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Deposition and Characterization of Innovative Bulk Heterojunction Films Based on CuBi_2O_4 Nanoparticles and Poly(3,4 ethylene dioxythiophene):Poly(4-styrene sulfonate) Matrix

María Elena Sánchez-Vergara ¹ , América R. Vázquez-Olmos ², Leon Hamui ^{1,*} , Alejandro Rubiales-Martínez ², Ana L. Fernández-Osorio ³ and María Esther Mata-Zamora ²

- ¹ Facultad de Ingeniería, Universidad Anáhuac México, Avenida Universidad Anáhuac 46, Col. Lomas Anáhuac, Huixquilucan, Estado de México 52786, Mexico; elena.sanchez@anahuac.mx
- ² Instituto de Ciencias Aplicadas y Tecnología, Universidad Nacional Autónoma de México, Circuito Exterior S/N, C.U., Coyoacán, Ciudad de México 04510, Mexico; america.vazquez@icat.unam.mx (A.R.V.-O.); alex91hirdck@gmail.com (A.R.-M.); esther.mata@icat.unam.mx (M.E.M.-Z.)
- ³ Facultad de Estudios Superiores Cuautitlán, Universidad Nacional Autónoma de México, A.P. 25, Cuautitlán Izcalli, Estado de México 54740, Mexico; ana8485@unam.mx
- * Correspondence: leon.hamui@anahuac.mx



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Abstract: This work presents the deposition and study of the semiconductor behavior of CuBi_2O_4 nanoparticles (NPs) with an average crystallite size of 24 ± 2 nm embedded in poly(3,4 ethylene dioxythiophene):poly(4-styrene sulfonate) (PEDOT:PSS) films. The CuBi_2O_4 NP bandgap was estimated at 1.7 eV, while for the composite film, it was estimated at 2.1 eV, due to PEDOT:PSS and the heterojunction between the polymer and the NPs. The charge transport of the glass/ITO/PEDOT:PSS- CuBi_2O_4 NP/Ag system was studied under light and dark conditions by means of current–voltage (I–V) characteristic curves. In natural-light conditions, the CuBi_2O_4 NPs presented electric behavior characterized by three different mechanisms: at low voltages, the behavior follows Ohm's law; when the voltage increases, charge transport occurs by diffusion between the NP–polymer interfaces; and at higher voltages, it occurs due to the current being dominated by the saturation region. Due to their crystalline structure, their low bandgap in films and the feasibility of integrating them as components in composite films with PEDOT:PSS, CuBi_2O_4 NPs can be used as parts in optoelectronic devices.

Keywords: mechanochemical synthesis; composite films; heterojunction; optical properties; electrical properties

1. Introduction

The evolution of electronic technology has been linked in a parallel way to the continuous miniaturization of its components, and to the development of new materials with improved optoelectronic properties. For instance, two-dimensional (2D) transition metal dichalcogenides (TMDs) have received a great deal of attention due to their superior electrical properties [1,2]. In TMDs such as MX_2 , M is a transition metal (Mo, W, Ti, Zr, Hf, V, Nb, Ta, Tc, Re, Pd, Pt) and X is a chalcogen (S, Se, Te) [3]. TMDs consist of a variety of materials with diverse electronic properties ranging from insulators (e.g., HfS_2), semiconductors (e.g., MoS_2 , MoSe_2 , WS_2 , WSe_2 , NbSe_2 and TaS_2), semimetals (e.g., TiSe_2 and WTe_2) and metals (e.g., NbS_2 and VSe_2) [1,3]. Additionally, the advantage of these 2D materials is their adjustable properties, a consequence of the compositional and structural features of their construction components, which allow their introduction in supercapacitors, batteries, solar cells and sensing applications [1]. Regarding their optoelectrical parameters, TMDs have shown good charge carrier mobility, a direct bandgap, good stability and good performance as a hole transport layer (HTL) [3,4]. For instance, a wide variety of TMDs have been investigated as counter electrodes for dye sensing, substituting the conventional Pt electrode,

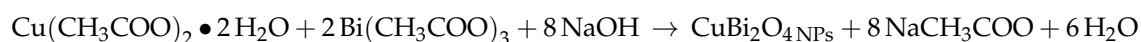
where an increase or decrease in the solar cell parameters has been reported depending on the TMD, number of layers, microstructure, deposition process and annealing process [2]. In addition to 2D chalcogenides, 2D oxides have been considered within the family of 2D materials [2,3]. The development of nanomaterials formed by transition metal oxides, conductors, superconductors, light emitters, dielectrics, magnetics and ferroelectrics proves that these types of metal oxides form a series of compounds that give place to a diversity of applications that can only be found in this type of material. In this regard, copper bismuth oxide (CuBi_2O_4) is an attractive p-type semiconductor with a bandgap of 1.5–1.8 eV [5], which could take advantage of a large portion of the visible spectrum for optoelectronic applications. The structure of CuBi_2O_4 , space group $P4/ncc$ and tetragonal symmetry was discovered by Boivin et al. in 2001 [6]. CuBi_2O_4 nanoparticles (NPs) have been obtained by different methodologies such as solid-state reaction [7–9], the hydrothermal method [10], the sonochemical approach [11] and the sol–gel method [12], as well as an innovative and environmentally friendly one-step synthesis method [13]. Until now, the main applications of this oxide are in photocatalysis, generation of hydrogen from H_2O , degradation of water contaminants such as dyes and as microbicides [5,13–16]. Moreover, under AM1.5 and EQE (external quantum efficiency) equal to 1, the maximum theoretical J_{sc} is 29 mA/cm^2 , which potentiates its use for solar cell applications [17]. Nevertheless, although CuBi_2O_4 NPs have a low bandgap [5,18–20], their semiconductor behavior has not been studied, and their possible application in optoelectronic devices has not been studied either. Regarding the above, it is required that CuBi_2O_4 NPs form part of semiconductor thin films which are integrated into various devices [20–25]. The study of the semiconductor behavior of CuBi_2O_4 NPs, when they are part of composite films, should be expanded. Composite films have gained importance in optoelectronics since they combine the electrical properties of NPs with the properties of the polymeric matrix in which they are embedded. The construction of these heterojunctions is an important aspect that can separate electron/hole pairs in semiconductors [23,26,27].

Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) is one of the most widely used polymers in the manufacture of composite films and in the manufacture of optoelectronic devices [28–36]. Some examples of the application of PEDOT:PSS in composite films with optoelectronic applications are as follows: Kepić et al. [37] used spherical nanoparticles of graphene embedded in PEDOT:PSS. Sarkhan et al. [38] used graphene oxide sheets embedded in the polymer. On the other hand, Stevens et al. [39] achieved an improvement in the thermoelectric performance of polymer nanocomposites, and Yeo et al. [40] also achieved an improvement in the electrical behavior of composite films with PEDOT:PSS and TMD nanosheets due to an improved electron transfer while being used as a hole extraction layer (HEL) [2,4]. Previous works regarding solar cells have shown that the TMD island morphology allows an efficient hole collection due to a larger contact area between the active layer and the composite layer, a reduced series resistance and an increased J_{sc} and power conversion efficiency (PCE) compared to PEDOT:PSS [4]. For example, the resulting conductivity and mobility of a PEDOT:PSS/ WS_2 composite film, compared to PEDOT:PSS, were found to be $14.3 \times 10^{-4} \text{ S cm}^{-1}$ ($5.7 \times 10^{-4} \text{ S cm}^{-1}$) and $1.73 \times 10^{-5} \text{ cm}^2/\text{Vs}$ ($6.54 \times 10^{-6} \text{ cm}^2/\text{Vs}$), respectively [4]. Additionally, it has been observed that an increase in the TMD concentration of a dye-sensitive solar cell counter electrode composite film (i.e., $\text{TiS}_2/\text{PEDOT:PSS}$) increases the J_{sc} and PCE, where increases of 12.74 mA/cm^2 (3.91%), 13.81 mA/cm^2 (5.91%) and 15.78 mA/cm^2 (7.04%), have been reported, respectively, for 0 wt%, 5 wt% and 10 wt% [2]. PEDOT:PSS forms a continuous film on either rigid or flexible substrates by various solution processing techniques, including spin casting, slot die coating, spray deposition, inkjet printing and screen printing [28–36]. PEDOT:PSS films are smooth and have a surface roughness of usually less than 5 nm (deposition technique-dependent) [41], and in the visible light range, PEDOT:PSS films are almost transparent and have a high work function of 5.0–5.2 eV [30]. Therefore, in this work, composite films of CuBi_2O_4 NPs in PEDOT:PSS were obtained by the spin coating technique, and they were morphologically and optically characterized. As an

approximation to determine the effect of PEDOT:PSS on CuBi₂O₄ NPs, the optical bandgap was calculated using the simple Tauc method, for the NPs and for the amorphous film. Moreover, a device made of glass/ITO/PEDOT:PSS-CuBi₂O₄/Ag was constructed, and its transport characteristics were studied from current–voltage (I–V) measurements.

2. Materials and Methods

Mechanochemical Synthesis and Characterization of CuBi₂O₄ NPs. Copper (II) acetate dihydrate Cu(CH₃COO)₂·2H₂O (99.9%, Aldrich, Saint Louis, MO, USA), bismuth (III) acetate Bi(CH₃COO)₃ (99.9%, Aldrich, Saint Louis, MO, USA), sodium hydroxide NaOH (98%, Aldrich, Saint Louis, MO, USA) and acetone CO(CH₃)₂ (99.5%, Aldrich, Saint Louis, MO, USA) were purchased and used as received, without further purification. Ultra-pure water (18 MΩ cm^{−1}) was obtained from a Barnstead E-pure deionization system (Thermo Scientific, Waltham, MA, USA). The nanoparticles of CuBi₂O₄ were obtained following the procedure reported by Vázquez-Olmos et al. [13], as follows: 5 × 10^{−4} mol (0.09 g) of Cu(CH₃COO)₂·2H₂O and 1 × 10^{−3} mol (0.38 g) of Bi(CH₃COO)₃ were ground in an agate mortar for approximately 10 min, and then 4 × 10^{−3} mol (0.16 g) of previously ground NaOH was added. The mixture was ground until a dark brown powder was obtained. This product was washed four times with water and twice with acetone. In each case, it was separated by centrifugation at 3000 rpm for 10 min and finally air dried. This procedure does not necessarily carry out any heat post-treatment and is environmentally friendly because it excludes the use of a large quantity of solvents. The chemical reaction is as follows:



The yield of the reaction was 85%, and it was carried out in triplicate to guarantee the reproducibility of the synthesis method.

