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Photo catalyticdegradation of methylene blue using $Y_4Ti_{2.25}Hf_{0.75}O_{12}$ nanomaterial

S. Anila[1] , J. K. Thomas[2,*] S Solomon[3]

[1] *Department of Physics, Mar Ivanios' College, Trivandrum, Kerala 695015, (India)*

ABSTRACT

Nanocrytalline $Y_4Ti_{2.25}$ $Hf_{0.75}O_{12}$ (YTHO) is successfully synthesized through single step auto ignited combustion technique. The structure of the sample is examined by X-ray Diffraction (XRD) technique. The crystalline size of the as prepared sample is analyzed by using Scherrer formula. The evaluation of the degradation of dye using YTHO is activated using UV light. Adsorption of dye on the as prepared nanoparticles, being the first and important step, is explored experimentally to study the degradation of the sample in dark room. A pseudo-second order reaction equation is found to be matching well with the experimental data for this sample suggesting that adsorption of methylene blue on YTHO is a surface controlled reaction step. Photocatalytic activity is analyzed by the degradation of methylene blue (MB) under UV light. The percentage degradation of the sample is 26.3 %. The rate of degradation is also analyzed for the sample.

Keywords: Methelyne Blue, Degradation, Adsorption, Pseudo-second order.

1. INTRODUCTION

Most of the compounds with general formula $A_nB_{n-1}O_{3n}$ ($n \geq 3$) are homologous series of trigonal structures. These types of compounds are derived from perovskite structures of intrinsic stacking faults in the cubic close packing of AO_3 mixed layers. The slabs of normal cubic perovskites are inter-grown with regions stacked in hexagonal close packing. [1-3].These compounds having rhombohedral symmetry with trigonal δ-phase have stability and self- consistency [4-8]. They also undergo reversible rhombohedral to fluorite-type phase transition and advanced oxidation process that has proven to be a promising method for elimination of toxic, bio-resistant organic and inorganic compounds from wastewater [17]. Recently photocatalysts have applicable in electrolytes for solid oxide fuel cells, oxygen sensors and refractory materials for high temperature furnaces [9-16]. The efficient treatment of industrial wastewaters and contaminated drinking has become of immediate importance in a world. An ideal waste treatment process will completely mineralize all the toxic species present in the waste stream without leaving behind any hazardous residues. It is very expensive and a high effort matter. Heterogeneous photocatalysis is one of the

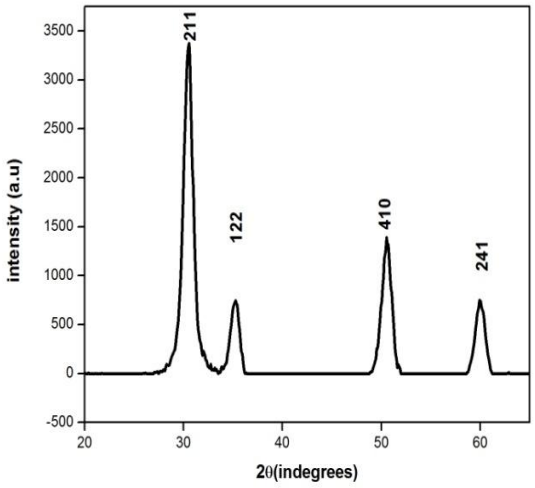
attracted many researchers due to their potential applications in solar energy conversion and environmental pollution decomposition. Titanium based materials have high stability, low cost, non-

toxicity and are active only under ultraviolet irradiation [18]. The advance oxidation process such as ionizing radiation, sonification and the combination of UV and ozone or hydrogen peroxide are able to destroy environmentally persistent pollutions due to their ability to generate the highly oxidizing species, OH radical. This radical can be generated at the suface of the titanium based material when being irradiating with UV light [19-24].

In this paper, we focus to prepare $Y_4Ti_{2.25}Hf_{0.75}O_{12}$ (YTHO) nanopowders by single step auto-igniting combustion technique and its photoctalytic studies.

2 EXPERIMENTAL

The single step auto-igniting combustion method is used to prepare nanostructured YTHO. In this technique, yttrium oxide (dissolved in hot dilute HNO_3), hafnium chloride (dissolved in distilled water) and titanium isopropoxide (dissolved in 25 ml of ethanol with two drops of HNO_3) are mixed in stoichiometric proportions to make a clear solution. The amount of citric acid is calculated based on total valency of the oxidizing and the reducing agents for maximum release during combustion and is then added to it as a complexing agent. The oxidant to fuel ratio of the system is adjusted by adding concentrated nitric acid and ammonium hydroxide and the ratio is kept unity. The solution containing precursor mixture is heated using a hot plate at



approximately 250 °C in a ventilated fume hood. The solution boils on heating and undergoes dehydration accompanied by foam. The foam then gets ignited by itself on persistent heating giving voluminous and fluffy product of combustion [25].

