



Recent Advances In Nano Science And Technology 2015 (RAINSAT2015)

Ceria doped titania nano particles: Synthesis and photocatalytic activity

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Abstract

Ceria (0.5, 1 and 2 mol %) doped titania nano catalysts were prepared by combustion synthesis method, using titanium isopropoxide as the starting material. The prepared catalysts were characterized by X-ray diffraction (XRD), Energy dispersive X-ray analysis (EDX), Scanning electron microscopy (SEM) and Infra red spectroscopy (FTIR). Total acidity of the prepared catalysts were determined by temperature programmed desorption of ammonia (TPD – NH₃). XRD pattern of 1% ceria doped titania obtained by calcinations at 873 K indicated that the samples were crystalline with a mixture of anatase and rutile phase. No peaks corresponding to cerium oxide were observed XRD patterns indicating that the amount of cerium is negligible on the surface of titania catalyst. The photo catalytic activity was evaluated for the degradation of methylene blue (MB) under visible light irradiation. The degradation rates of MB on cerium doped TiO₂ samples were higher than that of pure TiO₂. The introduction of structural defects (cationic ceria dopant) into the titania crystal lattice leads to the change of band gap energy. As a result, the excitation energy is expanded from UV light of anatase TiO₂ to visible light for ceria doped titania.

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Selection and Peer-review under responsibility of [Conference Committee Members of Recent Advances In Nano Science and Technology 2015.].

Keywords: : Ceria doped titania; Titanium Isopropoxide, Combustion synthesis method; photo degradation of Methylene blue.

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1. Introduction

Titanium dioxide TiO_2 has received good attention because of its interesting properties such as pigments [1], medical devices [2] and gas sensing [3]. The application of titanium dioxide as heterogeneous photocatalyst has attracting considerable attention for purification of air [4–6]. In particular, the attention has been recently focussed on the semiconducting and photosensitive behaviour, exploited in several applications concerning the environmental field, such as purification of air and water from pollutants [7] and solar cells for low-cost photovoltaic devices [8]. The photocatalytic performance of TiO_2 -based devices is largely influenced by the particle size, apparently at the nanometer scale. TiO_2 in anatase crystalline form has become the most promising photocatalyst for its efficient photocatalytic, non-toxic, low cost and oxidation activity. Due to the large band gap of pure anatase titania about 3.2 eV, all photon-driven applications of TiO_2 require ultraviolet light for excitation [9]. Many attempts have been made to narrow the band gap energy by modification of TiO_2 using metal ions doping [10, 11].

Despite the promising properties, applications have been limited, for the UV region, as it occupies only approximately 4% of the entire solar spectrum, while 45% of the solar energy corresponds to the visible light. More practical applications can be possible if the photocatalytic active region can be expanded to the visible light region (400–700 nm); the photoenergy can be used more efficiently [12]. Doping, within certain limits, serves to prolong the lifetime of charge carriers if the dopants have energy levels just below the conduction band or just above the valence band of to realize shallow charge carrier trapping. As reported in the literature, Co and Fe doping [13, 14] had increased the photocatalytic activity of TiO_2 under visible light. Many rare earth metal ions were reported to improve the photocatalytic activity of TiO_2 . Nd^{3+} ion doping reduced the band gap of nano- TiO_2 [15]. Xie et al. [16] reported that Sm^{3+} ions doping leads to considerable modification in the photocatalytic activity of nano TiO_2 for cango red dye degradation under visible light. Doping with cerium ions containing 4f electrons into the TiO_2 lattice can eliminate the recombination of electron–hole pairs significantly and also result in the extension of their wavelength response toward the visible region. Among lanthanides, cerium is arguably the most exciting for researchers in the field of catalysis and photocatalysis. Ceria (CeO_2) has a band gap ~ 3 eV and shows interesting optical properties and strong UV absorption. The catalytic activity of ceria is attributed to its high oxygen storage capacity which is largely due to two common valence state cerium (III) and cerium (IV). The ability of Ce^{3+} to oxidize to Ce^{4+} states leads to high oxygen mobility which in turn leads to a strong catalytic potential [17]. Li et al. [18] have reported that the introduction of Ce 4f level led to the optical absorption band between 400 and 500 nm and eliminated the recombination of electron–hole pairs and enhance the photocatalytic activity under UV or visible light illumination. Until now, there has been very little literature about the combustion synthesis of Ce^{3+} doped titania and its effect on the photocatalytic activity under visible light irradiation.

In this work, we report the synthesis of TiO_2 nanopowders, which was achieved by combustion method using titanium tetra isopropoxide $\text{Ti}(\text{O}-i\text{Pr})_4$ as the precursor and glycine as fuel. Cerium nitrate is used for doping cerium ions. The main advantage of the method was the reduction in of the number of processing steps and the cost-effectiveness of the starting reactants. The study was also aimed at extending the light absorption spectrum toward the visible region, and to investigate the effect of the doping content of Ce^{3+} ions on the photocatalytic activity towards the degradation of methylene blue.

2. Experimental

In combustion synthesis, pure and Ce^{3+} doped TiO_2 nanoparticles were prepared using analytical grade titanium iso-propoxide ($\text{Ti}(\text{OC}_2\text{H}_5)_4$) and cerium nitrate ($\text{Ce}(\text{NO}_3)_3$) as the source of the respective metals. Glycine was used as an organic fuel during the process. Titanium Isopropoxide and glycine in the 5:1 ratio was mixed well, transferred into a crucible and fired to the 500°C in a pre heated muffle furnace for 4 hours. The molar ratio of cerium ion doping was 0.5%, 1% and 2 % of titania. The combusted puffy and porous powder obtained was sieved. Powder X-ray diffraction (PXRD) measurements were performed on a PANalytical Xpert Pro X-ray Diffractometer using $\text{Cu-K}\alpha$ radiation ($\lambda = 0.154$ nm) at 40 kV, at a scanning rate of 2°min^{-1} . The crystallite size of TiO_2 was calculated using the modified Scherrer equation, $d = 0.9\lambda/\beta\cos\theta$. Fourier transform infrared (FTIR) spectra of the samples were

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