A study on methylene blue degradation: enhanced photocatalytic activity of Ag-ZnO nanocomposites

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Abstract
Silver/Zinc Oxide nanocomposites (Ag-ZnO NCs) were fabricated by varying the weight percentages of both Ag and ZnO for investigating its photocatalytic activity. The structural, morphology and optical response of the prepared nanocomposites were examined with PXRD, FESEM, TEM, EDAX, XPS, FT-IR, UV–vis-DRS and PL spectroscopy. The effect of Ag and ZnO concentrations on these nanocomposites was examined by analyzing the photocatalytic activity towards Methylene Blue (MB) dye degradation under the UV irradiation. The overall results suggested that, AZ1:1 NC achieved better photocatalytic activity than AZ1:2 and AZ2:1 composition. Therefore, the present study demonstrated the viability of the Ag-ZnO NCs in remediation of environmental pollutant and treatment of waste water.

1. Introduction

During the past few decades, there is a rapid growth of human population and technological development which in turn leads to an exponential growth in both water and air pollution arises from various industrial activities. These pollutants threaten the lives of the inhabitants throughout the world. At present, Heterogeneous semiconductors based photocatalysts are effective materials for degradation of organic pollutants through photocatalysis process by means of exploiting the energy from artificial or natural illumination. The efficiency of photocatalysts are typically depends on their specific surface area, appropriate optical band-gap, reusability and trapping of photo generated charge carriers [1, 2]. Among the various potential candidates, ZnO nanoparticles (NPs) and its Nanocomposites (NCs) have received large interest in diverse field owing to its unique properties like ZnO has wide and direct band gap, chemical stability, non-toxicity, large surface area and high photosensitivity [3, 4]. As an effective photosensitizer, ZnO have been successfully employed in light induced redox applications [5–8]. However, the practical utility of pure ZnO phase still confronts some challenges, i.e., its innate capability in the effective utilization of solar radiation and optical transparency lowers its photo degradation performance [9, 10] and rapid recombination of photo excited charge carriers resulting in least quantum yields [11].

Undoubtedly, several strategies have been evolved to modify and to improve the performance and photocatalytic efficiency of nanostructured ZnO by controlling the morphology of it, coupling it with metals, doping with non-metals and synergistic combination of ZnO with carbon materials [12–15]. Among various kinds of transition and noble metal semiconductor heterostructures, Ag-ZnO hybrid nanocomposites with different morphologies and sizes have received much interest since they exhibit good chemical and thermal
stability, eminent electronic property and notable enhancement in optical property [16, 17]. Therefore, incorporation of Ag could enable improvements in the absorption of certain wavelengths of incident light, because of the surface Plasmon resonance (SPR) and extend the photo responding range [18, 19]. Also, Ag can act as a charge carrier trap that suppresses the recombination rate due to the formation of a Schottky contact at the boundary of metal/oxide [20–22]. Recently, several studies have been explored in the photocatalysis of Ag-ZnO NCs for effective photodegradation of organic pollutants; however, the synergetic effects of the Ag contribution have not yet been explored in detail.

In the present study, we have prepared a series of Ag-ZnO NCs by combined wet impregnation and chemical reduction method. The investigation of structural, morphological, and optical properties of the nanocomposites have been carried out with appropriate characterization techniques. The photocatalytic performances of Ag-ZnO NCs were tested for methylene blue (MB) degradation in an aqueous solution with UV light irradiation under optimal conditions.

2. Experimental technique

2.1. Materials

Commercial ZnO nano powder with particle size less than 100 nm, Silver Nitrate (AgNO₃) and Sodium Borohydride (NaBH₄) were obtained from Merck, India. Deionised (DI) water was used for materials synthesis. All the chemicals used were analytically pure and utilize as received without further purification.

2.2. Synthesis of Ag-ZnO nanocomposites

Ag-ZnO nanocomposites were prepared by wet impregnation method. In brief, 1 g of ZnO nano powder was dispersed in 100 ml DI water and stirred for 1 h to attain the homogeneous suspension. After that, 1 g of AgNO₃ was dropped into the ZnO suspension and stirred magnetically for 30 min. Then, 1 g of NaBH₄ was added to the above mixture under continuous stirring for 1 h. Subsequently, the resulting precipitated particles were then separated by centrifugation and collected after washing with DI water and ethanol in sequence and finally heated at 60 °C for 6 h. The sample was labeled as AZ1:1. This producer was repeated to prepare a series of Ag-ZnO NCs, except for different weight percentage of AgNO₃ and ZnO in order to compare the properties of prepared materials with each other. The weight ratio of Ag to ZnO was changed in the ratio of 1:2 and 2:1 was donated as AZ1:2 and AZ2:1, respectively.

