

Surfactant Effect on Bandgap and Crystallite Size of ZnO–TiO₂–CeO₂ Nanocomposites



H. Srinivasa Varaprasad, P. V. Sridevi, and M. Satya Anuradha

Abstract Multiphase, mixed metal oxide material composites at nanosize with wide bandgap are capable of good electronic functionality at higher temperature compared with existing semiconducting materials. In this work, ZnO–TiO₂ semiconducting metal oxide doped with 0.1 M CeO₂ ternary composite is prepared by solid-state method and surfactants like hydroxypropyl cellulose (HPC) and Sodium dodecylbenzene sulfonate (SDBS) are used as reacting agents. Prepared nanocomposites were characterized by X-ray diffraction (XRD), FESEM, and UV–Visible spectroscopy for the observation of crystallite size, surface morphology, and bandgap calculation sequentially. Crystallite size was calculated by using Debye–Scherrer method and was reconfirmed with Williamson–Hall and size–strain plot methods. The results revealed that mixed metal oxide composite generates a new energy level at 2.6 eV. Nanocomposite modified with hydroxypropyl cellulose (HPC) exhibits good optical absorption, around 16–20 nm crystallite size is obtained and also homogeneous distribution of particles is observed.

Keywords Solid state · HPC · SDBS · Wide bandgap

1 Introduction

Nowadays, most of the researchers are focused on mixed metal oxide and its composites to enhance properties like optical, thermal, structural, morphological, electrical, physical, chemical, mechanical, bio-medical, and interdisciplinary applications [1, 2]. It is more secure to use two or more material combinations in the place of one material by carefully choosing and tuning combinations of metal oxides [3, 4]. ZnO and TiO₂ are such kind of materials which can form ZnTiO₃, ZnTiO₄ perovskites which attracts the attention toward dye degradation, photocatalysis, pigments, sensors, etc. [5–7]. The addition of metals and metal oxide to the binary composite may further

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© Springer Nature Singapore Pte Ltd. 2021
P. S. R. Chowdary et al. (eds.), *Microelectronics, Electromagnetics and Telecommunications*, Lecture Notes in Electrical Engineering 655,
https://doi.org/10.1007/978-981-15-3828-5_43

enhance the results. CeO_2 (3.5 eV) and SnO_2 (3.7 eV) are the metaloxides which have similar bandgaps of ZnO (3.37 eV) and TiO_2 (3.2 eV). The wide bandgap materials are capable of electronic functionality at higher temperatures compared with Si, Ge [8, 9].

All the materials at nanosize exhibit different properties compared with micron size. But the problem with nanomaterials is that they are highly reactive, oxidized very fast, and they get contaminated in the open atmosphere [10]. The surfactants are compounds that modify surface tension, material properties like particle shape, size, phase, surface morphology, and homogenies distribution of particles [11].

The properties of materials are varied with particle size, phase of the materials, calcination temperature, weight ratio, doping material, amount of dopants, catalysts, surface morphology, and preparation methods. The amount and phase distribution, inhomogeneity in the composition, size and shape distribution of crystallite and crystallographic orientations can be determined by diffraction lines of crystalline materials. The different methods to determine crystallite size and lattice strain from the diffraction lines are (1) Variance method, (2) Integral breadth method, (3) Warren–Averbach method, (4) Scherrer method, (5) Williamson–Hall method, (6) Size–strain plot method, etc. [12, 13].

The organization of the paper is as follows, materials used, preparation of CeO_2 – ZnO – TiO_2 Semiconducting ternary Nanocomposite, and characterization methods are given in Sect. 2. Section 3 describes the results and analysis of crystallite size and bandgap of the composite by using X-ray diffraction and UV–visible spectroscopy. Surface morphology observed from FESEM. Finally, Sect. 4 concludes.

