

Effect of Time and Amount of Ag Photodeposition over TiO₂ on Photo catalytic Properties

A thesis

Submitted in the partial fulfilment of the requirements for the award of degree of

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in

CHEMISTRY

Submitted by

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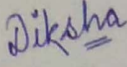
June, 2018

Dedicated to
My family, friends and teachers
For their love and support

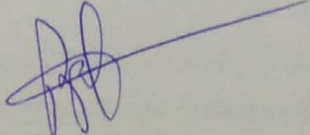
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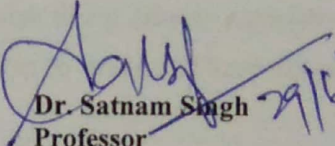
I hereby certify that the work presented in this thesis entitled "*Effect of Time and Amount of Ag Photodeposition Over TiO₂ on Photocatalytic Properties*" submitted in partial fulfilment of the requirements for the award of degree of Master of Science in Chemistry submitted to School of Chemistry and Biochemistry, Thapar Institute of Engineering and Technology, Patiala is an authentic record of my own work carried out under the supervision of Dr. Bonamali Pal and Dr. Satnam Singh. The matter embodied in the thesis has not been submitted to any other University for the award of any other degree or diploma. Works of other authors cited in this thesis have been duly acknowledged under reference section of this thesis.

Date: 29th, June, 2018


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This is to certify that the above statement made by the candidate is correct and true to the best of my knowledge.


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List of Abbreviations

SPR	Surface plasmonic resonance
NPs	Nanoparticles
CB	Conductance band
VB	Valence band
UV	Ultraviolet
Wt %	Weight percent
DRS	Diffuse reflectance spectrophotometer
DLS	Dynamic Light scattering
SEM	Scanning electron microscope
EDX	Energy dispersive X-ray
SA	Salicylic acid
IPA	isopropyl alcohol
DI	Deionized water
NC	Nanocomposite
Ag@TiO₂ / Ag-TiO₂	Silver photo deposited over TiO ₂
(Ag)₃₀ / (Ag)₆₀ / (Ag)₉₀@TiO₂	Silver photo deposited over TiO ₂ at different time intervals of 30 , 60 , 90 minutes

List of Symbols

kV	Kilo Volt
Mg	Milligram
ml	Milliliter
Rpm	Revolutions per minute
μL	Micro liter
e⁻	Electron
h⁺	Hole
Min	Minute
eV	Electron Volt
a.u.	Arbitrary unit
λ_{ex}	Excitation wavelength
E_g	Energy Gap

Abstract

This work investigate the influence of amount (1-5 wt %) and time (30-90 min) of Ag co-catalyst photodeposition over TiO₂ on the photocatalytic activity of different Ag-TiO₂ nanocatalysts for the degradation of salicylic acid under UV light irradiation. A considerable red-shift in the plasmon band (454 to 552 nm) with a significant color change (white to brown) of various Ag-TiO₂ nanocomposites were observed with increasing time and amount of Ag deposition over TiO₂ surface. It was also observed that the average hydrodynamic size 344 nm of bare TiO₂ is increased to 782 nm for (5 wt % Ag)_{90 min}-TiO₂ due to higher amount of Ag loading during 90 min. The EDX-mapping revealed higher amount (1.69 wt %) of Ag deposition during 90 min as compared to 0.21 wt % Ag after 30 min UV light irradiation. These 1, 3 and 5 wt% (Ag)_{90 min}-TiO₂ nanocatalysts always showed better photocatalytic activity (rate constant $k = 2.73 \times 10^{-2} \text{ min}^{-1}$) than 1 wt % (Ag)_{30/60 min}-TiO₂ composites ($k = 0.95 \times 10^{-2} \text{ min}^{-1}$) for the degradation of salicylic acid under UV light irradiation. Thus different photoactivity of 1-5 wt% Ag-TiO₂ nanocatalysts are correlated with the size and nature of Ag co-catalyst distribution over TiO₂ surface as a function of time and the amount of Ag deposition under UV light irradiation.

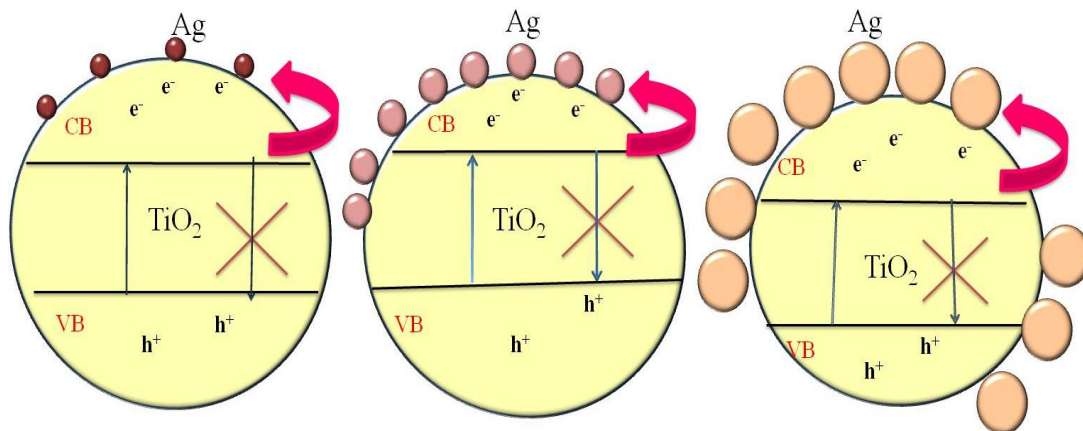
1. INTRODUCTION & LITERATURE REVIEW

Plasmonic metals (Au, Ag, and Cu) are gaining interest in the present days due to their unique optical properties related to collective oscillations of the surface electrons known as surface plasmonic resonance (SPR)¹⁻². Therefore these metals have been used in different shapes, sizes and forms to alter the optical and surface properties of TiO₂ photocatalyst. These photo deposited metals (Au, Ag, Cu) on the surface of TiO₂ can create traps to capture the photo induced electrons, leading to the drop in electron-hole recombination in photo catalytic processes and the increase in the absorption capability of TiO₂ particles, as the electrons gets transferred from metal nanoparticles (NPs) to the conductance band (CB) of TiO₂ because of their SPR effect. Literature reveals that Au-TiO₂ photocatalyst have been extensively used in environmental applications like degradation of toxic pollutants. It is known since the SPR band of Au NPs depends on shape, size and the chemical environment of AuNP, therefore any change in these will shift the frequency of SPR band³ leading to the changes in the interfacial properties of Au-TiO₂ photocatalyst. Currently most of research activities on Au-TiO₂ photocatalyst are in the field of photo degradation of pollutant dyes. For example, in 2003, *Falaras and co-workers* reported azo-dye degradation using Au-TiO₂ thin film⁴⁻⁶. They observed two times faster degradation of methyl orange w.r.t. rate obtained for bare TiO₂ material. Also, *Lu and co-workers* reported the conversion of phenol oxidation and chromium reduction catalyzed by mesoporus Au-TiO₂ nanocomposite with different amounts of Au loading in 2006⁷⁻⁸. *Gupta and co-workers* in 2016 reported the TiO₂ modification by Au for photocatalytic hydrogen (H₂) production. *Cubillos-Lobo and co-workers* in 2017 reported that optical absorption, oxidation state and particle size of the metallic Au species play an important role in the TiO₂ photocatalytic activity under visible-light irradiation. Although, Au-TiO₂ nanocomposite is widely used however, it has the disadvantage of being expensive.

