

Structural Modifications and Extended Spectral Response of CeO₂/CoPc Nanocomposites for Potential Applications

Kurup Kuniyil Babitha

Department of Physics, Nanoscience Research Centre (NSRC), Nirmala College, Muvattupuzha 686 661, Kerala, India

Department of Physics, Newman College, Thodupuzha 685 584, Kerala, India

Karathan Parakkandi Priyanka, Oppuveettunkal Paily Jaseentha, and Thomas Varghese*

Department of Physics, Nanoscience Research Centre (NSRC), Nirmala College, Muvattupuzha 686 661, Kerala, India

Aikkara Sreedevi

Department of Applied Science and Humanities, Thejus Engineering College, Thrissur 680584, Kerala, India

CeO₂/CoPc nanocomposites were synthesized by simple chemical method. Thermal behavior of these nanocomposites was studied by thermogravimetric and differential thermal analysis. The as-synthesized nanocomposite samples were characterized by various techniques. A decrease in band-gap energy together with an improved absorption intensity of the composite material confirms the role of the cobalt phthalocyanine in the absorption properties of CeO₂/CoPc composite. This study confirms structural modifications and extended spectral response of the synthesized CeO₂/CoPc nanocomposites. The results demonstrate that CeO₂/CoPc nanocomposite samples are promising materials for organic light-emitting diodes, solar cells, and optoelectronic devices.

Keywords: CeO₂/CoPc nanocomposites; structural properties; UV-visible absorption; photoluminescence

Introduction

Recently, the synthesis of organic–inorganic nanocomposite materials has attracted substantial attention from many of the researchers because of the potential of combining distinct physical properties of organic and inorganic components.¹ The organic material shows high thermal and chemical properties, nontoxicity, semiconductivity, and interesting optical properties.² A phthalocyanine containing one or two metal ions is called a metal phthalocyanine (M-Pc). The function of M-Pcs is almost universally based on electron-transfer reactions because of the 18 π electron-conjugated ring system found in their molecular structure. The most common polymorphic phases of phthalocyanines are α and β . Due to the semiconducting properties, M-Pcs are promising candidates for photovoltaic devices, photodetectors, organic transistors, organic electroluminescence devices, and sensors.³ Inorganic metal nanoparticles provide the potential for high carrier mobilities, band-gap tunability, a range of magnetic and dielectric properties,

and thermal and mechanical stability. There is a great deal of interest in exploring alternative luminescent materials for solid-state light applications, such as quantum dots (QDs) and inorganic–organic nanocomposites.⁴

In this study, we are focusing toward synthesis and characterization of cerium oxide/cobalt phthalocyanine (CeO₂/CoPc) nanocomposites. The knowledge about the surface morphology, optical absorption, and emission properties is essential for understanding the potential applications of this composite. CeO₂ was chosen because it is an important rare-earth semiconducting metal oxide and has interesting optical properties. CeO₂ nanostructures doping with various materials have drawn much interest because of their magnetically induced optical properties.^{5,6} Very few studies have focused on dopant-assisted enhancement of physical properties of CeO₂ nanostructures. To date, no studies have been reported on the structural and optical properties of CeO₂/CoPc nanocomposites. The aim of this work was to synthesis and study structural, thermal, optical, and photoluminescence (PL) properties of CeO₂/CoPc nanocomposites for potential applications.

*nanoncm@gmail.com

Experimental

Cerium oxide (CeO₂) nanoparticles produced by chemical precipitation method, cobalt phthalocyanine (CoPc) (Sigma-Aldrich Chemicals, Mumbai, India), dimethyl formamide, dimethyl sulphoxide, and ethanol (Merck, Whitehouse Station, NJ) were used for the synthesis procedures for the nanocomposite. Distilled water was used in all synthesis processes.

The composites were prepared using a standard method by coating CeO₂ nanoparticles with cobalt phthalocyanine. CoPc (1 wt%) dissolved in a solvent mixture containing 50% dimethyl sulphoxide, 30% dimethyl formamide, and 20% ethanol, at 60°C. CeO₂ nanoparticles prepared by precipitation method were described elsewhere.⁷ The required amount of synthesized CeO₂ was gradually added to this solution under constant stirring and heating, resulting in a suspension with homogeneous appearance. After complete solvent evaporation, the composite was dried at 100°C in a hot air oven for 15–20 h. A part of this sample was calcined at 350°C in a muffle furnace. The as-prepared CeO₂/CoPc nanocomposite sample and the sample calcined at 350°C are denoted as S1 and S2, respectively.

