RESEARCH PAPER

Fabrication of catalytically active nanocrystalline samarium (Sm)-doped cerium oxide (CeO₂) thin films using electron beam evaporation

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Abstract Samarium (Sm)-doped cerium oxide (CeO₂) thin films were fabricated using electron beam evaporation technique. The synthesized films were deposited either on glass or ITO substrates and studied their nature by annealing at different temperatures. The optical properties and other morphological studies were done by UV-Vis, XRD, XPS, SEM, EDS, and FT-IR analysis. XRD and XPS analysis clearly confirm the presence of Sm in the ceria site. From the SEM study, it was found that after annealing at high temperature (~ 300 or 500 °C), the particles size was reduced due to breakdown of large aggregates of particles which is also confirmed from UV-Vis, XPS, and XRD analyses. The FT-IR study proves the presence of -COO-, -OH, or ammonium group on the particles surface. The deposition of Smdoped CeO2 nanomaterials was found more feasible on

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N. Sutradhar · A. B. Panda Central Salt and Marine Chemical Research Institute (CSIR), G. B. Marg, Bhavnagar 364 002, Gujarat, India ITO substrate compared to that of glass substrate in terms of stability and depth of film thickness. The Sm-doped CeO₂ nanomaterial acts as a re-usable catalyst for the reduction of organic dye molecules in the presence of NaBH₄. The catalysis rate was compared by considering the electron transfer process during the reduction. The synthesized Sm-doped CeO₂ thin films might find wide variety of applications in various emerging fields like solid oxide fuel cells (SOFCs), oxygen sensor or as catalyst in different types of organic and inorganic catalytic reactions. The fabrication process is very simple, straightforward, less time consuming, and cost effective.

Keywords Samarium (Sm)-doped CeO_2 · Nanoparticles · Thin films · ITO · Glass · Catalyst

Introduction

Inorganic phosphors have attracted great attention due to their potential applications in flat panel display, field emission devices, cathode ray tubes, fluorescence applications, and application in optoelectronic devices (Mialon et al. 2009; Jadhav et al. 2009; Wang et al. 2007). The best phosphor material was found for rare earth oxides nanoparticles (NPs) doped with other material in comparison to other metal oxide nanomaterials (Das and Tan 2008; Wang et al. 2009). For these doped oxide NPs, the grain size plays a vital role as it affects emission lifetime and luminescence efficiency of NPs. Among the various rare earth oxide materials studied so far, cerium oxide (CeO₂) was found to be the best host material for other rare earth materials like samarium (Sm), erbium (Er), and europium (Eu). CeO₂ NPs have attracted great deal of interest due to its special properties like UV absorption capacity, high mechanical strength, high stability at elevated temperature, high hardness, high oxygen ion conductivity, and oxygen storage capacity (Gu and Meng 2007; Angel et al. 2008; Hassanzadeh-Tabrizi et al. 2008). Because of these unique properties, CeO₂ extensively used as gas sensor, luminescent material, UV-filters, catalyst in fuel cell technology, catalyst in oxidation of water, and so forth (Yamashita et al. 2002; Garzon et al. 2000; Larachi et al. 2002). Among the various doping materials, Sm-doped CeO₂ NPs are potentially important for the development of new luminescence devices (Souza et al. 2010). Moreover, Sm-doped CeO₂ NPs are the best material for solid oxide fuel cell (SOFC) applications in comparison to yttria-stabilized zirconium, which requires high operating temperature (Liu et al. 2010). There are extensive studies done on oxygen-ion conductivities of CeO2-based electrolytes doped with other rare earth ions like Sr²⁺, Y³⁺, Sm³⁺, Gd³⁺, etc. at various concentrations (Fu and Chen 2010; Steele 2000). Among these Sm^{3+} -doped CeO_2 observed to exhibit the highest oxygen-ion conductivity at a specific doping concentrations (Singh et al. 2007).

Several research paper reports that CeO₂-based thin films have high refractive index, dc permittivity, and transparency in the visible and IR region (Logothetidis et al. 2004; Patsalas et al. 2002). The normal band gap of CeO₂ films varies between 3.2 and 3.6 eV whereas higher value up to 4.1 eV is also reported for other different CeO₂ nanostructures. Due to these versatile properties, CeO₂-based films are attractive for research in optical, microelectronics, and optoelectronic devices (Logothetidis et al. 2004; Patsalas et al. 2002).

