



Research Article

Enhanced optoelectronic and semiconductor properties of electrodeposited hybrid films: Experimental and DFT-AIM investigation

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ABSTRACT

In this study, 2,2'-bithiophene-copper oxide (PBTh-CuO) hybrid films, containing 5 and 10 wt% CuO, were synthesized on FTO substrates via in situ electrochemical oxidative polymerization of 2,2'-bithiophene in CH₃CN containing 0.1 M LiClO₄. The resulting films were characterized using cyclic voltammetry, FTIR, UV-Vis spectroscopy, SEM, EDX, AFM, XRD, photoelectrochemical measurements, and Mott-Schottky analysis. In addition, density functional theory (DFT), COSMO and atoms in molecules (AIM) calculations were used to investigate the interfacial electronic properties of the hybrid materials. The incorporation of CuO induced significant structural, optical and electronic modifications compared with pristine PBTh. Increasing the CuO content from 0 to 10 wt% reduced the optical band gap from 1.88 to 1.81 eV, while the acceptor density increased from 2.12×10^{19} to 9.03×10^{19} and $3.4 \times 10^{20} \text{ cm}^{-3}$ for PBTh-CuO (5%) and PBTh-CuO (10%), respectively. AFM analysis revealed a substantial increase in surface roughness, from 10.9 nm for PBTh to 75.7 nm for the CuO-containing films. Theoretical calculations further corroborated the experimental findings, showing a progressive decrease in the HOMO-LUMO gap from 2.45 eV for PBTh to 1.45 eV for PBTh-CuO (5%) and 0.63 eV for PBTh-CuO (10%), accompanied by enhanced dipole moment and interfacial charge polarization. AIM analysis indicated that interface stabilization is dominated by strong S-O polar interactions, supplemented by weaker Cu-centered contacts. Consequently, the incorporation of CuO significantly enhances the optoelectronic and interfacial properties of PBTh, highlighting the potential of PBTh-CuO hybrid films for photoelectrochemical and optoelectronic applications.

1. Introduction

Converting solar energy into heat or electricity remains a research priority in sustainable energy systems. Despite silicon's stronghold in today's photovoltaic market, its associated manufacturer-to-device

energy and cost intensity creates an ever-present impetus for low-cost, scalable alternative semiconductor materials and processing routes [1–7]. Within this context, organic-inorganic hybrid materials have attracted considerable attention for their unique composition, which enables the exploitation of the solution-processability and structural

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tunability of conjugated polymers, combined with the inherent solid-state semiconducting properties of metal oxides [8–15]. Conducting polymers are particularly appealing for optoelectronic applications due to their ability to be prepared under relatively mild conditions and their tunable redox, optical, and charge-transport properties [12, 16–20]. Among these materials, polythiophene and its derivatives have been extensively studied for electrochromic devices [21], sensors [22], energy-storage systems [23,24], light-emitting devices [25], and photovoltaic applications [26–29]. In this regard, electrochemical polymerization is particularly advantageous, as it allows the growth of a film directly on the electrode surface, with good control over thickness and subsequent tuning of deposition conditions [18–20,24–26]. We focus on using such a hybrid system, copying the organics, combined with specific inorganic material to complete the combined energy function, because copper oxide serves as an appropriate inorganic partner, being a p-type semiconductor with a modest bandgap and high visible-light absorption [30–34], decent charge-transfer performance, and low price. Introducing CuO into a conjugated polymer matrix could induce local polarization (induce a dipole moment at the interface), enhance interfacial charge transfer from the conjugated Polymer to CuO via intermolecular hydrogen bonds formed between polar groups of the two materials, and alter the hybrid film's electronic structure [35,36]. These characteristics render PBTh–CuO composites potential materials for photoelectrochemical and similar opto-electronic systems [10–15].

It should be noted that CuO was selected as the matrix material due to its p-type semiconducting properties, good chemical stability, low cost and high surface area. The incorporation of CuO into the poly(2,2'-bithiophene) matrix enhances the charge transfer and provides additional electroactive sites. Also, the CuO nanoparticles help the conducting polymer growth and improve the adhesion and stability of the hybrid film on the FTO substrate. The synergetic interaction between CuO and PBTh contributes to improved electrochemical performance of the hybrid films [37–39].

The literature on conducting-polymer/metal-oxide composites is expanding. Still, studies that combine electrochemically deposited PBTh–CuO films with comprehensive structural characterization and semiconductor analysis, including atomistic DFT-AIM interpretations, remain scarce. Thus, this work aims to synthesize PBTh–CuO hybrid films via electrochemical deposition and evaluate how CuO loading affects their performance. By combining experimental techniques with theoretical analysis, we investigate the relationship between the material's structural, morphological, optical, semiconducting, and interfacial electronic properties. Specifically, we focus on how introducing CuO alters the hybrid material's band gap, charge-carrier density, interfacial polarization, and local bonding topologies.

2. Materials and methods

2.1. Materials and reagents

The monomer used was 2,2'-bithiophene (BTh, 99%, Sigma-Aldrich). Copper oxide (CuO, 98%) NPs were purchased from Neutrino Corporation, and acetonitrile (CH₃CN, 99.7% Sigma-Aldrich) was used. The supporting electrolyte consisted of 0.1 M anhydrous lithium perchlorate (LiClO₄, 99.99% Fluka) dissolved in distilled acetonitrile (CH₃CN, Aldrich).

2.2. Instruments

Electrochemical measurements were conducted using a Voltalab 301 potentiostat/galvanostat in a conventional three-electrode configuration. Bare or coated FTO substrates served as working electrodes, while a platinum wire and a saturated calomel electrode (SCE) served as the counter and reference electrodes, respectively. The surface morphology and elemental composition of the deposited films were examined by scanning electron microscopy (SEM) coupled with energy-dispersive X-

ray spectroscopy (EDX) on a JEOL JSM-7001 F microscope. Phase identification was performed by X-ray diffraction (XRD) using a Rigaku Smart Lab diffractometer equipped with monochromated CuK α 1 radiation ($\lambda = 1.54056 \text{ \AA}$), operated at 20 kV and 10 mA over a 2θ range of 20–80°. Photoelectrochemical measurements were performed under illumination from a 500 W halogen lamp at 100 mW cm^{-2} . Mott-Schottky measurements were carried out in CH₃CN/LiClO₄ (0.1 M) for PBTh and PBTh–CuO films. The thickness of the films was measured by a mechanical profilometer of the KLA- Tencor Alpha-Step D-500 type.

2.3. Preparation of a hybrid composite

The hybrid composite was electrochemically synthesized by cyclic voltammetry (CV) in an organic medium (CH₃CN) containing lithium perchlorate (0.1 M). Bithiophene (BTh, 0.01 M) and different concentrations of copper oxide (CuO, 5% and 10%) were added, with slight agitation to re-homogenize the solution. The electrochemical polymerization was conducted using fluorine-doped tin oxide (FTO) as the working electrode. Cyclic voltammograms were recorded over a potential range of 0 to 1.700 V/SCE at a scan rate of 25 mV/s. The resulting polymer film was washed successively with distilled water, ethanol, and acetone to remove residual bithiophene and counterions adsorbed on the electrode, and finally dried with an argon jet. In the absence of copper oxide, the experiment was conducted using bithiophene.

2.4. Numerical methodology

To complement the experimental characterization and clarify the role of CuO incorporation in the electronic structure of the polymeric matrix, a density functional theory study was conducted on three representative models: pristine PBTh, PBTh–CuO (5%), and PBTh–CuO (10%). This computational approach is justified by previous reports showing that the electronic and optical properties of polythiophene-based materials are highly sensitive to chain geometry, conjugation length, and interfacial interactions with inorganic phases [27–29]. In parallel, CuO is well known as a p-type semiconductor with a relatively narrow band gap and attractive photoelectronic properties, making it a relevant inorganic counterpart for hybrid photovoltaic materials [30–33]. All calculations were performed with the TURBOMOLE V7.7.1 program package via the TmoleX 2023 interface [40]. Geometry optimization and electronic-structure calculations were carried out using the PBE0 hybrid exchange-correlation functional [41] in conjunction with the def2-SVP basis set [42]. The Coulomb term was treated within the RI-J approximation, and long-range dispersion effects were included using the DFT-D3 correction with Becke–Johnson damping [43]. This level of theory offers a good compromise between computational cost and reliability for conjugated organic systems interacting with metal-oxide fragments, particularly when the objective is to compare relative trends in frontier orbitals, polarization, and charge redistribution across a homologous series of hybrid models [27–29,41–43]. The numerical settings extracted from the calculation files were kept identical across the three investigated systems to ensure strict comparability. The electronic density was integrated using a Lebedev spherical grid of size 3 with 302 angular points, a Chebyshev radial grid of size 3 with 114 integration cells, and Becke partitioning with sharpness 3. In the gradient evaluation, the neglect thresholds were fixed at 1.0×10^{-10} for both rithr 1 and rithr 2. The RI treatment employed 8 density bins, a maximum multipole moment of 14, a multipole precision parameter of 1.0×10^{-8} , and a moment summation threshold of 1.0×10^{-24} . All calculations were run in shared-memory parallel mode with 4 OpenMP threads and an RI memory allocation of 500 MB.

