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Ag/TiO$_2$ NANOCOMPOSITE: SYNTHESIS, CHARACTERIZATION, PHOTOCATALYTIC AND ANTIMICROBIAL ACTIVITIES

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***Abstract**:*
In this work, we report the synthesis, photo catalytic and antimicrobial activities of Ag/TiO$_2$ Nanocomposites prepared by easy, cost effective and less harmful co-precipitation method. The yield of the product is also good when compared to other methods. They were characterized by UV, XRD, FE-SEM and EDAX techniques. The X-ray diffraction (XRD) spectra reveal single phase anatase structure for the samples, formation of uniform spherical Ag doped TiO$_2$ nanocomposite is ascertained from the surface morphology of FE-SEM. From EDAX, metal composition is observed as Ag-2.33%, 2.72%, 7.90% and Ti-43.62%, 62.30%, 50.97%. The photocatalytic activity of the composite is tested with Rhodamine B dye, Ag-TiO$_2$ sample degraded the Rhodamine B dye (25ppm) in 150 min indicates good photocatalytic activity. An enhancement in bactericidal activity is also observed against bacterial strains Pseudomonousaeruginosa and serratia with increased Ag substitution. Pseudomonousaeruginosa exhibited good bactericidal effect than serratia.

***Keywords**: Nanocomposites, photocatalytic activity, Rhodamine B dye, Pseudomonousaeruginosa, serratia.*

I. Introduction

Water pollution is one of the most leading problems that badly affect the human and aquatic life [1]. Due to Increasing demand and shortage of clean water, the use of clean water and wastewater treatment processes becomes more and more challenged. Water treatment technologies like membrane filtration, advanced oxidation processes (AOPs) and UV irradiation hold great promise to provide alternatives for better protection of public health and the aquatic life [2]. Heterogeneous photo catalyst is recently emerged as an alternative technology of advanced oxidation processes (AOP) for bacteria inactivation [3] and organic pollutants oxidation[4]. Out of the various semiconductor photo catalysts used, TiO$_2$ (titanium dioxide) (band gap of ~3.2 eV) has been found to be the most suitable because of its nontoxic, insoluble, inexpensive, stable and high production of oxidative hydroxyl radicals (•OH)[5]. TiO$_2$ exhibits remarkable properties such as hydrophilicity as well as antibacterial and self-cleaning activity. Due to its optical activity, TiO$_2$ is often used in photo catalytic decomposition and more recently as photo catalyst for the reduction of CO$_2$ to methanol [6-7]. There are many approaches to synthesize TiO$_2$ and modified TiO$_2$ including hydrothermal, electrochemical, microwave, co-precipitation and sol-gel methods [8-9]. Among these methods, the co-precipitation method offers simple methodology, high control of surface area, average crystallite size, phase structure and morphology [10-11]. But the rapid recombination of electron-hole pair limits the efficiency of TiO$_2$ and it can be prevented by methods like doping, functionalization of the surface with metal particles, and reduction of particle size to the nanoscale.

Considerable research has been carried out to improve the electro catalytic and photo catalytic activity of TiO$_2$, with metal ion doping [12]. Transition metals doped on TiO$_2$ play the role of charge carrier trap, which allows for light absorption in the visible range and enhances surface electron excitation by visible-light excited plasmon resonance. TiO$_2$ doped with noble metal silver (Ag) have shown improved photo catalytic activity compared with its undoped counterpart [13-14]. This is due to the fact that Ag can trap the excited electrons and therefore reducing the recombination rate of photo induced electron-hole pairs. In this work, Ag doped-TiO$_2$ (AgTiO$_2$) in anatase form was prepared via co-precipitation method. The synthesized Ag-TiO$_2$ was then investigated for enhanced catalytic activity with regards to the oxygen evolution reaction. Photocatalytic degradation of Nanocomposite is tested for the degradation of organic Rhodamine B dye. It has been reported that doping of Ag can enhance the photocatalytic as well as antibacterial activity of TiO$_2$ under visible light illumination by promoting electron–hole separation [15-16]. Bactericidal activity is also observed against bacterial strains *Pseudomonousaeruginosa* and *serratia* with increased Ag substitution.

II. Materials and Methods

Materials: Titanium dioxide (97%) and silver nitrate (99%) were purchased from Aldrich. Rhodamine-B was purchased from Eastman and was of analytical grade and used without further purification. Deionized water was used in all experimental preparations. The samples were prepared by co-precipitation method.