In this respect Ag-TiO₂ nanocomposite is gaining attention, since the precursor AgNO₃ for the preparation of Ag NPs is cheap and easily available and moreover, Ag NPs can be photo deposited over the surface of TiO₂ quite easily. Literature reveals that a variety of studies have been undertaken using Ag-TiO₂ photocatalyst in the environmental applications, like; *Hermann and co-workers* in 1997 reported the photocatalytic degradation of organic pollutant malic acid using Ag-TiO₂ photocatalyst⁹⁻¹⁰. Apparent increase in activity was observed compared to pure TiO₂ catalyst since metallic Ag always produce an increase in activity as compared to oxidized

Ag⁺ ions. Also, *Yu and co-workers* reported the photocatalytic decolourization of methyl orange using Ag-TiO₂ thin films in 2005¹¹⁻¹². *O. Akhavan* in 2009 reported the photo degradation of *E.coli* bacteria in presence of Ag-TiO₂/Ag/a-TiO₂ nanocomposite under visible light irradiation¹³⁻¹⁴. It was observed that reduction in the rate of *E.coli* using the composite was 5.1 times higher as compared to bare TiO₂ catalyst. *Xiang and co-workers* in 2010 reported the photocatalytic degradation of Rhodamine B dye solution at ambient temperatures under UV light irradiation using Ag-TiO₂ photocatalyst. They observed the disappearance of color after 90 minutes of UV light irradiation indicating that the chromophoric structure of the dye was completely destroyed¹⁵. *Yang and co-workers* 2013 reported the photocatalytic activity of polypyrrole modified Ag-TiO₂ nanofibers¹⁶ by measuring the time dependant photo degradation of gaseous acetone under visible light irradiation. They concluded that the prepared Ppy-Ag-TiO₂ was stable and efficient in removal of organic pollutants. Further, *Kim and co-workers* in 2016¹⁷ reported the photocatalytic degradation of gaseous benzene using photo deposited Ag-TiO₂ nanoparticles. It was observed that the photo deposited Ag-TiO₂ NPs exhibited more efficient photocatalytic activity towards the photo degradation of benzene than bare TiO₂ under visible light irradiation. *Espino-Estevez and co-workers* also in 2016 reported the effect of Pd-TiO₂ and Ag-TiO₂ on the photocatalytic oxidation of diclofenac, isoproturon and phenol¹⁸.

The photodeposition test conditions of both metals determine their final oxidation state, with reduced particles of palladium and silver as well as silver oxides were found on the catalysts. The results indicated that the type of metal had different effects on the photo degradation mechanism depending on the nature of the pollutants. However, very little information is available regarding the modification in optical properties of Ag-TiO₂ photocatalyst w.r.t. increase in amount of Ag deposited over TiO₂ surface by varying the photodeposition time under UV light irradiation. Scheme 1 demonstrates the effect of change in the size of Ag NP and the increase in the number of Ag NPs with the increase in time of photodeposition for tuning the optical properties of Ag-TiO₂ photocatalyst for photodegradation of salicylic acid.



Scheme 1: Schematic representation of Ag deposition over TiO₂ with increasing amount (1, 3, 5 wt %) of Ag and UV light irradiation time (30, 60, 90 minutes).

2. Objectives

- ™ To prepare various Ag-TiO₂ photocatalysts with varying amount of Ag photodeposition at different time intervals.
- ™ To study the optical, structural and photocatalytic properties of the prepared Ag-TiO₂ photocatalysts.

3. EXPERIMENTAL SECTION

3.1. Chemical Reagents

Silver nitrate (AgNO₃, > 99%) was purchased from Sigma-Aldrich, IPA (isopropyl alcohol) – C₃H₈O was purchased from Rankem and Salicylic acid (SA), 99% was purchased from Loba Chemie, India. All chemicals were used without any further purification. Commercially available TiO₂ (P25; 70% Anatase + 30% Rutile phase) was received as a gift from Degussa corporation Germany. Deionized water (DI) was obtained from ultra-filtration system (milli-Q, Millipore) with measured conductivity of 35 mho cm⁻¹ at 25°C.

3.2. Methods

3.2.1. Photodeposition of Ag-TiO₂

The photo-deposition of Ag@TiO₂ was done as reported previously¹⁹⁻²¹. 100 mg of TiO₂ was dissolved in 5 ml of IPA (Isopropyl alcohol) and 5 ml of de-ionized water. The resultant solution was transferred in three different test tubes. Further, 934 μL of 1 wt% Ag solution (from the stock solution of AgNO₃) was added to the above TiO₂ solution in three test tubes. The test tubes were sealed and purged with argon to remove excessive oxygen in order to prevent oxidation. After 15 minutes of purging, the test tubes were continuously stirred using a magnetic stirrer and kept under UV light irradiation at different time intervals of 30, 60 and 90 minutes respectively. Subsequently the test tubes were removed after each interval and centrifuged for 10 minutes at 8000 rpm. The resulting nanoparticles (NPs) were washed thrice with DI water and lastly with ethanol. Finally, the nanoparticles were dried in order to obtain Ag@TiO₂ co-catalyst and prepared at different time intervals. In a similar manner 3 wt% and 5 wt% Ag@TiO₂ were also prepared.

3.2.2. Characterization techniques

Various techniques are used to characterize Ag-TiO₂ NCs. The technical details of these techniques are given below:

Ultraviolet-Visible (UV-Vis) Spectrophotometric analysis: The optical properties of Ag-TiO₂ were analyzed by UV-Vis (Specord 205) spectrophotometer. 5 mg of each prepared 30, 60, 90 min photo deposited Ag-TiO₂ co-catalyst was diluted by 2 mL of de-ionized water and their UV-Vis absorption spectra were obtained.

DRS (Diffuse reflectance spectrophotometer): The shift in surface plasmon bands were depicted by this instrument. Different catalysts of 30, 60 and 90 min photo deposited Ag-TiO₂ was taken and analyzed using Avntas DRS instrument, using BaSO₄ as a reference. Plasmon bands were observed at different wavelengths showing the change in the size of Ag NPs deposited over TiO₂.

Dynamic Light scattering (DLS) analysis: The average hydrodynamic particle size distribution of different 30, 60, 90 min photo deposited Ag-TiO₂ were analyzed by taking 2 mL of the solution using Malvern, zeta sizer.

Scanning electron microscope (SEM) analysis and elemental mapping: For SEM and elemental examinations, a single drop (10 μL) of the solution of the Ag-TiO₂ NPs were placed on a 300

mesh copper grid coated with a carbon film. The grid was left to dry at room temperature. SEM analysis was carried out using JSM-6510LV, electron microscope working at 30 kV.

Fluorescence Spectrophotometric analysis: Fluorescence measurements were analyzed by Perkin-Elmer LS55, interfaced to a PC for the reading and handling of the spectra. Quenching of different 30, 60, 90 min photo deposited Ag-TiO₂ co-catalysts were studied at λ_{ex} of 340 nm.

3.2.3. Photocatalytic activity of Ag-TiO₂

Firstly, a stock solution of salicylic acid (SA) was prepared by dissolving 5.5 mg of SA in 100 ml of DI water. 5 ml of this stock solution was taken in four different test tubes and 20 mg of prepared Ag-TiO₂ was added to each test tube. The test tubes were kept in a UV reactor and stirred continuously for 20, 40, 60 and 80 minutes, respectively. After each time interval, the test tubes were removed and centrifuged for 5 minutes at 6000 rpm. The supernatant solution from each test tube was collected and UV-Visible spectra of these samples were observed to determine the photocatalytic activity of Ag-TiO₂ for the photo degradation of salicylic acid.

4. Results and Discussion

4.1. Optical and Structural Analysis

Figure 1 shows the observed color changes in the Ag-TiO₂ nanocomposite during the photodeposition of Ag compared to bare TiO₂ solution. It was observed that the color of the solution changes from white to light brown with increasing Ag deposition time under UV light irradiation. The specific charge transfer transitions ($T_{2g} \rightarrow E_g$) between Ag co-catalyst and TiO₂ are accountable for the change in color at different time intervals (30, 60 and 90 min) of photodeposition.

Increasing time of Ag photo deposition over TiO₂

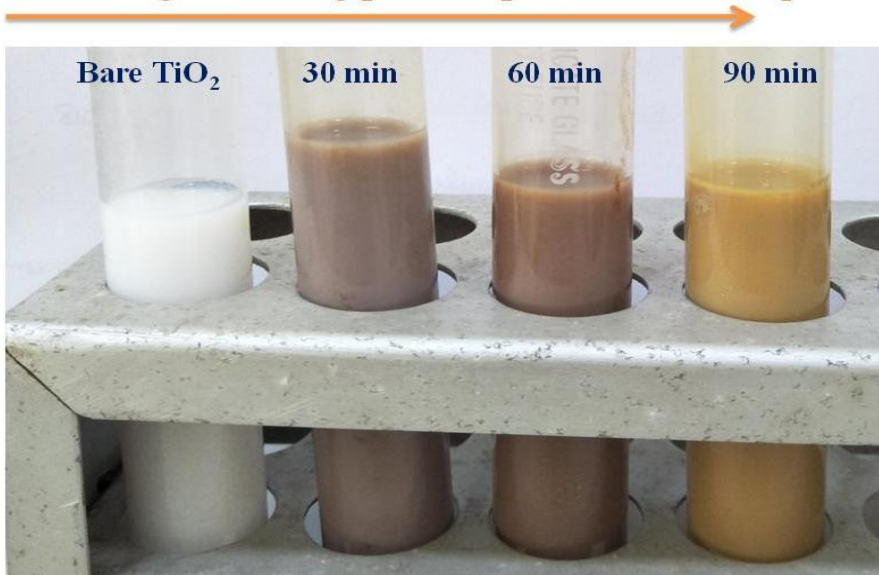


Fig.1: Changes in color intensity of Ag-TiO₂ nanocomposite during photodeposition of Ag at different time of UV light irradiation.

