



Silver doping on TiO₂ nanoparticles using a sacrificial acid and its photocatalytic performance under medium pressure mercury UV lamp

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ABSTRACT

Titanium dioxide nanoparticles were modified using a sacrificial organic acid carrier at low pH values where the zeta potential of the TiO₂ nanoparticles was found to be highly effective forming 0.05, 0.1, 0.5 wt.% Ag/TiO₂ nanocomposites. The organic carrier was acting both as an Ag ion carrier and a hole scavenger enhancing the photodeposition of Ag atoms. The formed nanocomposites were calcined at 300 and 400 °C under controlled atmosphere and later examined for photocatalytic performance using a 125 medium pressure mercury lamp decomposing formic acid as an organic pollutant. Morphological, crystallographical and UV–vis spectroscopy analyses were used to characterize the synthesized nanocomposites. The studies have revealed that non-calcined 0.5 wt.% Ag/TiO₂ nanocomposite has the best photocatalytic activity compared with other synthesized nanocomposites and that of the non-modified TiO₂ (P25). Further calcination of the synthesized nanocomposites has shown to be effective in lower Ag concentrations where 0.1 wt.% Ag/TiO₂ nanocomposite has the best photocatalytic activity at the 400 °C.

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1. Introduction

Titanium dioxide is a non-toxic, cheap, environmentally friendly metal oxide with seven known polymorphs. Anatase and rutile are well known crystal phases and have been frequently studied due to their non-selective organic compound decomposition and water splitting capabilities when illuminated with near UV light [1–3].

TiO₂ photocatalyst absorbs photons with wavelengths below 380 nm and generates electron and hole, which produce active oxygen species, such as O[•] and OH[•] radicals, and O₂⁻ ion, by the reaction with H₂O and O₂ adsorbed on the TiO₂ surface. The high oxidation potential of the active oxygen species have been applied for air purification, water purification, deodorization, self-cleaning, antibacterial coating, photocatalytic papers, etc. [4–8].

The UV dependence and high rate of electron–hole recombination in TiO₂ nanoparticles have been addressed as the main drawbacks for its practical applications [2]. Modifications of transient and noble metal ions such as Ag, Au, Cu, Fe, Pt, etc. have been accomplished using the photocatalytic reduction capabilities of the

metal oxide [5,9–14]. These metal ions show reduction potentials that are more positive than the conduction band edges of common semiconductors, increase the nanocomposites sensitization into the visible range. Furthermore they act as electron sinks for the exited electrons on the surface of TiO₂ delivering the exited electrons to oxygen molecules [9,15].

According to Gerischer and Heller [16], the reduction of oxygen to superoxide radicals was proposed to be the rate-limiting step in the photocatalytic oxidation of organics. When oxygen reduction is rate-limiting, electrons tend to accumulate on the photocatalyst surface and increase the rate of electron–hole recombination [17]. Thus, in the presence of metal deposits, the quantum yield of the reaction may be increased by improving the separation of charge carriers and the rate of oxygen reduction.

In this study formic acid has been used as a metal ion carrier as well as organic pollutant for measuring the photocatalytic performance of the synthesized nanocomposites and that of the non-modified TiO₂ in two consecutive separate processes. In the former process organic acid decomposition is accomplished at the same time as metal ion photoreduction onto the TiO₂ surface acting as hole scavengers enhancing the photoreduction of Ag ions to metal Ag [8].