Full geometry optimization was performed without symmetry constraints until all convergence criteria were met. The thresholds extracted from the optimization outputs were 1.0×10^{-4} a.u. for the energy change, 5.0×10^{-4} for the RMS displacement, 5.0×10^{-4} for the RMS gradient, 1.0×10^{-3} for the maximum displacement element, and $1.0 \times$

10-3 for the maximum gradient element. The pristine PBTh model converged after 123 optimization cycles, whereas PBTh-CuO (5%) and PBTh-CuO (10%) required 304 and 296 cycles, respectively. The higher number of cycles for the hybrid systems indicates a more complex potential-energy surface upon CuO incorporation, which is chemically consistent with the increased structural flexibility and interfacial polarization expected in organic/inorganic hybrids [10,14,15]. The optimized structures were then analyzed for total electronic energy, dipole moment, frontier-orbital energies, and atomic charge distributions (Table 1). The final total energies were found to be -8821.76746426205 a.u. for PBTh, -10536.84483070248 a.u. for PBTh-CuO (5%), and -12251.90218862372 a.u. for PBTh-CuO (10%). Because the three models differ in composition and total number of electrons, these absolute energies were not used alone to rank stability. Instead, the comparative discussion was based on descriptors that remain chemically meaningful across the whole series, namely HOMO and LUMO energies, HOMO-LUMO separation, dipole moment, charge redistribution, and local interfacial geometry. Solvation and surface polarization effects were also examined within the COSMO formalism [44]. In the three models, the COSMO cavity was closed and treated with $\epsilon = \infty$, $n_{\text{ppa}} = 1082$, $n_{\text{spa}} = 92$, $r_{\text{solv}} = 1.30$, $r_{\text{outf}} = 0.85$, and $n_{\text{sp}} = 32$. The number of surface segments was 4524 for PBTh, 4467 for PBTh-CuO (5%), and 4533 for PBTh-CuO (10%).

The exported COSMO coordinates were also used to determine local interfacial distances after conversion from bohr to angstrom. Natural population analysis was used to quantify charge redistribution induced by CuO incorporation. The PBTh-CuO (5%) system displayed an open-shell ground state with separate alpha and beta orbitals and an integrated spin density of 1.0000007006. In contrast, PBTh and PBTh-CuO (10%) converged as closed-shell systems. This distinction is important because it shows that the 5% CuO model is not merely an electronically perturbed closed-shell polymer but a genuinely spin-polarized hybrid interface. For completeness, the wavefunction norms were exactly 1.0000000000 for the three systems, while the virial values were 1.99575908811 for PBTh, 1.99611963636 for PBTh-CuO (5%), and 1.99638089786 for PBTh-CuO (10%), all very close to the ideal limit of 2. These results confirm the internal consistency of the converged electronic solutions and support the reliability of the descriptors used in the discussion below [40–45].

3. Results and discussion

3.1. Preparation of polythiophene

A visible color change was observed after CuO incorporation (Fig. 1), indicating that the deposited hybrid films differ optically from pristine PBTh. The PBTh film exhibited a brick-red appearance, whereas the PBTh-CuO film appeared darker blue, almost black, suggesting that CuO alters the polymer matrix's electronic environment. This visual observation is consistent with the spectroscopic and photoelectrochemical results discussed below.

Considerable research has focused on the electrochemical preparation of polythiophene (PBTh) films, particularly on optimizing electropolymerization conditions. Previous studies have shown that several parameters, including solvent composition (especially the presence or absence of water), temperature, monomer concentration, and the nature of the supporting electrolyte, strongly influence the properties of the deposited PBTh films. In particular, acetonitrile has been widely used as

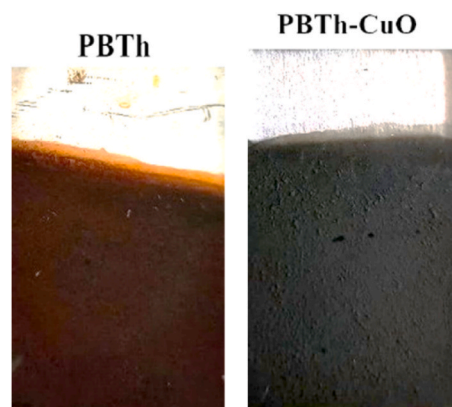


Fig. 1. Photographs of the electrodeposited PBTh and PBTh-CuO films on FTO substrates.

a suitable medium for the electropolymerization of thiophene derivatives, and the supporting electrolyte anion has been reported to affect film growth and electrochemical behavior significantly [13]. The film thicknesses determined by profilometric analysis, were approximately 900 and 1125 nm, respectively.

In this work, the electropolymerization of bithiophene was investigated by cyclic voltammetry. Fig. 2(a) shows successive cyclic voltammograms recorded over 10 cycles for PBTh formation in $\text{CH}_3\text{CN}/\text{LiClO}_4$ (0.1 M). During the first anodic scan, an oxidation wave appears at approximately 1.1 V/SCE, attributed to the formation of the bithiophene radical cation. This species serves as the key intermediate in polymerization, as coupling of radical cations initiates chain propagation and leads to the gradual formation of the conjugated polymer film on the FTO surface [14]. During the reverse scan, a broad cathodic peak centered around 0.36 V/SCE is observed, corresponding to the reduction of the deposited polymer layer. As the number of cycles increases, both the anodic and cathodic current densities rise, indicating continuous growth of the electroactive film on the electrode surface. This behavior is characteristic of successful electropolymerization and reflects the increasing thickness of the deposited conjugated layer [13]. Previous studies have also shown that freshly prepared monomer solutions can influence the polymerization threshold and the quality of the resulting films, due to the possible presence of oligomeric species in reused solutions [46].

Fig. 2(b) shows the corresponding voltammetric response in the presence of CuO. The overall electrochemical behavior remains consistent with film formation; however, the shape and intensity of the voltammograms indicate that the inorganic phase influences the deposition process and modifies the electrochemical response of the growing polymer matrix. This result suggests that CuO is not merely passively dispersed in the medium but actively contributes to interfacial film formation and affects the electronic properties of the hybrid layer.

In both systems, film formation is accompanied by electrochromic behavior arising from the conjugated Polymer's redox transitions. These reversible optical changes are typical of thiophene-based materials and stem from changes in electronic delocalization during oxidation and reduction. This behavior further confirms the successful formation of electroactive PBTh and PBTh-CuO films and highlights their potential for optoelectronic and photoelectrochemical applications [47].

Table 1

Key extracted numerical descriptors for PBTh, PBTh-CuO (5%), and PBTh-CuO (10%).

Model	Atoms	Basis functions	Occupied orbitals	Optimization cycles	Dipole moment (D)	HOMO (eV)	LUMO (eV)	HOMO-LUMO gap (eV)
PBTh	114	1354	337	123	1.0937	-5.10146	-2.64162	2.45984
PBTh-CuO (5%)	116	1399	356	304	6.9856	-4.34183	-2.88954	1.45229
PBTh-CuO (10%)	118	1444	374	296	46.4630	-3.96364	-3.33002	0.63362

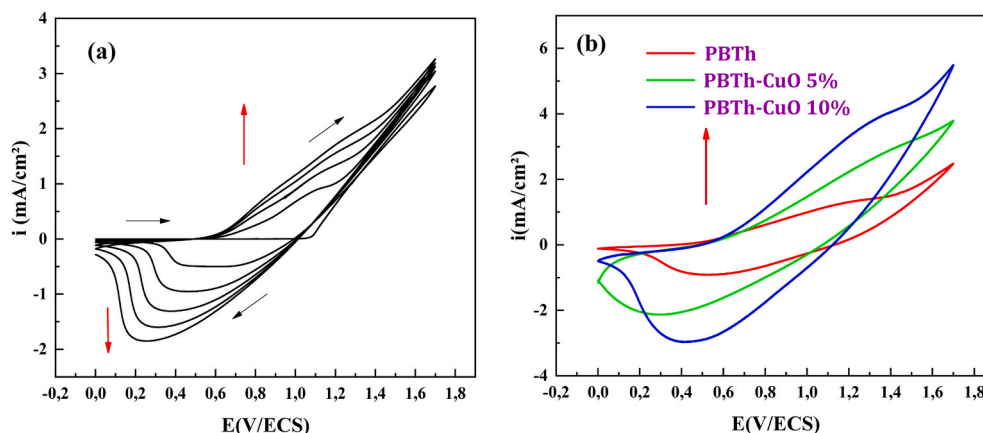


Fig. 2. Successive cyclic voltammograms recorded during the electropolymerization of (a) PBTh/FTO and (b) PBTh-CuO/FTO films in $\text{CH}_3\text{CN}/\text{LiClO}_4$ (0.1 M) at a scan rate of 25 mV s^{-1} .