DRS absorption spectra of 1 wt% Ag deposited over surface of TiO₂ at increasing time intervals and corresponding change in the plasmon bands is shown in figure 2 (a). Strong absorption bands at 460nm, 454 nm, and 452 nm for Ag were observed at different time intervals of 30, 60 and 90 min respectively in the Ag-TiO₂ photocatalyst. A red shift in the SPR bands was observed compared to absorption band of bare TiO₂ catalyst. This red shift in the photo deposited Ag-TiO₂ occurs due to transfer of 3d e⁻s from the C.B of TiO₂.

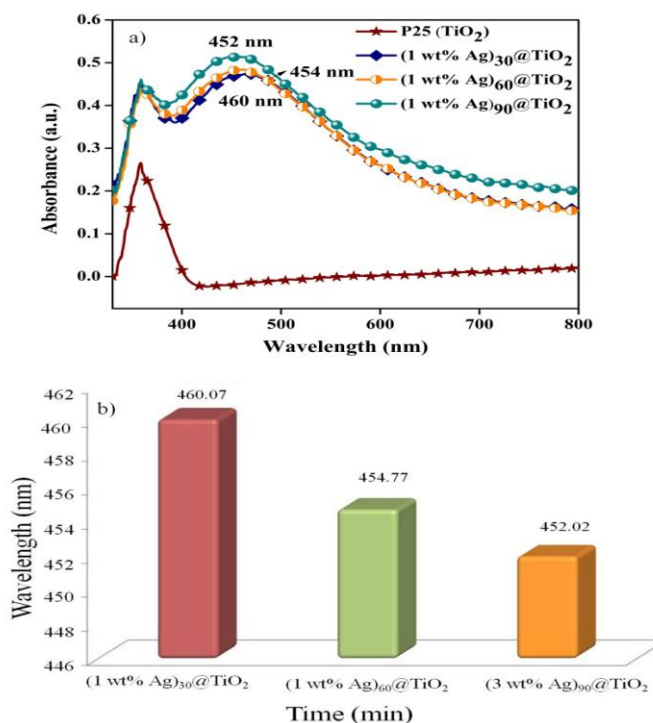


Fig 2: a) Absorption spectra of 1 wt% Ag deposition over TiO₂ after 30, 60 and 90 min UV light irradiation and corresponding change in Ag Plasmon band and b) Comparative histogram of 1 wt % Ag-TiO₂ at different time intervals.

Comparative histogram in figure 2 (b) Shows the shifts in plasmon bands corresponding to the color change indicated the increase in the size and distribution of Ag by progressive distribution of Ag NPs on the surface of TiO₂. Similarly, DRS absorption spectra of 3 wt% and 5 wt% Ag photodeposition at different time intervals are shown in figure 3 (a and b).

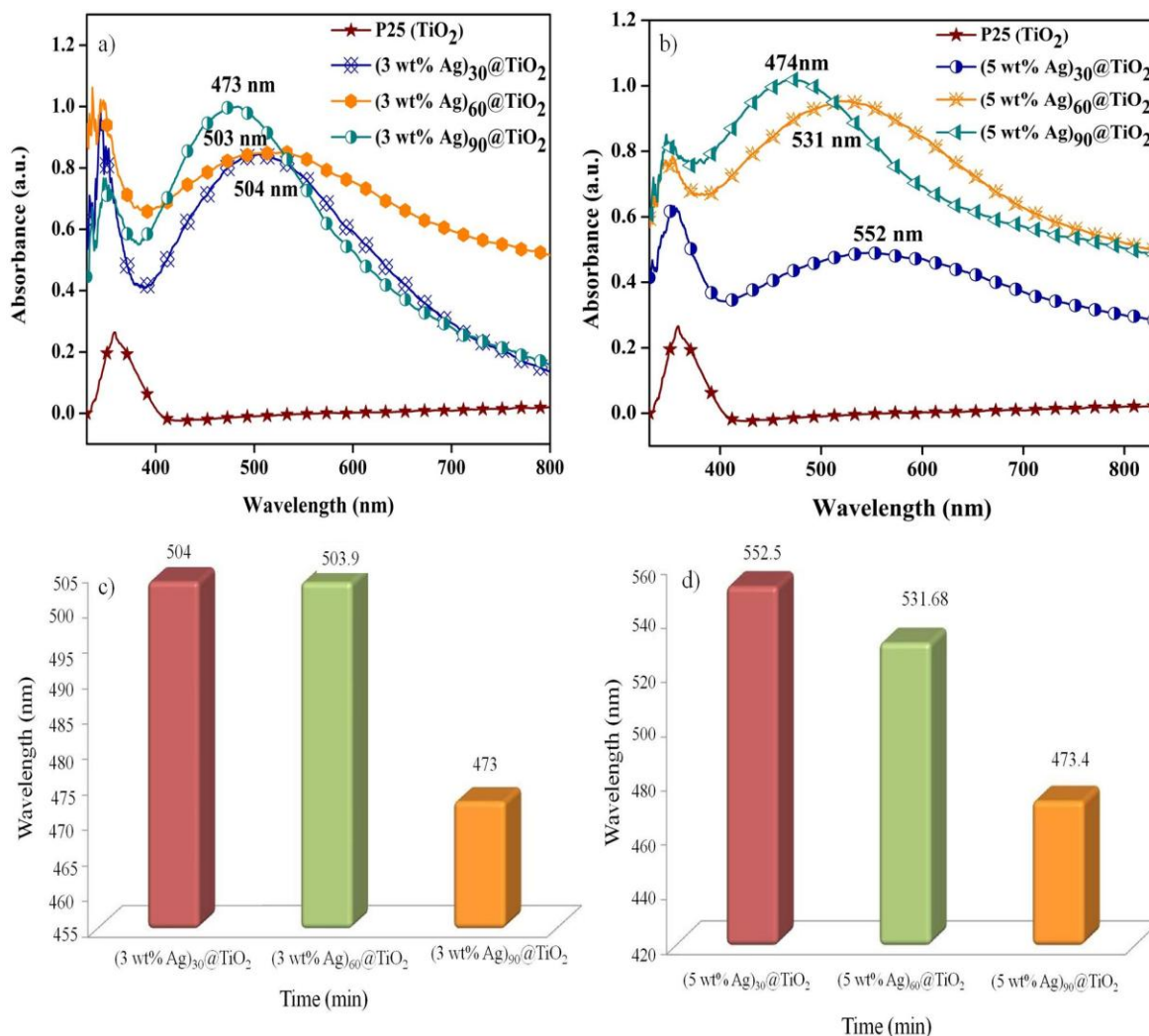


Fig.3: Absorption spectra of a) 3 and b) 5 wt% Ag deposition over TiO₂ after 30, 60 and 90 min UV light irradiation and corresponding change in Ag Plasmon band and c-d) Comparative histogram of 3 and 5 wt % Ag-TiO₂ at different time intervals.

The dynamic light scattering (DLS) results, illustrated in figure 4 and 5, shows a gradual increase in size of Ag-TiO₂ NC after successive increase in amount of Ag deposition of 1, 3 and 5 wt% at different time intervals. It has been observed from figure 3 that bare TiO₂ has an average size of 389 nm; however the size increased upto 526 nm after photodeposition of 1 wt% Ag under UV light irradiation.

