Structural, optical, photoluminescence and photocatalytic characteristics of sol-gel derived CeO$_2$-TiO$_2$ films

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CeO$_2$-TiO$_2$ films with different Ce/Ti mole ratios have been obtained using a simple sol-gel process. The films (1:0.25 and 1:0.5) containing more than 50% CeO$_2$ content show nanocrystalline characteristics. X-ray photoelectron spectroscopic study shows the variation of Ce$^{4+}$/Ce$^{3+}$ ratio with increasing TiO$_2$ content. Films with greater CeO$_2$ content exhibit higher porosity. The observed photoluminescence in the films is attributed to various defects resulting from crystallization and also to the relative amount of Ce$^{3+}$ in the mixed oxide matrix. The transparency in the films appears to be inversely related to their photoluminescence activity, since the 1:0.5 film, which exhibits the best photoluminescence response, is incidentally also the least transparent film. The presence of photocatalytic activity in these films shows their potential use as an efficient photocatalyst.

Keywords: Photochemistry, Photoluminescence, Photocatalysis; Luminescence, Thin films, Films, Sol-gel process, Ceria, Titania

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Photocatalytic reactions sensitized by TiO$_2$ and other semiconducting materials have attracted extensive interest for their potential for solving energy and environmental issues. Several cerium titanates have been investigated for their photocatalytic activity. Mixed CeO$_2$-TiO$_2$ films are reported to decolorize methyl orange solutions upon irradiation of the UV light. Luminescent properties of the rare earth oxides and other semiconductor and insulator oxides are widely used to study the active doping sites. Medical diagnostics, high-density optical storage, opto-electronic devices and flat panel displays are some of the major examples of the utility of these materials. The width and the relative intensity of luminescent emission bands are frequently affected by the nature of the lattice. This feature can be used to tune the emission of the materials depending on the practical applications. Thus, characteristics of rare earths luminescence in different compositions are of importance. Though there are some reports on bulk powders, only a few reports deal with rare earths oxides as thin films, which are of great importance for technological applications such as light emitting devices and flat panel displays. Sol-gel technology allows the architectural design of coatings and multilayered thin films in several types of geometries. This method can be used for fabrication of thin films of controlled thickness with the additional advantage of the possibility to dope them with a large variety of organic and inorganic compounds.

In the present study, CeO$_2$-TiO$_2$ films have been obtained using a simple sol-gel process. The structural, morphological, photoluminescence (PL) and photocatalytic characteristics of films with different Ce/Ti mole ratio have been investigated.

Materials and Methods
Preparation of deposition solutions and films
To 2.5 g of CeCl$_3$.7H$_2$O (Merck) dissolved in 30 ml of C$_2$H$_5$OH (Merck), 1.907 g of titanium propoxide (Aldrich) was added to obtain a deposition solution containing Ce/Ti mole ratio of 1:1. Apart from this composition, other mole ratios such as 1:0.25, 1:0.5 and 1:3 were also studied. These deposition solutions were stored at room temperature in closed glass vessels to prevent rapid precipitation of the alkoxide due to hydrolysis. During the experimental process, the room temperature was kept at 20±5°C and the humidity was maintained at 60±10%. Addition of alkoxide to the ethanolic solution of the cerium salt induced a color change so that the color of the deposition solutions was bright yellow. The intensity of the yellow color was observed to increase with increasing proportion of titanium propoxide. The gelation period of the sol decreased with the increased
proportion of titanium propoxide, and showed a strong dependence upon the ambient temperature and humidity.

Micro slide glass substrates were spin coated at 3000 rpm for 35 s by the freshly prepared deposition solutions to achieve the as-deposited mixed CeO₂-TiO₂ films. The as-deposited films thus obtained were dried at room temperature for 15 min., and subsequently densified for 5 min. in air at 500°C. Pale yellow homogeneous films with high adherence to the substrates and excellent chemical as well as mechanical stability were finally obtained.

