Synthesis and characterization of ZnO and Ti^{4+} modified ZnO nanoparticles and their photocatalytic performance

A report

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CERTIFICATE

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This is to certify that the dissertation entitled "**Synthesis and characterization of ZnO and Ti^{4+} modified ZnO nanoparticles and their photocatalytic performance**" being submitted by **MEENAKETAN SUNYANI** to the Department of Chemistry, National Institute of Technology, Rourkela, Orissa, for the award of the degree of Master of Science is a record of bonafide research carried out by him under my supervision and guidance. To the best of my knowledge, the matter embodied in the dissertation has not been submitted to any other University / Institute for the award of any Degree or Diploma.

N.I.T. Rourkela**.** **Dr. Aparna Mondal**
Date: *(Supervisor)*

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ABSTRACT

In the present work pure ZnO and Ti^{4+} doped ZnO nanoparticles were synthesized by co-precipitation method directly from an aqueous solution of zinc acetate dehydrate and sodium hydroxide. As-prepared precursor was calcined at 500°C and 600°C temperature for 2 h. The samples were characterized by X-ray diffraction (XRD), field emission scanning electron microscope (FESEM), and UV-DRS spectroscopy. Results show that the calcinations temperature and Ti^{4+} doping significantly affected the crystalline nature, and optical properties of the processed ZnO nanoparticles. The XRD spectra indicated that both pure ZnO and Ti^{4+} doped ZnO have hexagonal wurtzite structure at 500°C. By doping small amount of TiO_2 we obtained wurtzite structure at lower temperature. Both ZnO and Ti^{4+} doped ZnO nanostructures exhibited enhanced photocatalytic efficiency towards degradation of MB dye due to the enhanced surface area and high crystallinity of hexagonal plate like structures. Zn-600 shows highest photocatalytic activities due to higher crystallinity and lower band gap, which restricts their recombination of photogenerated charge carriers and higher surface area helps in increased adsorption of the dye for efficient degradation.

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1. Introduction

Nanoparticles have been a common material for the development of new cutting-edge applications in communications, energy storage, sensing, data storage, optics, transmission, environmental protection, cosmetics, biology, and medicine due to their important optical, electrical, and magnetic properties. The unique properties and utility of nanoparticles also arise from a variety of attributes, including the similar size of nanoparticles. Nanoparticles of particular materials show unique material properties, hence, manipulation and control of the material properties *via* mechanistic means is needed. In addition, synthesis of nanoparticles having uniform shape and size *via* easy synthetic routes is the main issue in nanoparticle growth.[2] Nanoscale metal oxides are attracting materials for engineering and scientific applications because of their unique physical and chemical properties. They can be used as catalysts, passive electronic components, and ceramics. Their unique properties and applications provide the main motivation for developing these nanomaterials. [1, 2, 3]

Recently, zinc oxide (ZnO) a wide band gap semiconductor has attracted significant research attention as a most promising candidate for ultraviolet light emitting and lasing device, because of its large binding exciton-binding energy.[4,5] It has extensive range of possible applications such as solar energy cells, photoelectric transformation materials and water or air purification as friendly photocatalyst. [6] Zinc oxide (ZnO) nanoparticles have their own importance due to their immense area of applications, e.g., gas sensor, chemical sensor, bio-sensor, cosmetics, storage, optical and electrical devices, window materials for displays, solar cells, and drug-delivery.[7,11] As a wide band gap material, ZnO is used in solid state blue to ultraviolet (UV) optoelectronics, including laser developments. In addition, due to its non-centrosymmetric crystallographic phase, ZnO shows the piezoelectric property, which is highly useful for the fabrication of devices, such as electromagnetic coupled sensors and actuators. [12] Titania/Zinc oxide coated on glass has advantages of absence of composite, easily reclaim after reaction particularly high surface activity.[13] Zinc oxide crystallizes in two main forms, hexagonal wurtzite and cubic zinc blende but the (B4 type) wurtzite structure is obtained only at optimum pressure and temperature [13,18]. The hexagonal wurtzite structure model of ZnO is shown in Fig. 1.