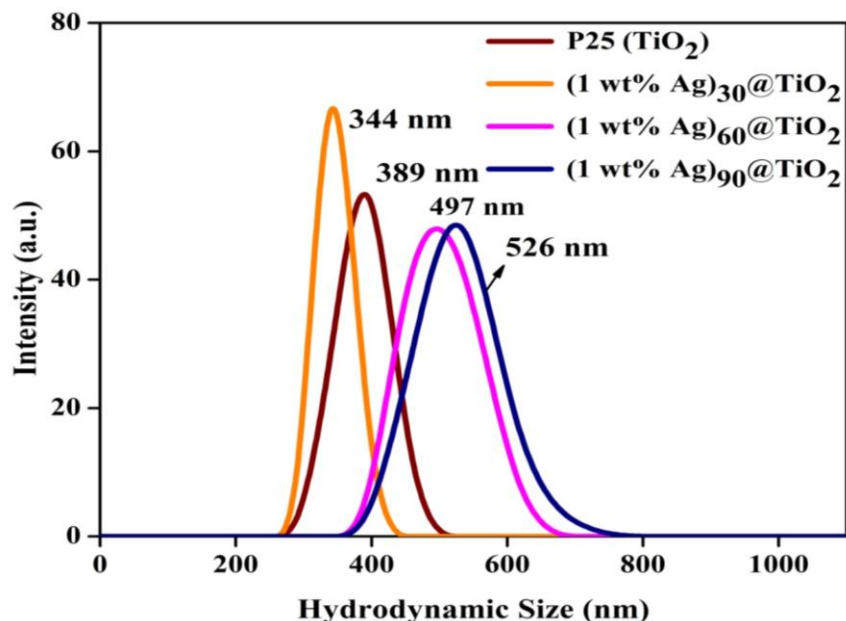


Fig.4: Dynamic light scattering (DLS) hydrodynamic size distribution of different Ag-TiO₂ nanocomposite after 1 wt% Ag photodeposition over TiO₂ at 30, 60 and 90min UV light irradiation.

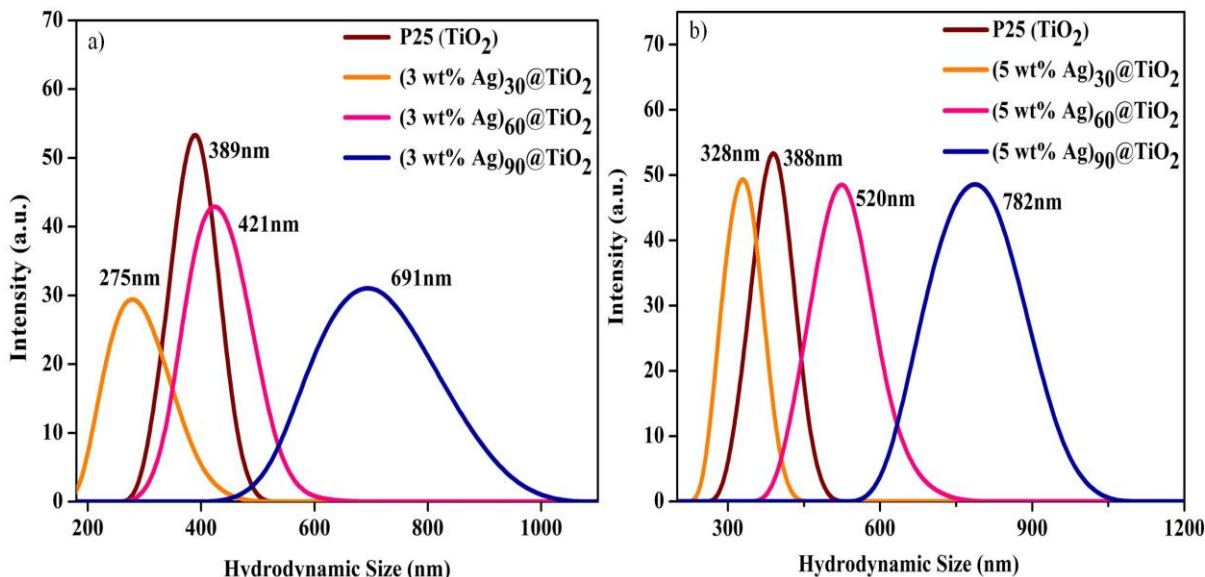
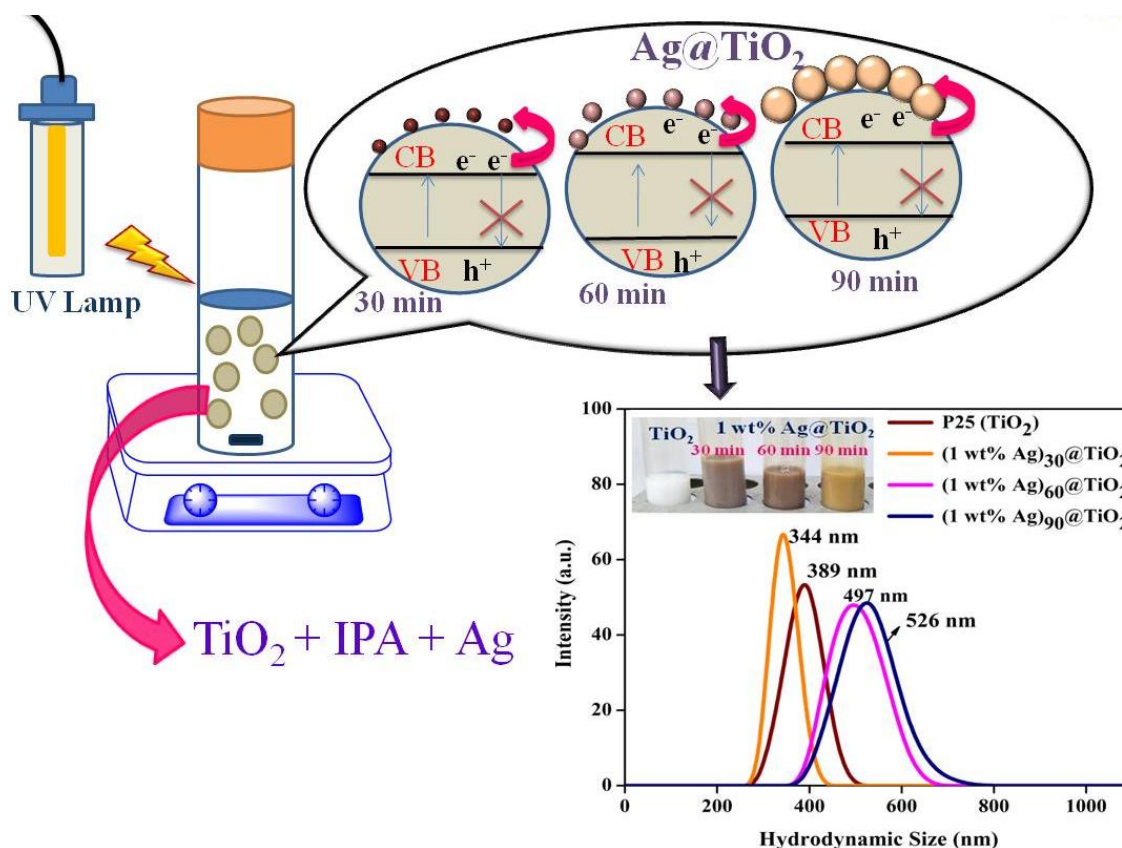


Fig. 5: Dynamic light scattering (DLS) size distribution of different Ag-TiO₂ nanocomposite after a) 3 and b) 5 wt% Ag photodeposition over TiO₂ at 30, 60 and 90min UV light irradiation.

Similar trends were observed when 3 and 5 wt% Ag was photo deposited over TiO₂ surface as the size increased upto 691 nm and 782 nm for 3 and 5 wt% Ag photodeposition respectively after different time intervals shown in figure 5. These results also indicate that the polydispersity of the samples at all times was very low and the particles were uniformly distributed within the



Scheme 2: Effect of Ag co-catalyst size over TiO₂ with increasing amount of Ag at different UV light irradiation time and their respective DLS particle size distribution compared to bare TiO₂.

solution. Scheme 2 summarizes the overall effect on the size of Ag-TiO₂ photocatalyst by varying the amount of Ag co-catalyst photodeposition at different increasing time intervals of UV light irradiation.

In order to study the trapping of photo generated e⁻ hole pair and their rate of recombination, photoluminescence (PL) studies were performed by exciting the photo catalysts at λ_{ex} of 340 nm. Figure 6 shows that the change in excitation bands occurs due to quenching of Ag-TiO₂ photocatalyst at different intervals of 30, 60, 90 min leading to prevention of (e⁻ - h⁺) recombination.