The thermal behavior of the sample was analyzed by thermogravimetric analyzer (TGA) and differential thermal analyzer (DTA) using Perkin Elmer STA 6000, at a heating rate of 10°C/min from room temperature to 730°C. The structural characteristics of the synthesized nanocomposite have been studied by X-ray powder diffraction (XRD) using Bruker D8 Advance X-ray diffractometer ($\lambda = 1.5406$ Å, step size = 0.020°, dwell time 65.6 s, 40 kV, and 35 mA) with Cu-K α radiation in 2 θ range from 5 to 80°. The particle size was estimated from the Scherrer's equation,⁸ given by $t = 0.9 \lambda / \beta \cos \theta$, with $\beta = \beta_{\text{obs}} - \beta_{\text{std}}$, where λ is the X-ray wavelength, β_{obs} the observed full width at half maximum (FWHM) of the peak, β_{std} the instrumental contribution to FWHM, and θ the Bragg's angle. Chemical sample analyses were performed by energy-dispersive X-ray spectroscopy using JEOL MODEL JED-2300 equipment with an accelerating voltage of 30 kV. For high-resolution transmission electron microscopic (HRTEM) studies, the CeO₂/CoPc powder was dispersed in ethanol using an ultrasonic bath. A drop of the suspension was placed on a copper grid coated with carbon film. After drying, the copper grid containing the nanoparticles was placed on a holder for the imaging process. TEM images of nanocrystalline CeO₂/CoPc powder samples were taken from a JEOL/JEM 2100 (Source: LaB6 and voltage: 200 kV). Fourier transform infrared (FTIR) spectra of the samples were recorded by Thermo Nicolet, Avatar

370 instrument in the range 4000–400/cm. Raman spectra were collected by Raman spectrometer, Bruker RFS-27, using Nd-YAG laser of wavelength $\lambda = 1064$ nm, operating at 4000–50/cm. Shimadzu 2600 UV-visible spectrophotometer was used to record the optical absorption spectra of the samples in a wavelength range of 100–900 nm. The absorption coefficient α is related to the photon energy $h\nu$ by the relation, $\alpha = \alpha_0(h\nu - E_g)^{1/2}$, where E_g is the optical band gap. Photoluminescence (PL) spectra were measured at room temperature using a Fluoromax-3 spectrophotometer having a 20-kW continuous powered high-pressure Xe lamp as the excitation source and an R928 photomultiplier as the photo-detector. The emission spectra were recorded in the range 350–650 nm at an excitation wavelength of 330 nm using an excitation slit width of 5 nm.

Results and Discussion

Thermogravimetric and differential thermal analysis (TG/DTA) was carried out from room temperature to 700°C at a rate of 20°C/min. Figure 1 depicts the TG/DTA curves of CeO₂/CoPc nanocomposites. TGA curves for samples S1 and S2 show a small weight loss from room temperature to 700°C. From room temperature to 400°C, weight loss is due to residual water evaporation. The decomposition of CoPc pyrolyzed between 500 and 1000°C.⁹ However, from 400 to 600°C, the weight loss is due to partial decomposition of macrocyclic structure, where low weight atoms (H and part of N) are lost from CeO₂/CoPc.¹⁰ The DTA curves of samples S1 and S2 show a strong endothermic peak below 100°C correlated to a weight loss confirming the combustion of organic residues due to the crystallization of residual amorphous phase. The endothermic peak positioned around 76.7°C of sample S2 suggests that the precursor decomposed almost around 100°C to become CeO₂/CoPc nanocomposites. Moreover, the TGA/DTA studies show that samples are thermally stable in the range 100–700°C.

The XRD spectra of (a) pure CeO₂, (b) CoPc, (c) S1, and (d) S2 samples are presented in Fig. 2. The average particle sizes of samples S1 and S2 obtained using Scherrer's equation are 7.3 and 7.77 nm, respectively. The small increase in particle size for S2 is due to thermally promoted crystallite growth. All peaks could be indexed to a pure cubic fluorite structure of CeO₂ (space group: *Fm3m*) with lattice constant $a = 5.411$ Å, which is in agreement with the JCPDS file No. 75-0076 for CeO₂. The peaks at 2 θ values 28.501°, 33.056°, 47.416°, 56.311°, 76.867°, and 78.907° correspond to

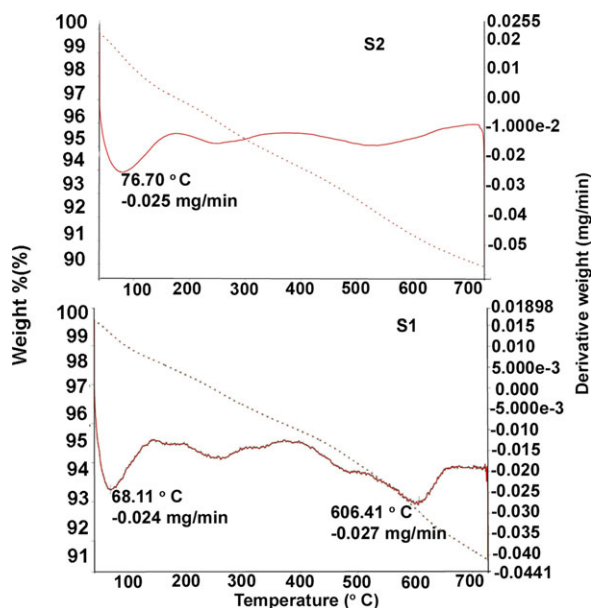


Fig. 1. TGA-DTA curves for CeO_2/CoPc nanocomposites.

planes (111), (200), (220), (311), (400), and (331), respectively, for CeO_2 . The peaks at 2θ values 6.66° , 14.85° , 18.39° , 25.29° correspond to planes (001), (002), (320), and (500) respectively, for α phase of CoPc.

