Photo-induced Oxidation and Reduction by Plasmonic Ag-TiO_2 nanocomposites under UV/Sunlight

A thesis

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

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Submitted by

Rudra Sharma

(Roll No. 301602036)

Under the supervision of

Dr. Bonamali Pal
Professor

Dr. Ranjana Prakash
Professor

School of Chemistry and Biochemistry
Thapar Institute of Engineering & Technology
Patiala-147004

June, 2018

Dedicated to

My Family, Teachers and Friends

Certificate

I hereby certify that the work presented in this thesis entitled "***Photo-induced Oxidation and Reduction by Plasmonic Ag-TiO$_2$ nanocomposites under UV/Sunlight***" submitted in partial fulfillment 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. Ranjana Prakash. 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.

Rudra

Date: 30·June·2018

Rudra Sharma

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

Dr. Bonamali Pal
Professor
Thapar Institute of Engineering
& Technology, Patiala- 147004

Dr. Ranjana Prakash
Professor
Thapar Institute of Engineering
& Technology, Patiala-147004

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Rudra

Date: 30 · June · 2018

Rudra Sharma

Table of Contents

List of Abbreviations

UV	Ultraviolet
DRS	Diffuse reflectance spectroscopy
DLS	Dynamic light scattering
PL	Photoluminscene
HPLC	High performance liquid chromatography
SEM	Scanning electron microscopy
EDS	Energy dispersive spectroscopy
NPs	Nanoparticles
m-ABA	m-Aminobenzoic acid
m-NBA	m-Nitrobenzoic acid
p-NBAL	p-Nitrobenzaldehyde
p-NBA	p-Nitrobenzoic acid
IPA	Isopropyl alcohol
CB	Conduction band
VB	Valence band
LSPR	Localised surface plasmon resosance
SPR	Surface plasmonic resosnace
DI	De-ionised

List of symbols

μL	Microlitres
mM	Millimolar
mg	Milligrams
wt%	Weight percentage
eV	Electron volt
e^-	Electron
h^+	Hole
min	Minutes
mL	Millilitres
kV	Kilovolts
λ	Wavelength
nm	Nanometer

Abstract

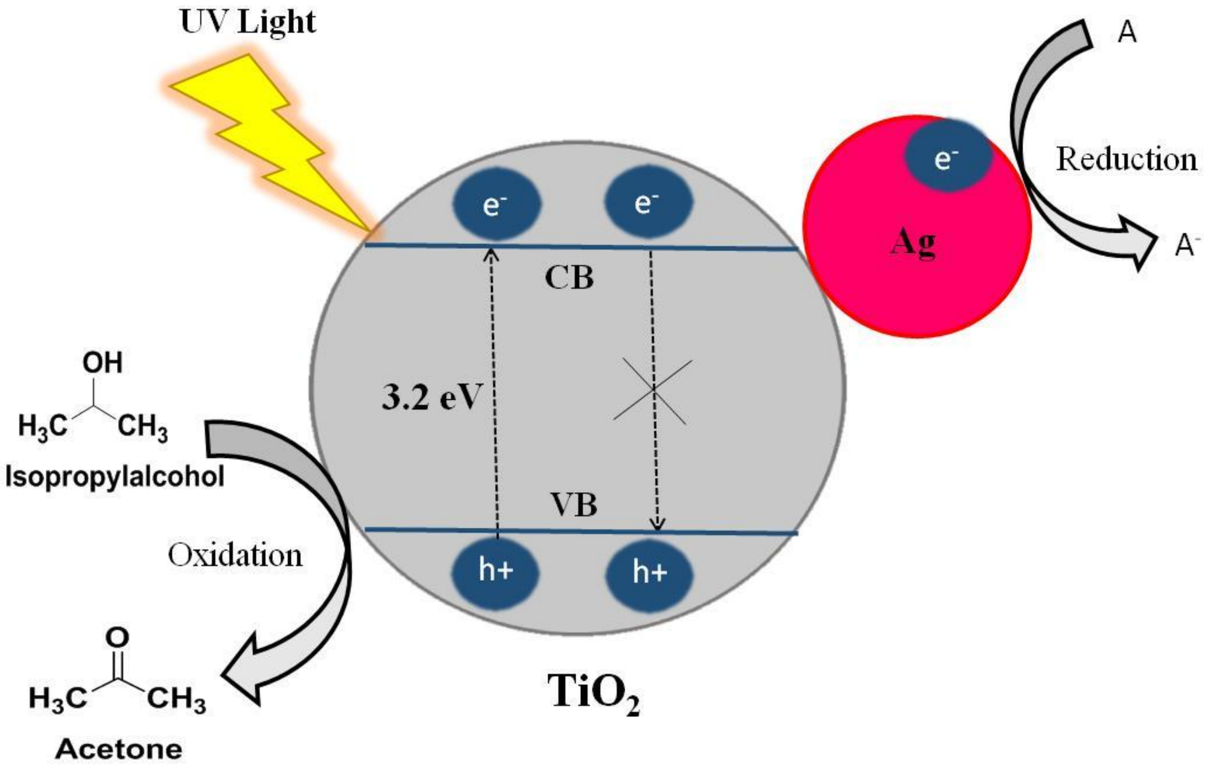
The present study demonstrates the effect of variable (1-3 wt%) amount of deposited Ag on TiO_2 surface for catalytic oxidation/reduction reactions under UV or sunlight irradiation. The physio-chemical properties of prepared Ag-TiO_2 nanocomposites were studied using different techniques (DRS, DLS, SEM-EDS). It was found that the hydrodynamic size of commercially available TiO_2 was nearly 252 nm which further increased by increasing amount of Ag co-catalyst deposition over TiO_2 where plasmonic absorption band at 463 nm is appeared in the optical absorption spectra (DRS) due to Ag deposition onto TiO_2. This observed change was due to enhancement of both number and size of loaded Ag nanoparticles on the surface of TiO_2. Moreover, photoluminescence intensity of Ag-TiO_2 was highly quenched with increased amount of Ag loading indicating lower recombination rate of photogenerated electrons and holes during photoexcitation. The 3 wt% Ag-TiO_2 nanocomposite showed highest photoactivity for oxidation of p-Nitrobenzaldehyde to Nitrobenzoic acid under UV and sunlight. However, 2 wt% Ag-TiO_2 proved to be more efficient during reduction of m-Nitrobenzoic to m-Aminobenzoic acid under UV irradiation. This is probably due to blockage of active site on the surface of catalyst. Thus, different amount of Ag (1-3 wt%) co-catalyst photodeposition is highly influenced the TiO_2 photocatalytic activity.

1. INTRODUCTION

The aromatic amines are considered to be important compounds for the synthesis of dyes, pharmaceuticals, food addictives, explosives industries etc. [1, 2]. In general, these compounds are synthesized by conventional methods like Bechamp reduction in which excessive transitional metals and strong acids are used, through catalytic hydrogenation using iron and hydrochloric acid, by using reducing agent such as $NaBH_4$ under high temperature conditions [3] or with iron powder, dilute acid. These conventional methods seem to be ineffective due to some drawbacks like requirement of harsh reaction conditions (such as high temperature, pressure) [4, 5], reducing agent, etc. Moreover, these synthetic techniques are not chemoselective in nature with poor product yield and perhaps destroy required intermediates. In contrast to these synthesis routes, photocatalytic approach is used nowadays.

