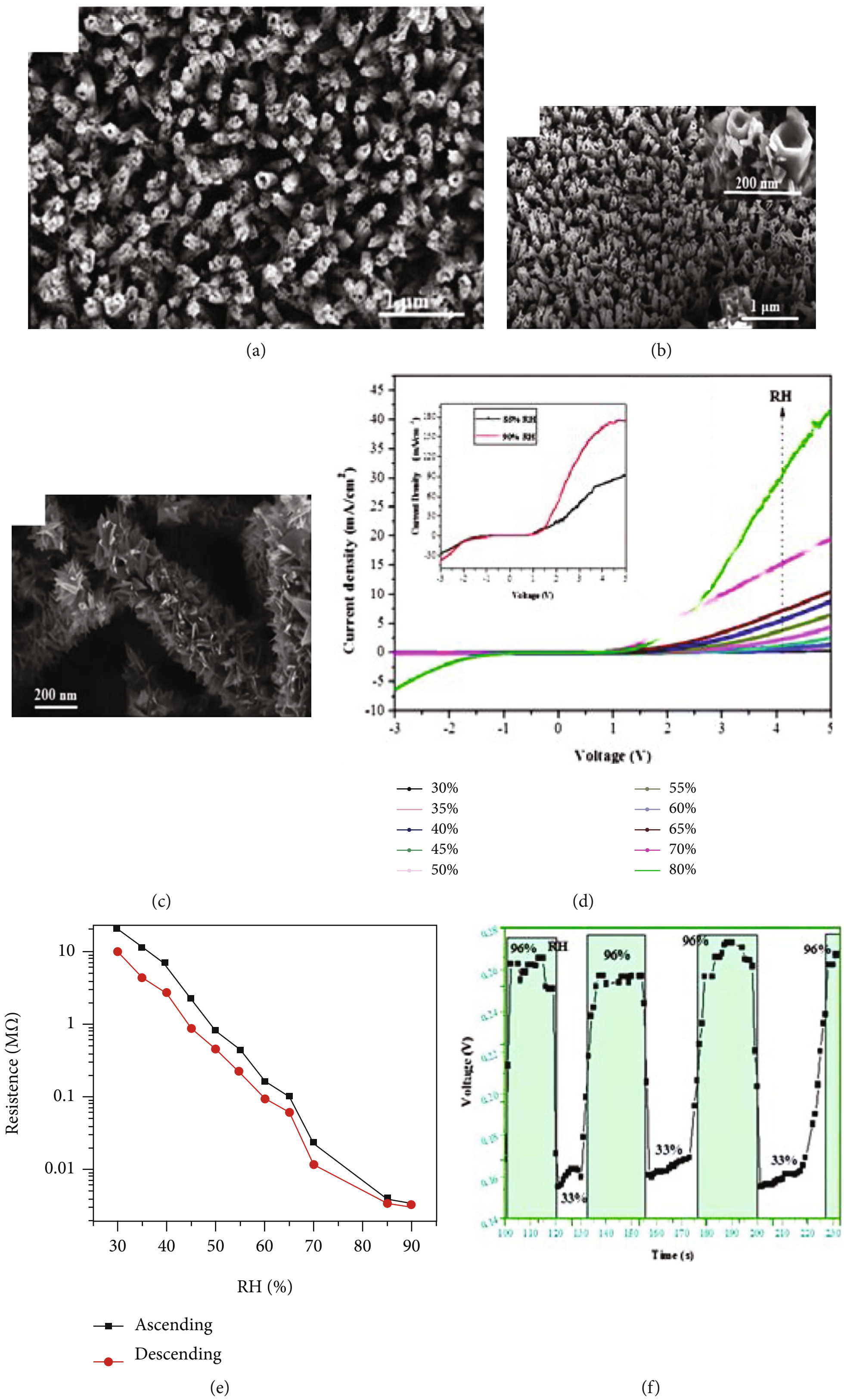


Figure 18: (a, b) Top and side views of the highly branched nanocorals. (c) Single CuO/ZnO nanocorals after hydrothermal growth for 4 h. (d) Current density–voltage characteristics of a typical nanocoral sensor at a different relative humidity (RH); the inset shows the J–V characteristics of the sensor at 85 and 90%RH. (e) DC resistance of a typical nanocoral sensor with increasing humidity and recovery cycle (ascending and descending). (f) Dynamic response of the nanocoral sensor when switched between 96% and 32%RH [84].

