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Optical properties of black carbon doped CuPC composites prepared by the slurry method

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Black carbon doped Copper phthalocyanine (CuPC) composites prepared with the slurry method were turned into pellets and their FTIR, XRD and UV properties were investigated. In XRD results, an increase in peak intensities was observed depending on the amount of BC doping. The optical properties of the composites, whose crystal and chemical structure were confirmed by XRD and FTIR analyzes, were analyzed by UV analysis. The forbidden energy gaps of CuPC and BC doped CuPC samples were calculated by converting the reflectance spectra to absorbance with the Kubelka Munk function. The increase and then decrease of Eg with BC doping is due to the structural relaxation that occurs when the molecular potential energy of the BC atoms entering the CuPC lattice first increases and then the BC atoms are fully placed in the CuPC structure. From the optical band absorption spectra, Eg values of 10% BC, 80% CuPC 20% BC and 70% CuPC 30% BC samples were found as 1.65 eV, 1.69 eV, 1.61 eV and 1.62 eV, respectively. It is evaluated that the organic composites can be used for optical applications.

Keywords: *CuPC, Black Carbon, Bandgap*

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1. Introduction

Copper phthalocyanine (CuPc), ($Cu_{32}H_{16}CuN_8$) is an organic dye with good absorption in the visible region. Due to their widespread ordered structure and thermal stability, phthalocyanines have been extensively studied in a number of applications such as photodynamic therapy, artificial photosynthesis, solar energy, chemical sensors and nonlinear optics applications. Such factors, combined with the various properties of phthalocyanine molecules, have led to a growing interest in their study. The thermal, optical, and electrical properties of phthalocyanines can be varied by changing the meso atoms, central atom, or periphery of the phthalocyanine ring. Water-soluble phthalocyanine complexes are utilized in applications such as nanotechnology, semiconductor technology, sensitivity to light for photodynamic therapy, sensors, nonlinear optics, polymers, and liquid crystals due to the unique optical and redox properties of phthalocyanines. [1,2]

Optical constants are important parameters as they explain the optical behavior of materials. Photon energy and band gap energy can be determined with the help of the absorption coefficient of the materials. The absorption coefficient expresses the attenuation of the photon energy per unit thickness [3-9]

2. Experimental

CuPC was purchased from Sigma Aldrich company. CuPC and Black Carbon (BC) organics used in the study were used as they are without any purification. The chemical structure of CuPC is given in figure 1. In order to improve the optical properties of CuPC and BC composites materials were prepared by adding different proportions of black carbon (BC) to CuPC

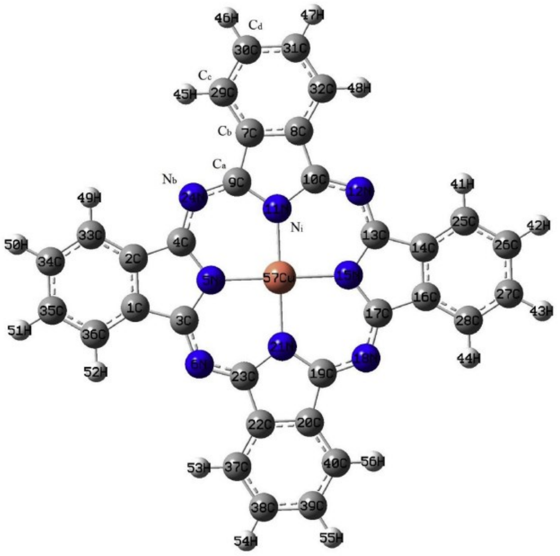


Fig. 1. Chemical structure of CuPc [2]

Initially, CuPC based composites have been prepared by slurry method and optica properties of the pellets have been investigated by reflectance spectrum characteristics.

In addition, the organic semiconductor CuPC is filled with black carbon to improve the optical properties of the pellets. For this, the total mass of the matrix material is taken at the appropriate value, CuPC: BC are homogeneously dispersed in NMP (N-methylpyrrolidone) in weight ratios of 100:0, 90:10, 80:20 and 70:30, then at 100 ºC. Composite materials were produced by drying.