3.2. FTIR characterization

The FTIR spectra of the PBTh film and PBTh-CuO hybrid films are shown in Fig. 3 and were recorded over the $4000\text{--}500 \text{ cm}^{-1}$ range. The PBTh/FTO spectrum exhibits a band at 777 cm^{-1} assigned to C-S stretching vibrations [2]. The band at 1628 cm^{-1} is attributed to C=C stretching within the thiophene ring, whereas the broad feature between 2330 and 2400 cm^{-1} reflects the extended conjugation of the PBTh backbone [34].

The band at 2341 cm^{-1} is associated with =C-H stretching linked to π -electron delocalization, while bands at 1050 and 1202 cm^{-1} are assigned to C-O and C=O stretching vibrations, respectively. The broad band near 3569 cm^{-1} is attributed to the =C-H group vibrations. For the PBTh-CuO films, additional weak bands in the $400\text{--}470 \text{ cm}^{-1}$ region are assigned to Cu-O vibrations [48]. In contrast, the main PBTh bands remain intact, indicating that the polymer framework is retained after CuO incorporation.

3.3. UV-visible spectroscopy characterization

The optical properties of the deposited films were characterized by UV-Vis spectroscopy across $350\text{--}1100 \text{ nm}$ (Fig. 4). Pristine PBTh exhibits a main absorption band at $\lambda_{\text{max}} = 464 \text{ nm}$ with an absorbance of 2.207, assigned to the $\pi \rightarrow \pi^*$ transition of the conjugated polymer backbone [49]. A second band near 850 nm indicates the formation of relatively long conjugated chains. After CuO incorporation, the absorption intensity increases markedly, reaching absorbance values of 2.768 for PBTh-CuO (5%) and 3.794 for PBTh-CuO (10%). This bathochromic shift is consistent with stronger electronic coupling within the hybrid material and qualitatively aligns with the DFT-predicted reduction of the frontier-orbital gap.

To estimate the optical gap (E_g) of the PBTh and PBTh-CuO films, plots of $(\alpha h\nu)^2$ versus $h\nu$ were constructed (Fig. 5), where α is the absorption coefficient, and $h\nu$ is the photon energy [3,4].

The optical gap was determined by extrapolating the linear region of each curve to the energy axis. The resulting E_g values are 1.88 eV for PBTh, 1.83 eV for PBTh-CuO (5%), and 1.81 eV for PBTh-CuO (10%). The progressive decrease in E_g with increasing CuO content indicates that CuO incorporation promotes electronic delocalization and enhances the light-harvesting potential of the hybrid films.

3.4. Morphological characterization by SEM

The surface morphology of the electrodeposited films was examined by SEM (Fig. 6). Pristine PBTh shows a relatively thick, porous deposit with an irregular granular morphology, consistent with the formation of

an amorphous polymer layer.

In contrast, the PBTh-CuO hybrid film exhibits clearly distinguishable inorganic domains embedded in the polymer matrix, confirming the successful incorporation of CuO into the conductive PBTh network. Overall, the SEM observations indicate that adding CuO substantially alters the film's surface texture and microstructural organization.

3.5. Energy dispersive X-ray (EDX)

Energy-dispersive X-ray spectroscopy (EDX) was used to confirm the elemental composition of PBTh and PBTh-CuO films (Fig. 7). The PBTh-CuO hybrid shows a strong sulfur signal at 2.3 keV from the thiophene-based polymer backbone, while oxygen appears around 0.5 keV . Copper signals near 0.9 , 8.0 , and 8.9 keV confirm that CuO is incorporated into the hybrid film. Chlorine signals are attributed to residues of the LiClO_4 supporting electrolyte, whereas Sn signals are attributed to the FTO substrate.

3.6. Atomic force microscopy (AFM) analysis

The topography of PBTh and PBTh-CuO films was further examined by atomic force microscopy (AFM), which provides direct information on surface texture and roughness (Fig. 8). The PBTh film exhibits a relatively smooth, homogeneous topography, whereas the PBTh-CuO film is more compact and heterogeneous, with pronounced protrusions attributed to inorganic domains. This morphological evolution is accompanied by a substantial decrease in roughness, from 75.7 nm for PBTh to 10.9 nm for PBTh-CuO. These results confirm that CuO incorporation strongly alters the surface organization of the polymer film. It is difficult to compare these results with the data in the literature because RMS parameters depend strongly on the scanning length and the thickness of the films.

3.7. XRD analysis

Fig. 9 shows the XRD pattern of the PBTh-CuO hybrid film deposited on FTO. The diffractogram reveals that the PBTh matrix is predominantly amorphous, with peaks wide, a centered peak at $2\theta = 13.27^\circ$ and 32.21° revealing the conducting amorphous nature of polythiophene. This result indicates that the polymer matrix remains largely disordered after electrodeposition, while CuO contributes a crystalline component to the composite structure. [50,51]. Additional diffraction peaks appear at $2\theta = 38.88^\circ$, 57.31° , 83.35° , and 90.66° , corresponding to the (022), (033), (051), and (022) planes, respectively, confirming the presence of a crystalline CuO phase in the hybrid material. These features support the successful incorporation of the inorganic oxide into the PBTh matrix

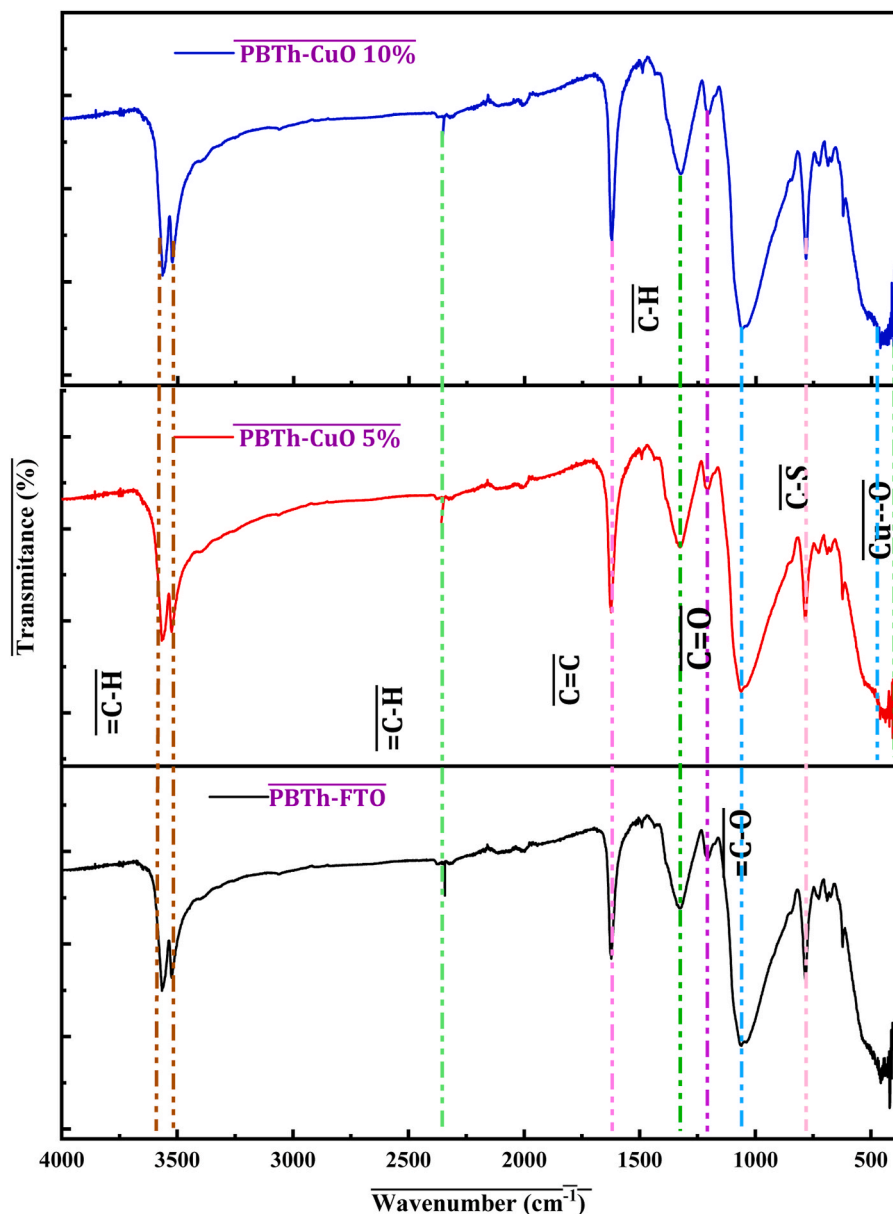


Fig. 3. FTIR spectra of PBTh and PBTh-CuO hybrid films containing 5% and 10% CuO.

and are consistent with the SEM and EDX results discussed above.

