Photocatalytic degradation of methyl orange using ceria, cassiterite and ceria-cassiterite nanocomposite

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Abstract

Nanosized ceria (CeO_2), cassiterite (SnO_2) and ceria-cassiterite (CeO_2-SnO_2) have been synthesized and studied its photocatalytic activity for methyl orange degradation under UV-Visible type radiation. Phase formation study was carried out by using x-ray diffraction technique and it's reveals that ceria (CeO_2) properly supported on the surface of cassiterite (SnO_2). Nano sized ceria, cassiterite and ceria-cassiterite nanocomposite were confirmed by transmission electron microscopy technique. The particle size of the CeO_2 and SnO_2 and their nano composite is in the range of 10-20 nm. Photocatalytic activity of the CeO_2-SnO_2 composite was improved as compared to CeO_2 and SnO_2. The enhanced photocatalytic activity is attributed to the increased visible light absorption and improved adsorption of the dye on the surface of the composite catalyst.

Keywords: Ceria, cassiterite, nanocomposite, photocatalytic degradation, methyl orange

1. Introduction

Effluents from textile industries contain a significant percentage of dyes that cause considerable environmental concerns. Dyestuffs are often non-biodegradable compounds and are hazardous to the living organisms. Photocatalytic degradation using solar radiation is a potential technique for the removal of the organic contaminants from water. Photocatalysts like TiO_2, CdS, WO_3, ZrO_2, and V_2O_5 have been investigated for the treatment of these effluents with the aim of mineralizing the dyes completely [1, 2]. When photocatalysts are dispersed on other oxides, its surface area increases and it can lead to enhanced photocatalytic activity. The increased activity was attributed to the increased surface acidity of the mixed oxide. Earlier researchers were studied TiO_2 dispersed on different supports like Al_2O_3, ZrO_2, CeO_2 and zeolite exhibited different photocatalytic activity for hydrogen generation from water-methanol mixture [3]. The highest activity was obtained for TiO_2 dispersed on ZrO_2 and the enhanced activity was ascribed to the increased optical absorption and increased lifetime of the charge carriers assisted by surface acidic sites.

SnO_2 is a special oxide material because it has a low electrical resistance with high optical transparency in the visible range. Due to these properties, apart from gas sensors, SnO_2 is being used in many other applications, such as electrode materials in solar cells, light-emitting diodes, flat-panel displays, and other optoelectronic devices where an electric contact needs to be made without obstructing photons from either entering or escaping the optical active area and in transparent electronics, such as transparent field effect transistors [4, 5]. SnO_2 owing to a wide bandgap is an insulator in its stoichiometric form. However, due to the high intrinsic defects, that is oxygen deficiencies, tin Also; SnO_2 is an n-type semiconductor and has many applications.

Similarly, CeO_2 is reported to be a predominantly ionic conductor, exhibits n-type conductivity under certain conditions. Cerium dioxide is an inexpensive and relatively harmless material that presents several characteristics that could be potentially advantageous for photocatalytic applications.

SnO_2 and CeO_2 nanomaterials reveal that they are promising materials for optoelectronic devices such as solar cells, conductive layers, and transistors due to its excellent electrical and optical properties [6- 9]. CeO_2 and SnO_2 are a well known photocatalyst having a bandgap of 3.4 eV and works under UV illumination [10]. Mesoporous structures [11] and nano wires of niobates [12] have been investigated and enhanced photocatalytic activity is reported for these catalysts compared to the bulk oxide due to their increased surface area and small particle size.

In the present work, we report the synthesis, characterization and photocatalytic activity of CeO_2, SnO_2 and CeO_2-SnO_2 novel photocatalytic system. It is expected that a combination of CeO_2 and SnO_2 can show synergistic effect in improving the optical absorption property resulting in enhanced photocatalytic activity. With this aim, CeO_2, SnO_2 and CeO_2-SnO_2 nanocomposite has been synthesized and studied its photocatalytic activity for the degradation of methyl orange dyes solution under UV-Visible light type irradiation.