3. Results and Discussion

3.1. Structural properties of CuPC and CuPC:BC composites

The information about the crystallographic structure, chemical composition, and physical properties of CuPC and CuPC:BC composites was determined by X-Ray diffraction analysis (XRD) X-Ray measurements is given in Figure 2-Figure 3. The most severe diffraction peak for CuPC was observed at 2θ = 6.99º. This peak is the main peak of CuPC and the presence of this peak confirms the crystal structure of CuPC. The XRD spectra of the composites were taken using a Bruker AXS (D8 Discover) X-ray diffractometer with CuKα (λ=1.5405 Å) radiation.

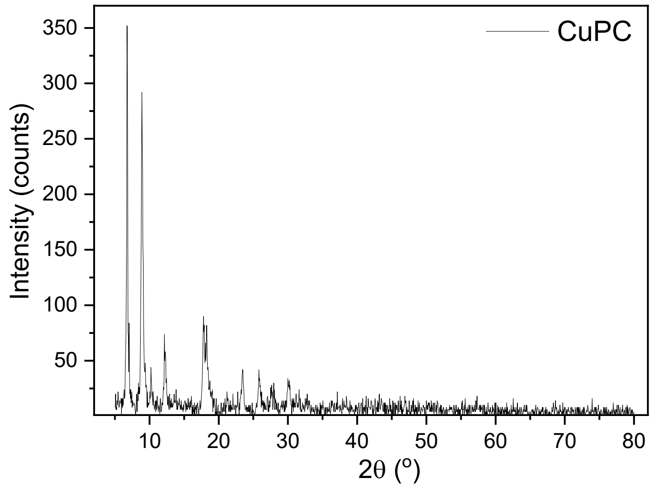


Fig.2. XRD patterns of the CuPC

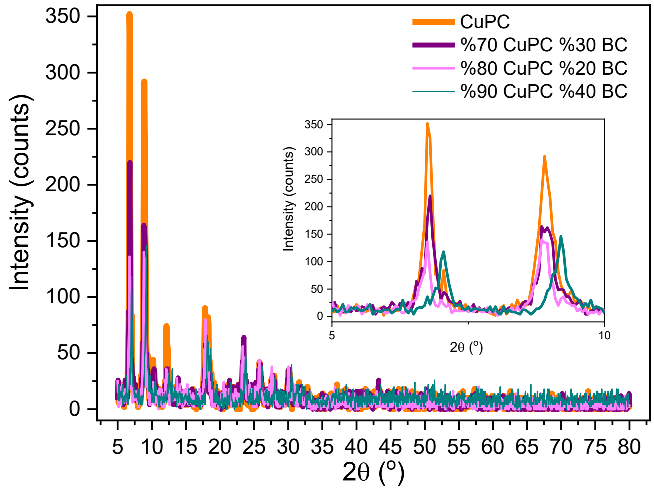


Fig.3. XRD patterns of the CuPC and CuPC:BC composites

XRD analysis of CuPC and its composites was performed. It was observed that the main peaks remained with BC doping, only the peak intensities changed. This change shows that black carbon enters the structure of CuPC. It was observed that the crystallization was not impaired by black carbon doping.

FTIR measurements of pelleted composites are performed using a Thermoscientific Attenuated Total Reflection (ATR) capped spectrophotometer. This spectroscopy was used to analyze the chemical structures of the CuPC and CuPC:BC composites. FT-IR spectra of the composites are shown in Fig. 4. The characteristics peak of C-O and C-C of the CuPC were observed at 1500-1700 cm^{-1} [10-15].