Characterization of films

X-ray diffraction (XRD) patterns of the films were recorded in the 2θ range from 5° to 70° at an incidence angle of 1° with a D8 Advanced Bruker diffractometer. Fourier transform infrared (FTIR) spectra of the films in the reflection mode were recorded in the wavenumber range of 400-4000 cm⁻¹ on a Perkin-Elmer (model BX2) spectrophotometer. The X-ray photoelectron spectroscopic (XPS) data were obtained on a Perkin-Elmer (P4I, model 1257) instrument. The surface morphology of the films was observed by scanning electron microscopy (SEM) on a JEOL JSM 840 scanning electron microscope. Optical transmittance and reflectance data of the films were measured in the range of 300-2000 nm using a UV 3101 PC Shimadzu spectrophotometer. The photocatalytic activity of the samples was evaluated by eosin (yellow) decomposition under UV-visible light irradiation. The irradiation was provided by 80 W mercury vapor light centered at 365 nm wavelength. The initial concentration of eosin (yellow) in water was fixed at 4 × 10⁻⁵ M. The extent of eosin decomposition was determined by measuring its absorbance at different time periods. Photoluminescence (PL) measurements were carried out at room temperature in the 300-700 nm range using a Perkin-Elmer LS055 spectrometer at an excitation wavelength of 240 nm.

Results and Discussion

Figure 1 shows the X-ray diffraction patterns of the CeO₂-TiO₂ films. It is evident from the figure that crystallization of CeO₂ has taken place in the 1:0.25 and 1:0.5 compositions along the (111) crystallographic plane only. The 1:1 and 1:3 compositions, however, exhibit amorphicity to X-rays. The CeO₂ crystallite size for the 1:0.25 and 1:0.5 films as found using the Debye Scherrer formula is 16 nm. Another important observation in the 1:0.5 composition is the crystallization of the mixed compound, CeO₁.₅₂TiO₂. Importantly, the diffraction peaks in these films are weak in intensity due to their small nano-range crystallite size. However, the d-values of CeO₂ and CeO₁.₅₂TiO₂ crystalline phases...
in the present work match very well with the $d$-values of CeO$_2$ and CeO$_{1.6}$TiO$_2$ phases reported in the literature. Furthermore, as is shown later in this study, the 1:0.5 composition demonstrates the highest PL activity. The existence of the mixed compound in 1:0.5 ratio is primarily responsible for this result. The absence of mixed compound in the 1:0.25 film seems to be the reason for its lower PL activity in comparison to that of the 1:0.5 film. The amorphous characteristics in 1:1 and 1:3 compositions have led to their lower PL response.

The elucidation of structural features using the FTIR study shows the formation of TiO$_2$ network in all the films. The films exhibit bands assigned to $\nu$(Ti-O-Ti) and $\nu$(Ti-O) near 544 and 798 cm$^{-1}$ (longitudinal optical mode) respectively. The red frequency shift of the LO mode of amorphous TiO$_2$ from $\sim$ 870 cm$^{-1}$ to $\sim$ 798 cm$^{-1}$ is a consequence of the presence of CeO$_2$ nanograins. The intensity of the band, which is assigned to longitudinal optical (LO) mode of amorphous TiO$_2$ phase, shows an increase with the increase in TiO$_2$ content in the films. This increased band intensity is also attributable to the higher thickness of these films. The degree of contribution from the $\nu$(Ti-O-Ti) and $\nu$(Ti-O) stretching vibrational modes varies for these films depending on their TiO$_2$ content. Importantly, the 1:0.25, 1:0.5, and 1:1 compositions exhibit relatively higher intensity of the band assigned to the $\nu$(Ti-O-Ti) mode. The 1:3 composition, however, shows a reverse trend and demonstrates more intensity for the band assigned to $\nu$(Ti-O) vibrational mode. This indicates that due to the higher proportion of Ti in the 1:3 composition, the TiO$_2$ network formed in this film is stronger. It also suggests that the conversion of Ti-O-Ti polymeric chains with different lengths to the oxide network is nearly complete in the 1:3 film.

