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Study of Structural and Optical Properties of Zinc-doped Titanium Dioxide Nanoparticles

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ABSTRACT. Titanium dioxide (TiO₂) nanoparticles have been extensively investigated for potential applications in various fields due to their unique physical and chemical properties. In this investigation, Zn-doped TiO₂ nanoparticles were prepared by sol-gel method and characterized for their structural and optical properties using X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), UV-Vis Spectroscopy and Photoluminescence (PL). The precursors titanium tetraisopropoxide and zinc chloride dopant were used as the source of titanium and zinc. Hydrochloric acid was used to maintain the pH of the solution during the process. A red shift of the light absorption edge of Zn-doped TiO₂ has been observed as compared to undoped TiO₂ nanoparticles. The crystallite sizes of Zn-doped TiO₂ nanoparticles ~8 nm were estimated by using Scherrer's formula.

Introduction. Titanium dioxide (TiO₂) material has been widely investigated and used as photocatalysts, sensors, catalysts for photo-electrochemical water splitting, for hydrogen storage and photovoltaic applications. This material is chemically and physically stable, inexpensive and non-toxic to the human being and our environment. TiO₂ exists in both crystalline and amorphous forms with three crystalline polymorphs of TiO₂ are anatase, rutile and brookite. These three polymorphs have different crystalline structures; anatase and rutile have tetragonal structure whereas brookite has orthorhombic structure. The structure of anatase and rutile can be described in terms of chains of TiO₆ octahedron. The two crystal structures differ by the distortion of each octahedron and by the assembly pattern of octahedral chains [1]. TiO₂ nanoparticles are synthesized via various methods such as Hydrothermal, Solvothermal, Electrodeposition, Sonochemical, Flame Pyrolysis and Sol-gel methods. Among these, sol-gel is one of the most preferable techniques for preparation of titanium dioxide particles in nanometer range because of its cost effectiveness, controlled particle growth and ability to produce nanoparticles with high degree of homogeneity [1-4]. Heterogeneous photocatalysis employs TiO₂ and UV light to give an efficient new route for the degradation of toxic substances, decomposition of water and hydrogen generation [5, 6]. TiO₂ nanoparticles show high reactivity and chemical stability under ultraviolet light, whose energy exceeds the band gap of 3.3 eV in the anatase crystalline phase TiO₂, thus limiting the reactivity in visible range. Many studies were carried out to decrease its band gap with lower rate of recombination of the electron-hole pair. It can be achieved by proper doping of metal ions, surface modification and dye photosensitization of TiO₂ surface [6, 7]. Several literatures have reported the tenability of TiO₂ particles through doping with transition metals like chromium, manganese, iron, cobalt, nickel, copper, zinc, etc. For dye sensitized solar cell application, optimal light harvesting can be attained by doping the metal in titanium dioxide which results in altering the optical band gap. In order to increase the photocatalytic activity of TiO₂ nanoparticles, various synthesis methods have been explored [8, 9]. Zn-doped TiO₂ powders

synthesized by sol–gel route showed the effect of doping on the crystalline phase, degree of crystallinity, particle size, distribution and morphology [10]. In addition, double-layer films doped with Zn-ions have also been reported with various morphologies and phase compositions which could enhance the cell efficiency of the dye-sensitized solar cell [11].

In this paper, we present the preparation of undoped and doped TiO₂ nanoparticles via sol-gel route. The prepared sample is studied for its structural and optical properties using different characterization techniques. The materials and experimental details are described in Section second and the obtained results are discussed in Section third. Finally, Section fourth concludes the paper.

Experimental Details. All the chemicals were analytical grade and used without purification. Titanium tetraisopropoxide (TTIP) with a purity of 97% (Aldrich, UK) was used as a titanium precursor; analytical grade hydrochloric acid (HCl, Merck) was used as catalyst for the peptization. Water–acid mixture (in the range of pH = 1–2) was stabilized at a constant temperature. TTIP was added to maintain the molar ratio of Ti:H₂O=1:100. As a result, white precipitates were formed and further peptized for 2 hours to form a stable sol. For the preparation of Zn-doped TiO₂ solution, zinc chloride (ZnCl₂, Finar) was dissolved in the water-acid mixture with 0.03 mol %. The solution was then heated at 100 °C for 3 hours to obtain as-synthesized Zn-doped TiO₂ powders. Subsequently, the as-synthesized powders were calcined at 450 °C for 2 hours to attain the crystallinity. The morphology and structure of the particles were studied using Scanning Electron Microscopy (SEM-JSM-6360). The crystalline nature of the nanoparticles were characterized using X-ray Diffractometer (Shimadzu, 6000) and the crystallite size was calculated using Scherrer's formula. The absorption spectra of nanoparticles were measured using UV-VIS spectrophotometer (Schimadzu, UV-1800) and Fourier transform infrared spectroscopy (FTIR) measurements have been performed with (Shimadzu, 8400) in the mid infrared area, ranging from 450-4000 cm⁻¹.

