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# Influence of Capping Agent on Structural and Optical Properties of Erium Oxide Nanoparticles Synthesized by Co-Precipitation and Green Method

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**Abstract:** The Monoethanolamine (MEA) capped cerium oxide Nanoparticles (CeO<sub>2</sub> NPs: B1) and *Gloriosasuperba* (*G. superba*) capped CeO<sub>2</sub> NPs (B2) were synthesized through co-precipitation and Green method. X-ray diffraction studies revealed that the synthesized MEA and *G. superba* capped CeO<sub>2</sub> NPs exhibited cubic phase. Morphological and elemental composition was studied FESEM and EDAX spectra. From the FTIR spectra, the Ce-O stretching band was observed at 505 and 508 cm<sup>-1</sup> for MEA and *G. superba* capped CeO<sub>2</sub> NPs respectively. UV-Visible absorption spectra, the band gaps of MEA and *G. superba* capped CeO<sub>2</sub> NPs were calculated at 2.6 and 2.95 eV, respectively. The photoluminescence measurements revealed that the broad emissions were composed of five different peaks observed for MEA capped CeO<sub>2</sub> NPs.

**Keywords:** Monoethanolamine; *G. superba*; capping agent; CeO<sub>2</sub>; XRD; FESEM.

## I. INTRODUCTION

Cerium oxide nanoparticles (CeO<sub>2</sub> NPs) are technological important material with desirable properties used wide applications, such as heterogeneous catalysts, high charge storage capacitors, corrosion-resistance materials, UV-protective coating and gas sensor materials [1-3]. In the literature, syntheses of nanoparticles have been achieved by various methods incorporated with physical and chemical way, such as hydrothermal, flame spray pyrolysis, sonochemical, microwave, sol-gel, and co-precipitation methods [4-9]. Though, these approaches are the most relevant methods. But these methods were very complex, time taken, expensive and hazardous chemicals. As a result of these confines, the green chemistry attitudes are remarkably considered to be the most worth protocol in the phyto-synthesis of metal oxide NPs owing to their plenty of rewards such as cost-effectiveness, large-scale commercial production, environment-friendly and pharmaceutical applications [10].

*G. superba* is a species of flowering plants belonging to Colchicaceae family. It is a perennial, greenish, climbing herb and native to South Africa. Its flower is a state flower of Tamil Nadu and national flower of Tamil Eelam[10]. Since 2000 B.C. it is being used as a traditional medicine by the tribes. Each part of the plant should be used in Siddha, Ayurveda and Unani system of medicine. *G. superba* leaf extract contains many organic components, such as asuperbine, colchicine, loriosine, gloriosol, phytosterils and stigmaterin[11].

In the present investigation, Monoethanolamine and *G. superba* leaf extract capped CeO<sub>2</sub> NPs were prepared through co-precipitation and green method. Synthesized CeO<sub>2</sub> NPs characterized by XRD, FESE, EDAX, UV-Vis and Photoluminescence spectra studies were carried out. From this result, *G. superba* capped CeO<sub>2</sub> NPs defect level was decreased. In PL results provides strong support for the further development of extensive optical device applications.

## II. SYNTHESIS AND CHARACTERIZATION TECHNIQUES

The following high purity chemicals such as Cerium nitrate, Monoethanolamine (MEA), and Sodium hydroxide were used as precursors without further purification.

The MEA added CeO<sub>2</sub> NPs synthesis following, Cerium Nitrate 0.1M with capping agent added MEA 0.05M were dissolved double distilled water separate 100ml beaker, then form a homogenous mixture. 0.8M of NaOH was separately dissolved in 100 ml of double distilled water. Then, NaOH solution was added drop wise to the homogenous mixture of Cerium nitrate solution, the pH 12.30 obtained and which yields violet precipitate. The solution with the violet precipitate was stirred at room temperature for 6 h. This solution was refluxed at room temperature for 24 h. Then, a clear solution was obtained, which found to be stable at ambient condition.

