Influence of Ag-Cu binary metal photo deposition over TiO_2 on its photocatalytic activity under Sunlight irradiation

A

thesis

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

MASTER OF SCIENCE

in

CHEMISTRY

Submitted by

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June 2018

Dedicated

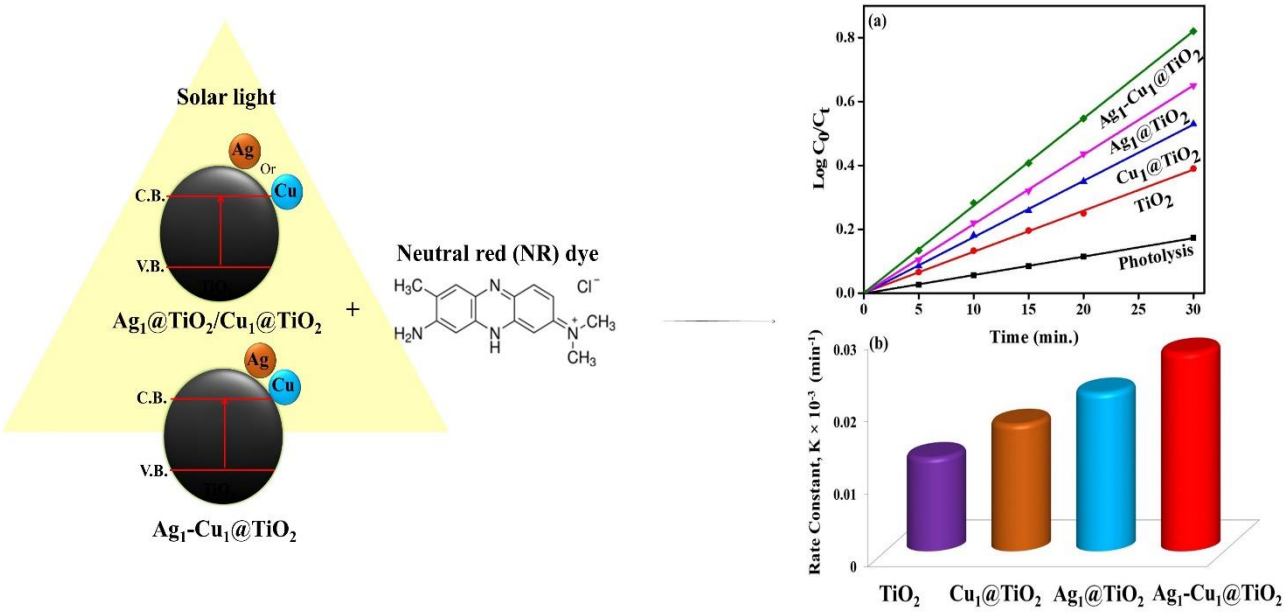
To

My Family

&

Teachers

Graphical Abstract



Scheme.1: Enhanced co-catalytic degradation by binary metal (Ag-Cu) deposition photocatalysts as compared to monometallic counterparts under solar irradiation.

Certificate

This is to certify that the project entitled "***Influence of Ag-Cu binary metal photo deposition over TiO_2 on its photocatalytic activity under sunlight irradiation***" being submitted by Deeksha in partial fulfilment of requirement for the award of degree for the Master of Science in School of chemistry and biochemistry, Thapar Institute of engineering and technology Patiala, is a record of student's own work carried out by her under our supervision and guidance. The report has not been submitted for the award of any other degree or certificate in this or any other university or institute.

Date: 29 June 2018

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A special word of appreciation for helpful and encouraging attitude of my mentor **Mrs. Sakshi Bhardwaj** for her guidance, support, encouragement and suggestions throughout the period.
Finally, yet importantly, I would like to express my heartiest thanks to my family for their blessings, my friends for help and wishes for the successful completion of this project.

Place: Patiala

Deeksha

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Contents **Page No**

List of Abbreviations

˚C	Degree Celsius
%	Percent
CB	Conduction band
VB	Valance band
µ	Micro
mM	Mili Molar
Nm	Nano-meter
NP’s	Nanoparticles
NR	Neutral red
SPR	Surface plasmon resonance
SEM	Scanning electron microscopy
DRS	Diffuse Reflectance Spectroscopy
DLS	Dynamic light scattering
SEM-EDS	Scanning Electron Microscopy- Energy dispersive Spectroscopy

List of schemes and figures

Figure.12. SEM-EDS analysis of Ag_3-$Cu_{3@}TiO_2$ for (a) 15 (b) 30 (c) 60 and (d) 90 min. photo-deposition time.

Figure.13. Photoluminescence spectrum of binary metal (Ag-Cu) deposited TiO_2 photocatalysts.

Figure.14. Dynamic light scattering (DLS) of different binary metal (Ag-Cu) deposited TiO_2 photocatalysts.

Figure.15: Change in UV peak intensities of Neutral red dye (0.2mM) when treated with different photocatalysts under 30 min. sunlight irradiations.

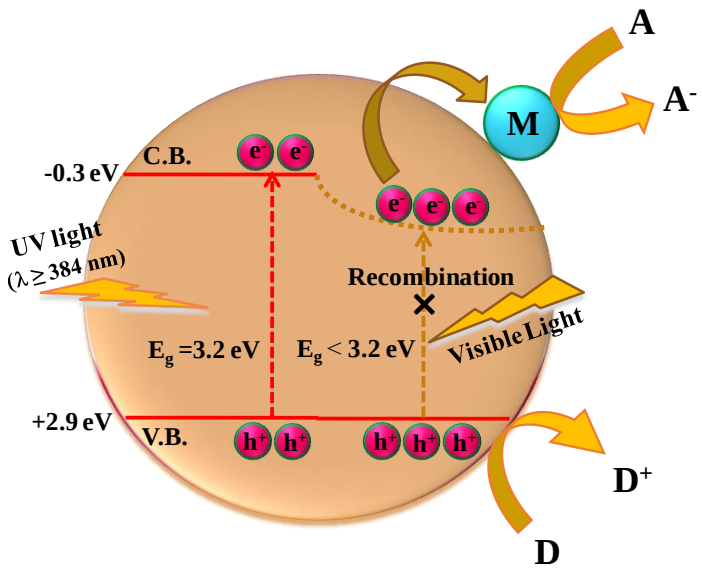
Figure.16: Time course study and corresponding k values for the photodegradation of neutral red dye using different catalysts.

Abstract

The present work demonstrates the preparation and photocatalytic activity of mono (Ag/Cu) and binary (Ag-Cu) metal deposited TiO_2 photocatalysts using photo-deposition method. Various properties of catalysts were studied by DRS, PL, DLS and SEM-EDS analysis. Ag-Cu@TiO_2 catalysts were found to display considerable red shift of plasmon band (460-700 nm) enhancement in a broad visible region in the absorption spectra. The effects of different amount (1-5) wt % of Ag-Cu binary metal and by varying photo-deposition time (15 - 90 min.) time on the photodegradation of Neutral red dye have been evaluated under solar light irradiation. DLS measurements showed that with increase in photo-deposition time, hydrodynamic size of various photocatalysts increase (from 72 nm of bare $TiO_2$to 386 nm for Ag/Cu deposited TiO_2) due to continuous growth of deposited Ag-Cu on TiO_2 surface. From the SEM-EDS analysis it was also confirmed that during the photo-deposition of binary metal (Ag-Cu), Ag metal with higher reduction potential gets deposited first followed by Cu. Further, the photocatalytic activity of various catalysts under solar irradiations revealed that binary metal deposited Ag_3-Cu_3@TiO_2always showed considerable increase in the photodegradation rate of dye relative to mono metal Ag/Cu-TiO_2 catalysts. It has been realized that the appropriate metal NP distribution and their growth control onto TiO_2 plays an important role for the effectiveness of a photocatalytic process.

Introduction:

Noble metal-TiO_2 photocatalysts have pulled in a lot of consideration over recent years [1,2]. Metal loading on the surface of TiO_2 not only lead to red shift absorption of solar spectrum but decreases the recombination rate of generated charge carriers also (Scheme. 2). Different metals such as Pd, Pt and Au etc. have been used in different interesting ways to enhance the photocatalytic efficiency of TiO_2 photocatalyst. For example, among Pd, Pt and Au photodeposited onto mesoporous RuO_2-TiO_2, Au modified catalysts showed remarkable photonic efficiency for CH_3OH oxidation [3]. It has been found that different metals like Fe^{+3} and Pt^{+4} exhibit different photooxidation rates depending on their work function, electron capturing tendency and oxidation states [4].



Scheme. 2: Effect of metal loading on TiO_2 surface for improved photocatalytic process.

Plasmonic metals such as Au, Cu and Ag due to their strong SPR, suitable redox potentials and easily reducible nature on the surface of TiO_2 make their utility more reproducible [5,6].

$$Ag^{+} + e^{-} \rightarrow Ag \quad (E^{\circ} = 0.799\,V)$$
$$Cu^{+2} + 2e^{-} \rightarrow Cu \quad (E^{\circ} = 0.337\,V)$$

In this respect, these metals have been photodeposited onto TiO_2 and have been applied for various photocatalytic application purposes. For example, under visible light irradiation Ag modified TiO_2 nanoparticles have been viewed as good photocatalysts for the degradation of Rhodamine B [7]. In another study, Cu, Ag and Au-TiO_2 catalysts have been compared for the degradation of methylene blue dye and activity order has been found in manner: Cu-TiO_2> Au-TiO_2> Ag-TiO_2[8].