Synthesis Of Ag-TiO_2 Nanocomposite: 20 ml of 3M TiO_2 was taken in 100ml beaker. Then 5 ml of 0.025M ammonium per sulfate and silver nitrate was taken in three different concentrations (0.05M, 0.1M and 0.15M) which were mixed with the above solution. 2.5ml of 0.5M NaOH solution was added to the above solution and stirred on a magnetic stirrer for one hour. After stirring, the solution was kept at 70˚C for 15 minutes and dried the sample. This powder was finely ground using mortar–pestle and kept for further use.

III. Results and Discussion

A. *UV- Visible Spectrum:*

UV spectra of the TiO_2 and Ag-modified TiO_2 samples were recorded in Jasco V-630 spectrometer. TiO_2 spectrum consists of a wide absorption band below ~370nm ascribed to electron transitions from the valence band (VB) to the conduction band (CB). Moreover, an interesting light response was found for Ag-loaded samples. Increase in Ag concentration induces a shift in light absorption to the visible range for wavelengths up to 800nm. UV spectrum of the 0.05% Ag loaded TiO_2 sample did not show a significant increase in visible absorption capacity of the material. In addition, 0.10M & 0.15M Ag-loaded samples shown a shoulder-like peak at ~460nm which has been proposed for Ag nanoparticles inducing visible light absorption. Atoms, ions and clusters of Ag show characteristic absorption peaks with irradiation wavelengths from 190nm to 500nm in UV spectra. The UV spectra clearly shows that when Ag is added to the TiO_2 which can shift the absorption range from UV to visible region.

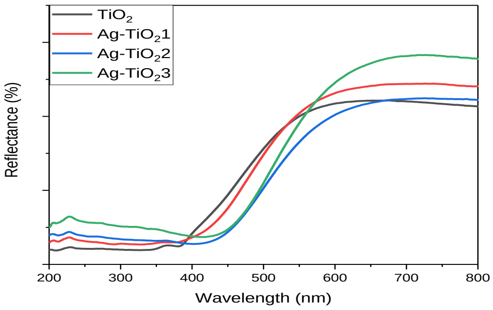


Figure 1. UV Spectra of the TiO_2 and Ag-TiO_2 Samples.

B. *Field Emission Scanning Electron Microscopy Scanning Electron Microscopy (FESEM):*

The figure (2, 3 & 4) shows the FESEM images of freshly synthesized spherical Ag-TiO_2 nanocomposite. It can be observed that the Ag-TiO_2 nanocomposite with pores in the nano range which exist in contact with each other and diameters were also in the nanometer range.

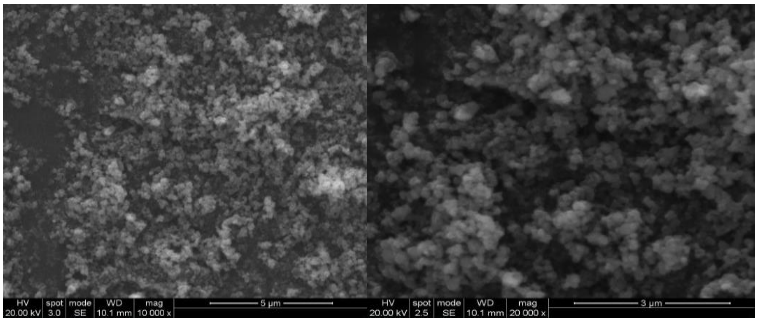


Figure.2 FESEM Images for Ag-TiO_2 (0.05M)

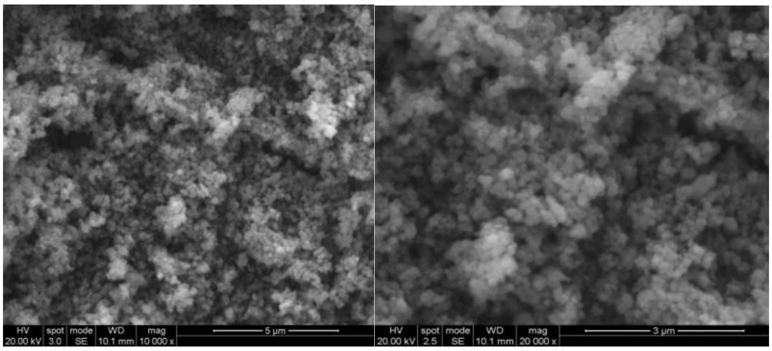


Figure.3 FESEM Images for Ag-TiO_2 (0.10M)