The 10 g of *G. superba* finely cut green leaves were added to 100 mL of double distilled water and boiled at 50-60 °C for 15 min. The obtained extraction was filtered using Whatmann No. 1. Thereafter, 0.1M of Ce (NO<sub>3</sub>)<sub>3</sub> .6H<sub>2</sub>O salt was added to 100 mL of *G. superba* leaf extract. This solution was stirred constantly at 80 °C temperature for 6h. A brown precipitate formed and then it was

become a yellowish brown in color on continuous stirring. A schematic diagram of *G. superba* capped CeO<sub>2</sub> NPs is shown in Fig. 1. Thereafter, the solution was washed several times with double distilled water and ethanol. The precipitate was dried at 120 °C. Finally, MEA capped CeO<sub>2</sub> and *G. superba* capped CeO<sub>2</sub> NP samples were annealed at 700 °C for 5 h.

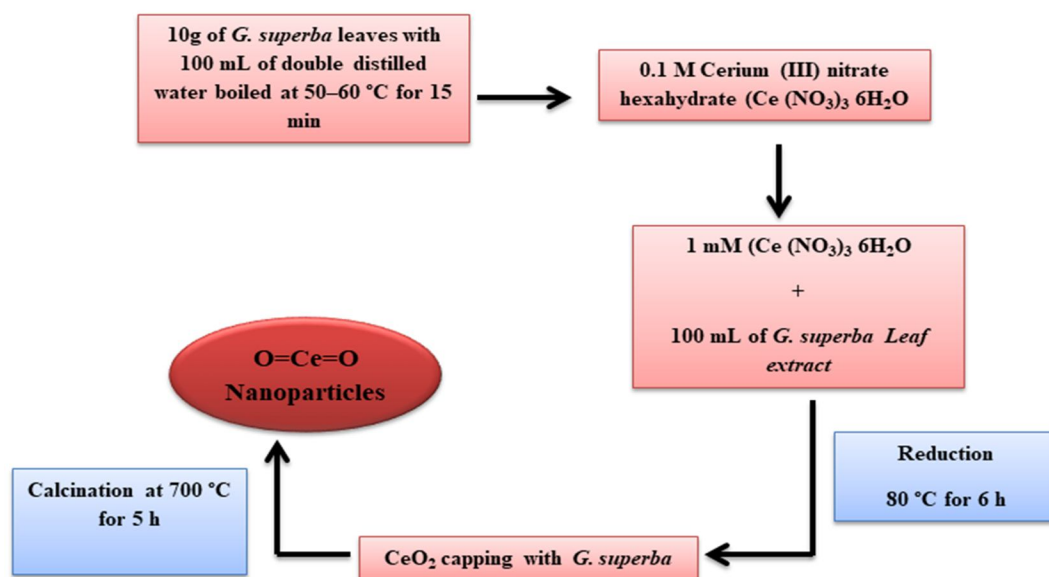


Figure 1. A schematic diagram of *G. superba* capped CeO<sub>2</sub> NPs

The MEA capped CeO<sub>2</sub> and *G. superba* capped CeO<sub>2</sub> NPs were characterized by X-ray diffractometer (model: X'PERT PRO PANalytical). The diffraction patterns were recorded in the range of 30°-80° for the MEA capped CeO<sub>2</sub> and *G. superba* capped CeO<sub>2</sub> NP samples where the monochromatic wavelength of 1.54 Å was used. The samples were analyzed by Field Emission Scanning Electron Microscopy (Carl Zeiss Ultra 55 FESEM) with EDAX (model: Inca). The absorption spectra of MEA capped CeO<sub>2</sub> and *G. superba* capped CeO<sub>2</sub> NP samples were studied in the range between 200 and 1100 nm by Lambda 35 spectrometer. Photoluminescence spectra were studied using Perkin Elmer-LS 14.