EDX spectrum of CeO_2/CoPc nanocomposite sample is displayed in Fig. 3. The peaks confirm that the product contains Ce, O, and C. The intense signal at 4.8 keV indicates that Ce is the major element. No peaks could be identified for Co and N, which is most likely due to the lower loading of CoPc (1 wt% of CeO_2).

TEM bright field (BF) and SAED images (inset) of sample S1 and S2 are shown in Fig. 4. The BF images demonstrate that particles are spherical or near spherical in shape. The particle size obtained from TEM images ranges from 6 to 9 nm for S1 and 6 to 12 nm for S2, which are in agreement with the XRD results. The appearance of strong diffraction spots (SAED) rather than diffraction rings confirms the crystalline nature of the nanocomposite. The size distribution and abundance of CeO_2/CoPc nanocomposites are plotted in the histogram in Fig. 5.

The FTIR spectra of CeO_2/CoPc nanocomposites are shown in Fig. 6. The spectra have several significant absorption peaks recorded in the range of 2000–400/ cm . The absorption peak at 848/ cm is due to metal-O bond. FTIR illustrated absorption band at 522/ cm is observed in both S1 and S2. This band is produced by CeO_2 , which is typical peak for the Ce-O stretching

vibration.^{11,12} The commonly used bands for orientation studies in phthalocyanines are 733/ cm (C–H out-of-plane deformation) and 1334/ cm (C = C in-plane stretching).^{13,14} The IR active band at 918/ cm in S2 is related to the metal ligand vibration, which shows the presence of CoPc in the sample. The presence of a band at 724/ cm suggests the presence of α phase of CoPc. The band at 977/ cm in sample S2 indicates the presence of β phase, attributed to change of phase from α to β as calcination temperature increases to 350°C for sample S2.¹⁵ FTIR bands for samples S1 and S2 are presented in Table 1, along with literature values for CoPc.

Figure 7 shows UV-visible absorption spectra of CeO_2/CoPc nanocomposite samples in the range 200–900 nm. Samples S1 and S2 show very good absorption in the regions 200–300 nm, centered on 240 nm. The absorption of CeO_2 in the UV region originates from the charge-transfer transition between the O 2p and Ce 4f states in O^{2-} and Ce^{4+} .^{7,16} The intense bands in the regions 300–400 nm (Soret band) and 650–700 nm (Q band) correspond to absorption peaks of metal phthalocyanines. The peaks at higher-energy and low-energy regions result from B (Soret band) band and Q bands respectively, which arise from π - π^* transitions.¹⁷ The absorption bands from 400–800 nm region are caused by the π - π^* transitions of the conjugated macrocycle of 18 π -electrons. The intensity of higher energy peak (Q1) is larger than the second peak (Q2) of Q bands, which represents the typical feature of CoPc α -phase for sample S1 and all of the peaks diminish as the calcination temperature goes to 350°C (S2). There is a red shift for the Soret band while a slight blue shift for Q1 and Q2 bands which is due to the phase transformation from α to β as the calcinations temperature changes.¹⁵ The two absorption maxima of S1 at the Q band with wavelengths of 607 and 675 nm correspond to α -phase of CoPc. The two maxima of peaks are separated by 68 nm. The absorption threshold edge at 503 and 517 nm for α and β phase determines the band gap of the CeO_2/CoPc nanocomposite samples. Figure 7 shows that sample S2 has smaller optical absorption intensity compared to sample S1. The reason is that surface defects will be reduced as calcination temperature of CeO_2/CoPc nanocomposites is increased to 350°C .

The plots of α^2 vs $h\nu$ for CeO_2/CoPc samples are shown in Fig. 8. In Table 2, the optical band-gap energies for the samples S1 and S2 are compared with our earlier report for CeO_2 nanoparticles.¹⁸ The lowering of band-gap values for the nanocomposite samples relative to pure CeO_2 is due to the presence of cobalt in the CoPc.¹⁹ The cobalt ions create oxygen vacancies and favor the formation of Ce^{3+} from Ce^{4+} . This increases

