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Copper phthalocyanine nanocrystals embedded into polymer host: Preparation and structural characterization

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Abstract Copper phthalocyanine Cu-Pc nanocrystals (NCs) dispersed in thin films of polystyrene (PS) matrix were fabricated by spin coating method at room temperature under normal atmospheric pressure on glass substrate. The films have been characterized by several characterization techniques. X-ray diffraction diagrams confirmed the incorporation of Cu-Pc nanocrystals in polystyrene matrix and determined the structure of the CuPc-NCs. Raman and FT-IR spectra of PS/Cu-Pc nanocomposite were also recorded. The observed Raman and FT-IR bands were assigned to phonon modes on the basis of their symmetry. The optical absorption spectra of PS/Cu-Pc nanocomposite films showed three absorption bands, one band positioned at 718 nm, another one located at 611 nm with a shoulder at 645 nm known as the Q-band, and the B-band was located at 336 nm. Discussion of the obtained results and their comparison with the previous data were also given.

1. Introduction

In the last years, considerable research efforts have been devoted to the fabrication and characterization of various organic semiconducting thin films. Metal phthalocyanine is one of the most important organic compounds which can be applied in electro-optic devices, photoconducting agents (Law, 1993), photovoltaic cell elements (Anthopoulos and Shafai, 2003), nonlinear optics (De la Torre et al., 1998), electrocatalysis (Bottger et al., 1997), and other photoelectronic devices. Many researchers have studied various metal substituted phthalocyanine (Janczak and Kubiak, 2001, 2007, 2009; Janczak and Idemori, 2003; Janczak, 2010). Among the metal substituted phthalocyanine, copper II phthalocyanine (Cu-Pc) was found to have superior properties (Auerhammer et al., 2002). It is well known that copper-phthalocyanine (Cu-Pc) is an organic semiconductor (Hanack and Lang, 1995). They are chemically and thermally very stable (Prince et al., 2001); most of them can easily form ordered thin films. Cu-Pc has a lower mobility of about 10^{-4} cm^2/V s compared to the conjugated oligomers such as α-hexathienylene (α-6T) with a mobility of approximately 10^{-2} cm^2/V s. However, recently, it was reported that high mobility of Cu-Pc thin films could be achieved by employing an elevated substrate heating temperature, which directly affects the crystal structure and morphology of the thin films; such studies have indicated that the orientation of the grains depends on the substrates, the deposition technique, and the heat treatment temperature.

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Semiconductor quantum dots (QDs) embedded in polymer films, so called ‘‘nanocomposite’’ film, have attracted a large amount of attention because they exhibit many useful optical and electrical properties (Subbiah and Mokaya, 2003). Many techniques like sol–gel, vacuum evaporation, solvent casting, spin coating, and Langmuir–Blodgett (LB) methods have been established to prepare nanocomposite thin films.

We report in this work the synthesis, the structural characterization, and optical properties of CuPc-NCs dispersed into a transparent polystyrene matrix by colloidal solution and deposited on a glass substrate using spin coating technique. We also report Raman and FT-IR spectra of Cu-Pc molecules dispersed in the polymer matrix to provide information about stretching and bending motions of the atoms in this molecule.

2. Experimental

Cu-Pc nanoparticles dispersed polymer system was prepared by colloidal solution. A host solution was prepared by dissolving amorphous polymer polystyrene (PS) in chloroform ($CHCl_3$) with a concentration of 0.020 g/ml. This solution was stirred at 50 °C for 2 h. A guest solution was prepared with 0.500 g of mechanically crushed Cu-Pc powder (obtained from Fluka) dispersed in 10 ml of chloroform. Both solutions were mixed and homogenized by magnetic agitation for 24 h. Glass slab substrates were degreased and rinsed thoroughly with distilled water before deposition of few CuPc-NCs droplets dispersed in PS solution. Films were deposited by spin coating technique. The rotation speed ranged from 2000 to 3000 rpm. All experiments were performed at room temperature.

