

Photodegradation of methylene blue by using Sm₂O₃-doped TiO₂ as a heterogeneous catalyst

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Abstract

In the present investigation the synthesis and characterization of Sm₂O₃-TiO₂ doped nanomaterial has been reported. The material was synthesized by sol-gel combined with a surfactant-assisted template method. The concentration level of Sm (III) additive was varied systematically from 0.5 to 5.0 wt. %. The calcination of prepared material was carried out at 500°C. The prepared material was characterized by sophisticated techniques like X-ray diffraction patterns (XRD), Fourier-transform infrared spectroscopy (FT-IR), Particle size and morphology was studied by transmission electron microscopy (TEM). The material obtained was nanocrystalline, having particle size in the range of 10–13 nm. Photocatalytic activities of the samples were studied with degradation of methylene blue. The modified 5 wt. % Sm-doped TiO₂ sample showed enhanced photocatalytic activity in comparison with the undoped samples.

Keywords: Sol-gel process, TiO₂, Sm₂O₃, Nanoparticles; Electron microscopy; Photocatalytic degradation

1. Introduction

Nanocrystalline materials have received considerable attention because of their structural, electronic, optical properties and their potential applications [1, 2]. In the past decade a large number of nanocrystalline metal oxides such as TiO₂, Cr₂O₃, MoO₃, ZnO, Sm₂O₃ [3-7] have been widely synthesized. These nanomaterials have been used as a photocatalyst [8, 9], Dye sensitized solar cells [10], rechargeable lithium batteries gas sensors, field emitters and in heterogeneous catalysis [11-14].

Various synthetic routes like sol-gel method [15], hydrothermal method [16], co-precipitation peptization method [17] have been studied for rare earth doped TiO₂ nanoparticles. However, among this method the sol-gel process is one of the most

successful techniques for the synthesis of nanosize ceramic powders, producing a narrow particle size distribution and showing considerable advantages over the above reported methods. These advantages include excellent compositional control, homogeneity on the molecular level due to the mixing of liquid precursor, and lower crystallization temperature. It is believed that nanoparticles of Sm₂O₃-TiO₂ ceramics could be possible to synthesize using similar surfactant synthetic strategy. We have used the cationic surfactant cetyl trimethyl ammonium bromide (CTAB) as a structure directing agent by mixing it in an alkoxide solution in order to modify the microstructure of the gels, which will certainly allow the formation of oxides with controlled particle size.

The degradation or decomposition by photocatalysis is a novel method for the treatment of air and water pollutant. Most of the photocatalytic studies use TiO₂ as a photocatalyst. Recently some studies have been carried out to evaluate the priority of other metal oxides such as ZnO, In₂O₃, SnO₂ and TiO₂ [18-21]. Here we report the photocatalytic activity of modified 5 wt.% Sm-doped TiO₂ catalysts.

2. Experimental

The reagent grade chemicals were used in the preparation of samples, Titanium butoxide (Sigma-Aldrich), Samarium nitrate (Sigma-Aldrich), cetyl trimethyl ammonium bromide (Qualigens Fine chemicals), without further purification.

Precursor solutions were prepared by the following method. An aqueous solution of various concentration (0.5, 1.0 and 5.0 wt%) Sm(NO₃)₃·5H₂O was prepared by using double distilled deionized water. Required amounts of Ti(OC₄H₉)₄ was added to 100 ml double distilled deionized water. The cationic surfactant CTAB (10%) was prepared in 50 ml ethyl alcohol and 10 ml isopropyl alcohol. The Various % of Samarium nitrate was dropped into the titanium butoxide solution along with CTAB. The system was kept

under stirring for 4 hours, resulted in the formation of a white coloured sol. The sol was then heated slowly up to 80°C and dried to produce a white fluffy gel. The dried gels were calcined at 500 °C temperatures for 2 h in an air with the help of muffle furnace.

2. Results and Discussion

The X-ray diffraction (XRD) patterns were recorded with a Bruker 8D advanced X-ray diffractometer using monochromatic Cu-K radiation (40 kV and 30 mA). The Fourier transform infrared spectroscopy (FT-IR) analysis was performed using a Shimadzu-8400 spectrometer. The microscopic nanostructures were observed using a transmission electron microscopy (TEM; FEI, Tecnai F30, HRTEM, FEG operated at 300 kV).

