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Synthesis, Characterization, and Application of Zr,Ce-TiO_2/SiO_2 Nanocomposite Thin Film as Visible-light Active Photocatalyst

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Abstract

A novel Zr,Ce-TiO_2/SiO_2 nanocomposite thin film was successfully prepared with various amounts of Zr^{4+} and Ce^{4+} as codopant ions for self-cleaning applications. A thin film was coated on a tile substrate by dip-coating and porous Zr,Ce-TiO_2/SiO_2 was obtained after heat treatment for 2 hours at 500 °C. The SEM images and XRD pattern showed that the optimum amount of doping ions in relation to Ti^{3+} is 0.1%. In this circumstance, the most monotony of film was seen and the main formed phase was anatase. The sample structures were characterized by infrared spectroscopy. The nanocomposite films were found to be active for photocatalytic decomposition of methyl orange as an organic pollutant.

.**Keywords:** Codoped TiO_2, Photocatalytic application, Self-cleaning, Visible light

1. Introduction

Nanocomposites have been a topic of intense research mainly because of their unique physical and chemical properties. Titania in particular has recently attracted so much interest owing to their potentials for revolutionary photocatalytic applications, optical properties, photovoltaic cells and gas sensors [1-6]. However, titania has relatively high band gap energy (3.2 eV) which limits its applications in visible light range of electromagnetic spectrum [7].

It is becoming increasingly difficult to ignore the kind of TiO_2 phase on the photocatalytic activity. It is well known that the best form is anatase phase for photocatalytic degradation. Among the different phases of TiO_2, anatase/rutile interface show that more activity because of the effect on the band gap. Efficiency of electron-pair separation is important for photocatalytic applications and optical properties. Furthermore, titania photocatalytic activity has been improved by doping with transition metal impurities since metal ion doping decreases the electron-hole recombination and increases production of OH^o in the photocatalytic activity [8-14]. The effect of doping on the photocatalytic depends on several factors such as type, concentration of ions and the method of ion doping [15].

Previous researches indicate that the addition of SiO_2 and dispersive agent to TiO_2 films create an extremely large surface and increase photoinduced super hydrophilicity [16-19].

This study focused on using Zr^{4+} and Ce^{4+} codopant were used for the synthesis of TiO_2/SiO_2 nanocomposite thin film on tile.

2. Computational details

2.1. Materials

Titanium tetra isopropoxide (TTIP), Zirconium (IV) Chloride and Cerium (IV) Nitrate (AR analytical grade, Merck Chemical Company) were used as Titanium, Zr^{4+} and Ce^{4+} sources for synthesis of the Zr,Ce-TiO_2 nanocomposite. Hydroxy Propyl Cellulose (HPC) was used as a dispersion, HNO_3, SiO_2 colloid solution (Ludox) and absolute ethanol were purchased from Merck Chemical Company. Double distilled water was used in all of the experiments.

2.2. Photocatalysis and Characterizations

SEM- XL30 scanning electron microscope was used to determine the microstructure of the thin film samples. X-Ray powder diffraction data were collected on SCIFERT- 3003 PTS. FT-IR spectra were obtained using a Thermo Nicolet NEXUS- 870. The photocatalytic degradation of methyl orange dilute solution were performed by measuring optical absorption at the 465 nm wavelength before and after the illumination of visible range of electromagnetic radiation by Varian UV-Vis Spectrophotometer. In photocatalytic experiments, light source was 400 W high pressure mercury vapor lamp (Osram). The solution of methyl orange in deionized water with a concentration of 5 ppm was chosen as a matter of photodegradation. This solution was set in the vicinity of thin film samples under visible light irradiation. The spectrum of Osram HQL (MBF-U) 400W- E40 lamp was reported by Aberoomand Azar et al. in 2011 [19].

2.3. Preparation of samples

The preparation of sample solution is described in details elsewhere [19,20]. First, TTIP was dissolved in absolute ethanol. Then this dispersed solution was added with molar ratio TTIP:C_2H_5OH:dispersion equals to $1{:}125{:}4.5\times10^{-3}$ $gg^{-1}_{sol.}$ and stirring until complete dissolution. Afterward, the mixture of C_2H_5OH, HNO_3, water, and SiO_2 with molar ratio of ethanol:HNO_3:H_2O:SiO_2 equals to 43:0.2:1:0.30 and various amounts of $Ce(NO_3)_4$ and $ZrCl_4$ (refer to Table-1) were added dropwise under vigorous stirring. The obtained colloidal suspension was transparent and stirred for 45 minutes and then aged for 48 hours until gel formed. Finally, the tiles were coated by dip-coating method, after pretreatment with fluoric acid.

