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DEVELOPMENT OF A NEW HUMIDITY SENSOR BASED ON (CARBOXYMETHYL CELLULOSE–STARCH) BLEND WITH COPPER OXIDE NANOPARTICLES

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We have synthesized a nanocomposite of a new type as a humidity sensor and studied its electric and optical properties. The carboxymethyl cellulose–starch–copper oxide nanocomposite is prepared with different concentrations of copper oxide nanoparticles. The DC electric conductivity of the carboxymethyl cellulose–starch–copper oxide system was tested at room temperature. The results show that the DC conductivity of the blend increases with the copper oxide concentration. The optical properties of the nanocomposite are measured in the range of wavelengths (220–800) nm. The results show that the absorbance of the blend increases with the concentration of copper oxide nanoparticles, whereas the energy band gap decreases. With the purpose to use the system as a humidity sensor, its electric capacitance was measured on different samples in the range of humidity (40–90) RH%. The experimental results have shown that the carboxymethyl cellulose–starch–copper oxide nanocomposite has a higher sensitivity in the humidity range (60–90) RH%.

Keywords: sensor, humidity, blend, copper oxide, nanocomposite.

1. Introduction

Humidity sensors are of importance for the specific control and reliable estimate of the content of water vapor supplied by industrial processes in the atmosphere. Such control is needed for the general improvement in the quality of life. Generally, a humidity sensor has to possess fast response and recovery time, high sensitivity, good stability, negligible hysteresis over periods of usage, and a large operation range for both humidity and temperature. The importance of the humidity sensing has been well understood, and many researchers have been focused on the development of humidity-sensitive materials. In particular, the monitoring of a moisture content in soil has

become a pre-requisite for a variety of processes such as those in agricultural areas prone to landslides. It is worth noting the application of laboratory tests of microsensors to geological and geotechnical engineering, which has emerged only recently owing to the complex boundary conditions that must be overcome in granular materials such as three-phase solid-water-air void structures and heterogeneous particle distributions. Nanostructures with metal oxides as promising materials have attracted much attention because of their extraordinary properties in different fields of optics, optoelectronics, catalysis, *etc.* In particular, they are used as biosensors and humidity sensors. The sensors made from metal oxides like aluminum oxide, titanium oxide, tin oxide, and iron oxide have been emerged as economical humidity sensors in recent years. Among all, cupric oxide (CuO)

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has attracted a considerable attention because of its peculiar properties. An important advantage of the use of CuO in devices is that it is non-toxic, and its constituents are available in abundance [1]. Many commercially available humidity sensors are based on ceramic materials due to their low cost and quite good performance. They offer major advantages with high resistance to chemical attacks, thermal stability, and mechanical strength. However, some problems can be mentioned, like the insufficient sensitivity over a wide humidity range in some types of sensing elements, reversibility and drift in the base line with time due to the chemisorption of various gases [2]. Humidity sensors are in demand in the industrial, environmental, and structural monitoring fields. One of the most frequent causes for the structural failure is the corrosion. A large number of structures degrade and fail due to the inefficient humidity monitoring. A lot of researches has been conducted to fabricate high-efficiency humidity sensors based on either a change in the resistance or mass of a thin film due to the presence of water molecules. More recently, the humidity sensors for the corrosion detection were fabricated using long-period gratings by calculating the resonant wavelength shift. In recent years, the research has been conducted to achieve a high level of sensitivity and selectivity in sensors [3]. Humidity sensors have gained increasing applications in the industrial processing and environmental control. For manufacturing highly sophisticated integrated circuits in the semiconductor industry, humidity or moisture levels are constantly monitored in the wafer processing. There are many domestic applications, such as the intelligent control of a living environment in buildings, cooking control for microwave ovens, and the intelligent control of laundry, *etc.* In the automobile industry, humidity sensors are used in rearwindow defoggers and motor assembly lines. In the medical field, humidity sensors are used in the respiratory equipment, sterilizers, incubators, pharmaceutical processing, and biological products. In agriculture, humidity sensors are used for green-house air conditioning, plantation protection (dry prevention), soil moisture monitoring, and cereal storage. In the general industry, humidity sensors are used for humidity control in the chemical gas purification, dryers, ovens, film desiccation, paper and textile production, and food processing [4].