Results and Discussion. Fig. 1 shows the XRD pattern of Zn-doped TiO₂ nanoparticles calcined at 450 °C. The diffraction peaks at $2\theta = 25.3^\circ$, 37.8° , 48.0° , 53.9° and 55.0° corresponds to the anatase phase of TiO₂ (JCPDS No. 96-500-0224). A low intense diffraction peak at $2\theta = 30.7^\circ$ is attributed to the brookite phase of TiO₂. Anatase is the predominant phase in the prepared sample. X-ray diffraction peak at 25.3° corresponds to the characteristic peak of crystal plane (101) of anatase and peak at 27.4° corresponds to a crystal plane (121) of brookite. The calculated crystallite size from Scherrer's formula is found to be around 8 nm.

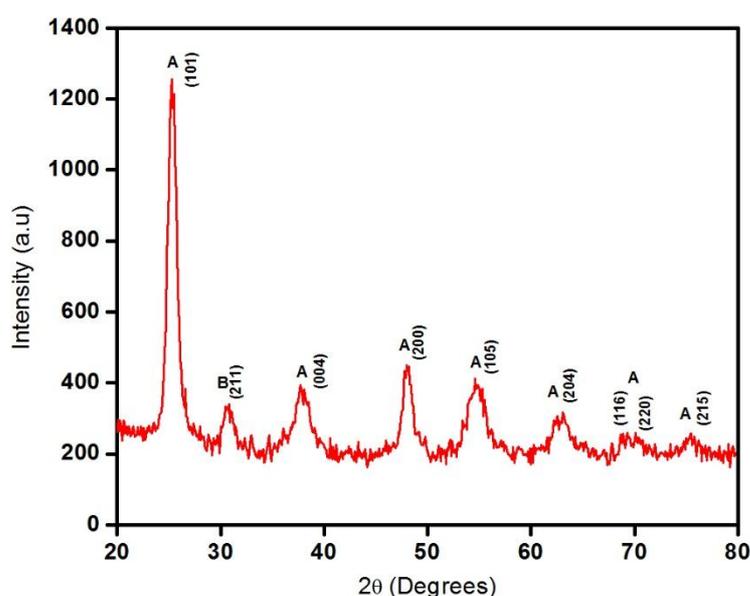


Fig. 1. XRD pattern of as-synthesized Zn-doped TiO₂ sample (A, anatase; B, brookite).

Fig. 2 depicts the scanning electron microscopy image of Zn-doped TiO₂ particles which shows the particle distribution of as-synthesized Zn-doped TiO₂ nanoparticles. The nanopowder exhibited a homogeneous spherical morphology of the particles.

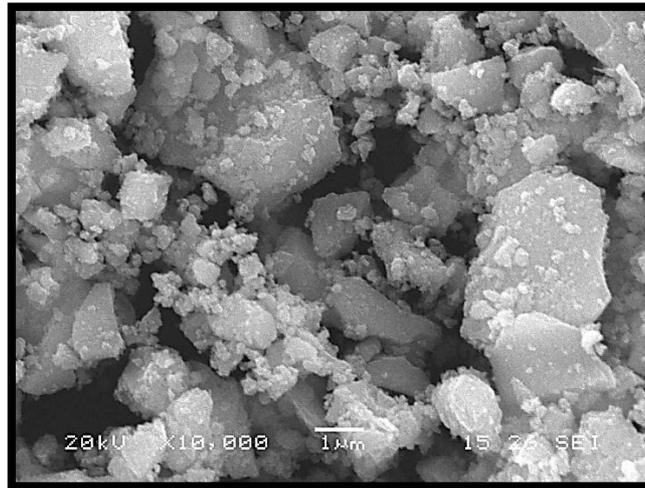


Fig. 2. Scanning Electron Microscopy image of as-synthesized Zn-doped TiO₂ nanoparticles.

Optical absorbance spectra of undoped and Zn-doped TiO₂ particles calcined at 450 °C were recorded and shown in Fig. 3. Absorption spectra shows the red shift of the light absorption edge of Zn-doped TiO₂ nanoparticles as compared to pure TiO₂ particles. The band gap energy can be estimated from the value of wavelength where the absorption edge starts to take off and the band gap energy of TiO₂ nanoparticles were observed to be decreased from 3.17 to 2.93 eV with Zn-doping. The red shift has been attributed to the formation of impurity by the dopant within the band gap states of TiO₂ [10].

