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Preparation and characterization of visible-light-activated tio₂ nanoparticles codoped with copper and samarium

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ABSTRACT

Enhancement of photocatalytic activity of titania in the visible region and stabilization of anatase phase are significant from the view point of water pollution abatement, since this will enable solar light mediated processes to be scaled up to meet industrial requirements. Recent research has focused on designing nano titania based catalytic systems due to the large surface areas and improved photogeneration of oxidant-reductant species that the nano particles offer. There are several methods for the synthesis of nanoTiO₂. Compared to bare TiO_2 , metal ion doped TiO_2 is advantageous, as the doped metal ion alters the band gap and surface adsorption properties. Iron, zinc, cadmium, lanthanum, cerium, cobalt and nickel ions doped TiO₂ have been reported in the literature for photocatalytic application. In this context, the present study aims at the co-doping of nano titania with a transition metal ion and a rare earth metal ion. Copper and Samarium ions have been chosen for this purpose as this co-doping has not been reported in the literature so far. In this paper we have synthesized Cu and Sm ions co-doped nano titania prepared by the solgel method. This catalyst was characterized by FTIR, XRD, TGA, SEM and UV- visible to analyze the band gap chatacteristics and the effect of calcination on the photodegradation of 4CP

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Introduction

Environmental cleaning using TiO2 photocatalysts has attracted a great deal of attention due to the increase in the level of environmental pollutions in the world [1]. Among various semiconducting materials, much attention has been given to TiO2 because of its high photocatalytic activity, high refractive index leading to a hiding power and whiteness, resistance to photocorrosion, chemical stability, low cost and non-toxicity [2,3]. For more than a decade, studies have mainly concentrated on the suspension of TiO2 fine powder because of its higher photocatalytic activity compared to TiO2 thin films [4-7]. From among the three principal crystalline forms of titania, rutile does absorb some visible light, while anatase absorbs only in the UV region. Unfortunately, rutile is not a good photocatalyst. It is also known that optimal photocatalytic efficiency is obtained with a mixture of anatase and a small percentage of rutile [8-11]. Titania has a large band gap (3.20 eV for anatase TiO2) and therefore, only a small fraction of solar light can be absorbed [6]. Many attempts have been made to sensitize titanium dioxide to the whole visible region, such as doping with transition metals [12], transition metal ions [13-17], nonmetal atoms [18-20] and organic materials [21-24]. Introduction of dopants allows titania to absorb in the visible region but this does not necessarily mean that the doped catalyst has a better photocatalytic activity. When the doping level exceedsan optimal limit, which usually lies at very low dopant concentration and low visible light absorption, the dopant causes recombination of sites and has undesirable effects on photocatalysis [25-28]. The sol-gel method is an attractive method for low temperature synthesis of TiO₂, and it is easier to realize metal doping [29]. Since this method is carried out in solution, this permits tailoring of certain desired structural characteristics such as compositional homogeneity, grain size, particle morphology and porosity. Preparation of transition metal doped TiO_2 nanoparticles by sol-gel method, characterization and investigation of their photocatalytic activity have been reported in recent literature [30-32]. Preparation of Cu- Sm co doped TiO_2 nanoparticles by sol-gel method has not been reported in literature. In this work, preparation and characterization of pure and Codoped TiO_2 nanoparticles is reported and photocatalytic degradation of 4CP [33-35] under Visible light is investigated.

Experimental

Material and Methods

Titanium tetraisopropoxide (TTIP) 99% (Spectrochem), isopropyl alcohol 99% (SRL), copper nitrate-98%(CDH), samarium nitrate, nitric acid, surfactants polyethylene glycol-6000 (Spectrochem) and triethanolamine (SRL) were used as received.

Synthesis of Catalysts

TiO₂ nanoparticles were synthesized by standard sol-gel methods [36]. TiO₂ sols were prepared by drop wise addition of 8.5ml titanium isopropoxide solution, which had been dissolved in 80 mL of isopropanol under vigorous stirring at room temperature. After continuous stirring for half an hour, solution of polyethylene glycol (0.5g), triethanolamine (2ml) and 5 ml of 0.5M nitric acid were added to that solution. The resulting solution was filtered and dried in the air oven (90 °C) for two hours. The obtained powder was calcined at various temperatures from 400 and 500°C for two hours.