2.3. Characterization

Powder x-ray diffraction (PXRD) measurements were performed using a X’Pert–PRO diffractometer with Cu—Kα radiation of wavelength (λ) of 1.54060 Å. The Fourier transform infrared spectra (FTIR) were recorded on a Thermo Nicolet 380 spectrometer in the range of 400–4000 cm⁻¹. The chemical state of nanocomposite was analyzed on a high resolution x-ray photoelectron spectroscopy (K–Alpha XPS, Thermo Fisher Scientific) using Al Kα radiation. The optical properties were investigated using UV–Diffuse Reflectance spectrophotometer (SHIMADZU/UV 2600) in the wavelength range of 200–800 nm and photoluminescence spectrophotometer (FLS 1000). The surface morphology and elemental composition were examined using a field emission scanning electron microscope (FESEM, Carl Zeiss microscopy ltd, UK & SIGMA) operated at 30 kV equipped with EDAX detector. The structural morphology of nanocomposites were analyzed by JEOL-2100 + High Resolution Transmission Electron Microscope (200 kV).

2.4. Photocatalytic experiments

The photocatalytic activities of Ag-ZnO NCs were examined towards photodegradation of methylene blue (MB) dye solution under ambient condition using 80 W Mercury vapour lamp as UV source. Typically, 100 mg of the photocatalyst was dispersed in 100 ml of MB aqueous solution with known concentration. The system was magnetically stirred in the absence of source light for 30 min to ensure that it attains the adsorption saturation. After that the suspension is exposed to the UV irradiation for 1 h. An aliquot part of 2 ml was withdrawn for every 10 min time interval and suspended photocatalysts were removed from the aqueous solution by ultracentrifugation. The residual concentration of MB dye in the solution was analyzed using UV–vis spectrophotometer. The photodegradation efficiency can be calculated using the equation (1) given below

\[ \text{Degradation}\% = \frac{C_0 - C_t}{C_0} = \frac{A_0 - A_t}{A_0} \]  

(1)

Where, \( C_0 \) and \( A_0 \) are concentration and absorption of MB at time 0, whereas \( C_t \) and \( A_t \) are concentration and absorption of MB at a certain time \( t \), respectively.

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3. Results and discussion

3.1. Structural and vibrational analysis

Figure 1(A) shows the P-XRD survey spectra of Ag-ZnO NCs. All the three samples exhibit the Bragg’s angles at $2\theta = 31.7^\circ$, 34.3$^\circ$, 36.2$^\circ$, 47.5$^\circ$, 56.5$^\circ$, 62.7$^\circ$, 66.2$^\circ$, 67.8$^\circ$, 69.0$^\circ$ and 72.6$^\circ$ can be assigned to wurtzite structured ZnO (JCPDS No. 36–1451) and their corresponding reflecting planes are (100), (002), (101), (111), (110), (103), (112), (201), (004), and (202) respectively. Furthermore, two additional peaks observed at 38.0$^\circ$, 44.2$^\circ$, 46.5$^\circ$ and 76.9$^\circ$ which corresponds to (100), (200), (220) and (311) planes of FCC structure of Ag (JCPDS No. 04-0783). Figure 1(B) shows the enlarged regional XRD patterns of the sample within the $2\theta$ angle of 36$^\circ$–38$^\circ$. From the figure, in comparison with AZ1:2 NC, the peak intensity of Ag in AZ1:1 and AZ2:1 NCs found to change gradually. Meanwhile, the peak intensity of (101) plane of ZnO was also found to be deteriorated in sequence. No characteristic peaks from any other impurity phases of ZnO or Ag were identified from the XRD pattern. It should be noted that, no remarkable shifts were observed in the Bragg’s angles and their corresponding crystallographic parameters of ZnO, implying that Ag did not incorporate into the ZnO crystal lattice, but could be deposited on the surface of ZnO as described previously. The average crystallite sizes of Ag-ZnO NCs were calculated using Debye–Scherrer formula to be 45 nm, 52 nm and 43 nm for AZ1:1, AZ1:2, and AZ2:1, respectively.