A Raman spectrum of 100 to 900 cm^{−1} was acquired by a dispersive Raman spectrometer, Nicolet Almega XR (Thermo Scientific Nicolet, Waltham, MA, USA), and detected by a CCD camera, at 25 s and a resolution of ~4 cm^{−1}. The excitation beam was a Nd:YVO₄ 532 nm laser, and the incident power on the sample was ~3 mW. FTIR analysis was performed on KBr pellets with powdered CuBi₂O₄ NPs, in a Thermo Nicolet Nexus spectrometer (Thermo Scientific, Waltham, MA, USA). X-ray diffraction patterns were acquired at room temperature with Cu Kα radiation (λ = 1.5406 Å) in a D5000 Siemens diffractometer (Bruker, Billerica, MA, USA); diffraction intensity was measured between 2.5° and 70°, with a 2θ step of 0.02°, for 0.8 s per point. The average crystal size (D) of the NPs was estimated from their diffractograms, using the Debye–Scherer formula, $D = \kappa\lambda/\beta\cos\theta$, where κ is the shape factor equal to 0.9, λ is the CuKα radiation, β is the full width at half maximum intensity of selected peaks (FWHM) and θ is the Bragg angle. High-resolution transmission electron microphotographs (HR-TEM) were obtained with a JEOL ARM200F analytical microscope (JEOL, Akishima, Tokyo, Japan) operating at 200 kV, by deposition of a drop of the powdered CuBi₂O₄ NPs dispersed in ethanol onto 300-mesh Cu grids coated with a carbon layer. UV–visible electronic absorption spectra of the powdered samples were obtained by the diffuse reflectance technique, with an Ocean Optics USB2000 miniature fiber-optic spectrometer (Ocean Optics, Dunedin, FL, USA).

Film Deposition and Characterization. Composite film deposition of CuBi₂O₄ NPs was carried out in air by spin coating in a Smart Coater 200 instrument (Laurell Technologies Corporation, North Wales, PA, USA). The composite films were deposited onto different substrates: ITO-coated glass slides, high-resistivity monocrystalline n-type silicon wafers (c-Si) and Corning glass. Substrates were previously submitted to a sonication cleaning process and dried in vacuum. The deposition was performed by a spin coating technique that produces thin and uniform films and involves spreading a liquid solution over the center of the substrate, which is subsequently rotated for 7 s at a constant angular velocity of 700 rpm. In order to obtain composite films, the solution to deposit in the current work was composed of PEDOT:PSS dissolved in water (Aldrich, Saint Louis, MO, USA) and

the CuBi_2O_4 NPs in suspension. The NPs added to the polymer PEDOT:PSS correspond to CuBi_2O_4 nanoparticles with an average diameter of 24 ± 2 nm. After the composite films were deposited, annealing at 120°C for 10 min took place, with the objective of eliminating the residual water from the polymer active layer, and the thickness of the films was 77.6 ± 5 nm. In order to study the morphology of the composite films, ZEISS EVO LS 10 SEM (Zeiss International Inc., Göttingen, Germany) was performed for the films deposited on glass substrates, and AFM measurements of the films on silicon substrates were performed in contact mode with a Nanosurf Naio microscope (Intercovamex, S.A. de C.V., Cuernavaca, Morelos, Mexico). In order to verify their stability, these films on silicon were analyzed using a Nicolet iS5-FT IR spectrometer (ThermoFisher Scientific Inc., Waltham, MA, USA), in the wavenumber range from 4000 to 500 cm^{-1} . The UV-visible spectra of the films on Corning glass were obtained on a UV-Vis 300 Unicam spectrophotometer (ThermoFisher Scientific Inc., Waltham, MA, USA), and the measurements were conducted in the wavelength range from 200 to 1100 nm. Finally, simple devices of glass/ITO/PEDOT:PSS- CuBi_2O_4 NP/Ag were manufactured (see Figure 1), and the electrical properties were obtained through current-voltage (I-V) measurements (of area $2.6\text{ cm} \times 2.6\text{ cm}$). A Keithley 4200-SCS-PK1 auto-ranging picoammeter (Tektronix Inc., Beaverton, OR, USA) was used with the four-point probe method, in a sensing station with lighting and temperature controller circuits from Next Robotix (Comercializadora K Mox, S.A. de C.V., Mexico City, Mexico). In the device, the external quantum efficiency (EQE) was obtained using a QUESA-1200 system (TFSC Instrument Inc, Intercovamex, S.A. de C.V., Cuernavaca, Morelos, Mexico) with an LED light source of 100 mW/cm illumination, AM1.5.