In literature, there are several reports for the synthesis of CeO_2 NPs but Sm^{3+} -doped CeO_2 NPs are not much. For example, CeO_2 NPs were synthesized by solution-based hydrothermal method (Xu et al. 2002). Anisotropic CeO_2 NPs were prepared by polyol method and thermostatic bath approach (Chen et al. 2006). Similarly, CeO_2 microplates of triangular shapes were prepared via the decomposition of cerium hydroxyl carbonates using well-known hydrothermal

process (Hyun et al. 2002). There are several techniques employed for the deposition of doped CeO₂ films on different substrates like spin-coating, sol-gel, sputtering, chemical vapor deposition (CVD), tape casting, and electron beam evaporation (Liu et al. 2009; Yi et al. 2010; Chen et al. 2010; Jasinski et al. 2003; Mansilla 2009). Among these vapor processing methods are more expensive and complex to make thin and dense film. Moreover, it is difficult to control their thickness, porosity, crystalline structure, and other parameters. The electron beam evaporation method was found suitable for making very thin and dense films with controllable thickness, porosity, and crystalline structure. Moreover, electron beam evaporation method found to be a very straightforward preparation process and results uniform, homogeneous and crystalline films in a very shorter time scale.

It is well known that nanoscale materials have been widely considered as effective catalyst because of their high surface area and high density of active sites. Different transition metals like Au, Ag, Pt, Ir NPs, etc. are found as outstanding candidates due to their high activity, stability, and selectivity under different reaction conditions (Kundu et al. 2004, 2009a, b, c, 2010; Yinghuai et al. 2008). It has been reported earlier that metallic NPs can be used as an excellent catalyst in many catalysis reaction like oxygen evolution reaction (OER) (Marshall et al. 2006), oxygen reduction reaction (ORR) (Liu and Zhang 2008), and for direct methanol fuel cell (Papageorgopoulos et al. 2007) reactions for methanol crossover problems. The catalytic rate of NPs strongly depends on the particle size and shapes. With the change in particle size and shape, the catalytic rate is also changed as reported by Kundu et al. for the reduction of aromatic nitro compounds using Au and Rh NPs as catalyst (Kundu et al. 2009a, b, c). Recently, oxide materials supported by other materials are also found for the use of different catalytic reactions (Carrettin et al. 2004; Zhou et al. 2010; Fu et al. 2003; Yeung and Tsang 2009). For examples, Au NPs supported by CeO₂ was used as a catalyst for CO oxidation (Carrettin et al. 2004). Recently, Zhou et al. (2010) synthesized Pt/CeO_2 nanocomposites by a microemulsion mediated method and observed high catalytic activity of Pt/CeO₂ nanocomposites for CO oxidation. Few others observed that rare earth oxides mainly ceria-based materials are attractive with extensive applications in conversion catalysts, three-way catalysts (TWCs), fuel cells, solar cells, gates for metal

oxide semiconductor devices, and phosphors (Fu et al. 2003). Another study on ceria-based materials towards exhaust emission has demonstrated that the capacity for rapid storage and release of oxygen at their surface is mainly associated with the ceria–noble metal interaction (Yeung and Tsang 2009).

In this study, we prepared nanocrystalline Sm-doped CeO_2 thin films by electron beam evaporation technique. The thin films of Sm-doped CeO_2 were deposited either on glass or on ITO substrates. The characteristics of the thin films on both the substrates were analyzed by UV–Vis, XRD, XPS, SEM, EDS, and FT-IR analyses. The fabricated Sm-doped CeO_2 thin film was found to serve as an effective catalyst for the reduction of organic dye molecules in the presence of NaBH₄ in a short reaction scale. To the best of our knowledge, the fabrication of doped oxide nanomaterials in thin film form and their catalytic activity for dye reduction has not been explored before. The preparation process of the thin film is simple, straightforward, less time consuming, and cost effective.

Experimental

Reagents

Sm-doped CeO₂ NPs were supplied from CSIR-Bhavnagar and used for our study to make the thin films. The detailed preparation procedure is given elsewhere (Sutradhar et al. 2011). We used two types of substrates, glass and indium tin oxide (ITO), both having dimensions 7.5×2.5 cm. A graphite crucible was used for keeping the Sm-doped CeO₂ nanopowders during electron beam evaporation. The glass and ITO substrate were purchased from local Balaji Scientific Company, Karaikudi, Tamilnadu. The graphite crucible was obtained from Shree Shastha Scientific Company, Karaikudi, Tamilnadu. Two different dye molecules like methylene blue (C₁₆H₁₈N₃SCl, MB) and rhodamine B (C₂₈H₃₁N₂O₃Cl, RhB) were purchased from Sigma-Aldrich and used as received. Sodium borohydride (NaBH₄) (Sigma-Aldrich) was used fresh daily for all the reduction reactions.