Several PL spectral bands were observed at 395 nm, 422 nm, 447 nm, 485 nm for bare TiO₂ and 1 wt% Ag co-catalyst deposition at different time intervals of 30, 60, 90 min respectively. These peaks were characterized by free excitation emission of the band gap²²⁻²⁴. Similarly, figure 6 shows the PL spectra of 3 and 5 wt% Ag depositions. It was observed that PL spectra of (1 wt % Ag)₃₀@TiO₂ was lower compared to 3 and 5 wt%

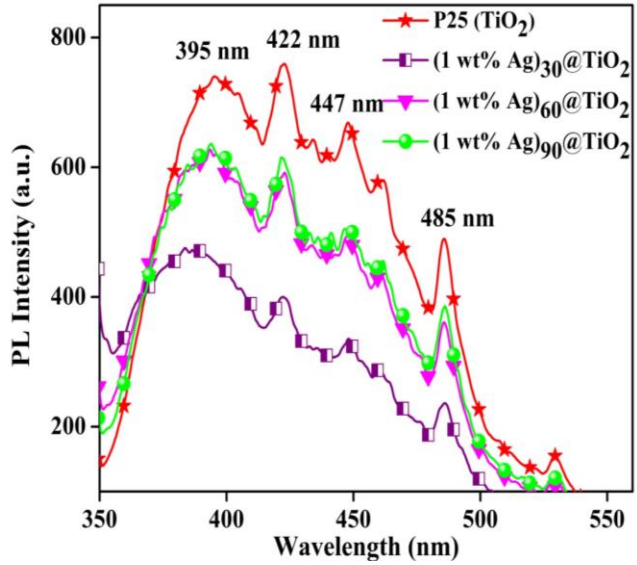


Fig. 6: PL (Photo Luminescence) spectra of 1 wt% Ag over TiO₂ sample obtained after 30, 60 and 90 min Ag deposition with UV light irradiation.

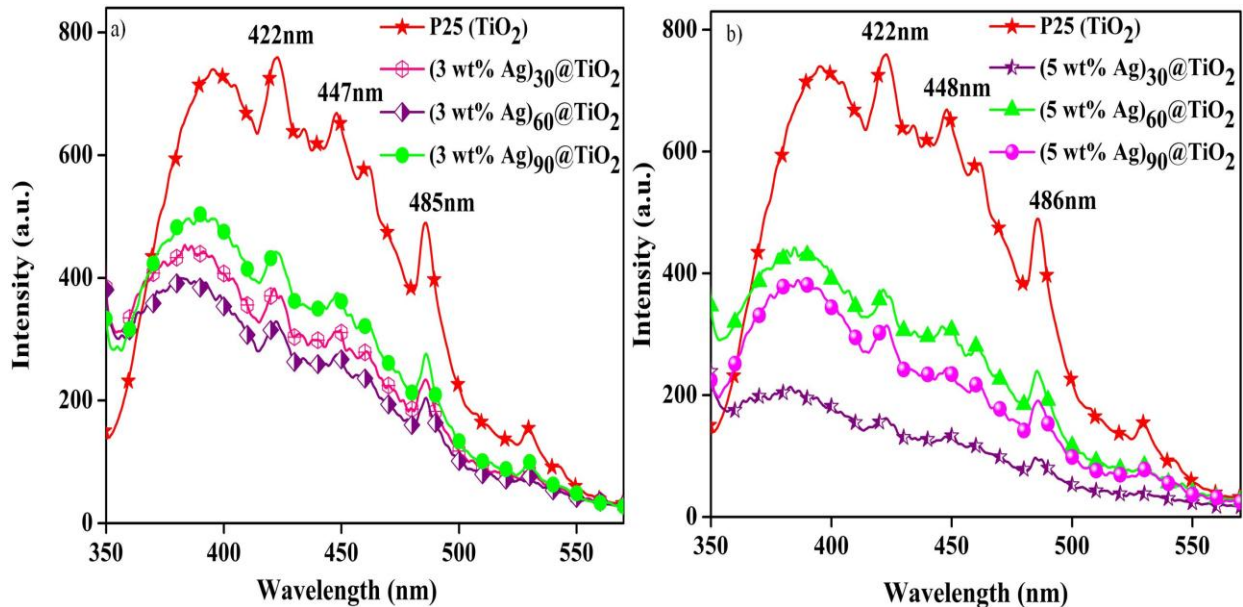


Fig.7: PL spectra of a) 3 and b) 5 wt% Ag over TiO₂ sample obtained after 30, 60 and 90 min Ag deposition with UV light irradiation.

Ag-TiO₂. Therefore, it has been concluded that increasing the amount of Ag deposition imparts more vacant sites as evident by their higher photo catalytic activities.

The SEM studies revealed the uniform dispersion of Ag NPs photo deposited over TiO₂ at different time intervals of 30, 60, 90 min respectively shown in figure 8.

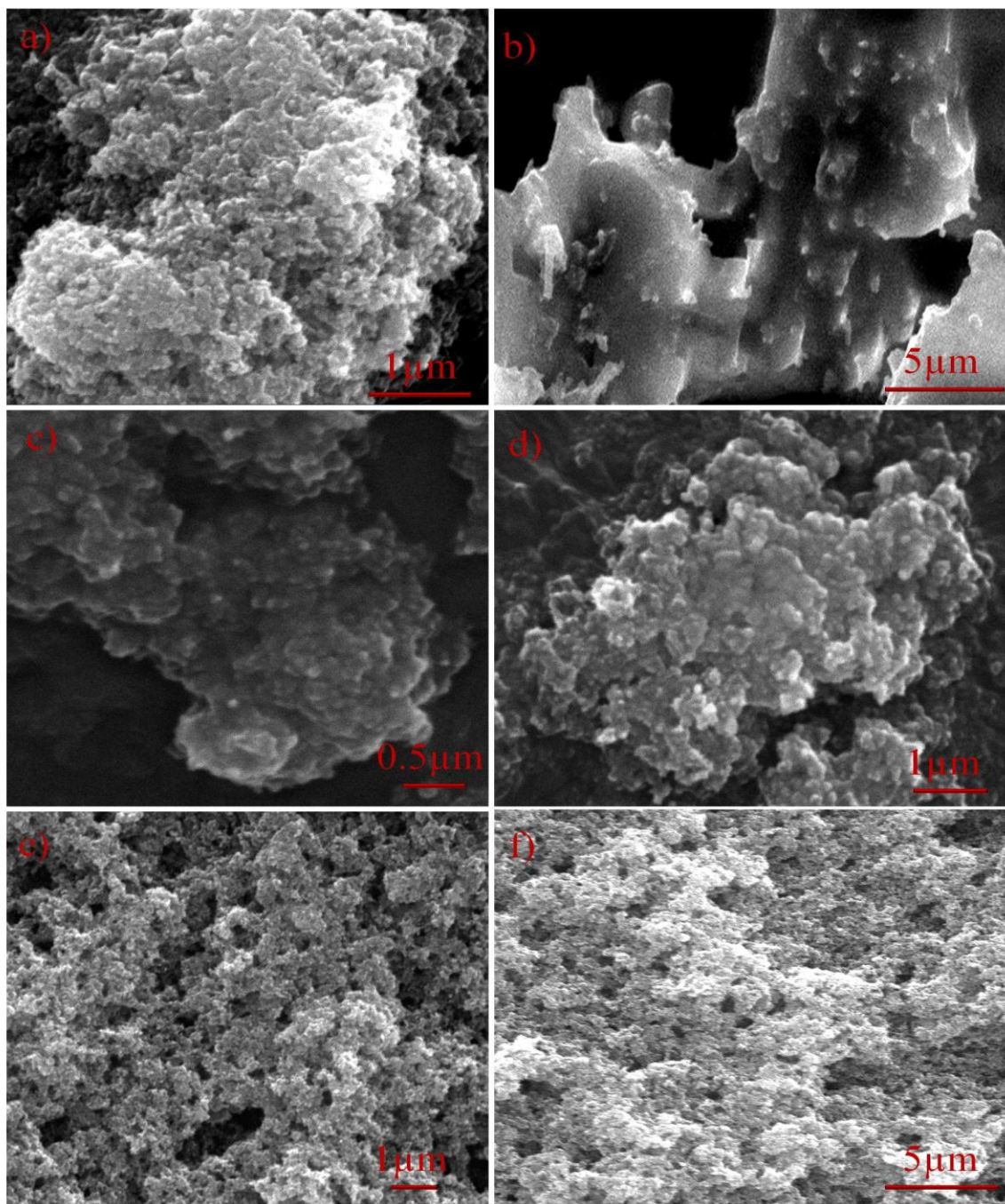


Fig.8: SEM images of Ag deposition over TiO₂ at a-b) 30 minutes, c-d) 60 minutes and e-f) 90 minutes under UV light irradiation.