2. Experimental details

Ceria (CeO_2) and cassiterite (SnO_2) has been synthesized by microwave method. All the chemicals are of analytical grade about 2.2565 g of $SnCl_4$ $2H_2O$ is dissolved in 100 ml Distilled water. 30 ml of above solution is taken in 250 ml Beaker and 45 ml 1M ammonia solution was added dropwise with constant stirring till precipitation completed and gel is formed. Then the solution was kept in (800 W EO-77 HORNO ELECTRICO, ORBIT) microwave oven at 353K for 30 min. The resulting gel was filtered through Whatmann filter paper No. 40 then it is dried at 353K for 24 Hrs in order to remove moisture or water molecule present in it. Then the precipitate obtained collected in silica crucible and calcination was carried out at 773K for 2 hrs finally ash colored tin oxide nanoparticles were formed. Similarly Cerium oxide has been synthesized. Also, 10% Ceria- cassiterite nanocomposite was prepared by sol–gel hydrolysis.

X-ray diffractometer (Philips model PW-1710) was used to identify the crystalline nature of the samples using CuKα radiation. FT-IR spectra were recorded in a Perkin-Elmer spectrometer using KBr pellets. Average grain size was measured using a scanning electron microscope (SEM JSM-JEOL 6360). Particle size was measured using a transmission electron microscope (TEM) (Philips, CM200, operating voltages 20–200 kV).

Photocatalytic reaction was conducted in a 100 ml Pyrex glass vessel containing 50 ml of the aqueous methyl orange dye solution (concentration: 50 ppm) having 50 mg of catalyst suspended in it. The UV-Visible type radiation was used. After every one hour of irradiation, 2 ml of the aliquot was withdrawn, centrifuged and quantitative determination was carried out using a spectrophotometer by measuring its absorbance at λ = 592, 411 and 330nm.

3.0 Results and discussion

3.1 XRD studies

Fig. 1 shows the powder X-ray diffraction (XRD) patterns of pure ceria, cassiterite and the composites having 10 percentage of CeO_2 on SnO_2 nanoparticles. The diffraction pattern of SnO_2 shows peaks corresponding to planes (111), (101), (200) (211), (002), (310), (301), (202) and (321) confirming the formation of SnO_2 (JCPDS Patterns No. 41-1445). Diffraction peaks corresponding to planes (111), (200) (220) and (311) of CeO_2 (JCPDS Patterns No. 75-0076) besides that of SnO_2, are seen in the CeO_2 coated samples indicating the biphasic nature of the samples.

3.2 FT-IR studies

Fig.2. shows the typical FT-IR spectra of ceria (CeO_2), cassiterite (SnO_2) and ceria-cassiterite (CeO_2-SnO_2) in the spectral region 400-1000 cm^{-1} sintered at 773K. The spectra have been used to locate the band positions. The lower frequency band is 478 cm^{-1} in CeO_2 and 488 cm^{-1} in SnO_2. Also, the higher frequency band is 822 cm^{-1} in CeO_2 and 619 cm^{-1} in SnO_2. The absorption bands observed within this range is an indication of the formation of single phase metal

oxides [13]. But ceria-cassiterite nanocomposite lowers the values of frequency band due to the different Sn-O and Ce-O starching frequencies in same samples and this is clearly observed in the **Fig. 2c**.

3.3. Scanning Electron Microscopy

The SEM images of CeO_2, SnO_2 and CeO_2-SnO_2 are shown in the **Fig.3(a-c).** It is observed that the average grain size is smaller than 0.1μm for all the compositions. It can be seen that the grains and crystallinity both uniformly observed in ceria and cassiterite. But SEM image of CeO_2-SnO_2 nanocomposite significantly indicates that the ceria is directly dispersed on the surface of cassiterite.

3.4 TEM analysis

Fig. 4 (a–c) depicts the transmission electron micrographs of CeO_2, SnO_2 and CeO_2-SnO_2 nanocomposite samples. It is evident from **Fig. 2(a-b)** that the average particle size of CeO_2 and SnO_2 is around 10-15 nm. **Fig. 2(c)** clearly shows the presence of a dispersed phase of CeO_2 on SnO_2.