Apart from doped frameworks, the composite nanostructures (binary/bimetallics) may combine the unique properties of semiconductors and noble metals/magnetic metals demonstrating multifunctional behaviors [9,10]. However, the simultaneous and effectivecontrol ofmorphology, structure,composition and distribution of metal nanoparticles is still a major concern. There exist several reports on the effective photocatalytic activity of binary metal doped TiO_2 nanoparticles. For example, effective aerobic oxidation has been attributed to the efficient charge separation on the Pt-Cu/anatase interface due to decrease in schottky barrier [11]. Au-Ag modified TiO_2 NP's have been proven to be effective photocatalysts for benzyl alcohol oxidation due to high thermal stability, tailorable shape and size of the catalysts [12]. Recent report on Ag-Cu binary mixture deposition onto TiO_2 revealed the effect of binary metal deposition for improved optical and photocatalytic degradations[13]. However, detailed study of the effective photocatalytic tendency of these binary depositions is still needed to be done. Also, there are no reports available on the effect of different UV irradiation timings during the preparation of photocatalysts for the effective photooxidation process. In this concern, the present study focus on three objectives:

(i) To Study the effect of single (Ag/Cu)/binary metal (Ag-Cu) deposition on TiO_2 activity by degrading Neutral red (NR) dye under sunlight irradiation (Scheme. 1).

(ii) To evaluate the effect of different wt % of Ag-Cu binary mixture on the degradation of neutral red dye under sunlight irradiation.

(iii) To evaluate the effect of varying photo-deposition time of binary metal photocatalyst (Ag_3-Cu_3@TiO_2) on the photocatalytic degradation of dye.

2. Experimental section:

2.1. Reagents:

Materials utilized were purchased from commercial companies with no further purification. Commercial form of TiO_2 (P25; 70% Anatase + 30% Rutile) was received as gift from Degussa corporation Gemany. Cupric nitrate ($Cu(NO_3)_2.3H_2O$) from LOBA Chemie, Silver nitrate ($AgNO_3$) from Sigma Aldrich, India, scientific were used. Neutral Red pH indicator AR ($C_{15}H_{17}ClN_4$) was obtained from S.D. Fine Chem Limited, India. Deionized water (DI) was obtained from an ultra-filtration system (Milli-Q, Millipore) with measured conductivity of 35 mho cm^{-1} at 25^0C.

2.2. Photocatalyst preparation:

Photo-deposition method was exploited for simultaneous deposition of Ag and Cu metals in differing proportions (1:1, 2:2, 3:3, 4:4, 5:5, 1:5, 2:4, 4:2, 5:1) and their monometallic counterparts [14]. In a typical procedure, TiO_2 (100 mg) was dispersed in a 50 vol% 10 mL aqueous IPA solution followed by addition of various volumes of $AgNO_3$ (0.01 M; 936 – 4680 μL), $Cu(NO_3)_2$(0.01 M; 1574 - 7870 μL) solutions in a test tube. The resulting solution was photo-irradiated under a mercury arc lamp (125 W, 10.4 mW/cm^2) in an inert atmosphere of argon with continuous magnetic stirring of2h. The above solutions were centrifuged (6000 rpm), washed with methanol and then with water and dried at 353 K overnight. In another method, photocatalysts were prepared under varying UV irradiations (15, 30, 60 and 90 min.) also. Ag(1 wt%)@TiO_2, Cu(1 wt%)@TiO_2, and Ag(1 wt%)-Cu(1 wt%)@TiO_2 have been abbreviated as Ag_1@TiO_2, Cu_1@TiO_2 and Ag_1-Cu_1@TiO_2, respectively. Catalysts with other wt % are abbreviated in a similar way. On the other hand, catalyst prepared with photo-deposition time; 15 min. has been abbreviated as Ag-Cu@TiO_2[15] and so others in same manner.

2.3. Characterization techniques:

Optical studies of metal deposited catalysts were done by Diffuse reflectance spectrophotometer (DRS, Avantes). Elemental detection was carried out with Energy Dispersive Spectroscope (EDS)

JEOL JSM-7600 F, 01 operating at 30 kV. The emission spectra of catalysts were studied using spectro-fluorimeter Perkin Elmer LS 55. Dynamic light scattering (DLS); Malvern, ZEN 3600 was used to determine the hydrodynamic size of catalysts.

2.4. Photocatalytic Oxidation:

Firstly, the calibration curve for NR dye was obtained with the solutions of different concentrations (0.1mM, 0.2mM, 0.3mM, 0.4mM and 0.5mM) by examination of these solutions under UV-Vis spectrophotometer.NR dye (0.2 mM; 5 mL) was then photodegraded under sunlight irradiation using the prepared catalysts (20 mg) for 30 min. duration. The reaction mixtures were taken out at regular time intervals, centrifuged and observed for their spectral studies**.**

3. Results and discussions:

Section. (a): Effects of mono (Ag/Cu)/binary metal (Ag-Cu) deposition on TiO2 activity for degradation of NR dye under sunlight irradiation.

3.1. Optical properties:

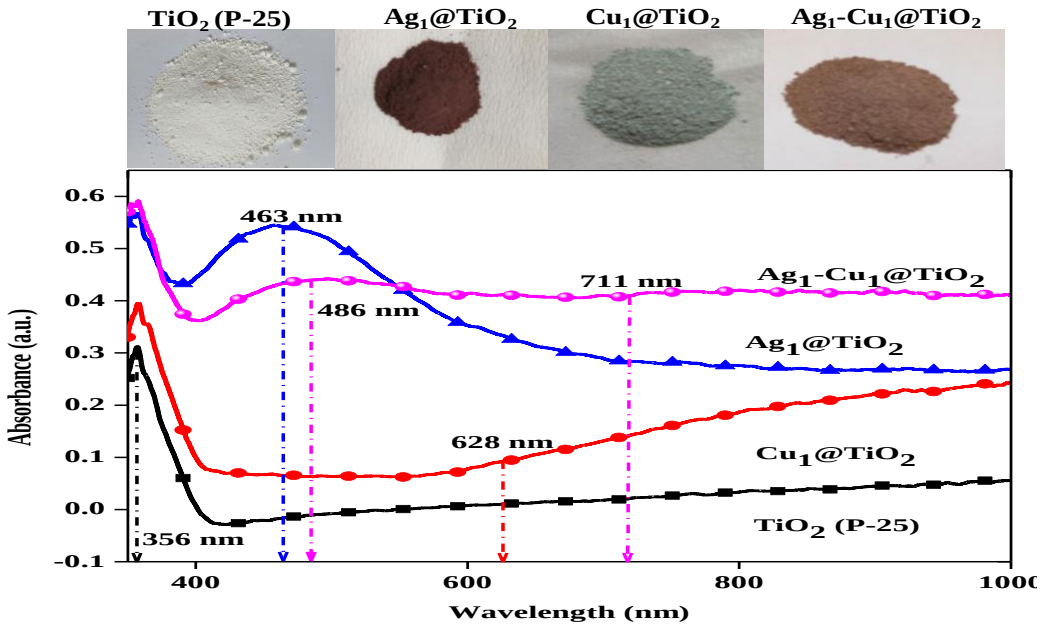


Figure.1: Diffuse reflectance spectra of mono (Ag/Cu) and binary metals (Ag-Cu) deposited TiO_2 photocatalysts.

Fig.1 shows the absorption/Diffuse reflectance spectra (DRS) of mono (Ag/Cu) and binary (Ag-Cu) metals deposited TiO_2photocatalysts. TiO_2 showed absorbance edge at 356 nm due to electron transfer from its valence band (V.B.) to the conduction band (C.B.). On the other hand, Ag and Cu mono-deposition showed SPR at 463 nm and 628 nm, respectively due to electronic exchange between metal's d-electronic states and TiO_2. However, Ag-Cu binary deposited catalysts led to red shift enhancement from ~ 400 nm to 720nm indicating their broad absorption range [15]. The colour change of catalyst solutions from white to brown and light blue for Ag and Cu and grey for Ag_1-Cu_1@TiO_2, respectively were observed.

Fig. 2 shows the photoluminescence spectra of various prepared photocatalysts which is a technique for the characterization of optical and electronic properties of semiconductors based catalysts. The charge carrier trapping and recombination rate were analysed in terms of quenching of PL peak by exciting the photocatalysts at wavelength of 340 nm. Several peaks at 396, 424, 448, 460 and 486 nm were obtained for various prepared photocatalysts. PL peaks for Ag_1-Cu_1@TiO_2 was found to exhibit greater quenching as compared to monometallic (Ag/Cu)@TiO_2 photocatalysts. This quenching reflects reduction in the recombination rate due to enhanced charge separation in case of binary metal deposition which lead to enhanced photocatalytic efficiencies [16].