X-ray diffraction patterns of the CuPc-NCs dispersed PS films were measured using an X-ray diffractometer model D8 Advance Bruker with Ni filtered Cu radiation generated at 40 kV and 30 mA (CuK_α = 1.542 A) as the X-ray source. Raman spectra were recorded in a back scattering configuration with a Jobbin Yvon micro Raman spectrometer coupled to a DX40 Olympus microscope. The absorption spectrum of the thin films was recorded using a UV–visible/NIR spectrophotometer (Perking Elmer, model Lambda 19) in the range of 290–800 nm. The FT-IR spectra of PS/Cu-Pc nanocomposite film samples were studied using the InfraLUM FT-02 Fourier-Transform Spectrometer. The spectra were recorded in the spectral range from 400 to 1500 cm^{-1}.

3. Results and discussion

The molecular structure of Cu-Pc has a square-planar configuration with metal ion in its centre as shown in Fig. 1. The figure also shows the atom labelling scheme of the molecule. The molecule has an overall symmetry of D_{4h}, which can be inferred from the figure. Moreover, recent DFT calculations also resulted in the idealized D_{4h} point group symmetry for this molecule (Li et al., 2005).

3.1. Optical absorption analysis

The B (Soret) band at 336 nm was observed in UV absorption region (Fig. 2). The other well known Pc molecule bands, namely the Q-bands appear at 611 nm (broad), 645 nm (shoulder) and 718 nm in the visible region. Comparing the obtained results to those of literature, we note that the Q-band was red shifted. The absorbance of the Q-bands in the solid film broadened and was red shift due to strong aggregations between neighbouring molecules. Four general types of Pc arrangement have been observed in spin-coated films and these are cofacial (C: face to face), herringbone (H), edge-to-edge (E) and isolated (I). Each of the four basic types of arrangement displays a characteristic visible absorption spectrum determined by the mature and extent of the intermolecular excitation coupling between the aromatic cores of neighbouring Pc molecules. A herringbone arrangement leads to strong Davydov splitting giving bands at both higher and lower wavelengths relative to the solution phase Q-band (Hassan et al., 2000). The intensity of the higher-energy maximum peak is smaller than the lower-energy peak (Fig. 2). This behaviour represents the typical features of the β-phase of Cu-Pc (Jungyoon et al., 2003; Yang et al., 2005). The origin of electronic absorption bands of the Cu-Pc can be explained on the basis of $\pi \rightarrow \pi^*$ excitation from HOMO, a_{1u} and a_{2u}, to LUMO, $2e_g$. Although metal d_{x2-y2} orbital of b_{1g} symmetry is half filled and lies between the HOMO, a_{1u}, and LUMO orbitals of the Pc ring, yet the d_{x2-y2} orbital does not take part in electronic transitions since transition from d_{x2-y2} to LUMO is forbidden. However, metal d-orbital can take part in non-radiative processes such as electrical conductivity. The broadening of the absorption bands is caused by the molecules aggregation (Bajema et al., 1971). Observation of more than one band in Q spectral region is due to the Davydov splitting (Karan et al., 2007). Therefore, bands’ positions in Q region depend on the interactions between the transition dipole moments and relative orientations from adjacent molecules (Karan and Mallik, 2007).

3.2. X-ray diffraction analysis

Fig. 3 shows the X-ray diffraction patterns for PS/Cu-Pc nanocomposite thin films deposited on a glass substrate. Note that Cu-Pc has different crystal phases: α-, β-, and χ-phases (Pirriera1 et al., 2009; Abkowitz and Sharp, 1968). The α-phase is

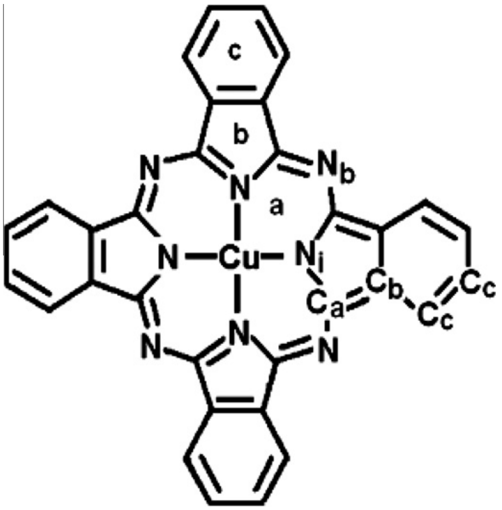

Figure 1 Molecular structure and atomic notation of Cu-Pc molecule.