3.5 Photocatalytic study

Photocatalytic activity of CeO_2, SnO_2 and 10%CeO_2-SnO_2 nanocomposite for the degradation of methyl orange under UV-Visible type irradiation is shown in **Fig 5.** There is hardly any change in the concentration of the dye when the solution is irradiated in the absence of catalyst. Under dark conditions, a slight change in the concentration of the dye is observed over a period of 7 hours due to its adsorption on the catalyst's surface (C/C_0=0.87). It can be seen from the figure that the photocatalytic activity increases in CeO_2-SnO_2 nanocomposite as compared to CeO_2 and SnO_2 and the catalyst degrades the dye almost completely in 7 hours. The enhanced photocatalytic activity of the composites can be attributed to a combination of factors such as increased optical absorption and increased adsorption of the dyes on the surface of the catalyst. When the composite sample is exposed to UV-Visible type irradiation, both CeO_2 and SnO_2 can get excited leading to enhanced photocatalytic activity. The enhanced adsorption of the dye on the composite sample can be attributed to the increased surface acidity. As methyl orange is a basic dye [14], an enhanced adsorption of the dyes takes place on the acidic surface of the composites [15]. Another reason for the UV-visible light activity of the composite catalyst can be due to the photobleaching process [16].

4. Conclusions

Nanosized ceria (CeO_2), cassiterite (SnO_2) and ceria-cassiterite (CeO_2-SnO_2) nanocomposite was successful synthesize by using microwave method. This method is cost-effective and environmentally friendly because of no by-product effluents. X-ray diffraction technique reveals that ceria (CeO_2) properly supported on the surface of cassiterite (SnO_2) and formation of single phase metal oxides. Nano sized ceria, cassiterite and ceria-cassiterite nanocomposite were confirmed by transmission electron microscopy technique. The particle size of the single oxide like CeO_2, SnO_2 and their nano composite is in the range of 10-20 nm. The photocatalytic activities of the prepared nanoparticles were measured by the photodegradation of methyl orange under UV-Visible type irradiation. The results indicated that the composites exhibit a synergistic effect in enhancing the photodegradation of methyl orange.

Reference

[1] Xu, Y.; & Schoonen, M.; American Mineralogist, vol. 2000, 85, 543-556.

[2] Blake, D.; National Renewal Energy Laboratory 1999.

[3] R. Sasikala; A. R. Shirole; V. Sudarsan; V. S. Kamble; C. Sudakar; R. Naik; R. Rao; S.R. Bharadwaj, Applied Catalysis A, 390 (2010) 245-252.

[4] J. F. Wager, “Transparent electronics,” Science, vol. 300, no. 5623, pp. 1245–1246, 2003.

[5] R. L. Hoffman, B. J. Norris, and J. F. Wager, Applied Physics Letters, vol. 82, no. 5, article 733, 3 pages, 2003.

[6] S. Bagherian, A. K. Zak, Mater. Sci. Semicond. Process. 56 (2016) 52-58.

[7] V. K. Tomer, S. Duhan, Sens. Actuators, B 223 (2016) 750-760.

[8] V. Ramasamy, G. Vijayalakshmi, Superlattices and Microstruct. 85 (2015) 510-521.

[9] J. Malleshappa, H. Nagabhushana, B.D. Prasad, S.C. Sharma, Y.S. Vidya, K.S. Anantharaju, Optik. 127 (2016) 855-861.

[10] Kominami Hiroshi , Oki Kazuhide , Kohno Masaaki , Onoue Sei-ichi , Kera Yoshiya and Ohtani Bunsho, *J. Mater. Chem.*, 2001,11,604-609.

[11] X. Chen, T. Yu, X. Fan, Applied Surface Science 253 (2007) 8500–8506

[12] Kenji Saito, Kazunori Koga and Akihiko Kudo, Dalton Trans., 2011, 40, 3909.

[13]R.D. Waldron, Phys. Rev. 99 (1955) 1727.

[14] A.K. Gupta, Anjali Pal, C. Sahoo, Dyes and Pigments 69 (2006) 224

[15] Fuat Guzel, Separation Science and Technology, 31(2). pp. 283-290, 1996.