The synthesized nanocomposites were characterized using crystallographical, morphological, UV–vis spectroscopic and photocatalytic decomposition analyses. Earlier published studies are

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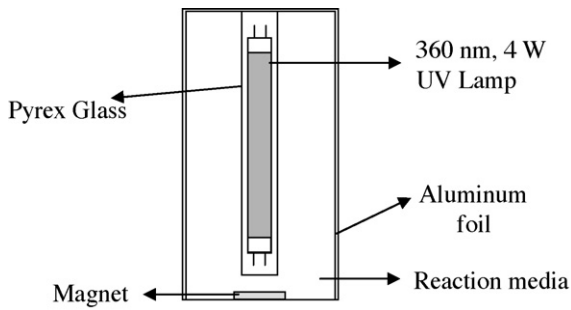


Fig. 1. Photo-reactor setup for photocatalytic reduction of the Ag onto TiO₂.

mainly engaged on higher silver contents and effect of further calcinations has been rarely reported. Effects of low concentrations of Ag and further calcination under controlled atmospheres have been studied on the photocatalytic activity of the synthesized Ag/TiO₂ nanocomposites under illumination of medium pressure mercury lamp. The potential routes for mechanisms are proposed and discussed.

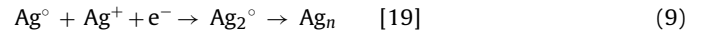
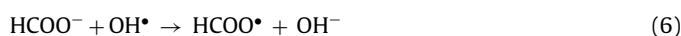
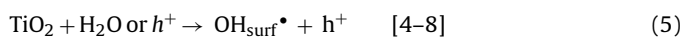
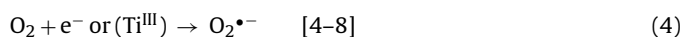
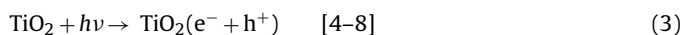
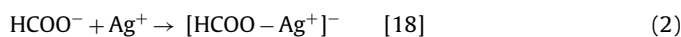
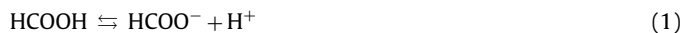
2. Experimental

2.1. Materials

Titanium dioxide (P25) was purchased and used as received from Degussa, Germany, Formic acid and Silver Nitrate (0.1 M) was purchased from Merck, Germany.

2.2. Ag/TiO₂ nanocomposite synthesis

TiO₂ (P25) (70% anatase and 30% rutile) was doped with silver atoms using formic acid as a sacrificial component in acidic media, producing 0.05, 0.1 and 0.5 wt.% silver with respect to TiO₂. Silver nitrate was used as source of silver ion, where premixed with 1 M formic acid in 25 ml of distilled water under dark conditions in a molar ratio of 10:1, formic acid to silver nitrate forming an organic–metal ion complex. Appropriate amount of TiO₂ was dispersed in 200 ml of distilled water and its pH was controlled at 2 using a 1 M nitric acid giving titanium dioxide a positive electrical charge due to its zeta potential. The pre-prepared complex was added to the suspension of TiO₂ and mixed under dark conditions for 1 hour adsorbing the formed organic–metal complex onto the TiO₂. Then it was subjected to a uni-wavelength 360 nm UV lamp for 2 h which was found suitable experimentally. Figs. 1 and 2 show the schematic of the designed photo-reactor and proposed model for Ag/TiO₂ nanocomposite formation. Eqs. (1)–(9) represent the photoreduction mechanism using the sacrificial acid. The slurry was filtered using a filter paper and washed with distilled water using a Buckner flask and dried at 60 °C using an oven. The dried nanocomposite was hand milled and subjected to a later calcination of 300 and 400 °C for 30 min using a furnace under argon controlled atmosphere.



2.3. Nanocomposite characterization

UV–vis spectroscopy measurements (250–800 nm) were performed on a Spectronic 401 – MILTON ROY to account for the absorption characteristics of the photocatalysts. For crystallographical analysis of the synthesized nanocomposites XRD patterns were obtained using TW3710 Philips X'Pert diffractometer using CuK α as radiation and CuK α as a filter ($\lambda = 1.54 \text{ \AA}$). Data were collected in the range of $20^\circ \leq 2\theta \leq 90^\circ$ a $0.02^\circ 2\theta$ -step and 2 s per step (40 kV and 30 mA). Morphological studies were conducted using a scanning electron microscopy (SEM, Viga II, 3×10^5 , USA).

