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Synthesis and Characterization of PVVH/ CuONanocompositefor Industrial Application

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Abstract

Polymer nanocomposite of poly(vinyl chloride-co-vinyl acetateco-2-hydroxypropyl acrylate) copolymer (PVVH) doped with different concentrations of Copper oxide nanoparticles (CuO NPs) is prepared using the casting method. The prepared nanocomposite samples are characterized using X-Ray Diffraction (XRD), Transmission Electron Microscope (TEM), Attenuated Total Reflection- Fourier Transform Infrared (ATR-FTIR), and optical properties are studied using the Ultraviolet-Visible technique (UV-Vis). XRD and ATR-FTIR of the prepared sample confirmed the interaction and complexation between PVVH and CuO NPs. Optical properties such as bandgap energy andUrbach energy indicate that the addition of CuO NPs into PVVH polymer induced variations in the number of available final states as a function of composition ratio. Also, CuO NPs changed the electronic structure PVVH by doping via deformation potential, formation of localized band states, and Coulomb interaction.

Keywords:PVVH;CuO NPs; XRD;Optical properties

1. Introduction

Nanotechnology and nanoscience now play an important and efficient role in our daily lives, which are greatly influenced by the advancements made in materials, particularly in the nanoscale range [1]. These innovative materials with better functionality are extremely valuable in a variety of sectors, including biology, medicine, materials science, industrial, engineering, and electrical applications [2, 3]. The use of fillers to improve the characteristics of polymers is widely known [4]. Fillers were initially employed to minimize the cost of polymeric products [5]. Fillers, on the other hand, have become an important aspect of many applications [6]. Polymers[7], polymer nanocomposites [8], and copolymers [9] are the focus of a new area of technology due to their excellent properties and wide range of applications [10]. PVVH is a copolymer consisting of three types of monomers and it is a flexible monomer that is commonly used in sensors [11]. It is an amorphous terpolymer that was preferred for its structure's sensitivity to temperature changes and transparency with an excellent film-forming ability [12, 13].

In most research and industrial applications, metal oxide nanoparticles are used [14]. Transition metal oxides are a common type of semiconductorsuch as9CuO has a variety of uses, including catalysis [15], solar energy conversion [16], gas sensing materials [17], and electronics [18]. CuO is one of the best materials for electrical, optical, sensing, and other applications due to its cheap cost production methods and outstanding electrochemical characteristics. CuO nanostructures can be used in a

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variety of gas-sensor applications [19]. A few previous researchers studied PVVH with other polymers or nanomaterials [20] and investigated the effect of graphene oxide NPs on PVVH [20] structural characterization, optical and dielectric properties. Also, PVVH/ $CoCl_2$composite structural, electrical, and optical properties were studied [21].Furthermore, the role of adding silica on PVVH [22] and studied the behavior of PVVH/ ZnO using TSDC technique [23].

The current research looks into the structural characteristics and band structure of CuO NPs–PVVH composites in depth. The solution casting method was used to successfully create CuO NPs loaded PVVH composite films. The goal of this study was to make CuO NPs–PVVH composite films with various loadings and analyze their structural and optical properties to create high-performance optoelectronic devices. The prepared samples were thoroughly evaluated for property enhancement.

2. Materials and Method

2.1. Materials

The PVVH copolymer (81 wt.% vinyl chloride; 15 wt.% percent 2-hydroxypropyl acrylate; 4 wt.% percent vinyl acetate) that has an average molecular weight equal to 33,000 g/mol was supplied by Aldrich Chemicals. CuO with a particle size less than 70 nm was supplied byNawah Company, Egypt. The common solvent in the current study, tetrahydrofuran (THF), was purchased from Fisher Scientific for chemicals.

2.2.Synthesis of PVVH/CuO NPs membranes

At 40°C, an appropriate amount of PVVH was dissolved in THF. CuO NPs were then added to the dissolved solution in mass fractions up to 0.005 wt% as listed in table (1). The solution was then sonicated to prevent agglomeration in the PVVH solution and stirred continuously at 40°C until a homogeneous solution was generated. The resultant solutions were cast onto Petri dishes and stored for about 6 hours in the dryer at 40°C as described in scheme1.