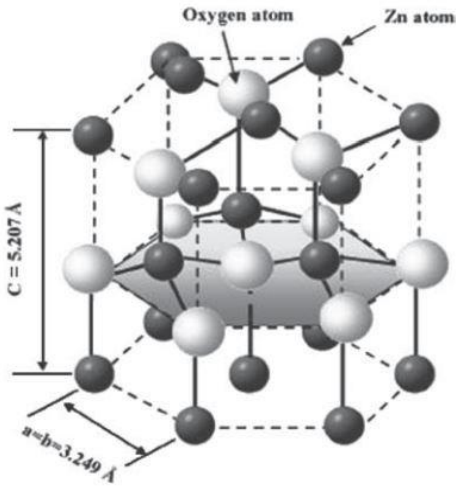

Fig. 1. *The hexagonal wurtzite structure model of ZnO. The tetrahedral coordination of Zn-O is shown.[2]*

ZnO usually appears as a white powder, nearly insoluble in water. The ZnO powder is widely used as an additive in various products including plastics, glass, cements, rubber, ceramics, lubricants, paints, ointments, adhesives, pigments, foods (source of zinc nutrients), batteries, ferrites, first aid tapes, fire retardants, etc. The wastes from the textile and dye industries are very poisonous, toxic and harmful for the livings under water and human beings [19, 20]. The organic dyes produce environmental hazardous, and irregularity non esthetical pollution for water based living parts.

Many attempts have been made to overcome this problem. Among these techniques, heterogeneous photocatalysis is a very popular process to reduce toxic and harmful waste materials like organic compounds [21]. As of late, the metal oxides, SnO_2, ZrO_2, Fe_2O_3, CdS and ZnO [22,23], have shown good photocatalytic activity toward the degradation of hazardous organics in to less toxic and harmful molecules under UV and sunlight. Kansal et al. [22] have reported the photocatalytic degradation of methyl blue and Rhodamine 6 G using commercially available ZnO, SnO_2, ZnS and CdS as photo-catalysts under UV/solar light irradiation. Lizama et al. reported ZnO is more efficient catalyst than TiO_2 in degrading Reactive Blue 19 (RB-19) in aqueous solutions [24]. ZnO semiconductors with direct wide band gap are highly efficient n-type semiconductors having high electron–hole binding energy (60 meV), and applications in photocatalysis have received a great deal of interest because of its good catalytic activity and quantum efficiency [25]. Various ZnO nanostructures have been used to degrade the harmful dyes by photo catalytic reaction under

sunlight. In this work we have utilized ZnO photocatalyst for the degradation of methylene blue.

Methylene blue (MB) is widely used as a colorant in textiles and food industry [26]. It is harmful and toxic to human beings and animals, and causes irritation of the skin, eyes and respiratory tract, the carcinogenicity, and developmental toxicity, neurotoxicity toward living beings [27]. India is a tropical country, so sunlight is an abundantly available natural energy source, which can be utilized for irradiation. Dyes can be degraded in the presence of photocatalyst upon irradiation with visible light because of their absorption in the visible region [28]. In this study, photocatalytic activity on MB dye by ZnO photocatalyst by solar light irradiation was studied. The effect of catalyst dosage and calcination temperature on the photocatalytic effect was investigated.

ZnO, as an important functional oxide, is a direct wide band gap (3.37 eV) semiconducting and piezoelectric material having many useful properties, such as optical absorption and emission, piezoelectricity, photocatalysis, and sensitivity to gases. Water contamination due to hazardous water soluble organic dyes and chemicals poses a severe threat to the environment. It has been known that ZnO is a suitable alternative to TiO_2 so far as band gap energy is concerned, and in fact higher photocatalytic efficiency compared with TiO_2 has been reported for ZnO. Mostly wurtzite hexagonal crystal structure of zinc oxide has been synthesized at higher temperatures. Xiao et al.[29] synthesised Co doped ZnO by a hydrothermal method with enhanced visible light photocatalytic activity as compared to undoped ZnO, degrading 100% methylene blue (MB) dye in 300 minutes. Therefore, in the present work a facile wet chemical method was employed to develop ZnO and Ti^{4+} doped ZnO hexagonal plates.