2.4. Photocatalytic performance test

Formic acid was taken as an organic pollutant in aqueous media subjected to synthesized nanocomposites and that of the non-modified Degussa TiO₂ (P25). 5 μl of 1 M formic acid was added to 0.1 g of the nanocomposite suspension and subjected to a 125 W medium pressure mercury lamp irradiation in 100 ml of deionized water using a 250 ml beaker. It was mixed using a magnetic stirrer, and its decomposition was tracked using a digital pH meter. The tests were repeated three times to assure for repeatability and reliability of the results.

3. Results and discussions

3.1. Crystallographic characterization

Fig. 3(a–d) shows the XRD patterns obtained from the synthesized nanocomposites and that of the non-modified TiO₂ (P25). The

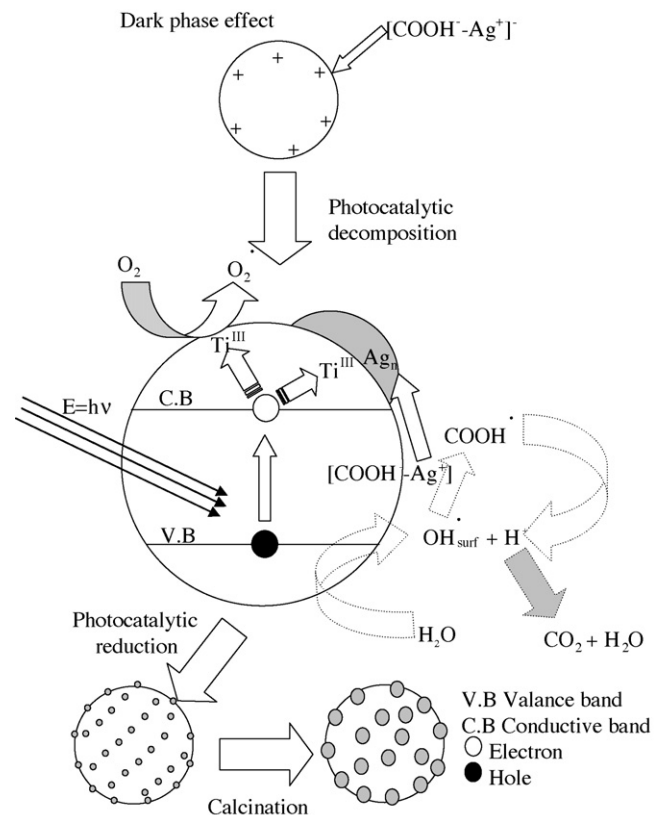


Fig. 2. The proposed mechanism for the photoreduction of Ag onto TiO₂.