**X-ray photoelectron spectroscopic studies**

The deconvoluted XPS core-level spectra of Ce in the binding energy range of 870-930 eV are shown in Fig. 2. The films show spin-orbit splitting of the Ce 3$d$ level, manifested as Ce$3d_{5/2}$ and Ce$3d_{3/2}$. Deconvolution of the peaks into ten components has been carried out. These films show the presence of Ce in both Ce$^{4+}$ [882.7 eV ($\nu$), 888.2 eV ($\nu'$), 899.2 eV ($\nu''$), 901 eV ($u$), 907.6 eV ($u'$), 916.7 eV ($u''$)] and Ce$^{3+}$ [882 eV ($\nu$), 886.2 eV ($\nu'$), 903.05 eV ($u$), 905 eV ($u'$)] states. The compositions containing higher ratio of Ce are observed to possess greater proportion of Ce$^{4+}$ state. With increasing Ti content in the samples, a small peak corresponding to the 3+ state of Ce appears at 886.2 and 903.05 eV for $3d_{5/2}$ and $3d_{3/2}$ spin-orbit states, respectively. This peak grows gradually with increasing Ti content suggesting thereby the Ce$^{4+}$$\rightarrow$Ce$^{3+}$ conversion. The reduction of Ce$^{4+}$/Ce$^{3+}$ ratio with increased Ti content in the films suggests the influence of Ti in facilitating Ce$^{4+}$ reduction. Earlier, XPS studies by Trinchi et al. have also shown an increase in the Ce$^{3+}$ content for...
samples containing lower Ce concentration. Additionally, in all their samples, Trinchi et al.\textsuperscript{15} have observed the presence of Ti in Ti\textsuperscript{4+} state. In the present study, although the Ti core-level intensity has shown an increase with the Ti content (core level spectra are not shown here), there is no evidence of peak broadening or formation of new transitions, thus discounting the formation of any sub-stoichiometric titanium oxide\textsuperscript{15,16}. Curve fitting of the XPS spectra has further confirmed that the Ce\textsuperscript{3+} content in the samples increases on increased addition of TiO\textsubscript{2}. The results obtained from curve fitting of variation in the ratio of Ce\textsuperscript{3+}/Ce\textsuperscript{4+} as a function of Ti content, shows that from the 1:0.25 to 1:1 composition, there is a marked increase in Ce\textsuperscript{3+} content, while from 1:1 to 1:3 composition, this change is less prominent and a state of saturation in Ce\textsuperscript{3+} content is reached.

Morphological properties

Figure 3 shows SEM micrographs of the CeO\textsubscript{2}-TiO\textsubscript{2} films with different compositions. The morphology of the films is decided by parameters such as preparation conditions and film thickness. The films comprise agglomerates of varying dimensions in the nano range. The agglomerate size for the 1:1 composition film is ~170 nm. The agglomerate size is reduced with enhanced TiO\textsubscript{2} proportion. The morphology of the 1:3 composition is seen to differ distinctly. Although in certain domains the 1:3 film has exhibited smaller grains, the average agglomerate size in 1:3 film is estimated to be around 300 nm. The granular nature of the 1:3 film, which contains a very high proportion of TiO\textsubscript{2} is dominated by the presence of TiO\textsubscript{2} agglomerates. Furthermore, the pore size in these films shows a decrease with the enhanced proportion of TiO\textsubscript{2}.

Optical properties

Figure 4 shows transmission and reflection spectra of films with different Ce/Ti mole ratios. Higher roughness in 1:0.25 and 1:0.5 films due to greater CeO\textsubscript{2} content has resulted in reduced visible region transmission. Best transmission characteristics observed for the 1:3 composition can be correlated to its lower roughness in comparison to the 1:0.25, 1:0.5

![Fig. 3 — SEM micrographs of the CeO\textsubscript{2}-TiO\textsubscript{2} films with different Ce/Ti mole ratios. [(a) 1:0.25; (b) 1:0.5; (c) 1:1; (d) 1:3].](image-url)
and 1:1 films. Also, irrespective of the Ce/Ti mole ratios, all the films are characterized by a unique feature, i.e., deposition of films from the coating solution just prior to the commencement of gelation has led to highly transparent films. Transparency in the films adversely affects their PL response. Therefore, the films in the present study have been deposited from freshly prepared sols, since such films are least transparent and thereby demonstrate high PL activity. Furthermore, in general, the films with high roughness due to high CeO$_2$ content are more reflecting than the smoother films containing lower CeO$_2$ content.

**Photocatalytic activity**

The films have shown potential for use as efficient photocatalytic agents. The absorption spectra of eosin (yellow) solution after 1 hr of UV-visible light irradiation in the presence of different Ce/Ti thin films is shown in Fig. 5. The percentage decomposition of eosin (yellow) absorption peak at 517 nm after 1 hr irradiation in the presence of 1:0.25, 1:0.5, 1:1 and 1:3 films is 73, 83, 62 and 90%, respectively. These results affirm the superior photocatalytic response of 1:3 film in comparison to other films. The decrease in intensity of the absorption peaks, both in visible and ultraviolet regions, with irradiation time indicates that the eosin (yellow) solution can be degraded using these films; 20 ml of $4 \times 10^{-5} M$ eosin (yellow) solution can be completely decomposed in 2 hrs using the 1:3 photocatalyst with surface area of 5.75 cm$^2$. The percentage decomposition of the most intense absorption peak at 517 nm after 1 and 2 hrs irradiation in the presence of 1:3 film is 90 and 96.3%, respectively. To compare the photocatalytic activity of 1:3 and TiO$_2$ films, the absorption spectra of eosin (yellow) solution after 2 hrs irradiation in the presence of 1:3 and TiO$_2$ films were also recorded. The percentage decomposition of eosin (yellow) absorption peak at 517 nm after 75 min. irradiation in the presence of 1:3 and TiO$_2$ photocatalysts is 93 and 96.5%, respectively. Although the photocatalytic response of TiO$_2$ film is superior in comparison to the 1:3 film, these results still affirm that addition of cerium to titanium oxide leads to an efficient photocatalytic agent. The major advantage of the 1:3 film over TiO$_2$ film is its better mechanical strength.