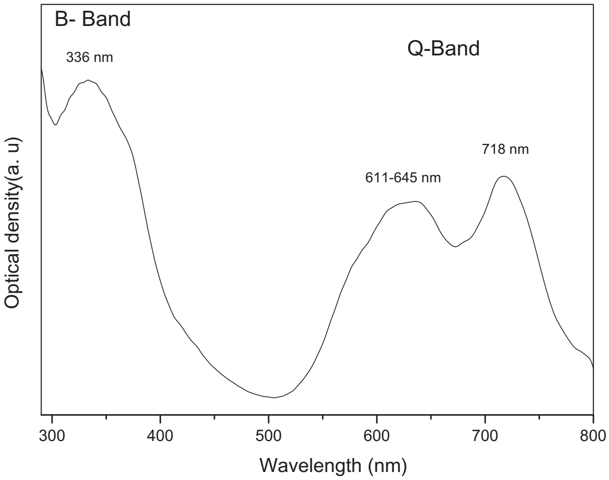

Figure 2 Absorption spectrum of Cu-Pc/PS thin films.

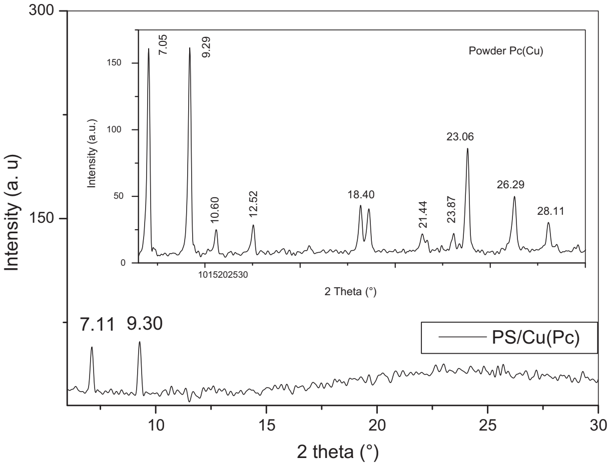

Figure 3 X-ray diffraction patterns of Cu-Pc/PS thin films.

metastable and undergoes a polymorphic transition to the stable β-phase when heated and when stored in certain organic solvents. The structure of the α-phase is known to be an orthorhombic crystal having unit cell dimensions: a = 25.92 Å, b = 3.97 Å and c = 23.9 Å. The structure of β-phase is a monoclinic crystal with the following unit cell dimensions: a = 14.68 Å, b = 4.98 Å, c = 19.6 Å and γ = 121.5°. The XRD patterns of PS/Cu-Pc guest host films exhibit sharp peaks at 2θ equal to: 7.11° and 9.30° which correspond respectively to the (100) and ($\bar{1}$02) Cu-Pc β-phases diffraction planes (Jungyoon et al., 2003). The observation of two peaks indicates that the thin films consist of randomly oriented CuPc-crystallites, as there is no preferential orientation of the crystals. The crystal sizes of dispersed CuPc-NCs in polystyrene matrix were estimated using the Scherrer formula (Baruchel et al., 1994):

$$D = \frac{0.9\lambda}{\Delta(2\theta)\cos 2\theta} \tag{1}$$

where λ is the X-ray wavelength, Δ is the full width at half maximum of the diffraction peak and θ is the peak angular position.

The calculated average crystal grain size is summarized in Table 1. The average particle size value was about 31 nm justifying hence the nanometric size of the particles.

3.3. FT-IR and Raman analyses

Figs. 4 and 5 represent respectively FT-IR and Raman spectra of Cu-Pc nanocrystals dispersed in the polymer matrix and deposited on glass substrates measured at room temperature

Table 1 Cu-Pc NCs radius calculation using the Scherrer formula (Eq. (1)).

