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Visible Light assisted Photocatalytic Acitivity of Zinc Titanate in Presence of Metallic Sodium

Sirajudheen P*

Department of Chemistry, WMO Imam Gazzali Arts and Science College, Koolivayal, Panamaram, Wayanad, Kerala, India

Abstract

Zinc titanate powder was synthesizd by an organic free co-precipitation peroxide technique. Zinc chloride and titanium (IV) isopropoxide were used as the primary material with the ratio of Zn:Ti was 1:1 and the later compound was prepared by mixing titanium chloride with isopropanol. The stoichiometric ratio of the synthesized zinc titanate was measured by using AAS. The synthesized powder was calcined at 800°C for 3 hours using the X-ray diffraction and the calcined zinc titanate powder crystalline phase formation was found to be cubic. FTIR was used for studying the bonding characteristics of ZnO and TiO_2. Disintegration temperature was analyzed by means of Thermogravimetric analysis. The photocatalytic activity was measured based on the degradation of methyl orange in aqueous solution in the presence of metallic sodium. The results showed that $ZnTiO_3$ particle exhibited good photocatalytic activity under visible range radiation.

Keywords: Zinc titanate; Cubic phase; Methyl orange; Photocatalytic activity

Introduction

Zinc titanate ($ZnTiO_3$), has a promising material as a gas sensor [1] (for ethanol, NO, CO, etc.), paint pigment [2], catalyst [3] and etc. Also $ZnTiO_3$ has been reported as a material with an exceptional electrical properties which could be a suitable contender as microwave resonator [4]. This material has a dielectric constant of 19, quality values of 30.0 GHz and the temperature coefficients of the resonant frequency of -55 ppm/qC [5]. The structures of titanium dioxide (TiO_2), $Zn_2Ti_3O_8$, $ZnTiO_3$ and Zn_2TiO_4 comprised of TiO_6 octahedra. In rutile and in $ZnTiO_3$, the connection of the TiO_6 octahedra results chains and/or layers. As a result of this resemblance, $ZnTiO_3$ is formed only in the presence of rutile [6].

Zinc titanates are generally synthesized by characteristic solid state reactions at high temperatures [7]. Due to some confines of solid-state synthesis, such as large grain size and uncontrolled and irregular morphologies, different kinds of alternative techniques have been depicted including mechano-chemical activation [8,9], molten salt synthesis [10], a semi chemical route combined with vigorous micro beads milling [11,12] and sol-gel method. But the sol-gel methods are generally complicated and the reagents used are expensive. In wet chemical processes for preparing highly quality of powders, better homogeneity, control morphology and smaller particle size are preferred.

The co- precipitation reaction technique has exciting characteristics such as its simplicity, its relatively low cost and the fact that it usually results in products with the preferred structure and composition [13]. The effort aimed to synthesize $ZnTiO_3$ powder by the co- precipitation peroxide method. The phase change was studied by X-ray diffraction (XRD). The chemical characterization of zinc titanate encompasses analysis of elements using AAS. The photocatalytic activity was measured based on the degradation of methyl orange in aqueous solution in the presence of metallic sodium.

Materials and Methods

Materials

Anhydrous Zinc chloride and Titanium chloride in isopropanol were used as starting materials for zinc titanate synthesis. Hydrogen peroxide and ammonia solutions from Merck are also used. All the chemicals were used without further purification. The crystalline structure of the samples was determined by powder XRD using BRUKER D8 Advance X-ray diffractometer using CuKα radiation. FT-IR spectra were recorded using KBr pellet method on Shimadzu IR affinity spectrophotometer in the range from 4000 cm^{-1} to 400 cm^{-1}. TGA experiments were carried out using SDT Q600 V20.9 instrument. The decolorization of methyl orange was measured by using UV-Visible Spectrophotometer of Shimadzu at 465 nm by incorporating the dye solution with zinc titanate in presence of metallic sodium, exposed to sunlight for different irradiation time, using UV-Visible Spectrophotometer. During the irradiation time, the solution was bubbled with air and the initial concentration of dye was 10.0 ppm.

Preparation of the sample

0.2 mol (0.272 g in 100 ml) zinc chloride was dissolved in 100 ml of water and 0.2 mol of titanium chloride in isopropanol was also prepared up to 100 ml and the two solutions are mixed together to get a homogenous solution. Then 15 ml of hydrogen peroxide and 20 ml of ammonia solutions are mixed and 165 ml of water is added to it. The homogeneous solution having zinc chloride and titanium tetra chloride are added to the second solution drop by drop by means of a burette. A precipitate was developed in the beaker it was allowed to settle for some time and filtered. The residue obtained was washed with water dried by using owen and calcined in Muffle furnace at 800°C about half an hour in a silica crucible [14]. The zinc titanate formed was powdered and used for further experiments.