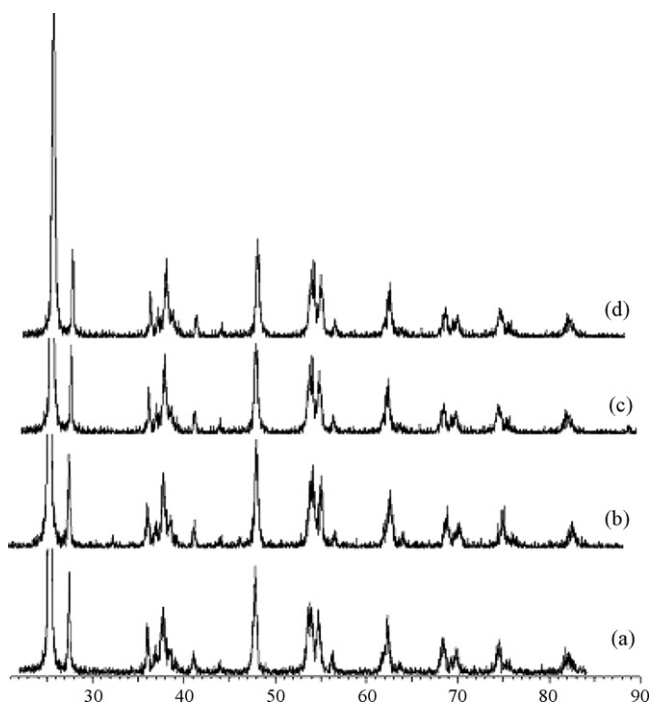


Fig. 3. XRD patterns of samples: (a) 0.1 wt.% Ag/TiO₂, (b) 0.5 wt.% Ag/TiO₂, (c) 0.5 wt.% Ag/TiO₂ calcined at 300 °C and (d) Non-modified TiO₂ (P25).

results reveal that there is no difference between the XRD patterns of the synthesized nanocomposites and that of the non-modified TiO₂ (P25). The peaks in the XRD patterns correspond to the anatase and rutile phases of the commercial TiO₂. No sign of crystal Ag is seen in the XRD results obtained from both calcined and non-calcined samples at all Ag-doped concentrations, suggesting either that the Ag is not in the crystal form or the extent of deposition is not detectable by XRD analysis.

3.2. Absorption characterization

Fig. 4(a–c) illustrates the UV–vis spectroscopy results of synthesized nanocomposites and that of the commercial TiO₂. The results show that the silver content has positive effect on the UV–vis absorption spectrum in all applied methods, increasing the absorption range from the UV range into the visible range. As it can clearly be observed from the UV–vis spectroscopy, non-modified TiO₂ has a semiconductor characteristic with a sharp decrease above its band gap limits while as for the synthesized nanocomposites has developed an intermediate character between the metal and metal oxide. Calcination has shown to have positive effect on absorption capabilities, where it is shown that 400 °C treated sample has more absorption with 0.5 wt.% silver content than the sample without heat treatment. For the samples of 0.05 and 0.1 wt.% silver content, the 300 °C treated nanocomposite has shown better absorption compared with that of non-calcination forms. Therefore calcination of nanocomposites has positive effect on the absorption spectrum from the UV range to the visible spectrum.

3.3. Surface morphological characterization

Fig. 5(a–d) illustrates the SEM micrographs of TiO₂ (P25) and that of 0.5 wt.% Ag/TiO₂ nanocomposite both calcined at 300 and 400 °C as well non-calcined forms. As it is clearly addressed from the presented micrographs, the calcined form is more aggregated, and growth of particles is seen as a result of sintering at 400 °C, reducing active surface area and affecting the size distribution. Cal-

cined nanocomposites up to 300 °C have shown less aggregation than the 400 °C and better size distribution.

3.4. Photocatalytic performance

Fig. 6(a–c) shows the photocatalytic study of the synthesized Ag/TiO₂ nanocomposites and that of non-modified TiO₂, photodecomposing formic acid as an organic pollutant. As can be clearly observed the nanocomposites are prepared at three different Ag contents of 0.05, 0.1 and 0.5 wt.% with respect to TiO₂ and further calcined at 300 and 400 °C under controlled atmospheres. Crystallographic studies have revealed that no significant change is observed in the synthesized nanocomposites in respect to that of pure TiO₂ (P25), suggesting that the changes in the photocatalytic performance can be addressed by different aspects of silver doping on TiO₂ (see Fig. 6(a)). Organic pollutant residue percent was calculated using Eq. (10) and plotted versus time as shown in Fig. 6.

$$\text{organic pollutant residue (\%)} = \left(\frac{C}{C_0} \right) \times 100 \quad (10)$$