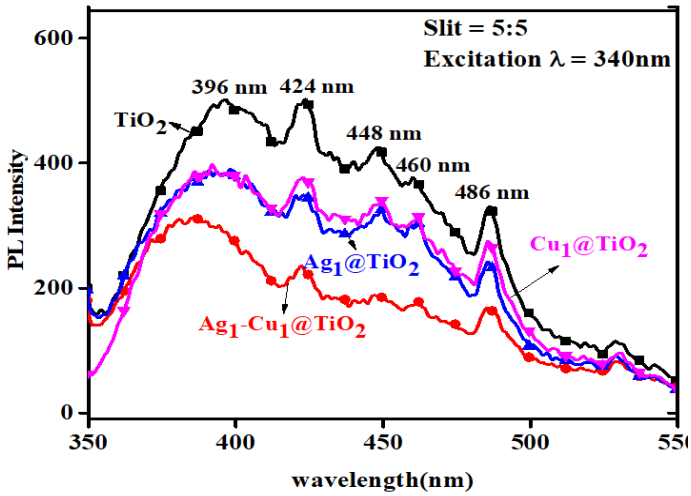


Figure. 2: Photoluminescence spectrum of mono (Ag/Cu) and binary metal (Ag-Cu) deposited TiO_2 photocatalysts.

3.2. Hydrodynamic size analysis: Changes in DLS absorption bands occurs due to different metal deposition and distribution on the TiO_2 surface which are reflected in Fig. 3. It shows that the average hydrodynamic size of TiO_2 (72 nm) increased to 175nm and 216 nm after the deposition of Ag (1wt%) and Cu (1wt%) respectively. On the other hand, by depositing binary metal Ag_1-Cu_1@TiO_2, size increased up to 386 nm. This occurs due to the simultaneous deposition

of two metals (Ag-Cu) in case of binary photocatalyst compared to single (Ag/Cu) metal which lead to larger hydrodynamic size.

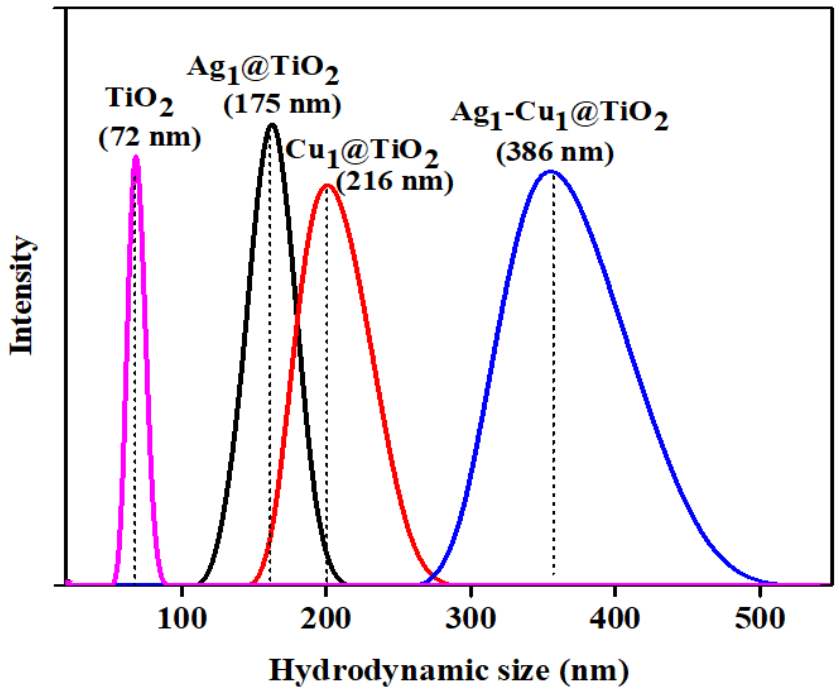


Figure. 3: Dynamic light scattering (DLS) of different prepared photocatalysts.

3.3. Photocatalytic activity:

Calibration curves are used to predict the concentration of an unknown sample. A straight line was observed which obey Lambert-Beer's law. Among various solutions, NR Dye with a concentration

of 0.2 mM having absorbance 1 was selected for further photocatalytic studies. The photocatalytic activity of synthesized photocatalysts was tested by photodegradation of Neutral Red (NR) dye, a waste water pollutant under sunlight irradiations. Fig. 5 shows changes in absorption peak intensities and corresponding colour change during the oxidation of NR for 30 min. duration using different photocatalysts. The maximum decrease in peak intensity was observed by Ag_1-Cu_1@TiO_2 catalyst under sunlight irradiation. However, photolysis in the absence of catalysts showed little degradation indicating the need of photocatalyst to carry out the degradation process.

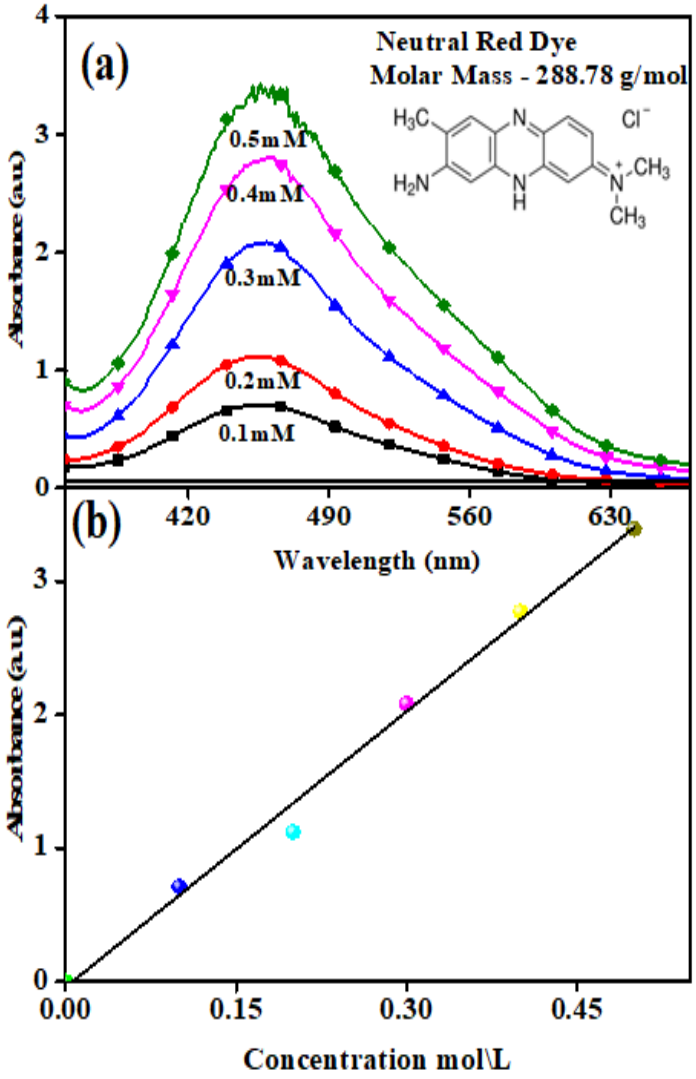


Figure. 4: Calibration curve for neutral red dye follows lamberts beer law.

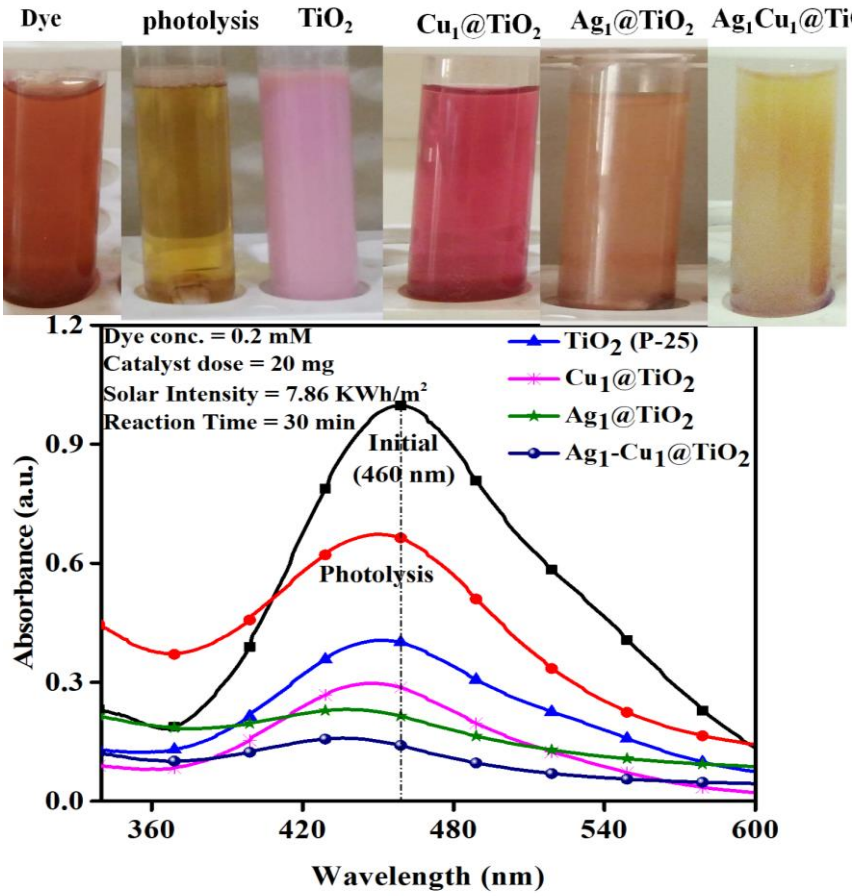


Figure. 5: Changes in UV absorption peaks and colour intensity of neutral red dye due to its photodegradation by different Ag/Cu and Ag-Cu@TiO_2 photocatalysts under 30min. sunlight irradiation.