Objective

- Synthesis of pure ZnO and Ti^{4+} doped ZnO nanocrystals through solution phase synthesis route using sodium hydroxide as the precipitating agent.
- To study and compare the properties of pure ZnO and Ti^{4+} doped ZnO.
- Structural characterization using XRD, UV-Vis DRS, BET and FESEM.
- The photocatalytic activities were evaluated for visible light driven degradation of an aqueous methylene blue (MB) solution.
- Study the effect of irradiation time, and calcination temperatures on photocatalytic degradation of methylene blue.

Experimental procedures

Synthesis of ZnO and Ti^{4+} doped ZnO nanostructure

In this experiment all the chemicals used are of analytical grade and used without further purification. ZnO nanoparticles were synthesized through hydrolysis of zinc acetate dehydrate [$Zn(C_2H_3O_2)_2.2H_2O$] in aqueous solution. First, [$Zn(C_2H_3O_2)_2.2H_2O$] was dissolved in deionized water. Then NaOH was added drop wise to [$Zn(C_2H_3O_2)_2.2H_2O$] solution until desired pH was achieved. Then after continuous stirring for 5 h, the precipitate was left for ageing. These precipitates were filtered, washed with distilled water and ethanol several time then collected and dried and finally grounded to powder. Similarly, for 5 mol % TiO_2 modified ZnO, Ti^{4+} salt was dissolved in deionized water and was mixed with [$Zn(C_2H_3O_2)_2.2H_2O$] solution and followed the procedure to prepare pure ZnO. These as-prepared powders were then calcined at 500°C and 600°C. The powders calcined at 500°C and 600°C were studied using different characterization techniques. Formation of pure ZnO phase was verified by XRD analysis. The shape and morphology of particles were studied by FESEM.

Photodegradation of organic dye

The photocatalytic activity of ZnO and Ti^{4+} doped ZnO was investigated by using methylene blue (MB). In a typical photocatalytic experiment, aqueous suspension of MB (100 mL, $1x10^{-5}$ M) and 0.1 g photocatalyst powder were placed in a 100 ml beaker with vigorous stirring under sun light and stirred for a period up to 4 h without any further adjustment of pH and then centrifuged. Sample aliquots were withdrawn from the reaction mixture at a regular time interval and centrifuged and then dye concentration in the residual solution was analysed by using a Shimadzu UV-2450 spectrophotometer. Changes in the concentration of MB were observed from its characteristic absorption band maximum at 664 nm. The decolourization efficiencies of the dyes were estimated by the equation: $[(C_i - C_f)/C_i] \times 100$, where Ci and C_f represent the concentration of dye in solution before after irradiation, respectively. Effect of various parameters such as irradiation time, and the calcination temperatures on decolourization efficiency were also investigated.

Result and Discussion

X-ray diffraction analysis

The crystal structure of the ZnO and Ti^{4+} doped ZnO nanopowders were investigated by X-ray diffraction patterns. Figure 2 and 3 show the XRD spectra of ZnO and Ti^{4+} doped

ZnO. These data are collected over 2θ range of 10°C to 80°C. All diffraction peaks of the products are well indexed as the hexagonal phase of wurtzite ZnO (space group $P6_3mc$) in the absence and presence of titanium. The XRD profiles confirm to the standard XRD pattern of wurtzite ZnO (JCPDS card no. 36–1451). The lattice parameters were found to be a = 3.249Å and c = 5.206 Å. The result indicates that the products are in pure phase. The mean grain size (D) of the particles was determined from the XRD line broadening measurement using Scherrer equation.

$$\mathbf{D=0.89\lambda / (\beta Cos\theta).}$$

Where λ is the X-ray wavelength (Cu Kα), β is the full width at the half- maximum (FWHM) of the ZnO (101) line and θ is the diffraction Bragg angle.