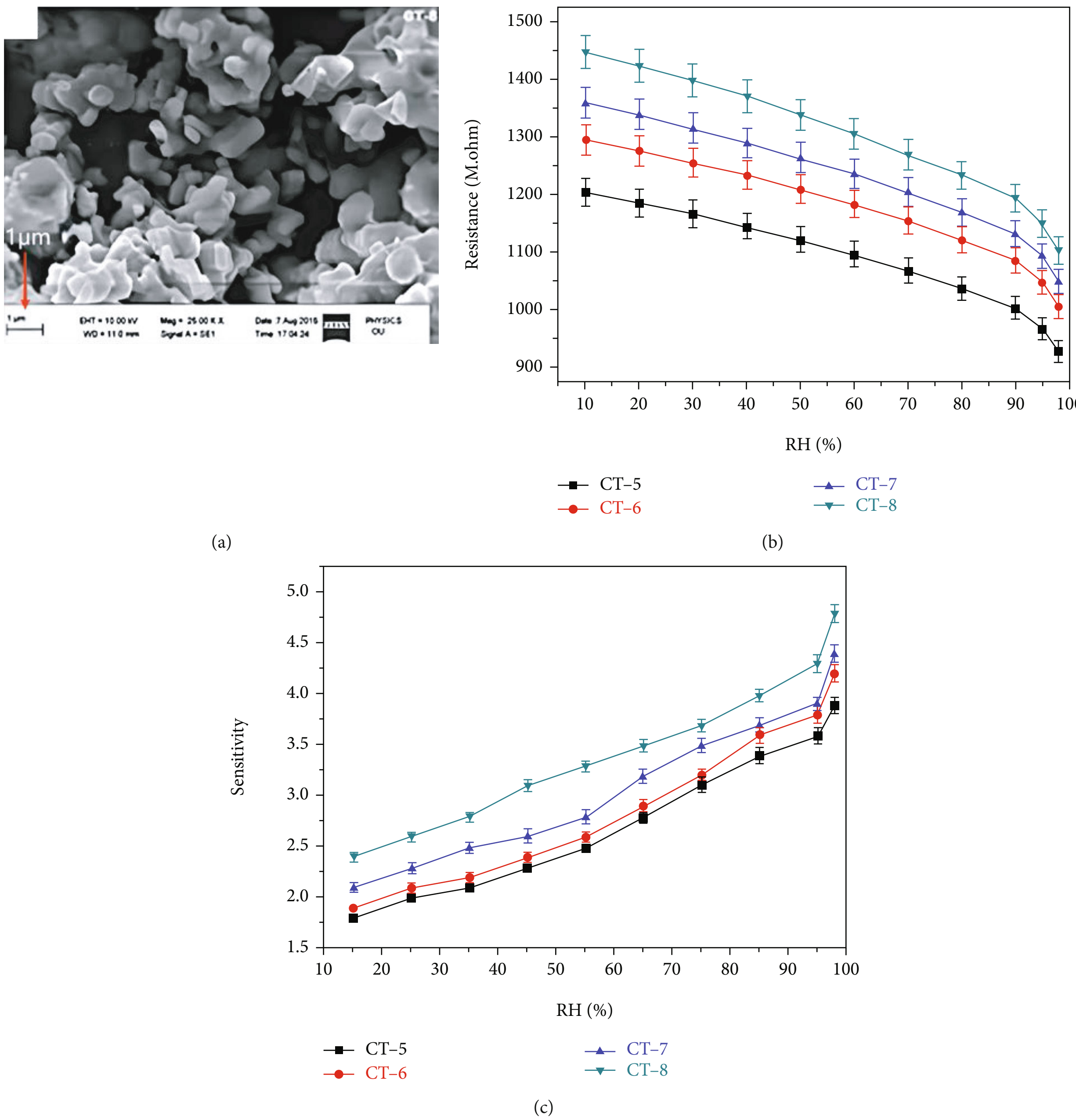
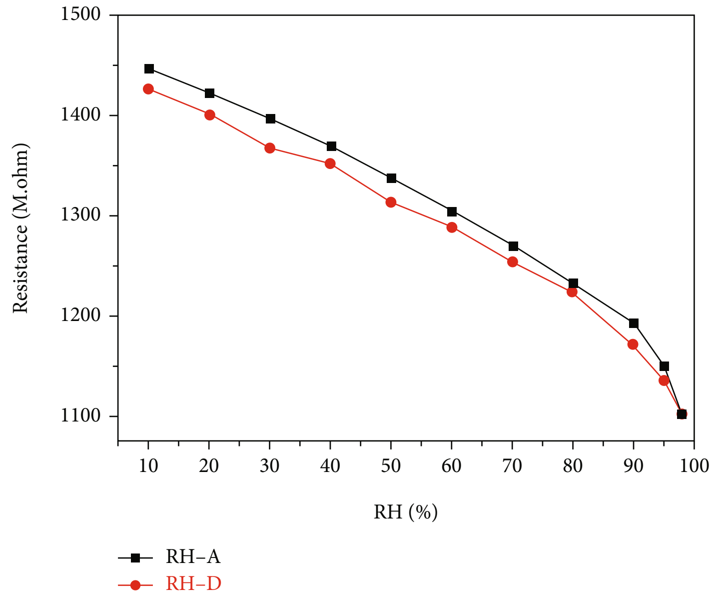