2 Composite Material Preparation

2.1 Materials

Commercially procured nanopowder materials ZnO (99.9% pure, 30 nm), TiO_2 (Anatase 99.9% pure, 25 nm), CeO_2 (99.9% pure, 35 nm) are used. Isopropanol ($\text{C}_3\text{H}_8\text{O}$), deionized water (H_2O), ethanol ($\text{C}_2\text{H}_6\text{O}$), and acetone ($\text{C}_3\text{H}_6\text{O}$) are used as medium and cleaning agents. Sodium hydroxide (NaOH) is used to adjust the value of pH. Hydroxypropyl cellulose (HPC), sodium dodecylbenzene sulfonate (SDBS) are used as reactive agents. All chemicals are used without any modifications.

2.2 Preparation for Nanocomposite

ZnO – TiO_2 (1:1) Nanocomposite is doped with 0.1 Mol of CeO_2 has been prepared by a solid slate method. The high purity commercially available nanopowders ZnO (99.9% pure) and TiO_2 anatase (99.9% pure) were equally weighted

and mixed according to stoichiometry. Then, 0.1 Mol percentage of CeO_2 (99.9% pure) nanopowder was mixed to prepare 1:1 ZnO–TiO₂ nanocomposite. The mixed nanopowder was milled for 45 min at 600 rpm in a 125 ml jar with 1:10 ZrO₂ balls with isopropanol as a medium by using high energy ball mill. The obtained wet powder was collected and magnetically stirred until xerogel is formed at 50 rpm by maintaining 55 °C temperature. Further 50 ml deionized water, 20 m Mol NaOH, 1 Mol hydroxypropyl cellulose (HPC)/1 Mol sodium dodecylbenzene sulfonate (SDBS)/1 Mol hydroxypropyl cellulose (HPC), and sodium dodecylbenzene sulfonate (SDBS) were added and magnetically stirred for 3 h at 250 rpm. Some of the formed gels were collected. The remaining gel was dried at 85 °C for 1 h on heat mount. White-colored fine nanosized powders were obtained. Then these nanopowders were sintered up to 450 °C for 2 h at the increment of 5 °C/min in the muffle furnace. 0.1 M CeO₂–ZnO–TiO₂ composites are named as C1A0 (Pure), C1B0 (HPC), C1C0 (SDBS), and C1D0 (Modified by HPC and SDBS).

2.3 Characterization

The crystallite size and phase structures of the ZnO–TiO₂ (1:1) doped with 0.1 Mol of CeO₂ nanocomposite powder were observed by X-ray diffraction peak analysis (PAN ANALYTICAL, XPERT PRO) at a scanning rate 2°/min in 2θ range from 10° to 90° within CuK α radiation with $\lambda = 1.54060 \text{ \AA}$ at 45 kV and 40 mA. The optical properties were calculated by UV–visible spectrophotometer (FILMETRICS F20, UV–VIS spectrophotometer). The micrographs are obtained by FESEM-EDS (JEOL Asia PTE Ltd) operated at 12 kV with 100 nm resolution.

3 Results and Discussion

3.1 X-ray Diffraction

The X-ray diffraction of the prepared sample modified by surfactants is as shown in Fig. 1 and it is analyzed with Philips Xpert high score plus software package. All the diffraction peaks exhibit ZnO, TiO₂, CeO₂ mixed phases structure. Crystallite size is calculated using Debye–Scherrer method, W–H method, and SSP method. The X-ray diffraction peaks of 0.1 M CeO₂ is doped to ZnO–TiO₂ modified by HPC are as shown in Fig. 2. The structure parameters of ZnO–TiO₂ doped with 0.1 M CeO₂ is represented in Table 1.

Debye–Scherrer method: The crystallite size can be calculated by the Scherrer method using Scherrer equation

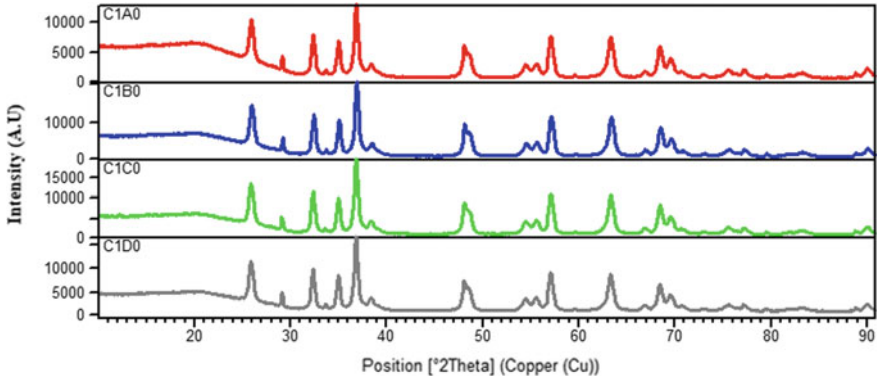


Fig. 1 XRD pattern of ZnO–TiO₂ doped with 0.1 M CeO₂ modified by HPC, SDBS, HPC, and SDBS