Instruments

Sm-doped CeO_2 thin films were prepared by electron beam evaporation technique using a HIND HIVAC

vacuum coating unit with electron beam power supply. The detailed preparation procedure is given below. The UV-visible (UV-Vis) absorption spectra were recorded in a Hitachi (model U-4100) UV-Vis-NIR spectrophotometer equipped with a 1 cm quartz cuvette holder for liquid samples. The scanning electron microscopy (SEM) analyses were done with HITACHI Model S-3000H instrument. The energy dispersive X-ray spectroscopy (EDS) analysis was done with the same SEM instrument with a separate EDS detector. The fabricated thin films were characterized by X-ray diffraction (XRD). The analysis was done with a scanning rate of 0.020 s⁻¹ in the 2θ range 20-80° using a PAN analytical Advanced Bragg-Brentano X-ray powder diffractometer (XRD) with Cu K_{α} radiation ($\lambda = 0.154178$ nm). The X-ray photoelectron spectroscopy (XPS) analysis was carried out using a ESCA model VG 3000 system X-ray photoelectron spectrometer with monochromatic Mg K_{α} line (1253.6 eV) radiation. The instrument integrates a magnetic immersion lens and charge neutralization system with a spherical mirror analyzer, which provides real time chemical state and elemental imaging using a full range of pass energies. The emitted photoelectrons were detected by the analyzer at a passing energy of 20 eV with energy resolution of 0.1 eV. The incident X-ray beam was normal to the sample surface, and the detector was 45° away from the incident direction. The analysis spot on the sample was 0.4×0.7 mm. The overall energy resolution was about 0.8 eV. Samples for the survey spectrum was recorded in the 0-1100 eV kinetic energy by 1 eV steps whereas high resolution scan with 0.1 eV steps were conducted over the following regions of interest: Ce3d, Sm3d, O1s, and C1s. The O1s and C1s spectra are not shown in the paper. The Fourier transform infrared spectroscopy (FT-IR) analysis was done with the model Nexus 670 (FTIR), Centaurms 10X (Microscope) having spectral range 11,000–375 cm^{-1} with a MCT-B detector.

Preparation of Sm-doped CeO₂ thin films by electron beam evaporation

A small amount (approx. 1 g) of Sm-doped CeO_2 powder was taken into graphite crucible. The powder was heated by means of electron beams collimated from the dc heated tungsten filament. Initially, the Smdoped CeO₂ powders were made into pellets and placed inside the vacuum chamber. Chamber was closed and evacuated using the rotary and diffusion pumps. After sufficient vacuum is achieved (i.e., high vacuum of the order of 1×10^{-5} mbar), the evaporation process was started. That powder surface was bombarded by 270° deflected electron beam with an accelerating voltage of nearly 5.4 kV and a power density of 1.5 kW/cm² that was focused on the surface of the pellets. That evaporated particles were deposited as thin films either on the glass or ITO substrates at a pressure about 1×10^{-5} mbar. The homogeneous distribution of evaporated particles on the substrate was attained by continuously rotating the substrate

during deposition. The distance of the substrate from the target material is ~11.5 cm. Thin and uniform layers of Sm-doped CeO₂ films are formed within 1 h. The observed films are uniform, transparent and adherent to both the substrates. The formation of the thin films by electron beam evaporation method was schematically shown in Scheme 1. The measured thickness of the coating was ~0.3 μ m. After the formation of films, we analyzed the samples at room temperatures (RTs) as well as after annealing at various temperatures. After taking these substrates several characterizations like UV–Vis, XRD, XPS, SEM, EDS, and FT-IR analyses were done to



Scheme 1 Schematic presentation for fabrication of Sm-doped CeO_2 thin films on different substrate by electron beam evaporation techniques

investigate the morphology of the thin films on both the substrates.

Reduction of organic dye molecules using Sm-doped CeO₂ thin films as catalyst

We studied the catalytic reduction of two different organic dye molecules like MB and RhB in the presence of NaBH₄ using Sm-doped CeO₂ thin films as catalyst. A stock solution of two different dyes (10^{-2} M) was prepared and a stock solution of NaBH₄ (0.1 M) was made fresh daily. The NaBH₄ solution was stored in the refrigerator in the dark. For the reduction reaction, the dye solution was diluted to a concentration of 10^{-5} M. The whole reduction reaction was carried out using a small 20 mL stopper glass bottle. For the catalytic reduction, 10 mL of (10^{-5} M) dye solution was mixed with 2 mL of (0.1 M) NaBH₄ solution and the solution was mixed well by shaking in hand. Finally, Sm-doped CeO2 thin films on ITO substrate were dipped in the solution, shaking in hand, and the progress of the reduction was monitored spectrophotometrically in situ using an UV-Vis spectrophotometer. The reduction of the dyes started within a couple of minute and completed in 65 min, as observed from the UV-Vis spectrum. After the completion of the reduction, the bluish color MB and the pinkish color RhB became colorless, which was further confirmed from the UV-Vis spectrum. After the complete reduction, the catalysis reaction rate was calculated and a comparison study was made.