3.8. Photoelectrochemical measurements

Fig. 10 shows the photocurrent response of PBTh and PBTh-CuO films under chopped illumination in $\text{CH}_3\text{CN}/\text{LiClO}_4$ at an applied potential of -400 mV vs. SCE.

Upon illumination, the current density shifts toward negative values, indicating cathodic photocurrent and confirming the p-type photoresponse of both films [6,10]. The transient response is reproducible across successive light-on/off cycles, indicating that the deposited layers are photoactive. At the same time, the effect of CuO loading should not be interpreted solely by the absolute photocurrent amplitude, but rather in combination with the optical-gap reduction, the higher carrier density, and the stronger interfacial polarization, as evidenced by Mott-Schottky analysis and theoretical calculations.

3.9. Mott-Schottky analysis

Mott-Schottky analysis is a widely used method for investigating the semiconductor/electrolyte interface. It provides access to key semiconductor parameters, particularly the charge-carrier density and the flat-band potential, by measuring the capacitance of the space-charge region as a function of the applied potential. In the present study, the Mott-Schottky behavior of PBTh and PBTh-CuO films was evaluated by plotting $1/C^2$ versus the applied potential [52]. For a p-type semiconductor, the Mott-Schottky relation is expressed as:

$$\frac{1}{C^2} = \frac{2}{\epsilon\epsilon_0 q N_A} \left(E - E_{fb} - \frac{kT}{q} \right)$$

where (C) is the capacitance of the space-charge layer, (ϵ) is the semiconductor's dielectric constant, (ϵ_0) is the vacuum permittivity, (q) is the elementary charge, (N_A) is the acceptor density, (E) is the applied potential, (E_{fb}) is

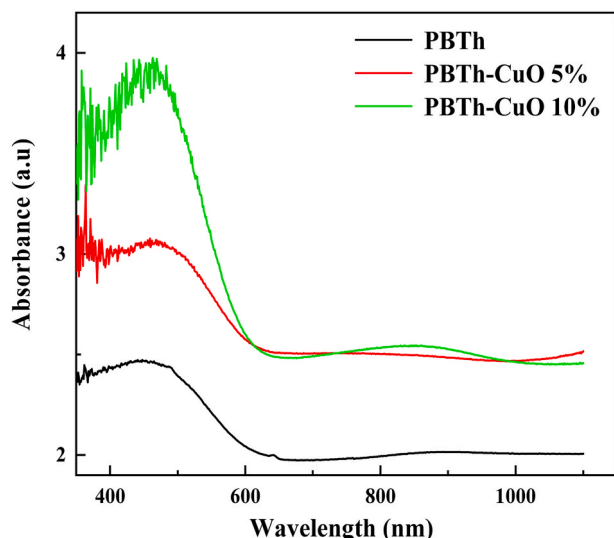


Fig. 4. UV-Vis absorption spectra of PBTh and PBTh-CuO films deposited on FTO.

the flat-band potential, k is the Boltzmann constant, and $(\text{cap } T)$ is the absolute temperature. A negative slope in the Mott-Schottky plot indicates p-type semiconducting behavior.

Fig. 11 presents the Mott-Schottky plots of PBTh/FTO and PBTh-CuO/FTO films containing 5% and 10% CuO. All curves were recorded in $\text{CH}_3\text{CN}/\text{LiClO}_4$ (10^{-1} M), with the frequency and amplitude fixed at 200 Hz and 10 mV/SCE, respectively. The negative slope of the linear region in the depletion domain clearly confirms the p-type semiconducting behavior of the investigated films. The experimental values of E_{fb} and NA are reported in Table 2. While PBTh exhibits an acceptor density of $2.12 \times 10^{19} \text{ cm}^{-3}$, this value increases to $9.03 \times 10^{19} \text{ cm}^{-3}$ for PBTh-CuO (5%) and $3.4 \times 10^{20} \text{ cm}^{-3}$ for PBTh-CuO (10%). This progressive increase indicates that CuO incorporation enhances the carrier

density and is expected to facilitate interfacial charge transport within the hybrid films [36,53]. Taken together, the experimental results already establish a clear trend before the theoretical discussion: CuO addition decreases the optical gap, increases the acceptor density, and substantially modifies film morphology.

The molecular modeling section is therefore used not as an isolated calculation but as a mechanistic framework to explain why the CuO-rich films exhibit stronger interfacial polarization and more favorable electronic properties.

3.10. Molecular modeling

• DFT calculations

The calculated results reveal a pronounced, systematic electronic reorganization of the PBTh matrix upon CuO incorporation. The most striking trend is the continuous decrease in the HOMO-LUMO gap, from 2.45984 eV for pristine PBTh to 1.45229 eV for PBTh-CuO (5%) and 0.63362 eV for PBTh-CuO (10%) (see Table 1). This corresponds to reductions of about 40.96% for the 5% CuO model and 74.24% for the 10% CuO model relative to pristine PBTh. Such a strong contraction of the frontier-orbital gap indicates that the metal-oxide phase does not act as a passive additive but rather as an electronically active component that substantially perturbs the conjugated polymer backbone. This behavior is fully consistent with the known sensitivity of polythiophene derivatives to structural perturbations and interfacial interactions [27–29], and it also qualitatively agrees with the experimental UV-visible results of the present manuscript, where the optical gap decreases from 1.88 eV for PBTh to 1.83 and 1.81 eV after CuO addition.

A closer examination of the frontier-orbital energies shows that the narrowing of the gap results from a combined upward shift of the occupied frontier level and a downward stabilization of the virtual frontier level. The HOMO energy becomes progressively less negative, moving from -5.10146 eV in PBTh to -4.34183 eV in PBTh-CuO (5%) and -3.96364 eV in PBTh-CuO (10%), whereas the LUMO decreases from -2.64162 eV to -2.88954 eV and -3.33002 eV, respectively. In

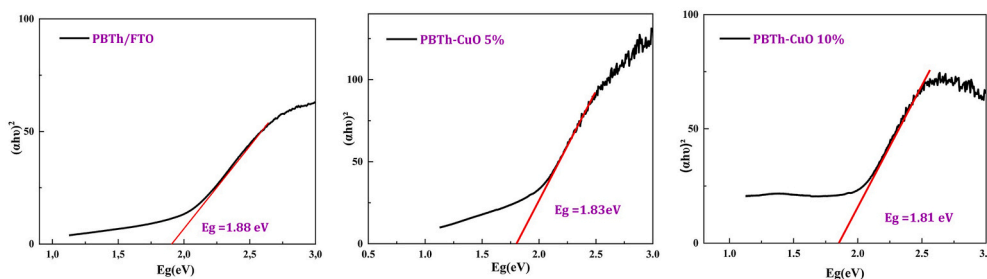


Fig. 5. Tauc plots of $(\alpha h\nu)^2$ versus $h\nu$ for (a) PBTh and (b) PBTh-CuO films containing 5% and 10% CuO.

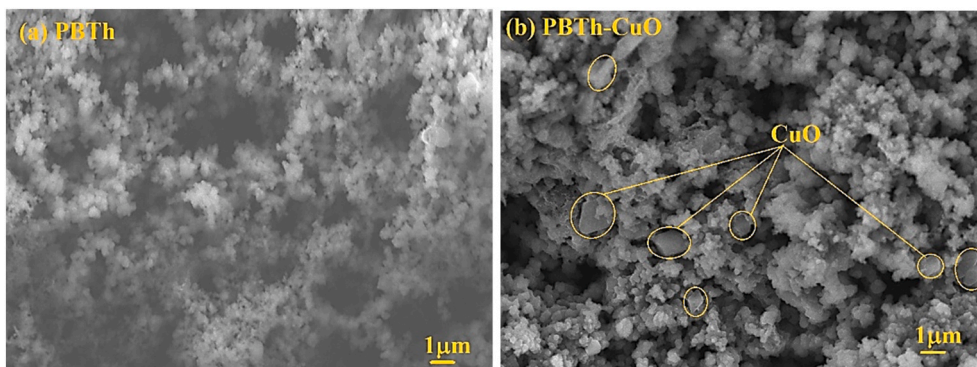


Fig. 6. SEM micrographs of PBTh and PBTh-CuO thin films deposited on FTO substrates.