Fig. 6 (a) demonstrate the graph of log C_0/C_t vs. time (min.) where C_t is the final conc. at a particular time and C_0 is the initial concentration of NR respectively. The reaction rates are observed to follow pseudo first order kinetics according to equation:

$\log C_0/C_t = kt/2.303$

where k is the pseudo first order rate constant. In order to investigate the relative photo-degradation rates of mono and binary mixture Ag_1-Cu_1@TiO_2 catalysts, k values have been evaluated and compared in Fig. 6 (b). Rate constant, k values of (0.013, 0.0176, 0.0219 and 0.0274) × 10^{-3} have been observed for TiO_2, Cu_1@TiO_2, Ag_1@TiO_2 and Ag_1-Cu_1@TiO_2, respectively.

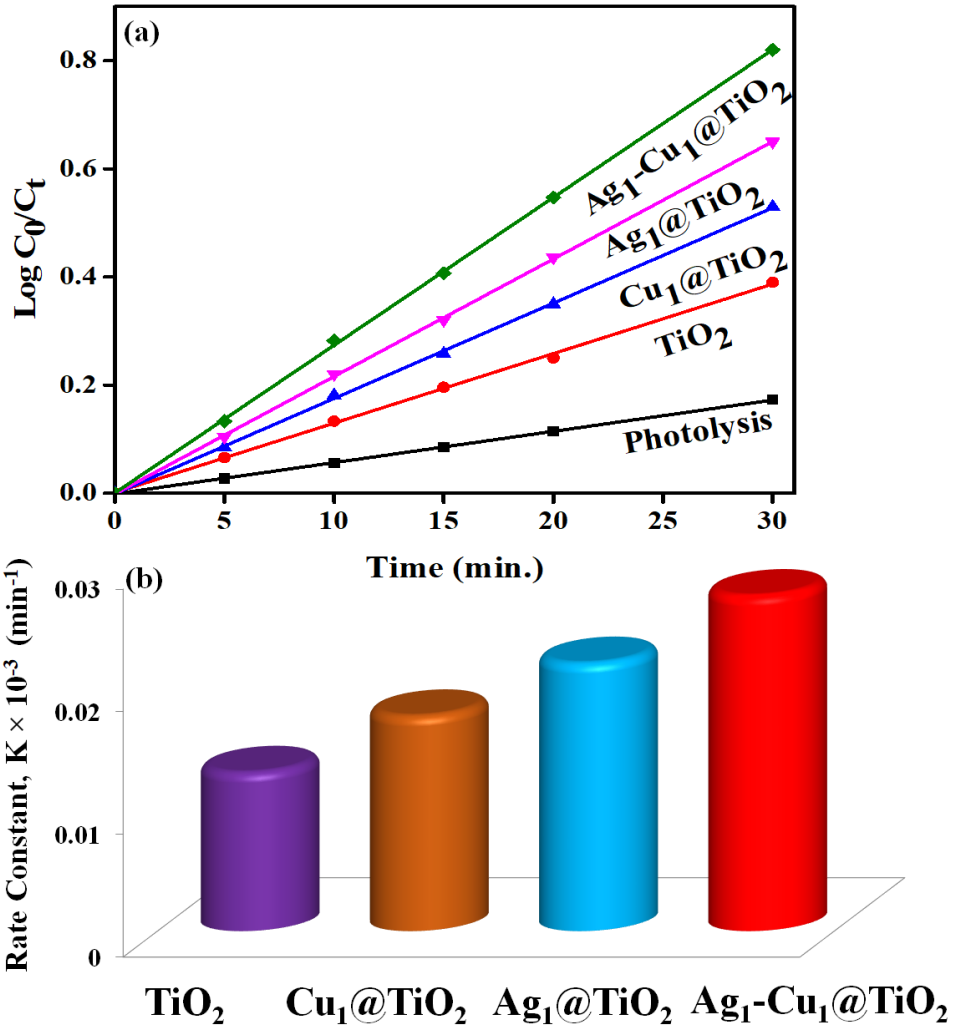


Figure. 6: Comparative photodegradation rate of neutral red dye by different photocatalysts under sunlight irradiations.

Section. (b): To evaluate the effect of different wt % of Ag-Cu binary mixture on the degradation of neutral red dye under sunlight irradiation.

3.4. Optical properties:

Fig. 7 (a) and (b) demonstrates the DRS of different wt% of Ag-Cu (Ag_1-Cu_1, Ag_2-Cu_2, Ag_3-Cu_3, Ag_4-Cu_4, Ag_5-Cu_5, Ag_1 -Cu_5, Ag_2-Cu_4, Ag_4-Cu_2, Ag_5-Cu_1)@TiO_2. It has been observed that as the % deposition of a particular metal increases, the corresponding peak intensity also increases in the similar manner. This occurs due to the presence of more metal NP's onto TiO_2 surface that possess

large quantum efficiency. Metal depositions were also confirmed by colour change of catalyst solutions.

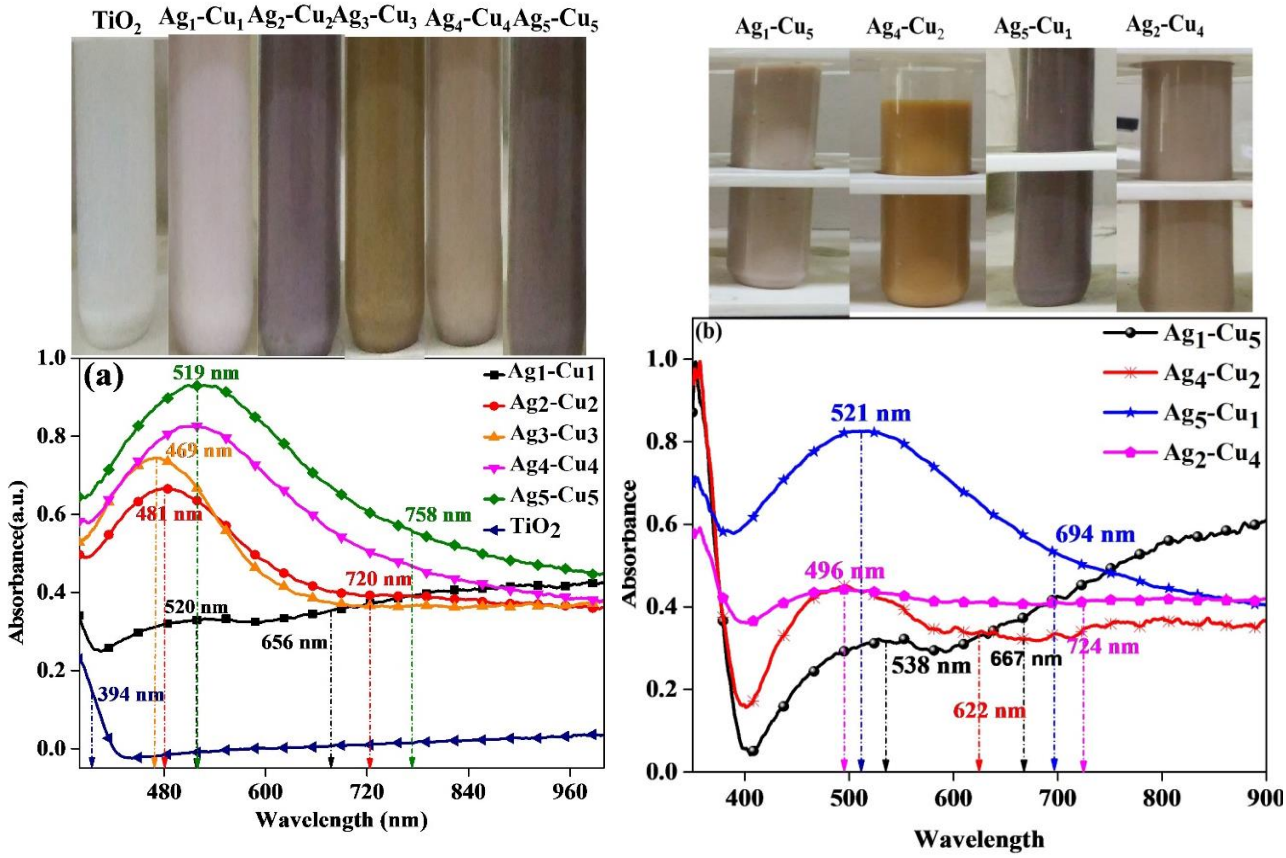


Figure. 7: Diffuse reflectance spectra and corresponding colour of different binary (Ag-Cu)@TiO_2 photocatalysts.

3.5. Photocatalytic Activity

The photocatalytic performance of different catalysts was examined for the degradation of NR under sunlight for 30 min. The maximum decrease in peak intensities was shown by Ag_3-Cu_3@TiO_2 photocatalyst. If the conc. of deposited metal is too high, it will cover the entire surface of TiO_2 hindering its photocatalytic efficiency. So, an optimized wt % of binary metal was needed to be evaluated which came out to be Ag_3-Cu_3@TiO_2. Fig. 8 depicts the changes in various NR peak intensities when treated with different Ag-Cu wt % photocatalysts. The maximum activity and corresponding colour change by Ag_3-Cu_3@TiO_2 is demonstrated in Fig.8.