Results and discussion

UV-Vis spectroscopic study

Figure 1A and B shows the UV–Vis absorption spectra of the Sm-doped (5%) CeO₂ thin films deposited on glass and ITO substrates, respectively. Both the cases, the absorption spectra are recorded by preparing the samples at RT and annealing at different temperatures up to 500 °C. Figure 1A shows three different bands for the same samples but prepared in three different temperatures using glass substrates. From the spectra it was seen that there is a sharp band ~300 nm but the spectra remains flat (without any hump or peak) in the region 350–2,500 nm range. The absorption band maxima (λ_{max}) for the sharp band at RT comes around 305 nm but with increasing temperature it decreases to 292 nm (at 500 °C). This might be due to the breakdown of bigger size particles to smaller particles with increasing temperature. Figure 1B shows the UV-Vis absorption spectra of the Sm-doped CeO₂ films on ITO substrates prepared exactly like on glass, i.e., at RT and annealing at different temperature up to 500 °C. Like before (glass substrate), there is a sharp absorption band around 300 nm but at higher wavelength the spectra becomes flattened without any noticeable peaks. The absorption band maxima shifted from 324 nm (at RT) to 284 nm (at 500 °C), which signify the formation of smaller particles at higher temperature having similarity with the glass substrates. It was reported in literature that metal NPs when formed smaller size particles the λ_{max} shifted toward shorter wavelength (blue shift) side whereas when the smaller particles aggregate to form bigger/larger size particles the λ_{max} value shifted toward longer wavelength (red shift) side (Pal 2004). We also analyzed the transmittance spectra of the films (not shown here) in addition of adsorption spectra both on glass and ITO substrates at different temperatures like RT, 300, and 500 °C. In all cases, all the films are having transmittance >65 % and there is no transmittance below 300 nm. From all the absorption data, the band gap energy (E_g) of the thin films was calculated using the Tauc's equation:

 $\alpha h v = A \left(h v - E_{\rm g} \right)^n$

where α is the absorption coefficient and *n* is a constant which depends on probability of the transition. Figure 1C shows the variation of $(\alpha hv)^2$ vs hv curve which is a straight line at higher hv values (>3.5) indicating direct optical transition. Putting energy axis x = 0, the band gap energy E_{g} can be calculated by extrapolating the linear portion of the graph. Figure 1E is recorded for the thin films on glass substrate, whereas Fig. 1D for the ITO substrate. According to the literature, the direct band gap comes in the range 3.2-3.5 eV which matched with our result also (Patsalas et al. 2002; Guo et al. 1995). Guo et al. (1995) and Murali (2008) observed band gap energy in the range 3.5-3.6 eV. Zhang et al. (2006) and Tsunekawa et al. (2003) observed band gap energy 3.9 and 4.1 eV, respectively. In our study for the glass substrate, we observed band gap energy 3.7, 3.8, and 3.9 eV at RT, 300, and 500 °C, respectively. Thus, the





Fig. 1 A The UV–vis absorption spectra of the Sm-doped (5%) CeO₂ thin films recorded in glass substrate. The absorption spectra is recorded at room temperature (RT) and annealing at 300 and 500 °C. **B** The UV–vis absorption spectra

of the Sm-doped CeO₂ films on ITO substrate prepared at different temperatures like glass substrate. **C**, **D** The variation of $(\alpha hv)^2$ vs *hv* curve on glass and ITO substrate, respectively

band gap energy is increased with increasing annealing temperature. On the other hand, the band gap energy decreases with increasing annealing temperature for the same sample prepared on ITO substrate. Here, we observed a band gap energy decrease from 4.3 eV (at RT) to 4.0 eV (at 500 °C). This variation of E_g values for different substrates, probably due to different adhesion and attaching mechanism with the substrates, as having good agreement with the previous reports by Zhang et al. (2006) and Tsunekawa et al. (2003). Scanning electron microscopy and energy dispersive X-ray spectroscopy analysis

The SEM images of the undoped CeO_2 and Sm-doped CeO_2 films on glass and ITO substrates are shown in Fig. 2. Figure 2A and B shows the SEM images of undoped CeO_2 samples using glass and ITO substrates, respectively. From the images, we can see the big size aggregates of CeO_2 particles without much individual particles. Figure 2C, D, and E are the SEM images of the Sm-doped (5 %) CeO_2 thin films



Fig. 2 A, **B** The SEM images of undoped CeO₂ on glass and ITO substrate, respectively. **C**, **D**, **E** The SEM images of the Sm-doped (5 %) CeO₂ film prepared at RT, annealed at 300 °C, and

annealed at 500 °C, respectively, using ITO substrate. F The average particles size distribution for the annealed sample at 500 °C

prepared on ITO substrates at various temperatures, respectively. Due to low coating thickness and instrumental problem we could not able to collect the images from the glass substrate for the doped samples. Figure 2C is the SEM image of the Sm-doped (5 %) CeO₂ thin film at RT. Similarly, Fig. 2D and E shows the SEM images of the Sm-doped (5 %) CeO₂ thin film annealed at 300 and at 500 °C, respectively. From the images, it was seen that initially at RT or at 300 °C temperature the particle size was large but after annealing to 500 °C, the particle size decreases. The approximate particle sizes for the RT or 300 °C annealed samples were $\sim 600 \pm 150$ nm ranges (histogram plot not shown here). Most of the places they formed aggregated big lumps. After annealing the samples to 500 °C, we observed mostly individual particles and the average size of the particle calculated from the histogram plot is $\sim 290 \pm 80$ nm as shown in Fig. 2F. Moreover, from these images we get an idea that with increasing temperature during annealing, the larger particle break down and produce smaller size particle but further analysis is needed to get a complete idea about the size change of the particles with different environment. EDS analysis was done to identify the elements present in the sample. The EDS spectra of the same thin film were taken using the ITO substrate during SEM study (not shown here). From the spectrum, we observed the expected peaks those came from the samples and from the substrate. Due to very less percentage (5 %) of doping material and thin film thickness, we have not observed any intense peaks for the Sm but observed clear evidences from XRD, XPS, and FT-IR analyses those are discussed later.