### III. RESULTS AND DISCUSSION

#### A. X-ray diffraction studies

Figure 2 shows the X-ray diffraction pattern of as synthesized MEA and *G. superba* capped CeO<sub>2</sub> NPs. The XRD peaks are at the (2θ) values of (28.58, 33.13, 47.53, 56.38, 59.09, 69.46 and 76.73) and (28.59, 33.12, 47.54, 56.40, 59.1, 69.48, and 76.7) corresponding to (111), (200), (220), (311), (222), (400), (331) and (420) planes of the both MEA and *G. superba* capped CeO<sub>2</sub> NPs respectively, with a space group of Fm $\bar{3}$ m (225). XRD results clearly show reflection peaks are sharp and well crystallized. The lattice parameters CeO<sub>2</sub> NPs is calculated according to the formula

$$\frac{1}{d^2} = \left( \frac{h^2 + k^2 + l^2}{a^2} \right)$$

The lattice constant 'a' value is obtained through the relation  $a = \sqrt{d^2(h^2 + k^2 + l^2)}$ . The calculated 'a' values are 5.4041 Å and 5.3935 Å for MEA and *G. superba* capped CeO<sub>2</sub> NPs respectively. Changing the capping agent during the synthesis process of CeO<sub>2</sub> NPs, the lattice parameter values and FWHM of the NPs were found to be slightly varied. The average crystallite size of the MEA and *G. superba* capped CeO<sub>2</sub> NPs are calculated by Debye Scherrer's relation

$$\text{Average crystallite size } D = \frac{k\lambda}{\beta \cos\theta}$$

Where, λ is the wavelength of the radiation (1.54056 Å for CuKα radiation), k is constant which is equal to 0.94, β is the peak width at half-maximum intensity, θ is the peak position. The MEA and *G. superba* capped CeO<sub>2</sub> NPs average crystallite sizes are calculated at 21.56 nm and 18.71 nm respectively. The crystallite size of *G. superba* capped CeO<sub>2</sub> NPs decreased as compared to that of MEA capped CeO<sub>2</sub> NPs. The reduction in the crystallite size is mainly due to the many organic components involved in the formation of nanoparticles, which is decreasing the nucleation and subsequent growth rate of the CeO<sub>2</sub> NPs.

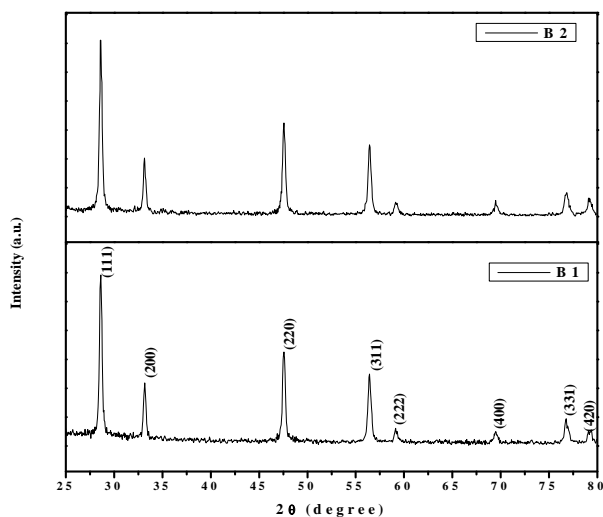


Figure 2. X-ray diffraction pattern of MEA and *G. superba* capped CeO<sub>2</sub> NPs.

**B. Morphological and Elemental composition of CeO<sub>2</sub>**

Figure 3 (a-b) shows the topographical analysis of as-synthesized MEA and *G. superba* capped CeO<sub>2</sub> NPs. From the FESEM image, the synthesized MEA and *G. superba* capped CeO<sub>2</sub> NPs exhibit cubic structure. The average particle size observed at 35 and 27 nm for both CeO<sub>2</sub>NPs respectively. *G. superba* leaf capped CeO<sub>2</sub> NPs possess decreased as compared to that of chemical synthesized MEA capped CeO<sub>2</sub> NPs. This size reduction may be presence of various organic components involved in the NPs formation. Metal element composition of CeO<sub>2</sub> NPs as shown in Fig. 3(c-d). From EDAX results, the Ce and O atomic percentage are observed at (31.13 % & 68.87%) and (73.62 % & 26.38%) for MEA capped CeO<sub>2</sub> and *G. superba* capped CeO<sub>2</sub> NPs respectively. The *G. superba* capped CeO<sub>2</sub> NPs oxygen percentage increase with decrease the cerium percentage as compared to that of MEA capped CeO<sub>2</sub> NPs, which may be NPs formed using *G. superba* plant extract.