Figure 19: Continued.



(d)

Figure 19: (a) SEM images of CuO/TiO_2 CT-8 (8.0% by weight of CuO in TiO_2) nanocomposites. (b) Resistance w.r.t. relative humidity. (c) Sensitivity w.r.t. relative humidity. (d) Hysterisis curve of CT-8 [85].

popular material in many fields [119]. So far, among the several graphene preparation methods known, chemical or thermal reduction of graphene oxide is less costly, which best meets the needs of practical applications [120–123].

Wang and colleagues [86] reported the synthesis of reduced graphene oxide- (rGO-) modified sea urchin-like CuO nanostructures (Figures 20(a) and 20(b)). Experimental observations show that the change of material impedance with humidity conforms to the general law of humidity sensing (Figure 20(d)). Sea urchin-like composite nanomaterials exhibit fast response (2 s) and recovery time (17 s) (Figure 20(c)), which is faster than the copper oxide humidity sensor. In addition, the repeatability of the composite material is also better. In the article, the author introduces the Schottky junction theory to explain the change in the sensor impedance. He believes that the reduced graphene oxide with good conductivity and CuO forms a Schottky junction, which increases the normal impedance of the composite material. As humidity increases, water molecules replace oxygen ions to release electrons, while attracting electrons to the surface. Under low humidity, the transport of charges is achieved by a hopping mechanism, and with the injection of electrons, the hole barrier is lowered, which will reduce the impedance in the Schottky junction. Under high humidity conditions, electrons are transported through the Grotthuss mechanism, and proton migration becomes easier, not only the surface impedance of copper oxide decreases, but also the impedance in the Schottky junction is greatly reduced. Therefore, the composite material exhibits a high response speed to humidity under high humidity conditions.

Ahmad [77] et al. reported that they prepared nanocomposites made of polyethylene oxide (PEO), oxidized multiwalled carbon nanotubes (MWCNT), and copper oxide (CuO) by electrospinning fiber. Among them, MWCNT and CuO are filled into polyethylene oxide as fillers. The data show that this composite exhibits a good response to humidity.

3.4. Doping with Other Inorganic Substances. In the selection of copper oxide doping materials, inorganic compounds such as potassium chloride (KCl) [87] and sulfuric acid (H_2SO_4) [124] are occasionally used to improve the moisture-sensitive properties of composites. When water vapor is adsorbed on the outer layer of the sensing element, such inorganic substances can be effectively dissolved into the adsorbed water and dissociated into an ionic state under the action of local charge density and strong electrostatic field. These ions can act as carriers to transfer charge carriers, thereby reducing the impedance of the sensing element [125, 126].

