RESEARCH PAPER

Fabrication and Characterization of Polymer Blend Doped with Metal Carbide Nanoparticles for Humidity Sensors

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ABSTRACT

Nanocomposites films of (polymer blend-ceramics) were prepared from (PVA-PAA) blend and (PVA-PAA) blend doped with niobium carbide nanoparticles for humidity sensors have low cost, easy fabrication, high sensitivity, lightweight and high corrosion resistance. The structural, electrical and optical properties of (PVA-PAA-NbC) nanocomposites have been studied. The D.C electrical properties of (PVA-PAA-NbC) nanocomposites were studied with different temperature range. The results showed that the D.C electrical conductivity (PVA-PAA) blend increases with increase in niobium carbide nanoparticles concentrations and temperatures. The activation energy of (PVA-PAA) blend decreases with increase in niobium carbide nanoparticles concentrations. The results of optical properties showed that the transmittance of (PVA-PAA) blend decreases with increase in niobium carbide nanoparticles concentrations. The (PVA-PAA-NbC) nanocomposites tested for humidity sensors and the results showed that the (PVA-PAA-NbC) nanocomposites have high sensitivity for humidity sensors.

INTRODUCTION

The demand for advanced materials possessing a good combination of desirable properties for wide range of applications in future technologies is increasing day by day. Lightweight, low cost, low temperature fabrication, mechanical strength, good environmental stability etc. are a few of the requirements to be met by such materials. Exploitation of nanomaterials, especially composites based on them, is nowadays a common approach to prepare new smart materials for future technologies. It is expected that some organic inorganic nanocomposites will have synergetic behavior of their organic and inorganic components, and therefore, potential applications of these nanocomposites in optoelectronic devices, sensors, electromagnetic interference shielding etc. may be explored. In a similar context, our group dedicated to the study of stability of electrical conductivity of materials tried to find out the stability of electrical conductivity of organic-inorganic nanocomposites mainly based on conducting polymers using inorganic nanoparticles with a supporting matrix of a thermoplastic polymer [1]. Polymers have several advantages, such as low cost, easy processing, flexibility, good mechanical properties and high strength. Polymeric nanocomposites consisting of inorganic nanoparticles and organic polymers represent a class of materials that have motivated considerable interest in recent years. The nanocomposites applications 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

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goods .. etc [2-7]. Semiconductor nanoparticles/ organic polymer composites have attracted considerable interest in recent years due to their sizedependent properties and great potential for many applications such as nonlinear optics, photoelectrochemical cells, heterogenerous photocatalysis, optical switching, and single electron transistors. The reason is that the polymer matrices provide for procceibility, solubility, and control of the growth and morphology of the nanoparticles. Various approaches have been employed to prepare nanoparticles/polymer composites. Therefore, more attention has been paid to the in situ synthesis of inorganic nanoparticles in polymer matrices to obtain new semiconducting properties by controlling nanoparticle size and shape (polymer used as capping agent for nanoparticles). PVA is a potential material having high dielectric strength, good charge storage capacity and dopant-dependent electrical and optical properties. PVA polymer 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 by growing inorganic nanoparticles inside polymer matrix [8]. PAA is a non-toxic, hydrophilic and biocompatible superabsorbent polymer with a three dimensional (3-D) network. PAA was chosen as a host polymer in this research due to its fascinating behaviors 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 favors the bond formation—for example, ionic, covalent, hydrogen and coordination–which can be used to form complexation with the nanoparticles. The ionization of the carboxylic group in PAA depends mainly on pH and ionic strength. The charge density of PAA is low in acidic media due to the poor degree of dissociation. The ions can just be dissociated well in the solution at higher pH values (pH > 5) [9]. Humidity sensors are very important key for applications in environmental monitoring, industrial process control and in day today life. The measurement of humidity is demanded in wide range of areas, including agriculture, horticulture, meteorological services, food processing, air conditioning and electronic processing. While electronic humidity sensors are commercialized, other types of humidity sensors which are thin, light-weight and cheap are still required for many applications. The constructive design of good humidity sensor is a rather complicated topic, because high performance humidity sensor claim many requirements including linear response, high sensitivity, fast response time, chemical and physical stability, wide operating range and low cost [10]. Ghadiry et al. [11] studied the nano-anatase TiO_2 for high performance optical humidity sensing on chip. They found that the proposed sensor was extensively compared with other state-of-the-art proposed counterparts from the literature and remarkable advantages were found. Since a high sensitivity of ~0.21 dB/%RH and high dynamic performances were demonstrated, this sensor is
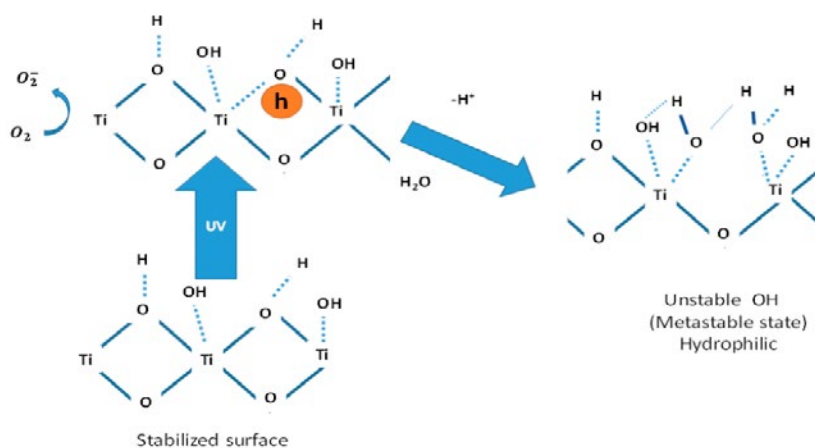