To overcome such limitations, photocatalytic methods are used in the presence of UV or visible light using semi-conductor (TiO_2, ZnO, CdS, etc.) as a photocatalyst under inert or air conditions depending upon the reaction requirements. TiO_2 is widely used catalyst [6,7] due to it higher chemical stability, non-toxic nature, cost effective and its suitable band gap energy (3.2 eV) for photo-oxidation [8] and photo-reduction reactions [9]. Apart from many advantages of TiO_2, it possesses few disadvantages also such as visibly inactive and higher recombination rate of excitons (e- and h+). It can be achieved by suitable metal (Pt, Au, Cu, Pd, Ag, etc.) deposition [10] to improve its reaction efficiency. Among various metals Ag is mostly used [11] because of its relatively low cost, non toxic, special oxygen adsorbed behavior. Photo deposition of Ag on TiO_2 support improves physical and chemical properties of TiO_2. Moreover, Ag is a plasmonic metal which absorbs the visible light and render a strong LSPR (Localised Surface Plasmon Resonance) effect [12-15] which enriches the photo catalytic activity by shifting UV light absorption of semiconductor to visible light absorption. Ag-TiO_2 nanoparticles are used for both redox reactions. Upon illumination, electrons from the valence band get excited and jump into conduction band of TiO_2 and the attached Ag NPs (nanoparticles) traps the electrons and serves as electron trapper [16-19] and itself gets reduced (Ag^+ to Ag^0) and it stores electrons for a longer time and thus decreases the recombination rate of charge carriers [20-22]. The stored electrons in the Ag activate the reduction reaction. In addition, these reactions require isopropyl alcohol (IPA) which is used as hole scavenger, and hence thereby traps the holes, oxidizes itself into acetone as shown in **Scheme 1.** These reactions are performed under the argon atmosphere.

While in case of oxidation, free photo-induced holes in the valence band are entrapped by the adsorbed reactant and get oxidized.



Scheme 1. Mechanism of photoreduction reactions with Ag-TiO_2 in the presence of IPA as a hole scavenger.

In general, by increasing the amount of the metal ions on the surface of catalyst, the number of deposited metal particles increase and these get well distributed over semi-conductor surface which further influence the photocatalytic activity. The effect of Ag loading on TiO_2 for redox reactions under different light sources has to be studied. In this regard, the following objectives are set.

2. Objectives

1. Preparation and characterization of Ag-TiO_2 nanocomposites.
2. To study the influence of Ag amount over TiO_2 surface for oxidation and reduction reactions in UV or sunlight.

3. Experimental

3.1 Material and Methods

p-NitroBenzaladehyde ($C_7H_5NO_3$), p-Nitrobenzoic acid ($C_7H_5NO_4$), *m*-Nitrobenzoic acid ($C_7H_5NO_4$), m-Aminobenzoic acid ($C_7H_7NO_2$), silver nitrate ($AgNO_3$), isopropanaol (C_3H_8O), methanol (CH_4O), ethanol (C_2H_6O) were purchased from Loba Chemicals, de-ionized (DI) water. Commercially available Degussa P25-TiO_2 was employed in all experiments, HPLC grade methanol and water were used for HPLC analysis.

3.2 Photodeposition of Ag on TiO_2 (P25)

To synthesize Ag loaded TiO_2, test tubes containing aqueous isopropyl solution (50 vol%),TiO_2 (P25, 50mg) along with 932 μL, 1864 μL and 2796 μL of $AgNO_3$ solution (0.01M) for 1wt% Ag-TiO_2, 2wt% Ag-TiO_2, and 3wt% Ag-TiO_2 respectively were sealed and introduced for argon purging for 15-20 min so to create inert atmosphere, then the test tubes were sealed with the septum and paraffin and irradiated by the UV light (125 W, 10.4Wcm^{-2}) under constant magnetic stirring for 5h in photochemical reactor. Then the obtained solution was centrifuged and washed with DI water five times and two times with ethanol. The suspension was dried in oven for 50°C for half an hour. After that dried powder was grinded by mortar pestle into fine powder.

4. Characterization techniques used

(1) *Diffused reflectance spectroscopy*

This technique was used to determine the reflectance/absorption of as prepared bare and Ag deposited samples in the UV/visible region by **Avantes Diffuse reflectance spectrophotometer.** Sample (2-5 mg) was taken on a glass slide and the light source probe was placed over the sample to record its reflectance/absorbance spectra by using $BaSO_4$ as a reference.

(2) *Dynamic light scattering (DLS)*

The mean hydrodynamic size distribution of bare and Ag loaded nanoparticles was determined by 1mg of each catalyst dissolved in 2 mL of DI water using **Malvern ZEN3600** particle size analyzer.

(3) *Photoluminescence analysis (PL)*

Photoluminescence was analyzed by **Perkin-Elmer LS55** spectrofluorimeter by taking 1mg/mL ethanol suspension of as prepared samples. These prepared catalyst were photoexcited at 320 nm with xenon lamp at room temperature.

(4) *Scanning electron microscopy and energy dispersive spectroscopy (SEM-EDS)*

SEM-EDS analysis was carried out on **JSM-6510LV** working at 30 kV by taking single drop of solution of all Ag loaded catalysts on 300 mesh copper grid coated with carbon film.

(5) *High performance liquid chromatography (HPLC)*

The samples of after reaction with all prepared catalyst were analyzed by **Agilent 1120 Compact LC** equipped with a Qualisil BDS C-18 column (250 mm × 4.6 mm, 5 μm), at $\lambda = 254$ nm with flow rate 1 mL/min with methanol : water (70:30) as solvent system.

5. Results and Discussion

5.1. Diffused Reflectance Spectroscopy (DRS)

Fig. 1 shows the variation in the optical absorption spectra which displays that the absorption

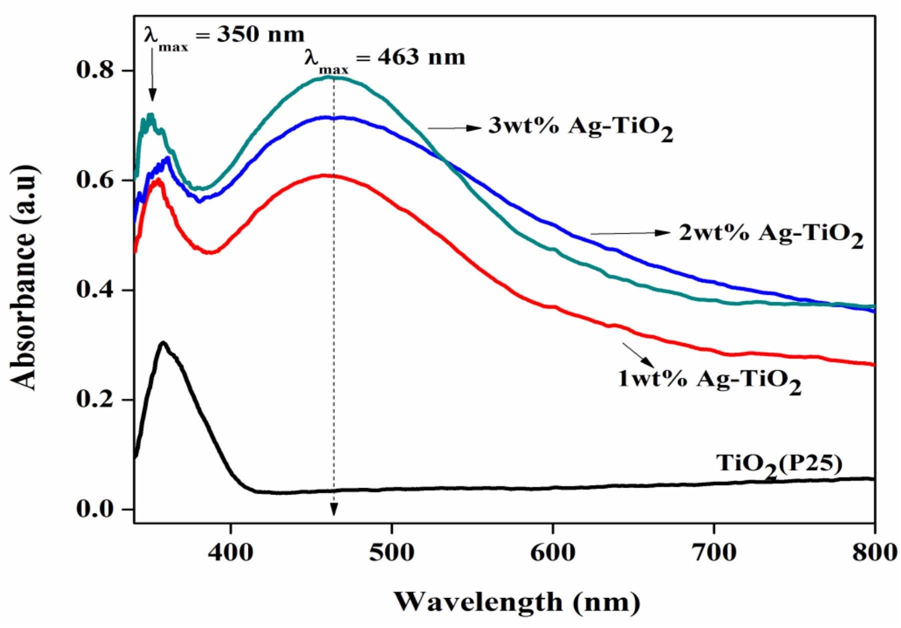


Fig. 1. Diffused reflectance spectra of various synthesized photocatalysts.

band below the 400 nm in a UV region indicates TiO_2 whereas the band appeared at nearly 463 nm is due to Ag loaded nanoparticles on TiO_2 support [23, 24]. This new band is attributed to surface plasmon resonance of Ag nanoparticles due to oscillations of conduction band electrons with incident light. Furthermore, difference in the intensities of the plasmon band was observed due to the difference in the concentration of Ag loading as the absorption value is related to the amount of the metal deposited. Higher the concentration of the Ag deposition, the greater is absorption in the visible region.