2θ (°)	Diffraction planes	Δθ (°) full width at half maximum (FWHM)	Radius size (nm) (R)
7.11	(100)	0.132	31.51
9.30	($\bar{1}$02)	0.133	31.32

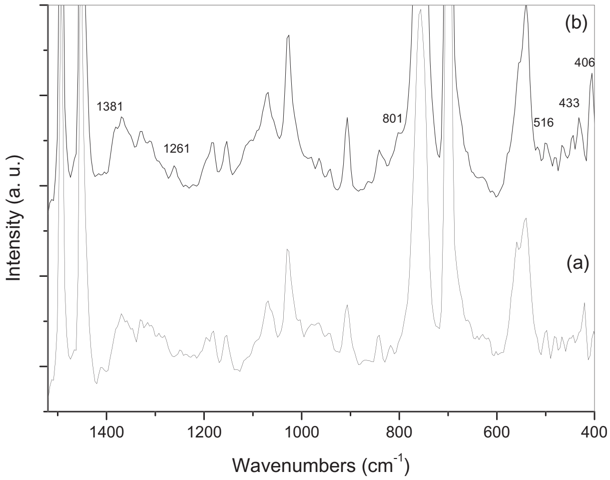

Figure 4 FT-IR spectra of (a) PS pure and (b) Cu-Pc/PS thin films.

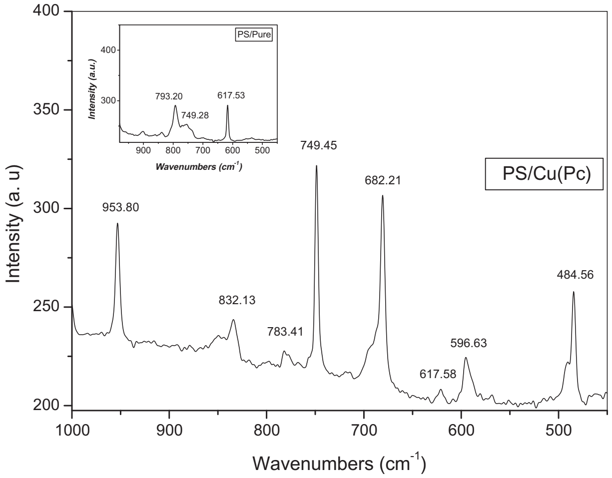

Figure 5 Raman spectra of Cu-Pc/PS thin films.

Table 2 Position, symmetry of vibration and assignment of observed FT-IR and Raman bands of PS/Cu-Pc nanocomposite.

Band (cm^{-1})			Symmetry and assignment [b,c]
Powder [a]	In polystyrene		
	FT-IR	Raman	
406	406		$E_g(E)$; $\rho_w(C_b–C_c–H)_{as}$
433	433		$A_{2u}(A_2)$; $\rho_w(C_b–C_c–H)_s$
480		484	$E_g(E)$; $[\rho_w(C_b–C_b), \rho_w(C_c–C_c)]_{as} + \rho_w(C_a–N_b)$
515	516		$B_{2g}(B_2)$; $\rho_\tau(c\ ring) + \rho_\tau(C_a–N_i–C_a)$
598		596	E_g; $(C_a–C_b) + \delta(C_c–H)$
689		682	$E_g(E)$; $\rho_w(C_a–N_i–C_a) + \rho_w(C_c–H)$
780		783	B_{1g}; $(C_b–C_c) + (C_a–N_i)_s + \nu[(C_a–N_i–C_a) + (C_b–C_a–N_b)]$
801	801		$E_u(E)$; $\eta(N_i–N_i) + [\nu(b\ ring, cring)]_{as} + \rho_\tau(C_c–C_c)_{as}$
864		832	$E_g(E)$; $\rho_w(C_c–H)_{as}$
955		953	$E_g(E)$; $\rho_w(C_c–H)$
1262	1261		$A_{2g}(A_2)$; $\rho_\tau(C_b–C_b)$
1385	1381		$A_{1g}(A_1)$; $\nu(Cu–N_i)_s + \delta(C_a–N_b–C_a)$

The subscript (s) and (as) represent the symmetric and asymmetric modes, respectively.

[a] Powder bands are based on references (Szybowicz et al., 2006; Su et al., 2005).

[b] Assignments are based on references (Janczak and Idemori, 2003; Prince et al., 2001; Tackley et al., 2000; Yang et al., 2005).