Fig. 1. Mechanism of surface wettability of TiO_2 film under UV light irradiation [11].

proposed for use in biomedical applications [11] as shown in Fig. 1.

MATERIALS AND METHODS

Nanocomposites films of (polyvinyl alcohol-poly-acrylic acid) blend and (polyvinyl alcohol-poly-acrylic acid) blend doped by niobium carbide nanoparticles were prepared by using casting method with different concentration of polymers (PVA (85 wt.%) and PAA (15 wt.%) was dissolved in distilled water. The niobium carbide nanoparticles was added to (PVA-PAA) blend with different concentrations are (1.5, 3, 4.5 and 6) wt.%. The electrical resistivity of (PVA-PAA-NbC) nanocomposites samples was measured for different range of temperature from (50 to 80)^{0}C by using Keithly electrometer type (2400 source mater). The optical properties of (PVA-PAA-NbC) nanocomposites were measured by using the double beam spectrophotometer (shimadzu, UV -1800^{0}A) in wavelength (240-800) nm. The (PVA-PAA-NbC) nanocomposites film was placed in box and the water vapor was used as a source of humidity. The control network monitored and controlled variations in humidity. The D.C electrical resistance of (PVA-PAA-NbC) nanocomposites film was measured by using the Keithley electrometer type 2400 source mater for different humidity range (30-90) %.

The D.C electrical conductivity (σ) of (PVA-PAA-NbC) nanocomposites was calculated by the equation [12]:

$$\sigma = \frac{d}{RA} \tag{1}$$

Where: A = area (cm^2), R = resistance (Ohm), d = thickness of sample (cm).

The activation energy for (PVA-PAA-NbC) nanocomposites defines by the following equation [13]:

$$\sigma = \sigma_0 \exp(-E_a)/K_B T \tag{2}$$

σ = electrical conductivity at T temperature, σ_0 = conductivity at absolute zero of temperature, K_B = Boltzmann constant, E_a = activation energy.

RESULTS AND DISCUSSION

The effect of niobium carbide nanoparticles concentration on D.C electrical conductivity of (PVA–PAA) blend is shown in Fig. 2. The figure shows that the electrical conductivity increases with increase in niobium carbide nanoparticles concentration, this behavior related to the niobium carbide nanoparticles and (PVA–PAA-NbC) nanocomposites having large number of free charge carriers available for the purpose of conduction. Hence, as the concentration of niobium carbide nanoparticles increases the number of free charge carriers also increases [14], as shown in Fig. 3.