2.1. XRD analysis

X-ray diffraction results show the crystal structures, phases and lattice modification of the Samarium doped TiO₂ composite shown in **Figure 1**. The peaks in **Figures 1(a)** is indexed to the cubic phase of Sm₂O₃ with a = 10.93 Å (JCPDS No. 74-1807). All the samples shows number of XRD peaks, positioned at 2θ° = 20, 28, 43, 46, 55 and 57 indicating hkl values due to planes (211), (222), (134), (440), (622), (444) that can be easily indexed as cubic nature of pure Sm₂O₃. The **Figures 1(b)** shows the XRD patterns of pure TiO₂. From Figure it shows that the peaks at 2θ° = 25.3, 37.8, 48.0, 53.9, 55.2, 62.6 and 75.1, indicating for the hkl as (101), (112), (201), (210), (203), (204) and (223) are corresponding to anatase phase of TiO₂ lattice parameter a=b=3.784 and c=9.512, from the JCPDS card 84-1285 [22]. Similarly **Figure 1 (c-e)** gives peaks for series of Samarium doped TiO₂ peaks at 2θ°= 28 is corresponds for (211) plane mainly due to presence of Sm₂O₃ while peak at 2θ°= 25 is corresponds for (101) plane for anatase phase of TiO₂

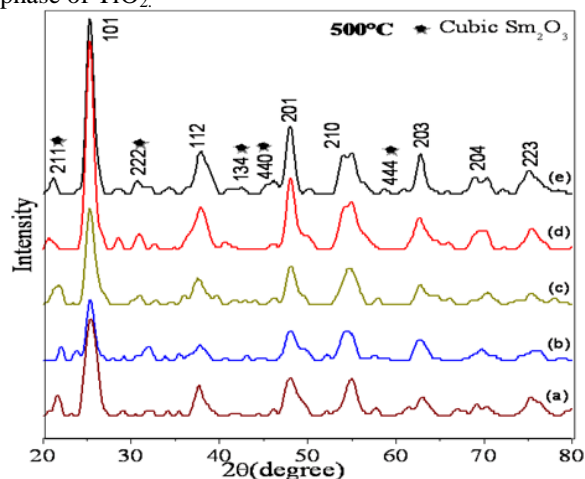


Figure 1: XRD patterns of a) Sm₂O₃, b) TiO₂, c) 0.5 wt%, d) 1.0 wt% and e) 5.0 wt% Sm doped TiO₂

2.2 SEM and EDS analysis

To study the surface topography and elemental composition, the SEM with EDS was investigated systematically. **Figure 2(a-b)** shows the variation in morphology of pure TiO₂ samples. It shows morphology of pure TiO₂ that gives mesoporous nature of anatase. **Figure 2(c and d)** shows image of 5 wt% Samarium addition in TiO₂. It can be seen that the samples shows decrease in the particle size and development of porous surface. From the SEM micrograph, the effect of addition of samarium clearly shows alteration in particle size and morphology with increasing porosity.

Elemental compositions of 5 wt% Samarium doped TiO₂ were represented in **Table 1**. The observed Sm: Ti: O atomic ratios 13.21: 66.34: 20.45 respectively, are fairly close to the expected bulk ratios indicating uniform distribution of the metal species inside the samples. It was supports that, the minimum stoichiometric ratio of desired elements in the 5 wt% sample is maintained.