The humidity monitoring is a necessary activity in many industry fields. The measurement of humidity is of great importance in chemical and medical industries such as respiration monitoring. In addition, the humidity sensing is essential in the civil and aerospace engineering. It is frequently monitored in giant structures such as planes and bridges to control the possible risk of a leakage due to the corrosion. In humidity sensors, the low response time, high sensitivity, repeatability, reversibility, and noise immunity are required. Furthermore, in situations where humidity changes rapidly, sensors with low response and recovery times are needed. Such applications include the control over processes in industry, meteorology, and a variety of other medical applications such as the human respiration monitoring. This shows the need for fast, highly sensitive, and low-cost humidity sensors. Moreover, the fabrication simplicity and low cost are also of importance in humidity sensors [5]. The addition of inorganic nanoparticles to polymers allows a modification of the polymer physical properties, as well as the implementation of new features in the polymer matrix. With decreasing the particle size, the surface/volume ratio increases, so that the surface properties become crucial [6, 7]. The applications of nanocomposites are quite promising in the fields of microelectronic packaging, medicine, automobiles, optical integrated circuits, drug delivery, injection molded products, sensors, membranes, aerospace, packaging materials, coatings, fire-retardants, adhesives, consumer goods, *etc.* [8, 9]. The composites have been widely used in the various fields such as military equipments, safety, protective garments, automotive, aerospace, electronics, and optical devices. However, these application areas continuously demand additional properties and functions such as high mechanical properties, flame retardation, chemical resistance, UV resistance, electric conductivity, environmental stability, water repellency, magnetic field resistance, radar absorption, *etc.* [10].

2. Materials and Methods

The carboxymethyl cellulose–starch–copper oxide nanocomposite has been prepared with different concentrations of components: carboxymethyl cellulose (81 wt.%), starch (19 wt.%), and copper oxide

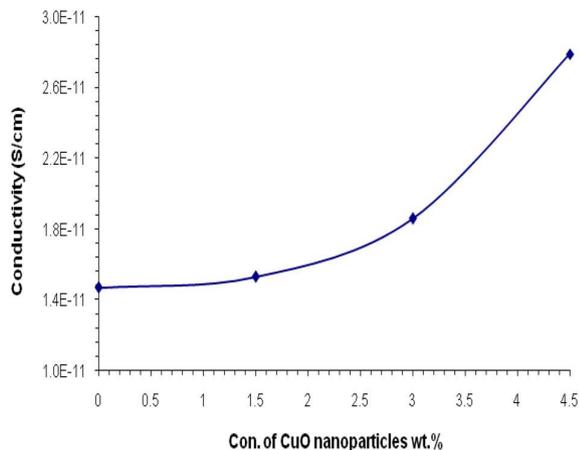


Fig. 1. Variation of the DC electric conductivity of the (CMC-starch) blend with different concentrations of copper oxide nanoparticles at room temperature

nanoparticles are added with concentrations of 0, 1.5, 3, and 4.5 wt.%. The nanocomposites prepared by the casting method in the template (Petri dish was 10 cm in diameter). The samples were prepared in the thickness range (32–52) μm . The optical absorbance of the nanocomposite was recorded by a UV/1800/Shimadzu spectrophotometer in the range of wavelengths (220–800) nm. The DC electric conductivity of nanocomposites was determined by measuring the DC electric resistance at room temperature, by using a Keithley electrometer 2400. The DC electric conductivity (σ_V) of nanocomposites can be calculated for a regular body with length L , constant area N , and electric resistance R , by using the relation [11]

$$\sigma_v = L/RN. \quad (1)$$

The absorption coefficient α of (CMC-starch-CuO) nanocomposites is determined by the relation [12]

$$\alpha = 2.303 \frac{A}{t}, \quad (2)$$

where t is the sample thickness, and A is the absorbance.

The electronic transitions can be defined by the relation [13]

$$\alpha h\nu = B_0(h\nu - E_g^{\text{opt}})^r, \quad (3)$$

where ν is the frequency, B_0 is a constant, h is Planck's constant, E_g^{opt} is the energy band gap between the valence band and the conduction band, and

r can take the values 2, 3, 1/2 or 3/2 for indirect allowed, indirect forbidden, direct allowed, and direct forbidden transitions, respectively.

