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Humidity Sensing Performance of Polymer Blend–Titanium Nitride Nanocomposites: Structural, Electrical, and Optical Properties

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Synthesis of new nanocomposite films of both the PVA–PAA blend and the PVA–PAA blend doped by titanium nitride nanoparticles is investigated for the sake of humidity sensors with low cost, light weight, flexibility and high sensitivity. The structural, electrical, and optical properties of PVA–PAA–TiN nanocomposites are studied. The results concerning electrical properties of PVA–PAA–TiN nanocomposites show that the electrical conductivity of PVA–PAA blend increases from $4.3 \cdot 10^{-11}$ S/cm to $6.1 \cdot 10^{-9}$ S/cm, if the titanium-nitride nanoparticles' concentration increases to 6 wt.%. In addition, the electrical conductivity of all samples of PVA–PAA–TiN nanocomposites increases by one order, when temperature increases from 50°C to 80°C. The activation energy for PVA–PAA blend decreases from 0.57 eV to 0.29 eV, when titanium-nitride nanoparticles' concentration increases. The optical-properties' results show that the transmittance of PVA–PAA blend decreases (to 83.5%) with increasing the titanium-nitride nanoparticles' concentration. The results concerning PVA–PAA–TiN-nanocomposites' applications for the sake of humidity sensors show that the PVA–PAA–TiN nanocomposites have high sensitivity for relative humidity.

Синтеза нових нанокompозитних плівок як суміші полівінілового спирту (ПВС)–поліакрилової кислоти (ПАК), так і суміші ПВС–ПАК, левованої наночастинками нітриду Титану, досліджується заради датчиків вологості з низькою вартістю, невеликою вагою, гнучкістю та високою чутливістю. Досліджено структурні, електричні й оптичні властивості нанокompозитів ПВС–ПАК–TiN. Результати щодо електричних властивостей нанокompозитів ПВС–ПАК–TiN показують, що електропровідність суміші ПВС–ПАК збільшується з $4,3 \cdot 10^{-11}$ См/см до $6,1 \cdot 10^{-9}$ См/см, якщо концентрація наночастинок нітриду Титану збільшується до 6 ваг.%. Крім того, електропровідність всіх зразків нанокompозитів

ПВС–ПАК–TiN збільшується на один порядок, коли температура підвищується від 50°C до 80°C. Енергія активації суміші ПВС–ПАК зменшується від 0,57 eV до 0,29 eV, коли концентрація наночастинок нітриду Титану збільшується. Результати щодо оптичних властивостей показують, що прозорість суміші ПВС–ПАК знижується (до 83,5%) зі збільшенням концентрації наночастинок нітриду Титану. Результати щодо застосування нанокompозитів ПВС–ПАК–TiN заради датчиків вологості показують, що нанокompозити ПВС–ПАК–TiN мають високу чутливість до відносної вологості.

Key words: humidity sensors, nanocomposites, titanium nitride, conductivity, transmittance.

Ключові слова: датчики вологості, нанокompозити, нітрид Титану, електропровідність, прозорість.

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1. INTRODUCTION

Humidity has an important influence on several industrial processes such as electronic, food or pharmaceutical manufacturing, food storage, *etc.* All these processes, which can be affected by humidity, require continuous monitoring of air humidity. In addition, proper humidity levels can be critical to the quality of the product and having the right humidity level can contribute to diminishing energy consumption [1]. Humidity sensors have gained advanced applications in industrial processing and environmental control. For manufacturing, highly sophisticated integrated circuits in semiconductor industry, humidity levels are constantly monitored in wafer processing. There are many domestic applications, such as intelligent control of the living environment in buildings, cooking control for microwave ovens, and intelligent controller. In automobile industry, humidity sensors are used in rear window defoggers and motor assembly lines. In medical field, humidity sensors are used in respiratory equipment, sterilizers, pharmaceutical processing, and biological products. In agriculture, humidity sensors are used for greenhouse air conditioning, plantation protection (dew prevention), soil moisture monitoring. In general industry, humidity sensors are used for humidity control in chemical gas purification, dryers, ovens, film desiccation, paper and textile production, and food processing. Humidity sensor plays an important role in every part of the Earth and automated industrial processes [2].