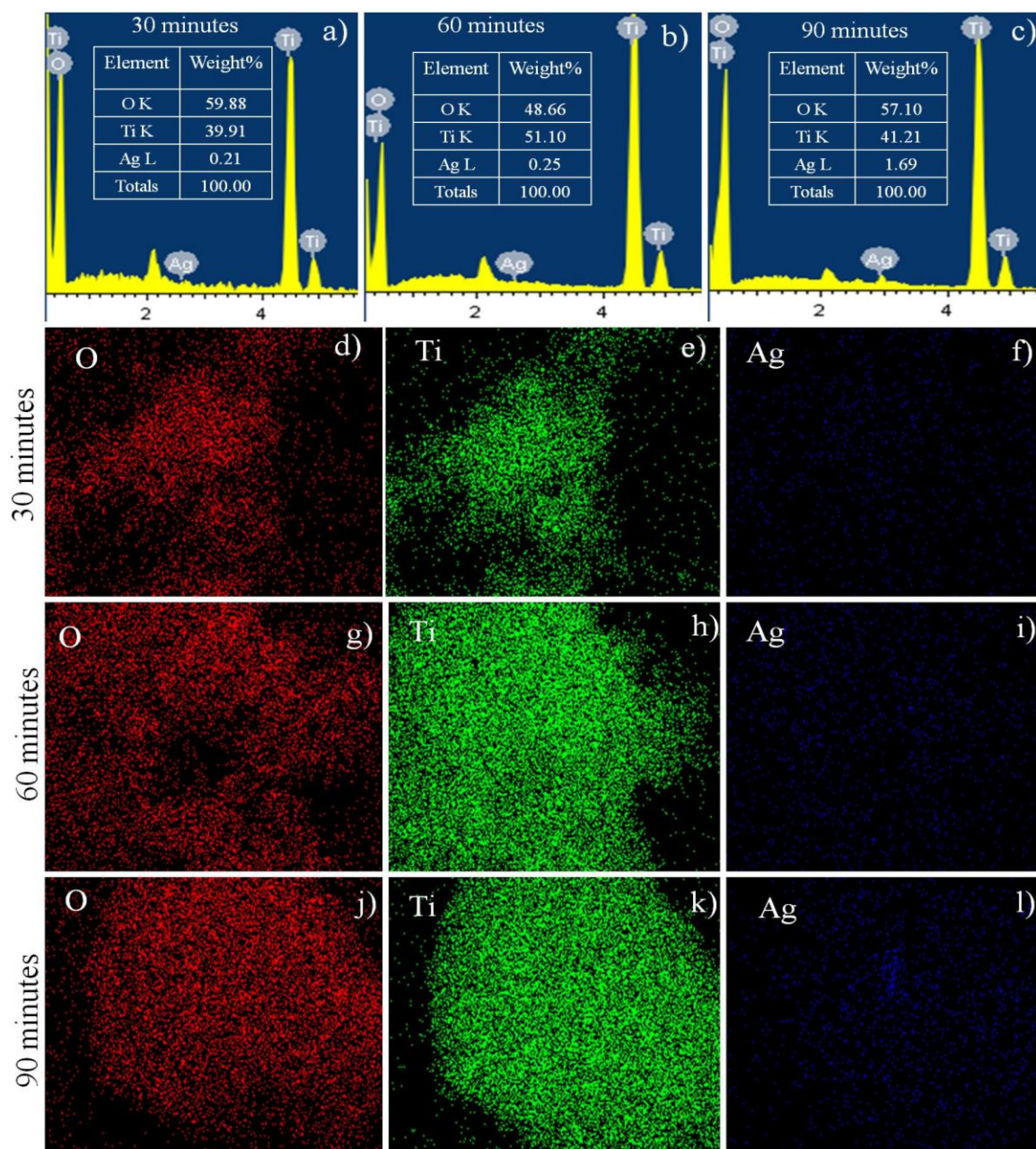


Fig.9: EDS spectra a-c) and corresponding Elemental mapping of 1 wt% Ag photodeposition over TiO_2 photocatalyst at d-f) 30 minutes, g-i) 60 minutes & j-l) 90 minutes of time interval under UV light irradiation.

In order to verify the presence of Ag photo deposited over TiO_2 at different time intervals of 30, 60 and 90 min figure 9 (a-c) shows the detected wt% of Ag to be 0.21, 0.25 and 1.69 wt% respectively, which was further confirmed by elemental mappings shown in figure 9 (d-l). The presence of O, Ti and Ag metal were represented by red, green and blue colors respectively. The

elemental mapping indicated the appropriate proportion of Ag at different time intervals of 30, 60, 90 min for 1 wt% Ag co-catalyst photo deposition over TiO₂ surface.

4.2. Photo degradation of Salicylic acid (SA)

To assess the photocatalytic activity of the different prepared Ag-TiO₂ photocatalysts, these were studied for the photo degradation of salicylic acid (SA) under UV light irradiation at 298 nm for 80 minutes.

Firstly, a calibration graph of salicylic acid (figure 10) was plotted. 0.4 mM solution was taken and the absorbance Vs concentration was plotted and all the further calculations were done using this relationship.

The absorption spectra of salicylic acid (0.4 mM, 5 ml) photo degradation by Ag-TiO₂ prepared at different intervals of 30, 60 and 90 min was obtained after 80 min UV light irradiation are shown in figure 11 and 12. It was observed from figure 11 that the bare SA gives an

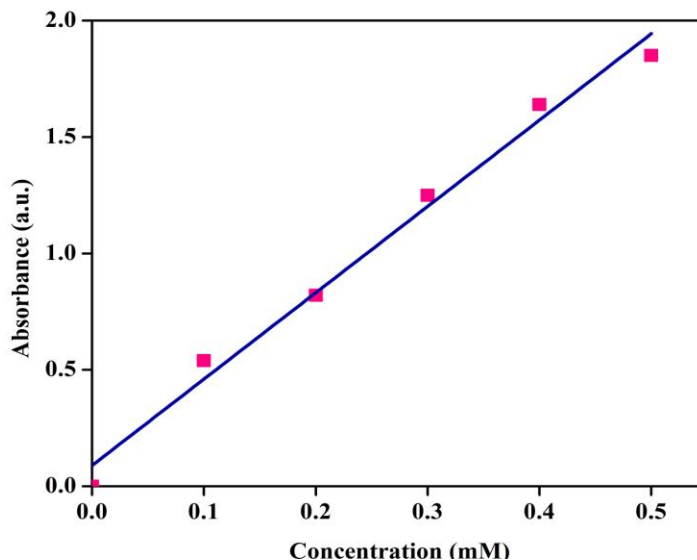


Fig.10: Calibration graph (Lambert-Beer's Law) of Salicylic acid (SA).

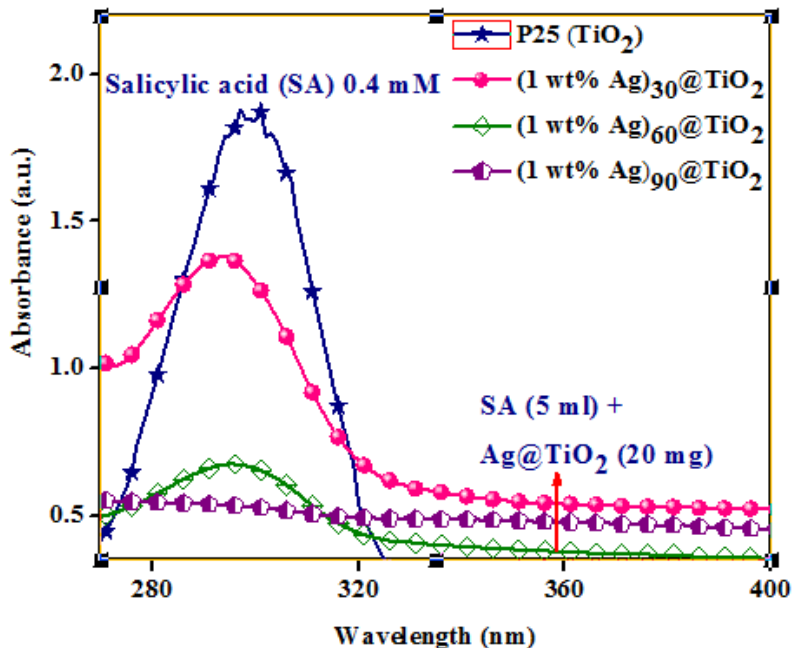


Fig. 11: Comparative absorption spectra of salicylic acid (0.4 mM, 5 ml) due to its photo degradation by different 1 wt% Ag over TiO₂ sample obtained after 30, 60 and 90 min Ag deposition under 80 min UV light irradiation.