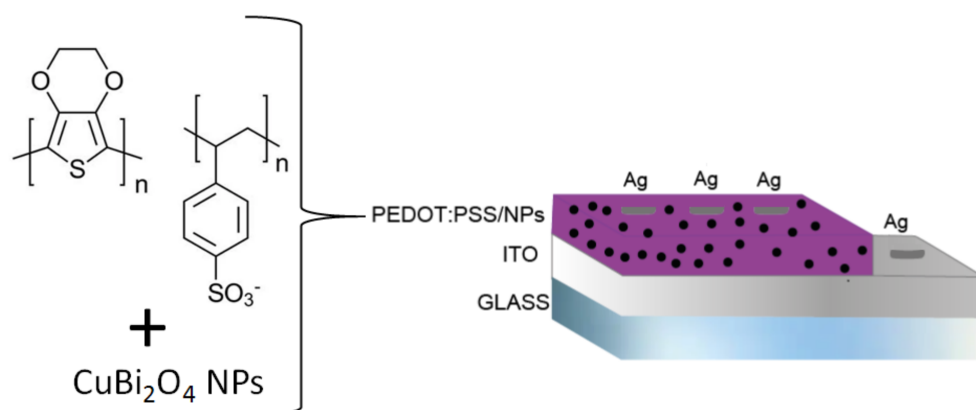


Figure 1. Device structure made of glass/ITO/PEDOT:PSS- CuBi_2O_4 NP/Ag.

3. Results and Discussion

CuBi_2O_4 NP characterization. The XRD pattern of the powdered CuBi_2O_4 NPs corresponds to that reported in the crystallographic card (International Center for Diffraction Data) ICDD 01-079-1810, for CuBi_2O_4 in a tetragonal crystalline structure, with spatial group $P4/ncc$ and crystal lattice parameters $a = b = 8.48\text{ \AA}$, $c = 5.79\text{ \AA}$ (Figure 2a). All peaks in the pattern correspond to the single crystalline phase [13,15,16], and there are no other diffraction peaks attributed to impurities. An average crystallite size of 24 ± 2 nm was estimated using Scherrer's equation on the (200), (211) and (202) diffraction peaks. Furthermore, the HR-TEM micrographs corroborate the formation of CuBi_2O_4 nanocrystals. In Figure 2b, a smaller isolated CuBi_2O_4 NP with 10.3 nm for each side is presented. The measured interplanar spacing of $4.2\text{ \AA}$ corresponds to the (200) plane, and in the corresponding FFT (fast Fourier transform), the indexed planes belong to the tetragonal crystal structure (ICDD 01-079-1810) of CuBi_2O_4 (Figure 2c), confirming the nanoparticle composition. The importance of the crystalline structure in these NPs lies in the fact that the charge transport is strongly conditioned by the order of the structure of the material:

when the order is of a higher level, the more favored overlap of the structures, which may define the energy bands and the spacing between them, will exist.

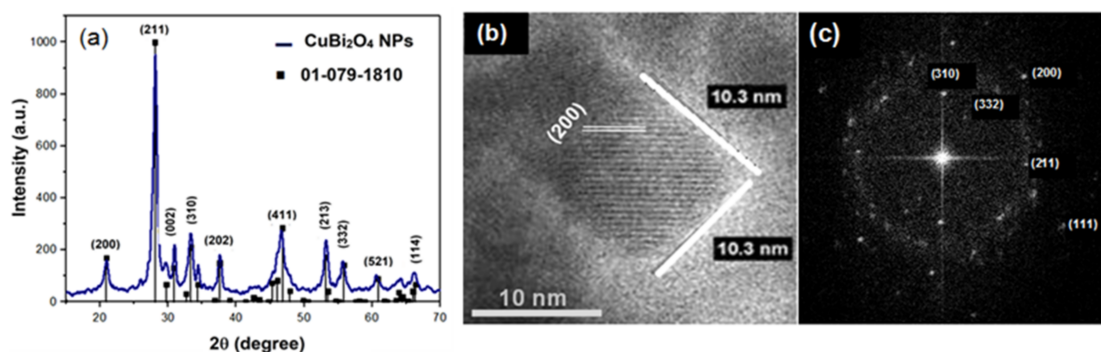


Figure 2. (a) Powder XRD pattern and (b) HR-TEM micrograph of CuBi_2O_4 NPs. In the corresponding FFT pattern (c), the indexed planes belong to the tetragonal crystal structure of CuBi_2O_4 .

On the other hand, six Raman bands centered at 88, 122, 182, 255, 392 and 573 cm^{-1} , characteristic of CuBi_2O_4 NPs, are observed (Figure 3a). These bands are associated with the bending vibration of Bi rhombohedra (B_{2g}), the translational vibration of the CuO_4 plane along the Z-axis (A_{1g}), the Cu–Cu vibration (E_g), the rotation of two stacked CuO_4 squares in opposite directions (A_{1g}), the Bi–O stretching vibration (A_{1g}) and the in-plane breathing of CuO_4 squares (A_{1g}), respectively. All these peaks correspond to those reported by other authors [41–45], whereas in the FTIR spectrum of the CuBi_2O_4 NPs (Figure 3b), two strong signals are seen at 517 and 411 cm^{-1} , which are, respectively, assigned to the stretching mode of the Bi–O bonds of BiO_6 and the stretching vibration of the Cu–O bond.

