



PHOTOCATALYTIC AND ANTIBACTERIAL ACTIVITIES OF TiO₂ AND SILVER AND ZINC DOPED TiO₂ NANOPARTICLES

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Abstract:

The TiO₂ and Ag and Zn doped TiO₂ nanoparticles were synthesized by sol-gel method. The sol-gel method is one of the versatile method to prepare doped and co-doped nanoparticles. sol gel method has emerged as simpler and better option than physical and chemical procedures as it is fast, clean and eco-friendly alternative that does not involve any costly instruments. Synthesis of doped and co-doped nanoparticles having good photocatalytic activity have great potential for the degradation of dye. We have tried to develop new effective antimicrobial reagents with good photocatalytic activities which are not resistant to disease causing microbes.

Keywords: Photocatalytic; Antibacterial; Nanoparticles.

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1. Introduction

Nanotechnology deals with nanometre sized objects. It is expected that nanotechnology will develop at several levels: materials, devices and systems. Nanoparticles were studied because of their size-dependent physical and chemical properties¹. Lots of applications of the nanomaterials to biological system and medicines are found in drug and gene delivery^{2,3}, bio detection of pathogens⁴, detection of proteins⁵, probing of DNA structure⁶, tissue engineering^{7,8}, tumour destruction via heating (hyperthermia)⁹, separation and purification of biological molecules and cells¹⁰, MRI contrast enhancement¹¹. Nanotechnology has also more applications in electronics, optics, optoelectronic devices, solar cells, fuel cells, food, water pollution treatment, chemical and biological sensors and many more. Use of the photocatalytic process to degrade organic dye pollutants with visible light has important industrial implications because it can use the relatively inexpensive solar light¹². Our main aim of research is to develop new, simple, cheaper, novel and green methods for the synthesis of doped and co-doped nanoparticles and to improve their photocatalytic activity or the degradation of dyes and antibacterial agent.¹³

These kind of natural chemical properties of nanoparticles have been changed by doping process such as size dependent variation of the band gap energy. Furthermore, impurity ion doped into these nanostructures can influence their electronic structure and transition probabilities. Ag and

Zn have been incorporated into TiO₂ Nanostructure by sol-gel processing. Doping TiO₂ nanoparticles, with transition metal ions and non-metals usually results in hampered enhancement efficiency of the photocatalyst. Several methods have been developed for synthesis of doped and co-doped nanoparticles. The sol-gel method is one of the versatile methods to prepare doped and co-doped nanoparticles. Metallic nanoparticles have emerged as a simpler and better option than physical and chemical procedures as it is fast, clean and eco-friendly alternative that does not involve any costly instruments.

2. Materials and Methods

2.1. Material

All chemicals used in this study (Titanium n-butoxide, Butanol, Ethanol, Glycerol) were AR grade. Nanoparticles were washed by deionized water.

2.2. Method

2.2.1. Preparation of TiO₂ Nanoparticles

5 ml of Titanium n-butoxide dissolved with 5 ml n-butanol drop by drop with continuous stirring in round bottom flask on magnetic stirrer. 36.4 ml ethanol and 13.6 ml acetic acid were taken in RB flask under ice cold condition and the mixture is subjected to stirring for 10 minutes. Then glycerol (0.3 ml) as gelling agent was added to it. Then Titanium n-butoxide solutions were mixed in it. This mixture was stirred vigorously for three hours. Kept this mixture in room temperature for gelation. Next day kept this solution in oven at 60⁰C then next day kept it at 100⁰C until the gelling reaction was completed. Then finally TiO₂ nanoparticle obtained in powdered form.⁶

2.2.2. Preparation of Ag Doped TiO₂ Nanoparticles

Titanium n-butoxide dissolved with n-butanol drop by drop with continuous stirring in round bottom flask on magnetic stirrer. Then added 0.5% AgNO₃. 36.4 ml ethanol and 13.6 ml acetic acid were taken in RB flask under ice cold condition and the mixture is subjected to stirring for 10 minutes. Then glycerol as gelling agent was added to it. Then Titanium n-butoxide solutions were mixed in it. This mixture was stirred vigorously for three hours.

Kept this mixture in room temperature for gelation. Next day kept this solution in oven at 60⁰C then next day kept it at 100⁰C until the gelling reaction was completed. Then finally Ag doped TiO₂ nanoparticle obtained in powdered form.