[16]de GJ, Soler-Illia AA, Candel RJ, Regazzoni AE, Blesa MA, (1997) Chem Mater 9:184.

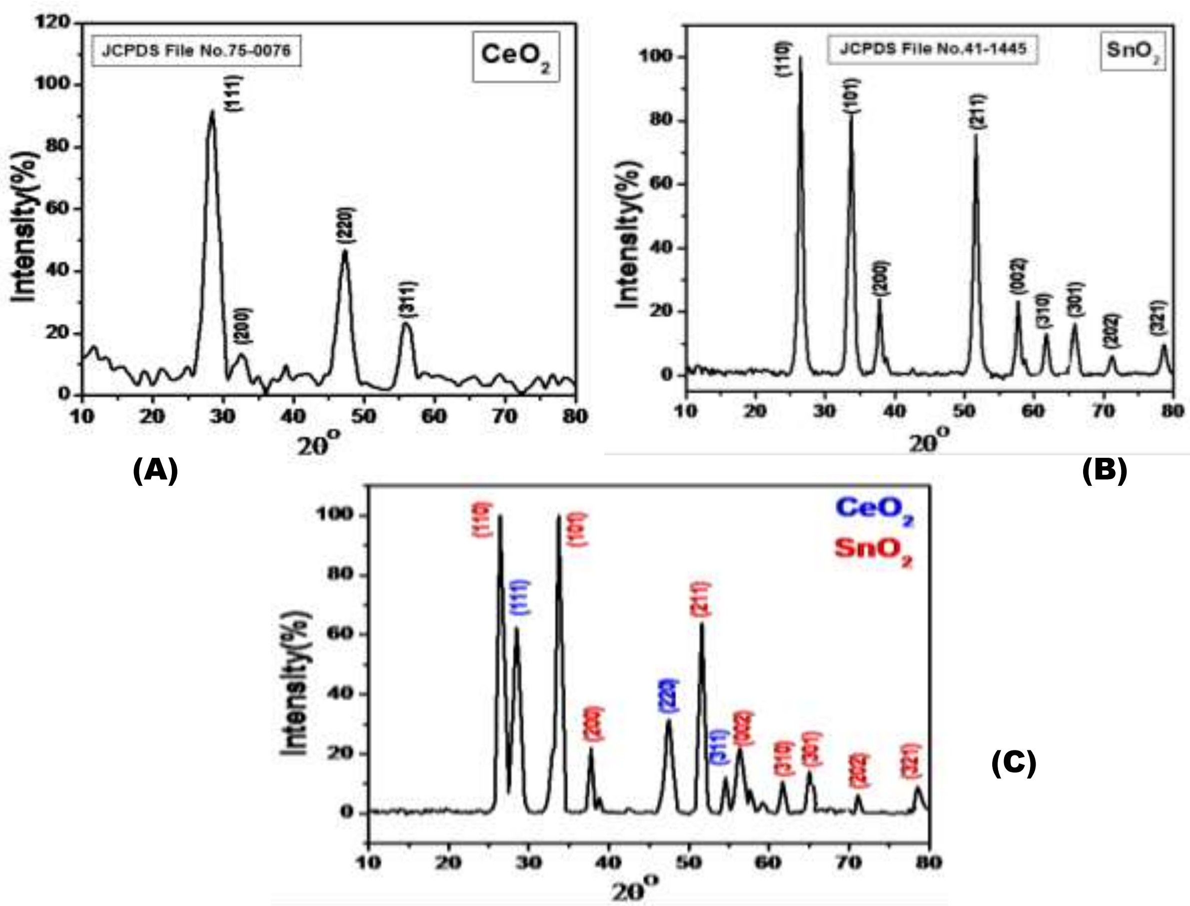