Qi et al. [87] reported the preparation of composite nanoparticles (KCZ/CZNs) using KCl-doped Cu–Zn/CuO–ZnO (CZ/CZNs). Through experiments, it was found between 11 and 95%RH; KCZ/CZNs showed a better linear correlation (Figure 21(a)), indicating that doping of KCl optimizes the impedance-humidity linearity. The response and recovery speed of the material has also been reliably verified (Figure 21(b)), with small hysteresis (Figure 21(c)) and shows good stability in the 60-day experiment.

In another experiment, Rahim et al. [124] recently reported the preparation of polyaniline and copper oxide- (PANI-CuO-) doped sulfuric acid (H_2SO_4) composites. The doped composite has higher conductivity, exhibits good response/recovery speed in experiments, and has excellent stability.

In general, doping copper oxide with additives increases the carrier density in the moisture-sensing material, which

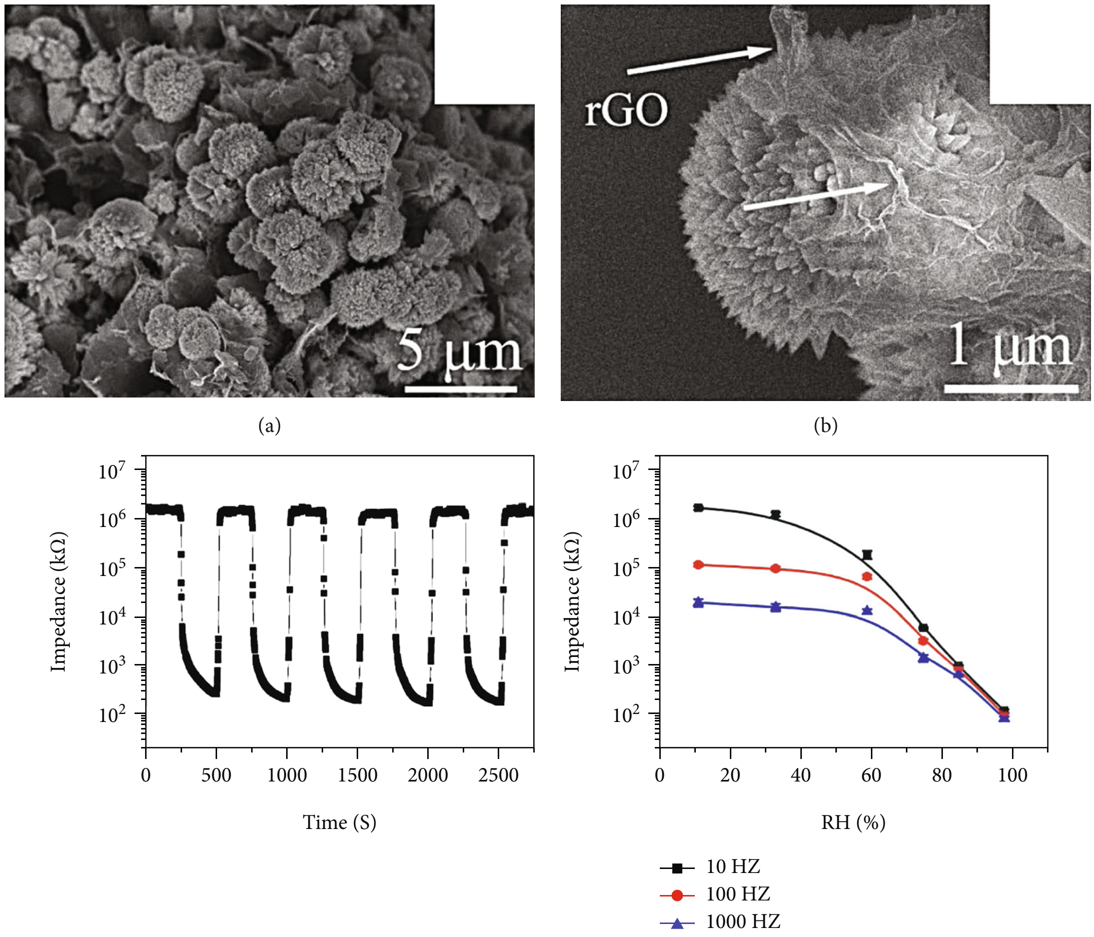


Figure 20: (a, b) SEM images of CuO/rGO composites. (c) Response and recovery properties of the sensors fabricated with the CuO/rGO composites. The curves were measured between 11% and 98%RH at 25°C. (d) Impedances of the sensors based on the CuO/rGO composites under different RHs measured at different frequencies [86].