2.2.3. Preparation of Zn doped TiO₂ Nanoparticles

Titanium n-butoxide dissolved with n-butanol drop by drop with continuous stirring in round bottom flask on magnetic stirrer. Then added 0.5% ZnCl₂. 36.4 ml ethanol and 13.6 ml acetic acid were taken in RB flask under ice cold condition and the mixture is subjected to stirring for 10 minutes. Then glycerol as gelling agent was added to it. Then Titanium n-butoxide solutions

were mixed in it. This mixture was stirred vigorously for three hours. Kept this mixture in room temperature for gelation. Next day kept this solution in oven at 60⁰C then next day kept it at 100⁰C until the gelling reaction was completed. Then finally Zn doped TiO₂ nanoparticle obtained in powdered form.

3. Results and Discussions

TiO₂ and silver, zinc doped TiO₂ nanoparticles were characterized by the SEM and XRD analysis.

The detailed study of morphology of the sample were performed by SEM. Instrument used was Make Jeol model –JSM-5400, acceleration voltage -10 KV .The microstructure of TiO₂ (fig 1) and Silver (fig2) and Zinc doped TiO₂ (fig 3) shown in figure.

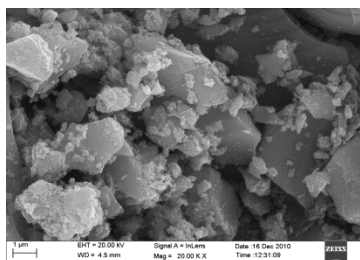


Figure 1: TiO₂ nanoparticles

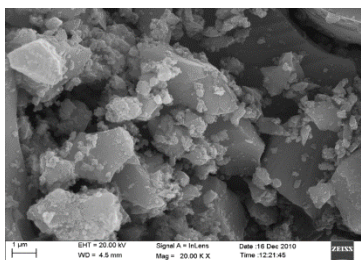


Figure 2: Silver doped TiO₂

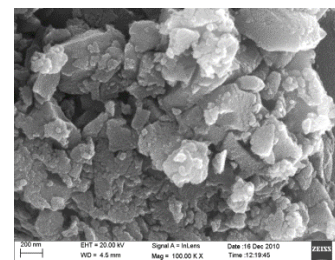


Figure 3: Zn doped TiO₂

The SEM Images shows the particles have nano sized.

The XRD diffraction spectrum of calcined powder was recorded using Instrument is panalyticle and empyrean respectively used target is Cu k-alpha with the wavelength target is 1.54 angstroms .It is well know that the calcination improve the crystallinity of particles.

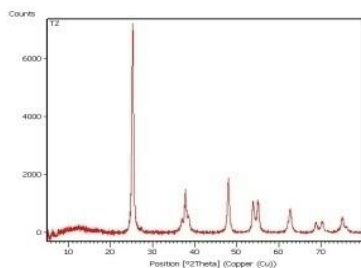


Figure 4: Zinc Doped TiO₂

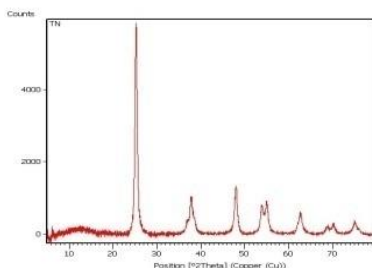


Figure 5: TiO₂ nanoparticles

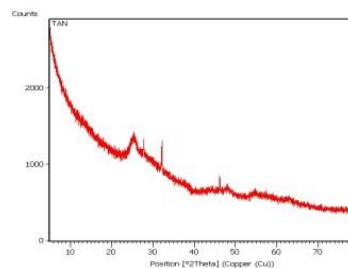


Figure 6: Silver doped TiO₂

TiO₂ nanoparticles have photocatalytic and antibacterial activity. Doping TiO₂ nanoparticles, with transition metal ions and nonmetals usually results in a hampered enhancement efficiency of the photocatalyst and improves antibacterial activity. Environmental cleaning using TiO₂ photocatalyst has attracted a great deal of attention due the increase in the level of environmental pollution in the world.