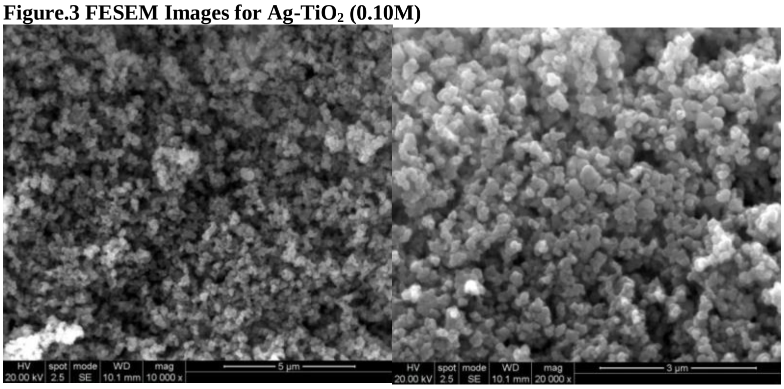


Figure.4 FESEM Images for Ag-TiO_2 (0.15M)

C. *Energy Dispersive Analysis Of X-Rays (EDAX)*

EDAX spectrum showed the presence of elemental silver and titanium shown in Figure. (5, 6 & 7) and metal composition, i.e., Ag-2.33%, 2.72%, 7.90% and Ti-43.62%, 62.30%, 50.97% were observed. It also showed the absence of any other impurity in the synthesized samples.

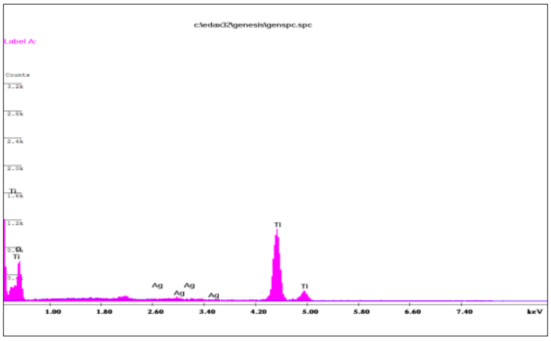


Figure.5 EDAX Images for Ag-TiO_2 (0.05M)

Element	Wight (%)
O	54.05
Ag	2.33
Ti	43.62
Total	100.00

Table 1 EDAX Analysis for Ag-TiO_2 (0.05M)

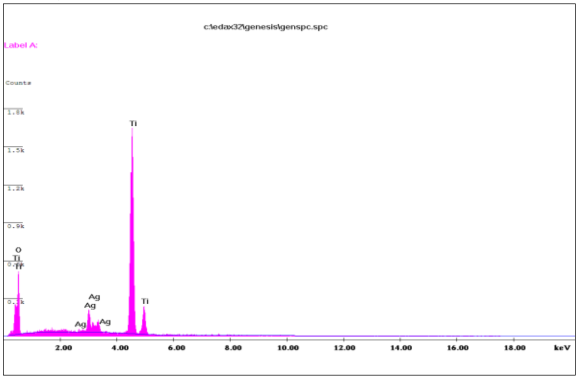
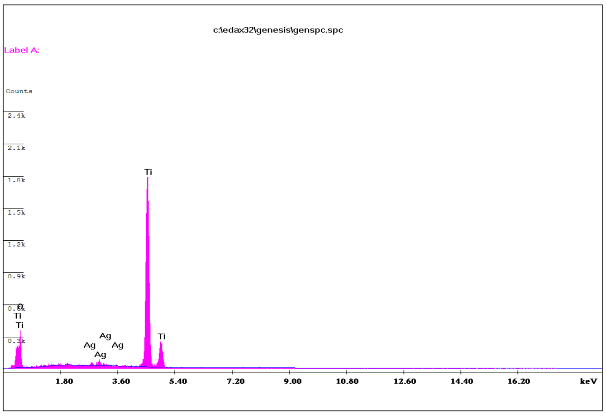


Figure.6 EDAX Images for Ag-TiO_2 (0.10M)