makes the adsorption process of water vapor easier, and also reduces the activation energy of the sensing reaction on the surface of the material. As a result, the sensitivity and response speed of copper oxide-based humidity-sensing materials at room temperature are improved. Compared with the surface modification of pure copper oxide materials, in general, doping additives can effectively improve the humidity-sensing performance of sensors. Among them, the strengthening effect of metal oxides is the most significant.

4. Conclusions

To sum up, we found that doping organic polymers, metal oxides, and carbon-based materials is an efficacious way to achieve breakthroughs in the performance of CuO-based humidity-sensing elements, especially the doping of organic polymers and metal oxides. Through doping, the contact site of the additive with the copper oxide will form a heterojunction, which can effectively improve the sensitivity of copper oxide-based humidity-sensing elements, which points out the direction for the development of higher-performance copper oxide-based humidity sensors in the future, and even humidity sensors of other semiconductor metal oxides. It must be pointed out that doping organic polymers and metal oxides also increase the difficulty and cost of sensor fabrication. Apart from that, with the enhancement of water adsorption on the sensing element outer layer, the desorption process becomes difficult. Therefore, such a well-balanced connection between the sensitivity and hysteresis of the moisture-sensitive materials becomes crucial.

5. Outlook

There is no doubt that the current humidity sensor is developing rapidly in the direction of miniaturization and high efficiency. However, the complex and changeable working environment has become a major challenge for the current humidity sensor application, which urgently requires us in the performance of sensing elements, including its sensitivity, response speed, hysteresis and stability have been further improved. In recent years, promising results have been achieved in improving the humidity-sensing performance of copper oxide-based humidity