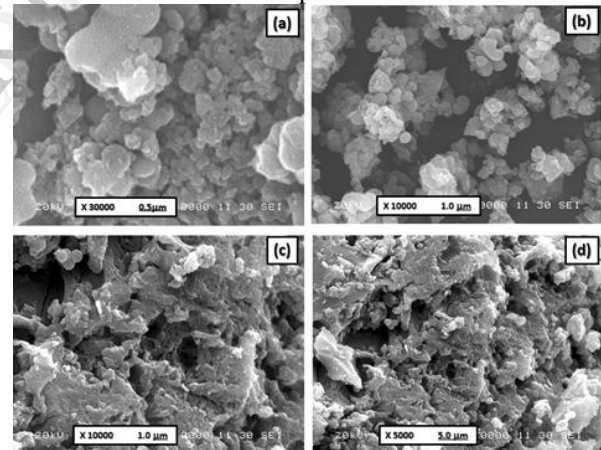


Figure 2: SEM images of (a-b) Sm₂O₃, (c-d) 5.0 wt% Sm doped TiO₂

Table 1: EDS analysis of 5 wt% Sm doped TiO₂

Entry	Element	Mass %	Atom %
1	Sm	13.21	3.19
2	Ti	66.34	50.34
3	O	20.45	46.47

2.3 TEM analysis

The TEM images shown in **Figure 3** indicate the obtained nano-sized particles have clarity. The TEM images of pure TiO₂ in **Figure 3 (a-b)** shows the presence of highly mesoporous nature of anatase TiO₂ with particle size varying in between 15 to 20 nm which is matching with XRD analysis.

It can also be seen that in Figure 3 (c and d) the average particle size of modified sample of 5 wt% Samarium doped TiO₂ is in the range of 10 to 18 nm. From the images, it is clearly seen that addition of samarium on TiO₂ surface improves the catalytic activity.

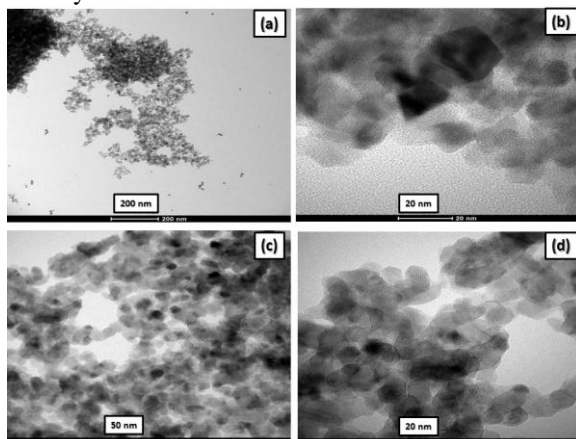


Figure 3: TEM images of (a-b) Sm₂O₃, (c-d) 5.0 wt% Sm doped TiO₂

2.4 FT-IR analysis

Figure 4 (a) shows the FT-IR spectra of pure TiO₂. A band at 877 cm⁻¹ is characteristic of terminal molybdenum oxygen double bond (Ti=O). The bands at 1416 and 1562 cm⁻¹ were attributed due to presence of acidic sites [23]. The broad band around 3417 cm⁻¹ is due to O-H stretching vibration modes of the adsorbed water on the surface of the powder [24]. The **Figure 4 (b-d)** shows the FT-IR spectra of 0.5, 1.0 and 5.0 wt% samarium doped TiO₂ respectively. A sharp band appears in the range 867-866 cm⁻¹ is due to the terminal Samarium-Oxygen double bond (Sm=O). The bands at 1416-1600 cm⁻¹ were attributed due to bending vibration mode due to adsorbed water and hydroxyl groups on metal surface. While broad band around 3350-3398 cm⁻¹ is due to O-H stretching vibration modes of the adsorbed water [25].

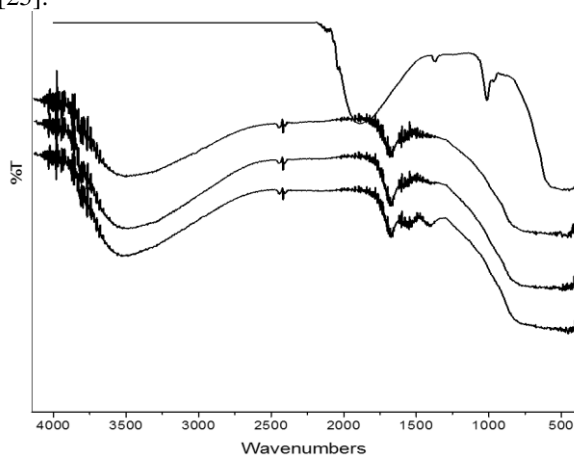


Figure 4: FT-IR spectrum of a) Sm₂O₃, b) 0.5 wt%, c) 1.0 wt% and d) 5.0 wt% Sm doped TiO₂