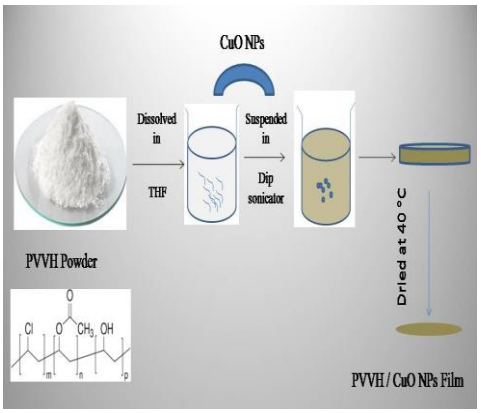
Table (1) Sample abbreviation and composition

Sample	PVVH (wt%)	CuO (wt%)
PVVH	100	0.000
PVVH/CuO1	99.999	0.001
PVVH/CuO2	99.998	0.002
PVVH/CuO3	99.997	0.003
PVVH/CuO4	99.996	0.004
PVVH/CuO5	99.995	0.005

2.3. Measurement Techniques

The PANalytical X'Pert Pro target Cu-K with secondary monochromator Holland radiation with a tube operating at (λ= 0.1540 nm and 45 kV) from 2θ range from 5–80° was used for XRD examination.

The JEM-2100F electron microscope was used to perform a high-resolution transmission electron microscope (HRTEM) with a 200 kV accelerating voltage. ATR –FTIR spectrum data was recorded using the VERTEX 80 (Bruker, Germany) spectrometer in the range 4000-450 cm^{-1}.



Scheme1: Steps of preparation of PVVH/ (wt%) CuO NPs.

The Jasco V-630 UV-Vis (Japan) spectrophotometer was used to detect UV-Vis absorption spectra in the wavelength range of 200-1000 nm.

3. Results and Discussion

3.1. *Structural* Studies

Fig. 1describes the diffraction patterns of PVVH loaded with different concentrations of CuO NPs. PVVH has an amorphous broad diffraction peak at 2θ equal 21.5° which reflects the amorphous nature of PVVH [21]. As seen for PVVH incorporated with CuO NPs, the diffraction peak shifted toward lower 2θ diffraction and there are no diffraction peaks appeared for CuO NPs, which confirmed the complete incorporation of CuO NPs into PVVH. Also, the XRD peak width of the produced samples was extended by the progressive addition of nanofiller amount after integrating CuO NPs due to the abundance of (C=O and/ or O-H) groups on the backbone of PVVH, which aids in the uniform dispersion of CuO NPs. This demonstrates

that the amorphous phase dominates in the complex system.

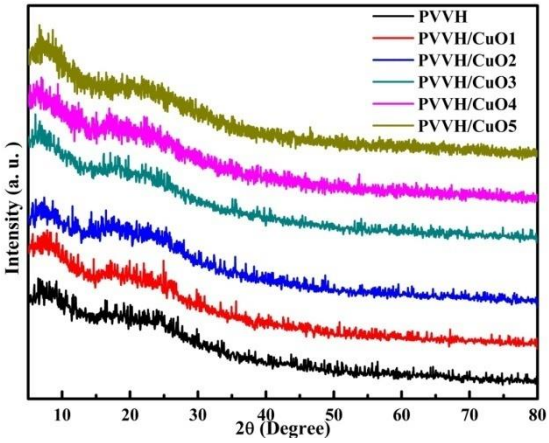


Fig. 1: XRD patterns of PVVH incorporated with different weight percentages of CuO NPs.

Fig. 2representsthe TEMof CuO NPs used as a dopant in the studied samples. Microscopic images show the presence of hexagonal morphology within the nanoscale.