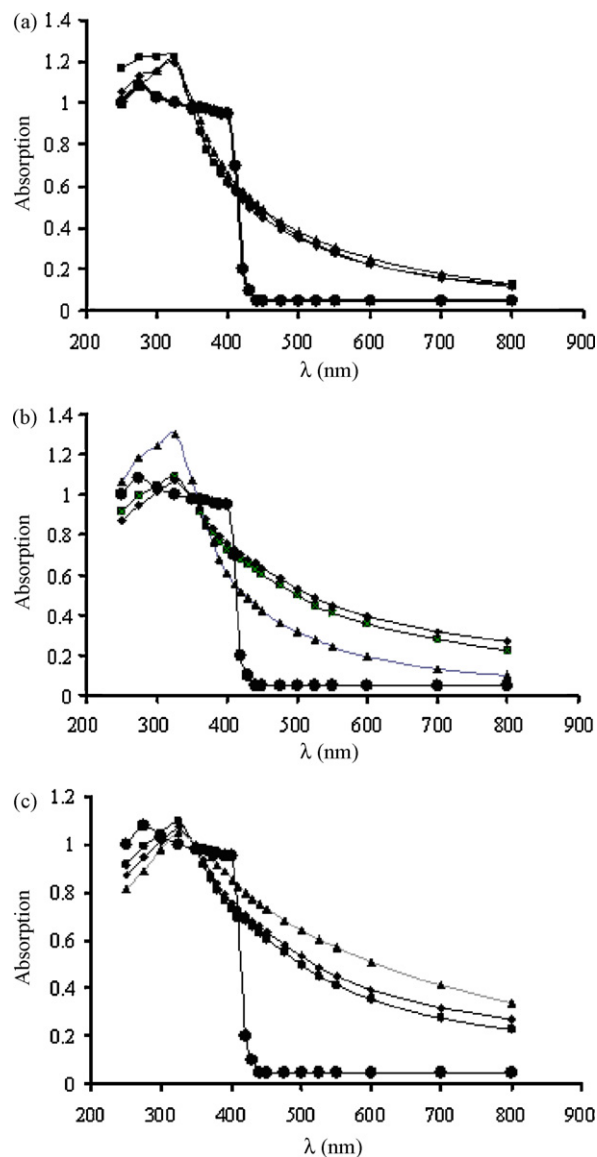


Fig. 4. UV–vis spectrometry analysis of TiO₂ and Ag/TiO₂ nanocomposites: (■) 0.05 wt.% Ag/TiO₂; (◆) 0.1 wt.% Ag/TiO₂; (▲) 0.5 wt.% Ag/TiO₂; (*) non-modified TiO₂ (P25), (a) non-calcined, (b) 300 °C calcined and (c) 400 °C calcined.