5.2. Dynamic Light Scattering (DLS)

A comparative graph representing hydrodynamic size of bare TiO_2 and its metal nanocomposites is shown in **Fig. 2**.The bare TiO_2 nanoparticles before have a mean diameter of 252 nm while

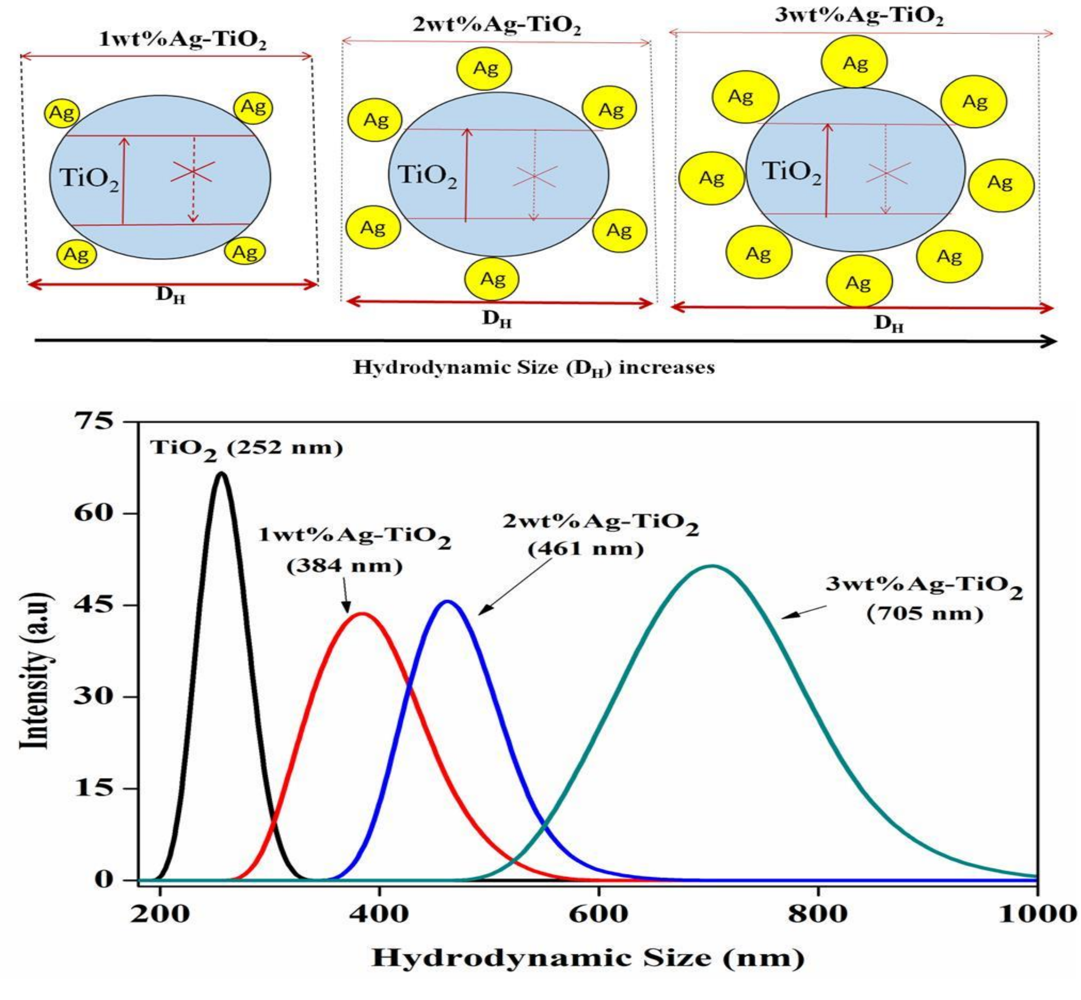


Fig. 2. Average hydrodynamic size of bare and Ag loaded TiO_2 nanocomposites.

after Ag deposition on TiO_2 their sizes grow to some extent. 1wt% Ag-TiO_2 composite exhibited an average size of 384 nm which roughly 130 nm higher than bare TiO_2. Moreover, 3 wt% loaded Ag-TiO_2 possessed highest hydrodynamic size (706 nm) as compared to other prepared catalysts. The increase is due to increases in the concentration of Ag nanoparticles. As the amount of co-catalyst is increased then number of deposited particles also enhanced along with their well distribution on the surface of TiO_2 which is also represented in incorporated scheme in **Fig. 2**. Thus, amount and way of distribution of metal naonparticles may affect the photocatalytic activity.

5.3. Photoluminescence (PL) Studies

The emission spectra of commercially available TiO_2 (P25) and prepared Ag (1-3 wt%) loaded TiO_2 is represented in **Fig 3**. The order of intensities is as described: TiO_2> 1wt% Ag-TiO_2> 2wt% Ag-TiO_2> 3wt% Ag-TiO_2.

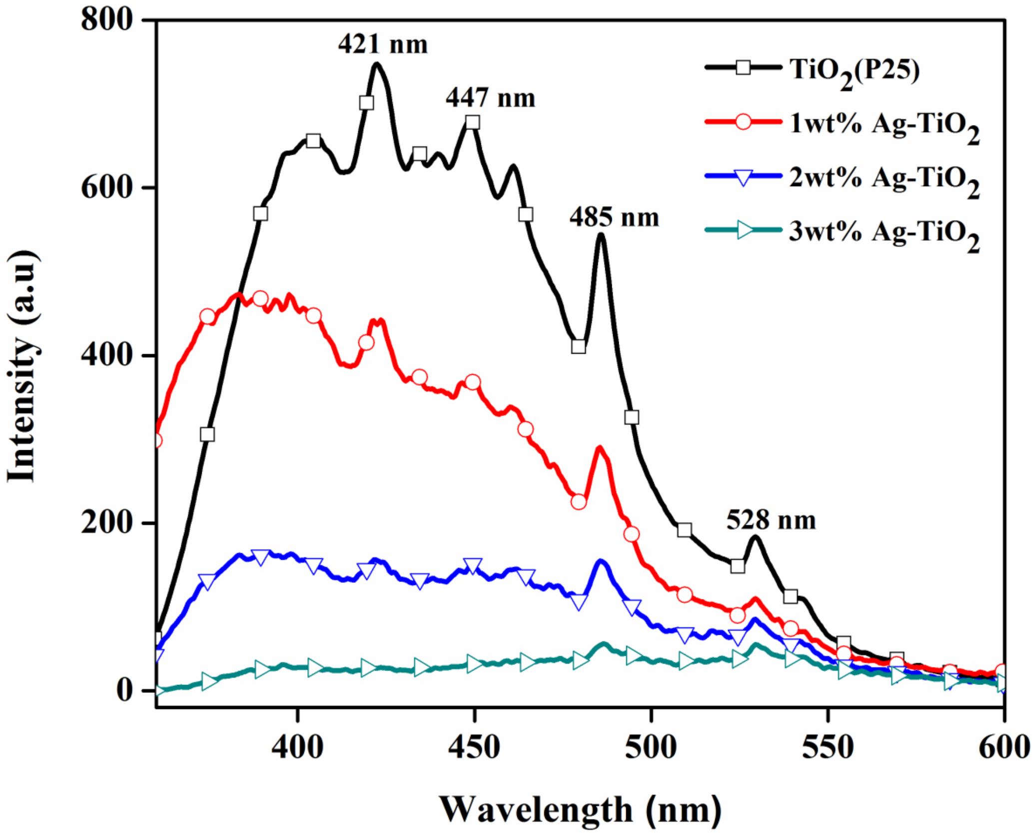


Fig. 3. Photoluminescence spectra of all synthesized Ag-TiO_2 (1-3 wt%) catalysts.