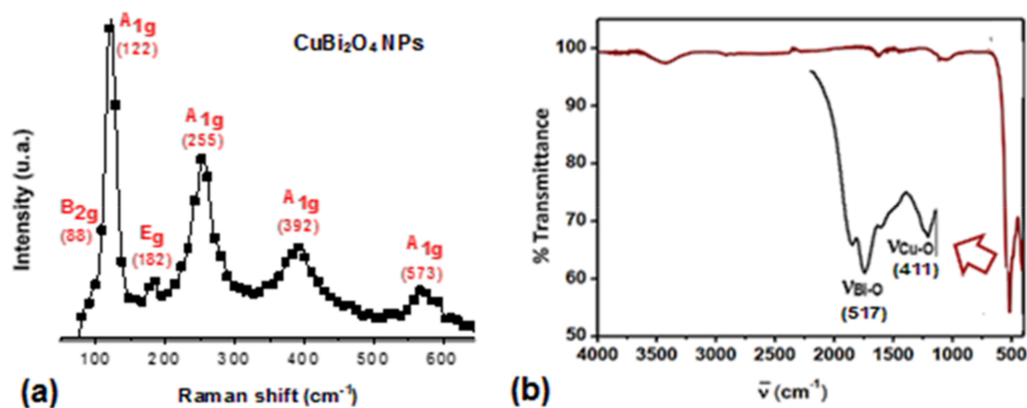


Figure 3. Spectra of (a) Raman and (b) FTIR of the CuBi_2O_4 NPs.

From diffuse reflectance spectroscopy (DRS), the UV–visible spectrum of the powdered CuBi_2O_4 NPs (Figure 4a) was obtained. This spectrum shows a wide absorption band between 300 and 790 nm, centered at 527 nm. The optical bandgap energy of the CuBi_2O_4 NPs was estimated at 1.7 eV from Tauc’s plot obtained from their DRS spectrum (Figure 4b). According to Tauc’s equation for a direct bandgap: $(\alpha h\nu)^2 = A^2(h\nu - E_g)$, where α is the absorption coefficient, $h\nu$ is the photon energy, E_g is the bandgap energy and A depends on the type of transition, when $\alpha h\nu = 0$, then $E_g = h\nu$. The bandgap energy is determined by plotting $(\alpha h\nu)^2$ versus $h\nu$ and finding the intercept on the $h\nu$ axis by extrapolating the plot to $(\alpha h\nu)^2 = 0$. Due to the size of the NPs obtained here, it is not expected that the bandgap energy would have shifted to the ultraviolet region.

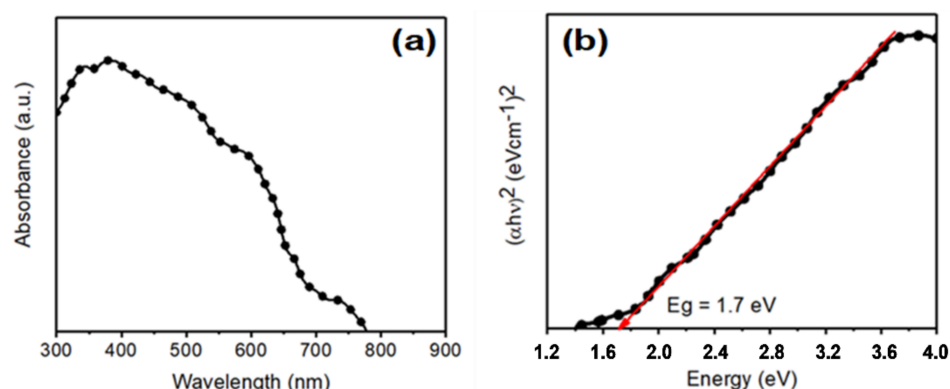


Figure 4. (a) UV–visible spectrum from DRS and (b) optical bandgap energy estimated by Tauc's plot method for CuBi_2O_4 NPs.

Characterization of composite films of PEDOT:PSS- CuBi_2O_4 NPs. Composite films with PEDOT:PSS were deposited by the spin coating technique in order to evaluate the use of the CuBi_2O_4 NPs as semiconductors in optoelectronics. The construction of a polymer–NP heterojunction will have the ability to separate photoexcited electron/hole pairs [26], where the polymer serves as a support for the NPs and as a hole injector layer [26,45]. Before carrying out the optical and electric characterization, the composite film was characterized in terms of its morphology by means of scanning electron microscopy (SEM) and atomic force microscopy (AFM). Figure 5a shows the microphotograph obtained at 250x, in which it is possible to observe the distribution of NPs along the polymer in the film. The CuBi_2O_4 NPs are distributed along the whole PEDOT:PSS polymer, meaning a proper charge transport along the PEDOT:PSS- CuBi_2O_4 NP system is expected. In order to complement the information provided by SEM, AFM measurements were conducted. Figure 5b shows the image for a $2\ \mu\text{m} \times 2\ \mu\text{m}$ area. The obtained RMS (root mean square) for this film was 24.76 nm, and the roughness average was 19.83 nm. These results were expected, considering that the size of the CuBi_2O_4 NPs is $24 \pm 2\ \text{nm}$. In the zones where the NPs are present, the roughness is greater than in the zones where only PEDOT:PSS is present. It is expected that this bulk heterojunction between the polymer and the metal oxide will promote electric charge transport throughout the film [26,45,46]. The interface between PEDOT:PSS and all the NPs generates a large interfacial area due to the NPs' size, which is desirable for photoinduced charge separation and charge transport [26].