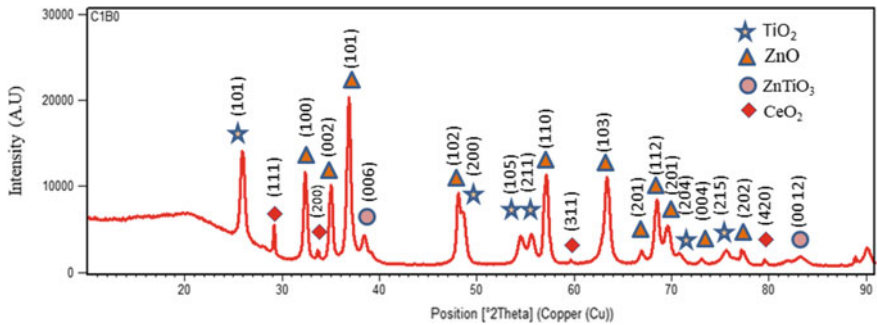


Fig. 2 XRD pattern of ZnO–TiO₂ doped with 0.1 M CeO₂ modified by HPC

$$D = \frac{K\lambda}{\beta_{hkl} \cos \theta} \tag{1}$$

Where D is crystallite size in nanometers, $k = 0.94$. The wavelength of radiation $\lambda = 1.5406 \text{ \AA}$ (CuK α radiation), β_{hkl} = full width at half maximum (FWHM) of the peak in radians, and θ = Bragg angle.

Lattice strain of the material particles can be calculated by the relation

$$\varepsilon = \frac{\beta_s}{4 \tan \theta} \tag{2}$$

Figure 3 shows the $\cos \theta$ versus $1/\beta$. The obtained crystallite sizes of 0.1 M CeO₂ are added ZnO–TiO₂ modified composite is as shown in Table 2.

W-H Plot Method. The crystallite size can be calculated by Williamson–Hall method. According to the Williamson–Hall method, the reflections can be determined from the relation

Table 1 X-ray diffraction parameters of ZnO–TiO₂ doped with 0.1 M CeO₂ modified by HPC

S.No.	Compound name and phase	2θ	Hkl	Unit cell	Crystal structure	ICOD
1	ZnO (zincite)	32.40, 35.03, 36.86, 48.06, 57.13, 63.40, 66.93, 68.48, 69.61, 73.10, 77.27	(100), (002), (101), (102), (110), (103), (201), (112), (201), (004), (202)	$a = b = 3.22 \text{ \AA}$ $c = 5.17 \text{ \AA}$ $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$ Volume = 46.67 \AA^3	Hexagonal	01-075-1526
2	TiO ₂ (anatase)	25.84, 48.57, 54.35, 55.48, 63.32, 75.52	(101), (200), (105), (211), (204), (215)	$a = b = 3.75 \text{ \AA}$ $c = 9.42 \text{ \AA}$ $\alpha = \beta = \gamma = 90^\circ$ Volume = 132.8 \AA^3	Tetragonal	00-002-0406
3	ZnTiO ₃ (ecandrewsite)	38.32, 83.83	(006), (00 12)	$a = b = 0.355 \text{ \AA}$ $c = 0.140 \text{ \AA}$ $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$ Volume = 0.28 \AA^3	Trigonal (hexagonal axis)	00-026-1500
4	CeO ₂ (cerium oxide)	29.08, 33.60, 57.07, 79.53	(111), (200), (311), (420)	$a = b = c = 5.41 \text{ \AA}$ $\alpha = \beta = \gamma = 90^\circ$ Volume = 158.34 \AA^3	Cubic	00-001-0800

$$\beta_{hkl} \cos \theta = \frac{K\lambda}{D} + 4\varepsilon \sin \theta \quad (3)$$

where D = crystallite size, ε = lattice strain.