X-ray diffraction analysis

Figure 3 shows the XRD pattern of Sm (5 %)-doped CeO₂ thin films. We took the XRD pattern both on glass and ITO substrates at RT and after annealing at 300 and 500 °C temperature. From the glass substrate, the pattern we obtained has no specific peaks at RT as well as after annealed at different temperatures like 300 and 500 °C (not shown here). This confirms the absence of crystalline nature in the sample. Now, the same sample is deposited on ITO substrate and analyzed by XRD. Figure 3 shows the XRD pattern of Sm-doped CeO₂ thin films on ITO substrate that prepared at RT and after annealing at different



Fig. 3 The XRD pattern of Sm (5 %)-doped CeO_2 thin films taken using ITO substrate. The sample was prepared at RT and after annealing at different temperature

temperatures. For RT sample, we observe only one intense peak at 2θ value 28.52, having d_{spacing} is 3.12 Å, signify the (111) plane of diffraction for cubic fluorite structure of CeO₂ which matched with standard JCPDS (89-8436). The grain size calculated from the XRD line width is ~ 48 nm. After annealing the sample at different temperatures we observed several other peaks. After annealed to 100 °C, we observed three other different peaks for CeO₂ in addition with CeO_2 (111) peak with a slight shift from undoped CeO_2 . The peaks are observed at different 2θ values like 30.12 (for the ITO substrate for (033) plane), 50.40, and 59.96 (not shown here), respectively. It indicates that with increasing temperature the crystallinity of the sample becomes better compared to RT. Now with further increase in temperature (at 300 °C), the well intense CeO₂ (111) peak disappeared but other peaks for the substrate and the host matrix remains in the same place with slight decrease in peak height. This signifies the little change in crystallinity in the sample. Now, when the sample was annealed at 500 °C, all the peaks for host CeO₂ almost disappeared and only the substrate peak was observed at the same 2θ value for (033) plane of diffraction with a noticeable decrease of intensity. The approximate peak positions were indicated with black arrows. Zivkovic et al. prepared various % of Sm-doped CeO₂ samples and observed that after 15 % doping, the host peaks mostly disappeared (Zivkovic et al. 2011). Their results found similarity with our results although the doping % was less in our case. The crystalline size of the material after annealing to 200 °C was 17.14 nm whereas after 300 °C, it decreases to 13.70 nm. It was reported in literature that although the Sm ions have larger ionic radii, they occupy the ceria sites due to the high doping (>5 %) percentage (Fujihara and Oikawa 2004). This high level of doping (5 %) can create more oxygen vacancies in ceria host for charge compensation. Thus, the formation of the nanocrystalline structure indicated by XRD was matched with the SEM images as shown in Fig. 2. Table 1 shows the XRD data those are calculated at various temperatures for the ITO substrate.

X-ray photoelectron spectroscopic study

XPS was carried out to identify the chemical composition and valence state of the elements in the Sm-doped CeO₂ nanomaterials. Figure 4 shows the XPS analysis of Sm-doped CeO₂ nanomaterials. The part (A) of Fig. 4 shows the overall survey spectrum containing peaks for Ce, Sm, O, and C. The part (B) shows the Ce core level spectrum of CeO_2 in the region 860–925 eV. From the spectrum, it is shown that both +3 and +4 valence states are present there due to very high non-stoichiometric nature of the material. The main intense peak of Ce³⁺ $3d_{3/2}$ and $Ce^{3+} 3d_{5/2}$ are located at a binding energy of 901.5 and 882.2 eV, respectively. The other peaks for $Ce^{4+} 3d_{3/2}$ and $Ce^{4+} 3d_{5/2}$ are shown at binding energies of 916.6 and 898.3 eV, respectively. Thus, from the Fig. 4 part (B) it is clear that dominating spin-orbit doublet of $3d \text{CeO}_2$ is for Ce^{3+} and the smaller doublet is for Ce⁴⁺ at higher binding energies. From the deconvolution result, we also observed additional satellite peaks for Ce^{3+} but not in Ce^{4+} . It is reported earlier that rare earth compounds having unpaired electron can give raise an extra satellite peak due to photoelectron energy gain and photoelectron energy loss. Moreover, Ce^{3+} has one 4f electron but Ce⁴⁺ has no. Thus, the extra electron can go additional electronic transition and give raise the satellite peaks. These spectra are fully consistent with the previous results by others (Sutradhar et al. 2011; Reddy et al. 2010). Figure 4, part (C) shows the Sm3d peaks which confirm the doping of Sm in CeO_2 nanomaterials. The peak intensity is not that much