3.1. Photocatalytic Activity of Nanoparticles

The nanoparticles reduce the dye solution can be studied by spectrophotometrically. The graphs are taken by Labindia V UV-Vis spectrophotometer. Different dilution of dye and different concentration of nanoparticles on different time intervals have been studied .¹⁴

Absorption Studies

Toluidine blue solution: - prepared different conc. Of dye and Monitored the spectra of this solution Table (1) show the absorption spectra of Toluidine blue solution with different dilution.

Table 1: Firstly take 20 ml dye and put on sunlight, absorption spectra of selected dye on different time intervals have been studied

S.No.	Time	Azur I		Aniline Blue		Toluidine Blue	
		λ_{max}	Absorbance	λ_{max}	Absorbance	λ_{max}	Absorbance
1.	10 min	290	0.845	235	0.922	285	0.943
2.	20 min	290	0.776	235	0.907	285	0.920
3.	30 min	290	0.758	235	0.903	285	0.885
4.	40 min	290	0.641	235	0.881	285	0.768
5.	50 min	290	0.639	235	0.877	285	0.758

Take 20 ml selected dye and 0.001 gram TiO₂ nanoparticles were added in different dye. In presence of TiO₂ nanoparticles, dye absorption spectra suffered a slight red shift in the band peak position, which indicated that the absorption of different dye on to the TiO₂ nanoparticles. TiO₂nanoparticles were added different solution of dye and put on sunlight. In presence of TiO₂ nanoparticles dye absorbance decreases dye on different time intervals have been studied:-

Table 2: Toluidine Blue +0.001 gm TiO₂ nanoparticles

S.No.	Time	Azur I		Aniline Blue		Toluidine Blue	
		λ_{max}	Absorbance	λ_{max}	Absorbance	λ_{max}	Absorbance
1.	10 min	290	0.742	235	0.728	285	0.665
2.	20 min	290	0.615	235	0.604	285	0.468
3.	30 min	290	0.422	235	0.399	285	0.348
4.	40 min	290	0.338	235	0.282	285	0.328
5.	50 min	290	0.285	235	0.212	285	0.256

Take 20 ml selected dye and 0.001 gram Ag doped TiO₂ nanoparticles were added in different dye. In presence of Ag doped TiO₂ nanoparticles, dye absorption spectra suffered a slight red shift in the band peak position, Which indicated that the absorption of different dye on to the Ag doped TiO₂ nanoparticles. Ag doped TiO₂ nanoparticles were added different solution of dye and put on sunlight. In presence of Ag doped TiO₂ nanoparticles absorbance of dye decreases on different time intervals have been studied:-

Table 3

S.No.	Time	Azur I		Aniline Blue		Toluidine Blue	
		λ_{max}	Absorbance	λ_{max}	Absorbance	λ_{max}	Absorbance
1.	10 min	290	0.486	235	0.832	285	0.717
2.	20 min	290	0.276	235	0.750	285	0.387
3.	30 min	290	0.248	235	0.663	285	0.299

Take 20 ml selected dye and 0.001 gram Zn doped TiO₂ nanoparticles were added in different dye. In presence of Zn doped TiO₂ nanoparticles, dye absorption spectra suffered a slight red shift in the band peak position, Which indicated that the absorption of different dye on to the Zn doped TiO₂ nanoparticles. Zn doped TiO₂ nanoparticles were added different solution of dye and put on sunlight. In presence of Zn doped TiO₂ nanoparticles absorbance of dye decreases on different time intervals have been studied:-

Table 4

S.No.	Time	Azur I		Aniline Blue		Toluidine Blue	
		λ_{max}	Absorbance	λ_{max}	Absorbance	λ_{max}	Absorbance
1.	10 min	290	0.512	235	0.822	285	0.622
2.	20 min	290	0.348	235	0.728	285	0.432
3.	30 min	290	0.320	235	0.615	285	0.342
4.	40 min	290	0.217	235	0.512	285	0.225

This study shown the Silver doped and Zinc doped TiO₂ have better photocatalytic activity than TiO₂ nanoparticles.

Antibacterial Activity

An antibacterial substance is an agent that interferes the growth and reproduction of bacteria. In particular, silver ions have strong inhibitory and bacterial effects and possess a broad spectrum antimicrobial activity.