Element	Wight (%)
O	34.98
Ag	2.72
Ti	62.30
Total	100.00

Table. 2 EDAX Analyses for Ag-TiO_2 (0.10M)



Element	Wight (%)
O	41.14
Ag	7.90
Ti	50.97
Total	100.00

Figure.7 EDAX Images for Ag-TiO_2 (0.15M)

Table. 3 EDAX Analyses for Ag-TiO_2 (0.15M)

D. X-Ray Diffraction (XRD)

The XRD pattern of Ag-TiO_2 contras the formation of dual phases including the anatase phase of TiO_2 and the face centered cubic (FCC) lattice of Ag. The Ag exhibits 5 major peaks at 2θ values of 22.7, 37.8, 48.15, 62.6 and 75.2 degrees, assigned to the corresponding (101), (111), (200), (220) and (311) indices respectively. Five peaks indexed at (101), (111), (200), (220) and (311) matches well with JCPDS card (89-4837) of Ag-TiO_2 nanocomposite. From the Figure (8, 9 & 10) clearly shows there is no other phase in XRD except anatase.

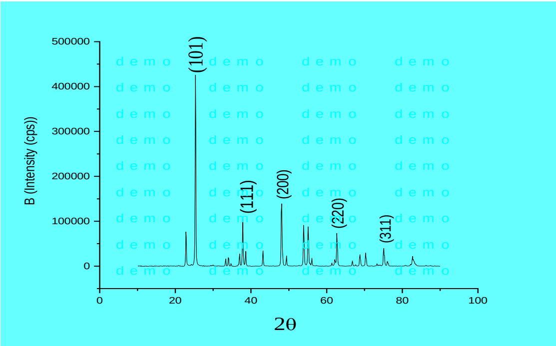


Figure.8 XRD Images for Ag-TiO_2 (0.05M)

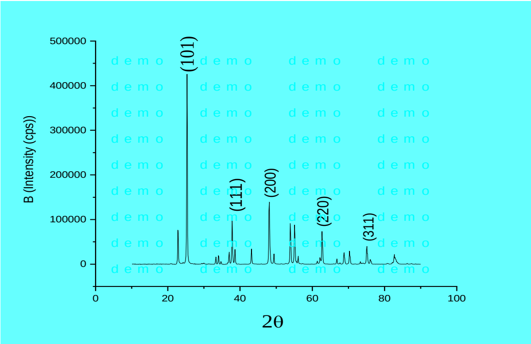


Figure.9 XRD Images for Ag-TiO_2 (0.10M)

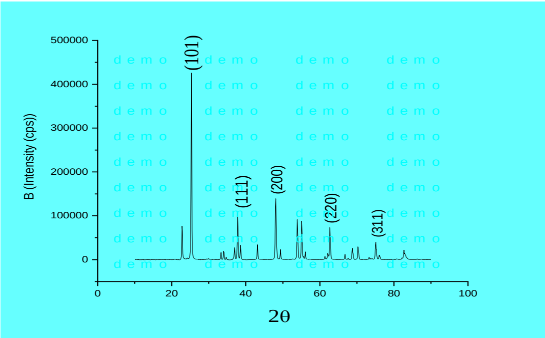


Figure.10 XRD Images for Ag-TiO_2 (0.15M)

PHOTOCATALYTIC ACTIVITY

25 mg of Ag-TiO_2 (0.05 M, 0.10 M and 0.15 M) was taken in 25 ml of Rhodamine-B. Control is taken along with the Ag-TiO_2 naocomposites. After 2 minutes sonication samples were kept in dark room. Then UV was taken for all those samples after 150 minutes degradation and with the time interval of 30 minutes. Figure.11 shows the UV spectrum of Rhodamine-B. Figure 12, 13 and 14 shows the UV-spectra of Ag-TiO_2 loaded

Rhodamin-B. 25 ppm of Rhodamine-B dye was prepared and the reading was noted by using UV-spectrophotometer, which is shown in figure.15, From the figures, it is clear that the Ag-TiO_2 concentration increases, degradation ability also increases Ag-TiO_2 (0.15 M) loaded in Rhodamine-B got degraded completely at 150 minutes time interval. Thus it can act as a very good photocatalyst.