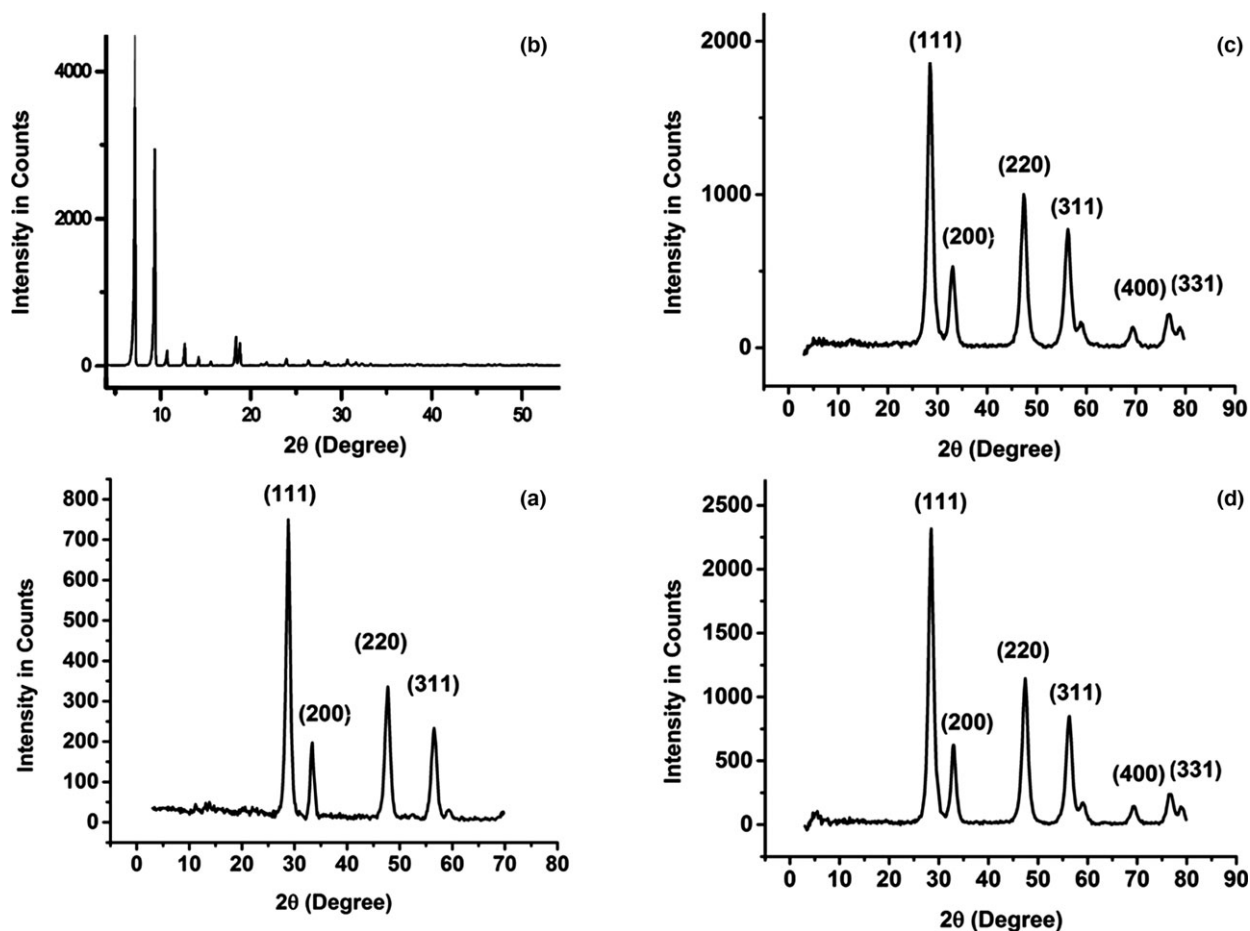


Fig. 2. XRD spectra of pure CeO₂, CoPc, and CeO₂/CoPc nanocomposite samples.

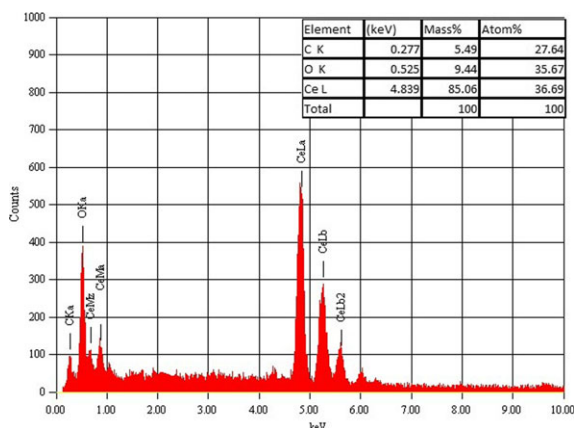


Fig. 3. EDX spectrum of CeO₂/CoPc nanocomposites.

the amount of Ce³⁺ states, resulting in the formation of localized energy states that are closer to the conduction band, and thereby decreasing the band gap. Also, average

particle size of CeO₂/CoPc nanocomposites (S2) increases with calcination temperature. This in turn broadens the HOMO (highest occupied molecular orbit in the valence band) and the LUMO (lowest unoccupied molecular orbit in the conduction band) energy levels, which leads to narrowing of the band gap. Moreover, CeO₂/CoPc nanocomposites can help us to extend the optical absorption spectra of CeO₂ from the UV region to the entire span of visible light in addition to enhanced absorption intensity, suggesting visible light-driven photocatalytic application of the nanocomposite.

The room temperature PL emission spectra ($\lambda_{\text{ex}} = 330$ nm) for CeO₂/CoPc nanocomposite samples are shown in Fig. 9. It has been reported in the literature that CoPc does not show fluorescence because of strong spin orbit interaction.²⁰ However, a weak emission peak is observed at the 394 nm in the Soret band region. The PL emission for CeO₂/CoPc nanocomposites can be assumed to be the transition from 4f band of cerium to the 2p band of O. The broad emission band ranging