Figure 1(B) shows the FTIR spectrum of AZ1:1, AZ1:2, and AZ2:1 NCs. The Absorption bands centered at 3474 cm$^{-1}$, 1615 cm$^{-1}$, and 1389 cm$^{-1}$ are attributed to stretching vibration of O–H group of residual water molecules caused by surface absorbed moisture onto ZnO surface [23, 24]. A significant band located at 518 cm$^{-1}$ indicated the characteristic stretching mode of ZnO [25]. No other vibrational modes related with interaction between Ag and ZnO were detected, indicating that there is no bond formation occurred between Ag and ZnO [26].

To clarify the elemental and chemical states of pure Ag and AZ1:1 NC, XPS analysis is conducted and the corresponding results are shown in figure 2. The XP spectra of pure Ag (figure 2(A)) showing that the material contains only Ag and C. All peaks for AZ1:1 NC (figure 2(B)) was assigned to Zn, O, Ag and C. No other peaks corresponding to any other element was observed, which confirmed the purity of synthesized samples. The existence of the carbon element could be ascribed to the hydrocarbon contaminants occurred on vacuum treatment before the XPS test. High resolution spectra of Ag3d species obtained from the pure Ag and AZ1:1 NC is presented in figure 2(C). The spectra depicted two intense peaks at 368.5 and 374.5 eV are ascribed to the binding energies of Ag 3d$_{5/2}$ and Ag 3d$_{3/2}$, which corresponds to the zero valence state of silver. It can be found that the peak positions of Ag 3d remains unchanged in pure Ag and AZ1:1 NC, which suggested that there is no possible interaction between Ag and ZnO in the composite which is consistent with XRD and FTIR studies. Figures 2(D) and (E) shows the high resolution XP spectra of the Zn 2p, and O 1 s core levels, respectively. The two peaks appearing in figure 2(D) were centered at 1022.6 and 1045.6 eV, which were assigned to Zn 2p$_{3/2}$ and Zn 2p$_{1/2}$. In figure 2(E), the O 1 s profile can be deconvoluted into two asymmetrical peaks. The peak at 531.6 eV corresponded to the chemisorbed oxygen of the surface hydroxyls and the 530.1 eV peak is associated with the lattice oxygen of ZnO [27, 28]. These binding energy values and XRD results unambiguously confirm that Ag is

Figure 1. (A) PXRD pattern (B) Enlarged view of (101) and (100) peaks and (C) FT-IR spectra of AZ1:1, AZ1:2 and AZ2:1 NCs.
present only in the metallic form. The valence band maximum position for AZ1:1 was determined using the high-resolution XP valence band spectra (figure 2) and it measured to be 2.50 eV.

3.2. Morphological analysis

Figure 3 shows the FESEM image of AZ1:1, AZ1:2 and AZ2:1 NCs. All the three NCs exhibit similar surface morphologies. It clearly shows that the tiny Ag platelets were densely aggregated on the surface of ZnO nanorods. Further, the EDAX profile of AZ1:1 (figure 3(D)) clearly depicts the appearance of all expected elements in the results, i.e., Zn, Ag, and O and no other foreign contaminants were detected, confirming the prepared NC was free from impurities.

The structure of the samples were further characterized by TEM. As displayed in (figure 4), the structure of ZnO mainly consists of microrods with mean particle size of approximately 130–150 nm in diameter and 250–300 nm in length. It also reveals smaller Ag NPs with typical size of 70–90 nm in diameter distributed partially over the surface of ZnO microrods.

3.3. Optical properties

Figure 5(A) represents the UV–vis–diffuse reflectance spectra of Ag/ZnO NCs. From the figure, it is clear that all the Ag/ZnO NCs shows high reflectance in visible region and low reflectance in UV region with minimum reflectance ($\lambda_{\text{min}}$) observed at a wavelength of 374, 350 and 353 nm for AZ1:1, AZ1:2 and AZ2:1, respectively. This indicates that the absorption band edge was more active in UV region and the band gap values of Ag/ZnO NCs...
were calculated based Kubelka-Munk function. It showed in figure 5(B), that the band gap energy of AZ1:1, AZ1:2, and AZ2:1 was measured as 3.01, 3.09 and 3.05 eV respectively. However, these results revealed that the incorporation of Ag did not widely change the band structure, provides additional evidence for that there is no interaction between Ag and ZnO, which is consistent with the XRD and FTIR outcomes.