Several kinds of humidity sensors are available based on different transduction principles, such as resistive, capacitive, optical, and surface acoustic wave. However, resistive-type sensors have the ad-

vantage to be cheaper and easier to read out over the other ones. Typically, rigid substrates like ceramic, glass, or silicon are used as the fundamental building blocks of humidity sensors; but, recent advancements in the field of printed electronics show increased potential for the substitution of rigid substrates by flexible ones, since the latter potentially reduce the cost of sensors and offer good mechanical flexibility. Examples of flexible sensors integrating additional electronic functions like readout electronics, thermal compensation systems, and other sensors have opened a new route towards multifunctional sensors fabricated on flexible substrate [3]. Inorganic-organic nanocomposites are extremely promising for applications in light-emitting diodes, microelectronic packaging, automobiles, medicine, drug delivery, injection moulded products, optical integrated circuits, sensors, fire-retardants, membranes, aerospace, coatings adhesives, packaging materials, consumer goods, *etc.* [4-10].

The properties of nanocomposites films can be adjusted by varying the composition. Their fabrication shares the same advantages of organic device technology, such as low cost production and the possibility of device fabrication on large area and flexible substrates. Polyvinyl alcohol (PVA) is a potential material having high dielectric strength, good charge storage capacity and dopant-dependent electrical and optical properties. It has carbon chain backbone with hydroxyl groups attached to methane carbons. These OH groups can be a source of hydrogen bonding and hence assist the formation of polymer composite [11]. Polyacrylic acid (PAA) is a non-toxic, hydrophilic and biocompatible superabsorbent polymer with a three dimensional (3D) network. PAA was chosen as a host polymer in this research due to its fascinating behaviours such as excellent stability in acidic and basic media, high ionic conductivity, strong adhesive properties, superior selectivity and permeability and high ability to associate with a variety of multivalent metal ions in solution. PAA can suppress the crystallization and form stable complexes with metal. The main reason for choosing PAA as a host polymer is because of its high charge density based on carboxylic (-COOH) functional group. This functional group favours the bond formation, for example, ionic, covalent, hydrogen and coordination ones, which can be used to form complexation with the nanoparticles [12]. Lim *et al.* [13] studied the polyvinyl alcohol nanocomposites containing reduced graphene oxide coated with tannic acid for humidity sensor. The results showed that the PVA nanocomposites showed excellent humidity sensing properties over the wide relative humidity range and the long-term stability due to the conductive property of the reduced GO and the enhanced mechanical strength by the effective incorporation of rGO-TA into the

PVA matrix [13].

2. MATERIALS AND METHODS

Nanocomposites films of polyvinyl alcohol–polyacrylic acid blend and polyvinyl alcohol–polyacrylic acid blend doped with titanium nitride nanoparticles were prepared by using casting method. The films of PVA–PAA–TiN nanocomposites were prepared by dissolving 1 gm of PVA and PAA in 30 ml of distilled water with concentrations 85 wt.% PVA and 15 wt.% PAA by using magnetic stirrer to mix the polymers for 1 hour to obtain solution that is more homogeneous. The TiN nanoparticles were added to PVA–PAA blend with concentrations 1.5, 3, 4.5 and 6 wt.%. The samples of nanocomposites were prepared with thickness range 115–122 μm . The D.C. electrical conductivity of films was measured by measuring the D.C. electrical resistance by using the Keithley electrometer type 2400 source mater at different temperature 50–80°C. The optical properties of PVA–PAA–TiN nanocomposites were measured by using the double beam spectrophotometer (Shimadzu, UV-1800Å) in wavelength 240–820 nm. The each one of PVA–PAA–TiN nanocomposites samples was placed in box and the water vapour was used as a source of humidity. The control network monitored and controlled variations in humidity. The electrical resistance of PVA–PAA–TiN nanocomposites for different-humidity range 40–90% was measured by using the Keithley electrometer type 2400 source mater.

The D.C. electrical conductivity (σ) of PVA–PAA–TiN nanocomposites can be calculated by using the equation [14]:

$$\sigma = L/(RS), \quad (1)$$

where S —the open cross-sectional area, L —the length, and R —the electrical resistance of a sample.

The electrical conductivity of PVA–PAA–TiN nanocomposites increases with increasing temperature according to the relation [15]:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{k_B T}\right), \quad (2)$$

σ —conductivity at temperature T , σ_0 —conductivity at absolute temperature zero, E_a —activation energy, k_B —Boltzmann constant.