The structure of the as prepared samples is characterized by X-ray diffractometer (Model Bruker D-8) with Nickel filtered CuK_α radiation in the range 20-60° in step size of 0.0840.

Photocatalytic experiments are performed by trial and error methods [26, 27]. Initially, 10 mg of MB is dissolved in one litre of distilled water and stirred well. Then 2 mg of YTHO is dispersed in the MB solution for 30 minutes using ultrasonic agitation. The unwanted powder from the solution is removed using filter paper. The experimental setup is kept in a dark room and the solution is well stirred continuously for half an hour to ensure adsorption or desorption equilibrium state. The equilibrium

concentration of the sample is taken for measuring the initial value of absorption before the UV irradiation. Thereafter, 15 W of UV lamp is irradiated to a bottle of solution, in which the solution is kept at a distance of 5 cm from UV lamp. For every 30 minutes, 25 ml of solution is taken into a tube for measuring absorption using UV-Visible Spectrophotometer (JASCO V-650). This process is continued from 30 minutes to 120 minutes. Percentage of degradation and rate of degradation as a function of irradiation time are determined.

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3 RESULTS AND DISCUSSIONS

3.1 X-ray DIFFRACTION

Fig. 1. shows the XRD pattern of the as prepared sample, YTHO. All the peaks are indexed using JCPDS File No: 29-1389and the structure of both samples are found to be rhombhohedral, which confirm the phase formation of both the samples. Lattice constants of YTHO are calculated as a = 9.48 Å and c =8.66Å respectively. The broadening of the peak in sample may be due to the lattice strain and the nano-sized crystalline nature of the sample [28].

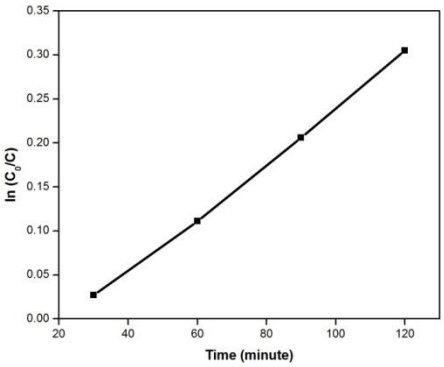
Fig. 1.The XRD pattern of YTHO

The average crystallite size is determined by Scherrer equation [28],

$$D = \frac{k\lambda}{\beta cos\theta} \quad \ldots\ldots\ldots\ldots (1)$$

where λ is the wavelength of X-ray radiation (1.54060 Å), β is the Full Width at Half Maximum (FWHM) of the peak and θ is the diffraction angle. The reflection, (211) of YTHO is identified and the crystallite sizes are found to be 12.65 nm. This result confirms that the preparation of as prepared compounds by combustion technique offers ultrafine nanopowders. Ulta fine nanoparicles of hafnium based materials are applicable in optical system due to their smaller size of the compound [25].

3.2 PHOTOCATALYTIC ACTIVITY



Photocatalytic activity of YTHO is evaluated by studying the degradation of MB solution. The MB solution with the respective samples dispersed in it is irradiated with 15 W of UV light and the degradation of the sample is evaluated in steps of 30 minutes time interval, upto 120 minutes. Absorbance of YTHO is shown in Fig. 2. The spectrum of the sample indicates the absorption band of the dye decreased rapidly around 665 nm and have a small shoulder around 600 nm. The absorption decreases from YTHO samples. This implies that the

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absorption of the material decreases with increase in time. Upon irradiation, the peak at 662 nm has a progressive slight blue shift due to hypsochromic effect [29, 30] The photocatalytic activity meaurements shows the elimination of dark blue colour of MB with increasing irradiation time. The decrease of MB dye concentration as a function of irradiation time is shown in Fig. 3. and its rate is also shown in Fig.4. This result indicates the photodegradation process of the sample is faster due to the absorption of cataionic MB dye on the sample.

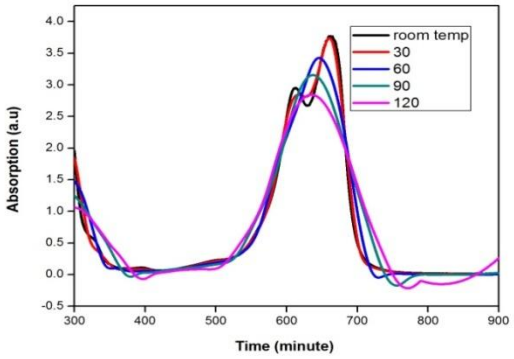
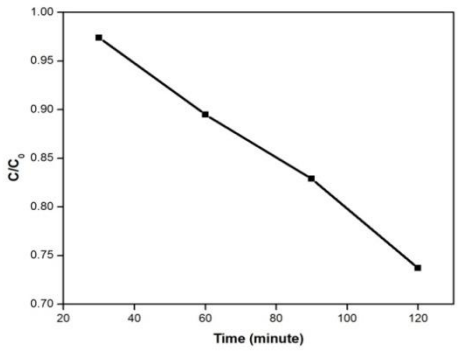


Fig. 2. UV absortion spectra of MB after reacting with YTHO at different time



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4.