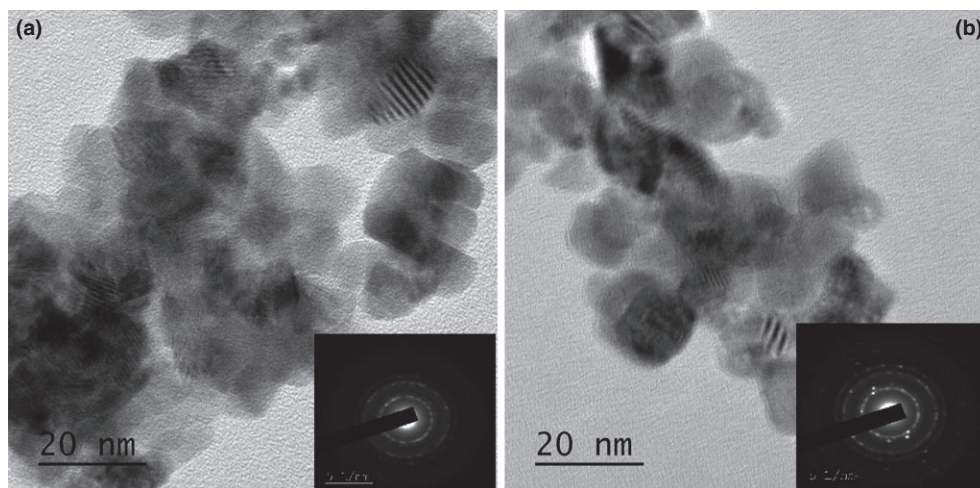


Fig. 4. TEM images of CeO_2/CoPc nanocomposite samples (a) S1 and (b) S2.

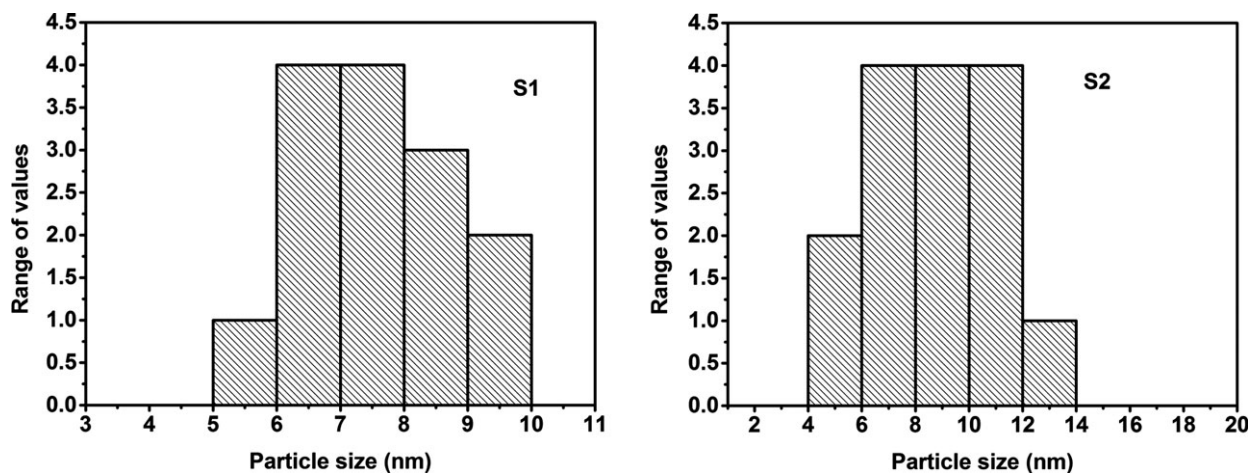


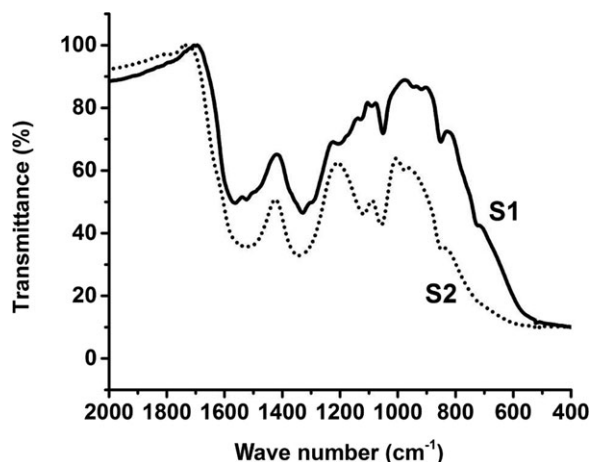
Fig. 5. Size distribution of CeO_2/CoPC nanocomposites.

from 350 to 575 nm of the samples S1 and S2 could be the result of defects, including oxygen vacancies in the crystal with electronic energy levels below the 4f band.²¹ Intense blue bands are observed at 435 nm (2.85 eV) and 448 nm (2.77 eV), respectively, for samples S1 and S2. A strong blue emission at 465 nm (2.66 eV), blue-green emission at 481 and 490 nm, and a good green emission at 540 nm (2.29 eV) are also observed for both the samples. The strong emission at 465 nm is related to the defects such as dislocations, which is helpful for fast oxygen transportation.¹⁸ It can be seen from Fig. 9 that the PL intensity of the sample S2 is much stronger than that of S1, which is attributed to phase change of CoPc from α to β that confirms the FTIR result.²²