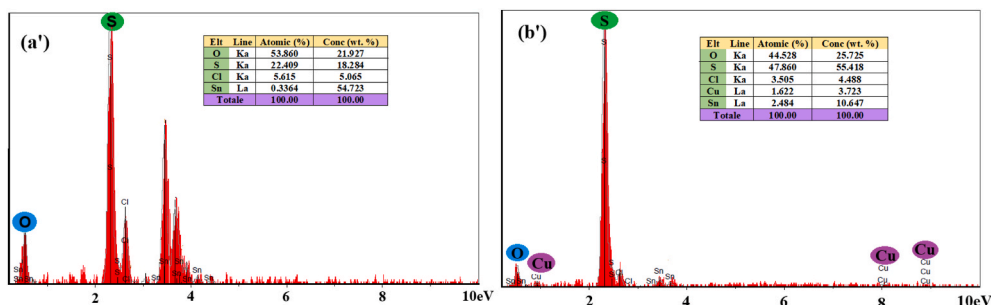


Fig. 7. EDX spectra of the (a')PBTh and (b') PBTh-CuO films deposited on FTO.

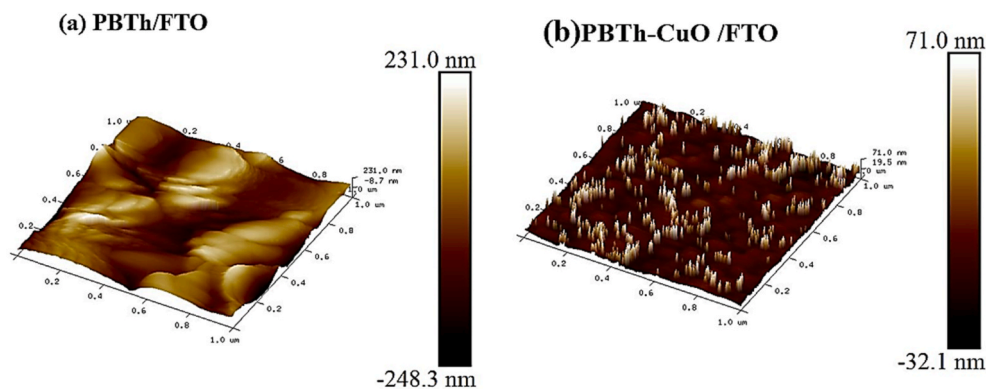


Fig. 8. Two-dimensional and three-dimensional AFM topographies of PBTh and PBTh-CuO films deposited on FTO.

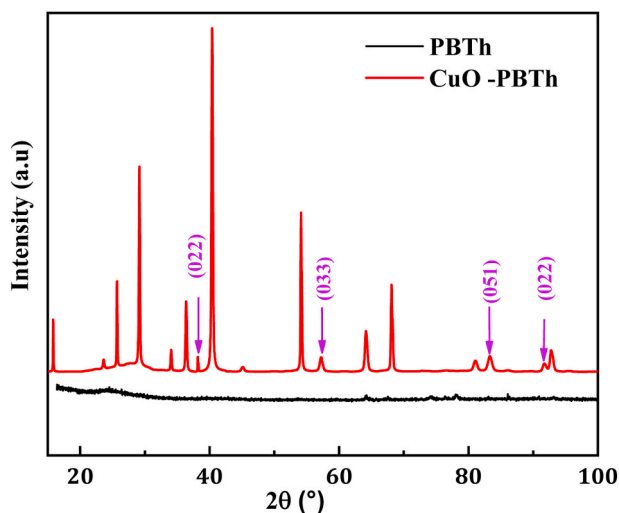


Fig. 9. XRD pattern of the PBTh-CuO hybrid film deposited on FTO.

physical terms, CuO incorporation destabilizes the Polymer's electron-rich frontier states and stabilizes the hybrid system's electron-accepting states. This dual effect is characteristic of strong interfacial electronic coupling in organic/inorganic composites [10,14,15] and supports the idea that CuO facilitates charge transfer within the PBTh matrix. From the viewpoint of photovoltaic or photoelectrochemical applications, this is a favorable trend because it may enhance carrier separation and reduce the energetic barrier for excitation.

Global conceptual DFT descriptors derived from the frontier orbitals support this interpretation. Using the standard finite-difference approximation, the ionization potential decreases from 5.10146 eV for PBTh to 4.34183 eV for PBTh-CuO (5%) and 3.96364 eV for PBTh-CuO

(10%) (Table 3). In comparison, the electron affinity increases from 2.64162 eV to 2.88954 eV and 3.33002 eV, respectively. As a result, the chemical hardness falls sharply from 1.22992 eV to 0.72615 eV and then to 0.31681 eV, whereas the softness rises from 0.40653 eV to 1 to 0.68857 eV⁻¹ and finally to 1.57823 eV⁻¹. In parallel, the electrophilicity index increases from 6.09341 eV for pristine PBTh to 9.00177 eV and 20.98950 eV for the hybrid models. According to conceptual DFT, lower hardness and higher softness indicate a more polarizable and electronically more responsive system [54], while a larger electrophilicity reflects a greater tendency to accept electronic charge. Therefore, the progressive CuO loading transforms PBTh into a softer, more polar, and more electrophilic hybrid material.

The dipole moment provides another clear signature of this transformation. The total dipole moment increases from 1.0937 D in PBTh to 6.9856 D in PBTh-CuO (5%), then rises dramatically to 46.4630 D in PBTh-CuO (10%). This corresponds to an increase of about 538.7% for the first hybrid and 4148.2% for the most CuO- rich model. Such a change is far too pronounced to be interpreted as a simple steric effect. It demonstrates that CuO incorporation induces intense charge separation and a highly anisotropic distribution of electronic density. In hybrid polymer/oxide materials, this type of internal polarization is generally associated with stronger local electric fields and improved interfacial charge separation [10,14,15]. The computational result, therefore, provides a plausible atomistic explanation for the experimentally observed enhancement in the optical response of the CuO-containing films. The natural population analysis confirms that this polarization is localized at the polymer/oxide interface. In pristine PBTh, sulfur atoms bear a moderate positive charge, with an average value of +0.41494, whereas carbon atoms are on average - 0.24357 and hydrogen atoms +0.26321. After CuO incorporation, the mean sulfur charge rises to +0.45982 in PBTh-CuO (5%) and +0.49040 in PBTh-CuO (10%), while the average carbon charge becomes slightly more negative, reaching - 0.25302 and - 0.25884, respectively. This indicates a global redistribution of electron density from a relatively homogeneous

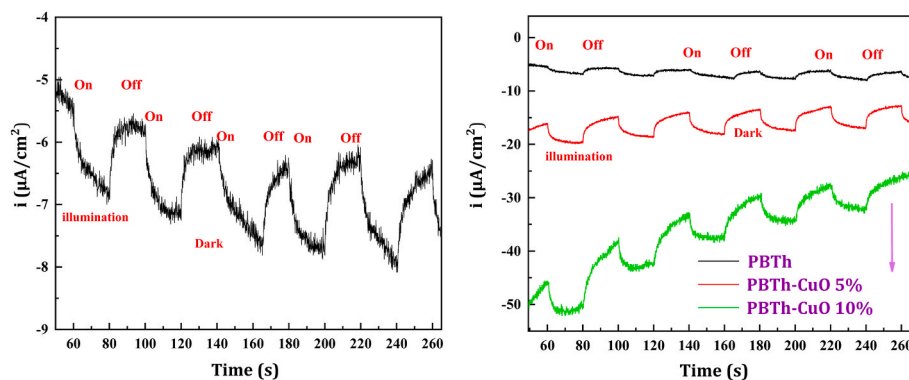


Fig. 10. Chronoamperometric photoresponse of PBTh and PBTh-CuO films in $\text{CH}_3\text{CN}/\text{LiClO}_4$ (10^{-1} M) under alternating dark and illuminated conditions at 100 mW cm^{-2} .