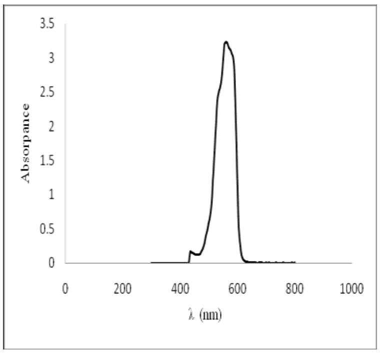


Figure.11Photo Catalytic Activity for Rhodamine-B

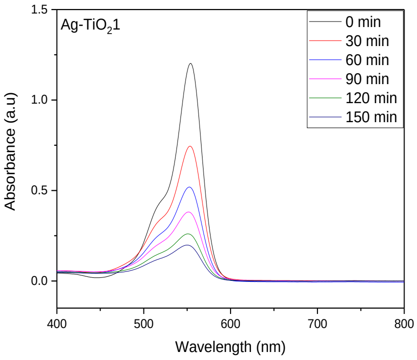


Figure.12 Photo Catalytic Activity for Ag-TiO_2 (0.05M)

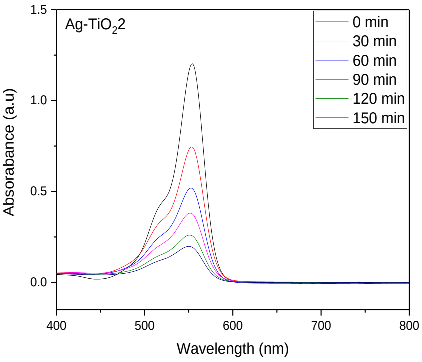


Figure.13 Photo Catalytic Activity for Ag-TiO_2 (0.10M)

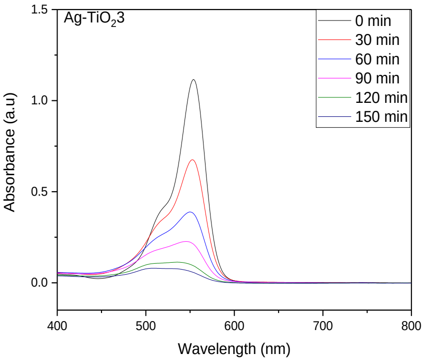
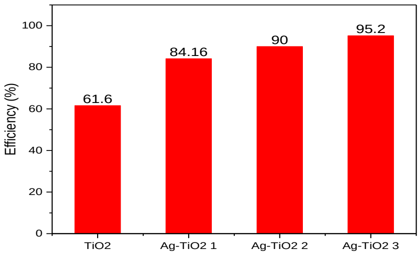


Figure.14 Photo Catalytic Activity for Ag-TiO_2 (0.15M)



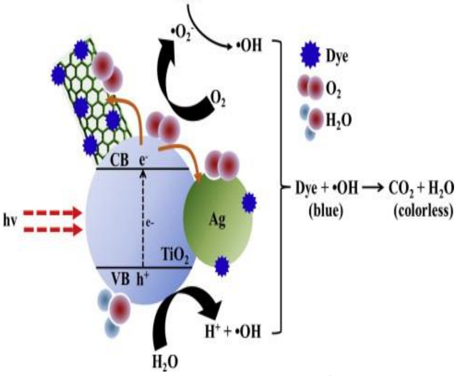


Figure.15 Photo Catalytic Efficiency for Ag-TiO_2 (0.05M, 0.10M and 0.15M)

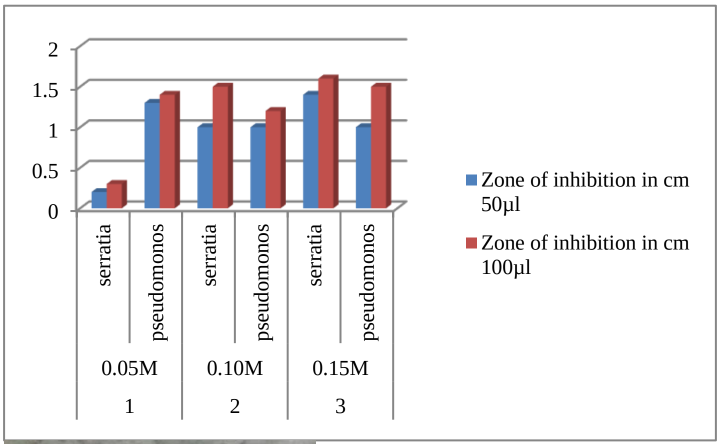
Figure.16. Mechanism of Photo Catalytic Activity.