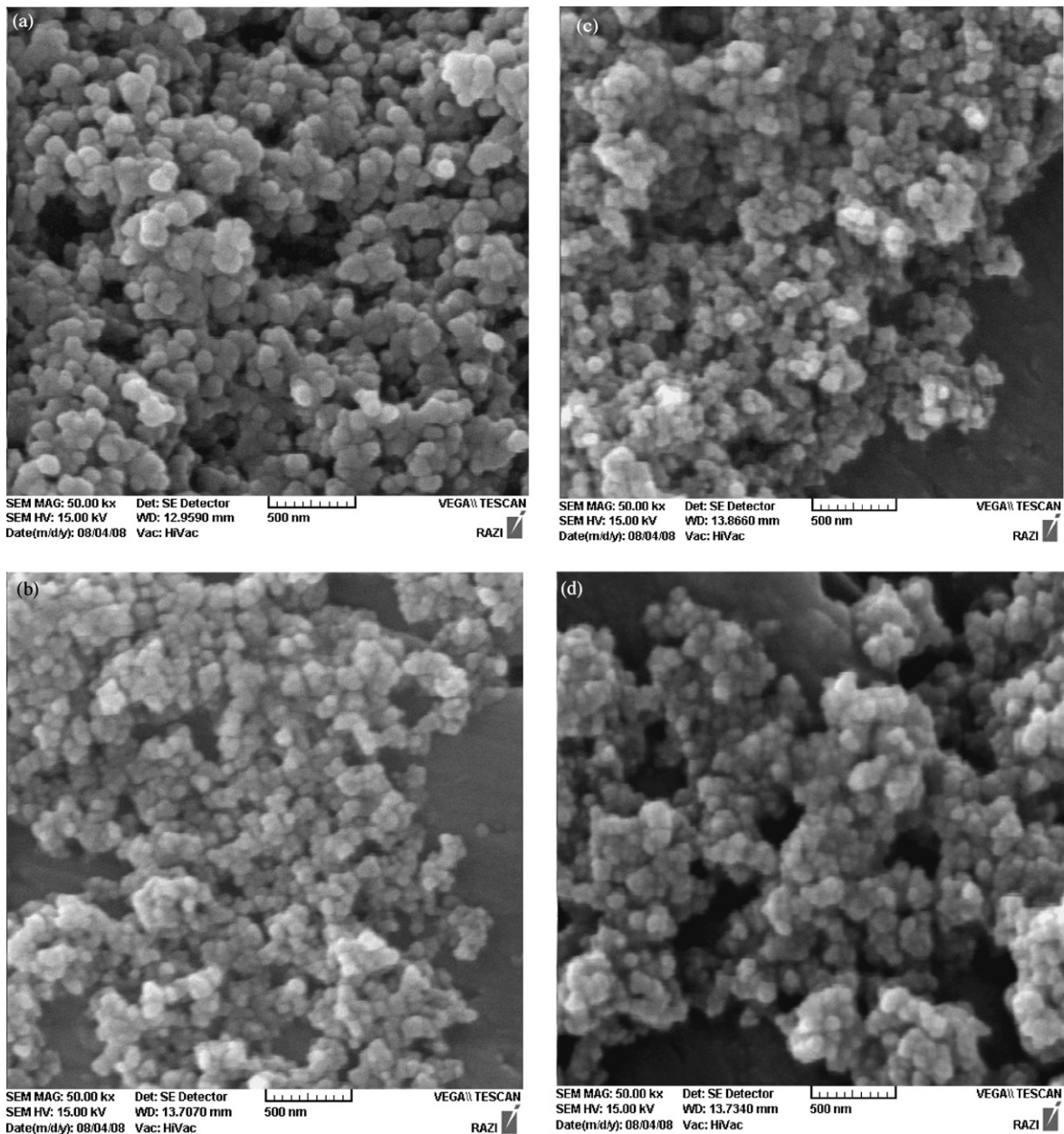


Fig. 5. SEM micrographs of samples (a) TiO_2 (P25), (b) 0.5 wt.% Ag/TiO_2 , (c) 0.5 wt.% Ag/TiO_2 calcined at 300°C and (d) 0.5 wt.% Ag/TiO_2 calcined at 400°C .

where C_0 is the initial organic content and C is the organic content at time t .

The photocatalytic studies have revealed that non-calcined 0.5 wt.% Ag/TiO_2 nanocomposite has the best photodecomposition activity under 125 W medium pressure mercury lamp. The synthesized 0.05 and 0.1 wt.% Ag/TiO_2 nanocomposites have shown the same photocatalytic activity, photodecomposing the organic pollutant with a similar trend and duration, which are still more effective compared to that of non-modified TiO_2 (P25).

Photocatalytic studies of the calcined Ag/TiO_2 nanocomposites upto 300°C have revealed that the photocatalytic activity of the 0.5 wt.% silver content has decreased when compared to that of non-calcined form. This may be due to the aggregates formed as a result of higher silver content making a soft media on the tough ceramic substrate, making it more susceptible to form aggregates resulting in less effective surface area for photocatalytic performance which is also confirmed by the SEM micrographs (see Fig. 5).

Growth of silver atoms forming uniform layers on the surface of ceramic can be another reason for low photocatalytic activity seen from the 0.5 wt.% calcined samples, blocking the light from entering the TiO_2 bulk to generate electron–holes. This is even seen to be more obvious when calcination temperature was increased to 400°C (see Fig. 7), which had the best absorption in the visible region among all samples, suggesting that the shifts alone into the visible region cannot assure the photocatalytic enhancements. This can be explained by formation of silver clusters in terms of their migration and combination [20].