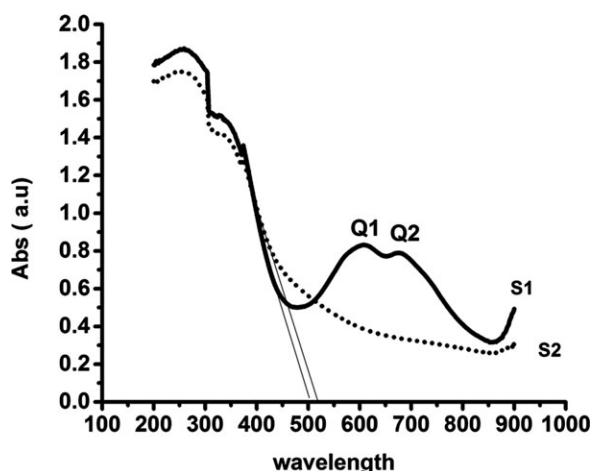
The emission peaks of sample S2 (Fig. 9) became red-shifted because of particle size elevation caused by

calcination. It is interesting that the PL intensity for CeO_2/CoPc nanocomposite samples is smaller than that for our earlier report for pure CeO_2 sample.¹⁸ The presence of Co can improve the life time of excitations by proper transferring and trapping of photo-excited charges through synergistic effect of optimum concentration of the CoPc and associated crystal defects. Hence, the intensity of PL spectra is lower for CeO_2/CoPc nanocomposite samples. The above property can be used to enhance the efficiency of dye-sensitized solar cells. Moreover, CoPc of appropriate concentration helps to enhance photo-efficiency and photo-activity of CeO_2 nanoparticles for potential applications in dye-sensitized solar cells²³ and photocatalysis.

Figure 10 exhibits the CIE chromaticity diagram of the synthesized nanocomposite samples S1 and S2. The

Fig. 6. FTIR spectra of CeO₂/CoPc nanocomposite samples.Table 1. FTIR band assignments of CeO₂/CoPc nanocomposites

S1	S2	CoPc ¹⁶	Band assignments
522	523	—	Ce-O stretching
724	—	721	C-H out-of-plane deformation
851	844	—	Metal-O bond
918	—	911	Metal ligand vibration
—	977	—	β-phase
1051	1057	—	C-H in-plane deformation
1090	—	1087	C-H in-plane deformation
1127	1118	1117	C-H in-plane bending

Fig. 7. Absorption spectra of CeO₂/CoPc nanocomposite samples.

greenish blue color emission is obtained with CIE coordinates (0.176, 0.262) for S1 and blue-green emission with coordinates (0.197, 0.295) for S2, when excited

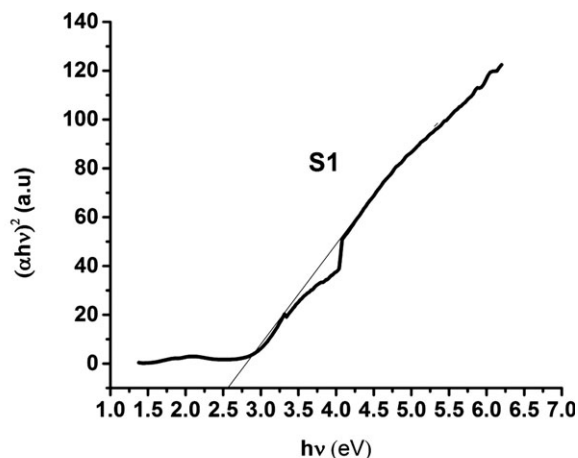
Fig. 8. α^2 vs. $h\nu$ plots of CeO₂/CoPc nanocomposites.

Table 2. Band-gap and excitonic energy level values for the nanocomposite

Sample	Absorption edge (nm)	Band gap (eV) (α^2 vs $h\nu$)	λ_{max} in Q band (nm)	
			Q1	Q2
S1	503	2.59	607	675
S2	517	2.31	—	—
CeO ₂ ¹⁸	456	3.5	—	—

with 330 nm which is in the near-UV region. In brief, the synthesized nanocomposite with suitable concentration of CoPc can be used to construct CeO₂ phosphors for near-ultraviolet (NUV) light-excited blue-green light-emitting diodes (LEDs) and optoelectronic devices.²⁴

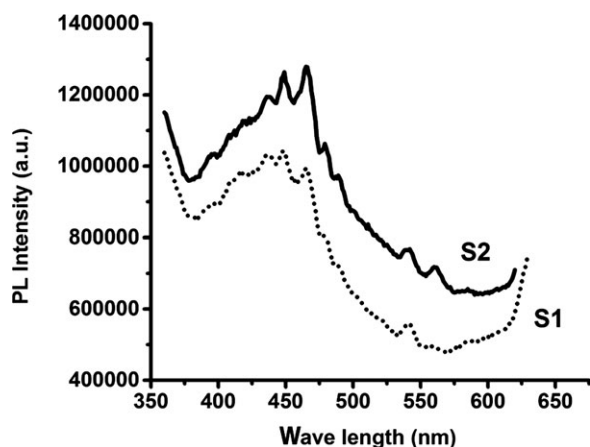


Fig. 9. Photoluminescence spectra of the nanocomposite samples.