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Metal ions-doped TiO₂ samples were prepared according to the above procedure in the presence of the corresponding metal ion salts as precursors to give a total doping of 0.05 mole%. The metal ion concentrations were varied as: $Cu^{2+}(0.01 \text{ mole}\%)$ -Sm³⁺ (0.04 mol%) and Cu (0.04 mol%)- Sm (0.01 mole%). The appropriate amount of metal ions precursors were as added to the distilled water before hydrolysis of titanium isoprpoxide and the remaining procedures were the same as described above. The schematic of preparation is shown in Fig. 1.

Photocatalytic degradation of 4- chloro phenol (4CP) using synthesized titania samples

The photocatalytic activity of undoped, single metal doped and Cu – Sm ions co-doped TiO₂ nanoparticles were examined through their activity for the photocatalytic degradation of 4-chlorophenol [37-40]. Photocatalytic degradation of aqueous solutions of 4-chloro phenol was carried out in a multi lamp Haber photo reactor fitted with eight numbers of high pressure mercury lamp having emission maximum at 254 nm wavelength. In a typical reaction, 100 ml of 4CP was taken in a clear quartz tube and the titania catalyst was added to it. Aeration was provided using an air circulatory pump. Aliquots of samples were withdrawn at regular intervals and centrifuged. The degradation of 4CP was monitored by measuring the absorbance of the samples spectrophotometrically at its λ_{max} of 225 nm. Effects of calcination temperature of photocatalyst on the degradation of 4CP were studied.



Figure 1. Schematic diagram of preparation of Cu-Sm doped TiO2

Results and Discussion

Undoped and copper-samarium ions co-doped nano titania particles were prepared by sol-gel method. Crystallite size, surface area, pore size, pore volume, thermal stability, surface oxygen vacancies, surface morphology and structural features of synthesized TiO₂ nanoparticles were studied through spectral and thermal analyses. The photocatalytic activity of the synthesized titania samples was evaluated through the degradation of a standard organic compound, namely 4-chloro phenol. The results of the study are presented below.

Catalyst Characterization

Fourier Transform Infrared Spectroscopic (FT-IR) studies of synthesized nano titania samples

The FT - IR spectral data are carefully examined in order to ascertain the relevant structural features of the as- prepared and

calcined TiO_2 and the spectra are presented in Fig.2 (a – c). Fig. 2 (a) shows the IR spectra for as - prepared TiO₂. It is interesting to note from this figure that narrow bands in the range of 3600 - 2800 cm⁻¹ and the maximum of 3355 cm⁻¹ occur due to the position of the interacting hydroxyl groups of the organic solvents. The structural features appearing as the stretching vibrations of the - CH₂, and - CH bands nearly at 2968, 2929, 2897, 2498, 1482 and 1250 cm⁻¹ are assigned to the organic residues which are originating from the preparation route. The FT-IR of the titania sample calcined at 400 °C for 2 hrs is shown in Fig 2(b). It shows minor changes in vibrational frequencies that can be attributed to the appropriate changes occurring as a result of removal of most of the weakly adsorbed interacting organic impurities and the hydroxyl groups. Fig.2 (c) shows the IR spectra of titania calcined at 500 °C for 1 hr. The band noticed at $\sim 500 \text{ cm}^{-1}$ may be attributed to the formation of a structure that is containing a Ti - O linkage, which fairly confirms the formation of Ti - O band and also confirms the characteristics of the high purity product. From Fig 2(c), it is interesting to note that the spectra have not shown any peak corresponding to the organic impurities and also to the hydroxyl groups used for this TiO₂ preparation. This confirms the removal of all the organic residues that arise from the preparatory route on calcination at 500 °C.



Figure 2. FTIR spectra of TiO_2 as prepared (a), calcined at 400° C (b) calcined at 500° C(c).