Fig. 4 shows the variation of D.C electrical conductivity for (PVA–PAA) blend and (PVA–PAA) blend doped by niobium carbide nanoparticles
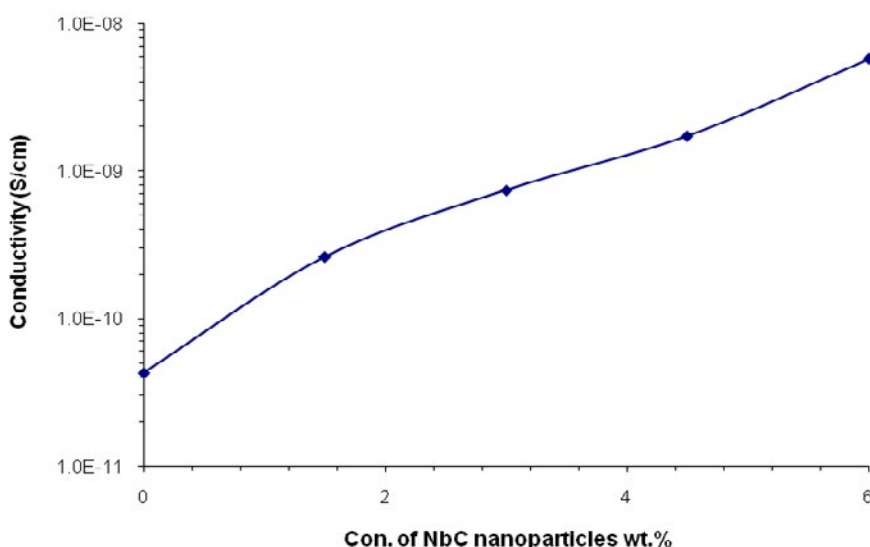

Fig. 2. The effect of niobium carbide nanoparticles concentration on D.C electrical conductivity of (PVA–PAA) blend.

with temperature. The magnitude of ionic conductivity was found to increase with increase in temperature in all compositions of the (PVA-PAA-NbC) nanocomposites. This may be explained on the basis of an increase in either ionic mobility or the concentration of carrier ions. In some polymer composites, change of conductivity with temperature is due to segmental motion, which results in an increase in the free volume of the system. When temperature is increased, the vibrational energy of a segment is sufficient to push against the hydrostatic pressure imposed by its neighboring atoms and create a small

amount of space surrounding its own volume in which vibrational motion can occur. Therefore, the free volume around the polymer chain causes the mobility of ions and polymer segments and hence the conductivity increases. The increase of temperature causes the increase in conductivity due to the increased free volume and their respective ionic and segmental mobilities. This increase in free volume would facilitate the motion of ionic charges [15]. The increase in the conductivity with temperature is also partially due to the transition from crystalline/ semi-crystalline phase to amorphous phase. According
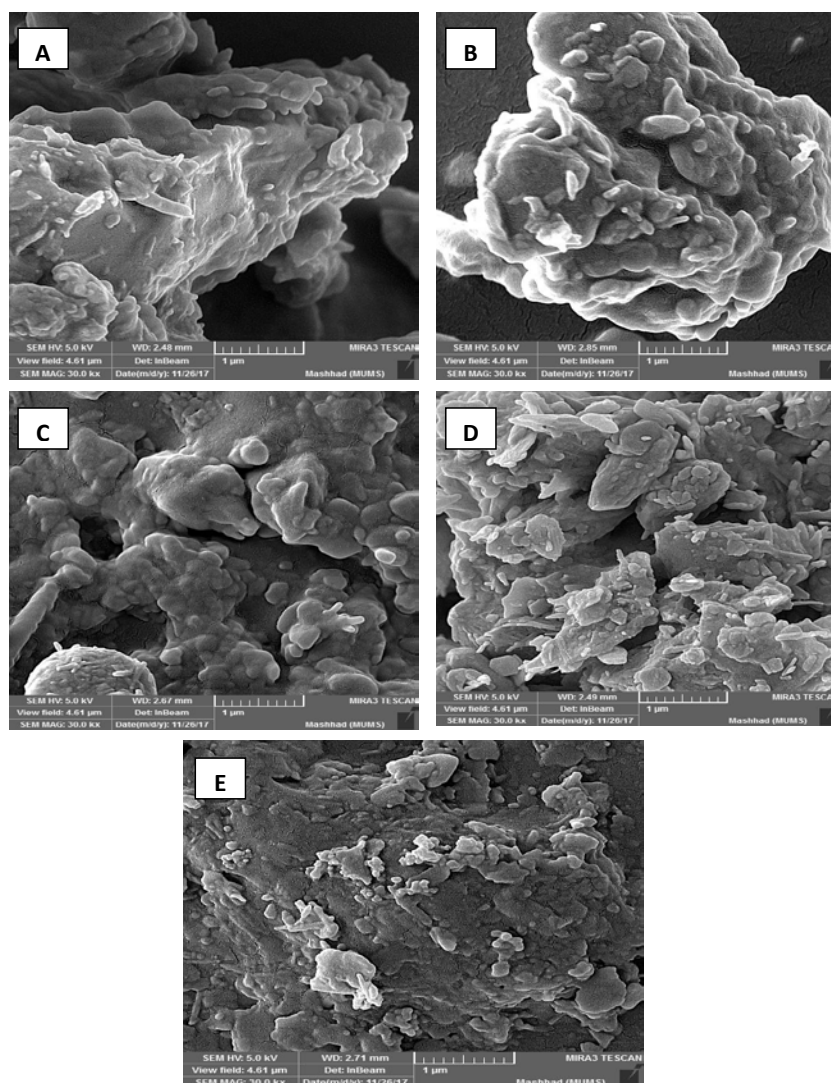