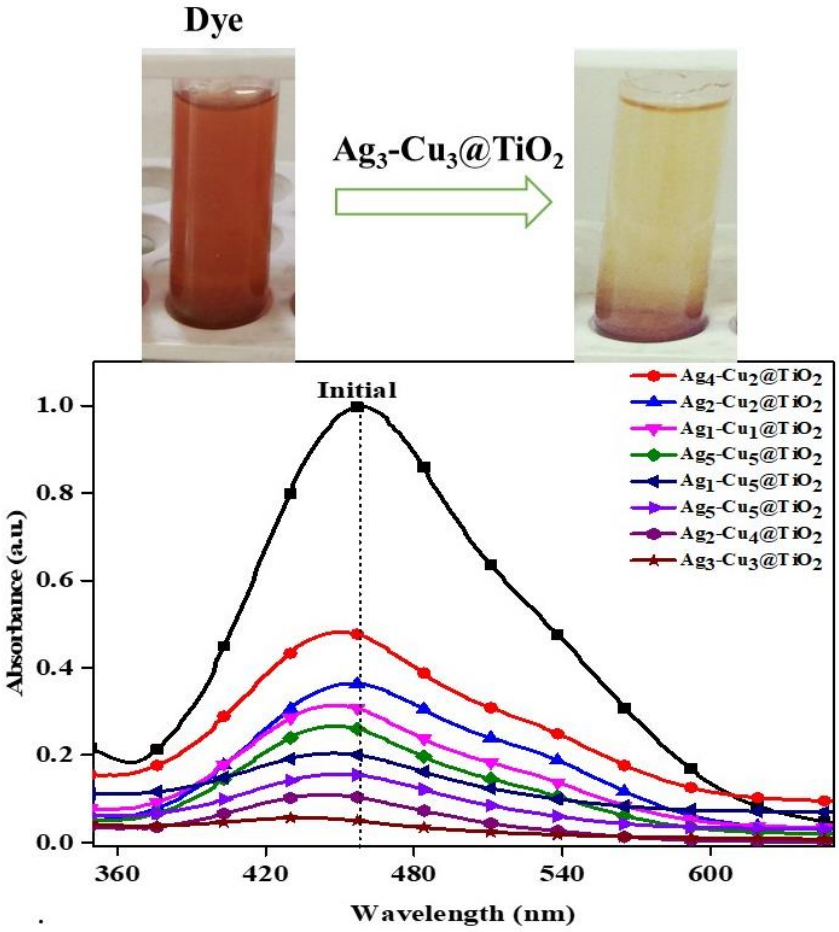


Figure. 8: Change in UV peak intensity of neutral red dye (0.2mM; 5 mL) when treated with different photocatalysts (20 mg) for 30 min. duration under sunlight irradiations.

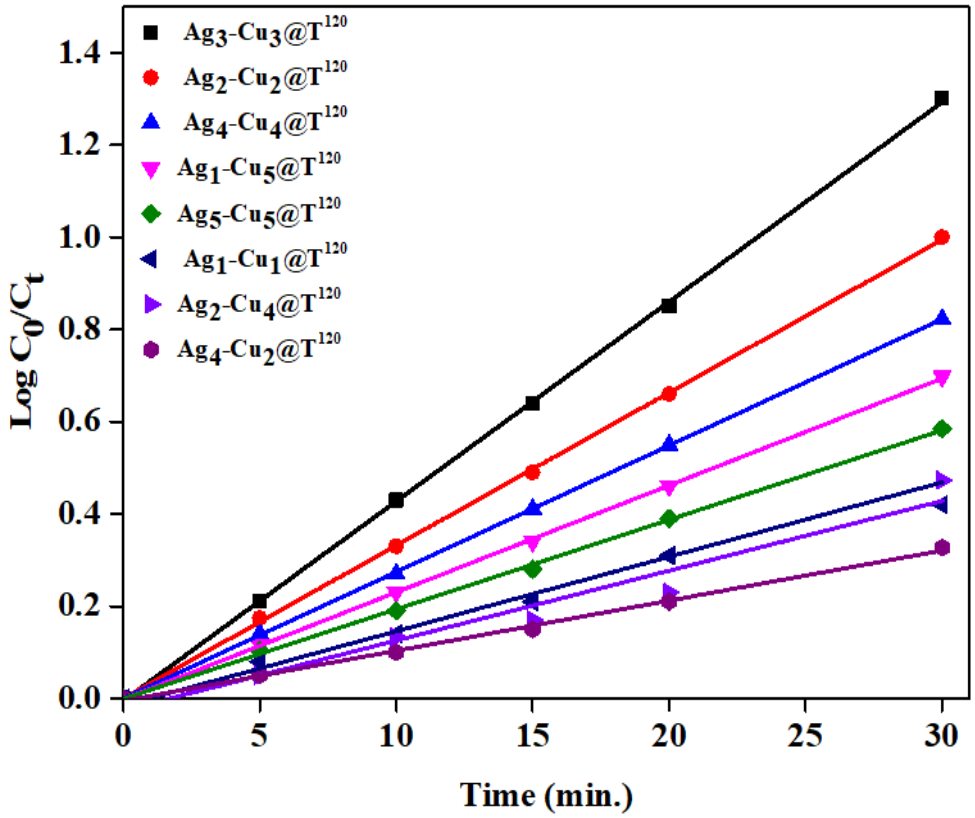


Figure. 9: Pseudo first order kinetic plot for the degradation of neutral red dye using various catalysts.

Fig. 9 demonstrate the graph of log C_0/C_t vs. time (min.) where C_t is the final conc. at a particular time and C_0 is the initial concentration of NR. The reaction rates followed pseudo first order kinetics according to the equation:

$\log C_0/C_t = kt/2.303$

where k is the pseudo first order rate constant. In order to investigate the relative photodegradation rates of different Ag-Cu@TiO_2 catalysts, k values have been evaluated and compared in Fig.10.

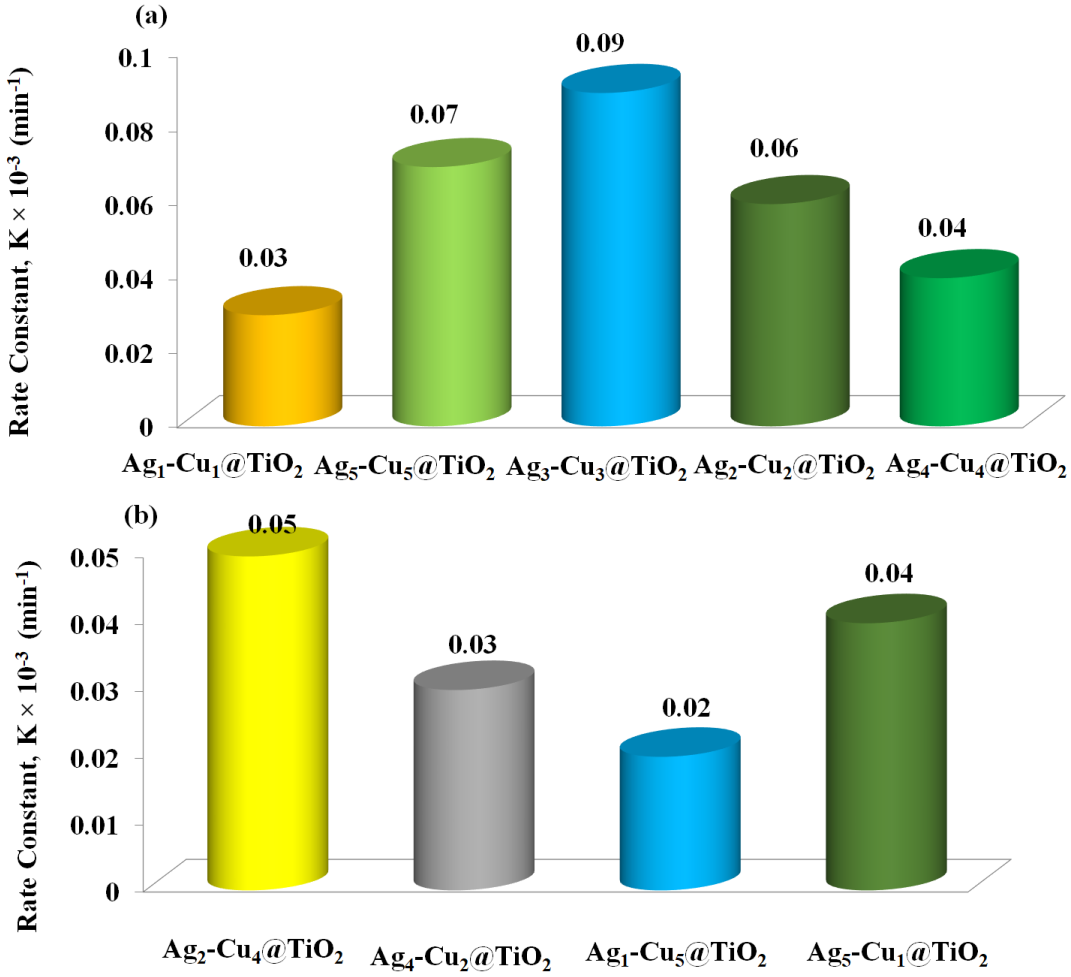


Figure. 10: Rate constant, k values observed for the degradation of dye using different photocatalyst under sunlight irradiations.