Table: 1. Crystallite size of ZnO and Ti^{4+} doped ZnO powders calcined at different temperatures

Sample name	2-theta (deg.)	FWHM (deg.)	Crystallite size (nm.)
Zn-500	36.2999	0.2160	40
Zn-600	36.3179	0.2276	38
ZnTi-500	36.3189	0.1988	43
ZnTi-600	36.4118	0.1959	44

No characteristics peaks for titanium dioxide are observed. It is due to small size of titanium dioxide with its low concentration in the solid phase mixture which is well dispersed. Ti^{4+} facilitates the formation of wurtzite phase at lower temperature.

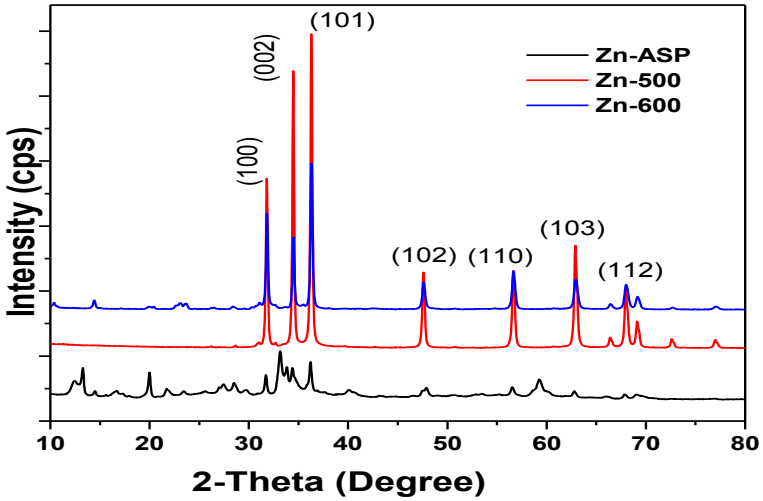

Fig. 2. XRD patterns of (a) Zn-Asp, (b) Zn-500, and (c) Zn-600. 500 and 600 denoted calcined temperatures.

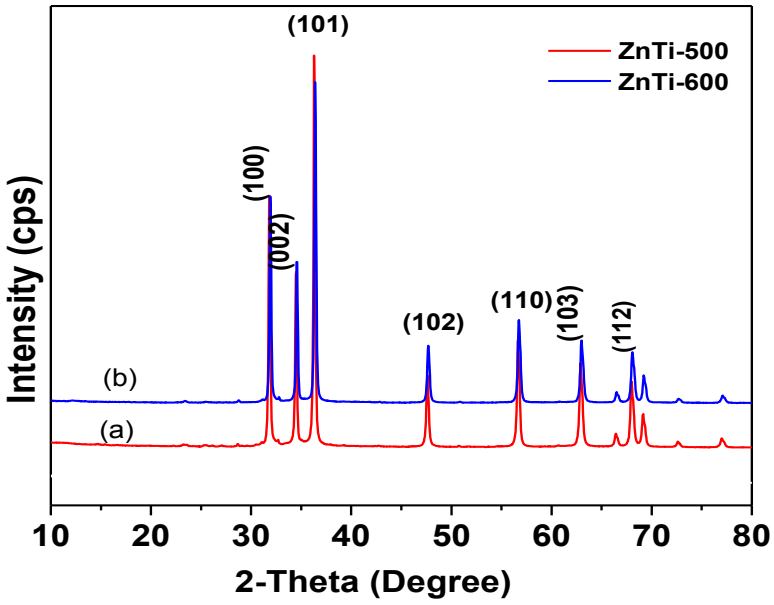

Fig. 3. XRD of Ti^{4+} modified ZnO: a) Zn-Ti 500, and b) ZnTi-600.