Figure 5(C) shows the PL spectra (excitation at 325 nm) of AZ1:1, AZ1:2, and AZ2:1 NCs. It could be seen from figure 5(C), a distinct shift in peak position was observed with AZ1:1, which showed a high intense peak near 410 nm, while AZ1:2 and AZ2:1 showed the intense peak at 380 nm. Excitation of AZ1:1 at 325 nm gave several peaks between 400 nm to 600 nm. The peaks observed < 400 nm is usually attributed to the near band edge (NBE) emission arises from the recombination of free excitons [26]. The peak originated at 410 nm could be ascribed to the radiative defect states. The emission peaks in the visible region (430–550 nm) are generally ascribed to surface defects and ionized oxygen vacancies [29]. Evidently, it can be seen that, the intensity of the peaks were varied with variation of concentration of both ZnO and Ag in our preparation. Moreover, the intensities of PL spectra decreased in the following order AZ1:2, AZ2:1 and AZ1:1, respectively. Thus, it was proven that a minimum intensity of PL spectra means maximum will be the separation effect on the photogenerated electron-hole pairs [30, 31]. These results suggest that AZ1:1 NC could exhibit the best photocatalytic performance in the present case.

3.4. Photocatalytic activity
The photocatalytic activities of AZ1:1, AZ1:2 and AZ2:1 nanocomposites were evaluated by measuring the decolorization at natural pH of dye solution (pH = 6.75), whose results are shown in figure 6. Photodegradation of the dye molecules was observed during every 10 min interval under the UV light irradiation in the presence of...
photocatalysts. It is clear that the AZ1:1 shows remarkable enhancement in photodegradation of compared with AZ1:2 and AZ2:1, which degrade 98.0% of degradation efficiency at a time period of 60 min. But, the AZ1:2 and AZ2:1 could degrade 90.6% and 95.0% of efficiency in the same interval of time. However, the efficiency of photocatalytic activity depends on the appropriate mass ratio of Ag to ZnO. Since the AZ1:2 and AZ2:1 NCs exhibit relatively less photocatalytic activity than AZ1:1, this could be attributed to the aggregation of Ag NPs on the surface of ZnO will hinder the dye adsorption leading to inhibit the degradation process in case of AZ2:1. On the other hand, the excess amount of ZnO makes the degradation of MB over Ag nanoparticles negligible and therefore, it exhibits lower photocatalytic activity compared with other NCs. In other words, higher the content of either Ag or ZnO could be detrimental to the photocatalytic performance. The AZ1:1 NC was therefore the optimum weight ratio in present case and possesses the best performance which is in accordance with optical studies.

3.5. Impact of solution pH

The impact of pH on the rate of degradation of MB was investigated over AZ1:1 NC by altering the range of pH from 2 to 10, with 10 ppm of aqueous MB solution containing 1 g l\(^{-1}\) of catalyst dose and the irradiation time of 60 min as shown in figure 7. It was found that the highest dye removal efficiency (98.8%) was obtained at pH 10 and 98.5% at pH 8, whereas 98.0% of degradation was achieved at natural pH (\(\sim 6.75\)) of dye solution, while the least efficiency of degradation was observed in pH 4 and 2, where the decomposition rate was fell below 50%. The above result indicates that the percentage of degradation was high in alkaline medium. This phenomenon might be explained in terms of type of charge present on the surface of AZ1:1 composite at different pH values. According to literature, the alkaline medium leads the catalyst surface to attain negative charges, hence the cationic MB dye can easily be adsorbed on the catalyst surface due to the electrostatic interaction between them, thereby enhancing the degradation rate. Another possible reason is that under alkaline condition, there will more number of hydroxyl radicals directly available for reaction, hence increase the degradation rate [32, 33]. On the other hand, in the strong acidic medium, the electrostatic repulsion between protonated dye and positively charged catalyst surface cause a reasonable fall in the degradation efficiency. These outcomes were fully supported with previous scientific reports [34, 35].