XRD—experimental values								
Position (2θ)	Height (cts)	FWHM (2θ)	d-spacing (Å)	Relative intensity (%)				
$CeO_2 + 5 \% Sm$	ITO (RT)							
28.6175	225.90	0.1800	3.11934	100.00				
$CeO_2 + 5 \% Sm$	n—ITO (100 °C)							
28.6090	39.69	0.2007	3.12026	53.92				
30.1203	73.62	0.2676	2.96705	100.00				
50.4064	22.34	0.4015	1.81043	30.34				
59.9639	11.75	0.9792	1.54144	15.96				
$CeO_2 + 5 \% Sm$	n—ITO (200 °C)							
28.6396	64.31	0.2786	3.11699	100.00				
30.0957	61.98	0.3346	2.96942	96.38				
50.5196	20.32	0.5353	1.80664	31.60				
60.0789	13.83	0.9792	1.53876	21.51				
$CeO_2 + 5 \% Sm$	n—ITO (300 °C)							
30.0971	54.72	0.3346	2.96929	100.00				
50.3086	21.43	0.6691	1.81373	39.16				
60.0414	9.90	0.9792	1.53964	18.08				
$CeO_2 + 5 \% Sm$	n—ITO (500 °C)							
30.2087	20.83	0.4896	2.95611	100.00				

Table 1XRD calculatedvalues at differenttemperatures for the ITOsubstrate







Fig. 4 The XPS spectrum of Sm-doped CeO_2 nanomaterials. The part (**A**) shows the overall survey spectrum containing peaks for Ce, Sm, O, and C. The part (**B**) shows the Ce core level

strong due to low doping concentration of the material. The core level Sm $3d_{3/2}$ and Sm $3d_{5/2}$ peaks are observed at binding energies of 1107.4 and 1080.45 eV, respectively. The main XPS peak for O1s is shown around 529.4 eV (not shown here). A small hump is also noticeable at 531.6 eV which is assigned to the adsorbed oxygen in CeO₂. The peak position of oxygen is slightly shifted due to incorporation of Sm ion with CeO₂ when we compared the peaks with pure CeO₂ nanomaterials (Reddy et al. 2010). From the deconvolution results, we got another small intense peak for O1s at 533.3 eV which is not due to the presence of Ce³⁺ or Ce⁴⁺ but probably due to the presence of OH on the sample surface. The C1s peak was observed in between the range of 280–295 eV (not shown here). Hence, these

spectrum of CeO_2 in the region 860–925 eV. Part (C) shows the Sm 3d peaks which confirm the doping of Sm in CeO_2 nanomaterials

XPS analysis clearly confirms the doping of Sm and successive formation of Sm-doped CeO₂ nanomaterials.

Fourier transform infrared spectroscopic study

FT-IR was usually employed for an additional probe to evidence the presence of OH group as well as other organic or inorganic species in the sample. As discussed earlier, Sm-doped CeO₂ was prepared using the hydrothermal condition by the reaction of SmCO₃ with CeCO₃ in the presence of NH₄CO₃. Figure 5 shows the FT-IR spectra of 5 % Sm-doped CeO₂ nanomaterials at different calcination temperatures using different substrates. Figure 5A shows the FT-IR spectrum for the above sample when we used glass as





substrate. In the Fig. 5A, we observed three spectrum indicated with A (at RT), B (after annealed to 300 $^{\circ}$ C), and C (after annealed to 500 °C). For each case, we take the sample out from the system, annealed inside a furnace at a specific temperature and then measured the data. For RT and 300 °C sample, we observed a broad peak in the range $3000-3600 \text{ cm}^{-1}$ due to stretching of O-H bonds vibrations. When we annealed the sample up to 500 °C, this band is weaker but remains still probably due to adsorption of moisture during testing. We observed a strong peak at 2356 cm^{-1} for the sample studied at RT and annealed at 300 °C. The same peak was found weaker when we annealed to 500 °C. This broad peak is for the -N-H stretching vibration due to the presence of ammonium carbonate with the nanomaterials. At higher temperature (500 °C), this peak includes weaker due to removal of the compound from the nanomaterials surface. A small intense peak at 1772 and 1641 cm⁻¹ for RT and 300 °C annealed sample respectively is due to the presence of carbonyl group in ammonium carbonate on the surface of Sm-doped CeO₂ nanomaterials. These bands are not visible when we annealed the same sample at 500 °C which confirms the removal of the compound from the nanomaterials surface at higher temperature. Although there is a shifting of carbonate peak towards lower wavelength signify that there might be a complexation of cerium carbonate with ammonium carbonate. In addition to the high intense band at 900–1300 $\rm cm^{-1}$, the band due to stretching frequency of Ce-O can be observed below 700 cm⁻¹ mostly in the range 400–650 cm^{-1} . These results found similarity with other reports for CeO2 or Sm-doped CeO2 (Zhang et al. 2007; Phoka et al. 2009). Now, when we analyzed the sample that deposited on ITO substrate, we observed similar type of result like glass substrate. These results for three different temperatures like RT, 300, and 500 °C are shown in Fig. 5B. From the figure, it was seen that for RT sample there is no sharp peak in the range $3000-3600 \text{ cm}^{-1}$, signify the absence of water or the % is very less. However, in the other two cases, we observed small intense peaks probably due to absorption of moisture from air during analysis. The strong peak at 2355–2358 cm^{-1} is due to -N-H stretching vibration, as discussed earlier for the same sample prepared in glass substrate. We observed another peak at $\sim 1596 \text{ cm}^{-1}$ for the sample annealed at 300 and 500 °C but not clearly visible for the RT sample. That peak is signified for the asymmetric stretching vibration of the -COO⁻ group. The -COO⁻ peak is not fully noticeable for RT sample where the -OH stretching peaks is also not fully visible. This speaks that moisture is adsorbed in other two samples more during the analysis. The presence of -COO⁻ peak proved that it is attached with the nanomaterials