Fig. 3. SEM images for (PVA-PAA-NbC) nanocomposites.
A- Pure (PVA-PAA)   B- 1.5 wt.% NbC nanoparticles
C- 3 wt.% NbC nanoparticles   D- 4.5 wt.% NbC nanoparticles
E- 6 wt.% NbC nanoparticles

to the vacancy diffusion theory, for the protons to jump from one lattice site to other lattice site, need energy to break bonds with neighbors and to cause the necessary lattice distortions during jump. This energy comes from the thermal energy of atomic vibrations (Ea ~ k_BT). Due to the thermal energy supplied, a small free volume is created around segments. At low temperatures Arrhenius model was assumed where the cation transport and its contribution to conductivity is a result of

cation jump into neighboring vacant sites and hence, increases the proton conductivity to a higher value. This hopping mechanism between coordinating sites is essentially in the region below T_g [16]. The activation energy E_a of (PVA-PAA-NbC) nanocomposites can be estimated from the slope of ln σ versus 1/T plot as shown in Fig. 5 by using equation (2), Fig. 6 shows the variation of activation energy for (PVA–PAA) blend with different concentrations of niobium
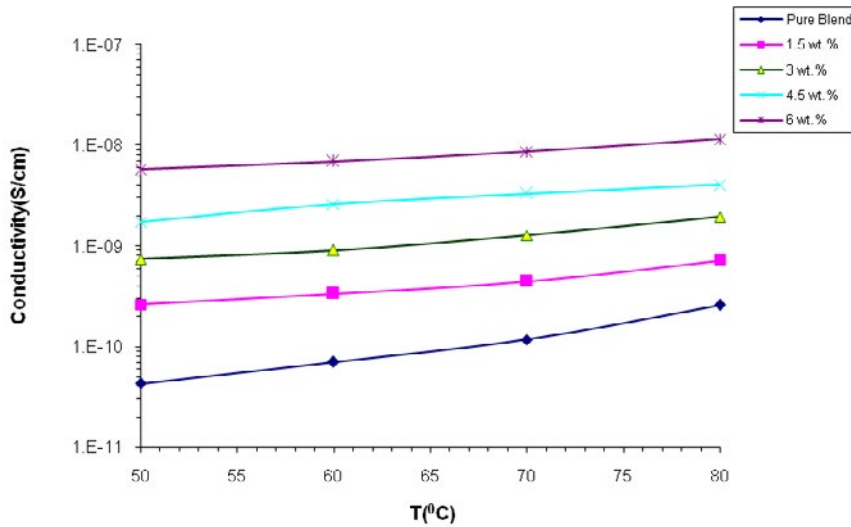