3.6. Influence of catalyst amount

After the optimization of the pH value, the influence of catalyst concentration was studied by varying the amount of catalyst from 0.5 g l\(^{-1}\) to 1.5 g l\(^{-1}\) containing 10 ppm MB aqueous solution at pH 10. The obtained results were depicted in (figure 8), demonstrated that by increasing the catalyst dosage leads to an increase in degradation efficiency up to 1 g l\(^{-1}\), and a further increase of catalyst dose causes a fall in degradation rate. The reason for above observation could be explained by considering the fact, while initially increasing the catalyst amount up to a certain critical limit, introduces more and more active sites on the catalyst surface that can generate more radical ions in the reaction medium which gave the best degradation rate in the presence 1 g l\(^{-1}\) of
AZ1:1 NC. However, when the quantity of catalyst exceeds this optimum value, the degradation activity was found to be decreased due to hindrance of photons penetration caused by turbidity of suspension at higher concentration and hence reduce the number the photons reaching the overall catalyst active sites effectively and as a result degradation declined [36]. Therefore, 1 g l$^{-1}$ of AZ1:1 NC was taken as optimum dose and applied for further studies.

### 3.7. Impact of initial dye concentration

The influence of initial dye concentration on the rate of degradation was examined by varying the initial concentration from 10 ppm to 30 ppm with optimized parameters stated above, whose results are presented in figure 9. It is obvious that the maximum rate of degradation was obtained for 10 ppm and beyond this limit, the effect is reversed. This abatement is may be due to blanket effect under the high concentration of dye. At this condition more dye molecules were adsorbed on the catalyst surface and acted as a screen for the incoming photons and prevents them to reach the catalyst surface. Hence, reduced the formation of active radicals (O$_2^-$ and OH) in the reaction medium which are responsible for the degradation process and thereby decrease the degradation rate at elevated concentrations.
3.8. Kinetic studies

The kinetics of the reaction for the photodegradation of MB was investigated with AZ1:2, AZ2:1, and AZ1:1 catalyst as a function of time by a pseudo-first order kinetics (equation (2)).

\[
\ln \left( \frac{C}{C_0} \right) = -kt
\]

where \(C\) and \(C_0\) are the concentrations of MB at time \(t\) and \(t_0\) respectively, \(k\) is the apparent first order rate constant.

The plot of \(-\ln \left( \frac{C}{C_0} \right)\) against time was found to be fit in straight line as shown in figure 10. This signifies that the photodegradation reaction obeys pseudo–first order kinetics [37, 38]. The apparent rate constant values obtained were 0.0009367, 0.00535 and 0.01066 min\(^{-1}\), for AZ1:2, AZ2:1, and AZ1:1, respectively. The observed results show that AZ1:1 nanocomposite exhibits higher catalytic activity compared to AZ1:2 and AZ2:1.

3.9. Stability and recycling capabilities

The photo-stability and reusability of AZ1:1 NC against degradation of MB was also evaluated, for this the catalyst was recycled and reused for four successive cycles with same physical parameters. The results are shown in figure 11. At the end the fourth cycle, the photocatalytic degradation efficiency was found to be significantly...
high without negligible or no deterioration in its performance. It clearly demonstrates that AZ1:1 NC can be beneficial for recycling and reusability applications.

Finally, several studies have investigated the catalytic efficiency of different materials for Methylene Blue degradation from aqueous solutions, as shown in table 1. The results reveal that the Ag/ZnO composite prepared in this work has an outstanding catalytic performance for removal of Methylene Blue in water under UV irradiation.

3.10. Band structure of AZ1:1 NC and mechanism analysis
The electronic band structure of the AZ1:1 photocatalysts can be predicted using optical analysis and XPS [43]. The valence band measured using valence band XPS confirmed the valence band maximum position of AZ1:1 to be 2.50 eV (figure 2(E)). UV–visible DRS analysis showed that AZ1:1 NC had a band gap of 3.01 eV (figure 5(B)). The conduction band minimum of the photocatalysts can be determined by subtracting the band gap from the valence band maximum energy. Combining these results, the conduction band minimum energy for AZ1:1 NC was calculated to be −0.51 eV. Based on these observations, scheme 1(A) presents a schematic diagram of the band structure of the AZ1:1 photocatalyst.