absorption band at 298 nm and as the time of deposition increased, a decrease in the intensity of absorbance band of SA was observed from 1.87 to 0.54 a.u for 1 wt%

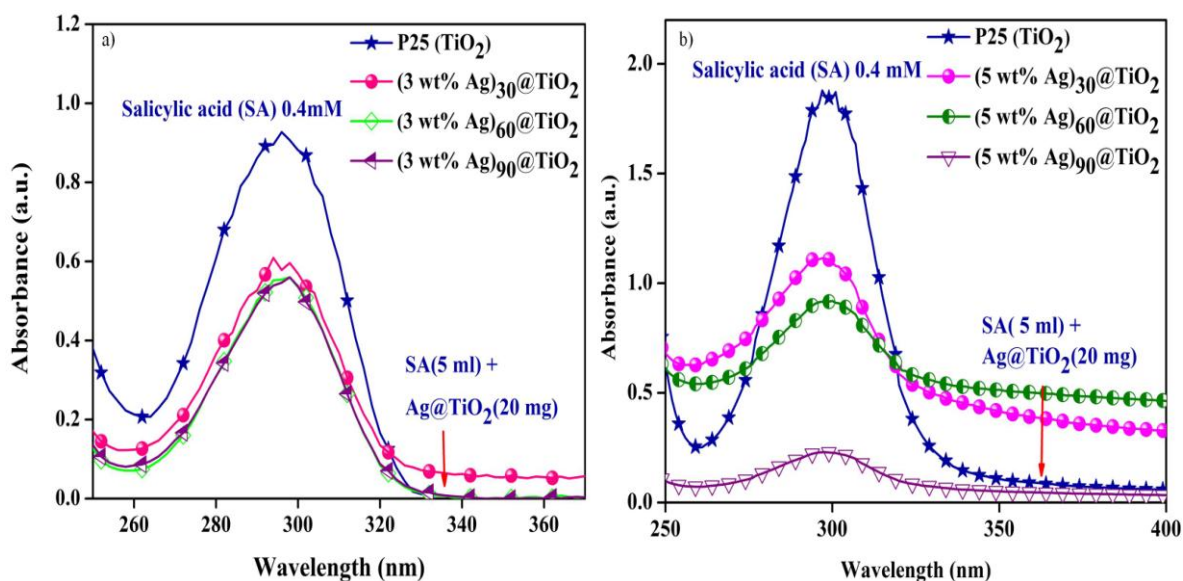


Fig.12: Comparative absorption spectra of salicylic acid (0.4 mM, 5 ml) due to its photo degradation by different a) 3 and b) 5 wt% Ag over TiO₂ sample obtained after 30, 60 and 90 min Ag deposition under 80 min UV light irradiation.

Ag photo deposited over TiO₂ after 80 min. Similar trends were observed for the photo degradation of SA with 3 and 5 wt% of Ag photo deposited over TiO₂ after 80 min respectively (figure 12). It was observed that maximum decrease in peak intensity was attained with (5 wt% Ag)₉₀-TiO₂. This higher catalytic efficiency exhibited by the photocatalyst can be attributed to the combined co-catalytic effects of Ag which helps in the increase in interfacial contact area, leading to increased transfer of charge²⁵ and decreased recombination rate of charge carriers²⁶ because of synergistic effect of Ag²⁷.

Figure 13 and 14 shows the $\log C_0/C_t$ Vs time (min) graph where C_0 is the initial concentration and C_t is the concentration at different time intervals of SA photo degraded by 1, 3 and 5 wt % Ag over TiO₂ for 20-80 min. Pseudo first order rate kinetics was observed according to the equation:

$$2.303 \log C_0/C_t = kt$$

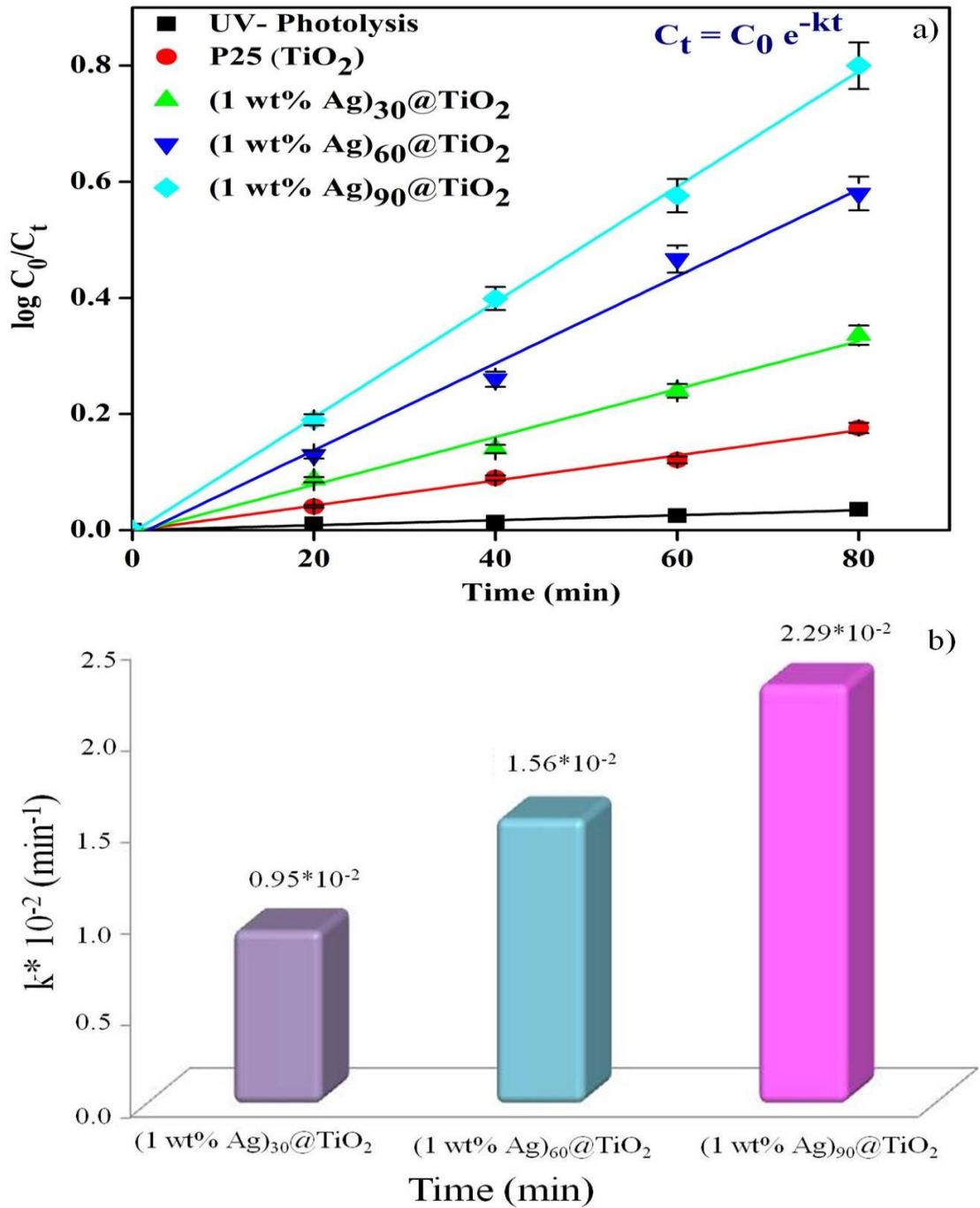


Fig.13: a) Time course of salicylic acid (0.4 mM, 5 ml) photo degradation by 1 wt% Ag over TiO₂ sample obtained after 30, 60 and 90 min Ag deposition with UV light irradiation for 20-80 min and b) Comparative histogram showing rate constant of different Ag-TiO₂ catalysts.