Fig. 3. Decreasing the concentration of MB dye.

The percentage of degradation (D) can be calculated as

$$D\ \% = \frac{(C_0 - C_1)}{C_0} x\ 100 \quad \ldots\ldots\ldots\ldots\ldots (2)$$

Fig. 4. The rate of decreasing the concentration of MB dye.

where C_0 is the initial dye concentration, C_1 is the dye concentration after photodegradation [31]. The degradation of YTHO are shown in Fig. 5. and the rate of degradation are shown in Fig. 6. The percentage of degradation after 2 hours irradiation is 26.3 % for YTHO. This effect is mainly based on two conditions, one is the concentration of the colourant dye to be degraded and other is the increase in the amount of UV light absorbed by the dye, which decreases transmittance and the number of photons that collide with catalyst molecules. As a consequence, fewer recombinations of electron-hole pairs are produced and a greater reaction time is needed to produce the OH^0 radicals needed for degradation of the dye [32, 33]. The oxidation and reduction can take place at the surface of the photoexcited semiconductor photocatalyst. Recombination between electron and hole occurs unless oxygen is available to scavenge the electrons to form superoxides (O^{2-}), its protonated form the hydroperoxyl radical (HO2) and subsequently H_2O_2 [34].

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The rate of degradation is calculated by pseudo second order kinetic model,

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^{\,2}} + \left(\frac{1}{q_e}\right) t \quad \ldots\ldots\ldots\ldots (5)$$

where K_2 is the second order equation rate constant, the values of K_2 is different in initial dye concentration for all absorbant, t is the different time interval for 30, 60, 90 and 120 minutes, q_e and q_t be the initial and after the time absorption capacity [26]. Rate of degradation of YTHO shows higher degradation. This result confirms that the colour change of MB increases in the samples with increase in time for 2 hours, thereby increasing the degradation which results in the enhancement of photocatalytic activity.. The earlier reports confirmed that the degradation rate increases with intensity of radiation during photocatalytic degradation. Surface defects and nano-sized particles are the other main reasons of photocatalytic activity. due to the photodegradation of the sample is used for removal of waste water and decompose organic pollutions [17].

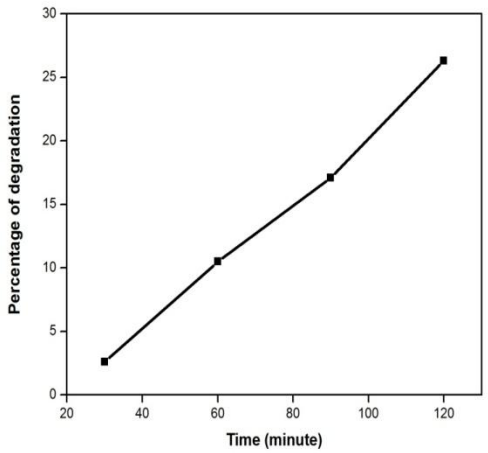
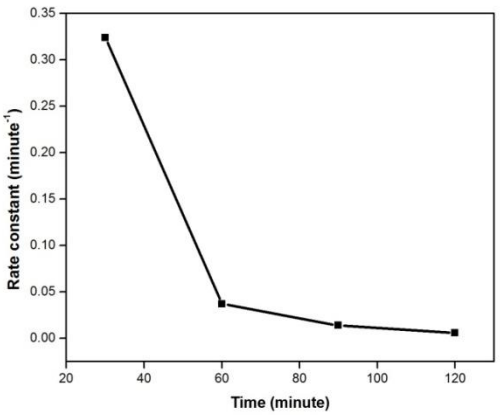


Fig. 5.Percentage of degradation of MB for YTHO with different time of irradiation

Fig. 6. Rate constant of YTHO with different time.



4 CONCLUSIONS

Nanocrystalline $Y_4Ti_{2.25}Hf_{0.75}O_{12}$ (YTHO) is synthesized by single step auto-igniting combustion method. The sample has rhombohedral crystal structure and the particle size is below 12.65 nm. The sample show the enhancement of photocatalytic activity. The percentage of degradation is about 26.3 % and rate constant are also analyzed. The enhancement photocatalytic acivity of the sample is used for the removal of waste water and decompose organic pollutions.

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