The samples of nanocomposites for humidity sensors were prepared by casting the solution of nanocomposites on glass slides (2×2) cm^2 in dimension after the cleaning by ethanol and distilled water and were left to dry for three days. The sample was placed in a box, and water vapor was used as a source of humidity. The control network monitored and controlled variations in humidity. The electric capacitance for the humidity range (40–90) % was measured, by using an LCR meter (HIOKI 3532-50 LCR HI TESTER) at 10 KHz.

3. Results and Discussion

Figure 1 shows the variation of the DC electric conductivity of a (CMC-starch) blend with different concentrations of copper oxide nanoparticles at room temperature. As shown in the figure, the electric conductivity of a (CMC-starch) blend increases with the concentration of copper oxide nanoparticles. This may be due to an increase in the number of mobile charge carriers and to an increase in the amorphous nature of the polymer blend, which reduces the energy barrier there by facilitating the ion transport [14].

The study of the fundamental absorption edge in the UV region is a useful method for the investigation of optical transitions and the electronic band structure in crystalline/noncrystalline materials. The UV-Vis absorption spectra of a (CMC-starch) blend and a (CMC-starch) blend doped with copper oxide nanoparticles are shown in Fig. 2. As is seen, the absorbance increases with the content of copper oxide nanoparticles in the blend. In the UV region, we observe the absorption band, which is a characteristic of the (CMC-starch) blend and is assigned to $\pi - \pi^*$ electronic transitions [15]. The absorbance of (CMC-starch) blend increases with the concentration of copper oxide nanoparticles; this occurs, because the layer of covalent bonds is formed between (CMC-starch) blend chains and additives, which increases the absorption of the incident light especially at the shortest wavelengths. The electrons in the outer orbits transit to the higher energy levels and occupy vacant positions of the energy bands. Thus, a part of incident light does not penetrate through the blend. However,

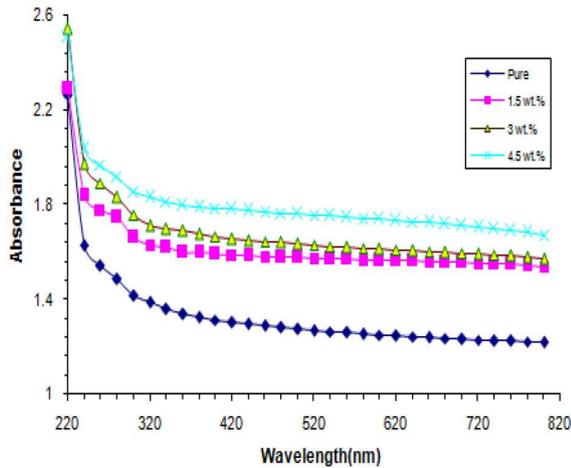


Fig. 2. UV-Vis absorption spectra of a (CMC-starch) blend and a (CMC-starch) blend doped with copper oxide nanoparticles

the conduction band of the (CMC-starch) blend needs photons with high energy, after which it has low absorbance [16].

Figure 3 shows a variation of the energy band gap for allowed indirect transitions of the nanocomposite. As is seen, the energy gap of (CMC-starch) blend is decreased, as the concentration of CuO nanoparticles increases. The decrease in the optical energy band gap with increasing the concentration of CuO nanoparticles may be explained on the basis of the fact that the incorporation of small amounts of a dopant forms charge transfer complexes in the host matrix. These charge transfer complexes increase the electric conductivity by providing additional charges, resulting in a decrease of the optical energy gap. As the dopant concentration is increased, the dopant molecules start bridging the gap separating the two localized states and lowering the potential barrier between them, by facilitating the transfer of charge carriers between two localized states [17].

Figure 4 shows the variation of the capacitance for the (CMC-starch-CuO) nanocomposite with humidity at 10 KHz. From the figure, the capacitance of the nanocomposite increases with the humidity. The sensing mechanism is based on the absorption and desorption process between the surface structure and humidity. At a low humidity, the tips and defects of the films present a high local charge density and a strong electrostatic field, which promotes water dis-