[c] The ν, δ, ρ and η denote stretching, in-plane bending, out-of-plane bending and heaving motion, respectively.

(RT). Large number of FT-IR and Raman bands appears in the spectra. In order to simplify the assignment of observed bands, we assume that the composite film consists of Cu-Pc molecules since Cu-Pc crystals are molecular solids with two molecules of Cu-Pc per unit cell. The molecule has 57 atoms and, therefore, 165 normal modes of vibrations. These vibrations can be broadly divided into two groups: one consisting of in-plane vibrations of symmetry A_{1g}, A_{2g}, B_{1g}, B_{2g}, E_u and other consisting of out-of-plane vibrations of A_{1u}, A_{2u}, B_{1u}, B_{2u}, E_g symmetry. Out of these, only the vibrational modes of symmetry species A_{2u} and E_u show IR activity. Therefore, its IR spectra consist of a few intense out-of-plane bands of the A_{2u} symmetry and in-plane bands of the E_u symmetry. We have utilized a simpler, qualitative approach to interpret the FT-IR and Raman data of Cu-Pc on the basis of recently reported normal coordinate calculations (Li et al., 2005; Tackley et al., 2000). These calculations along with the reported resonance Raman and IR studies of these complexes (Maggioni et al., 2005; El-Nahass et al., 2005; Su et al., 2005; Aroca and Thedchanamoorthy, 1995) simplified considerably the assignment of IR and Raman bands of Cu-Pc. Most of the bands are straight forward to assign, since their positions are close to the reported values (Li et al., 2005; Maggioni et al., 2005). It is expected that the mode compositions obtained in this study should be reasonably accurate and the major contributing motions should be correct. The observed FT-IR and Raman bands and their assignments are listed in Table 2. The bands of Cu-Pc powder of FT-IR and Raman are assigned on the basis of the references (Singh et al., 2008a,b).

The IR bands in 700–800 cm^{-1} region of the spectra of Pcs are often used to identify different polymorphs, α-, β-, and χ-, etc., because of their sensitivity to the crystal packing arrangements in thin films (Robinet et al., 1989; Szybowicz et al., 2006). In the spectrum of PS/Cu-Pc thin films, it was observed that the band at 783 cm^{-1} has been assigned to the $(C_b–C_c)$ and $(C_a–N_i)_s$ stretching motion and $(C_a–N_i–C_a)$ and $(C_b–C_a–N_b)$ in-plane bending (Li et al., 2005). We note that the molecules of NCs-CuPc are dispersed in PS matrix consisting of in-plane vibrations of symmetry A_{1g}, B_{1g}, B_{2g}. In the case of B_{1g} modes, the atomic shift is symmetric and relative to the two-fold axis C_2' through the central copper atom Cu, and the benzene rings. In the case of B_{2g} modes, the atoms are shifted symmetrically relative to the C_2' axis through the N_i and N_b atoms (Fig. 4) (Basova and Kolesov, 2000). The Raman spectra of PS/Cu-Pc in 400–1500 cm^{-1} region are shown in Fig. 5, we find that the vibrations are mainly composed of the dihedral plane deformations involving the aromatic CH groups and ring radial vibrations of the isoindole moieties (Giancane et al., 2011). We observe C–H bending modes at 596, 682, 832 and 953 cm^{-1}. The vibrational symmetry of this mode under D_{4h} group is E_g.

4. Conclusions

The preparation of CuPc-NCs using colloidal solution and their well incorporation in PS matrix is reported and supported by complementary investigations. Structural characterization, using X-ray diffraction indicates the incorporation of Cu-Pc crystals in the host matrix with their preferential orientation. Raman scattering spectra, UV–VIS absorption, and Infrared reflectivity measurements (FT-IR) allowed us to determine the complete set of vibration modes of CuPc-NC crystals dispersed in polymer matrix. Raman spectra showed that the molecules of Cu-Pc dispersed in PS matrix consist of out-of-plane vibrations, FT-IR spectra showed that the molecules of Cu-Pc dispersed in PS matrix have two types of vibration: one consisting of in-plane vibrations and other consisting of out-of-plane vibrations.

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