In contrast for the samples of 0.1 wt.% silver content and calcination temperature of 300°C has shown that they have better performance comparing to the non-calcined form. This increase in the photocatalytic activity may be due to activation of nanocomposite and effective dispersion of silver on the surface of the ceramic taking more effective sites for electron–hole separation. This photocatalytic activity was found to be enhanced even more when calcined upto 400°C reducing the time of decomposition from

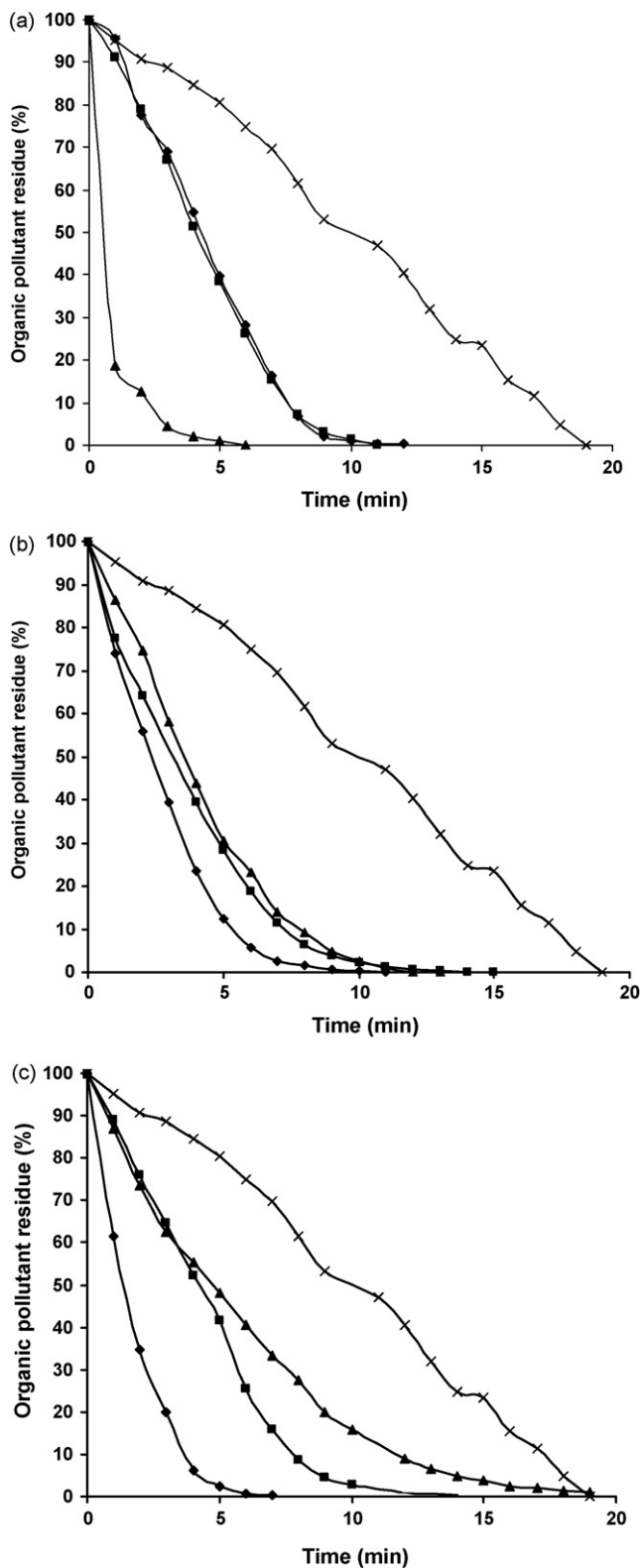


Fig. 6. Photocatalytic activity of TiO_2 and Ag/TiO_2 nanocomposites: (■) 0.05 wt.% Ag/TiO_2 , (◆) 0.1 wt.% Ag/TiO_2 , (▲) 0.5 wt.% Ag/TiO_2 and (×) non-modified TiO_2 (P25), (a) non-calcined, (b) 300 °C calcined and (c) 400 °C calcined.