ANTIBACTERIAL ACTIVITY

The antimicrobial activity has been observed to vary as a function of surface area in contact with the microbe, therefore nanocomposite with large surface area ensures a broad range of reactions with the bacterial surface. *Serrtia* and *Pseudomonas aeruginosa* microbial cultures were subjected to analyze their susceptibility/ resistance pattern to test samples by well diffusion method using Mueller Hinton agar medium for bacteria. Sterile medium was dispensed into sterile Petri dishes aseptically. Enriched broth cultures (24 h for bacteria culture, incubated) were used as inoculums. Using sterile cotton swab, the test organisms were swabbed over the surface of the agar plate aseptically. In each of these plates, wells (10 mm) were cut out using sterile cork borer. The samples were dissolved in the acetone and different concentration (50 & 100 g /ml) of the sample was loaded onto the wells. Incubated the plates at 37^0 C (for 24 h for bacteria) upright position of the plates. Solvent was used as control. After the incubation, the diameters of inhibition zones were observed. The inhibition zone was compared with the control sample. From the result (table 4. ;Figure 17-20), it is observed that prepared Ag-TiO_2 nanocomposites showed good antibacterial activity. Also when concentration of Ag increases antibacterial activity also increases. The antibacterial activity of Ag-TiO_2 nanocomposites against *pseudomonas* is better than the activity against *serratia*.

Sl. No.	Nanocomposite (Ag-TiO_2)	Name of Organism	Zone of inhibition in cm	
			50µl	100µl
1	0.05M	Serratia	0.2	0.3
		Pseudomonas	0.5	0.8
2	0.10M	Serratia	0.8	1.3
		Pseudomonas	1.0	1.4
3	0.15M	Serratia	1.0	1.6
		Pseudomonas	1.5	1.8

Table.4 Antibacterial Activity of Ag- TiO_2 Nanocomposite



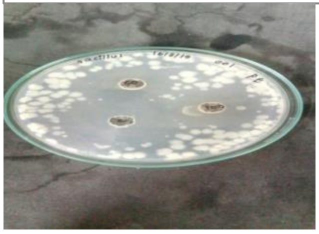


Figure.16 Antibacterial Activity of Ag-TiO_2 (0.05M, 0.10 M an0.15M) **Figure.17 Antibacterial Activity of Ag-TiO_2 (0.05M)**

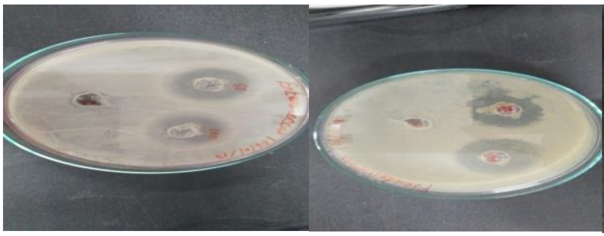


Figure.18 Antibacterial Activity of Ag-TiO_2 (0.10M) **Figure.19 Antibacterial Activity of Ag-TiO_2 (0.15M)**

CONCLUSION

In this work we synthesized Ag-TiO_2 nanocomposite by easy, cost effective, less harmful, less timing and good yield co-precipitation method. Ag doped TiO_2 nanocomposites were prepared by varying the concentration of Ag. Nano composites were characterized by UV, XRD, FESEM and EDAX. UV spectrum ascertained the formation of Ag doped TiO_2 nanocomposites which is evident from the shift in energy band gap changed from UV to Visible. The X-ray diffraction (XRD) spectra reveal single phase anatase structure for the samples with

20nm size, formation of uniform spherical Ag doped TiO_2 nanocomposite is ascertained from the surface morphology of FE-SEM. From EDAX, metal composition, i.e., Ag-2.33%, 2.72%, 7.90% and Ti-43.62%, 62.30%, 50.97% were observed. The antibacterial activity of the prepared sample exhibited good antibacterial effect on *Pseudomonosaeruginosa* than *serratia*. From photo catalytic study, it was observed that the prepared Ag-TiO_2 sample degraded the Rhodamine B dye (25ppm) in 150 min. Thus Ag-TiO_2 can act as a good photo catalyst and good antibacterial agent.

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