The Raman scattering spectra of CeO_2/CoPc nanocomposites are recorded in the spectral range of 50–2000/cm, displayed in Fig. 11. The frequency region 550–1650/cm corresponds to heavy atom-nitrogen (Co-nitrogen) in-plane stretching and bending vibrations as well as displacements on the C-N-C bridge bond of the phthalocyanine molecule. The structural studies of CeO_2 on the basis of Raman spectroscopy is described elsewhere.¹⁸ Both the samples S1 and S2 show Raman-active band at 460/cm. This mode is attributed to the fluorite

structure, which is due to a symmetrical stretching mode of the Ce-O8 vibrational unit.²⁵ The Raman mode at 460/cm for S1 is slightly shifted to 460.58/cm for S2 due to particle size increase caused by calcination. In addition to Raman mode at 460/cm for CeO_2 , Fig. 11 confirms Raman-active modes of the symmetry A_{1g} at 567/cm, 848/cm, B_{1g} at 689/cm, 1541/cm, and B_{2g} at 1451/cm for CoPc.²⁶

Raman-active mode for CeO_2/CoPc nanocomposites (Fig. 11) at 460/cm is attributed to a symmetrical stretching mode of the Ce-O8 vibrational unit, as discussed above. The vibrations of the CoPc planar molecule having 57 atoms and possessing D_{4h} point group symmetry can be classified into following irreducible representation (taking into account only internal vibrations)²⁶:

$$\Gamma_{\text{vib}} = 14A_{1g} + 13A_{2g} + 14B_{1g} + 14B_{2g} + 13E_g + 6A_{1u} + 8A_{2u} + 7B_{1u} + 7B_{2u} + 28E_u,$$

where A_{1g} , B_{1g} , B_{2g} , and E_g are Raman-active modes. The nondegenerate A_{1g} , B_{1g} , and B_{2g} modes are in-plane vibrations, and double-degenerate E_g mode is the out-of-plane vibration. The Fig. 11 exhibits Raman-active modes of the symmetry A_{1g} at 567/cm, 848/cm, B_{1g} at 689/cm, 1541/cm, and B_{2g} at 1451/cm. However, the intensity of all these modes is small for the calcined sample S2. All these Raman bands are associated with vibrations of C–N–C bridge bonds and vibrations of central atom of phthalocyanine molecule (Co) connected with nitrogen atoms. Moreover, Raman results also confirm the presence of CeO_2 and CoPc in the composite samples.

Conclusion

In the present investigation, CeO_2/CoPc nanocomposite sample is obtained by chemical method under optimum conditions. The thermal studies confirm that the composite is thermally stable in the range 100–700°C. The structure of the nanoparticles has been characterized by XRD, TEM, FTIR, and Raman studies, and their results confirm the formation of CeO_2/CoPc in the sample. UV-visible absorption studies indicate that nanocomposite has good light absorption in the UV and visible region. A decrease in band-gap energy together with an improved absorption intensity of the composite has been observed. PL spectra and CIE diagram show wide emission peaks in the blue-green region, when excited with near-ultraviolet light. Moreover, the systematic investigations found that the desired thermal,

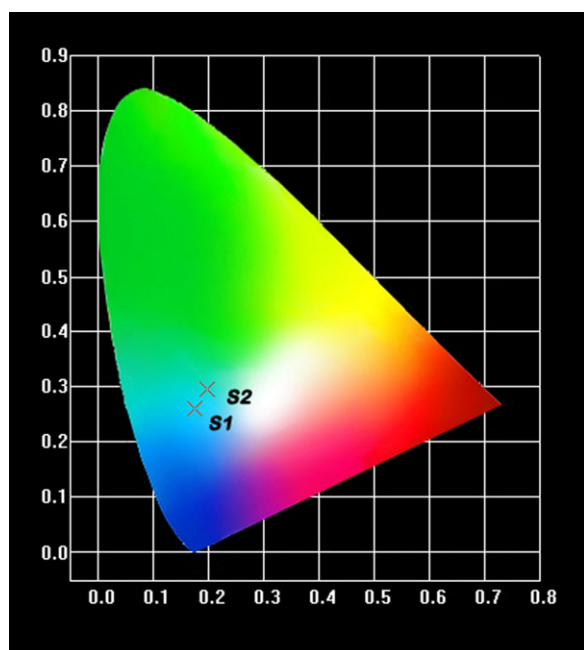


Fig. 10. CIE chromaticity diagram of CeO_2/CoPc nanocomposite samples.