Figure 4 shows the $\beta \cos \theta$ versus $4 \sin \theta$. The obtained crystallite sizes of 0.1 M CeO₂ is doped with ZnO–TiO₂ modified composite is as shown in Table 2.

Size–Strain Plot Method. The crystallite size can be calculated by size–strain method. The equation related to the SSP Method is

$$(d_{hkl} \beta_{hkl} \cos \theta)^2 = \frac{K}{D} (d_{hkl}^2 \beta_{hkl} \cos \theta) + \left(\frac{\varepsilon}{2}\right)^2 \quad (4)$$

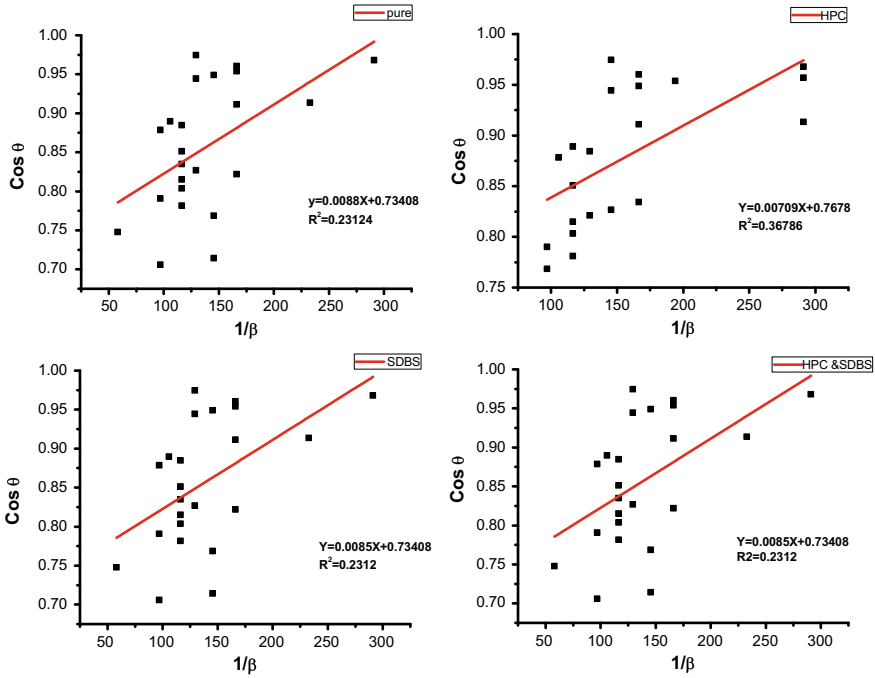


Fig. 3 Scherrer plot of ZnO–TiO₂ doped with 0.1 M CeO₂ modified by HPC, SDBS, HPC, and SDBS

Table 2 Crystallite size of ZnO–TiO₂ doped with 0.1 M CeO₂ modified composite in different methods

0.1 M CeO ₂ added ZnO–TiO ₂	Debye–Scherrer method (nm)	W–H plot method (nm)	Size–strain plot method (nm)
Pure	16.46	17.13	15.04
+HPC	20.43	21.91	19.06
+SDBS	17.04	18.91	16.23
+HPC and SDBS mixed	17.04	18.13	16.04

Figure 5 shows the $(d\beta\cos \theta)^2$ versus $d^2\beta\cos \theta$. The obtained crystallite sizes of 0.1 M CeO₂ is added to ZnO–TiO₂ modified composite is shown in Table 2.