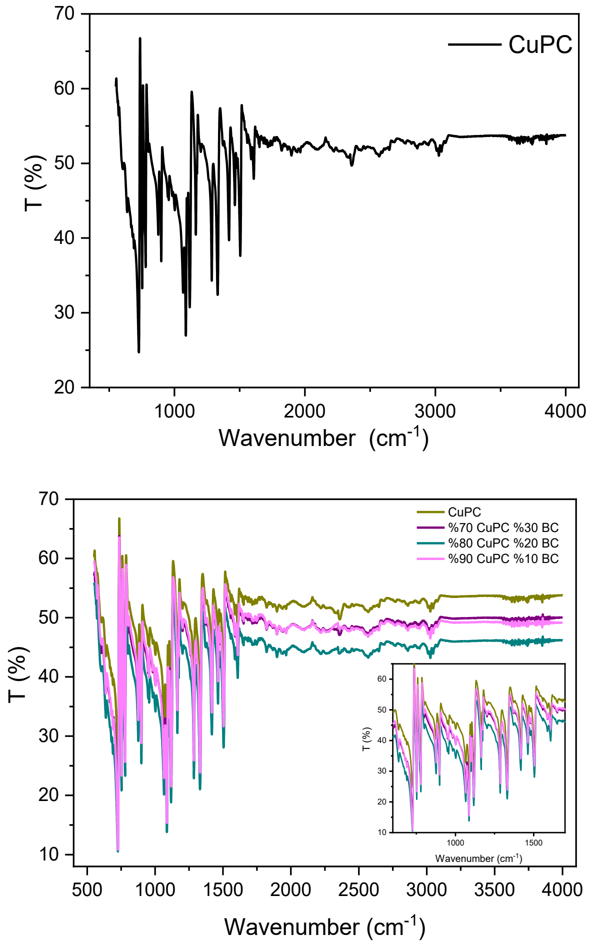


Fig.4. FT-IR spectra of the CuPC and CuPC:BC composites

3.2. Optical Spectroscopy Results of CuPC organic semiconductor and its composites

The optical properties of CuPC organic semiconductor were analyzed by reflection spectra. Double beam SHIMADZU UV 3600 spectrophotometer was used to investigate optical properties of pellets. Reflection spectra of CuPC composites doped with BC are given in Figure 6. As can be seen from Fig. 6. the reflectance curve of CuPC decreases with decreasing wavelength and shows a reflection limit of around 550 nm. This limit changes with BC doping. The reflectance value of CuPC decreases with the BC additive and shows the lowest value at the highest additive amount. With BC doping, the reflectance value of CuPC decreases regularly. This shows that the BC additive enters the structure of CuPC. To calculate the bandgap energy of CuPC and BC doped CuPC composites the reflectance spectra of the samples were converted to absorbance with the Kubelka-Munk function;

$$F(R) = \frac{(1-R)^2}{2R} \quad (1)$$

where R reflectance. and is F (R) is the Kubelka-Munk function. With the help of the Kubelka-Munk function, the relationship between the optical band gap can be expressed by the Tauc equation.

$$F\,(R)h\nu = A(h\nu - Eg)^n \quad (2)$$

in this equation, A is an energy independent constant, υ is the photon frequency, h is the Planck constant, Eg is the optical band gap, and n is the type of optical transitions.
It is n=1/2 for direct transition, n=2 for indirect transition, n=3/2 for forbidden direct transition, and n=3 for forbidden indirect transition [10-16].

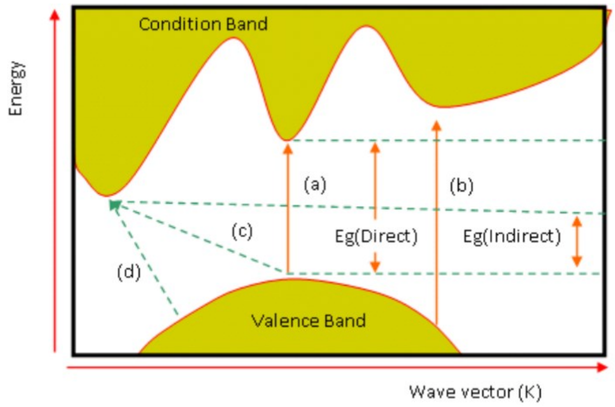


Fig.5. The optical transitions (a) Allowed direct, (b) Forbidden direct; (c) Allowed indirect, (d) Forbidden indirect [4-7]