Section. (c): To evaluate the effect of varying photo-deposition time of binary metal photocatalyst (Ag_3-Cu_3@TiO_2) on the photocatalytic degradation of dye.

3.6. Optical properties:

Fig. 11 represents the DRS of different Ag_3-Cu_3@TiO_2 photocatalysts prepared under varying UV irradiations for different time intervals (15 min., 30 min, 60 min and 90 min). It was found that as time of photo-deposition increases, peak intensity increases due to enhancement of SPR effect. It shows that as UV irradiation time during preparation of the photocatalyst is increased, more and more number of metal NP's begin to deposit on TiO_2 surface. In this regard, intensity of absorbance

of catalysts in the corresponding manner. It was observed that during the initial process of binary metal (Ag-Cu) deposition, the colour was brown due to deposition of Ag. While as the deposition process was continued the colour started to change from light brown → light purple → dark purple due to the simultaneous deposition of Cu metal also. Since, the photo-deposition of any metal depends on its reduction potential, this colour change can be attributed to the fast deposition of Ag metal (0.799 V) as compared to Cu (0.337 V).

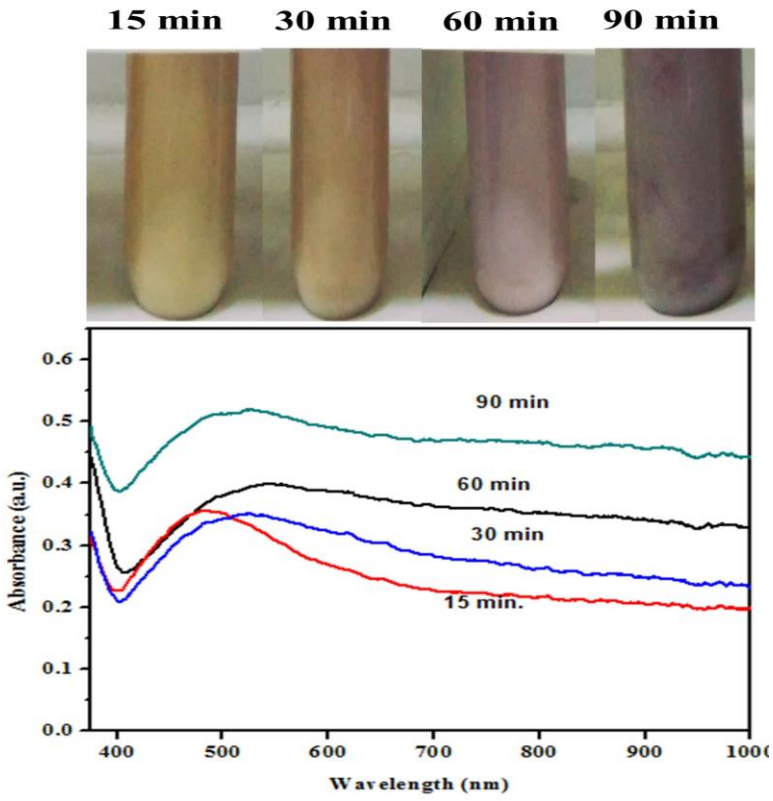


Figure. 11: Diffuse reflectance spectra of different Ag_3-Cu_3@TiO_2 photocatalysts prepared under varying UV irradiations.

3.7. SEM-EDS analysis:

The SEM-EDS analysis confirms the deposition of both metals (Ag and Cu) onto TiO_2 surface (Fig. 12). Interestingly, it was found that during binary metal (Ag-Cu) deposition, only Ag metal was deposited first within initial 15 min. instead of Cu. Further, continuous UV irradiation of the

photocatalyst lead to the deposition of Cu metal afterwards (30 to 90 min.). It has also been reported that photoreduction of Cu^{+2} particles on the surface of semiconductor (SC) is accelerated in the presence of Ag^{+} ions leading to the formation of ternary system (Ag-Cu-SC) [17]. Hence, during the photo-deposition process, Ag^{+} ions with higher reduction potential (0.799 V) accept electrons first from the C.B. of TiO_2 while Cu^{+2} ions with lower reduction potential (0.337 V) get reduced afterwards.

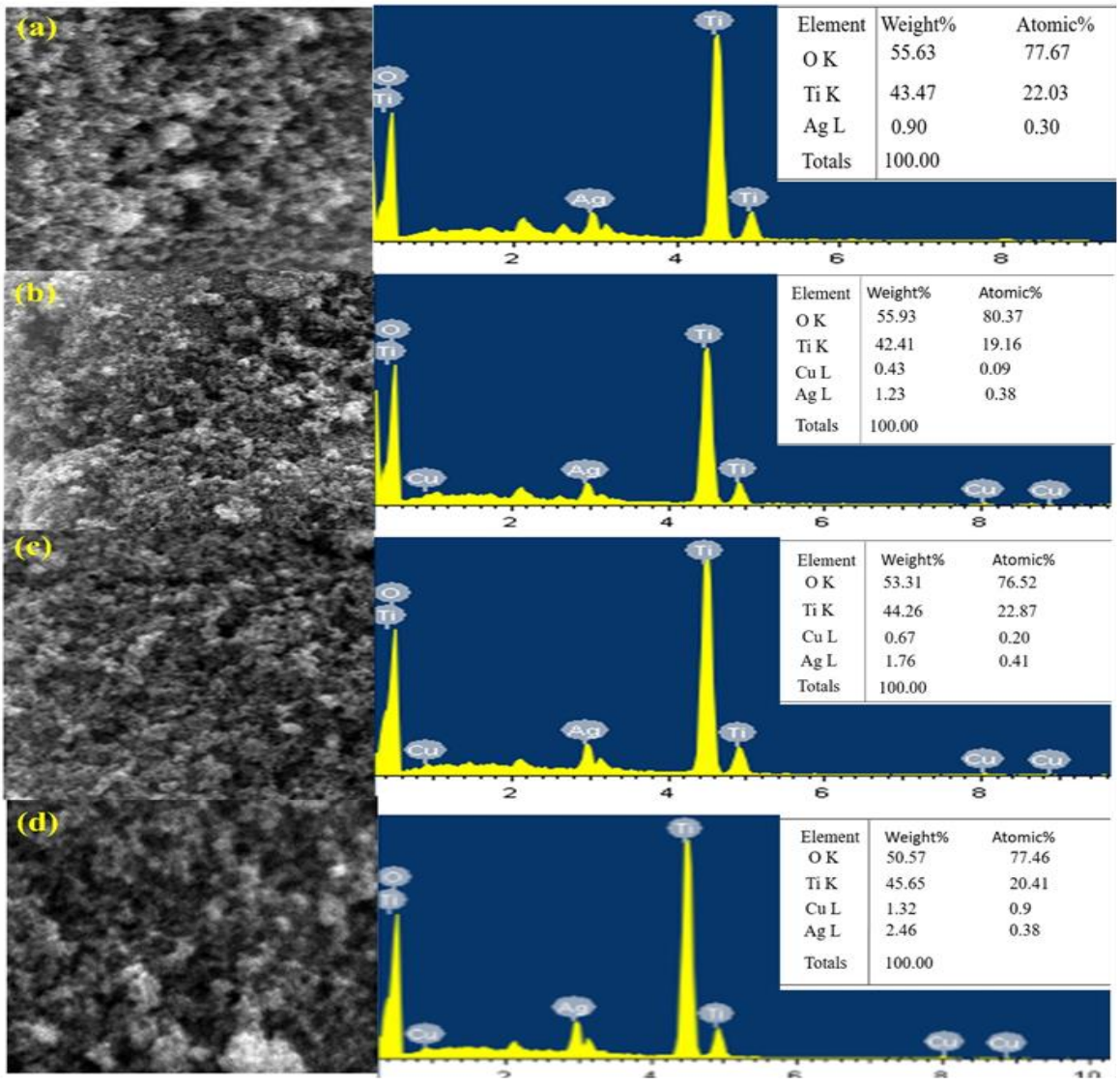


Figure. 12: SEM-EDS analysis of Ag_3-Cu_3@TiO_2 for (a) 15 (b) 30 (c) 60 and (d) 90 min photo-deposition time.

3.8. Photoluminescence Spectra:

Fig. 13. depicts the PL spectra of different photocatalysts at exciting wavelength of 340 nm. Several peaks at 410, 437, 464, 477 and 500 nm were obtained. Quenching of PL peaks was observed with the increase in photo-deposition time which shows decrease in recombination rate.