***Corresponding author:** Sirajudheen P, Department of Chemistry, WMO Imam Gazzali Arts and Science College, Koolivayal, Panamaram, Wayanad, Kerala, India, Tel: 04935272674; E-mail: sirajpalliyalil@gmail.com

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Photocatalytic activity

The photocatalytic efficiency of the synthesized powders was calculated by deprivation of a model aqueous solution of methyl orange in presence of metallic sodium. The initial concentration of methyl orange aqueous solution was 10 ppm exposed under visble light irradiation. During analysis varying amount of zinc titanate sample was added to methyl orange solution and it was exposed under visible light irradiation with constant weight (0.02 g) of sodium. During the irradiation time, the solution was bubbled with air. The photo-bleaching of methyl orange was strongly affected by the presence of zinc titanate in the present of metallic sodium. As the contact time increases, the degradation of methyl orange was also increases.

Result and Discussion

Results of structural and thermal analyses

The X-ray diffraction patterns of prepared $ZnTiO_3$ calcinated at different temperatures are shown in Figure 1. Neither ZnO nor TiO_2 phases were observed in the spectra. At 600°C, the samples undergo solid state reaction to form cubic structure. On increasing the calcination temperature from 600°C to 700°C, the crystallainity of cubic phase $ZnTiO_3$ also increases It was evidenced from the increased intensity peaks of $ZnTiO_3$ at 30.45° and peak at 35.37° [15]. When using the same precursors [16] at 800°C, several peaks related to the hexagonal $ZnTiO_3$ appears, but the cubic crystals are still dominant.

The Differential Thermal Analysis (DTA) curve of the formerly heat treated at 400°C sample elucidates two endothermic (120 and 380°C) and two exothermic peaks at 450 and 540°C. The exothermic lines might related to the combustion of the organic residues and crystallization of the sample with development of $ZnTiO_3$ phase (540°C) and the endothermic effects can be ascribed to the dehydratation of the sample. Both exothermic peaks (at 450°C and 540°C) are not observed in the DTA curve of the formerly heat treated sample at 500°C. This shows that the last exothermic effect is related to the crystallization process which is in good agreement with the X-ray diffraction results (Figure 2). The results are well-matched to those obtained by Hosono et al. and Wang et al. [15,16].

The Fourier Transform Infrared Spectrum (FTIR) of the prepared zinc titanate ($ZnTiO_3$) samples was shown in Figure 3. Dominant bands at 730 cm^{-1} , 490 cm^{-1} and 450 cm^{-1} along with a sharp band at 420 cm^{-1} are observed in the IR spectra of $ZnTiO_3$. It is identified that, the bands in the absorption range 700-400 cm^{-1} might be associated to the vibrations of TiO_6 units in $ZnTiO_3$ [16,17]. According to the X-ray diffraction data for this sample, only one phase ($ZnTiO_3$) was noticed. It is also known that, bands corresponding to ZnO_n polyhedra are in the same absorption range [18,19]. The IR spectrum of $ZnTiO_3$ is connected to the increased intensity of the band centered at 420 cm^{-1}. As it is known this band is typical for the vibrations of TiO_6 units [20,21] and the weak band near 450 cm^{-1} could be related to the Ti-O stretching vibrations in $ZnTiO_3$ [17,22]. A characteristic band at 730 cm^{-1} appeared at 800°C. This can be assigned to the Zn-O-Ti bond structure in cubic $ZnTiO_3$ [23].

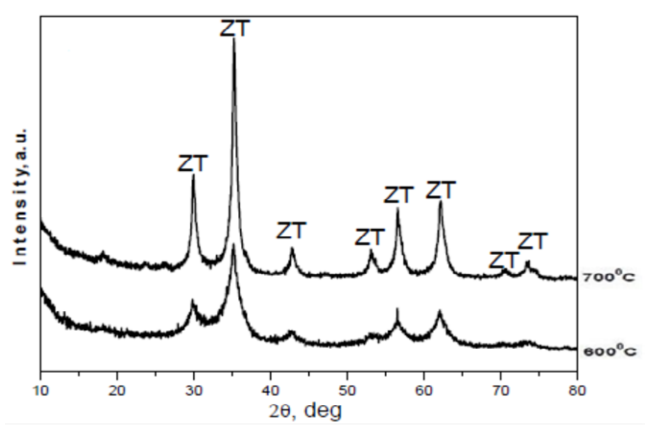

Figure 1: XRD of $ZnTiO_3$.