Fig. 4. The variation of D.C electrical conductivity for (PVA–PAA) blend and (PVA–PAA) blend doped by niobium carbide nanoparticles with temperature.
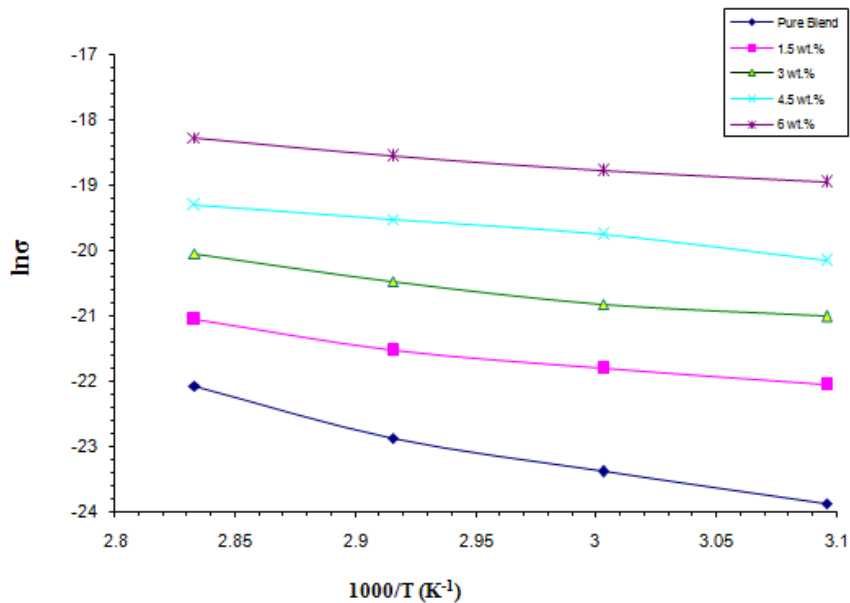

Fig. 5. ln σ versus 1/T plot for (PVA-PAA-NbC) nanocomposites

carbide nanoparticles. It is obvious that the values of the activation energy decreases with increase in dopant concentration. The decrease in activation energy upon doping with niobium carbide nanoparticles can be explained as being due to the formation of molecular aggregates. The charge carriers become more localized, which gives the increase in the trapped carrier density. These molecular aggregates results to the inhomogeneous distribution of the dopant as well as the nonbonding part of the dopant [17].

Fig. 7 shows the variation of transmittance spectra for (PVA-PAA-NbC) nanocomposites with wavelength of the incident light. From the figure, decrease of the transmittance for all samples of nanocomposites at UV region, this is due to the excitations of donor level electrons to the conduction band at these energies. The transmittance of (PVA-PAA-NbC) nanocomposites decrease with the increase in niobium carbide nanoparticles concentrations, this is due to the agglomeration of nanoparticles with increasing concentration and increase of the number of charge carriers [18].

Fig. 8 shows the variation of electrical resistance for (PVA-PAA-NbC) nanocomposites with relative humidity range (40–90)%. As shown in figure, the electrical resistance of nanocomposites decreases
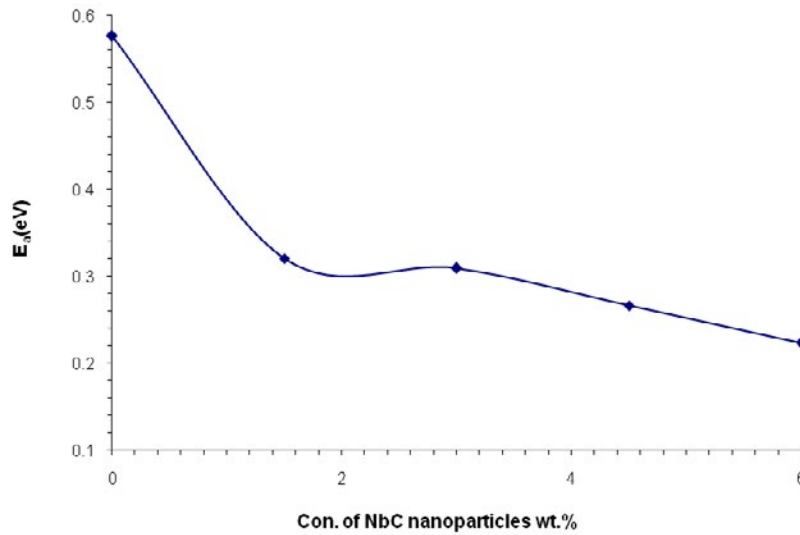