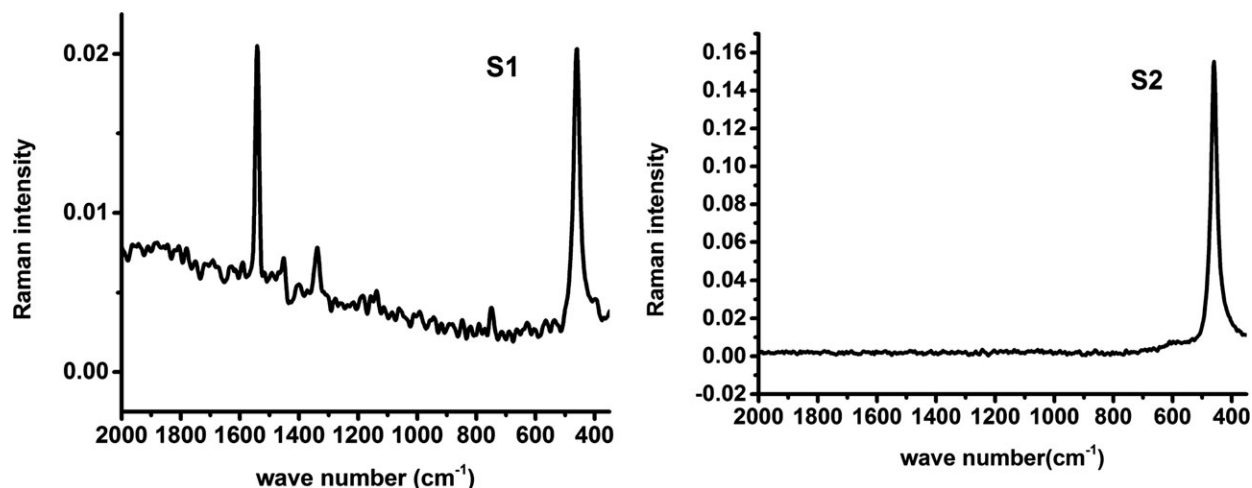


Fig. 11. Raman-active modes of CeO₂/CoPc nanocomposites.

structural, optical, and photoluminescence properties of CeO₂/CoPc nanocomposites make it as a promising material for photocatalytic, solar cells, NUV light-excited LEDs, and optoelectronic applications.

Acknowledgments

The authors acknowledge their thanks to NSRC, Nirmala College Muvattupuzha, Newman College Thodupuzha, and M.G University Kottayam for providing the opportunity to undertake this study. They are also thankful to SAIF, Cochin, and SAIF, IITM, Chennai, for providing facilities for characterization.

References

1. A. A. Anees, M. A. M. Khan, K. M. Naziruddin, A. A. Salman, M. Alhoshan, and M. S. Alsali, *J. Semiconductors*, 32 043001–043006 (2011).
2. N. Kobayashi, *Bull. Chem. Soc. Jpn.*, 75 1–19 (2002).
3. C. C. Leznoff and A. B. P. Lever, *Phthalocyanines: Properties and Applications*, Wiley, New York, 1989.
4. A. Sterning, J. Bernardi, K. Mc Kenna, and O. Diwald, *J. Mater. Sci.* 50 8153–8165 (2015).
5. Y. Q. Song, H. W. Zhang, and Q. Y. Wen, *J. Appl. Phys.* 102 043912 (2007).
6. A. Tiwari, *et al.*, *Appl. Phys. Lett.* 88 142511 (2006).
7. K. K. Babitha, K. P. Priyanka, A. Sreedevi, S. Ganesh, and T. Varghese, *Mater. Charact.* 98 222–227 (2014).
8. B. D. Cullity, *Elements of X-Ray Diffraction*, Addison-Wesley, Reading, MA, 1967.
9. B. N. Achar, K. S. Lokesh, G. M. Fohlen, and T. M. Mohan Kumar, *React. Funct. Polym.* 63 63–69 (2005).
10. F. V. Burgos, *et al.*, *Fuel* 99 106–117 (2012).
11. S. B. Khan, M. Faisal, M. M. Rahman, and A. Jamal, *Sci. Tot. Environ.* 409 2987–2992 (2011).
12. F. Niu, *et al.*, *Mater. Lett.* 63 2132–2135 (2009).
13. R. Aroca and A. Thedchanamoorthy, *Chem. Mater.* 7 69–74 (1995).
14. D. Li, D. Peng, L. Deng, Y. Shen, and Y. Zhao, *Vibrat. Spectrosc.* 39 191–199 (2005).
15. B. Joseph and C. S. Menon, *E. J. Chem.* 5 86–92 (2008).
16. S. Phoka, P. Laokul, E. Swatsitang, V. Promarak, S. Seraphin, and S. Maensiri, *Mater. Chem. Phys.* 115 423–428 (2009).
17. K. R. Rajesh and C. S. Menon, *Indian J. Pure Appl. Phys.* 43 964–971 (2005).
18. K. K. Babitha, A. Sreedevi, K. P. Priyanka, B. Sabu, and T. Varghese, *Indian J. Pure Appl. Phys.* 53 596–603 (2015).
19. S. Jayapalan, S. R. Kugalur, S. Padmanaban, M. Devanesan, and T. R. Ramasamy, *Mater. Sci. Semicond. Process.* 26 218–224 (2014).
20. W. Bala, *et al.*, *J. Optoelectro. Adv. Mater.* 11 264–269 (2009).
21. A. H. Morshed, M. E. Moussa, S. M. Bedair, R. Leonard, S. X. Liu, and N. E. Masry, *Appl. Phys. Lett.* 70 1647–1649 (1997).
22. B. A. Al-Asbahi, M. H. H. Jumali, C. C. Yap, and M. M. Salleh, *J. Nanomaterials* 1–7 (2013) doi:10.1155/2013/561534.
23. M. Lira-Cantu and F. C. Krebs, *Sol. Energy Mater. Sol. Cells* 90 2076–2086 (2006).
24. F. Hussain, M. Hojjati, M. Okamoto, and R. E. Gorga, *J. Compos. Mater.* 40 [17] 1511–1575 (2006).
25. I. Kosack, V. Petrovsky, H. Anderson, and P. Colomban, *J. Am. Ceram. Soc.* 85 2646–2650 (2002).
26. B. A. Kolesov and T. V. Basova, *Thin Solid Films* 304 166–169 (1997).