Fig.3illustrates ATR-FTIR of PVVH doped with different concentrations of CuO NPs. In the PVVH spectrum, there is broadband at 3444 cm^{-1} which is related to the O-H stretching group. Bands at 2970 cm^{-1}, 2920 $cm^{-1,}$ and 2852 cm^{-1} are related to the stretching vibrations of C-H groups. Bands at 1730 due to C=O stretching, 1238 due to stretching of the C-O ester group, and at (1373 cm^{-1}, 1328 cm^{-1}, 1237 cm^{-1}, 1169 cm^{-1}, 1102 $cm^{-1,}$ and 1052 cm^{-1}) are related to C-O stretch of secondary alcohol that combined with C-C vibration [24, 25].

Bands at 689 cm^{-1} and 611 cm^{-1} are attributed to C-Cl and the wagging mode of C-H, respectively. The effect of CuO nanofiller insertion with PVVH bonding was demonstrated by changes in peak troughs in the nanocomposite spectra. For PVVH doped with different concentrations of CuO NPs, the band intensities are increased by increasing filler concentration. Also, there is a new band that appeared at 490 cm^{-1} and its intensity increased with CuO NPs [26]. All the above results confirmed the interaction of (C=O, secondary O-H) with CuO NPs and strong absorption of CuO NPs on the surface of PVVH and this agreed with XRD results.

3.2. Optical Properties

The optical properties of PVVH incorporated with different weight percentages are studied using UV-Vis spectroscopy as seen in Fig. 4. PVVH has two bands at 205 nm, which is due to the n-π* transition of the C-Cl bond, and at 277 nm, which is due to π-π* transition that is assigned to C=O unsaturated bonds [21]. The rise in absorbance in the 200–250 nm region is found to be connected to the sample's bandgap, confirming the amorphous structure of PVVH.

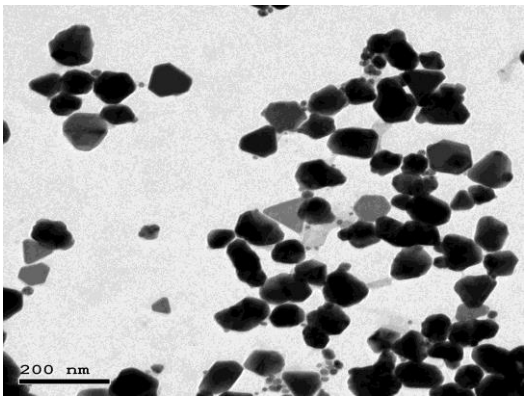


Fig. 2 TEM image of the studied CuO

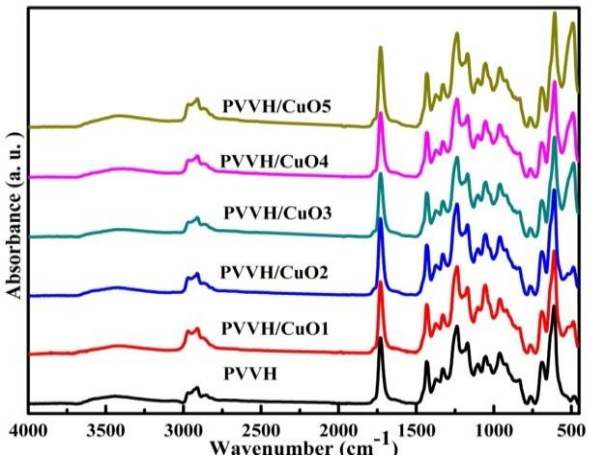


Fig. 3: ATR-FTIR spectra of PVVH incorporated with a different weight percentage of CuO NPs.

Its amorphous nature was further revealed by XRD investigation. CuO-loaded PVVH samples showed an absorption edge in the 240–300 nm regions. The absorption edge of the nano-CuO–PVVH composites was red-shifted, indicating that the optical band gap of PVVH may be modified using small amounts of nanofiller. The samples' red shift in absorption edge revealed hydrogen bonding between the CuOnanofiller and the –OH groups or C=O group in PVVH polymer. Because the absorbance increase is connected with the charge-transfer transition. The optical absorption edge changed to higher wavelength values when the CuOnanofiller concentration increased.