Fig.1 XRD Patterns of (A) CeO_2 (B) SnO_2 and (C) CeO_2-SnO_2

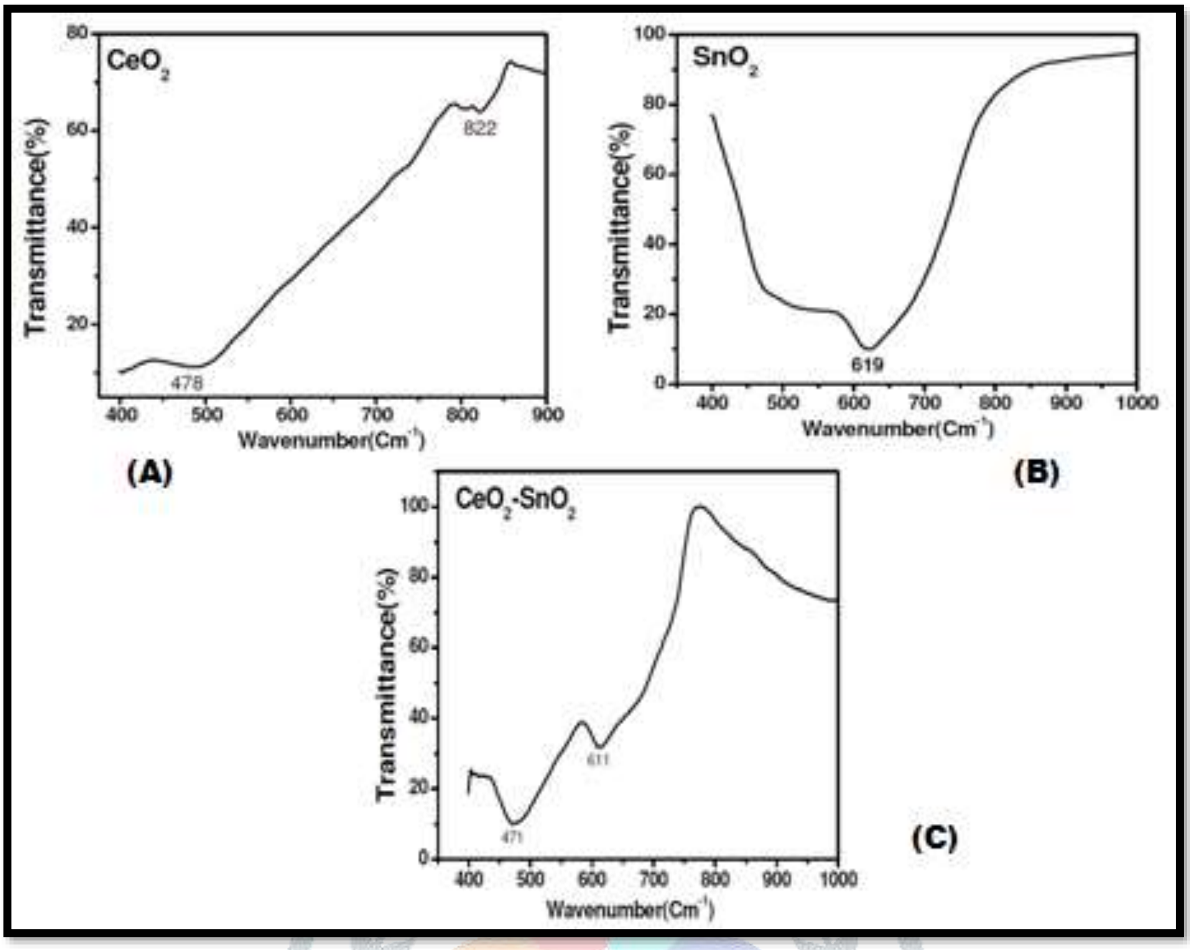

Fig.2 FT-IR Spectra of (A) CeO_2 (B) SnO_2 and (C) CeO_2-SnO_2