The photocatalytic process of Ag/ZnO heterostructures support under UV light irradiation is based on the mechanism related to the photo-induced charge generation, separation and migration at Ag/ZnO interfaces [45]. Normally, when two materials with different work functions are combined with each other, a Schottky barrier will be established and electrons will transfer from the materials with a low work function to the materials with a high work function. The Fermi energy of Ag is higher than that of ZnO due to the larger work function of ZnO [46]. This leads to the transfer of electrons from the Fermi level of Ag to the Fermi level of ZnO, until the two levels reach equilibrium and form a new Fermi energy level [47]. As shown in scheme 1(B), in Ag/ZnO NC, Ag NPs (equation (1)) can absorb UV light to produce plasmon-induced electrons and holes. The UV light driven photocatalysis of Ag/ZnO heterostructures is initiated from the Ag component as illustrates in scheme 1(B). When they are illuminated by UV radiation, the equilibrated Fermi level electrons are excited into the ZnO conduction band via surface plasmon resonance (SPR) oscillations of Ag nanostructures through the electric force driven by the incident photons. The conduction band (CB) and valence band (VB) energy levels of ZnO were calculated ca. −0.51 and 2.5 eV versus SHE, respectively. The plasmon-induced electrons of Ag nanoparticles and photoexcited of MB dye will be quickly injected into the conduction band of ZnO (equation (2)). From the photochemistry point of view, it was possible to reduce O$_2$ to O$_2^-$, E$^\circ$(O$_2$/O$_2^-$) = −0.28 V SHE) [48] through one electron reduction process because the CB potential of ZnO (−0.51 eV versus SHE) was more negative than the single electron reduction potential of oxygen (equation (3)). The photogenerated holes from the valence band of ZnO (+2.5 eV) or Ag NPs produce of OH of H$_2$O by oxidizing holes and produced radicals can be effective for the degradation of organic pollutants (equations (4)–(6)).

\begin{align*}
\text{O}_2 + 2e^- + 2H^+ \rightarrow \text{H}_2\text{O}_2 \quad \text{(1)}
\end{align*}

\begin{align*}
\text{O}_2 + 2e^- \rightarrow \text{O}_2^- \quad \text{(2)}
\end{align*}

\begin{align*}
\text{O}_2 + 4e^- + 4H^+ \rightarrow 2\text{OH}_2^- \quad \text{(3)}
\end{align*}

\begin{align*}
\text{H}_2\text{O}_2 + 2e^- \rightarrow 2\text{OH}^- \quad \text{(4)}
\end{align*}

\begin{align*}
\text{OH}^- + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{OH}^- \quad \text{(5)}
\end{align*}

\begin{align*}
\text{H}_2\text{O}_2 + \text{OH}^- \rightarrow 2\text{OH}_2^- \quad \text{(6)}
\end{align*}

The possible, taking place photoreaction equations were listed following:
Table 1. Photodegradation performance of different catalysts for Methylene Blue.

| Catalyst                      | Technique      | Operating conditions                                      | Removal efficiency (%) | References |
|-------------------------------|----------------|-----------------------------------------------------------|------------------------|------------|
| Ag doped ZnO NPs             | Photocatalysis | UV light, [MB]$_o$ = 20 ppm, Catalyst dosage = 20 mg      | 92.4% degradation within 150 min | [39]       |
| Ag@Ag doped ZnO NC           | Photocatalysis | UV light, [MB]$_o$ = 5 ppm, Catalyst dosage = 200 mg      | 98.6% degradation within 90 min | [40]       |
| ZnO/Ag$_2$O/NDC NC           | Photocatalysis | Visible light, [TC]$_o$ = 30 ppm, Catalyst dosage = 1000 mg | 90.7% degradation within 90 min | [41]       |
| Ag/ZnO core–shell NPs        | Photocatalysis | Sunlight, [MB]$_o$ = 0.15 ppm, Catalyst dosage = NA       | 95.8% degradation within 80 min | [42]       |
| PbS NPs                      | Photocatalysis | UV light, [MB]$_o$ = 10 ppm, Catalyst dosage = 50 mg       | 75.9% degradation within 180 min | [43]       |
| Ag/ZnO NC                    | Photocatalysis | UV light, [MB]$_o$ = 30 ppm, catalyst dosage = 7.5 mg.     | 83.5% degradation in 60 min | [44]       |
| Ag/ZnO NC                    | Photocatalysis | UV light, [MB]$_o$ = 10 ppm, catalyst dosage = 1000 mg.    | 98.8% degradation in 60 min | This work  |
Ag NPs + hv(UV light) → Ag NPs(h+ + e−)  

Ag NPs(e−) + ZnO → ZnO(e− CB) + Ag NPs(h+)  

O2 + ZnO(e− CB) → O2− + ZnO(E0 = −0.28V, versus SHE)  

H2O + h+(Ag NPs or ZnO) → OH + H+(E0 = 2.27V, vs SHE)  

Dyes + O2 −→ OXProd.  