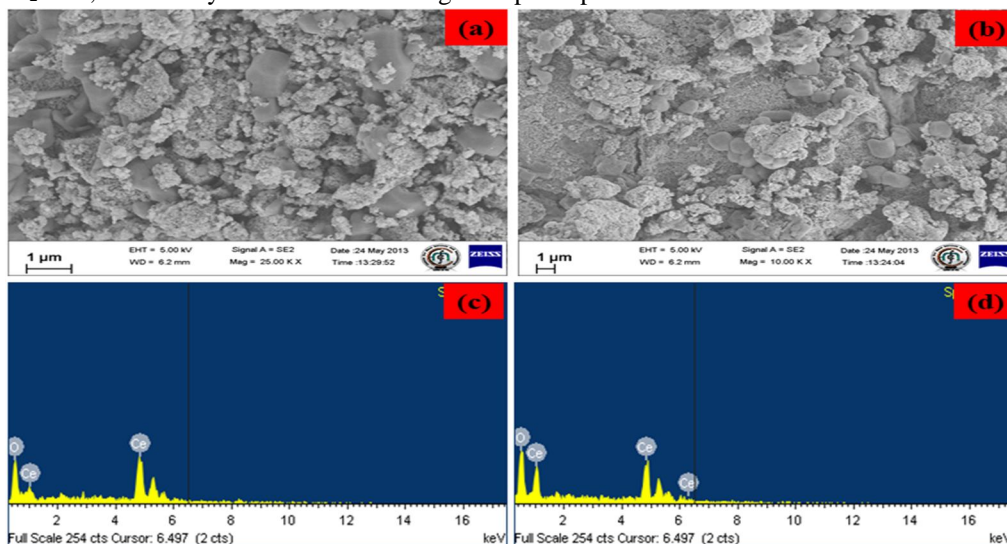


Figure 3 (a-b). FESEM image of MEA and *G. superba* capped CeO<sub>2</sub> NPs and (c-d) EDAX spectra of MEA and *G. superba* capped CeO<sub>2</sub> NPs.

**C. Ft-ir Spectroscopic Studies**

FT-IR spectrum of MEA and *G. superba* capped CeO<sub>2</sub> NPs shown in Fig. 4. The broad absorption O-H peak observed at 3750-3000 cm<sup>-1</sup> [12] From the FTIR spectra, the O-H stretching of residual alcohols, water and Ce-OH found for 3422 and 3442 cm<sup>-1</sup> for MEA and *G. superba* capped CeO<sub>2</sub> NPs respectively. The C-H vibration characteristic bands are observed at 2939 and 2911 cm<sup>-1</sup> for CeO<sub>2</sub>

NPs [13] Absorption band at  $1641\text{ cm}^{-1}$  is ascribed O-H symmetric stretching for MEA capped  $\text{CeO}_2$  NPs [13]. The Ce-O-Ce stretching frequency are found to be  $1008$  and  $1044\text{ cm}^{-1}$  for MEA and G. superba capped  $\text{CeO}_2$  NPs respectively. The Ce-O-C bending mode vibration is observed at  $687$  and  $682\text{ cm}^{-1}$  for both  $\text{CeO}_2$  NPs [14,15]. From the FT-IR results, the strong Ce-O stretching vibrations is centered at  $505$  and  $508\text{ cm}^{-1}$  for MEA and G. superb a capped  $\text{CeO}_2$  NPs respectively.