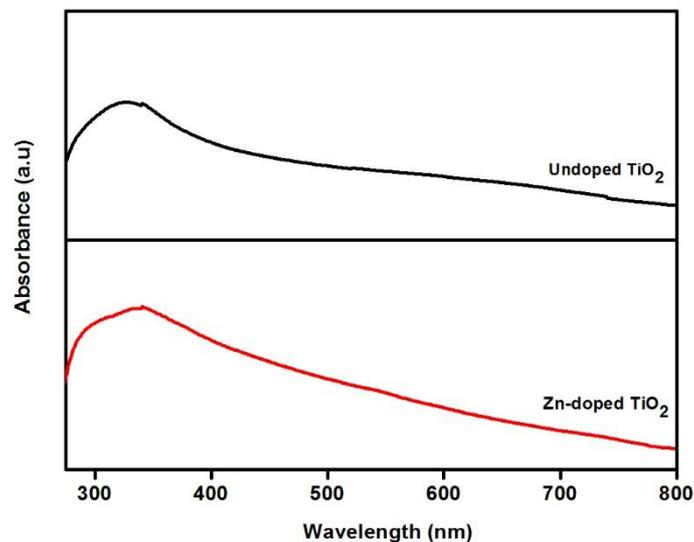


Fig. 3. UV-vis absorbance spectra of undoped TiO₂ and Zn-doped TiO₂ calcined at 450 °C.

Fig. 4 depicts the FTIR spectra of as calcined Zn-doped TiO₂ nanoparticles. A broad peak appearing at 3100–3600 cm⁻¹, precisely at 3325cm⁻¹ is attributed to the stretching vibration of O–H hydroxyl groups representing physically adsorbed water as the moisture. The peak observed at 1632 cm⁻¹ is attributed to the bending modes of adsorbed water. Another peak at 2973 cm⁻¹ is assigned to the C–H

vibrations. This could be because of the organic residues remained in TiO₂ even after calcination. The sharp peaks appearing at 1128, 1088 and 1046 cm⁻¹ can be attributed to C-O vibration while peaks at 500 cm⁻¹ to 900 cm⁻¹ corresponds to O-Ti-O bands [12, 13].

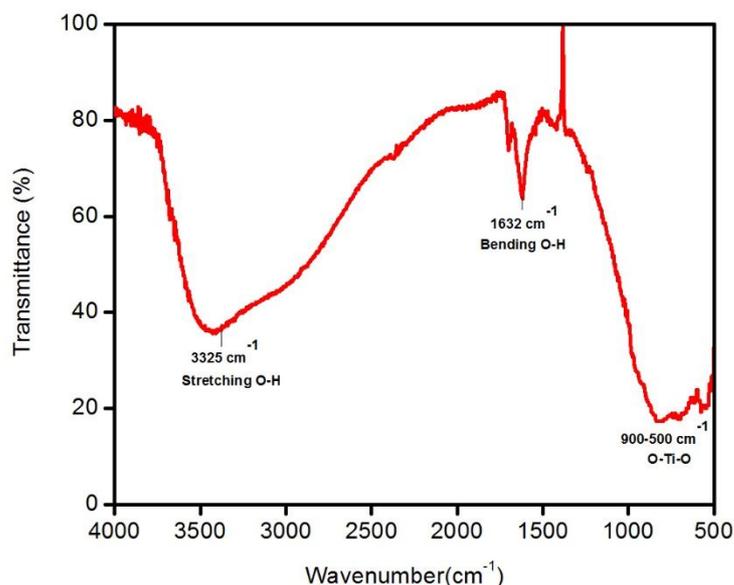


Fig. 4. FTIR spectrum of as-synthesized Zn doped TiO₂ sample

Summary. In this work, Zn-doped TiO₂ nanoparticles were successfully synthesized by sol-gel method and studied for their structural and optical properties. XRD pattern showed anatase crystalline phase of Zn-doped TiO₂ nanoparticles. A low intensity XRD peak has also been observed which is attributed to the brookite phase. Scanning electron microscopy study has confirmed the prepared particles of homogeneous spherical morphology. The absorption spectra of the as-synthesized nanoparticles showed strong absorption below 400 nm and a red shift was observed in Zn-doped TiO₂ as compared to the undoped TiO₂ nanoparticles.

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