Optical properties

Fig. 4 shows the optical absorbance spectra of ZnO and Ti^{4+} doped ZnO nanopowders calcined at 500°C, and 600°C for 2h, prepared by using NaOH as a precipitating agent. All the samples showed high UV-shielding properties below 400 nm. Ti^{4+} doped samples showed higher absorbance in the UV region as compared to pure ZnO. No significant changes in the band gap was observed for the Ti^{4+} doped ZnO samples calcined at 500 and 600°C. But for the pure ZnO samples with increasing calcination temperature the band gap decreases. So the results suggest that the pure ZnO samples would show higher photocatalytic activity under solar light irradiation.

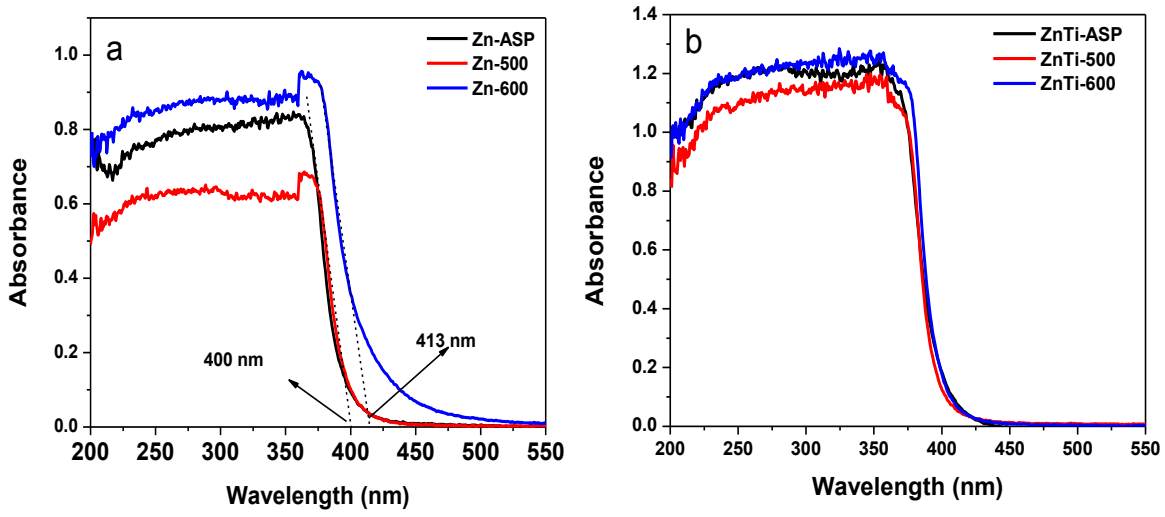

Fig. 4. Uv-vis DRS spectra of (a) ZnO and (b) Ti^{4+} doped ZnO samples.