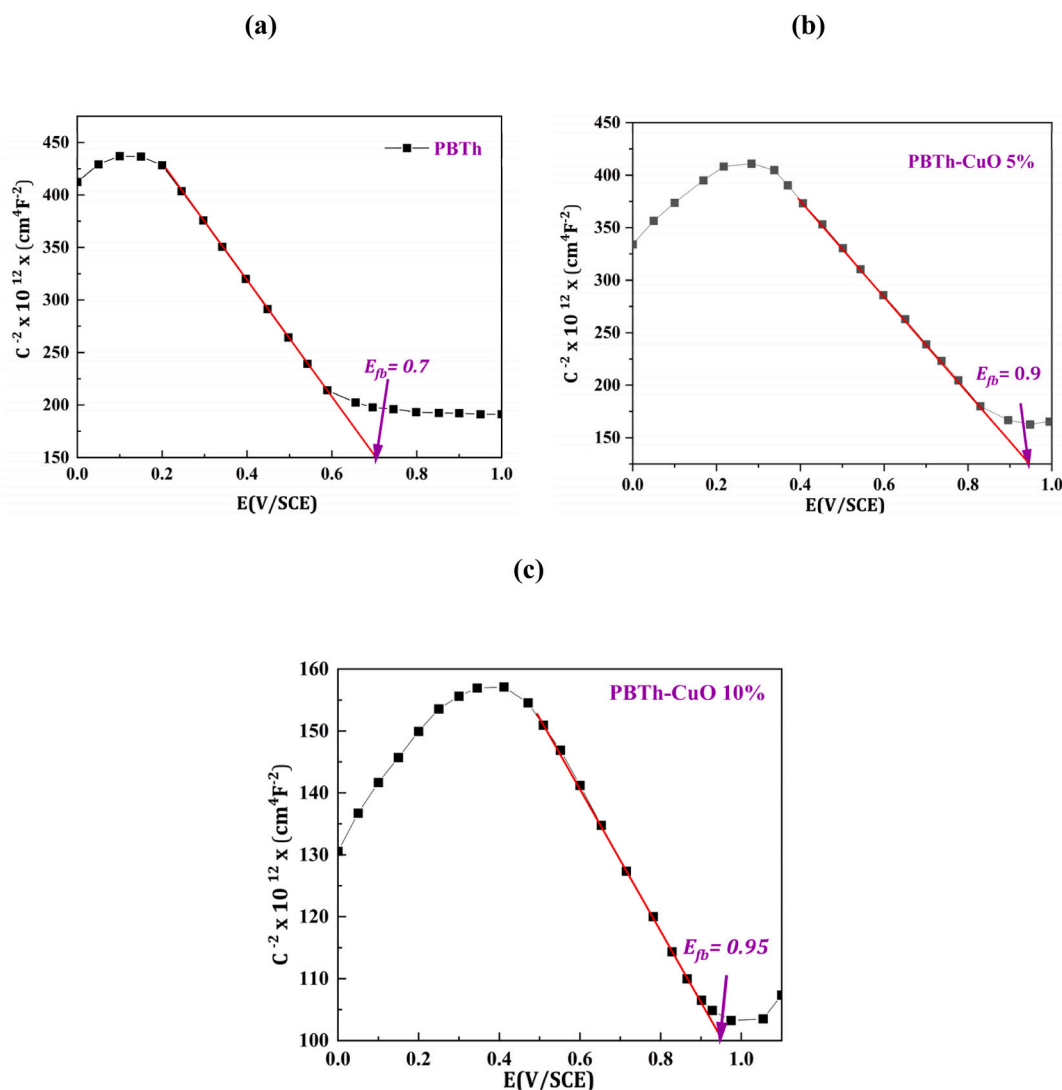


Fig. 11. Mott-Schottky plots recorded in $\text{CH}_3\text{CN}/\text{LiClO}_4$ (10^{-1} M) at 0.2 kHz for (a) PBTh/FTO, (b) PBTh-CuO/FTO (5%), and (c) PBTh-CuO/FTO (10%).

conjugated framework to a more polarized interfacial architecture. The local interfacial charges are even more revealing (Table 4). In PBTh-CuO (5%), the Cu center carries a charge of +0.91981, the O atom - 1.05909, and the nearest sulfur atom + 1.14808. In PBTh-CuO (10%), the first CuO unit gives charges of +0.93677 for Cu, - 1.03420 for O, and +1.18378 for the neighboring sulfur atom, while the second CuO unit

gives + 0.88615, - 1.06913, and +1.11720, respectively. These sulfur charges are much higher than in pristine PBTh, proving that the CuO entities generate strong localized polarization centers in the sulfur-containing segments of the chain. This point is chemically important because sulfur atoms are central to the conjugation pathway and electronic delocalization in thiophene-based polymers [27–29].

Table 2Experimental values of E_{fb} and NA, obtained.

Sample	Type	N_A (cm ⁻³)	E_{fb} (V/SCE)
PBTh	P	2.12×10^{19}	0.7
PBTh-CuO (5%)	P	9.03×10^{19}	0.89
PBTh-CuO (10%)	P	3.4×10^{20}	0.94

Their strong perturbation by CuO suggests direct electronic communication between the inorganic fragment and the conjugated polymer backbone.

The optimized geometries reinforce this conclusion. After converting the COSMO coordinates from bohr to angstrom, the nearest interacting triad in PBTh-CuO (5%) shows Cu-O, Cu-S, and O-S distances of 1.977 Å, 2.823 Å, and 1.587 Å, respectively. In PBTh-CuO (10%), the first CuO site shows 2.001 Å, 2.855 Å, and 1.566 Å, whereas the second site shows 1.969 Å, 2.797 Å, and 1.596 Å, respectively. The Cu-O bond distances remain around 2.0 Å, indicating that the oxide fragment retains its local integrity. At the same time, the relatively short Cu-S and O-S separations show that the CuO units are positioned close enough to the sulfur-rich PBTh domains to generate effective interfacial coupling. In other words, the calculations do not support a picture of isolated CuO particles embedded passively inside the Polymer. They instead support a compact hybrid interface, where short-range interactions facilitate charge redistribution.

The COSMO analysis further shows that adding CuO modifies not only the electronic levels but also the molecular surface's polar character (Fig. 12) (see Fig. 13).

The COSMO cavity area increases from 4168.26 Å² for PBTh to 4228.96 Å² for PBTh-CuO (5%) and 4291.25 Å² for PBTh-CuO (10%), while the cavity volume rises from 9341.27 bohr³ to 9515.55 bohr³ and 9779.35 bohr³, respectively. These increases are modest compared with the much larger changes in dipole moment and orbital gap. This is important because it indicates that the enhanced electronic response of the hybrid systems cannot be explained solely by size effects. Rather, it arises from the redistribution of the screening charge over the molecular surface. Consistent with this, the dielectric energy becomes more negative along the same sequence, with values of -0.0515525320 a.u., -0.0607447539 a.u., and -0.0902788428 a.u., indicating progressively stronger electrostatic stabilization in the polarizable continuum [53]. A more detailed look at the COSMO-derived surface-charge descriptors

leads to the same conclusion. The weighted average absolute surface charge density increases from 0.003993 in PBTh to 0.004253 in PBTh-CuO (5%) and 0.004604 in PBTh-CuO (10%). Simultaneously, the maximum positive surface charge density grows from +0.018217 to +0.020893 and +0.023066, while the most negative value changes slightly from -0.022409 to -0.022421 and -0.022639. The fraction of nearly neutral surface area, defined as the proportion of surface with $|\sigma| \leq 0.005$, decreases from 19.37% in PBTh to 18.41% and 17.01% in the two hybrid systems.

The strongly polar surface fraction, defined as $|\sigma| \geq 0.015$, increases from 0.00394% to 0.09109% and 0.19609%. These results indicate that incorporating CuO enriches the molecular surface with highly polarized regions, supporting improved interfacial charge separation and increased electrostatic heterogeneity. Notably, in the 5% CuO model, PBTh-CuO (5%) appears as an open-shell system with separate alpha and beta orbital manifolds and an overall spin density of 1.0000007006. This suggests that the 5% model is not a simple closed-shell perturbation but a genuinely spin-polarized interface. Nonetheless, the overall trends—such as gap narrowing, dipole enhancement, and stronger interfacial charge separation—remain consistent with those of closed-shell systems. The continuation of these trends across different electronic states reinforces the interpretation. Overall, increasing CuO concentration drives a gradual transition from a less polarized, harder polymer to a highly polar, electronically soft, and charge-separated hybrid material. Among the three systems studied, PBTh-CuO (10%) shows the most significant activation, with the smallest HOMO-LUMO gap, largest dipole moment, highest electrophilicity, and strongest interfacial charge localization. These theoretical findings align well with experimental observations, including the red shift, reduced optical gap, increased carrier density, and improved photoelectrochemical response in CuO-containing films described in the manuscript. Ultimately, the molecular modeling supports the conclusion that CuO incorporation is an effective strategy to enhance PBTh's optoelectronic and interfacial properties, making it more suitable for hybrid photovoltaic applications.