Table 5

S.no.	Nanoparticles	Zone of inhibition	Bacteria
1.	TiO ₂	23 mm	Staphylococcus
2.	Zn dped TiO ₂	25 mm	Staphylococcus
3.	Ag Doped TiO ₂	30 mm	Staphylococcus
4.	TiO ₂	21 mm	E-Coli
5.	Zn doped TiO ₂	23 mm	E-Coli
6.	Ag doped TiO ₂	25 mm	E-Coli
7.	TiO ₂	20 mm	Pseudomonas aourginosa
8.	Zn doped TiO ₂	21 mm	Pseudomonas aourginosa
9.	Ag doped TiO ₂	24 mm	Pseudomonas aourginosa

4. Conclusions

TiO₂ and Silver and Zinc doped TiO₂ nanoparticles were synthesized by sol gel method. The morphology study was demonstrated the particles have nano sized and the nanoparticles have photocatalytic and antibacterial activity.

References

- [1] Trung, Tran. , Cho, Won-jel. , Ha, Chang-Sik. , “Preparation of TiO₂ nanoparticles in glycerol-containing solutions, Science Direct Material Letters 57 ,2746-2750 (Elsevier) (2003)
- [2] Shen, Guozhen, Hee Cho Jung. Jin Kyoung Yoo, Gyu- Chul Yi. and Cheol jin Lee, ”Synthesis and Optical Properties of S-Doped ZnO Nanostructures : Nanonails and Nanowires”, Journal Of Phys. Chem. B , 109, 5491-5496, (2004-05)
- [3] Peng W.Q., Cong G.W., Qu S.C., Wang Z.G., ”Synthesis and photoluminescence of ZnS:Cu nanoparticles” Science Direct Optical Materials 29 ,313-317, (2006)
- [4] Rema Devi, B.S., Raveendran, R .and Vaidyan A V. ””Synthesis and characterization of Mn²⁺ -doped ZnS nanoparticles, PRAMANA, Journal of physics, Indian Academy of Science, . 68 No. 4, April (2007)
- [5] YU Huang Zheng xuxu, Zhongyi ,YIN, Feng, TAO , FANG Beibei , and HOU Keshan,”Preparation of Nitrogen-doped TiO₂ Nanoparticle Catalyst and Its Catalytic Activity under Visible Light” Chinese Journal Chemistry Engineering 15(6) 802-807 (2007)
- [6] Zaleska, Adriana, ”Doped – TiO₂ A Review” Recent Patent on Engineering ,2.,157-164, . (2008).
- [7] Akpan., U.G.,Hameed B.H, “The advancements in sol-gel method of doped-TiO₂ Photocatalysts.” Applied catalysis A: General 375 (2009)
- [8] Hamadian, M., Reisi- Vanani, A. , and Majedi A., “Sol- Gel Preparation and Characterization of Co/TiO₂ Nanoparticles” Application to the Degradation of Methyl Orange” Journal of the Iranian Chemical Society, 7,S52-S58 ,(2010)
- [9] Rahulan, K.Mani, Ganeshan, S. and Aruna, P., Synthesis and optical limiting studies of Au-doped TiO₂ nanoparticles from advances in natural science” “ Nano science and nano technology 2 , 025012 (2011)
- [10] Kokila, P. , Senthilkumar, V., Nazeer, K. Prem, ” Preparation and photo catalytic activity of Fe³⁺ -doped TiO₂ nanoparticles” Archives of Physics Research, , 2 (1): 246-253 (2011)
- [11] Chauhan, Ruby , Chaudhary ashadevi kumar Rampal: “structures of opticle properties of Zn_{1-x}Ni_xO and nano particles by coprecipitation method” Journal of optoelectronics and Biomedical materials III(1) , (2011)
- [12] Das,K.K.; Das,S.N.; Dhundasi,S.A.; “Nickel , its adverse health effects and oxidative stress “. Indian Journal of Medical Research ,128(4):117-131,(2008)
- [13] Roy, Kaushik; Sarkar, C.K.; Ghosh,C.K. “Photocatalytic activity of biogenic silver nanoparticles synthesized using yeast (Saccharomyces cerevisiae)extract,”Appliednanoscience5:953-959. (2014)
- [14] Ganesh, K.;Gupta, A.K.; Kumar,P.P.;Sekhar,P.S.C.;”Preparation and characterization of Ni-doped TiO₂ Materials for photocurrent and photocatalytic applications.

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