The emission bands at 421 nm and 447 nm represent near absorption trap sites whereas peaks at 485 nm and 528 nm correspond to far absorption edge of TiO_2 [25]. The emission band appeared at nearly 395 nm is because of recombination of charge carriers. The increase in the amount of Ag loading also increases the number of electrons trapper sites which further extends the separation of photo induced electrons (e^-) and hole (h^+) and lower recombination rate and shows quenched emission peak. More quenching enhances reaction efficiency by providing more number of electrons and holes for reduction and oxidation reactions.

5.4. Scanning Electron Microscopy (SEM)

The morphology of TiO_2 and Ag/TiO_2 NPs was studied by scanning electron microscopy (SEM) elucidated in **Fig. 4**. Although the morphology of nanoparticles is not very clear but variable deposited Ag metal is also supported by EDS as explained below. Few changes are observed in SEM images by varying metal loading.

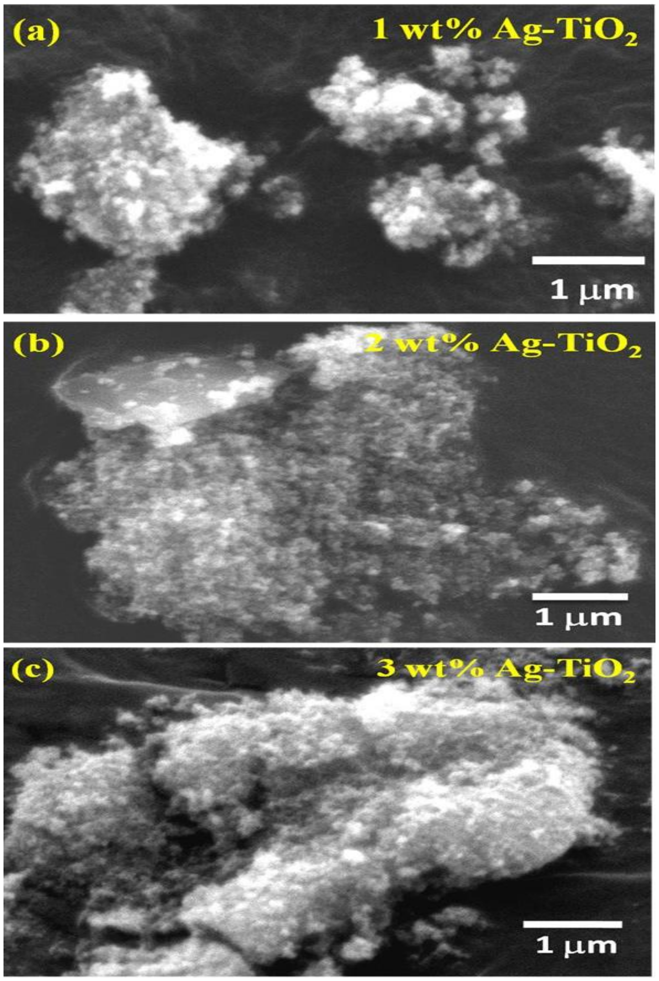
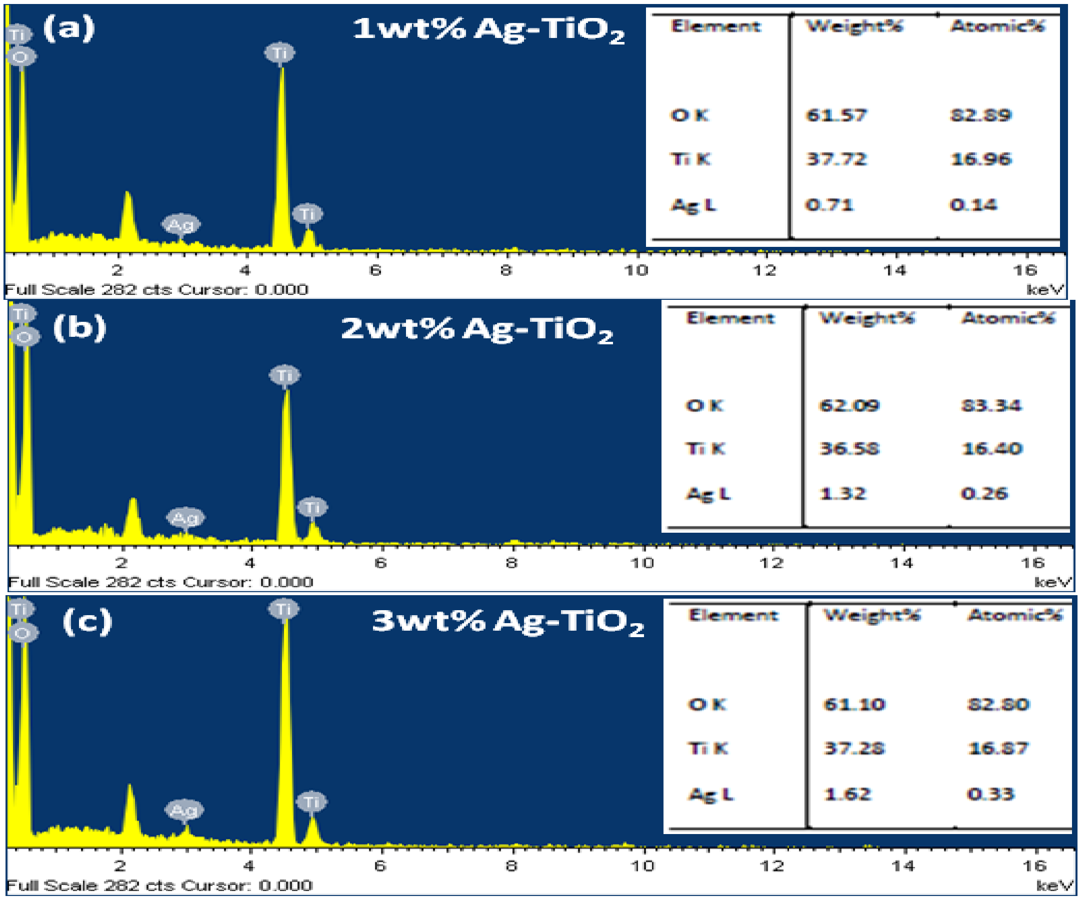


Fig. 4. SEM images of Ag loaded TiO_2 nanoparticles

5.5. Energy Dispersive X-Ray Spectroscopy (EDS)

The composition of particles was studied by energy dispersive X-Ray spectroscopy. The spectrum as shown in **Fig. 5** confirms the presence of Ag (silver), Ti (titanium), O (oxygen) atoms after metal deposition. It reflects that 0.71, 1.32 and 1.62 wt% has been shown in EDS point mapping for 1-3wt% Ag loading on TiO_2 surface. This variation in readings of actual deposition and observed amount is because this technique is used for particular points on the catalyst surface on which metal ions may be less as expected.