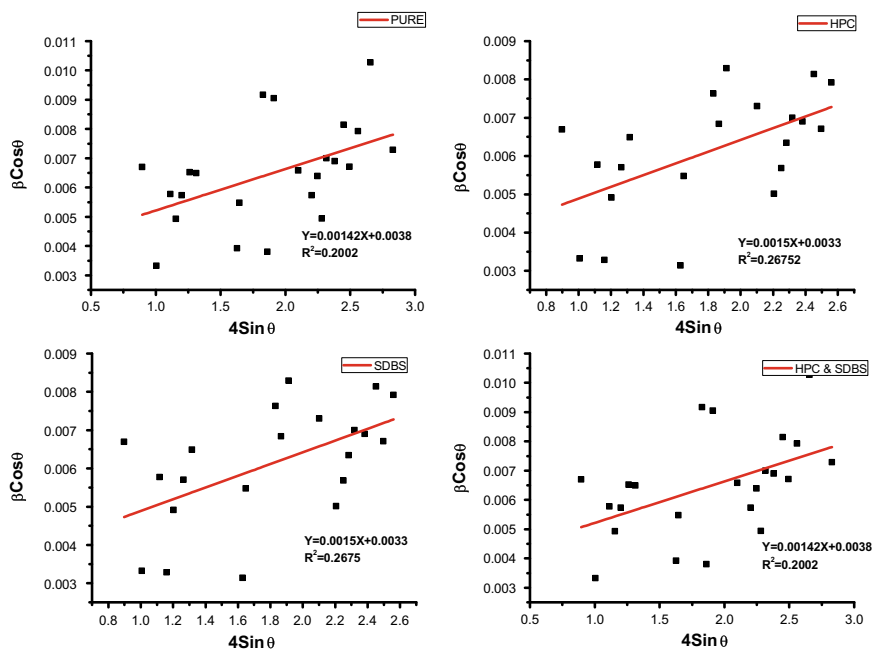


Fig. 4 Williamson–Hall plot of ZnO–TiO₂ doped with 0.1 M CeO₂ modified by HPC, SDBS, HPC, and SDBS

3.2 Surface Morphology

FESEM images of 0.1 M CeO₂ doped to ZnO–TiO₂ and modified with HPC, SDBS, HPC, and SDBS are as shown in Fig. 6. The FESEM results showed that the particles are spherical in shape and uniform in size. The average diameter of the particle is approximately 35 nm. Identification of ZnO, TiO₂, and CeO₂ is not possible in the image because of similar electron density of Zn and Ti. Hydroxy propyl cellulose modified composite appears as much bright and dispersed.

3.3 UV Visible Spectroscopy

Absorbance. UV–Visible absorption spectra are shown in Fig. 7. From the figure, all the bands exhibit red shift, composite shows maximum absorption in this UV region and shifts toward the visible region. Because of maximum absorption of TiO₂, CeO₂ is in UV region and absorption of ZnO is in visible region. The maximum absorption was observed at 351 nm is 88.76% due to hydroxy propyl cellulose. SDBS modified composite is at wavelength of 362 nm is 51.88%, SDBS and HPC mixed composites