3. RESULTS AND DISCUSSION

Figure 1 shows the variation of D.C. electrical conductivity of

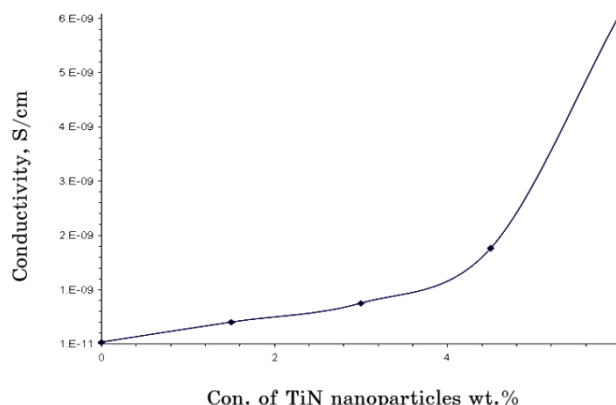


Fig. 1. Variation of D.C. electrical conductivity of PVA-PAA blend with concentration of TiN nanoparticles at 50°C.

PVA-PAA blend with concentrations of TiN nanoparticles at 50°C. The D.C. electrical conductivity of PVA-PAA blend is increasing with the increase in TiN nanoparticles' concentration and is noticeably increasing, when the concentration of TiN nanoparticles reach to 4.5 wt. %.

The increase of electrical conductivity with increasing TiN nanoparticles' concentration is attributed to the increase of the charge-carriers' number with increasing TiN concentration [16]. When the concentration of TiN nanoparticles reaches to 4.5 wt. %, the TiN nanoparticles form a continuous network in the nanocomposite as shown in Fig. 2. At low concentrations of TiN nanoparticles (1.5 wt. % and 3 wt. %), the nanoparticles are located in clusters, the clusters are contacted at concentration of 4.5 wt. % for PVA-PAA nanocomposites [17].

The effect of temperature on the D.C. electrical conductivity of PVA-PAA-TiN nanocomposites is shown in Fig. 3. This figure shows that the electrical conductivity of all samples is increased with increase the temperature. The behaviour of electrical conductivity with temperature attributed to the increase the mobility and number of charge carriers inside the PVA-PAA-TiN nanocomposites [18], where PVA-PAA chains and TiN nanoparticles could act as traps for the moving charge carriers by hopping process, the increase in temperature causes to moving the polymers chains and releasing the trapped charges [19]. So, the increase of current in PVA-PAA-TiN nanocomposites with the increase of the temperature is attributed to two parameters: mobility and number of charge carriers. The increase is exponential [20].

Figure 4 shows the variation of $\ln\sigma$ with $1000/T$ for PVA-PAA-TiN nanocomposites to calculate the activation energy for nanocom-

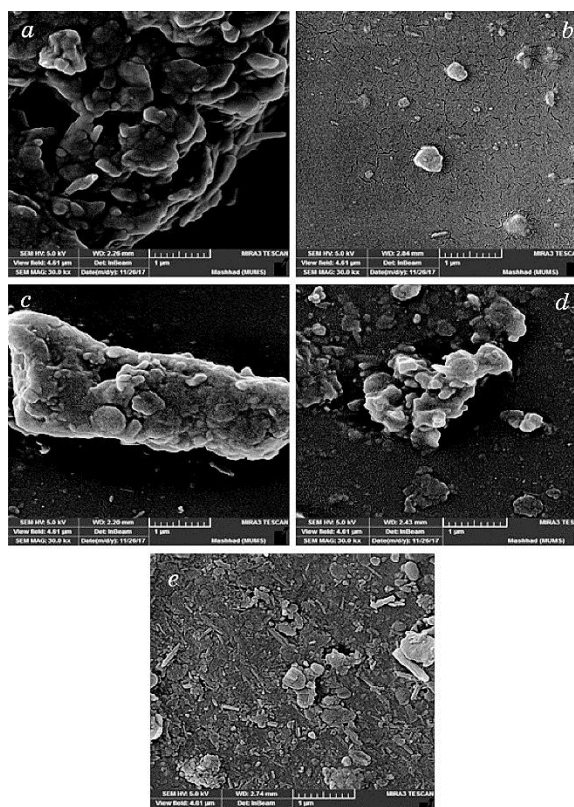


Fig. 2. SEM images of PVA-PAA blend and PVA-PAA blend doped with titanium-nitride nanoparticles: (a) pure PVA-PAA blend; (b) 1.5 wt.% TiN nanoparticles; (c) 3 wt.% TiN nanoparticles; (d) 4.5 wt.% TiN nanoparticles; (e) 6 wt.% TiN nanoparticles.

posites. The experimental results show that the activation energy values are ranging from 0.576 eV to 0.295 eV for PVA-PAA-TiN nanocomposites. The high value of activation energy for PVA-PAA blend attributed to existence of free ions in the polymers. The decrease of activation energy of PVA-PAA-TiN nanocomposites with the increase of the nanoparticles' concentration related to increase in localization of charge carriers causing higher electrical conductivity that is attributed to effect of space charge contribution, which may play an important role in the charges' transport [21, 22].