FESEM analysis

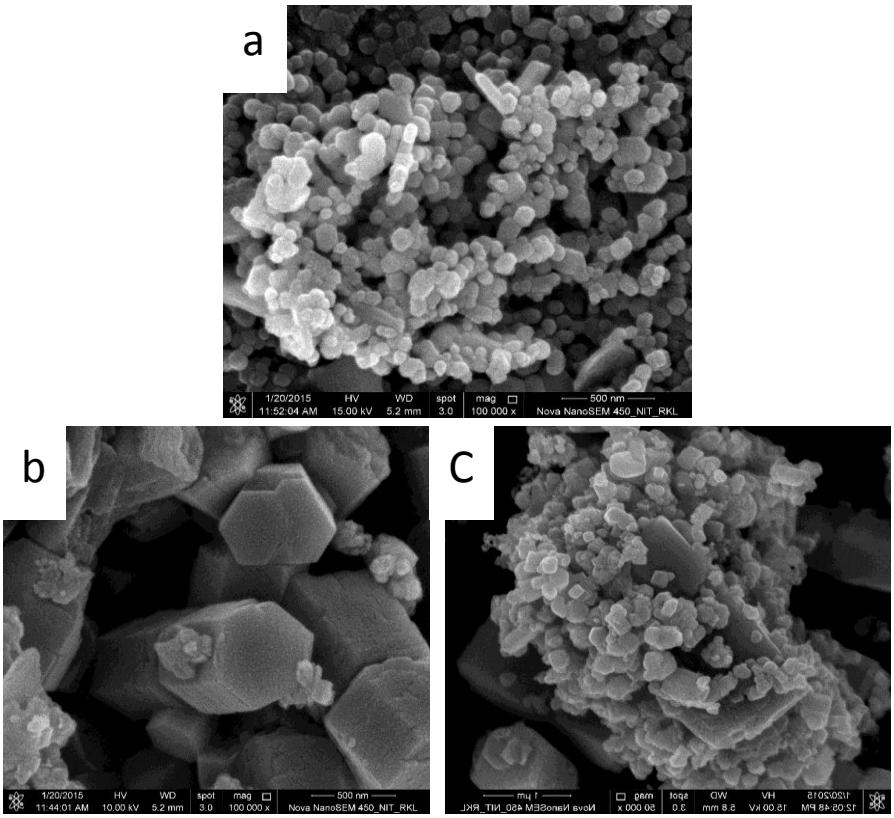

Fig. 5. FESEM images of (a) Zn-500 (b) ZnTi-ASP and (c) ZnTi-500.

Figure 5 shows the FESEM images of pure ZnO and Ti^{4+} doped ZnO nanoparticles. The ZnO sample calcined at 500°C exhibits clearly the formation of hexagonal morphology. Ti^{4+} doping further increased the size of the hexagonal plate (diameter 85-540 nm). The size of the plates increases (diameter in the range 100-200 nm) on increasing the calcination temperature to 500°C.

Photocatalytic application

Degradation of methylene blue

The photocatalytic activities of the obtained ZnO and Ti^{4+} doped ZnO have been investigated in the solar light by the decomposition of methylene blue as model pollutant. Firstly, 100 mg of powder was dispersed into 100 ml of the 10^{-5} (M) methylene blue solution. Figure 4 shows that the decomposition of methylene blue solution as function of time. All the samples degrade the methylene blue solution in just four hours. On increasing the calcination temperatures, the degradation efficiency increases for both the ZnO and Ti^{4+} doped ZnO samples as can be seen from Fig. 6. The is due to the higher crystallinity of the samples. However, it is interesting to observe that the pure ZnO showed higher degradation efficiency

than the doped one. This is due to lower band gap of the pure ZnO sample. Ti^{4+} may have enhanced the recombination of electron and hole pair, which are generated during the solar light irradiation. As was also evidenced from the FESEM that the particle size of ZnO was lower than the Ti^{4+} doped samples. So, higher surface area in pure ZnO might have increased the adsorption of dye and hence higher degradation efficiency was observed.