2.5 Photocatalytic Catalytic Activity results

To evaluate the photocatalytic activity of prepared series of modified Samarium-doped TiO₂ towards dye degradation, photocatalysis experiments were carried out in round-bottomed pyrex glass cells with cut off wavelength 320 nm. The irradiation system was equipped with mercury lamps 250W (Philips UV), light bulb. Methylene blue (MB) was used as the model pollutant for degradation. The suspensions of catalyst in dye solution were subjected to UV light radiation for 120 min. The solution of the dye with desired concentration (5 mgL⁻¹, pH 8) and 0.2 g of the catalyst was prepared in double distilled water. For irradiation experiment, 100 mL aqueous solution was taken in the photoreactor. The pH of the reaction mixture was adjusted by adding a dilute aqueous solution of HCl or NaOH. The solutions were stirred intermittently. After every 20 min, 2 ml aliquots were pipetted out and then centrifuged. The photocatalytic degradation of the dye was monitored using UV spectroscopic analysis technique (Varian Cary 500 spectrophotometer). The absorbance of the clear supernatants was determined at 660 nm wavelength against appropriate blanks. The rate of decolourization was observed in terms of change in intensity at λ max of the dye. The decolourization efficiency (%) has been calculated as:

Efficiency = $\ln(C_0/C)$, Where C₀ is the initial concentration of dye and C is the concentration of dye after photoirradiation.

First, the photocatalytic experiments were carried out using different catalysts at dye concentration (5 mgL⁻¹). The percentage of degradation increased with increasing UV exposure time shown in **Figure 5**. The variation of photodegradation % of MB using different catalysts was done under the UV irradiation for 120 minutes.

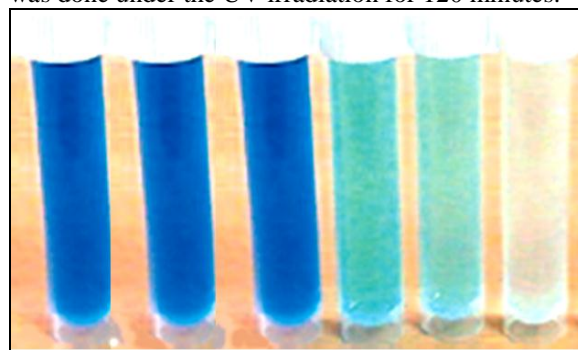


Figure 7: Photocatalytic degradation photograph of various catalysts (a) blank sample, (b) Sm₂O₃, (c) TiO₂, (d) 0.5% Sm doped TiO₂, (e) 1.0% Sm doped TiO₂, (f) 5.0% Sm doped TiO₂

1.0% Sm doped TiO₂, (f) 5.0% Sm doped TiO₂, for Methylene Blue degradation at pH 8 for 120 min.

The observed photocatalytic efficiency increased with addition of Samarium doping. The difference between photoactivities of these samples is possibly due to their different microstructures, as shown from SEM and TEM results. It was seen that, the 5 wt. % modified Samarium-doped TiO₂ sample showed maximum dye degradation in 120 min. The rate of degradation was found to be higher shown in Figure. This is may be due to the comparatively increased porosity and decreased crystallite size of the sample with successive addition of Samarium in TiO₂. It seems a great ability to capture photons is exhibited efficiently by nanocrystalline material; it is due to rough and porous surface area.

4. Conclusions

In summary the present paper describes a new, efficient and eco-friendly route for the synthesis of series of samarium doped TiO₂. The catalyst can be prepared with easily available and from inexpensive reagents by simple Sol-Gel method. The prepared catalyst is reusable and non-hazardous. A simple procedure combined with low toxicity and reusability of the catalysts, provides an economic and waste-free chemical methods. From the results, it was found that, increase in weight % of Samarium increases the porosity, crystalline nature and also which will improve the surface area of the nanocomposite material. The modified 5 wt.% TiO₂ sample showed enhanced photocatalytic degradation of methylene blue activity in comparison with the un-doped samples.

Acknowledgments

The authors are grateful to the Principal, New Arts, Commerce and Science College Ahmednagar and Shri Dnyaneshwar Mahavidyalaya, Newasa, Ahmednagar, India for providing the all required facilities to carry out the work.

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