Table 1. Formulation of sample thin films

No. of samples	Samples content	Amount of Ce^{4+} (molar ration vs. Ti^{4+})	Amount of Zr^{4+} (molar ration vs. Ti^{4+})
S_1	$Zr-TiO_2/SiO_2$	0.2%	-
S_2	$Zr,Ce-TiO_2/SiO_2$	0.15%	0.05%
S_3	$Zr,Ce-TiO_2/SiO_2$	0.1%	0.1%
S_4	$Zr,Ce-TiO_2/SiO_2$	0.05%	0.15%
S_5	$Ce-TiO_2/SiO_2$	-	0.2%

3. Results

The effect of Zr^{4+} and Ce^{4+} on the microstructure

FT-IR spectra of the samples with different amounts of Zr^{4+} and Ce^{4+} are shown in Figure 1. The stretching bands at 2060- 3600 cm^{-1} are assigned to symmetric vibration of surface hydroxyl group [21, 22]. The strong band at 3100- 3700 cm^{-1} is attributed to hydroxyl group that is obtained from TTIP hydrolysis. The strong bands at about 1630 cm^{-1} have been assigned to H-OH bending vibration of physically adsorbed

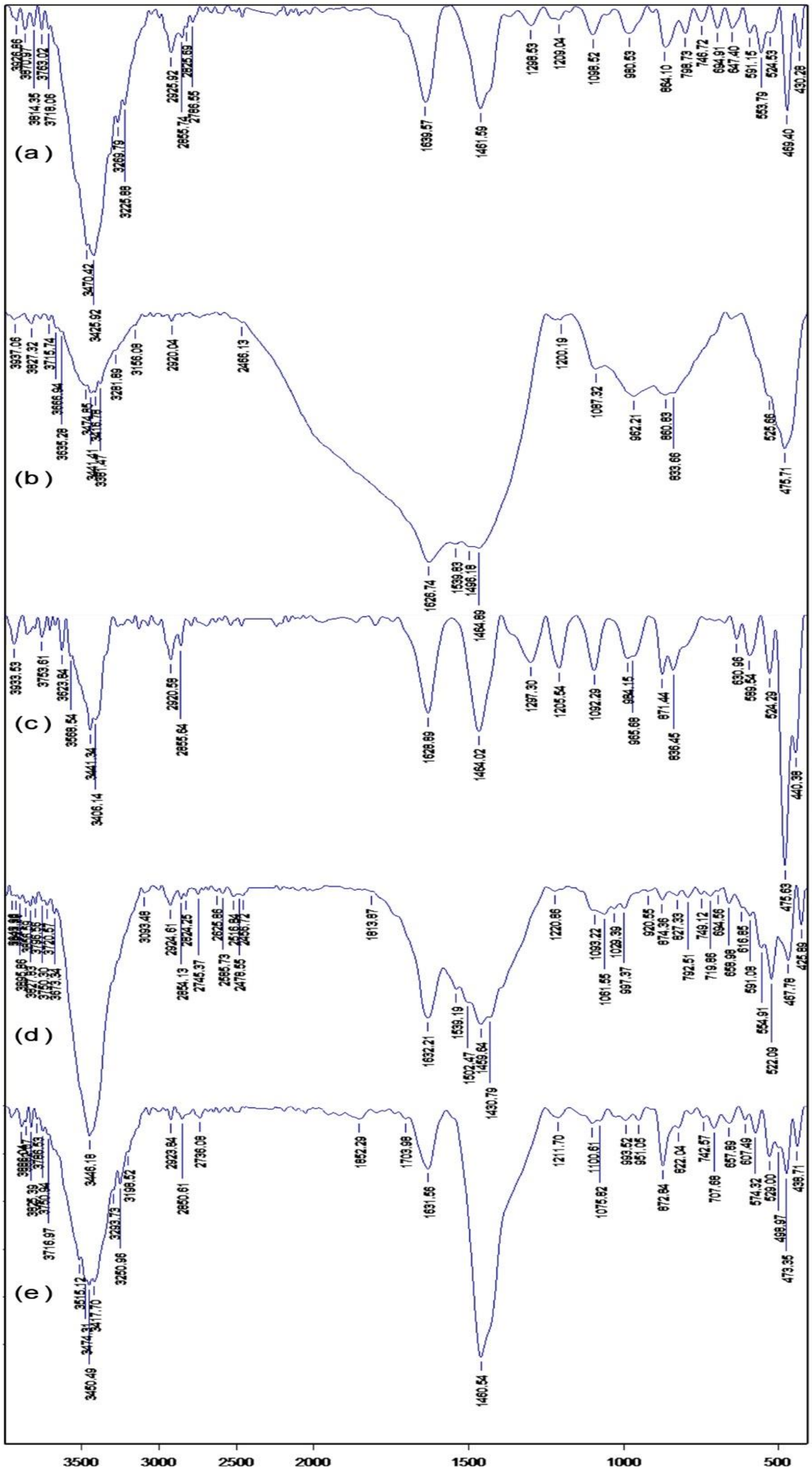

Fig 1. The FT-IR spectra of synthesized nanocomposites: (a) S_1 (b) S_2 (c) S_3 (d) S_4 (e) S_5

water and hydroxyl group [7,23,24]. The band around 791 cm^{-1}, along with a weak band around 960 cm^{-1} are commonly assigned to vibration of Si-O-Ti band [25]. The bands around 1100 cm^{-1} can be related to asymmetric stretching of the Ti-O bands [26, 27].

The SEM images are illustrated in Figure 2. Having Zr^{4+}, Ce^{4+} metal ions or the mixture of them on the thin film would have influence on particle size. When Zr^{4+} metal ion was added to nanocomposite, monotonous of film was decreased. In sample 4 that molar ratio of doping ions is 0.1% vs. Ti^{3+}, nanocomposite particle size was decreased and distribution was come narrow and coating was monotonously with minimum agglomeration. The analysis EDX in Figure 3 are shown in the presence of Zr^{4+} and Ce^{4+} as doping ions and Ti^{3+} for TiO_2.

