Synthesis, physico-chemical characterization and effect of cobalt doped TiO₂ nanoparticle catalyst prepared by sol-gel method

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Anatase TiO_2 and Co doped TiO_2 were prepared through sol-gel method. Powder XRD pattern confirms the formation of crystalline anatase TiO_2 and amorphous Co- TiO_2 . DR UV-Vis absorbance shows that band gap of TiO_2 is reduced to ~ 2.0-2.5 eV upon Co doping suggesting that these materials can absorb in the visible range also. FT-IR spectra confirmed that the Co- TiO_2 is similar to that of pure TiO_2 . Raman spectra exhibit all the bands corresponding to anatase TiO_2 . However, for Co- TiO_2 the peaks corresponding to the presence of Co clusters also appeared. BET surface area of TiO_2 is $82 \text{ m}^2\text{g}^{-1}$ and is reduced (60-45 m^2g^{-1}) upon Co doping. Nanosize (~20 nm) of the Co doped TiO_2 was confirmed from Transmission electron (TE) micrograph studies. Methylene blue dye degradation study have also carried out to exploit the catalytic activity of as prepared materials.

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1. Introduction

The world's energy demand is constantly rising and is expected to more than double by 2050 compared to today's level because of population growth, the rapid economic rise of many developing countries, and sustained high energy consumption. Finding methods for safe energy carriers is therefore a primary target for research today [1]. Solar energy is the largest source of renewable energy on the Earth [2-5]. The most critical issue is the development of a special class of new photosensitive materials for efficient and clean conversion of solar energy. TiO_2 and TiO_2 based oxide systems are the most promising due to its resistance to corrosion and photocorrosion, less toxicity etc. [6]. The activity of TiO₂ strongly depends on its morphology, particle size and distribution, crystallinity and crystal structure. Anatase is having the highest photocatalytic activity, while rutile has the highest chemical stability [7]. However, the efficiency is rather low since TiO_2 is active only under ultraviolet (UV) light because of its wide band gap, (~3.2 eV for anatase and $\sim 3.0 \text{ eV}$ for rutile) [6]. Thus, for efficient photosensitive applications it is necessary to extend the photoresponse of TiO₂ to the visible region by either modification of its optical properties or by reducing the rate of recombination of electron-hole pairs. Among many methods, doping is one of the most promising for sensitizing TiO₂ to visible light and also to keep electronhole pairs separate [8]. Different metal ions such as V, Ni, Cr, Mo, Fe, Sn, and Mn have been doped into TiO_2 to improve the visible-light absorption [6]. Synthesis parameters are crucial since photosensitive activity is greatly influenced by the amount and size of the dopants. Sol-gel is one

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of the most widely used methods for preparing nanoparticles, due to its high homogeneity, low processing temperature, stability and versatility of processing [9]. The possibility to obtain materials with controlled structural features and morphology, low particle size and high crystallinity makes this method more attractive for the preparation of nanosized materials with high surface area and photosensitive activity [10]. In the present work, nanosized TiO₂ and Co doped TiO₂ materials were prepared through simple sol-gel method. Detailed structural characterization was done in order to understand and utilize these nanosized materials effectively for photosensitive applications.

2. Experimental

2.1. Material Preparation

The chemicals used are; Titanium (IV) tetraisopropoxide (Ti[OCH(CH₃)₂]₄), TTIP, and Co(NO₃)₂.6H₂O- (98%, Merck Ltd., Mumbai), Isopropyl alcohol (IPA), Conc. HNO₃ and distilled water . All the chemicals were of AR and used as received. In the sol-gel method for TiO₂ preparation, TTIP (55 mL) was dissolved in IPA (72 mL) and hydrolysed with dH₂O (15 mL) under vigorous stirring (3 h, pH ~ 3) at room temperature. The gel obtained was dried overnight and calcined at 773 K to obtain TiO₂. For Co-TiO₂ preparation the same procedure was followed with various weight % of Co by taking corresponding amounts of Co(NO₃)₂.6H₂O solution. The materials were named as 0.1-2.0 Co-TiO₂ (0.1-2.0 weight % Co) respectively.