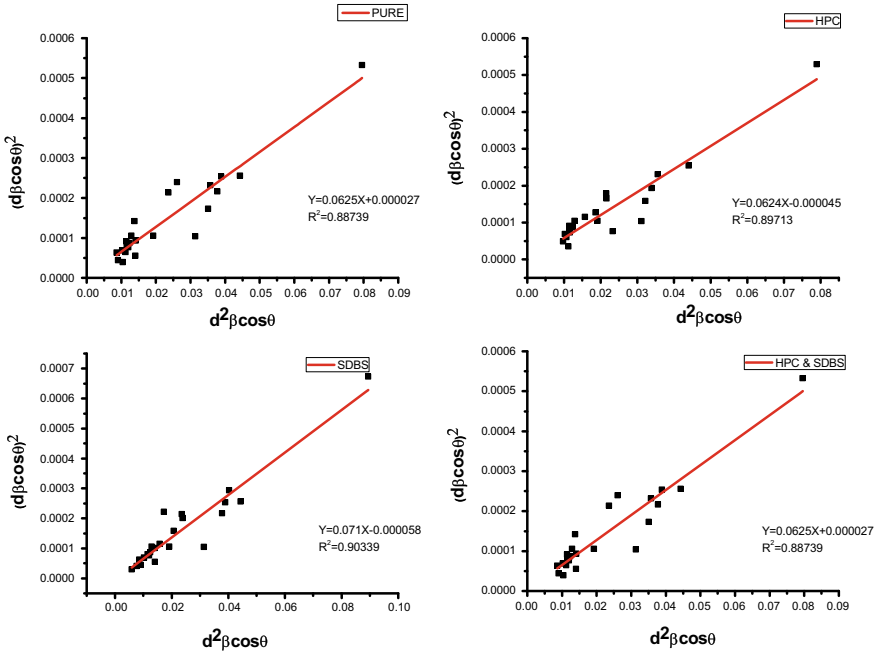


Fig. 5 Size–stain plot of ZnO–TiO₂ doped with 0.1 M CeO₂ modified by HPC, SDBS, HPC, and SDBS

maximum absorption is 368 nm and is only 33%, pure composite is at 363 nm and is 48.15%.

Bandgap calculation. The bandgaps are estimated from the Tauc-Plot Technique by plotting a line from the linear portion of high photon energy to zero absorption coefficients as shown in Fig. 8. The relation between the absorption edge and photon energy ($h\nu$) can be written as

$$\alpha h\nu = A(h\nu - E_g)^{n/2} \tag{5}$$

The list of bandgaps is tabulated in Table 3.

The optical bandgaps of ZnO, TiO₂, and CeO₂ are 3.3 eV, 3.2 eV, and 3.19 eV. But the estimated bandgap of the nanocomposite is 2.4–2.6 eV. The reduction in the bandgap is because of composite which generates new energy levels of TiO₂, ZnO incorporation with CeO₂. The maximum bandgap reported at 0.1 M CeO₂ is doped to ZnO–TiO₂ modified by HPC is 2.6 eV [14].

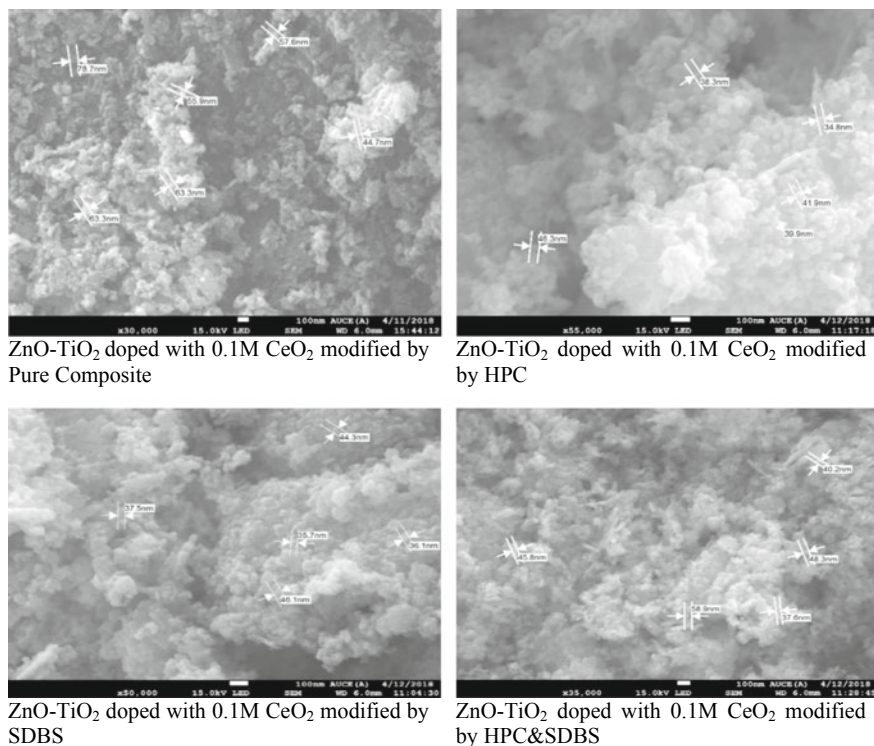


Fig. 6 FE-SEM images of ZnO–TiO₂ doped with 0.1 M CeO₂ modified by HPC, SDBS, HPC, and SDBS