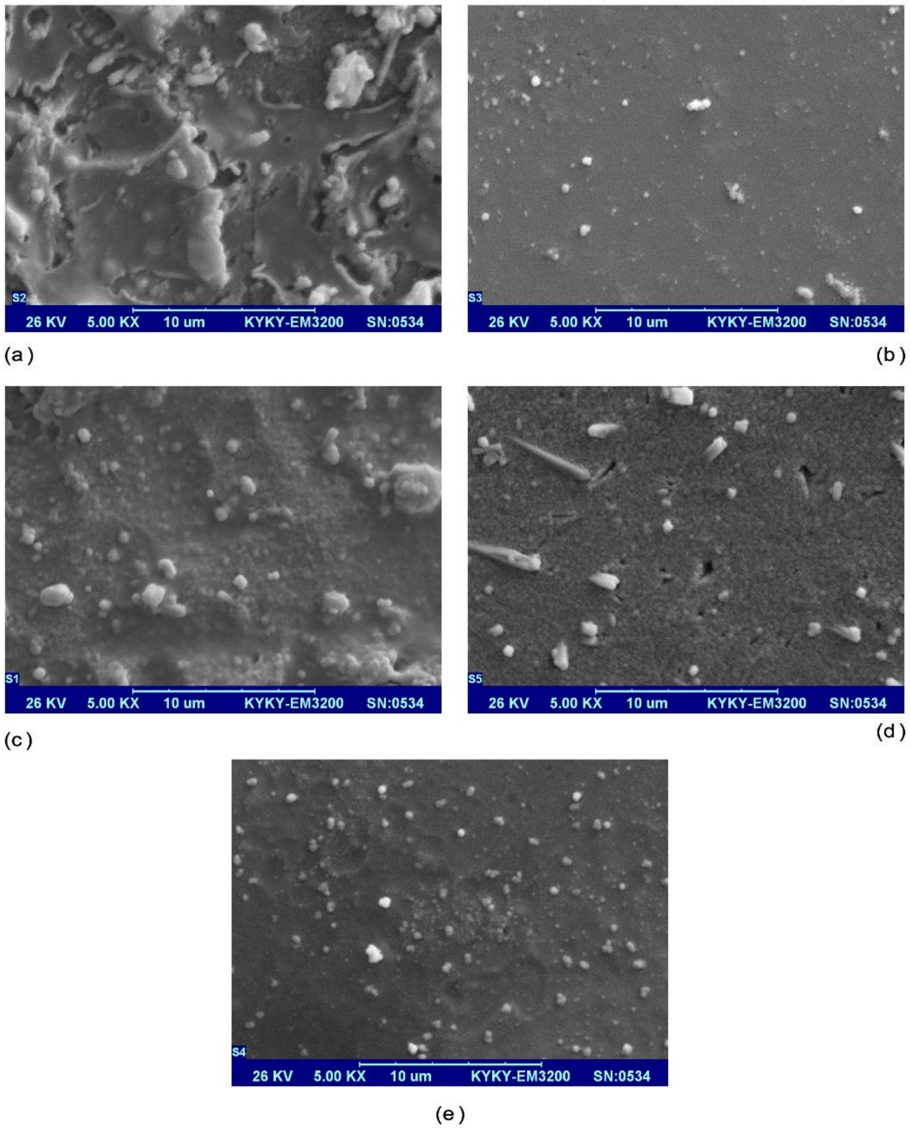

Fig.2. SEM images for the sample films: (a) S_1 (b) S_2 (c) S_3 (d) S_4 (e) S_5

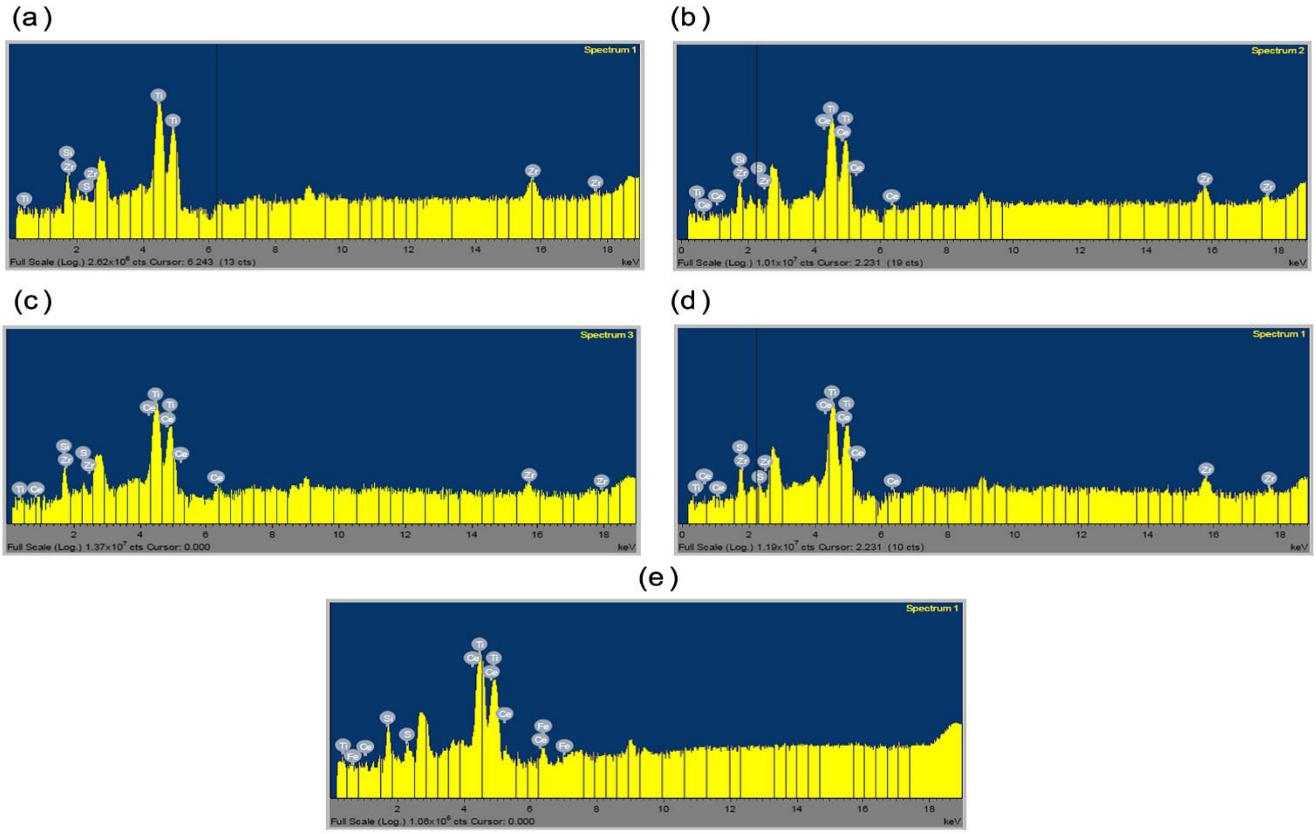

Fig. 3 The EDX analysis of Zr,Ce-TiO_2/SiO_2 thin films: (a) S_1 (b) S_2 (c) S_3 (d) S_4 (e) S_5

The effects of Zr^{4+} and Ce^{4+} on the anatase phase

The XRD patterns of S_1, S_2, S_3, S_4 and S_5 are shown in Figure 4a-e. The characteristic peak was appeared at $2\theta=25^{\circ}$ indicating an anatase structure and evidence of mixed rutile and anatase phases have not been observed. According to the Figure 4 proportions of anatase phase in the samples were different and the sample 3 was crystalline and has only anatase form. We expect that the sample 3 would be the best for self-cleaning activity. It might be concluded that at 500 ºC, the addition of Ce^{4+} and Zr^{4+} have facilitated the formation of anatase phase.