**Photoluminescence characteristics**

The emission spectra of films with different Ce/Ti mole ratio are shown in Fig. 6. The emission spectra of different compositions are characterized by three peaks near 440, 486 and 517 nm. All emission spectra ($\lambda_{ex} = 240$ nm) show a prominent band centered at 440 nm attributed to the oxygen related defects in the CeO$_2$-TiO$_2$ films. Dominant defects in CeO$_2$ are oxygen vacancies. The intensity of the band at 440 nm increases with increasing CeO$_2$ content up to 1:0.5 and then decreases for the 1:0.25 composition. The emission of the 1:0.5 composition is the most intense, while it is the weakest for the 1:3 film. The formation of the mixed compound, i.e., CeO$_{1.6}$-2TiO$_2$, may be considered to be the reason for its best PL characteristics. Incidentally, the
transmission for the 1:0.5 composition is observed to be the least and the highest for the 1:3 composition. In general, it has been observed that the transparency in the films adversely affects their PL response, i.e., the least transparent films exhibit the highest PL intensity. The peaks at 486 and 517 nm are characteristic of the Ce$^{3+}$ state. The XPS studies have confirmed the presence of Ce$^{4+}$ and Ce$^{3+}$ states in all the compositions. Trivalent Ce ion has only one electron in the 4$f$ state. The ground state of Ce$^{3+}$ is split into 2$F_{7/2}$ and 2$F_{5/2}$. The next higher state originates from the 5$d$ state and 4$f$-5$d$ transitions are parity allowed. Unlike the 4$f$ electron with the shielding effect of the outer shell 6$s$ and 5$p$ electrons, the shift of the 5$d$ and hence the $d$-$f$ emission band of Ce$^{3+}$ ion is heavily dependent on the local crystal field surrounding the Ce$^{3+}$ ion$^{17}$. Thus, the emission wavelength of Ce$^{3+}$ is very sensitive to the crystallographic environment$^{18}$. The decreased PL intensity of the 1:0.25 film in comparison to that of the 1:0.5 film shows that the concentration quenching is observed when the cerium concentration is increased due to the increase of intra-ionic non-radiative relaxation between Ce ions. When the splitting of 5$d$ state is large and the energy difference between the lowest 5$d$ sublevel and the ground state of 4$f$ configuration of Ce$^{3+}$ is small, the red shift of emission takes place. Interestingly, a red shift of emission is observed when the concentration of TiO$_2$ is increased. When the TiO$_2$ concentration is high, the unit cell of CeO$_2$ becomes larger. This leads to the lowest sublevel of the 5$d$ state of Ce$^{3+}$ getting further lowered in energy due to a stronger crystal field when the TiO$_2$ concentration is high. Red shift of emission from 516 nm in 1:0.25 composition to 521 nm for the 1:1 composition is observed.

Conclusions

Studies on spin coated CeO$_2$-TiO$_2$ mixed oxide films obtained from cerium chloride and titanium propoxide based deposition solutions have revealed that the addition of Ti to Ce in the deposition solution yields mixed oxide films with excellent chemical and mechanical stability. The XPS studies have confirmed the presence of Ti in + 4 state and Ce in + 3 and + 4 states. The Ce$^{3+}$/Ce$^{4+}$ ratio in the films is influenced by the TiO$_2$ content. The films containing higher amount of TiO$_2$ show the presence of higher Ce$^{3+}$ content. The 1:0.5 composition has exhibited the best photoluminescence characteristics. The least transmission observed in this composition is one of the reasons for its excellent PL response. Formation of both CeO$_2$ and CeO$_{1.6}$-2TiO$_2$ phases in 1:0.5 composition is also postulated as the cause behind its best PL response. The nanocrystalline nature gives these films unique properties that have consequently led to their usefulness in photocatalysis as well. The 1:3 film has shown the best properties for utility as an efficient photocatalyst.

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References