The variation of activation energy with TiN nanoparticles concentration is shown in Fig. 5. The activation energy of PVA-PAA-TiN nanocomposites decreases with the increase of the TiN nanoparticles' concentration for all samples of nanocomposites. This behav-

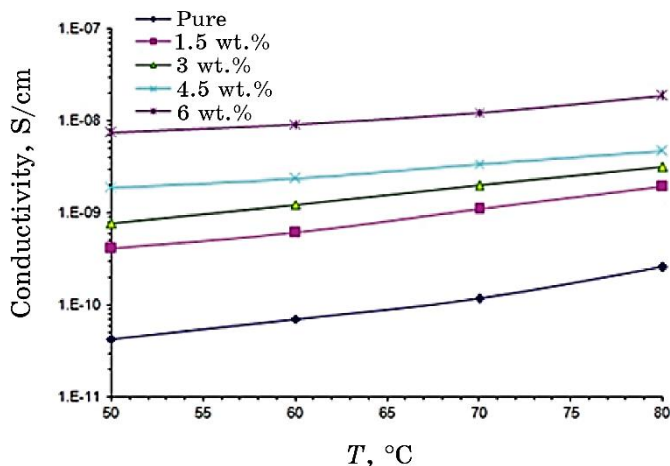


Fig. 3. Effect of temperature on the D.C. electrical conductivity of PVA-PAA-TiN nanocomposites.

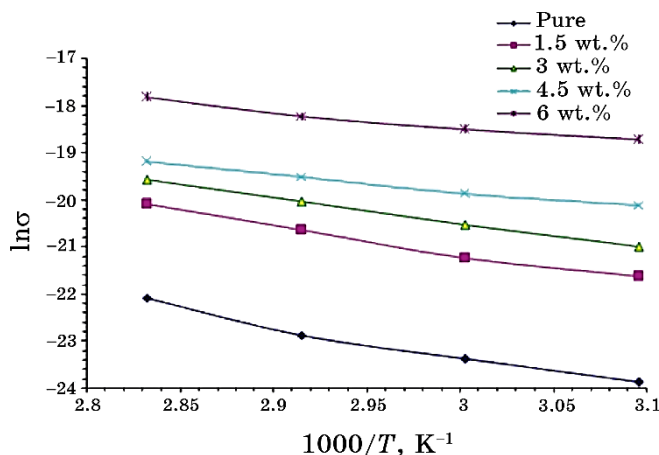


Fig. 4. Variation of $\ln\sigma$ with $1000/T$ for PVA-PAA-TiN nanocomposites.

ion is due to creating local energy levels in the energy gap, which act as traps for charge carriers [22]. At high TiN nanoparticles' concentration, the activation energy has lower values, which are attributed to formation a continuous network of nanoparticles in the nanocomposite [23].

Figure 6 shows the variation of transmittance for PVA-PAA-TiN nanocomposites with wavelength of the incident light. The figure shows that decrease in transmission of all samples at UV region; this is due to the excitations of donor level electrons to the conduction band at these energies.

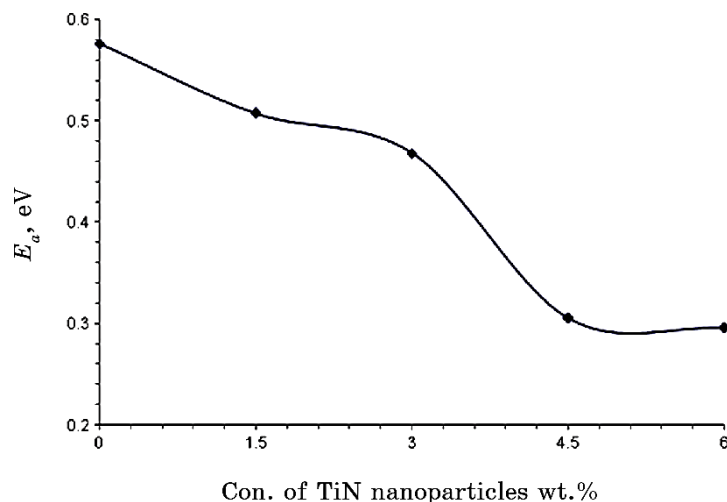


Fig. 5. Variation of activation energy with TiN nanoparticles' concentration.