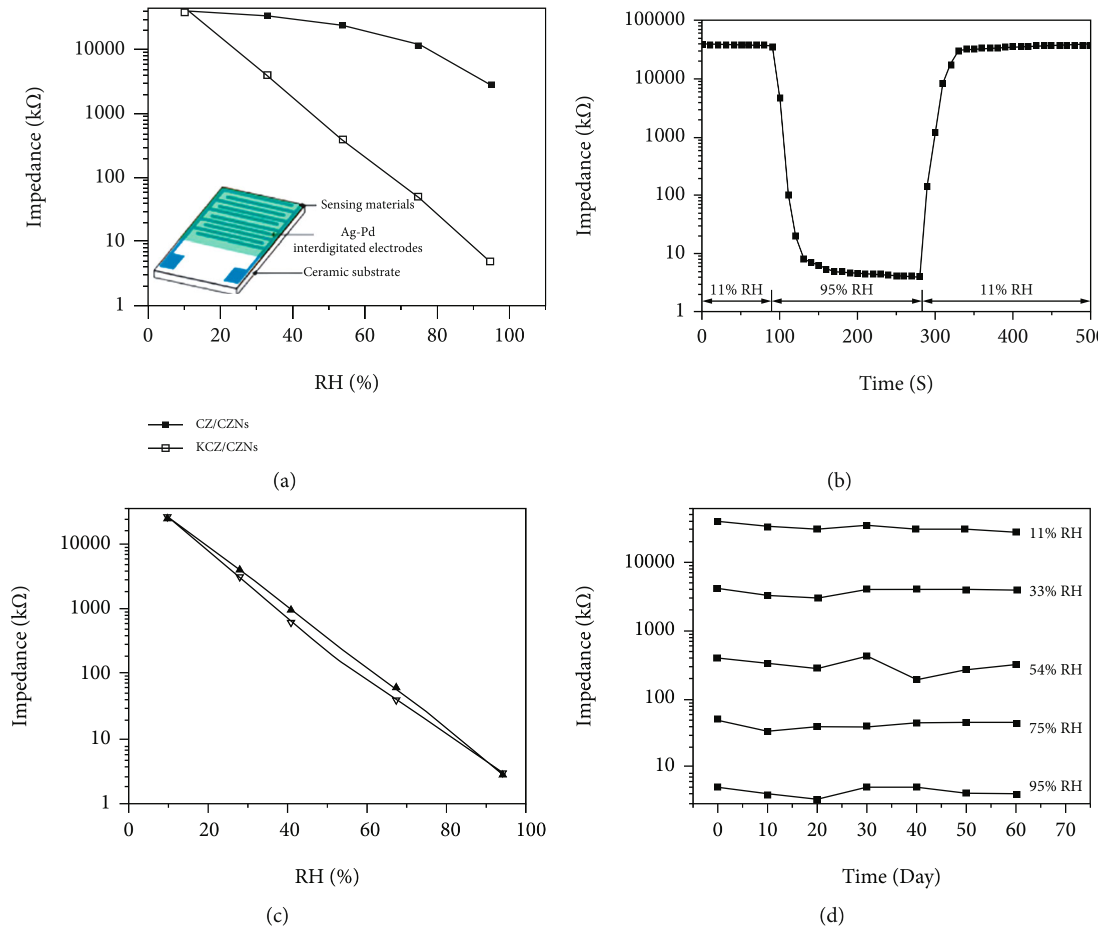


Figure 21: (a) The dependence of impedance on RH for pure and KCl-doped Cu–Zn/CuO–ZnO nanoparticles measured at 1 V, 100 Hz, and the inset shows the structure of the humidity sensor applied in our measurement. (b) Response of KCl-doped Cu–Zn/CuO–ZnO nanoparticles measured at 1 V, 100 Hz. (c) Hysteresis of KCl-doped Cu–Zn/CuO–ZnO nanoparticles measured at 1 V, 100 Hz. (d) Long-term stability of KCl-doped Cu–Zn/CuO–ZnO nanoparticles measured at 1 V, 100 Hz [87].

sensors. Fortunately, by modifying the surface of copper oxide and doping with different additives, considerable results have been achieved in improving the humidity sensitivity, especially the sensitivity, of copper oxide-based humidity sensors. Grain size, specific surface area, surface defects, and porosity are the main factors that affect the moisture-sensing properties of pure copper oxide. Smaller nanometer size enables the material to have a larger specific surface area, which increases the material's exposure to the atmosphere. Surface defects facilitate the adsorption of water vapor on the outer layer of the material, and the larger porosity can promote the condensation of water molecules. However, simple surface modification can only improve the humidity-sensitive properties of copper oxide to a certain extent, and it is difficult to make further performance improvements.

Nowadays, how to further ameliorate the humidity sensitivity of copper oxide-based moisture-sensitive materials is still a daunting challenge. Although many achievements have been made in bettering the performance of copper oxide-based moisture-sensitive materials, the performance of some humidity sensors, especially the sensitivity and stability, still cannot meet the needs of harsh environments, which requires further research. On the surface morphology modification of pure CuO, novel nanostructures can be synthesized by optimizing the structure and improving the process parameters, such as high-density nanofibers with a shell-core three-layer structure, which have better stability. In addition, doping additives are also effective measures to improve the humidity-sensing properties of copper oxide-based humidity-sensing materials. According to our previous detailed report, we found a considerable part of previous research on metal oxide doping has concentrated on n-type semiconducting metal oxides, in order to form a p-n junction with copper oxide, but there are few reports on p-type semiconductor metal oxides, which may be a good research direction and deserve further exploration. In fact, for improving the humidity-sensing properties of humidity-sensing materials, there have been experiments using a synergistic idea of combining multiple optimization strategies to further modify the surface morphology on the basis of doping additives, but there are still few reports. Finally, we sincerely hope that our work can contribute to the improvement of the humidity-sensing performance of copper oxide and even other kinds of semiconductor metal oxide humidity sensors.

Data Availability

All data can be obtained through contacting Pro. Wen Zeng.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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