Element	Weight%	Atomic%
O K	61.57	82.89
Ti K	37.72	16.96
Ag L	0.71	0.14

Element	Weight%	Atomic%
O K	62.09	83.34
Ti K	36.58	16.40
Ag L	1.32	0.26

Element	Weight%	Atomic%
O K	61.10	82.80
Ti K	37.28	16.87
Ag L	1.62	0.33

Fig. 5. EDS spectra of prepared Ag-TiO_2 (1-3 wt%) representing variable elemental amount.

5.6. Photocatalytic activity

The photo-oxidation and photo-reduction of 5 mL (0.5 mM) p-Nitro benzaldehyde (p-NBAL) and m-Nitro benzoic (m-NBA) acid respectively was performed under sunlight and UV light for 5h using (50 mg) bare TiO_2 and different weight% Ag-TiO_2. For photo-reduction, isopropyl alcohol (IPA) and argon atmosphere was given whereas photo-oxidation was carried out in the presence of oxygen and the photocatalytic activity is evaluated by HPLC (high performance liquid chromatography).

These are general calculations of concentration and percent conversion for reactants and products:

Amount of reactant reduced (C_{RF}) = ($C_0 \times P_F$) / P_0

Amount of product produce (C_{PF}) = C_0 -C_{RF}

Where P_0 is the peak height of authentic sample of reactant and P_F is the peak height of reactant after the reaction. C_0 is the initial concentration of the authentic samples. C_{RF} and C_{PF} is the concentration of reactant left and product formed after the reaction.

%Conversion = ($C_F \times 100$) / C_0

Where C_F is the final concentration of product and reactant after the reaction and C_0 is the initial concentration before the reaction. All calculations have been done with similar method.

5.6.1. Photo-oxidation of p-Nitrobenzaldehyde (p-NBAL)

The authentic sample p-NBAL shows a sharp peak with 270 mAu height at t_R = 4.4 min. as shown in **Fig. 6**. When this reactant was treated with bare TiO_2 under UV light, a small peak appeared nearly at similar t_R (3 min) as that of authentic product sample i.e, p-Nitrobenzoic acid (p-NBA). Further, this peak started gradually increasing when reaction was carried out with metal loaded TiO_2. It can been seen form HPLC pattern that highest amount of product formed (1.16 μmol) with 3 wt% Ag-TiO_2 which is nearly two times higher than 1wt% Ag-TiO_2 catalyst.

Similarly, the oxidation reaction was carried out in sunlight under same reaction conditions. The HPLC pattern (**Fig. 7**) shows that the concentration of (2.5 μmol) of p-NBAL decreased up to 0.1 μmol, 0.25 μmol, and 0.8 μmol with TiO_2 and 1wt%, 2wt% and 3wt% Ag-TiO_2 NPs respectively and hence it was observed that 3wt% Ag-TiO_2 have high concentration (1.6μmol) of product at retention time of 3 min. among all different synthesized nanocomposites. Thus, it was concluded that higher deposited amount of Ag (3 wt%) on TiO_2 support due suppression of photogenerated charged species which indirectly increase the reaction efficiency. The holes are easily available at valence band (VB) of TiO_2 which resulted into oxidation of reactant. A comparative of p-NBAL in both light sources i.e UV and sunlight has been shown in **Fig. 8** which clearly indicates that sunlight has highly effected product formation in case of 3 wt% Ag-TiO_2.

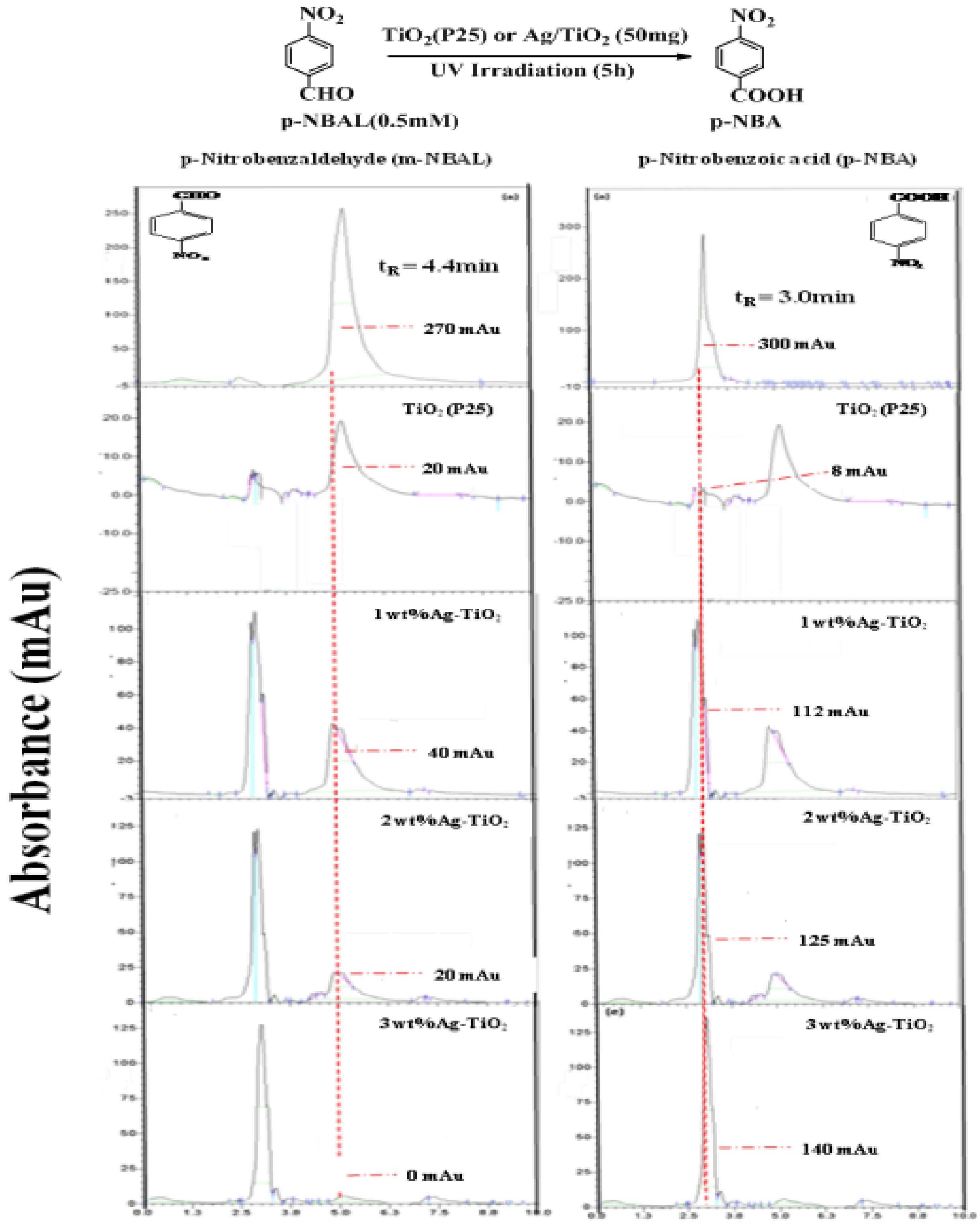


Fig. 6. HPLC pattern of p-NBAL oxidation with bare and Ag loaded TiO_2 catalysts under UV light.