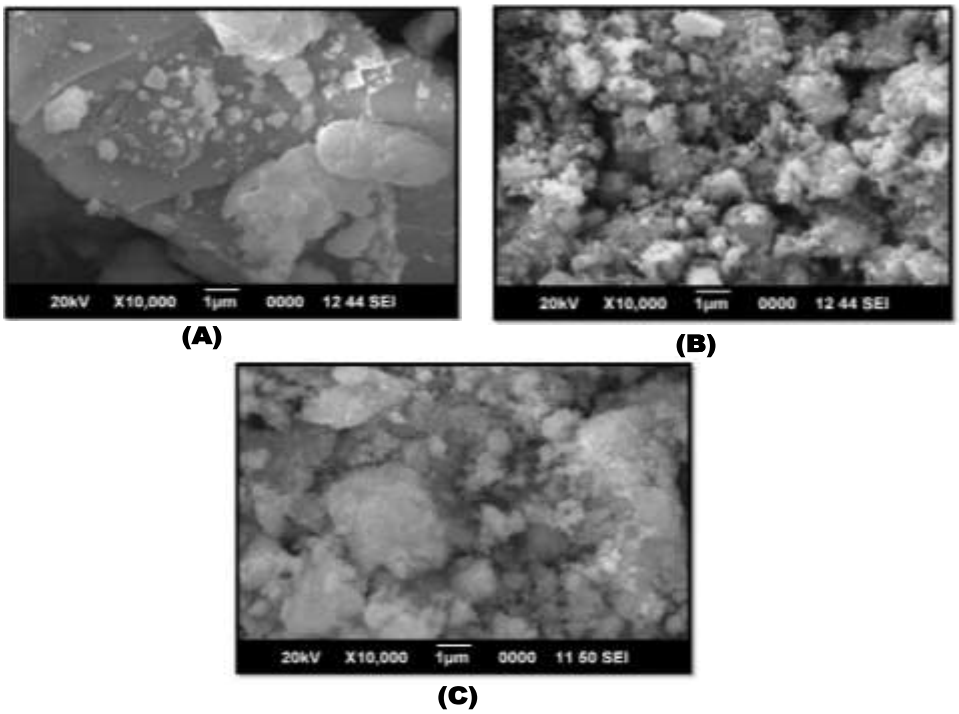

Fig.3 SEM Images (A) SnO_2 (B) CeO_2 and (C) CeO_2-SnO_2

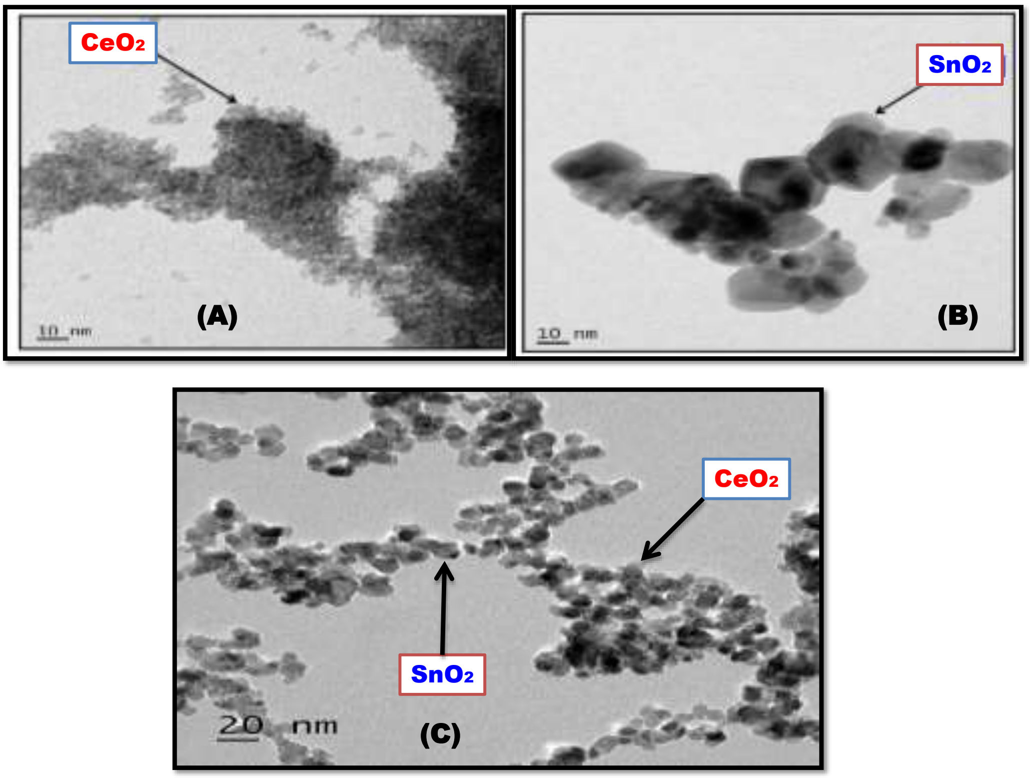