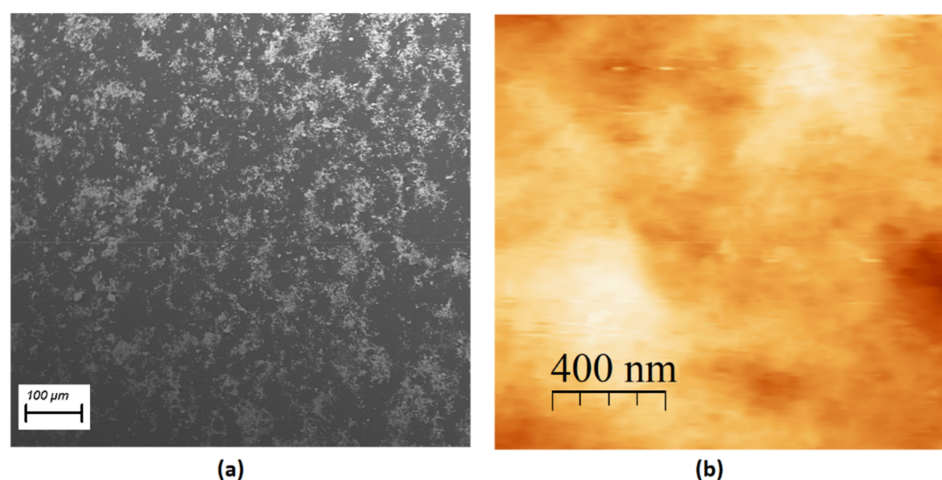


Figure 5. (a) SEM and (b) AFM of CuBi_2O_4 NPs in PEDOT:PSS.

Although CuBi_2O_4 NPs seemed to present thermal and chemical stability, IR spectroscopy was conducted in order to check that no material degradation occurred during the spin coating deposition. In Figure 6a, the spectrum shows signals at $413\ \text{cm}^{-1}$ and $523\ \text{cm}^{-1}$,

corresponding to the $\nu\text{Cu-O}$ bond and the stretching vibration of the $\nu\text{Bi-O}$ bond, respectively. In addition, the typical bands in PEDOT:PSS, such as 1172, 1131, 1006, 960, 802 and 690 cm^{-1} , were identified [47–49]. The C-O-C bending vibrations in the ethylenedioxy group occur between 1172 and 1131 cm^{-1} , while C-S-C stretching vibrations in the thiophene ring occur between 960 and 690. The 1006 cm^{-1} band is assigned to the O-S-O symmetric stretching mode in PSS, and the C-H angular deformation of the aromatic ring in PSS presents a band at 802 cm^{-1} [47,48]. From the previous results, it is deduced that there was no degradation of the NPs, nor of PEDOT:PSS, during the deposition of the composite films.

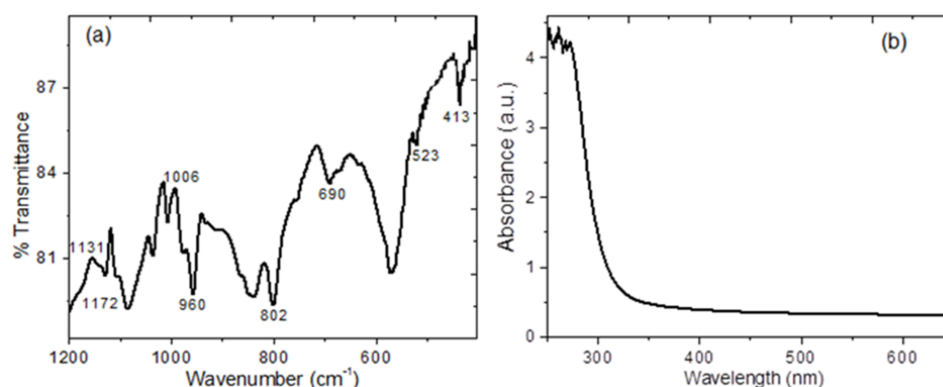


Figure 6. Spectra of (a) FTIR and (b) UV-Vis of PEDOT:PSS- CuBi_2O_4 NP films.

Regarding the absorbance of the film measured from UV-Vis spectroscopy, shown in Figure 6b, the characteristic absorption band of the NPs centered at 527 nm is not observed, and this is because the NPs are embedded within the polymer matrix, and they form an amorphous film. In amorphous semiconductor films, a tail in the absorption spectrum encroaches into the gap region [50]. This tail in the optical absorption spectrum, as a consequence of the disorder which characterizes these semiconductors, makes the absorption edge of an amorphous semiconductor difficult to define experimentally. As a result, several models have been developed to describe the bandgap [51]. The Tauc model has served as the standard empirical model whereby the optical gap of an amorphous semiconductor may be determined. The Tauc model has been applied to amorphous films, as well [51]. Additionally, although this is a simplified approach that can lead to errors in the determination of the optical bandgap, it is the same approach that was used to obtain the bandgap in the NPs. The above offers an idea about the increase or decrease in the bandgap when the NPs are introduced into the polymer. In this case, the Tauc bandgap obtained with a value of 2.1 eV is significantly greater than that of the NPs previously observed. It is important to mention that in the case of composite films with a heterojunction, the Tauc bandgap is calculated for indirect transitions [52]. In this amorphous semiconductor, optical transitions are described as a first approximation by non-direct transitions with no conservation of electronic momentum, for allowed indirect transitions [53]. Although the optical bandgap is higher for the film, it is in the range of semiconductors. The above is explained by the presence of PEDOT:PSS and the heterojunction which is formed between this polymer and the NPs. According to the SEM and AFM results, the heterojunction involves self-assembly of nano-scale heterojunctions by phase separation of PEDOT:PSS and the CuBi_2O_4 NPs. Due to the phase separation, charge-separating heterojunctions are formed throughout the bulk of the material [54]. This type of heterojunction may have advantages in the electric charge transport, due to the greater contact surface that promotes charge carrier transfer and exciton diffusion in devices, especially those of the photovoltaic type [26,54,55].