Dyes + OH −→ OXProd.

4. Conclusions

In summary, Ag-ZnO NCs were successfully synthesized by wet impregnation method. Physico-chemical properties of prepared NCs were studied using PXRD, FTIR, FESEM, TEM, EDAX, UV-Vis-DRS and PL techniques. PXRD patterns of NCs shows the synthesized ZnO was hexagonal wurtzite structure. FTIR spectra reveal that no bond formation occurs between Ag and ZnO in the NC. FESEM image confirm the existence of tiny Ag platelets were densely aggregated on the surface ZnO microrods and TEM displayed that Ag nanoparticles were partly distributed on the surface ZnO microrods. DRS spectra shows high reflectance in visible region and low reflectance in UV region, presenting the catalysts was more active in UV region. PL spectra shows near band edge emission of ZnO and also an increase in separation of electrons and holes in the Ag-ZnO NCs. Moreover, the Ag-ZnO NCs exhibits excellent photocatalytic performance towards degradations of MB removing more than 90% of dye in all cases under consideration, implying the potential viability of system for treating toxic contamination in waste water treatment. In fact, AZ1:1 exhibits the enhanced photocatalytic activity toward MB degradation (98.8%) under UV irradiation with the high-rate constant of 0.01021 min−1, which presenting the importance of synthesis optimal parameters (i.e., the dependence on the proportion of Ag and ZnO in the composite) and its influence in the catalytic performance of the system.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).
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References