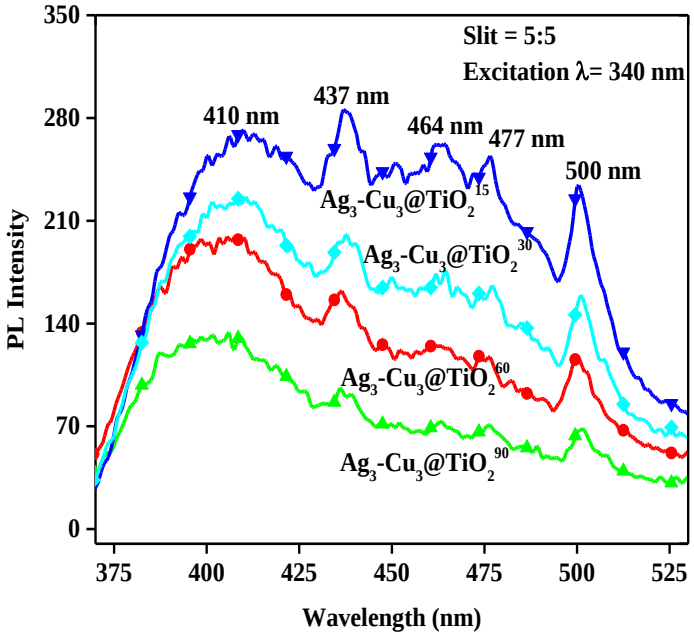


Figure. 13: Photoluminescence spectrum of binary metal (Ag-Cu) deposited TiO_2 photocatalysts.

3.9. Particle size Distribution (Dynamic light Scattering):

Hydrodynamic size of various photocatalysts prepared under different timing of UV irradiation are shown in Fig. 14. It was found that due to continuous growth Ag and Cu metal NP's onto TiO_2 surface with increase in photo-deposition time, overall size of the catalysts also increased. More deposition and growth of metals lead to increase in

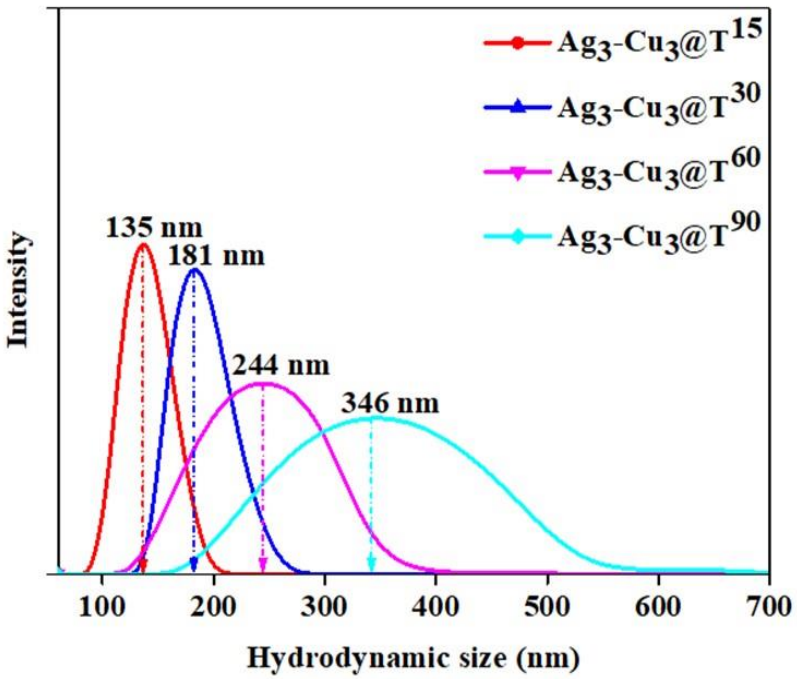
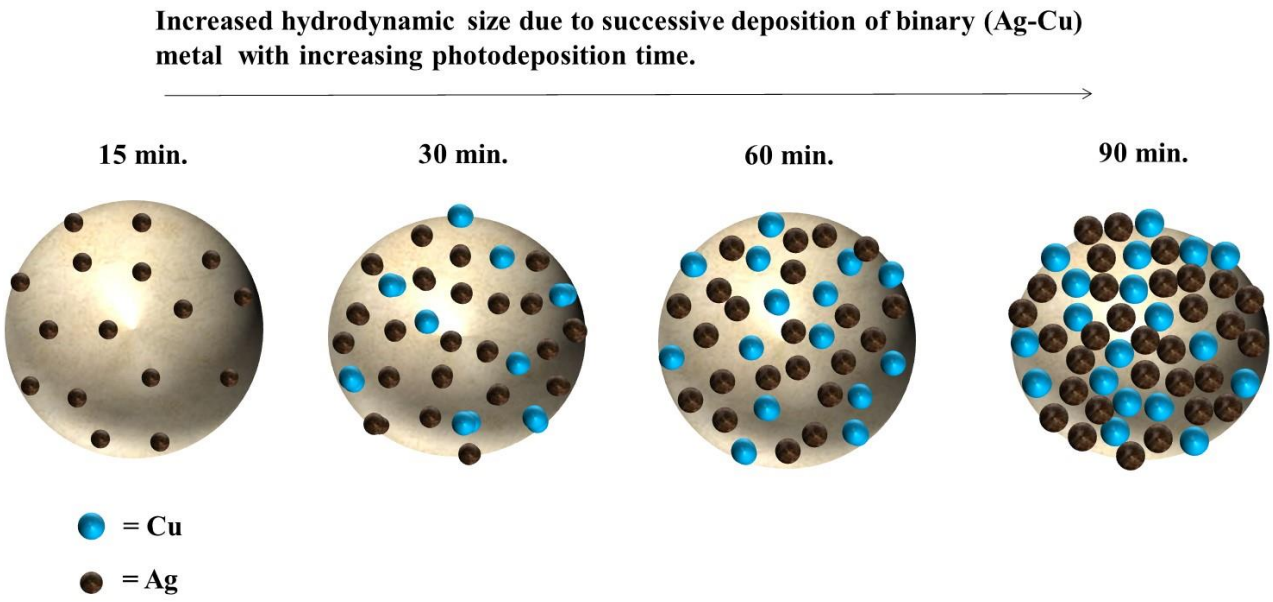


Figure. 14: Dynamic light scattering (DLS) of different binary metal (Ag-Cu) deposited TiO_2 photocatalysts.

effective average diameter of various photocatalysts and thus the hydrodynamic size also (Scheme. 3).



Scheme. 3: Continuous growth of binary metal (Ag-Cu) onto TiO_2 surface with increase in photo-deposition time.

3.9.1. Photocatalytic Activity:

The maximum decrease in peak intensities for NR was shown by Ag_3-Cu_3@TiO_2[30] catalyst as compared to other co-catalysts photodeposited in different timing. The UV absorption peaks of NR Dye treated with different photocatalysts under sunlight irradiation and their corresponding colour change has been shown in Fig. 15. Inspite of maximum PL quenching observed in Ag_3-Cu_3@T^{90}, the best photoactivity performance by 30 min UV irradiated Ag_3-Cu_3@TiO_2 catalyst might be due to appropriate and optimized dispersion of both metals (Ag and Cu) so that combined functional behaviour of every metal can come into play.

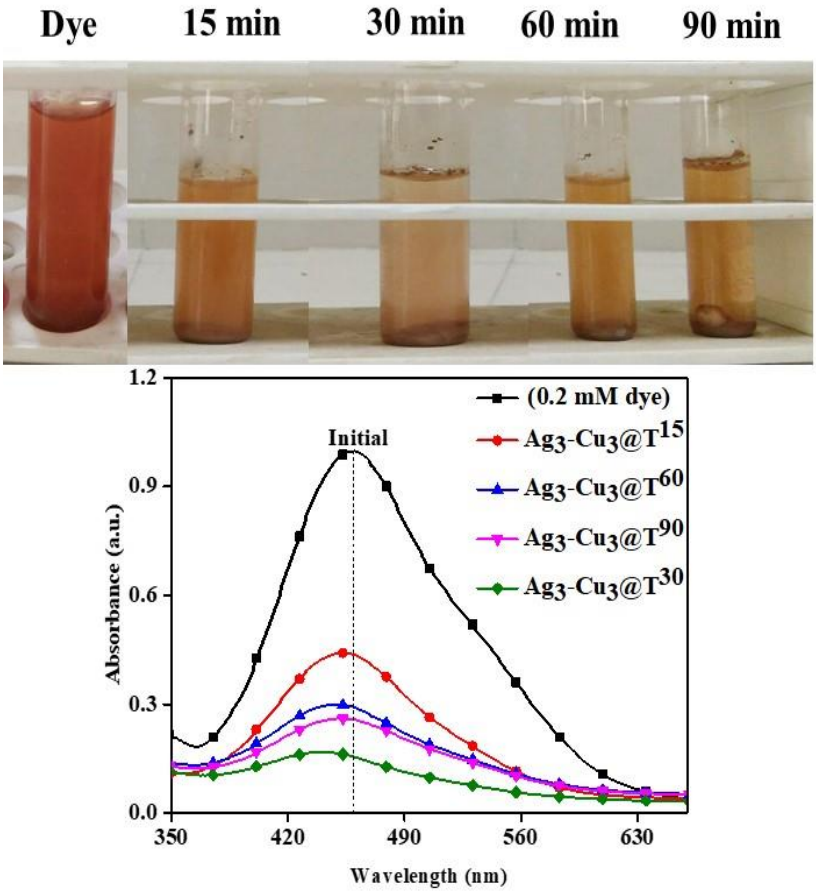


Figure. 15: Change in UV peak intensities of Neutral red dye (0.2 mM) when treated with different photocatalysts under 30 min. sunlight irradiation.