2.2. Material Characterization

The phase formation was confirmed using powder X-Ray Diffraction (AXS Bruker D5005 X-ray diffractometer, Germany, 40 kV and 30 mA, CuK α ($\lambda = 1.54$ A°) radiation with Ni filter). The absorption data was recorded on DR UV-Visible spectroscopy (Varian, Cary 5000). The vibrations as well as stretching modes were studied using FT-IR (Perkin Elmer over the range 400-4000 cm⁻¹) and Raman spectroscopies (Thermo DXR Raman Microscope). The surface area and pore volume was measured on BET surface area analyser (NOVA 1200, Quantachrome, USA). Thermal data was collected using TA instrument SDT Q 600V 8.3Build 101 and TE micrographs were collected on JEOL-JEM 2200 FS.

3. Results and discussion

The powder XRD patterns of TiO_2 and various Co-TiO_2 are shown in Figure 1.The patterns show the characteristic planes of anatase TiO_2 [6,7]. The pattern of 0.1Co-TiO_2 exhibits peaks similar to pure TiO_2. As the Co doping increases, the pattern becomes amorphous [10]. For 0.5-2.0 Co-doping, reduction in intensity of peaks suggests amorphous nature after doping of Co into TiO_2 [13]. For Co-TiO_2, no diffraction patterns of the dopants could be observed possibly due to the quantity of Co ions doped to TiO_2 was too small to be detected by XRD [11]. The average crystallite size of the materials calculated using the Debye-Scherrer equation is about ~ 20 nm [12]. Complete removal of water and organic precursors was confirmed by TG-DSC and 773 K was selected as the calcination's temperature.

The DR UV-Vis spectra of TiO₂ and Co doped TiO₂ are shown in Fig. 2. The DR spectrum of TiO₂ consists of a broad intense absorption around 413 nm (band gap energy ~ 3.0 eV, $\lambda_{edge} = 1239.8/E_{bg}$) [13]. Spectra of Co-TiO₂ shows a red shift in the absorption. Increase in the concentration of Co doping into TiO₂ resulted in a prominent change or shift of band edge from UV to visible region (2.8-2.3 eV) [14]. Trend of these band gaps agree rather well with the observation that metal oxides typically show decreased band gap energies with increasing particle size or with a change of phase [11]. The spectra of Co-TiO₂ materials consist of an additional peak around 550 nm. With increase in Co doping, the sharpness and intensity of absorption band between 500 and 600 nm is also increased. This can be attributed to Co²⁺ \rightarrow Ti⁴⁺ charge-transfer interactions [14]. Metal ion doping on TiO₂ can expand its photo-response to visible region through formation of impurity energy levels [15].



Fig. 1. Powder XRD pattern of TiO₂ and Co-TiO₂ materials.



Fig. 2. DR UV-Vis spectra of TiO₂ and Co-TiO₂ materials.

In FT-IR spectrum (Fig. 3) of TiO₂, the band found at ~ 564 cm⁻¹ is due to the Ti-O stretching vibration. The same peak, with more broadening, appears in Co-TiO₂ materials proves that after Co doping also TiO₂ anatase phase still exists, but having a low crystalline degree [9]. The absorption bands in the range 1100-1000 cm⁻¹ are attributed to the –OR groups linked to Ti. The peak at ~1640 cm⁻¹ and in the range 3500-2800 cm⁻¹ are the characteristics bending and stretching vibrations of adsorbed molecular water respectively [7,13]. Absence of any absorption in the range 1085-1050 cm⁻¹ suggests formation of TiO₂ as confirmed by thermal data [7].

Fig. 4 shows the Raman spectra of the prepared materials. In the spectra, Raman active modes of anatase TiO_2 are appear as E_g , B_{1g} , A_{1g} respectively [16, 17]. The Raman peak shifts to lower wavenumbers as the Co doping increases. Two additional Raman peaks at around 475-480 cm⁻¹ and 687-690 cm⁻¹ are observed in the Co doped TiO_2 may due to the clusters of Co or cobalt oxides. These spectra indicate that the doped Co enter into TiO_2 lattice, which may result in a disorder of the crystal structure and the presence of oxygen vacancies in Co-TiO₂ lattice [16].