Figure 3. XRD pattern of nano titania particles dried at 150° C (a) and calcined at 500° C (b)

XRD spectrum

The diffraction data of undoped and codoped TiO₂ samples are shown in Figure 3, 4 and 5. The XRD peaks of undoped TiO₂ at 25.5, 37.77, 48.0, 53.5, 63 and 70 (20) indicated the presence of TiO₂ in anatase phase. Sm and Cu ions co-doped TiO₂ also showed the same peaks indicating that titania was in anatase phase in the doped samples as well. Additionally, comparison between codoped and single metal ion doped TiO₂ revealed that, the relative intensity of major peak at 25.5 of anatase phase decreased significantly in codoped TiO₂, indicating that Sm and Cu co doping inhibits the phase transformation from amorphous to anatase in solid structure, leading to higher thermal stability. There were no separate peaks for Sm_2O_3 and CuO at 38.8, 47.5 and 55.6 (2 θ). The calcination temperature had some effect on structure of prepared catalyst. The catalysts were calcined at $400-600^{\circ}$ C was in anatase phase. The major peak was sharper with increasing calcination temperature. It means that the crystallinity of catalyst was higher in higher calcination temperature, 600°C. Additionally the crystallite size of the catalyst was calculated by using Debye-Scherer equation (1)

 $t = k\lambda/Bcos\theta$ (1) Where t is the crystallite size, k is the constant (0.89), λ is the wavelength of X-ray source (Cu α =1.54A⁰), B is full width of half max (FWHM) in radians. Here FWHM is 0.5radians and the crystallite size was 17nm for Sm and Cu co-doped TiO₂ photocatalyst.



Figure 4. XRD spectrum of a) 0.1M Cu-TiO2 at 500° C b) 0.1M Cu-TiO2 at 400° C c) pure TiO₂ at 500° C d) pure TiO₂ at 400° C





The thermal stability of pure and non-calcined titania is represented in Fig.6. The desorption of the solvent and water was the reason for 23% weight loss at 100% $^{\circ}$ C on the catalyst

surface. The second weight loss from 100°C to 470°C resulted from stronger desorption of organic solvent which were trapped on the catalyst. At higher temperature in the range of 500°C to 1000°C there was no weight loss. This suggested that the sample can be subjected to calcination at temperatures above 400 $^{\circ}$ C. 3.1.4 Scanning electron microscopy (SEM) analysis of metal ions co-doped titania



Figure 6. SEM images of copper and samarium ions codoped TiO₂ of different nanometers



Figure 7. TGA of as prepared and calcined Titania





Figure 7 shows the SEM images of the copper and samarium ions codoped TiO_2 . Its resolution was about 10,000X

magnification. The results showed that, the size of catalysts was in nanometer range, as suggested by the XRD data. The estimated size of undoped TiO_2 was larger than that of Cu-Sm ions codoped TiO_2 . There was no definite morphology and the codoped titania sample appears as multilayered.



Figure 9. Effect of calcination temperature for photodegradation of 4CP using as prepared and calcined codoped TiO₂

Effect of Calcination temperature of Nano $\text{Ti}O_2$ and Co doped $\text{Ti}O_2$

Calcination temperature of the catalyst plays an important role in the photocatalytic degradation of organic impurities in the aqueous phase. In the present study, degradation of 4CP was carried out with as prepared nano TiO₂, calcined TiO₂ at 500⁰ C, 0.05 mole % Cu²⁺ / 0.1 mole % Sm³⁺ co-doped nano titania calcined at 400 and 500 ^oC. It could be seen from the Figure. 8 and 9 that the rate of photocatalytic degradation was enhanced by increasing the calcination temperature of the catalyst and complete degradation of 4CP occurred within three hours in the presence of the 0.05 mole % Cu²⁺ / 0.1 mole % Sm³⁺ co-doped nano titania calcined at 400 and 500 ^oC. This can be attributed to the increase in the crystallinity of the anatase phase at 500^oC.

Conclusions

Copper and samarium codoped TiO₂ were synthesized by simple sol gel process. An increase in calcinations to 500° C, the crystallite size increased and transformation of anatase to rutile phase retarded. Characterization results showed that co doping can improve the photo catalytic properties, decrease in particle size and inhibition of phase transformation. Amount of copper on codoped TiO₂ had significant effect in catalytic activity and smaller amount was the most efficient. Sm ion could hinder the growth of the particles during calcination and the phase transformation which occurred at high temperature. The results of XRD showed that all samples were calcined at 400 to 600° C preserved the anatase structure and doping inhibited the increase of crystallite size.

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