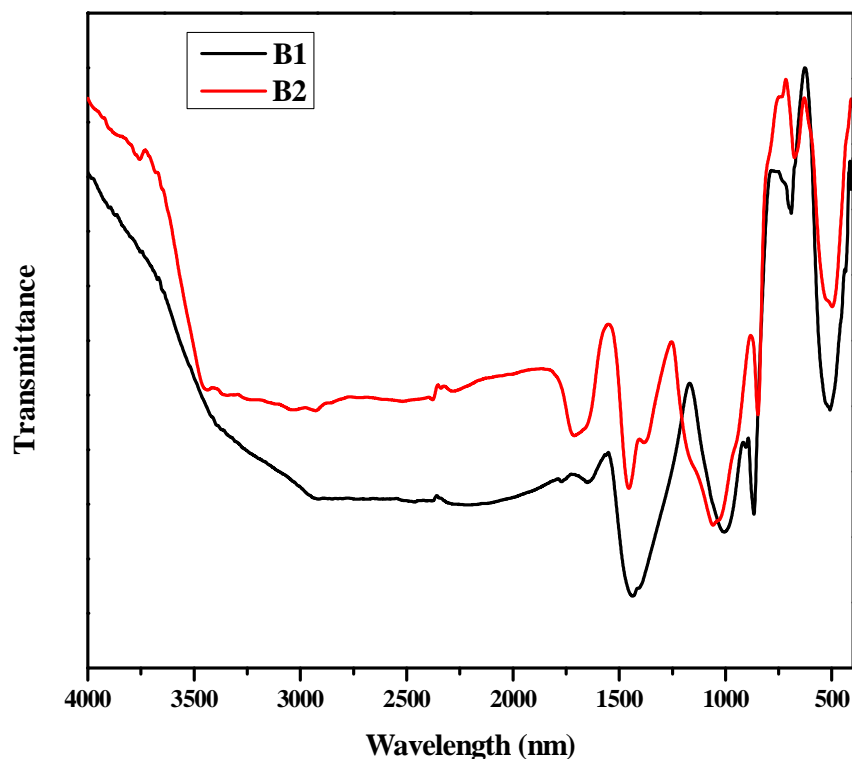


Figure 4. FT-IR spectra of MEA and G. superba capped  $\text{CeO}_2$  NPs.

#### D. UV-Vis Spectroscopic Studies

Figure 5 shows the UV-Vis absorption spectrum of MEA and G. superba capped  $\text{CeO}_2$  NPs. From the UV-Vis results, the absorption edge peaks are located at  $317$  and  $313\text{ nm}$  for MEA and G. superba capped  $\text{CeO}_2$  NPs, due to the photo excitation of electrons from the valence band to the conduction band. The absorption edge peak red shift is observed for MEA capped  $\text{CeO}_2$  NPs as compared to that of G. superba capped  $\text{CeO}_2$  NPs. This impact, the reduction of  $\text{CeO}_2$  band gaps caused by the G. superba capping effect. The band gap is calculated using tauc relation [16]. Considering direct band transition in  $\text{CeO}_2$  NPs, a plot between  $(\alpha h\nu)^2$  Vs.  $h\nu$  and extrapolating the linear portion of the absorption edge to find the intercept with energy axis is shown in Fig. 5 (a-b). Calculated band gaps of MEA and G. superbacapped  $\text{CeO}_2$  NPs values are found to be  $2.6\text{ eV}$  and  $2.95\text{ eV}$  respectively. The band gap of G. superba capped  $\text{CeO}_2$  NPs possess more than that of MEA capped  $\text{CeO}_2$  NPs, increasing the band gap may be due to the many organic components involved in the formation of nanoparticles. This result obey the quantum confinement effect shows the particles are in few nanometer level [10].