through bidentate coordination bonding. The all other peaks from the range 400–1261 cm^{-1} is due to stretching vibration of Ce-O as discussed earlier for the glass substrate. The main peak at 1261 cm^{-1} is shifted with increasing heating probably due to more oxygen vacancies. However, this claim is not fully clear at this stage and further study is warranted. Thus, based on the above analysis, we conclude that Smdoped CeO₂ nanomaterials surface are probably bound with functional group like -OH or -COO⁻. The presence of ammonium group also confirms that the -N-H stretching peaks come mostly from the NH₄CO₃ used during the synthesis process. Moreover, in both the samples (glass and ITO), the adsorbed water molecules are on the surface of the Sm-doped CeO₂ nanomaterials.

Catalytic reduction of organic dye molecules using Sm-doped CeO_2 thin films as catalyst

In this catalysis study, we choose two different dye molecules with different chemical structures and surface charge. We chose one cationic dye, MB and one anionic dye RhB for the entire catalysis study. It is well known that textile dyes and other commercial colorants have become a major concern to environmental pollution (Stylidi et al. 2003). Many dye molecules were used as commercial colorants in dye industry as they are highly soluble in water and used for deep dyeing. As a result, waste water becomes contaminated and scientists are searching a suitable method to degrade these dyes to prevent the waste water contamination. Here, we studied the catalytic efficiency of Sm-doped CeO₂ thin films for the reduction of two different organic dye molecules using NaBH₄ as a reducing agent. For the catalysis study, a thin film of Sm-doped CeO₂ on ITO substrate (surface area $\sim 1.2 \text{ cm}^2$ and film thickness $\sim 0.3 \,\mu\text{m}$) was dipped in the solution containing the dye and NaBH₄. Once the reduction is complete, the substrate was taken out from the solution, washed several times with DI water, dry it and reused for several cycles. This is very important to note that the catalyst we used as a thin film on ITO substrate can be reused several times which is not possible for the other nanomaterials those are made in solutions. There are a couple of methods reported in literature for the degradation of dye molecules (Kamat et al. 1991; Kosanie and Trickovic 2002). Most of the methods require harsh condition for the reduction, multiple steps, longer time, and moreover do not seem to be environmental friendly. There are several groups studied the dye reduction in surfactant media using UV-irradiation (Kosanie and Trickovic 2002; Kundu et al. 2006). Here, in our study, we reduced the dye molecules using NaBH₄ in the presence of Sm-doped CeO₂ thin films as a catalyst. The reduction was done at RT and the major advantage was that we could follow the reaction steps using UV-Vis spectrophotometer. The pH of aqueous MB and RhB (10^{-5} M) solutions are 7.50 and 6.76, respectively, and for 0.1 (M) NaBH₄ is 10.5. In our study, the reduction of the dyes using NaBH₄ is very slow in the absence of thin films of Sm-doped CeO2 nanomaterials. On the other hand, the reduction of the dyes in the presence of Smdoped CeO₂ thin films but in the absence of NaBH₄ does not take place at all even after a couple of days. Thus, a proper combination of dye molecules, NaBH₄ and the thin films of nanocrystalline Sm-doped CeO₂ is important. The absorption maxima of MB and RhB are peaked at 663.5 and 551 nm in the UV-Vis spectrum respectively. The dye solution mixed with NaBH₄ and Sm-doped CeO₂ thin films was dipped in the solution mixture; the reduction started spontaneously which could be easily monitored using an in situ UV-Vis spectrophotometer. Figure 6A shows the successive reduction of MB curve with time and the reduction is completed just after an hour. Figure 6B shows the corresponding \ln (Abs) vs time (T, min) plot for the same and the rate constant value for the reduction is 5.73×10^{-2} min⁻¹. Similarly, Fig. 6C and D shows the successive reduction of RhB absorption maxima (at 551 nm) with time and the corresponding ln (Abs) vs time (T, \min) plot, respectively. The reduction is completed just after 29 min and the constant value for the rate reduction is 1.61×10^{-1} min⁻¹. The overall concentrations of the dye molecules, concentration of NaBH₄, surface area of the ITO substrate used as catalyst, reduction time, and rate constant values were summarized and are listed in the Table 2. From the Table 2 it is clear that the reduction is much faster with RhB and slower with MB. Both the processes maintained the first-order reduction kinetics. In the reduction, NaBH₄ molecules transfer electron to the dye molecule via Sm-doped CeO₂ thin films and the dye molecule gets reduced and became colorless. The picture of the oxidized form of the dye molecule is shown in insets of Fig. 6A and C for MB