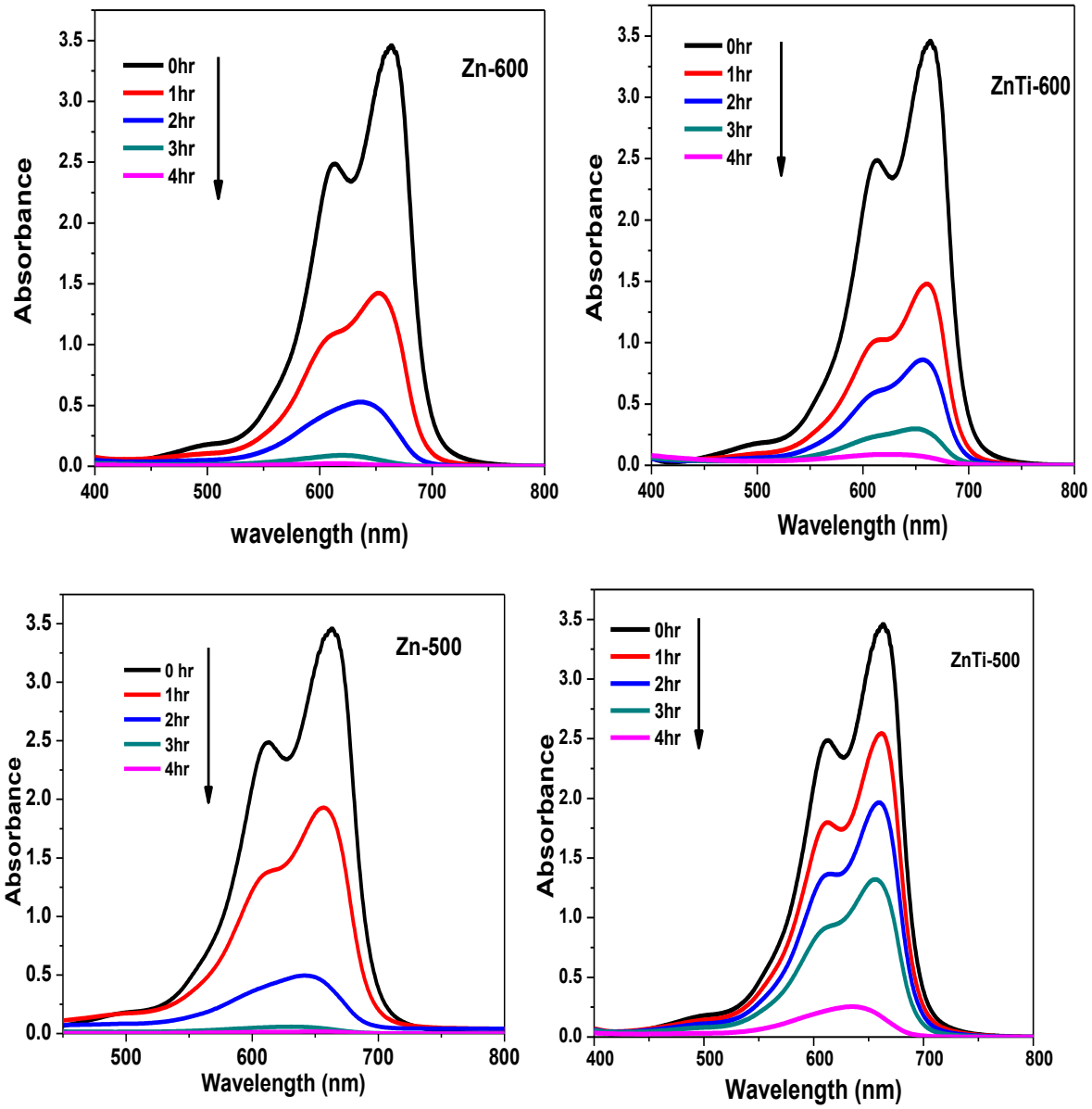

Fig. 6. Degradation of methylene blue solution by (a) Zn-600, (b) ZnTi-600, (c) Zn-500, and (d) ZnTi-500 samples. Catalyst amount 100 mg/L.

Conclusion

- ✓ We have synthesized wurtzite ZnO and Ti^{4+} doped ZnO hexagonal plates by a facile wet chemical method.

- ✓ The structural, optical and photocatalytic properties of ZnO and Ti^{4+} doped ZnO nanostructures have been investigated.
- ✓ By doping small amount of TiO_2 we obtained wurtzite structure at lower temperature.
- ✓ Both ZnO and Ti^{4+} doped ZnO nanostructures exhibited enhanced photocatalytic efficiency towards degradation of MB dye due to the enhanced surface area and high crystallinity of hexagonal plate like structures.
- ✓ Zn-600 shows highest photocatalytic activities due to higher crystallinity and lower band gap, which restricts their recombination of photogenerated charge carriers and higher surface area helps in increased adsorption of the dye for efficient degradation.

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