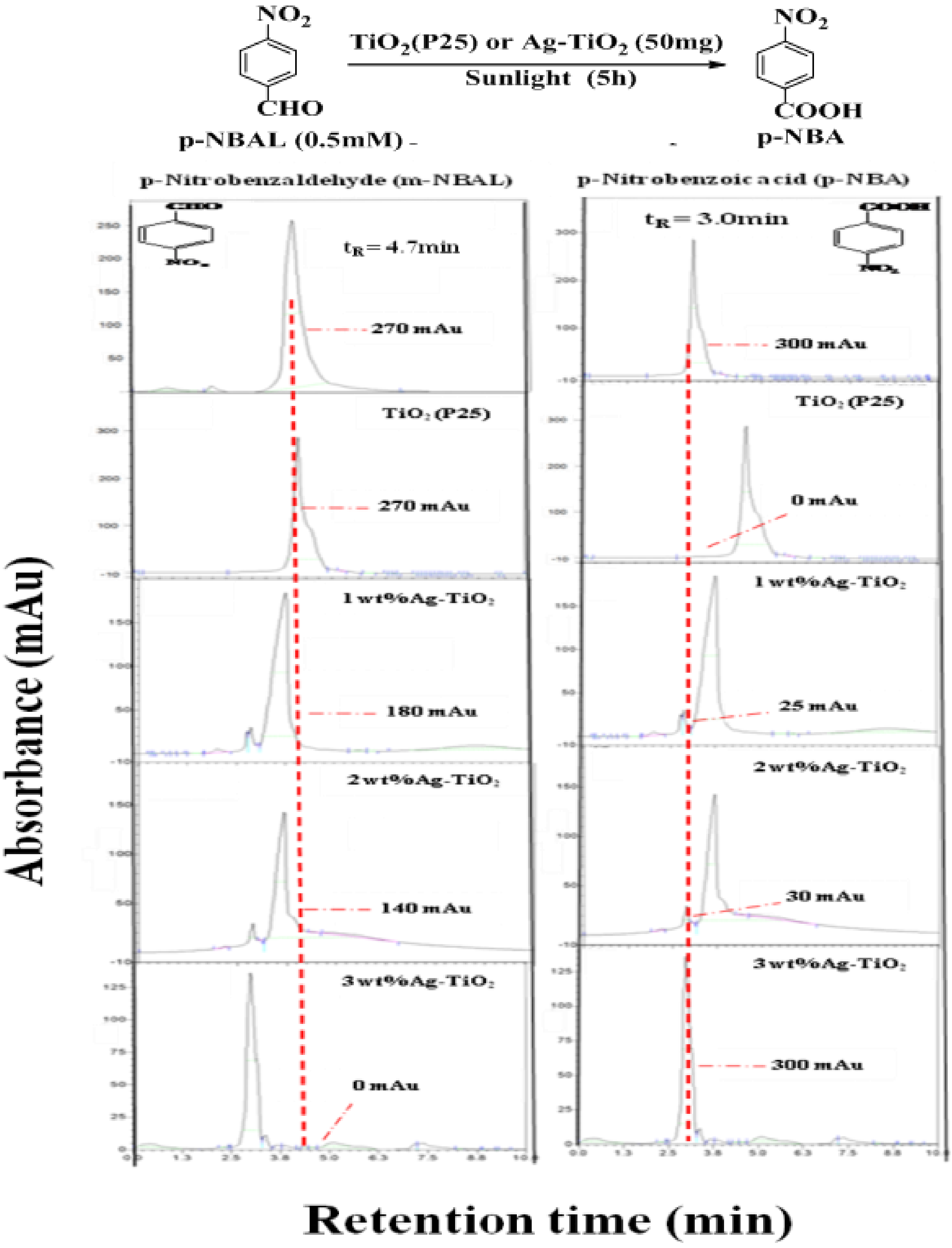


Fig. 7. HPLC pattern of p-NBAL oxidation with bare and Ag loaded TiO_2 catalysts under Sunlight.

5.6.2. Photo-reduction of m-Nitrobenzoic acid (m-NBA)

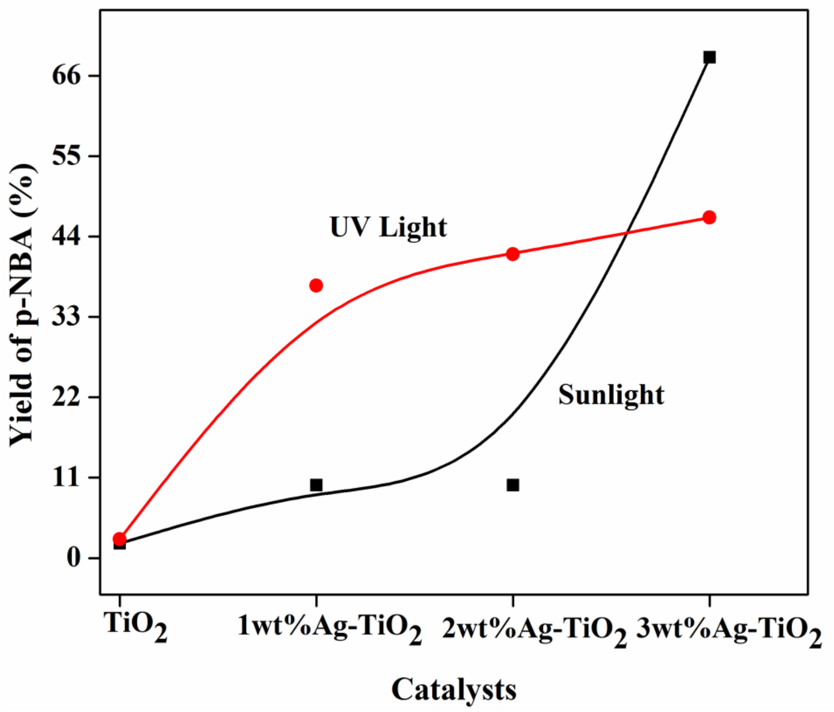


Fig. 8. Comparative (Yield%) graph of product (p-NBA) formation after p-NBAL oxidation in UV and sunlight.

HPLC chromatograph in **Fig. 9** exhibited one major peak of each authentic reactant and product sample detectable at peak height 1700 mAu and 540 mAu with retention time of 3.2 min and 2.5 min respectively. The reactant peak (t_R=3.2 min) started decreasing with 1 wt% and 2 wt% Ag-TiO_2 and another new peak at lower retention time was noticed under UV light. However, when the reactant was treated with 3 wt% prepared catalyst, a low amount of reactant was found to be reduced under similar reaction conditions. It indicates that 2 wt% Ag-TiO_2 was highly efficient but its efficiency was decreased when TiO_2 was loaded with 3 wt% amount of co-catalyst which shows that it is probably due to blockage of active sites of the catalyst.