Fig. 6 The UV–vis absorption spectrum for the reduction of dye molecules with NaBH₄ using Sm-doped CeO₂ thin films as catalyst. **A** UV–vis spectrum for the successive reduction of MB at 663.5 nm and **B** is the ln(abs) vs time (*T*) plot having the rate constant value of 5.73×10^{-2} min⁻¹. **C**, **D** are the UV–vis

spectrum for the successive reduction of RhB at 551 nm and ln(abs) vs time (*T*) plot, respectively, having rate constant value of 1.61×10^{-1} min⁻¹. The insets of (**A**, **C**) show the corresponding oxidized form of the dye images and (**B**, **D**) show their colorless reduced product

Table 2 The final concentrations of the dye molecules, concentration of NaBH₄, surface area and thickness of the thin films, reduction time and rate constant values for the reduction of dye molecules using Sm-doped CeO_2 thin films as catalyst

Name of the dye molecules	Final conc. dye (M)	Final conc. of NaBH ₄ (M)	Surface area of the Sm- doped CeO_2 thin film (cm^2)	Approx. thickness of the Sm-doped CeO_2 thin films (μ m)	Time for full reduction (min)	First-order rate constant $(k) (\min^{-1})$	Correlation coefficient (<i>R</i>)	Standard deviation (SD)
Methylene blue (MB)	8.92×10^{-6}	8.92×10^{-3}	1.2	0.3	55	5.73×10^{-2}	0.964	0.407
Rhodamine B (RhB)	8.92×10^{-6}	8.92×10^{-3}	1.2	0.3	25	1.61×10^{-1}	0.981	0.305

and RhB, respectively. The reduced colorless forms of dyes are shown in the insets of Fig. 6B and D for MB and RhB, respectively. The fastest reduction for RhB is probably due to better adsorption of the dye on the

surface of the Sm-doped CeO_2 thin films. The RhB structure contains both N and O on its skeleton which can absorb strongly with the NPs surface resulting fast electron transfer. The slow reduction rate observed for



MB in comparison to RhB is probably due to weaker adsorption of the dye on the surface of the Sm-doped CeO₂ thin films so the electron transfer is somewhat slower. The overall dye reduction process is schematically shown in Scheme 2. At this point, we are not fully confirmed about the insight mechanisms of the different reduction rates for different dyes. In future, we will investigate by changing the thickness of thin film, annealing the thin film at different temperatures and changing the size and shapes of the nanomaterials to get a clear idea about the reaction mechanisms. In summary, using the Sm-doped CeO₂ thin films as reusable catalyst it is possible to reduce various organic dyes that might find important applications in dying industry and for environmental studies.

Conclusion

In conclusion, we have successfully fabricated Smdoped CeO₂ thin films by electron beam evaporation technique. We deposited the thin films both on glass and ITO substrates and studied their nature at RT and by annealing at different temperatures. The optical property and other morphological studies were done by UV–Vis, XRD, XPS, SEM, EDS, and FT-IR analysis. XRD, XPS, and FT-IR analyses clearly confirm the presence of Sm in the ceria site. From the SEM study, it was found that after annealing at high temperature (~300 or 500 °C), the particle size reduced due to breakdown of larger particles. This was matched with the results from UV–Vis, XRD, and XPS analyses. FT-IR study proves the presence of – COO-, -OH, or ammonium group on the particles surface. The deposition of Sm-doped CeO₂ nanomaterials was found more feasible on ITO substrate compared to glass in terms of stability and depth of film thickness. This present process might give an idea for the easy fabrication of other doped oxide materials with different morphology. The fabricated Sm-doped CeO₂ thin films show excellent catalytic activity for the reduction of different organic dye molecules in the presence of NaBH₄. The Sm-doped CeO₂ nanomaterials participate during the electron transfer process from the BH₄⁻ ions to the oxidized form of the dye molecules. The synthesized thin films might find wide variety of applications like SOFCs, oxygen sensor or as catalyst in different organic and inorganic catalytic reactions. The fabrication process is very simple, straightforward, less time consuming, and cost effective.

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