Fig.4 TEM Images (A) CeO_2 (B) SnO_2 and (C) CeO_2-SnO_2

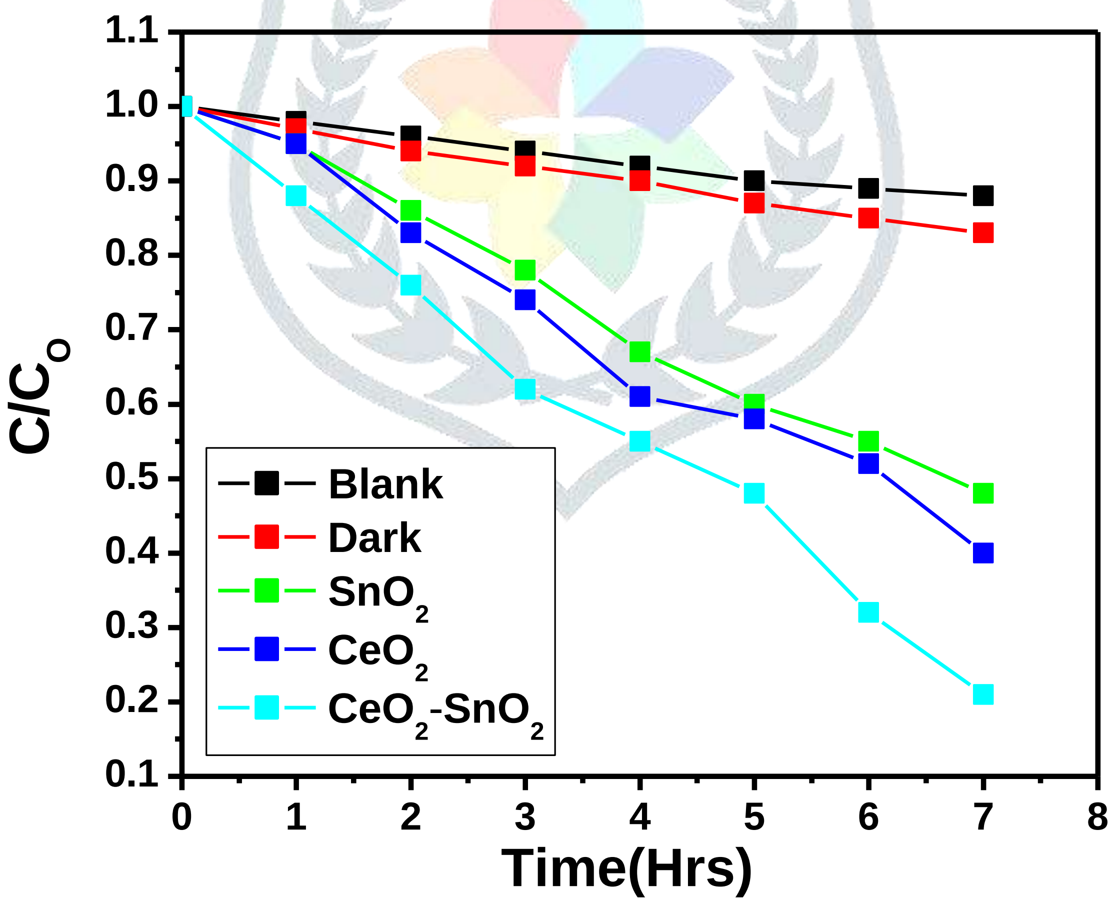

Fig.5 Photocatlytic study of (A) CeO_2 (B) SnO_2 and (C) CeO_2-SnO_2