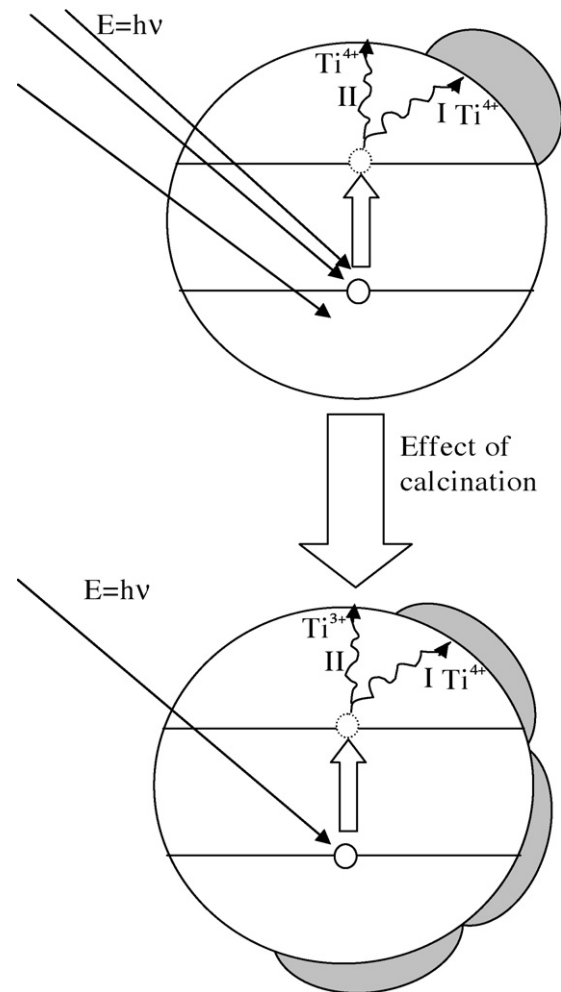


Fig. 7. Proposed model for effect of calcination on photocatalytic performance of Ag/TiO_2 nanocomposites.

10 min in the case of non-calcined 0.1 wt.% silver content to 9 and 6 min in case of 300 and 400 °C calcined nanocomposites respectively. It is suggested that calcination can act as an activating stage.

In the case of 0.05 (wt.%) silver content no significant difference has been observed between the non-calcined and 300 °C calcined nanocomposite. However at 400 °C the nanocomposites have shown less photocatalytic activity, which might be due to aggregates reducing the specific surface area of the nanocomposite and less effective distribution of silver atoms on the TiO_2 surface forming non-successful silver clusters.

4. Conclusion

Silver was successfully doped on TiO_2 (P25) nanoparticles using a sacrificial acid. Doping was performed in acidic conditions taking advantage of high zeta potential of the ceramic to adsorb the formed complex and further illumination with a UV lamp resulted in the nanocomposite formation. The following conclusions can be drawn:

- (1) Modifying Ag on TiO_2 nanoparticles has shown to be beneficial towards its photocatalytic performance, where 0.5 wt.% Ag/TiO_2 nanocomposite has the best performance among all non-calcined samples, at the modified range of experiments.
- (2) Calcination has shown to have activating properties on the synthesized nanocomposites and be more effective at lower

concentrations, where 0.1 wt.% Ag/TiO₂ nanocomposite has the best photocatalytic activity at 400 °C.

- (3) Visible light sensibilization was approved by the UV–vis spectroscopy analysis revealing the modification of TiO₂ nanoparticles by Ag and then formation of Ag/TiO₂ nanocomposites. Ag was not detectable by XRD analysis due to its low content.

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