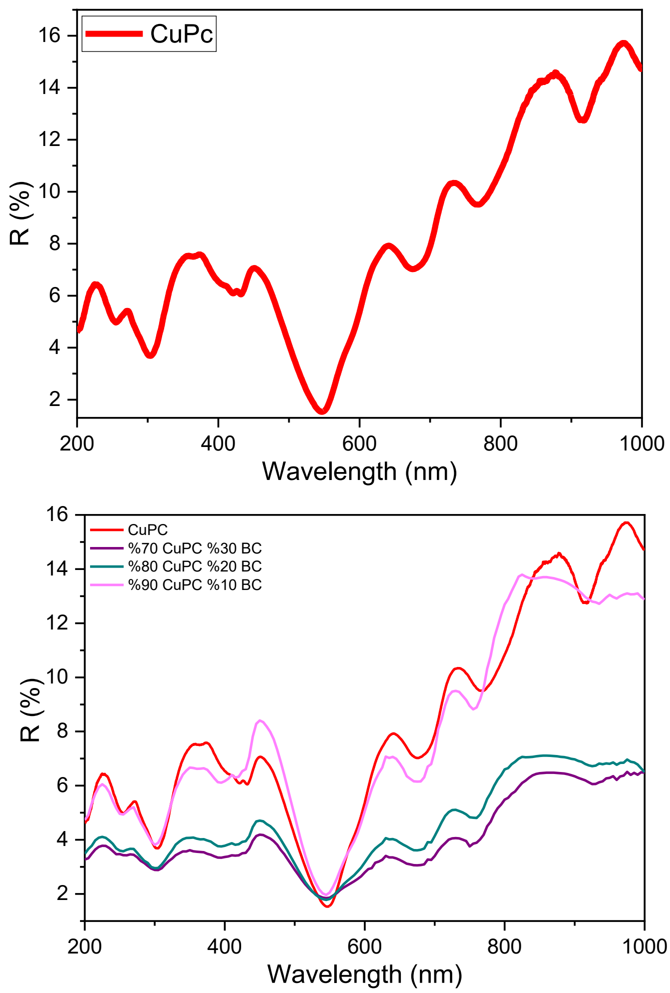


Fig.6. Reflection spectra of CuPC and its composites

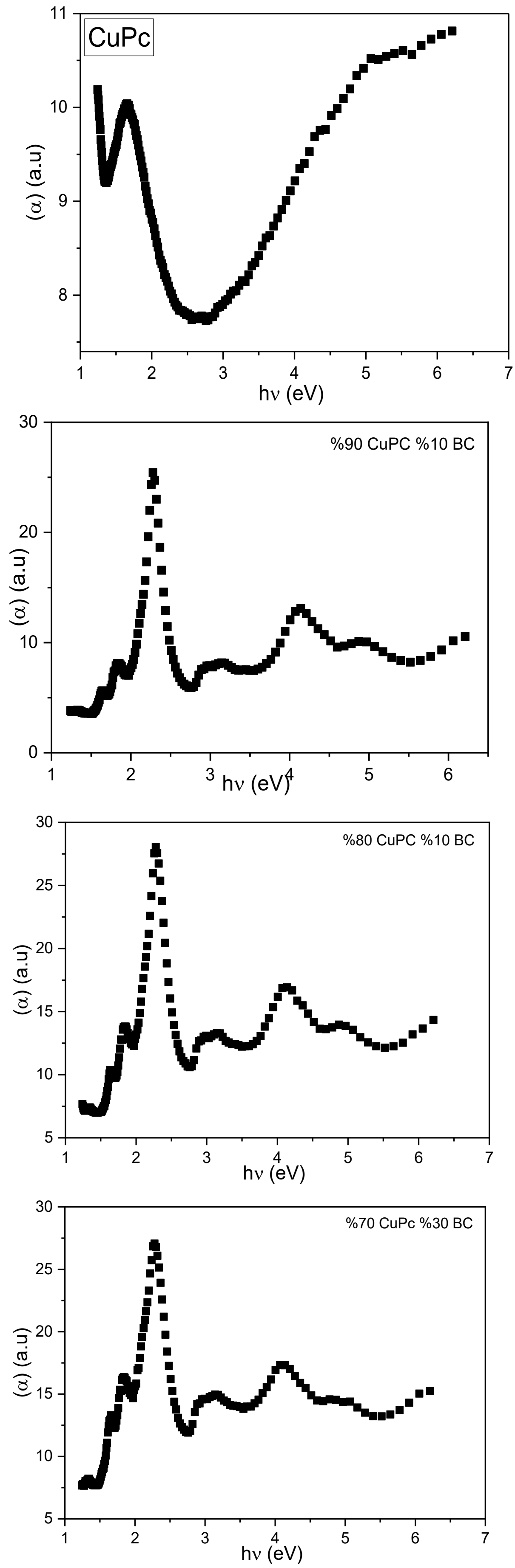
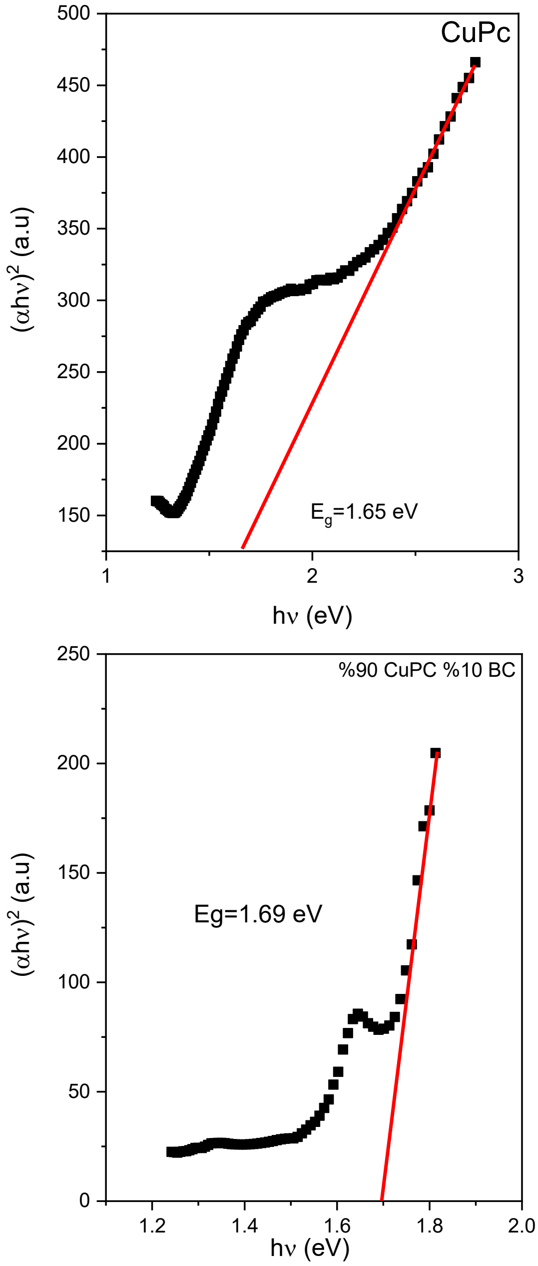


Fig.7. Absorbance spectra of CuPC organic semiconductor

As seen in Figure 7, absorbance spectra change with BC doping. The absorbance of CuPC shows a peak around 1.5 eV. The formation of this peak is due to electron transfer from the valence band to the conduction band of CuPC. With BC doping, new peaks around 2.30 eV are formed in the structure of CuPC:BC composites. These peaks are due to the molecular interaction of BC and CuPC atoms. The absorbance of CuPC:BC composites increases with increasing photon energy. The composites show a peak around 1.80. The presence of this peak is due to the transition of electrons from the valence band to the conduction band in CuPC:BC composites.