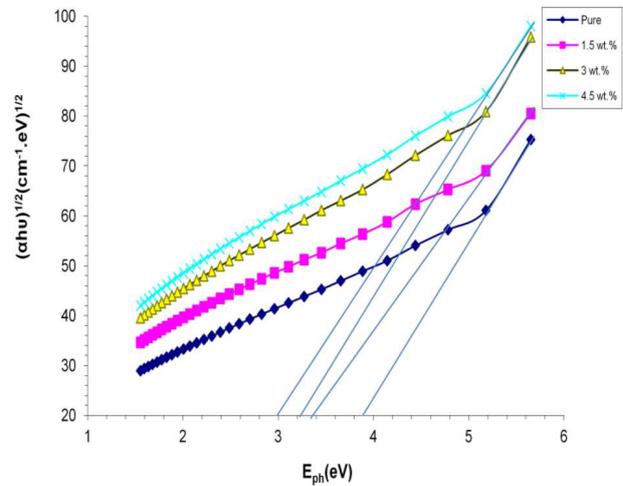


Fig. 3. Variation of the energy band gap for allowed indirect transitions of (CMC-starch-CuO) nanocomposites

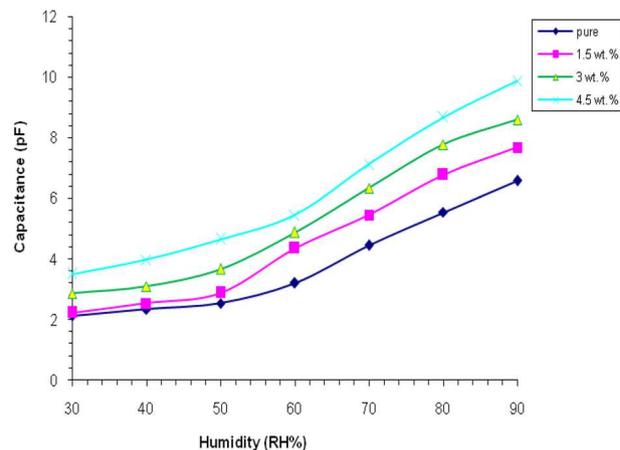


Fig. 4. Variation of the capacitance for the (CMC-starch-CuO) nanocomposite with humidity at 10 KHz

sociation. The dissociation provides protons as charge carriers of the hopping transport. At a high humidity, one or several serial water layers are formed among films, and the electrolytic conduction between sensing materials takes place along with photonic transport and becomes dominant in the transport process [18]. The result clearly indicates that, in the lower humidity range, the change of the capacitance with % RH is not significant, whereas it is sharp at higher %RH. The variation of the dielectric constant occurs due to a different level of moisture absorbed by pores of the nanocomposite material ac-

ording to the moisture content in the closed atmosphere. The water molecule has six degrees of freedom. When the water molecule enters the pores, it loses its degree of freedom, and a change of the state would take place from moisture vapor to liquid, and the overall dielectric constant of the material will be increased. In the low RH range, the less number of water molecules enter the pores, which leads to a small change in the capacitance. But, at higher RH, water molecules tend to form clusters in pores of the polymeric nanocomposite material. Therefore, a sharp change of the capacitance occurs at high RH range [19].

4. Conclusions

1. The DC electric conductivity of a (CMC-starch) blend increases with the concentration of copper oxide nanoparticles.

2. The absorbance of a (CMC-starch) blend increases with the concentration of CuO nanoparticles.

3. The energy band gap of a (CMC-starch) blend is decreased with the concentration of CuO nanoparticles.

4. The (CMC-starch-CuO) nanocomposites have higher sensitivity to the relative humidity in the range (40–90) %.

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РОЗРОБКА НОВОГО СЕНСОРА ПЕРЕВІРКИ
ВОЛОГИ НА ОСНОВІ СУМІШІ КАРБОКСИМЕТИЛ
ЦЕЛЮЛОЗА–КРОХМАЛЬ З НАНОЧАСТИНКАМИ
ОКИСУ МІДІ

Резюме

Ми синтезували нанокompозит нового типу як сенсор вологості і вивчили його електричні і оптичні властивості. Нанокompозит складається з карбоксиметил целюлози, крохмалю та наночастинок оксиду міді і приготований з різни-

ми концентраціями компонент. Ми вимірювали електричну провідність при постійному струмі і при кімнатній температурі і знайшли, що провідність системи зростає з концентрацією оксиду міді. Вимірювання оптичних властивостей нанокompозиту в діапазоні довжин хвиль 220–800 нм показало, що з ростом концентрації наночастинок оксиду міді поглинання зростає, тоді як ширина забороненої зони зменшується. З метою використовувати систему як сенсор вологості, виміряна її ємність для різних зразків в інтервалі відносної вологості 40–90%. Дані показали, що система має найбільшу чутливість в інтервалі 60–90%.