Fig. 3. FT-IR spectra of TiO_2 and Co- TiO_2 materials.



Fig. 4. Raman spectra of TiO₂ and Co-TiO₂ materials.

The BET surface area of TiO₂ (82.8 m²g⁻¹) is higher than of TiO₂-P25 (53.6 m²g⁻¹). Higher surface area can be attributed to the nanosize TiO₂ formed through adopted sol-gel method (Table 1). The higher surface area can be useful to get high efficiency of photosensitive organic transformation/pollution abatement applications as it implies larger contact surfaces exposed to the reagents [17]. There is a decrease in surface area of the materials as the Co doping increases. Accordingly, the particle size also increases. For 2.0Co-TiO₂, the surface area decreased drastically with corresponding increase in particle size. This can be related to the slower hydrolysis rate of titanium alkoxide in isopropanol, allowing particles to grow in size which results in agglomeration of particles [18]. The specific surface area determined by BET method is tabulated in Table 1.

Sl.No.	Material	BET surface area (m ² g ⁻¹)	Particle size (nm)
1.	$TiO_2 - P25$ (commercial)	53.6	26.5
2.	TiO ₂	82.8	17.1
3.	0.1 Co-TiO ₂	67.9	20.9
4.	0.5 Co-TiO ₂	62.2	22.4
5.	1.5 Co-TiO ₂	58.1	24.8
6.	2.0 Co-TiO ₂	45.4	31.2

Table 1. BET surface area and Particle size of the materials.

TEM images shown in Figure 5 confirms the formation spherical and needle shaped morphology for the as prepared cobalt doped TiO₂ materials. The dark metallic rich paricle deposition is due to cobalt doping into the titanium dioxide lattice. The average particle size of as prepared Cobalt doped titanium dioxide catalysts obtained between 15-20 nm particle size with respect magnified scale of value of 20 nm in the Figure 5. In the next step is to evaluate the photosensitive activity of prepared Cobalt doped TiO₂. Figure 6 (a-b) shows the photocatalytic activity results under visible light irradiation for the dye degradation process. The increase in the cobalt addition in tio2 photosensitive materials increase drastically the decomposition of the methylene blue dye compounds (Fig. 6 a-c). After the addition of higher amount of 1.5 moles of cobalt in TiO₂ (Fig.6d) addition is shows the complete dye degradation process with in 3-4 hours of reaction process. Over addition of cobalt above 1.5 moles results in deactivate the photosensitive activity for TiO₂. Hence, the optimized amount of 1 to 1.5 moles of cobalt addition in titanium dioxide catalyst could provide the best results for dye degradation in water treatment process.



Fig. 5. Transmission electron micrograph of 0.1 Co-TiO₂.



Fig. 6. Visible light driven photo catalytic activity of different amount of Cobalt doped TiO_2 catalyst (a) pristine TiO_2 (b) 0.1 Co-doped TiO_2 (c) 0.5 Co-doped TiO_2 (d) 1.5 Co-doped TiO_2 .

4. Conclusions

The nanosized TiO₂ and Co doped TiO₂ materials were successfully prepared by simple sol-gel method. X-ray diffraction pattern shows crystalline anatase TiO₂ and amorphous nature with higher Co doping. FT-IR confirms the complete hydrolysis of precursors to form crystalline TiO₂. Raman spectra show the peaks corresponding to anatase TiO₂ and formation of Co clusters or Co oxides with higher (0.5- 2.0 wt %) Co doping. DR UV-Visible spectra suggest a shifting in TiO₂ absorbance to visible region with Co doping. BET surface area decreased with increase in Co doping. TE micrographs confirmed the formation of 10-20 nm particles for Co-TiO₂ materials. These small size higher surface area materials can be utilized efficiently for photosensitive transformations of organic dye in waste water under direct solar visible light.

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