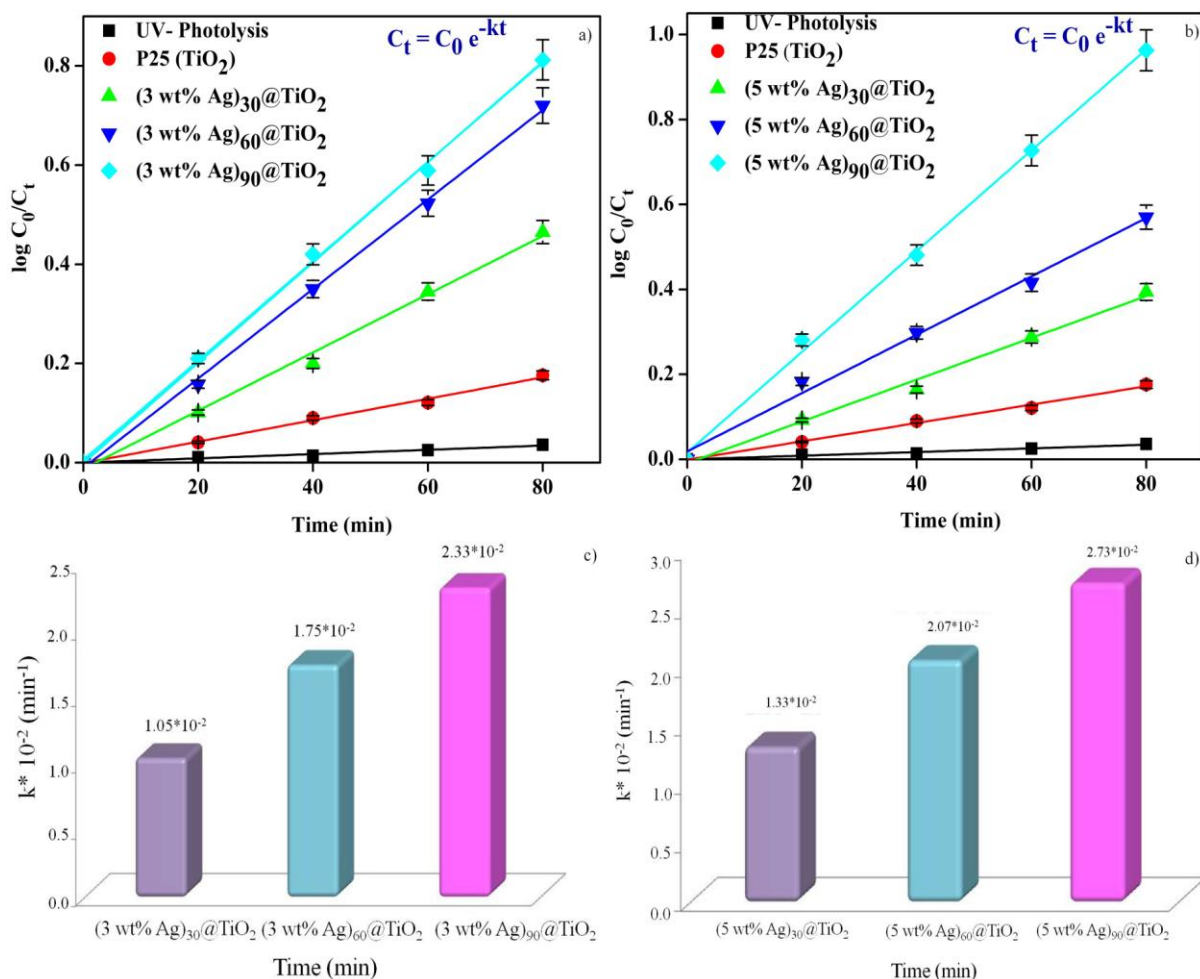
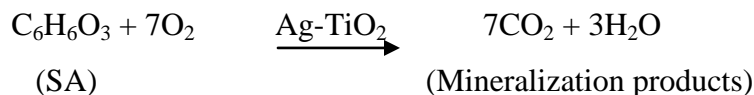
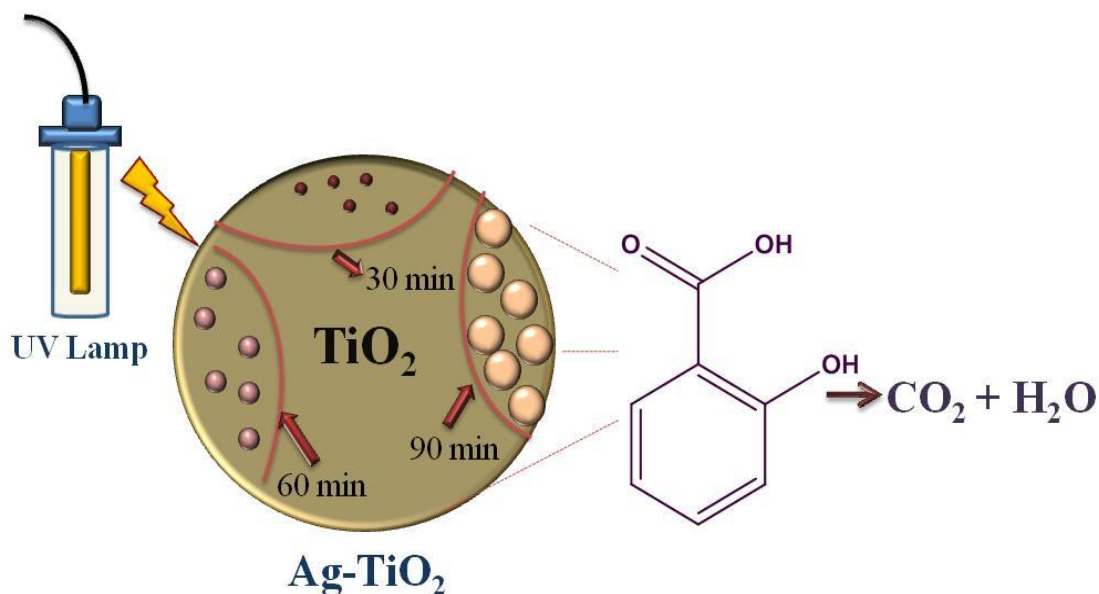


Fig.14: a-b) Time course of salicylic acid (0.4 mM, 5 ml) photo degradation by 3 and 5 wt% Ag over TiO₂ sample obtained after 30, 60 and 90 min Ag deposition with UV light irradiation for 20-80 min and c- d) Comparative rate constant of different Ag-TiO₂ catalyst.

where, k is the rate constant for pseudo first order rate kinetics. It was seen that in the absence of the catalyst, zero or negligible photo degradation indicating the need of photocatalyst to initiate the photolysis process. The k values for (1 wt % Ag)₃₀@TiO₂, (1 wt % Ag)₆₀@TiO₂ and (1 wt % Ag)₉₀@TiO₂ catalysts photo degraded SA for 20, 40, 60, 80 was $0.95 \times 10^{-2} \text{ min}^{-1}$, $1.56 \times 10^{-2} \text{ min}^{-1}$ and $2.29 \times 10^{-2} \text{ min}^{-1}$ respectively and the regression coefficient (R^2) value of 0.98 is in good concurrence.

A complete balanced equation for the degradation of SA scheme 3 can be written as:





Scheme 3: Schematic representation of salicylic acid photo degradation by Ag-TiO₂ prepared at different time intervals of Ag co-catalyst under UV light irradiation.

5. Conclusion

In summary, three varying amounts of Ag (1, 3 and 5 wt%)-TiO₂ were prepared at different increasing time intervals of 30, 60 and 90 minutes of Ag photo deposition. Initially a color change in the samples from white to light brown was observed, resulting in the change of size and distribution of Ag nanoparticles. The prepared Ag-TiO₂ photocatalysts were characterized by various techniques. A red shift in the SPR bands of Ag-TiO₂ was observed with an increase in the hydrodynamic size of the prepared photocatalyst from 344 nm to 782 nm compared to bare TiO₂ observed by DLS studies. To determine the recombination rate of Ag-TiO₂, PL studies were carried at λ_{ex} of 340 nm. Also the increased wt% of Ag at different time intervals was confirmed by EDX- mapping studies as the weight increased from 0.21wt% for 30 min to 1.69 wt% for 90 minutes of photo deposition. Finally, the effectiveness of the prepared Ag-TiO₂ photocatalyst was studied for salicylic acid degradation for 20-80 minutes under UV light irradiation. Complete degradation of salicylic acid was observed after 80 minutes and was found to follow the pseudo first order rate kinetics ($k- 2.73 \times 10^{-2} \text{ min}^{-1}$). Overall it can be concluded that with the increase in wt % and time of Ag photo deposition over TiO₂, resulted in the enhancement of photo catalytic properties.

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