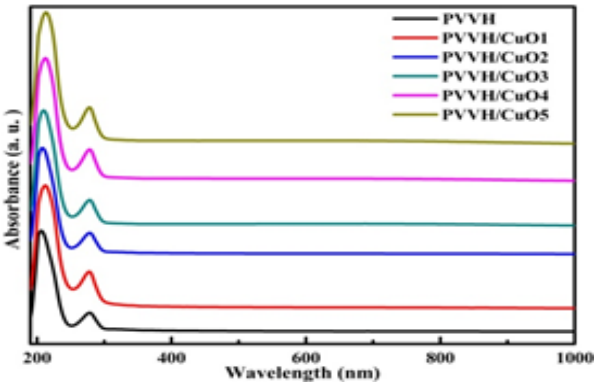


Fig. 4: UV-Vis of PVVH incorporated with a different weight percentage of CuO NPs.

The value of information received from the absorption coefficient, such as the electronic band structure and the optical energy band gap, is attributed to its importance. The absorption coefficient (α) can be calculated from the thickness of prepared films (d) and Absorbance (A) using the following equation [27]:

$$\alpha = \frac{2.303}{d} A \qquad (1)$$

Fig.5 represents the relation between absorption coefficient and photon energy (hυ), the intercept of the linear portion of the curve with the x-axis of photon energy gives the value of the absorption edge. As noticed from Fig.5, the values of the absorption edge of the prepared sample have changed and decreased compared to PVVH. This shows how the addition of CuO NPs changes the band structure and leads to the formation of localized states.

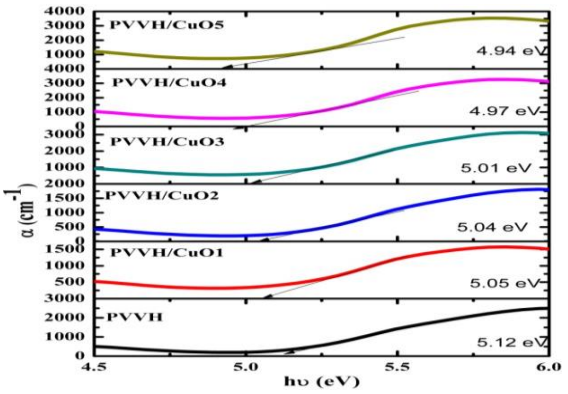


Fig. 5: Relation between absorption coefficient and photon energy of PVVH incorporated with a different weight percentage of CuO NPs.

The random fluctuations of the internal field associated witha structural disorder in many amorphous solids can explain the exponential dependency of energy in amorphous and crystalline materials. As a result, the number of electronic transitions in the band edge tails between localized states is expected to drop exponentially as energy is increased. For many amorphous materials, the electronic transitions at the band edge decrease exponentially with energy, as shown by the following relationship.

$$\alpha = \alpha_0 \exp\left(\frac{h\upsilon}{E_u}\right) \qquad (2)$$

Where E_u is defined as theUrbach tail, and α_0 is a constant. As seen in Fig. 6, band tail energy is computed by inverting the slope generated by the relationship between lnα and hυ. As seen, band tail values are increased compared to the PVVH polymer. This explained that adding CuO NPs to PVVH causes tail states by interrupting the band's edge through deformation potential, Coulomb interaction, and internal field fluctuations. As a result of the intermolecular interaction between the PVVH component and the CuO NPs, the optical characteristics of the polymer composite system change, causing disorder.

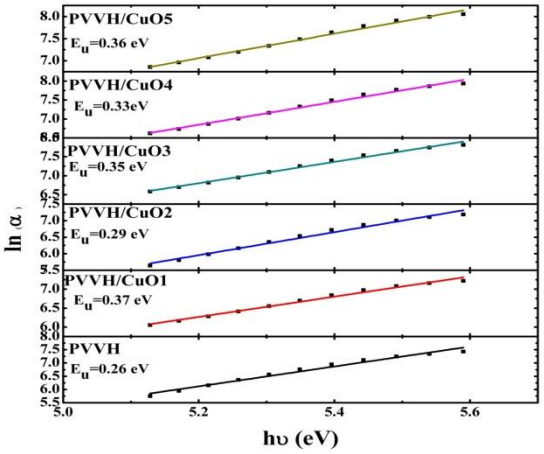


Fig. 6: Relation between ln α and hυ of PVVH incorporated with a different weight percentage of CuO NPs.