Moreover, reduction of same compound was also carried out in the presence of sunlight as elucidated in **Fig. 10**. The concentration of the authentic reactant before the reaction was (2.5 μmol) and after the reaction with TiO_2 it decreases upto 2.37 μmol which shows that only a amount of reactant has been reacted to produce corresponding amine. Almost same amount of product formed with 1 wt% and 2 wt% Ag-TiO_2 whereas when m-NBA was treated with 3 wt% deposited photocatalyst, the product yield was higher. By comparing the above results, it was noticed that the concentration corresponding amine formed was more in UV irradiation as that of sunlight as shown in **Fig. 11**.

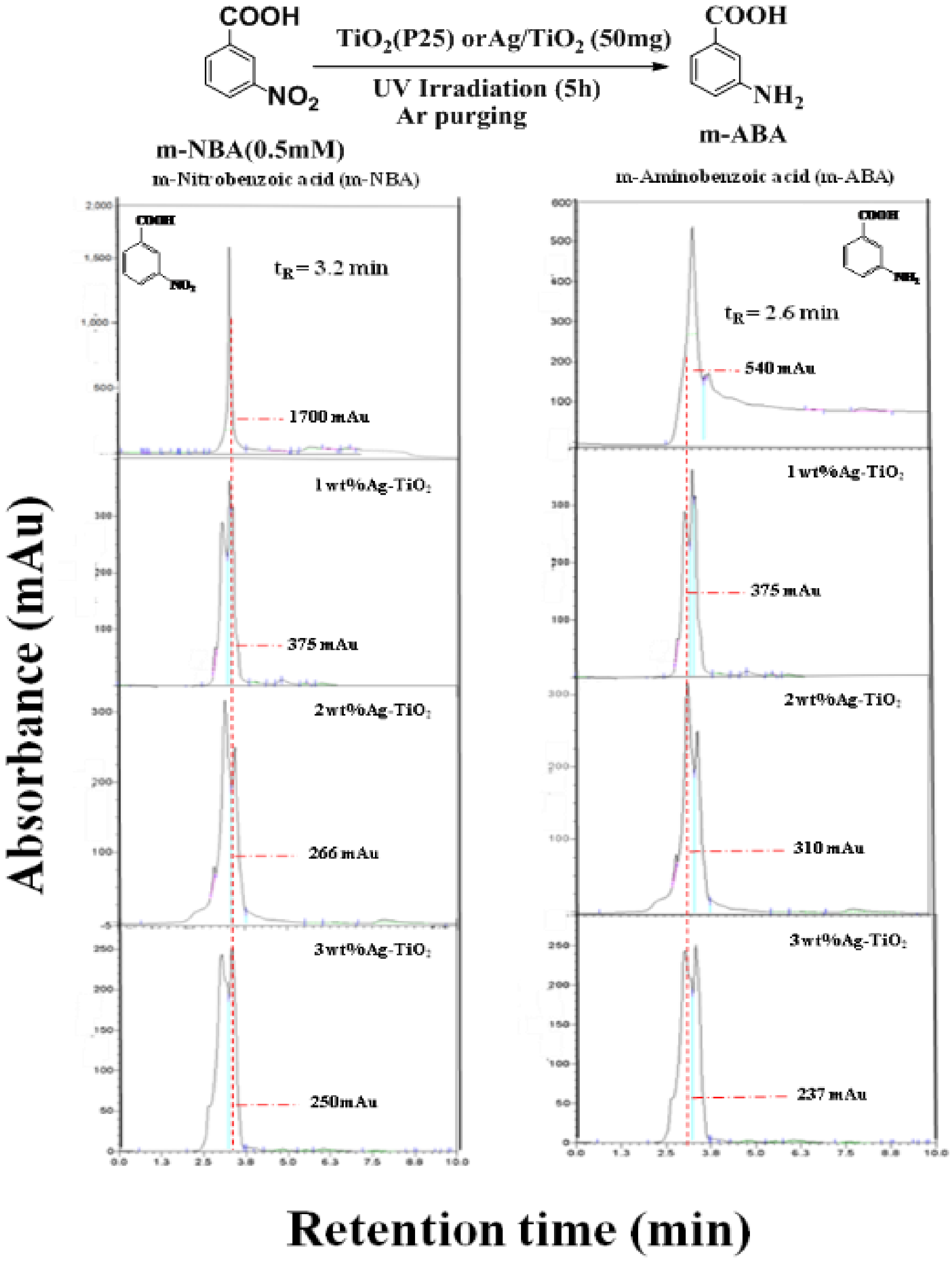


Fig. 9. HPLC pattern of m-NBA reduction with bare and Ag loaded TiO_2 catalysts under UV Light.

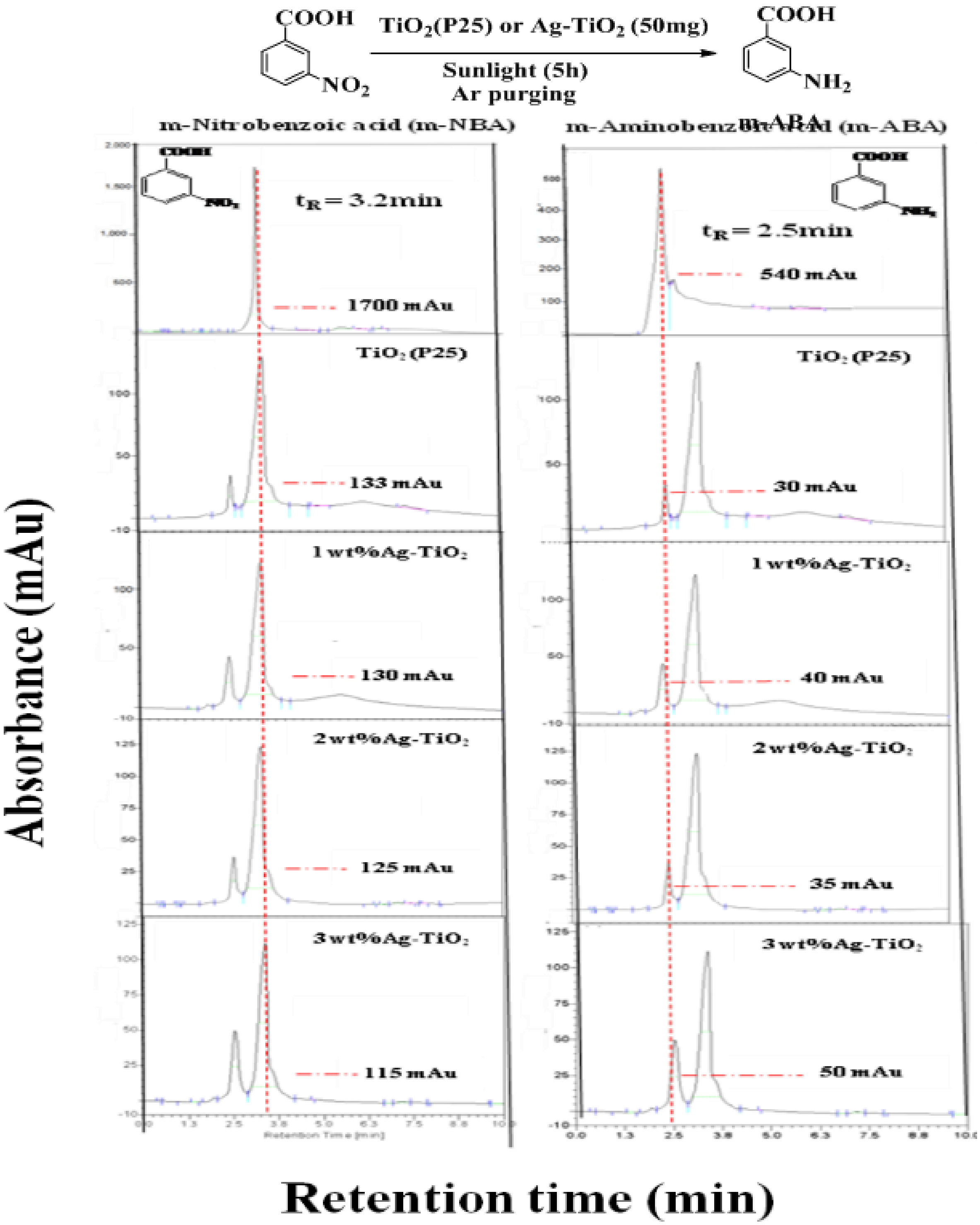


Fig. 10. HPLC pattern of m-NBA reduction with bare and Ag loaded TiO_2 catalysts under Sunlight.