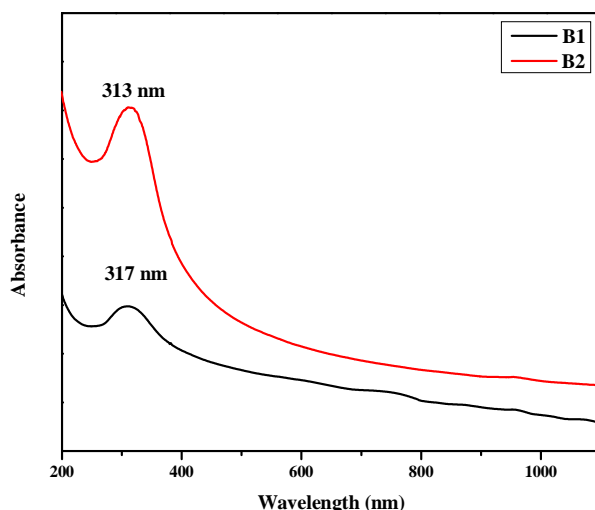


Figure 4. UV-Visible spectra of the MEA and G. superba capped CeO<sub>2</sub> NPs.

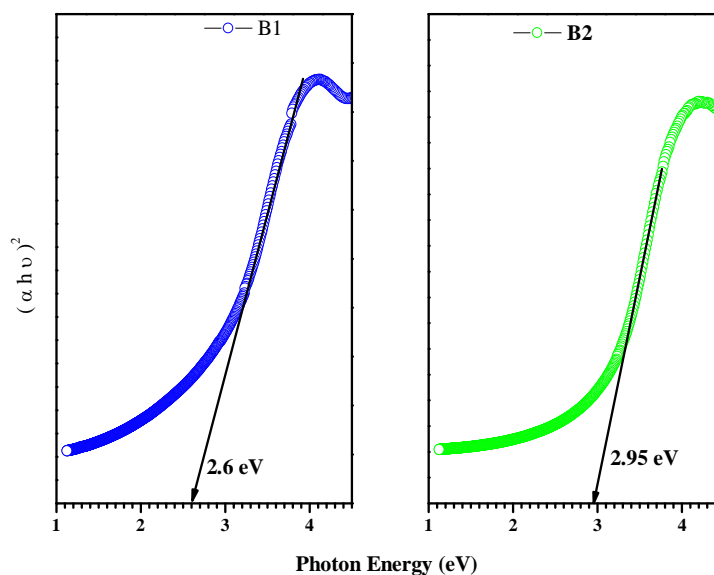


Figure 5 Band gaps of MEA and G. superba capped CeO<sub>2</sub> NPs.

### E. Photoluminescence spectroscopic studies

The room temperature photoluminescence emission spectra of MEA and G. superba capped CeO<sub>2</sub> NPs are shown in Fig. 6(a-b). The synthesized MEA and G. superba capped CeO<sub>2</sub> NPs were observed in the excited wavelength 325 nm. The PL emission wavelength is observed at (366 nm, 387 nm, 400 nm, 458 nm and 489 nm) and (389 nm, 414 nm, 439 nm, 457 and 482 nm) for MEA and G. superba capped CeO<sub>2</sub> NPs respectively. In case of MEA capped CeO<sub>2</sub> NPs, the two UV emission peaks observed at 366 nm and 387 nm are corresponding to the near band edge (NBE) emission, this is due to the recombination of free exactions[17]. The violet emission center at 400 nm, which is due to the charge transitions from the 4f band to the valence band of CeO<sub>2</sub> [18]. Blue emission observed at 458 nm is attributed to the localization of the energy levels among the Ce 4f and O2p bands. The blue-green emission centered at 485 nm, is described to surface defects. Blue shift observed for G. superba capped CeO<sub>2</sub> NPs emission values (389 nm, 414 nm, 439 nm, 457 and 482 nm) as compared to that of MEA capped CeO<sub>2</sub> NPs. This may occur from different origins, such as

electron phonon coupling, lattice distortion, localization of charge carriers due to interface effects and point defects. In PL spectra the defect level emission was reduced G. superba capped CeO<sub>2</sub> NPs. The optoelectronic properties mainly depend on the reduction of defect level in material, which influenced by electron phonon coupling interaction. In the present investigation, G. superba capped CeO<sub>2</sub> NPs defect level was decreased. In PL results provides strong support for the further development of extensive optical device applications.