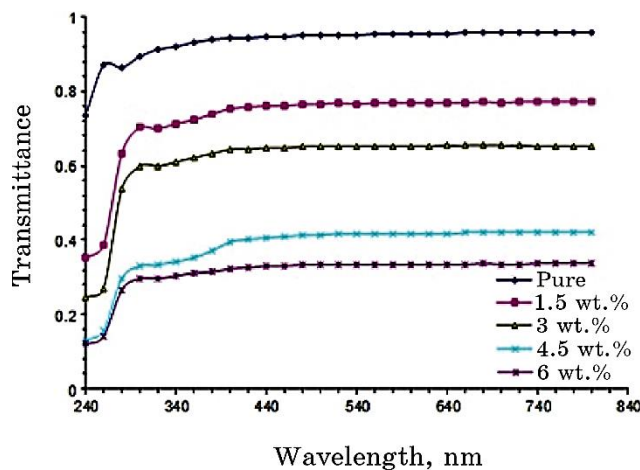


Fig. 6. Variation of transmittance for PVA-PAA-TiN nanocomposites with wavelength of the incident light.

The low transmittance of samples at UV region is attributed to the energy of photon enough to interact with atoms; the electron excites from a lower to higher energy level by absorbing a photon of known energy. The changes in the absorbed and transmitted radiation can decide the types of possible electron transitions [24].

At visible and near infrared regions, the transmittance of all samples has high values. This behaviour attributed to the energy of

incident photons does not enough in energy to interact with atoms. Thus, the photons will be transmitted when the wavelength increases [25]; hence, the transmittance increases.

In addition, Figure 6 shows that the transmittance decreases with increase in TiN-nanoparticles' concentration; this is due to the agglomeration of nanoparticles with increasing concentration and increase of the number of charge carriers [26].

Figure 7 shows the variation of electrical resistance for PVA-PAA-TiN nanocomposites with humidity at room temperature. From the figure, the electrical resistance decreases with increase in humidity. This behaviour may be attributed to the following possibilities. (i) At low *RH*, mobility of TiN ions in the composite is restricted due to curling up of polymer chains. As humidity increases, polymer chain uncurls and becomes aligned by absorbing water molecules paving way for faster hopping of charge carriers, resulting in increased sensing response of the composite. (ii) Porosity of the polymers may facilitate absorption of water molecules as *RH* increases causing a decrease in the impedance of the composite [27]. The resistance changes with increasing the humidity levels occur because of adsorption and capillary condensation of water. At low humidity levels, chemisorption takes place leading to the formation of two surface hydroxyls with the charge transport occurring by the hopping mechanism, while, at high humidity levels, water is physisorbed on the top of the chemisorbed layer. When water molecules are available at low humidity, they chemisorb on grain surfaces of the ceramic to form hydroxyl groups as surface charge carriers. When initial water molecules are adsorbed, each water molecule

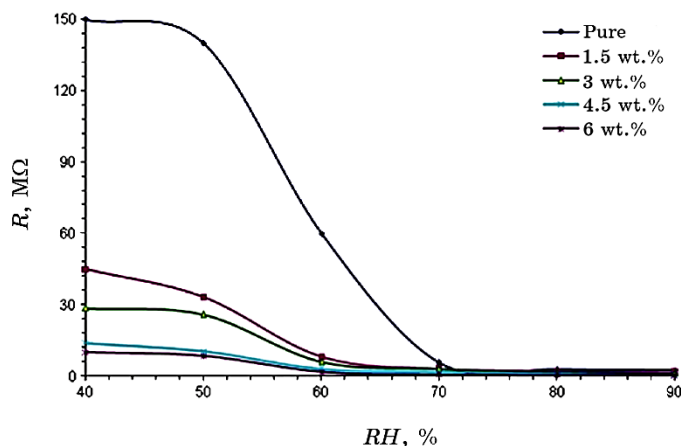


Fig. 7. Variation of electrical resistance for PVA-PAA-TiN nanocomposites with humidity at room temperature.

is hydrogen-bonded to two hydroxyls, and the dominant surface charge carriers will be H_3O^+ . When still more water is adsorbed, clustering of the water molecules takes place, forming a liquid-like multilayer film of hydrogen bonded water molecules, where each water molecule is only singly bonded to a hydroxyl group. Since dissociation of H_3O^+ into H_2O and H^+ is energetically favourable in liquid water, the dominant charge carrier in high moisture environment is H^+ [28–30].

4. CONCLUSIONS

The D.C. electrical conductivity of PVA–PAA blend increases with an increase in TiN nanoparticles concentration and temperature.

The activation energy of PVA–PAA blend decreases with an increase in titanium-nitride nanoparticles concentration.

The optical transmittance of PVA–PAA blend decreases with an increase in titanium nitride nanoparticles concentration.

The PVA–PAA–TiN nanocomposites have high sensitivity for relative humidity with low cost and low weight.

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