Furthermore, comparative histograms are shown (**Fig. 12**) which confirm that amount of co-catalyst and presence of different light source has highly affected both oxidation and reduction reactions.

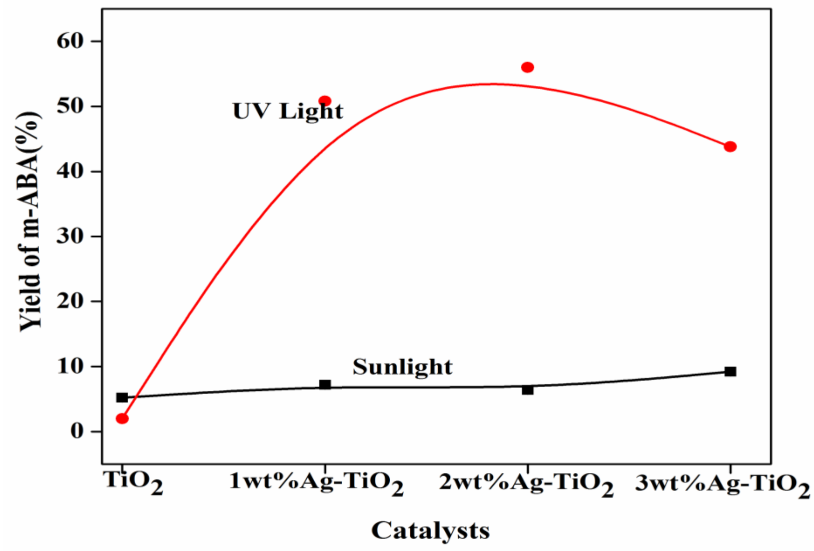


Fig. 11. Comparative (Yield%) graph of product (m-ABA) formation after m-NBA reduction in UV and Sunlight.

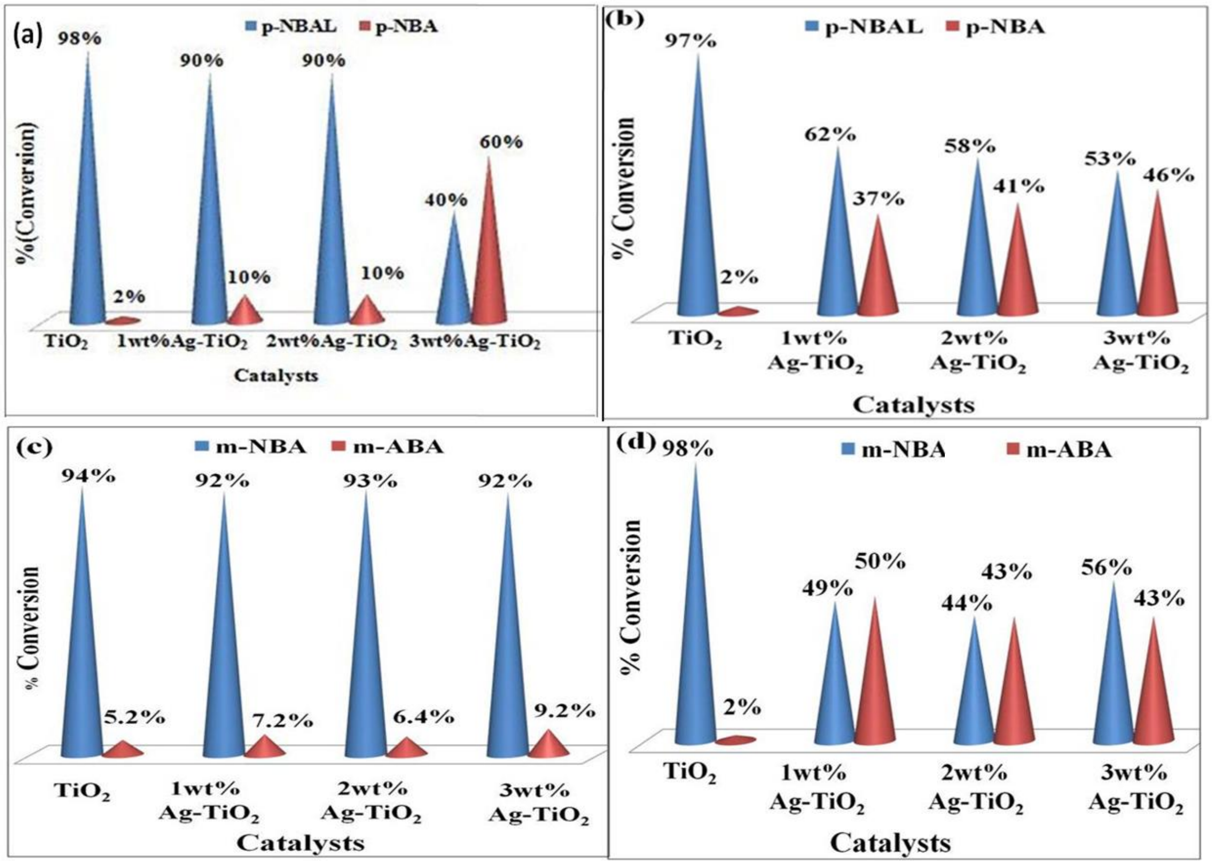


Fig. 12. Comparative (% Conversion) graphs of oxidation reaction of p-NBAL in (a) sunlight; (b) UV light and reduction reaction of m-NBA in the presence of (c) sunlight; (d) UV light.

6. Conclusion

In summary, it is demonstrated that all prepared Ag-TiO_2 (1 wt%, 2 wt% and 3 wt%) were potentially used for both photo-oxidation and photo-reduction of p-NBAL and m-NBA respectively to corresponding products. Ag metal ions had been effectively photodeposited on the surface of TiO_2 which resulted into increment of size of nanocomposites. These synthesized nanoparticles were found to be highly active under sunlight as well due to surface plasmon resonance (SPR). Both amount of co-catalyst and presence of particular light source (UV or sunlight) affected the product yield and selectivity. Oxidation of p-NBAL with 3wt% Ag-TiO_2 was nearly twice as that of 1wt% Ag-TiO_2 whereas 2 wt% Ag-TiO_2 was more efficient in case of reduction of m-NBA under UV light. Therefore, appropriate amount of co-catalyst and its distribution is influential for redox reactions in the presence of light source.

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