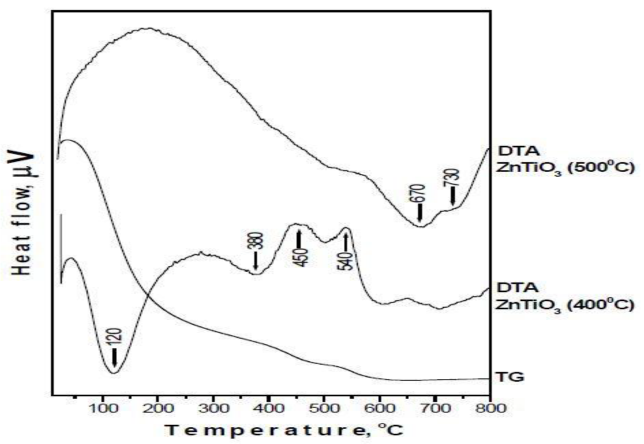

Figure 2: DTA curve of $ZnTiO_3$.

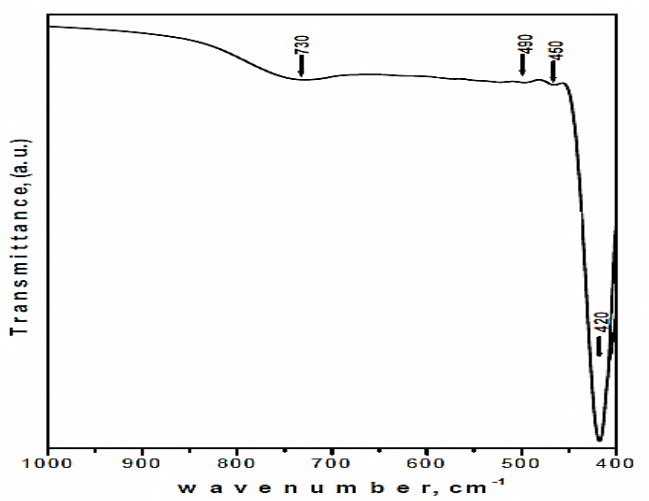

Figure 3: FTIR spectra of $ZnTiO_3$.

Photocatalytic activity

The photodegradation of methyl orage was performed by adding varying amount of zinc titanate particle in 10.0 ppm methyl orange solution exposed under visible light irradiation [16] by taking 0.02 g of sodium. Figure 4 shows the photobleaching of the dye with different amount of zinc titanate exposed to visible light irradiation for different duration [24]. If the dye concentration is increased, the number of dye molecule in the solution is also increased which eventually affect the degradation rate [16]. The photo-bleaching of methyl orange was

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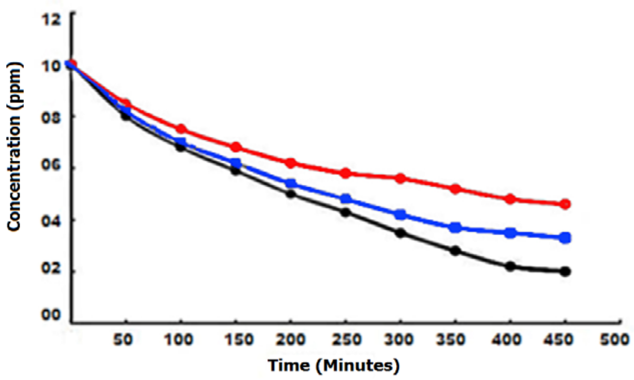

Figure 4: Photo degradation of Methylene blue solution with $ZnTiO_3$ With differentconcentration (Red- 0.05, Blue- 0.1 and Black- 0.2 in % respectively).

strongly affected by the presence of zinc titanate present in the system [25]. As the exposure time increases, the degradation of dye also increases [26]. This is due to increased photon absorption by zinc titanate which is catalysed by metallic sodium, which leads more transfer of photoelectrons and photo holes between valance band and conduction band and there by generating hydroxyl radical and super radical oxygen in the photo catalysis cell. These radical ions are responsible for the degradation of the methyl orange [24,27]. As the concentration of zinc titanate increased, more absorption of photon from the visible light leads to more degradation of the dye. The concentration of methyl orange was decreased to 2.0 ppm when solution containing 0.2% of zinc titanate under the visible light exposure of 4.15 hours.

Conclusion

The zinc titanate powders were prepared by co- precipitation peroxide method and its physical properties are studied by using XRD, FTIR and TGA. The stoichiometric ratio of the synthesized zinc titanate was measured by using AAS, it showed that the prepared zinc titanate contains about 40% of zinc and 23.68% of titanium and the compound displays dominant cubic structure. The concentration of methyl orange was diminished from 10.0 ppm to 0.2 ppm by introducing 0.2% zinc titanate in presence of 0.02 g of sodium exposed to sun light for 90 minutes duration. The photo bleaching of the dye under visible light with $ZnTiO_3$ confirms the photocatalytic activity of zinc titanate under visible light condition.

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