The process of electron transport between the bands of a material is referred to as interband absorption. Basic absorption is linked to band-to-band transitions and is constrained by a set of selection laws [28-30]. One approach to determining bandgap energy E_g is the Mott and Davis formulas, [31] which plot the relationship between $(\alpha h\upsilon)^{1/r}$ and hυ gives the values of bandgap energy by

extrapolating the linear part of the curve with the photon energy axis. The value of r is determined by the type of transition that best fits a set of data linearly [32]. r takes 1/2 for direct transitions and 2 for indirect transitions.

$$(\alpha h\upsilon) = B\,(h\upsilon - E_g)^{1/r} \qquad (3)$$

where B is constant. PVVH and PVVH loaded with varying concentrations of CuO NPs are plotted in Fig. 7 as $(\alpha h\upsilon)^{1/2}$ and $(\alpha h\upsilon)^{2}$ with hυ. When compared to pure PVVH, both direct and indirect bandgap values are decreased. The change between the valence and conduction bands of energy states causes a decrease in energy gap values. That is to say, the inclusion of CuO NPs causes a structural alteration in the PVVH structure. It's also important to note that the direct and indirect energy gaps are both inversely related to E_u values. All of the studies showed that adding CuO NPs to PVVH alters the structure and order of PVVH polymer.

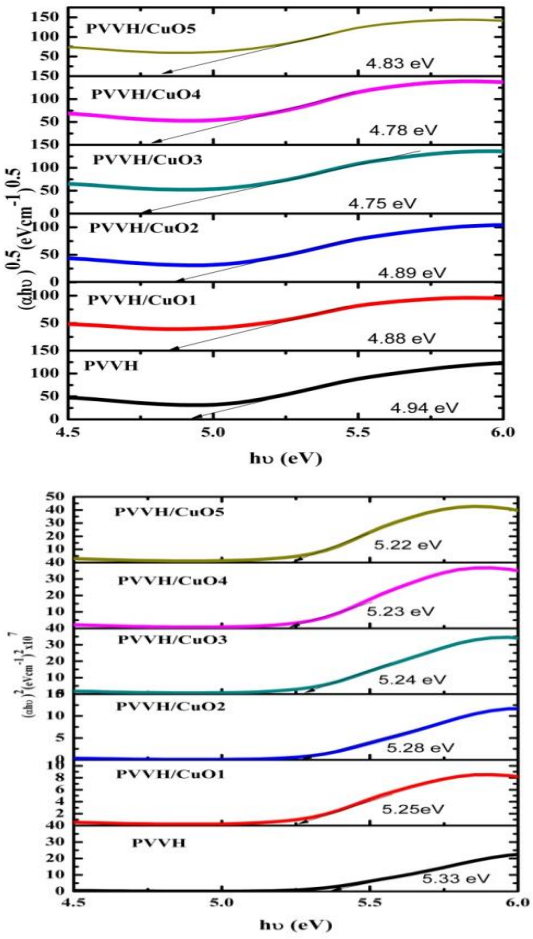


Fig. 7: Relation between $(\alpha h\upsilon)^{1/2}$ and $(\alpha h\upsilon)^{2}$ against hυ for of PVVH incorporated with a different weight percentage of CuO NPs.

4. Conclusions

The PVVH/CuO NPs composite films were simply made using a solution casting method. Nano-CuO has changed the desirable features of the PVVH matrix, according to structural and optical analyses. According to the XRD results, adding CuO NPs changed the amorphous nature of PVVH, leading the intensity of PVVH peaks to decrease and the broadening to increase. The ATR-FTIR technique confirmed the complexation between PVVH and CuO NPs by changing the intensities and shifting of PVVH bands. The shifting of the absorption edge, bandgap, Urbach energy, and variations of the optical bandgap could be important in optical communications, waveguide design, and optoelectronic device design. This referred to polymeric molecular linkages, as well as strong hydrogen bonds between OH or C=O groups of PVVH and nanofiller.

5. Conflicts of interest

The authors declare that there is no conflict of interest.

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