The electric characterization of the structure of PEDOT:PSS- CuBi_2O_4 NPs is important to verify the above-mentioned aspects. According to the scheme for the device: glass/ITO/PEDOT:PSS- CuBi_2O_4 NP/Ag, in Figure 1, when an external voltage is applied

to the electrodes ITO and Ag, electrons are injected from ITO to PEDOT:PSS, and from the polymer, they then flow to the NPs or to the Ag contact. However, under illumination, the absorbed photons within the CuBi_2O_4 NPs generate an electron/hole pair that must travel to the interphase to induce charge separation where electrons migrate to the Ag. The evaluation of the electric behavior in the device was conducted both in natural-light and in dark conditions, using the four-point probe method. Figure 7a shows the current–voltage (I–V) curves obtained. It can be observed that the device presents a marked change under illuminated conditions compared to the dark conditions, indicating a photoelectric behavior and that the device presents an appealing photosensitivity. It is important to note that only a slight change is observed in reverse bias.

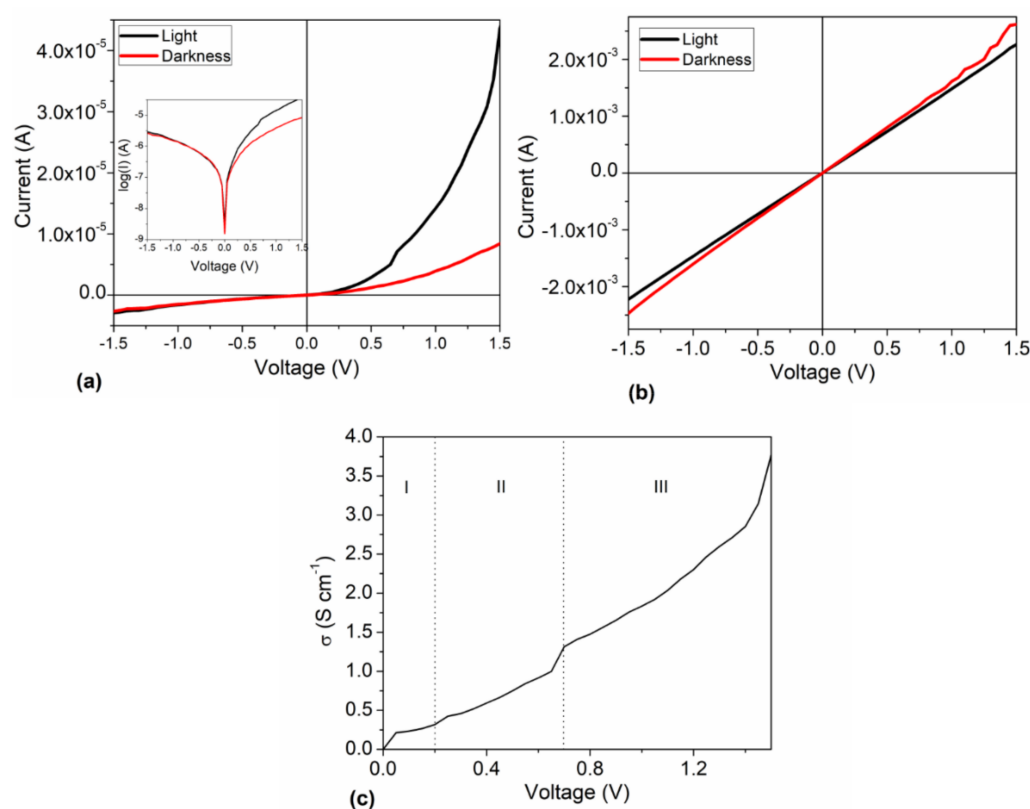


Figure 7. I–V graphs in light and dark conditions for (a) PEDOT:PSS-CuBi₂O₄ NP and (b) PEDOT:PSS devices. (c) σ –V graphs in light conditions for PEDOT:PSS-CuBi₂O₄ NP devices.

Moreover, the I–V characteristic curve behavior of the device is similar to that of a Schottky diode, where a small leakage current in reverse bias is observed. The resulting curve presents a threshold voltage of 0.067 V, a saturation current of 4.578×10^{-9} A and an ideality factor of 0.945. Additionally, a generated photocurrent of 1.448×10^{-9} A is observed at 0 V under light conditions. The latter indicates that the device starts operating at a very low voltage with an exponential output, and that also the device operation is close to the ideal diode where the ideality factor equals 1, which is evidence of its proper function as a photovoltaic device, as a consequence of an efficient charge separation and transport. On the other hand, the device characteristic presents three different conduction mechanisms: ohmic behavior, trapped charge limited current (T-CLC) and space charge limited current (SCLC) [56], which affect the resulting conductivity at different applied voltages. The resulting curve shows a current variation between 10^{-9} and 10^{-5} A (0 to 1.5 V), as it can be observed in the semi-logarithmic curve inset. However, under illuminated conditions, the device shows a current variation between 10^{-8} and 10^{-4} A (0 to 1.5 V), inducing a change in the current of as much as approximately one order of magnitude. From the curve obtained under light conditions, the asymmetry in the