To calculate the bandgap energy of the CuPC:BC composites, graphs $(\alpha h\nu)^2$ –hν of the composites of the samples were drawn and given in Fig. 8.



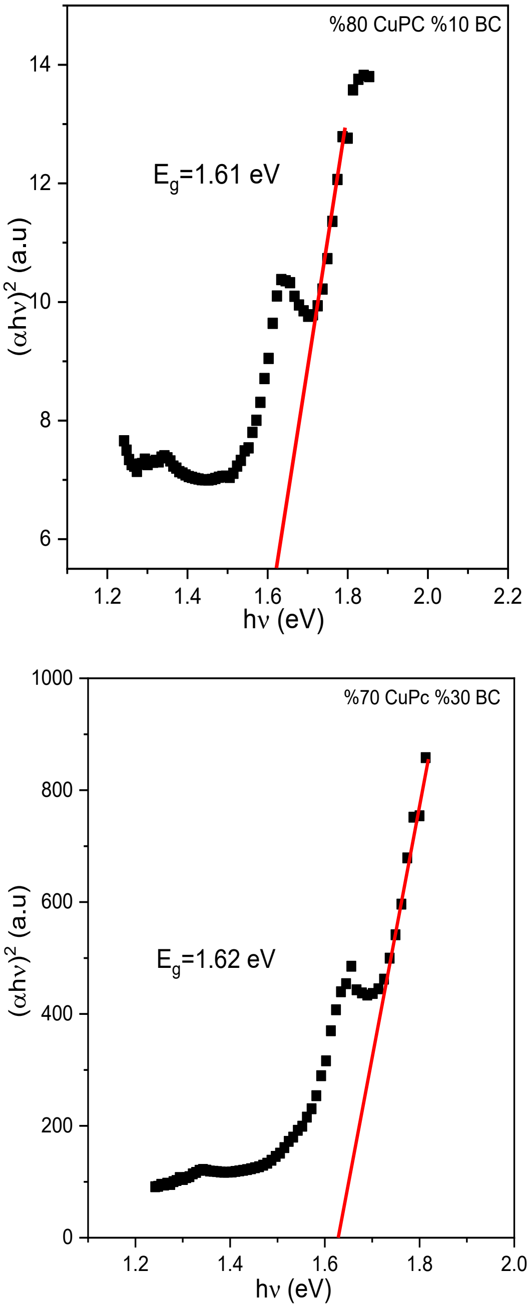


Fig. 8. (αhν)2 –hν spectra of CuPC and its composites

Eg values of 90% CuPC 10% BC, 80% CuPC 20% BC and 70% CuPC 30% BC samples were calculated as 1.65 eV, 1.69 eV, 1.61 eV and 1.62 eV, respectively. The Eg value of CuPC is in agreement with the studies in the literature [17-20].

4. Conclusion

As a result, it was observed that crystallization was not impaired by black carbon doping in XRD analysis. Molecular bond characterization was made by FTIR analysis of pure CuPc and Black carbon doped CuPC composites in pellet form and the functional groups and bonds in the structure of organic composites were determined. C-O and C-C characteristic peak values of CuPC were observed in all composites. It was observed that the absorbance spectra obtained from the reflectance curves of 90% CuPC 10% BC, 80% CuPC 20% BC, 70% CuPC 30% BC doped composite pellets changed with BC doping. Their composites showed the first peak value at an average of 1.80 eV. This peak indicates that electrons move from the valence band to the conduction band in CuPC:BC composites.
Finally, forbidden energy ranges were calculated from the graph of $\alpha h\nu^2$ versus hν with the help of absorbance curves of organic pellets. The Eg value of CuPC is in agreement with the studies in the literature. It is due to the structural relaxation that occurs when the molecular potential energy of the BC atoms entering the CuPC lattice first increases and then decreases with the BC doping, and then the BC atoms are fully placed in the CuPC structure.

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