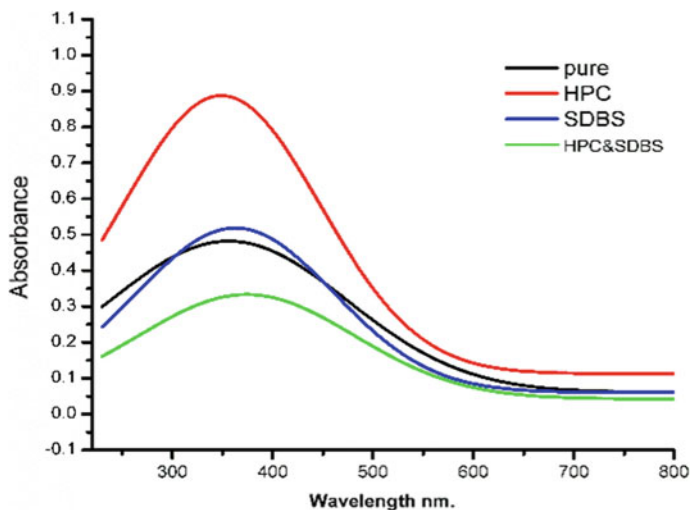


Fig. 7 UV–visible absorption spectra of ZnO–TiO₂ doped with 0.1 M CeO₂ modified by HPC, SDBS, HPC, and SDBS

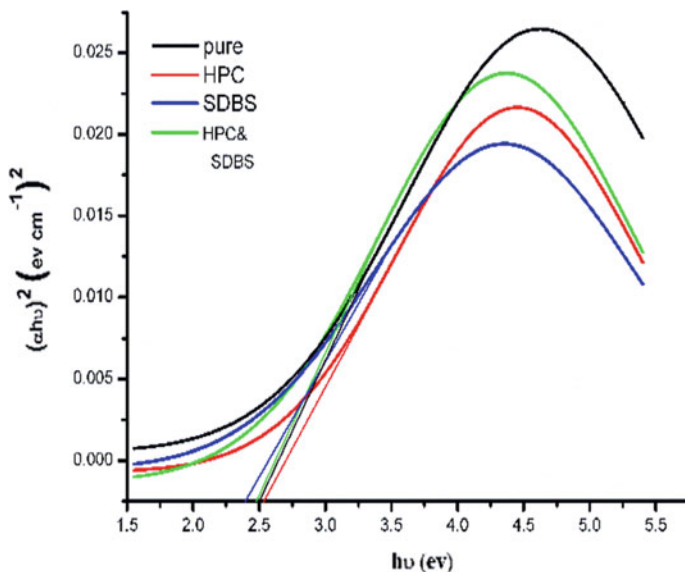


Fig. 8 Tauc-plot of ZnO–TiO₂ doped with 0.1 M CeO₂ modified by HPC, SDBS, HPC, and SDBS

Table 3 Tauc-Plot of ZnO–TiO₂ doped with 0.1 M CeO₂ modified by HPC, SDBS, HPC, and SDBS

S. No	Surfactant	The optical energy bandgap E_g = $1240/\lambda$ in eV	Energy bandgap from Tauc-Plot in eV
1	Pure	3.36	2.5
2	HPC	3.53	2.6
3	SDBS	3.42	2.4
4	HPC and SDBS	3.36	2.5

4 Conclusion

A solid-state method was approached to prepare CeO₂–ZnO–TiO₂ semiconductor composites with different surfactants. TiO₂ holds anatase phase and no other impurity elements are observed in the composite. Incorporation of TiO₂ to ZnO with addition of CeO₂ generates a new energy level at 2.6 eV. Absorption of the composite modified by hydroxy propyl cellulose is greatly enhanced due to the weak binding and quick absorption at lower activation energy barrier of HPC. SDBS, mixed HPC & SDBS does not show much impact on composite, so surfactant HPC is more suitable to ZnO, TiO₂ semiconducting metal oxide nano composites and mixed HPC do not show much impact on composite, so HPC is more suitable surfactant to ZnO, TiO₂

semiconducting oxides. Prepared semiconducting materials with the obtained semiconducting properties may be useful to optoelectronic, microelectronic, and sensing applications.

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