Fig. 6. The variation of activation energy for (PVA–PAA) blend with different concentrations of niobium carbide nanoparticles.
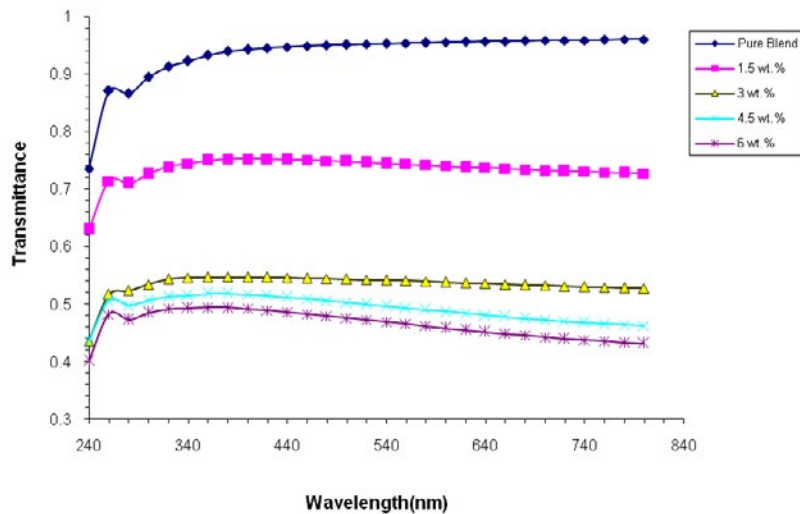

Fig. 7. The variation of transmittance spectra for (PVA-PAA-NbC) nanocomposites with wavelength of the incident light.
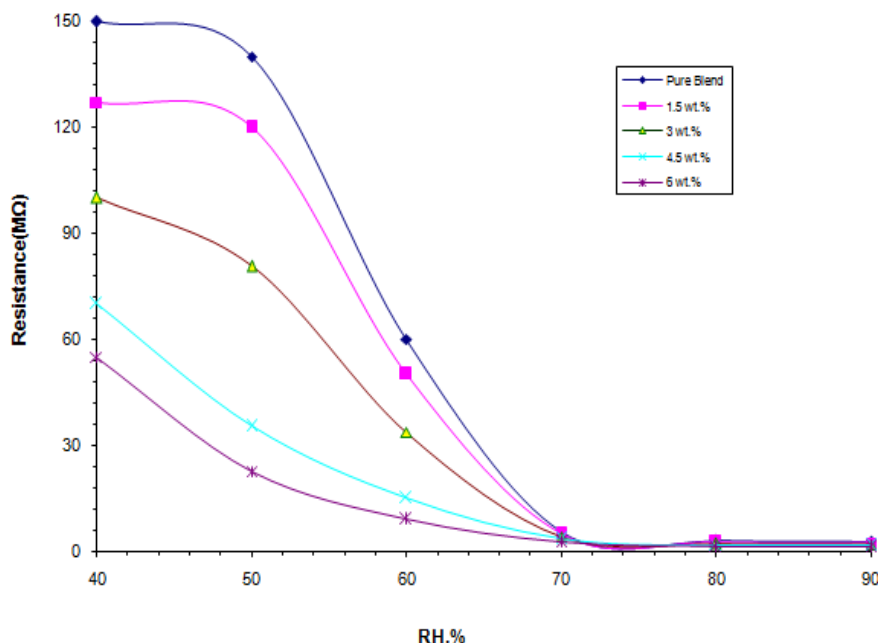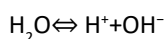
Fig. 8. The variation of electrical resistance for (PVA-PAA-NbC) nanocomposites with relative humidity range (40–90)%.