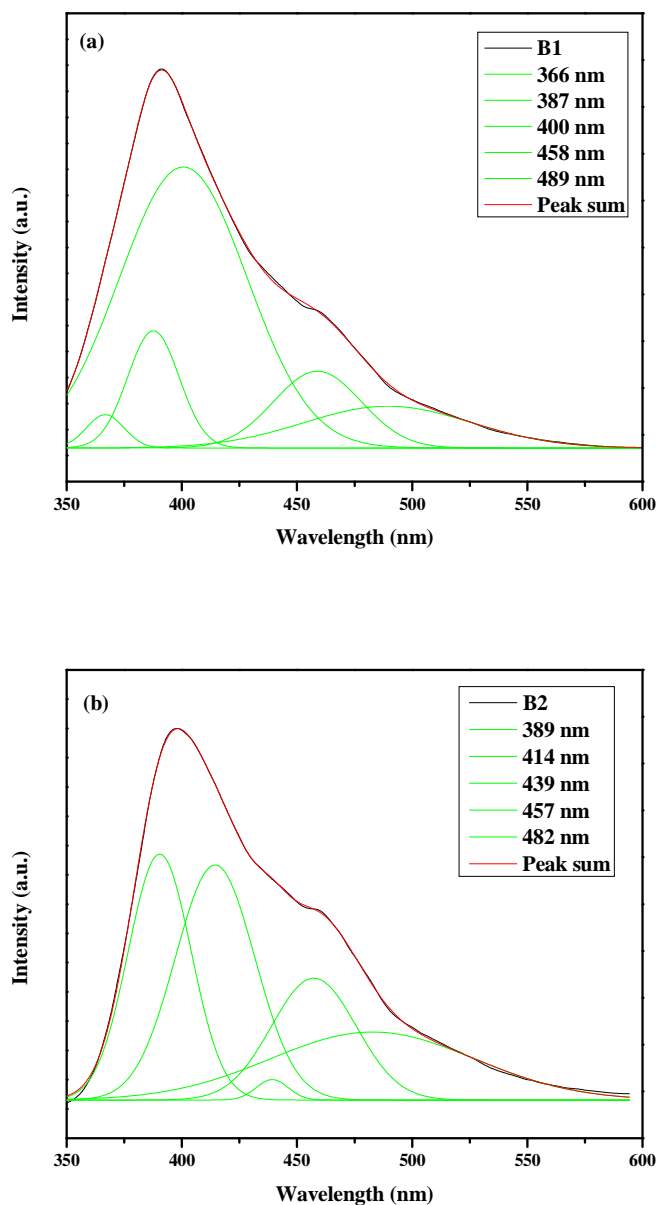


Figure 6 Photoluminescence spectra of MEA and G. superba capped CeO<sub>2</sub> NPs.

#### IV. CONCLUSIONS

In summary, the CeO<sub>2</sub> NPs were synthesized by co-precipitation and green method. Synthesized MEA and G. superba capped CeO<sub>2</sub> NPs were exhibited cubic phase, identified by X-ray diffraction studies. In the FESEM image, the both CeO<sub>2</sub> NPs were formed cubic structure. The Ce and O elemental composition were identified using EDAX spectra. Vibrational functional groups were identified using FT-IR spectra. From the UV-Vis studies, the absorption peaks edges were observed at 317 and 313 nm for both CeO<sub>2</sub> NPs respectively. In PL emission spectra the defect level emission was reduced G. superba capped CeO<sub>2</sub> NPs as compared to

the MEA capped CeO<sub>2</sub> NPs. The optoelectronic properties mainly depends on reduction of defect level in material, which influenced by electron phonon coupling interaction. In the present investigation, G. superba capped CeO<sub>2</sub> NPs defect level was decreased. In PL results provides strong support for the further development of extensive optical device applications.

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