• AIM topological analysis of the PBTh-CuO interface

To gain a more rigorous understanding of the local interactions responsible for the electronic reorganization of the hybrid systems, a topological analysis of the electron density was performed within the framework of Bader's Quantum Theory of Atoms in Molecules. This

Table 3

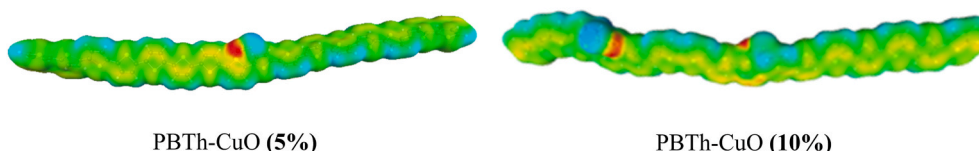
Global conceptual DFT descriptors derived from frontier-orbital energies.

Model	Ionization potential, IP (eV)	Electron affinity, EA (eV)	Hardness, η (eV)	Softness, S (eV ⁻¹)	Electrophilicity, ω (eV)
PBTh	5.10146	2.64162	1.22992	0.40653	6.09341
PBTh-CuO (5%)	4.34183	2.88954	0.72615	0.68857	9.00177
PBTh-CuO (10%)	3.96364	3.33002	0.31681	1.57823	20.98950

Table 4

Local interfacial geometric and charge descriptors extracted from the optimized structures.

Model	Interfacial atoms	q(Cu)	q(O)	q(S nearest)	Cu-O (Å)	Cu-S (Å)	O-S (Å)
PBTh-CuO (5%)	Cu73, O72, S66	+0.91981	-1.05909	+1.14808	1.977	2.823	1.587
PBTh-CuO (10%), site 1	Cu2, O1, S19	+0.93677	-1.03420	+1.18378	2.001	2.855	1.566
PBTh-CuO (10%), site 2	Cu75, O74, S68	+0.88615	-1.06913	+1.11720	1.969	2.797	1.596

**Fig. 12.** COSMO-surfaces of the PBTh-CuO systems.

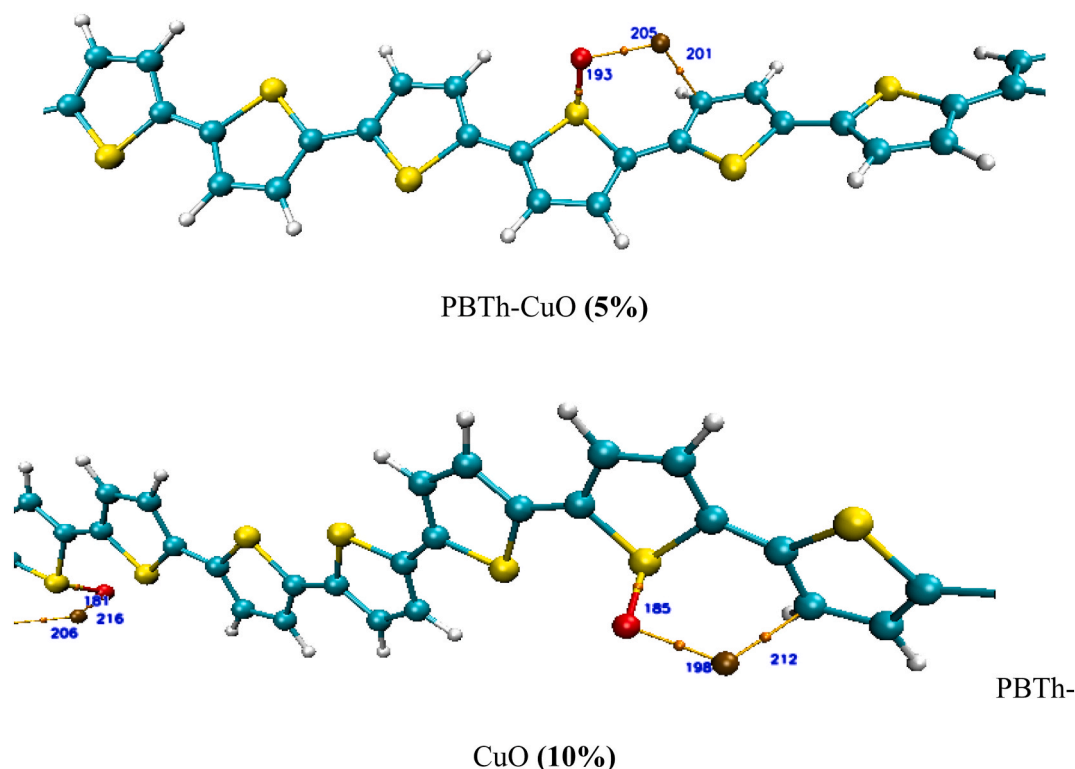


Fig. 13. AIM study of the PBTh-CuO systems.

approach is particularly relevant here because frontier orbital analysis, the strong increase in dipole moment, and the local charge redistribution already indicate that CuO is not a passive filler but an electronically active component that perturbs the PBTh backbone at short range. In the present work, the AIM analysis focused on bond-critical points (BCPs) visually identified in the interfacial region of the PBTh-CuO (5%) and PBTh-CuO (10%) models. The selected BCPs correspond to the local contacts that directly connect the CuO fragment to the sulfur-rich polymer environment and therefore provide the most chemically meaningful picture of the interface. The experimental results reported in the manuscript show that increasing the CuO content lowers the optical gap from 1.88 to 1.83 and 1.81 eV and increases the carrier density from 2.12×10^{19} to 9.03×10^{19} and $3.4 \times 10^{20} \text{ cm}^{-3}$, strongly supporting the idea that interfacial electronic coupling becomes progressively more effective with CuO incorporation.

In the PBTh-CuO (5%) model, three relevant BCPs were identified in the interfacial region (Table 5), namely CP193, CP201, and CP205. Among them, CP193 is by far the most important because it connects S66 and O72 and exhibits an electron density $\rho(r)$ of 0.20616 a.u., a positive Laplacian $\nabla^2\rho(r)$ of 0.25696 a.u., and a negative total energy density $H(r)$ of -0.20598 a.u. This combination is characteristic of a

closed-shell but strongly stabilizing interaction, meaning that the contact is not a classical shared-shell covalent bond. Yet it cannot be reduced to a weak electrostatic attraction. In chemical terms, it is more appropriate to describe this interaction as a strong polar coordination-like S...O anchor. By contrast, CP201, which corresponds to a C46...Cu73 contact, shows much lower values, with $\rho(r) = 0.05538$ a.u., $\nabla^2\rho(r) = 0.24344$ a.u., and $H(r) = -0.00543$ a.u. This indicates a much weaker interaction, although still slightly stabilizing. CP205, corresponding to O72...Cu73, is similarly weak, with $\rho(r) = 0.05507$ a.u., $\nabla^2\rho(r) = 0.44545$ a.u., and $H(r) = +0.01037$ a.u., which identifies it as a predominantly electrostatic closed-shell contact. Therefore, the PBTh-CuO (5%) interface is not controlled by a single metal-centered bond but by one dominant S...O anchoring interaction accompanied by weaker Cu-centered secondary contacts.

The interfacial topology becomes more complex in the PBTh-CuO (10%) model. In this system, six relevant BCPs were identified in the selected region, namely CP181, CP185, CP198, CP206, CP212, and CP216 (Table 6). The two strongest are CP181 and CP185, both corresponding to S...O contacts. CP181, which connects S19 and O1, shows $\rho(r) = 0.21328$ a.u., $\nabla^2\rho(r) = 0.38223$ a.u., and $H(r) = -0.21215$ a.u. CP185, which connects O74 and S68, gives $\rho(r) = 0.20347$ a.u., $\nabla^2\rho(r) = 0.21111$ a.u., and $H(r) = -0.20356$ a.u. The slightly higher electron density of CP181 compared with CP185 indicates that CP181 is the strongest interfacial anchor in the selected region. In both cases, the positive Laplacian combined with the negative $H(r)$ value clearly indicates a strong polar closed-shell interaction with significant stabilizing character. These data show that at 10% CuO loading, the interface is no longer organized around a single dominant contact but rather around two major S...O anchoring interactions, which substantially reinforce local interfacial cohesion. The four remaining BCPs in the PBTh-CuO (10%) model correspond to weaker secondary interactions. CP198, associated with O74...Cu75, exhibits $\rho(r) = 0.05638$ a.u., $\nabla^2\rho(r) = 0.45923$ a.u., and $H(r) = +0.01046$ a.u., whereas CP216, corresponding to O1...Cu2, gives $\rho(r) = 0.05148$ a.u., $\nabla^2\rho(r) = 0.40829$ a.u., and $H(r) = +0.00991$ a.u. Both interactions are therefore weak and primarily

Table 5

AIM topological parameters for the main interfacial BCPs in PBTh-CuO (5%).