current magnitude is more evident depending on the polarity of the external voltage and indicative of a pure ideal diode behavior. Meanwhile, obtaining such low current values for darkness conditions, as mentioned previously, is indicative of high resistance inside the device. This could be associated with the NPs that compose the bulk heterojunction and some of the interphases present in the architecture of the device. When comparing these results with those obtained for a device made mainly of a pristine PEDOT:PSS film (Figure 7b), it is observed that the latter device exhibits an ambipolar and ohmic behavior. However, higher current values are observed for the same applied voltage range, indicating apparently higher conductivities. Additionally, unlike the glass/ITO/PEDOT:PSS-CuBi₂O₄ NP/Ag device, no significant influence of the light or dark conditions is observed on charge transport. The difference in the behavior between the two devices is due to the presence of the CuBi₂O₄ NPs. Despite that, the CuBi₂O₄ NPs generate the n-p junction with the PEDOT:PSS, where these nanoparticles have a semiconductor behavior, which allows them to be used in optoelectronic devices, preferably under light conditions. The difference between the curves measured in light and dark conditions (Figure 7a) also indicates the possible use of these NPs in light-emitting diodes. To understand the conduction mechanisms of the device, the voltage-dependent conductivity (σ) in the heterojunction device was assessed at room temperature and is shown in Figure 7c. The graph has been divided into three different regions corresponding to the three different regimes of charge transport [57] previously mentioned. In the first regime, the behavior follows Ohm's law, and it depends on the residual charges present inside the device [58]. During the second regime, the conductivity is dominated by the diffusion of the charges along the device and its interfaces [59]. Meanwhile, in the third regime, the conductivity is dominated by carrier drift or the saturation region [60]. The change in charge transport regimes is associated with the accumulation of charges inside the device, mainly by traps; however, the observed continuous increase in the conductivity (Figure 7c) indicates the feasibility of using the films with CuBi₂O₄ NPs as components for diode-type devices. Each of the mentioned regions results in a different slope which is a consequence of the conduction mechanisms involved in the device conductivity at different voltages. On the other hand, conductivity values at room temperature for PEDOT:PSS/CuBi₂O₄ NPs (Figure 7c) are in the range for semiconductor materials (10^{-6} to 10^2 S cm⁻¹) [61]. The inclusion of CuBi₂O₄ NPs in PEDOT:PSS increases the conductivity, where the conductivity of pure PEDOT:PSS was about 39 S cm⁻¹ [62], and the obtained conductivity values for the device were as high as 4 S cm⁻¹ at 1.5 V, which is higher than the value of the pristine PEDOT:PSS (2 S cm⁻¹, Figure 7b). Additionally, these results indicate a higher conductivity compared to other 2D/PEDOT:PSS composite materials [4]. According to Pasha et al. [52–65], the reason for the improvement in the conductivity in PEDOT:PSS/CuBi₂O₄ NPs films can be attributed to the formation of more charge carriers, due to the large interfacial area in the polymer, and to the fact that the charge carriers also find electrical pathways to easily hop between the PEDOT and PSS polymer chains. Additionally, the NP-polymer interface promotes the generation of electron/hole pairs. One of the most important parameters in characterizing light-emitting diodes and solar cells is the external quantum efficiency (EQE). This parameter refers to the number of photons emitted by the device in respect to the number of charges injected [65]. The value obtained for the device glass/ITO/PEDOT:PSS-CuBi₂O₄ NP/Ag was 0.8. Although this is a low value, it can be increased in future works by optimizing the device with the inclusion of interfacial layers, in order to obtain devices with a sandwich-type architecture, and by device engineering, adjusting the film thickness. The interfacial films can be blocking layers, injector layers and hole or electron carrier layers. The incorporation of interfacial materials between the electrodes and the film with CuBi₂O₄ NPs may favor the contact between both, having a significant impact on the charge extraction and collection processes. However, it is evident in the current study that due to the CuBi₂O₄ NPs' crystalline structure and low bandgap, as well as the possibility of being integrated as components in composite films of a polymer matrix (PEDOT:PSS),

the proposed bulk heterojunction based on these NPs can be used as an active layer in optoelectronic devices.

4. Conclusions

CuBi₂O₄ NPs with an average crystallite size of 24 ± 2 nm were obtained by an uncomplicated one-step synthesis method. The bandgap of the composite PEDOT:PSS-CuBi₂O₄ NP film was evaluated considering indirect transitions in the heterojunction film that allowed the evaluation of its behavior as a component of a diode-type device. A resulting threshold voltage of 0.067 V, a saturation current of 4.578×10^{-9} A, an ideality factor of 0.945 and a generated photocurrent of 1.448×10^{-9} A were observed. Under natural-light conditions, the CuBi₂O₄ NPs presented electric behavior characterized by three different mechanisms: at low voltages, the behavior follows Ohm's law; when the voltage increases, charge transport occurs by diffusion between the NP-polymer interfaces; and at higher voltages, this occurs due to the current being dominated by carrier drift or the saturation region. Thanks to their crystalline structure, their feasibility in being integrated as components in composite films of a polymer matrix and their low bandgap, CuBi₂O₄ NPs are candidates to be part of optoelectronic devices.

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