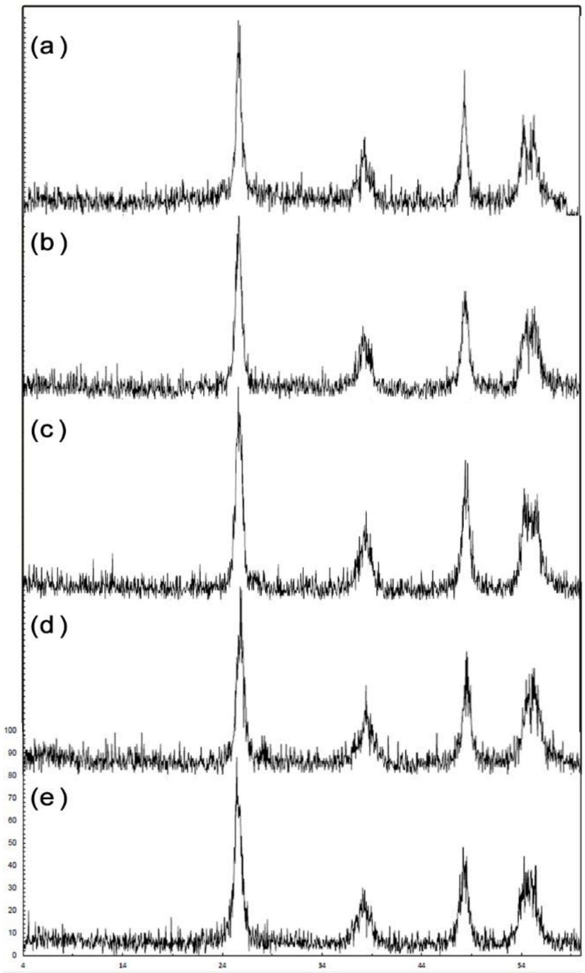

Fig. 4 XRD patterns of sol-gel synthesized nanocomposites: (a) S_1 (b) S_2 (c) S_3 (d) S_4 (e) S_5

The effects of Zr^{4+} and Ce^{4+}on the self- cleaning ability

Table 2 shows the relationship between the amount of Zr^{4+} and Ce^{4+} metal ions on photocatalytic activity of the samples. It is found that the photocatalytic activity would be improved by addition of Zr^{4+} to Ce^{4+} as a second doping ion. The decomposition time of methyl orange, in electromagnetic visible light range, would be reduced, when molar ratio of Zr^{4+} and Ce^{4+} were 0.1% vs. Ti^{3+}.

The amount of Zr^{4+} or Ce^{4+} is one of the most important parameter in photocatalytic degradation since these changes have a severe effect on the microstructure of the films. By addition of certain amount of Zr^{4+} to Ce^{4+}, the Zr,Ce-TiO_2/SiO_2 obtained porous films and decreased particle size in the suitable condition. As a result, the adequate self-cleaning activity of sample 3 under visible light would be attributed to the spongy microstructure.

Table 2. The self-cleaning ability of sample nanocomposites

Sample	S_1	S_2	S_3	S_4	S_5
Percent decompose of methyl orange solution over 4 hours	89.24	76.68	90.26	78.22	88.72

5. Conclusion:

The five types of Zr,Ce-TiO_2/SiO_2 photocatalyst thin films with various amounts of Ce^{4+} and Zr^{4+} were prepared by using the sol- gel method. The results indicate that addition of Ce^{4+} and Zr^{4+} as a codopant has influence on distribution and monotonous coating of TiO_2/SiO_2 thin film. The amount of codopant dictates the distribution of Zr,Ce-TiO_2/SiO_2 films. $Zr_{0.1\%}$, $Ce_{0.1\%}$-TiO_2/ SiO_2 nanocomposite thin film has the best uniform particle distribution among samples with low agglomeration, spongy microstructure and photocatalytic activity.

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