as relative humidity increases. It is universally suggested that protons (H^+) and hydroxide ions (OH^-) are quickly diffused due to surface collision or self-ionization of water molecules, and this leads to initial separation of (H^+, OH^-) ions as:

$$H_2O \Leftrightarrow H^+ + OH^-$$

Due to the amphoteric nature of water, and hence auto ionization reaction of water vapour on a surface, a H_2O molecule loses nucleus of one of its hydrogen, H^+, atoms
to become a hydroxide ion, OH^-. The released hydrogen nucleus immediately protonates another H_2O molecule to form an oxonium (hydronium) ion, H_3O^+. This is a simplest theory of water vapour interaction with a surface and is exemplified as follows:

$$H_2O + H_2O \Leftrightarrow H_3O^+ + OH^-$$
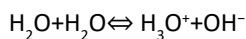
In environments with low humidity levels, when the sensor surface is slightly covered by water vapour molecules and only dissociated hydroxyl functional groups are present, the charge carriers are protons (hydrogen ions) and proton migration proceeds through hydrogen hopping between adjacent hydroxide ion sites. At higher humidity values, when a continuous water layer

is formed charge transfer still arises by proton hopping between neighbouring sites of water vapour molecules. Formation of more water layers facilitates the dissociation to produce hydronium groups. Easy dissociation of physisorbed multi water layers could be along the high electrostatic fields in the chemisorbed layer. When surface coverage with water molecules is complete, diffusion of H_3O^+ on hydroxide ions is dominant, but H^+ transfer by OH^- between neighbouring water molecules also occurs. The charge carrying continues when H_3O^+ transfers (releases) a proton to a neighbouring H_2O molecule and forms another H_3O^+. The procedure is carried out by dancing of protons (hydrogen ions) from one water vapour molecule to another, thereby leading to a remarkable change of resistance. When ceramic oxides are exposed to atmospheric moist air, in the first stage of the interaction a few water vapour molecules are chemically adsorbed (chemisorption) at the neck of the crystalline grains on activated sites of the surface, which is accompanied with a dissociative mechanism of vapour molecules to form hydroxyl groups (two hydroxyl ions per water molecule). As an interaction between the surface ions of the grain necks and the adsorbed water, the hydroxyl group of each water molecule is adsorbed on metal cations which are present in the grains surfaces and possess high charge carrier density and

strong electrostatic fields, thus providing mobile protons. The protons migrate from site to site on the surface and react with the neighbour surface O^{2-} groups (oxygen) to form a second hydroxyl (OH^-) group. The chemisorbed layer is the first formed layer so once it has formed on the surface it will not change further by exposure to humid air. As a second stage, after chemical completion of the first layer, subsequent water vapour layers are physically adsorbed (physisorption) on the first formed hydroxyl layer, and stack to form the physisorbed hydroxyl multilayer. After forming the first physisorbed layer, another water molecule adsorbs via double hydrogen bonding to two neighbouring hydroxyl groups. As water vapour continues to increase in the surface, an extra layer forms on the first physisorbed layer, therefore the physisorption changes from monolayer to multilayer. These layers are less ordered than the first physisorbed layer, and water vapour molecules in these layers may be only singly bonded to local hydrogens. Finally, by forming the more layers, a large amount of water molecules is physisorbed on the necks and flat surfaces, hence singly bonded water vapour molecules become mobile and able to form continuous dipoles and electrolyte layers between the electrodes, resulting in an increased dielectric constant and bulk conductivity, hence the electrical resistance decreases [19,20].

CONCLUSIONS

The D.C electrical conductivity of (PVA–PAA) blend increases as niobium carbide nanoparticles increase. The conductivity of all samples for (PVA-PAA-NbC) nanocomposites increases with increase in temperature. The activation energy of (PVA–PAA) blend decreases with increase in niobium carbide nanoparticles. The optical transmittance of (PVA–PAA) blend decreases niobium carbide nanoparticles as increase. The (PVA-PAA-NbC) nanocomposites humidity sensors have high sensitivity for relative humidity with low cost and low weight.

ACKNOWLEDGMENT

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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