[1] Chatterjee D and Dasgupta S 2005 J. Photochem. Photobiol., C 6 186
[2] Ramaswamy V, Jagtap N B, Vijayanand S, Bhanage D S and Awati P S 2008 Mater. Res. Bull. 43 1145
[3] Luo Q P, Lei B X, Yu X Y, Kuang D B and Su C Y 2011 J. Mater. Chem. 21 8709
[4] Kim Y S and Kang S H 2011 Nanotechnology 22 235707
[5] Andrade G R, Nascimento C C, Lima Z M, Teixeira-Neto E, Costa I P and Gimenez I F 2017 Appl. Surf. Sci. 399 573
[6] Li S, Ma Z, Zhang J, Wu Y and Gong Y 2008 Catal. Today 139 109
[7] Kuriakeo S, Choudhary V, Satpati B and Mohapatra S 2014 Beilstein J. Nanotechnol. 5 639
[8] Han Z, Ren L, Cui Z, Chen C, Pan H and Chen J 2012 Appl. Catal. B-Environ. 126 298
[9] Yildirim O A, Unalan H E and Durucan C 2013 J. Am. Ceram. Soc. 96 766
[10] Lu Y, Lin Y, Wang D, Wang L, Xie T and Jiang T 2011 J. Phys. D: Appl. Phys. 44 315502
[11] Liu Y, Wei S and Wei G 2015 J. Hazard. Mater. 287 59
[12] Wang M S, Zhang Y P, Zhou Y J, Yang F W and Seong S G 2013 Cryst Eng Comm. 15 1754
[13] Misra M, Kapur P, Nayar M K and Singla M 2014 New J. Chem. 38 4197
[14] Chen D M, Wang K W, Yao W Q and Zhu Y F 2014 Appl. Catal. B-Environ. 147 554
[15] Fu H, Xu T, Zhu S and Zhu Y 2008 Environ. Sci. Technol. 12 8064
[16] Georgekutty R, Seery M K and Pillai S C 2008 J. Phys. Chem. C 112 13563
[17] Kamat P 2002 J. Phys. Chem. B 106 7729
[18] Suh H M S, Choi J R, Hah H J, Koo S M and Bae Y C 2004 J. Photoch. Photobiol. A. 163 37
[19] Zhang Q, Liu J K, Wang J D and Luo H X 2014 Ind. Eng. Chem. Res. 53 13236
[20] Fu Q and Wagner T 2007 Surf. Sci. Rep. 62 431
[21] Zeng H, Cai W, Liu P, Xu Z, Zhou H, Kleinhans C and Kalt H 2008 ACS Nano. 2 1661
[22] Barreca D, Gasparotto A and Tondello E 2011 J. Mater. Chem. 21 1648
[23] Tian Q, Wu W, Yang S, Liu J, Yao W, Ren F and Jiang C 2013 Nanoscale Res. Lett. 12 221
[24] Guo X, Fu Y, Hong D, Yu B, He H, Wang Q, Xing L and Xue X 2016 Nanotechnology 27 375704
[25] Moussa H, Girot E, Mozet K, Alem H, Medjahdi G and Schneider R 2016 Appl. Catal. B-Environ. 185 11
[26] Subhban M A, Awal M R, Ahmed T and Younus M 2014 Acta Metall Sin-Engl. 27 223
[27] Sankar Ganesh R, Navaneethan M, Patil V L, Premnam S P, Muthamizhchelvan C, Kawasaki S, Atil P S P and Hayakawa Y 2018 Sens. Actuators B: Chem. 255 672
[28] Zare A, Saadati A and Shilbani S 2023 Mater. Res. Bull. 158 112048
[29] Ahmad M, Ahmed E, Hong Z L, Khalid N R, Ahmed W and Elhissi A 2013 J. Alloys Compd. 577 717
[30] Khan M M, Ansari S A, Amal M I, Lee J and Choa M H 2013 Nanoscale 5 4427
[31] Liqiang J, Yichun Q, Baiqi W, Shudan L, Baojiang J, Libin Y, Wei F, Honggang F and Jiazhon S 2006 Sol. Energy Mater. Sol. Cells 90 1773
[32] Meshesha D S, Matangi R C, Tirukkovalluri S R and Bojja S 2017 J. Asian Ceram. Soc. 5 136
[33] Vasiljevic Z Z, Dojcinovic M P, Vujanic J D, Costaj A, Ognjanovic M, Tadic N B, Stojadinovic S, Brankovic G O and Nikolic M V 2020 R. Soc. Open Sci. 7 200706
[34] Priyadharshini S S, Shubha P, Shivlingasingha J, Adil S F, Kuniyi M, Hatsman M R, Shaik B and Kavalli K 2002 Crystals 12 22
[35] Parvizi E, Tayebee R, Koushacki E, Abidzadeh M F, Maleki B, Audebert P and Galmiche L 2019 RSC Adv. 9 23818
[36] Paul D R, Sharma R, Nehra S P and Sharma A 2019 RSC. Adv. 9 15381
[37] Guo H, Ke Y, Wang D, Lin K, Shen R, Chen J and Weng K 2013 J. Nanopart. Res. 15 1457
[38] Zhang H, Liu D, Ren S and Zhang H 2017 Res. Chem. Intermed. 43 1529
[39] Saravanadevi K, Kavitha M, Karpagavayagam P, Srinivasaiah K and Vedhi C 2022 Mater. Today Proc. 48 352
[40] Yousefi H R and Hashemi B 2019 J Photochem Photobiol A Chem. 375 71
[41] Alhokhany N, Ahamed T and Alshehri S M 2022 J. Environ. Chem. Eng. 10 107681
[42] Rajbongshi H, Bhattacharjee S and Datta P 2017 Mater. Res. Express 4 022501
[43] Aijbade P A, Mbuyazi T B and Oluwalana A E 2021 J. Inorg. Organomet. Polym. Mater. 31 2197
[44] Zhang Y, Liu H, Zhang J, Dong H, Liu X, Jia H and Xu B 2014 Superlattices Microstruct. 65 134
[45] Xu J, Teng Y and Teng F 2016 Sci Rep. 6 32457
[46] Liu Y, Wei S and Gao W 2015 J. Hazard. Mater. 287 59
[47] Zhang X, Chen Y L, Liu R Sh and Tsai D P 2013 Rep. Prog. Phys. 76 046401
[48] Liang Y, Guo N, Li L, Li R and Gan S 2015 Appl. Surf. Sci. 332 32