CP	Connected atoms	$\rho(r)$ (a. u.)	$\nabla^2\rho(r)$ (a. u.)	$H(r)$ (a. u.)	Interpretation
CP193	S66...O72	0.20616	+0.25696	-0.20598	strong polar stabilizing interaction, main interfacial anchor
CP201	C46...Cu73	0.05538	+0.24344	-0.00543	weak secondary stabilizing contact
CP205	O72...Cu73	0.05507	+0.44545	+0.01037	weak closed-shell electrostatic contact

Table 6
AIM topological parameters for the main interfacial BCPs in PBTh–CuO (10%).

CP	Connected atoms	$\rho(r)$ (a.u.)	$\nabla^2\rho(r)$ (a.u.)	$H(r)$ (a.u.)	Interpretation
CP181	S19...O1	0.21328	+0.38223	−0.21215	strongest interfacial anchor in the selected region
CP185	O74...S68	0.20347	+0.21111	−0.20356	strong polar stabilizing anchor
CP198	O74...Cu75	0.05638	+0.45923	+0.01046	weak closed-shell electrostatic contact
CP206	C27...Cu2	0.05352	+0.23419	−0.00471	weak secondary stabilizing contact
CP212	Cu75...C64	0.05854	+0.26243	−0.00633	weak secondary stabilizing contact
CP216	O1...Cu2	0.05148	+0.40829	+0.00991	weak closed-shell electrostatic contact

electrostatic. CP206 and CP212 correspond to Cu...C contacts, with CP206 [C27...Cu2] characterized by $\rho(r) = 0.05352$ a.u., $\nabla^2\rho(r) = 0.23419$ a.u., and $H(r) = -0.00471$ a.u., and CP212 [Cu75...C64] by $\rho(r) = 0.05854$ a.u., $\nabla^2\rho(r) = 0.26243$ a.u., and $H(r) = -0.00633$ a.u. These contacts remain weak, but their slightly negative $H(r)$ values indicate a small stabilizing contribution. Taken together, these results show that the PBTh–CuO (10%) interface is best described as a cooperative multi-contact network, where the main S...O anchors are supported by weaker O...Cu and Cu...C interactions that help lock the local geometry and enhance interfacial polarization. A direct comparison between the 5% and 10% models reveals a clear concentration effect. In the 5% hybrid, the interface is dominated by a single strong S...O anchor.

In contrast, the 10% hybrid features an interface with two strong S...O anchoring interactions and four auxiliary secondary contacts. This topological enrichment is fully consistent with the stronger interfacial polarization, larger dipole moment, smaller HOMO–LUMO gap, and higher electrophilicity reported in the manuscript's molecular modeling section. It also qualitatively aligns with the experimental increase in carrier density and the reduction in the optical gap observed as the CuO content increases. Therefore, the AIM analysis not only confirms the presence of local interactions but also provides a direct atomistic explanation for the improved electronic activation of the CuO-rich hybrid material. Overall, the experimental and theoretical datasets converge on the same interpretation: increasing CuO content does not simply add an inorganic filler but progressively builds a more electronically polarized and interfacially coupled hybrid material (Table 7). This convergence among spectroscopy, semiconductor analysis, DFT descriptors, and AIM topology is one of the main strengths of the present study.

From a mechanistic perspective, the present AIM data suggest that the beneficial effect of adding CuO is not governed solely by direct Cu...S bonding. Instead, the dominant stabilization arises from strong S...O interfacial contacts, while the Cu atom contributes mainly through weaker auxiliary contacts with oxygen and carbon. This indicates that electronic communication between the oxide fragment and the PBTh chain is mediated by a more complex, cooperative interfacial arrangement than might initially be assumed. This conclusion is important because it helps explain why the CuO-rich model exhibits the most pronounced electronic softening and charge separation in the manuscript.

Table 7
Integrated summary of the main experimental and theoretical effects induced by CuO incorporation in PBTh.

Descriptor	Observed trend	Interpretation
Optical gap, Eg	1.88 → 1.83 → 1.81 eV	CuO progressively narrows the optical gap and enhances visible-light response.
Acceptor density, NA	$2.12 \times 10^{19} \rightarrow 9.03 \times 10^{19} \rightarrow 3.4 \times 10^{20} \text{ cm}^{-3}$	CuO increases carrier density and strengthens semiconductor behavior.
Roughness	10.9 → 75.7 nm	CuO strongly modifies surface organization and increases interfacial area.
DFT HOMO-LUMO gap	2.45984 → 1.45229 → 0.63362 eV	Theoretical calculations confirm progressive electronic softening.
Dipole moment	1.0937 → 6.9856 → 46.4630 D	CuO induces strong charge separation and interfacial polarization.
AIM topology	From one dominant S...O anchor at 5% to a richer multi-contact network at 10%	The interface becomes more cooperative and electronically coupled at higher CuO loading.

3.11. Comparative analysis of PBTh–CuO and previously developed conducting polymer hybrid films

Table 8 compiles recent studies in the field of conducting polymers/metal oxide hybrid films incorporating various metal oxide dopants such as CdO₂, TiO₂. While previous works mainly focused on band gap reduction, the present study provides additional advances, including a significant increase in acceptor density determined by Mott-Schottky analysis, a combined the correlation between experiments and theoretical approach (DFT, COSMO, and AIM), the identification of the stabilizing S...O interfacial interactions and a systematic evaluation of CuO loading effects (5% and 10 wt %). Therefore, the present work not only demonstrates enhanced optoelectronic properties compared with pristine PBTh but also provides a deeper understanding of the interfacial mechanisms governing the performance of PBTh–CuO hybrid films, which represents a significant advancement toward their application in photoelectrochemical and optoelectronic devices.

4. Conclusion

PBTh–CuO hybrid films were successfully synthesized by electrochemical polymerization of 2,2'-bithiophene in the presence of CuO nanoparticles on FTO substrates. Experimental characterization confirmed the successful incorporation of CuO into the PBTh matrix and revealed significant modifications in morphology, surface roughness, optical properties and semiconductor behavior. The optical band gap decreased from 1.88 eV for pristine PBTh to 1.81 eV for PBTh–CuO (10%). At the same time, Mott-Schottky analysis demonstrated the preservation of p-type conductivity accompanied by a substantial increase in carrier density, reaching $3.4 \times 10^{20} \text{ cm}^{-3}$ for PBTh–CuO (10%). Theoretical DFT calculations supported these experimental findings by showing reduced HOMO-LUMO energy gaps, enhanced electrophilicity,

Table 8

Comparing the developed hybrid films with other reported composites.

Material	Oxide content (wt %)	Optical band gap (eV)	Main improvement	Ref.
PMMA/PANI-WO ₃	3 - 10.0.	3.80-3.18	Enhanced electrical behavior and Thermal stability	[23]
PVA/ZnO- MoO ₃	25	3.5-2.6	high dielectric constant and optical properties	[24]
PVA/NaAlg-CoFe ₂ O ₄	0.5-2	4.53-3.37	AC conductivity and dielectric	[36]
PBTh/CdO ₂ /CdO	-	3.40- 2.5	Photocurrent	[55]
PBT/EVMG/TiO ₂ @SiO ₂ -g-EVMG	0.3- 2.	-	superior mechanical performance and UV resistant	[56]
PBT/TiO ₂	—	-	Photoelectrochemical behavior	[57]
PBTh-CuO	5-10	1.83-1.81	Higher acceptor density, reduced optical band gap, and enhanced interfacial polarization	This work

and increased interfacial polarization after CuO incorporation. AIM analysis indicated that strong S...O interactions play a key role in stabilizing the hybrid interface and facilitating charge redistribution. Photoelectrochemical measurements confirmed the photoelectroactivity of the prepared PBTh and CuO-PBTh films. In addition, the photocurrent intensity decreased with increasing CuO content. In summary, the combined experimental and theoretical results demonstrate that CuO effectively tailors the structural and electronic properties of PBTh, highlighting the potential of PBTh-CuO hybrid films for advanced photoelectrochemical and optoelectronic applications.

CRediT authorship contribution statement

Souhila Abaci: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing – original draft. **Leila Lamiri:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing – original draft. **Noureddine Khellaf:** Conceptualization, Formal analysis, Funding acquisition, Investigation, Validation, Visualization, Writing – original draft. **Assia Tounsi:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing – original draft. **Naima Maouche:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing – original draft. **Samia Latreche:** Investigation, Validation, Visualization, Writing – original draft. **Mabrouk Khemliche:** Investigation, Validation, Visualization. **Abdul Ahad:** Funding acquisition, Investigation, Methodology, Resources, Writing – review & editing. **Byong-Hun Jeon:** Funding acquisition, Investigation, Methodology, Resources, Validation, Visualization, Writing – review & editing. **Hyun-Jo Ahn:** Investigation, Validation, Visualization, Writing – review & editing. **Yacine Benguerba:** Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Resources, Software, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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