The graph of log C_0/C_t versus time (min.) are shown in Fig. 16 (a) where C_t is the final conc. at a specific time and C_0 is the primary conc. of NR individually. The reaction rates are seen to follow pseudo first order kinetics as demonstrated by the equation:

$$\log {}^{C_0}/_{C_t} = {}^{kt}/_{2.303}$$

where k is the pseudo first order rate constant. To examine the relative photodegradation rates of Ag_3-Cu_3@TiO_2 catalysts, k values have been calculated and compared as shown in Fig.16 (b).

Calculated values of rate constant, k (0.027, 0.051, 0.0412 and 0.044) × 10^{-3} have been observed for Ag_3-Cu_3@T^{15}, Ag_3-Cu_3@T^{30}, Ag_3-Cu_3@T^{60} and Ag_3-Cu_3@T^{90}, respectively.

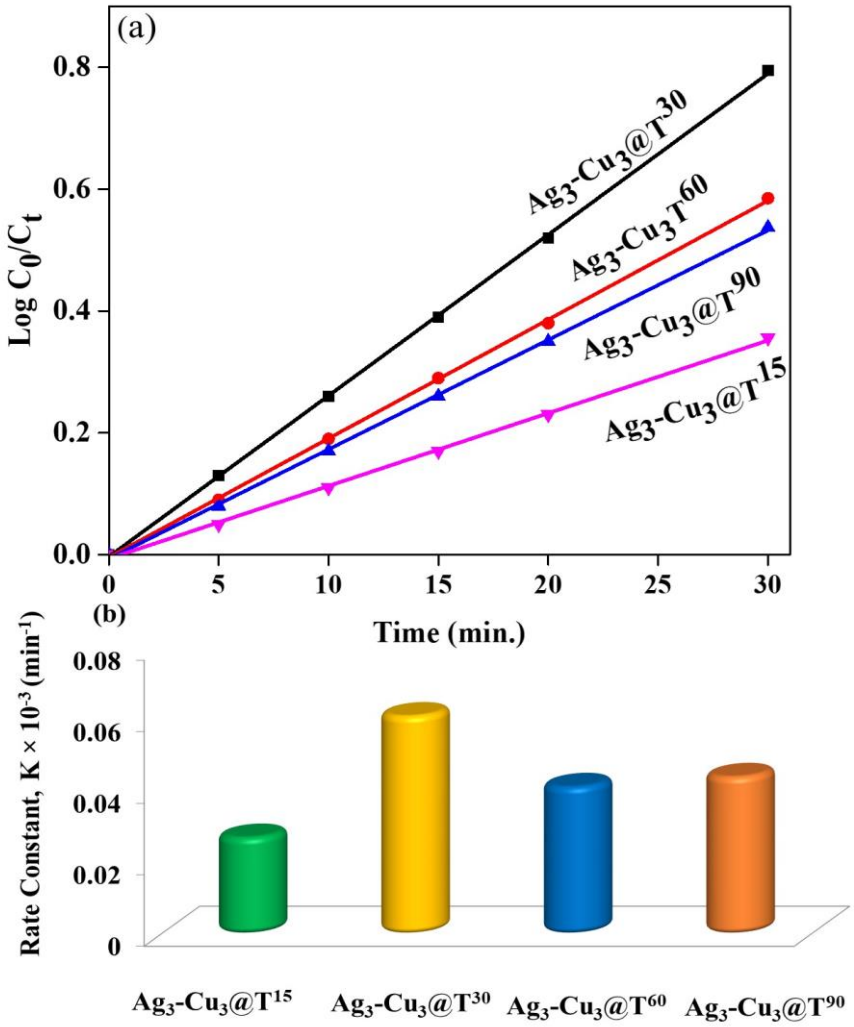


Figure. 16: Time course study and corresponding k values for the photodegradation of neutral red dye using different catalysts.

4. Conclusion:

Binary deposition of Ag and Cu metal led to enhanced degradation of NR dye due to greater photonic absorption, enhanced charge separations and interfacial charge transfer process. Method of synthesis of a photocatalyst, appropriate metal distribution onto TiO_2 surface and controlled growth of NP's are crucial factors determining the effectiveness of a photocatalytic process. It has been seen that dual metals on the TiO_2 surface play an effective and significant role for the photo-oxidation of environmental pollutants. Furthermore, these binary metal systems can be manipulated for future applications to remove other hazardous materials.

References:

1. Chatterjee, A.K.; Sarkar, R.K.; Chattopadhyay, A.P.; Aich, P.; Chakraborty, R.; Basu, T., A simple robust method for synthesis of metallic copper nanoparticles of high antibacterial potency against E. *coli*. *Nanotechnology* 2012, 23(8), 085103.

2. Fujiwara, K.; Müller, U.; Pratsinis, S.E., Pd Subnano-Clusters on TiO_2 for Solar-Light Removal of NO. *ACS Catalysis* 2016, 6(3), 1887-1893.

3. Ismail, A.A.; Bahnemann, D.W.; Al-Sayari, S.A., Synthesis and photocatalytic properties of nanocrystalline Au, Pd and Pt photodeposited onto mesoporous RuO_2-TiO_2 nanocomposites. *Applied Catalysis A:General* 2012, 431, 62-68.

4. Pal, B.; Kaur, R.; Grover, I.S., Superior adsorption and photodegradation of eriochrome black-T dye by Fe^{3+} and Pt^{4+} impregnated TiO_2 nanostructures of different shapes. *Journal of Industrial and Engineering Chemistry* 2016, 33, 178-184.

5. Poscucci, B.; Otero, G.S.; Belelli, P.G.; Illas, F.; Branda, M.M., Comparative density functional theory based study of the reactivity of Cu, Ag, and Au nanoparticles and of (111) surfaces toward CO oxidation and NO_2 reduction. *Journal of Molecular Modeling* 2014, 20(9), 2448.

6. Liu, E.; Kang, L.; Wu, F.; Sun, T.; Hu, X.; Yang, Y.; Liu, H.; Fan, J., Photocatalytic Reduction of CO_2 into Methanol over Ag/TiO_2 Nanocomposites Enhanced by Surface Plasmon Resonance. *Plasmonics* 2014, 9(1), 61-70.

7. Xiang, Q.; Yu, J.; Cheng, B.; Ong, H.C., Microwave-Hydrothermal Preparation and Visible-Light Photoactivity of Plasmonic Photocatalyst Ag-TiO_2 Nanocomposite Hollow Spheres. *An Asian Journal* 2010, 5(6), 1466-1474.

8. Sangpour, P.; Hasemi, F.; Moshfegh, A.Z., Photoenhanced Degradation of Methylene Blue on Cosputtered M:TiO_2 (M = Au, Ag, Cu) Nanocomposite Systems: A Comparative Study. *The Journal of Physical Chemistry C* 2010, 114(33), 13955-13961.

9. Monga, A.; Bathla, A.; Pal, B., A Cu-Au bimetallic co-catalysis for the improved photocatalytic activity of TiO_2 under visible light radiation. *Solar Energy* 2017, 155, 1403-1410.

10. Rojas, H. A.; Martínez, J. J., Díaz, G., Gómez-Cortés, A. The effect of metal composition on the performance of Ir–Au/TiO_2 catalysts for citral hydrogenation. *Applied Catalysis A: General* 2015, 503, 196-202.

11. Shiraishi, Y.; Sakamoto, H., Sugano, Y.; Ichikawa, S.; Hirai, T.; Pt–Cu bimetallic alloy nanoparticles supported on anatase TiO_2: highly active catalysts for aerobic oxidation driven by visible light. *ACS nano* 2013, 7(10), 9287-9297.

12. Guan, Y.; Zhao, N.; Tang, B.; Jia, Q.; Xu, X.; Liu, H.; Boughton, R. I., A stable bimetallic Au-Ag/TiO_2 nanopaper for aerobic oxidation of benzyl alcohol. *Chemical Communications* 2013, 49(98), 11524-11526.

13. Bhardwaj, S.; Pal, B., Photodeposition of Ag and Cu binary co-catalyst onto TiO_2 for improved optical and photocatalytic degradation properties. *Advanced Powder Technology* 2018, In Press.

14. Behnajady, M. A.; Modirshahla, N.; Shokri, M.; Rad, B., Enhancement of photocatalytic activity of TiO_2 nanoparticles by silver doping: photodeposition versus liquid impregnation methods. *Global NEST Journal* 2008, 10(1), 1-7.

15. Gupta, N.; Pal, B., Photocatalytic activity of transition metal and metal ions impregnated TiO_2 nanostructures for iodide oxidation to iodine formation. *Journal of Molecular Catalysis A: Chemical* 2013, 371, 48-55.

16. Ansari, M. O.; Khan, M. M.; Ansari, S. A.; Lee, J.; Cho, M. H., Enhanced thermoelectric behaviour and visible light activity of Ag@ TiO_2/polyaniline nanocomposite synthesized by biogenic-chemical route. *RSC Advances* 2014, 4(45), 23713-23719.

17. Stroyuk, A. L.; Shvalagin, V. V.; Kuchmii, S. Y., Photochemical synthesis and optical properties of binary and ternary metal–semiconductor composites based on zinc oxide nanoparticles. *Journal of Photochemistry and Photobiology A: Chemistry* 2014, 173(2), 185-194.

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