Ag$_2$S-Sensitized NiO–ZnO Heterostructures with Enhanced Visible Light Photocatalytic Activity and Acetone Sensing Property

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Supporting Information

ABSTRACT: Visible light-driven Ag$_2$S-grafted NiO–ZnO ternary nanocomposites are synthesized using a facile and cost-effective homogeneous precipitation method. The structural, morphological, and optical properties were extensively studied, confirming the formation of ternary nanocomposites. The surface area of the synthesized nanocomposites was calculated by electrochemical double-layer capacitance ($C_{dl}$). Ternary Ag$_2$S/NiO–ZnO nanocomposites showed excellent visible light photocatalytic property which increases further with the concentration of Ag$_2$S. The maximum photocatalytic activity was shown by 8% Ag$_2$S/NiO–ZnO with a RhB degradation efficiency of 95%. Hydroxyl and superoxide radicals were found to be dominant species for photodegradation of RhB, confirmed by scavenging experiments. It is noteworthy that the recycling experiments demonstrated high stability and recyclable nature of the photocatalyst. Moreover, the electrochemical results indicated that the prepared nanocomposite exhibits remarkable activity toward detection of acetone. The fabricated nanocomposite sensor showed high sensitivity (4.0764 μA mmol L$^{-1}$ cm$^{-2}$) and a lower detection limit (0.06 mmol L$^{-1}$) for the detection of acetone. The enhanced photocatalytic and the sensing property of Ag$_2$S/NiO–ZnO can be attributed to the synergistic effects of strong visible light absorption, excellent charge separation, and remarkable surface properties.

1. INTRODUCTION

Environmental imbalance due to fading of natural resources, rise in greenhouse gases, and growing pollution through urbanization and industrialization is a global concern. The unchecked and untreated discharges into the environment pose serious threat to both biotic and abiotic components of the environment. Researchers across the globe have devoted their efforts to check these issues by developing smarter and advanced technologies for sustainable future. From past few decades, semiconducting metal oxide nanostructures have received considerable attention owing to their novel characteristics and potential applications. The distinguished features of the metal oxide nanomaterials are remarkably assessed for remediation of the environment through various processes such as photocatalysis, hazardous chemical sensing, wastewater decontamination, and solar energy conversion and storage.

Semiconductor nanomaterials have the potential to degrade organic pollutants such as textile dyes, drugs, and fertilizers and to simultaneously find excellent applications such as chemosensors for the detection of acetone, formaldehyde, ammonia, LPG, and alcohols.

Semiconductor photocatalysis is the advanced oxidation technique to be researched for the treatment of multiple contaminants including textile dyes, pesticides, and biphenyls. Semiconductor photocatalysis, an advanced oxidation process, involves the formation of highly reactive species upon absorption of light, which can degrade the plethora of pollutants. However, the large band gap semiconductors suffer a drawback, that is, they absorb UV light which is only 4% of the solar spectrum. To shift the absorption of these semiconductors to the visible region, several procedures are followed, such as metal ion doping, formation of polymer nanocomposites, and metal organic frameworks. To further improve the visible light response and photocatalytic performance, ternary composites are preferred. Ternary nanocomposites are promising materials for usage as photocatalysts, electrochemical sensors, and energy storage devices and exhibit improved light absorption and power density, improved stability, and better catalytic activity.

Semiconductor nanomaterials have also been studied as chemosensors because of their remarkable variation in electrical resistance on exposure to target analytes and excellent chemical stability. An ideal chemosensor is one which operates at room temperature, possesses high sensitivity and reproducibility, fast response and recovery time, low detection limit, and low cost, and is eco-friendly. Nanomaterials have been utilized as effective and efficient chemical sensors for the detection of hazardous and toxic volatile organic compounds (VOCs) from the environment. Semiconducting metal oxides such as SnO$_2$, ZnO, In$_2$O$_3$, TiO$_2$, NiO, and Fe$_2$O$_3$ have been investigated as potential sensors for the detection of toxic chemicals from the environment. Chemosensors based on heterostructured...
nanomaterials have received much attention as compared to enzymatic sensors owing to their reliable, sensitive, simpler, and economical approach.36–38

ZnO is a n-type semiconductor with a wide band gap of 3.3 (eV) having high electron mobility. ZnO turns out to be an efficient photocatalyst for pollutant degradation because of its excellent redox properties.37,38 Moreover, ZnO has been studied in chemical sensing because of its intriguing properties such as low cost, good thermal and chemical stability, and better electronic properties. However, because of wide band gaps, absorption is restricted to the UV region.39 On the other hand, NiO is a p-type semiconductor with a wide band gap of 3.4 (eV) having high hole concentration. NiO promotes the interfacial charge transfer and finds extensive application in chemical and gas sensing, heterogeneous catalysis, photocatalysis, and magnetism.40–45 Formation of a heterojunction between n-type and p-type semiconductors is an effective strategy to avoid charge carrier recombination and simultaneously improves its photocatalytic and sensing performance. The heterostructures show enhanced electrical properties for chemical and gas sensing, photocatalysis, and fuel cell electrodes. In photocatalysis, fast recombination of electron–hole pairs can be suppressed and the efficiency of net charge transfer in the reaction system can be improved by forming heterostructures.46,47 In chemosensing, combining n- and p-type nanostructures leads to the formation of a more extended depletion layer, thus improving sensitivity and response time.48

Ag2S, a low band gap semiconductor (1.1 eV), has been widely used in several fields such as photography, IR detectors, photoconductors, electrochemical sensing, and photocatalysis because of its excellent and efficient photooxidative properties.49–52 Moreover, Ag2S has high absorption coefficient and possesses negligible toxicity compared to other narrow band gap materials.53,54 Owing to its remarkable properties such as chemical stability, narrow band gap, high absorption coefficient, and excellent optical and electronic properties, surface plasmon resonance (SPR), a ternary nanocomposite, was made by coupling it with a semiconductor binary metal oxide, which will facilitate separation of photoinduced charge carriers and show efficient electronic properties and strong absorption in visible light because of localized SPR (LSPR) effect.55

In the present study, the facile synthesis of p–n heterojunction between n-type ZnO and p-type NiO (NZ) by low cost and a simple precipitation method was reported. The as-prepared binary metal oxide was further grafted by Ag2S to form Ag2S/NiO–ZnO (AZN) ternary nanocomposites. The prepared ternary nanocomposite had some advantages over binary metal oxides as surface plasmon resonance of Ag, enhancing the visible light absorption and electronic properties of the ternary nanocomposite. The enhancement in the visible light photocatalytic efficiency, effective charge separation, and simultaneously better electronic properties can make the synthesized nanocomposite a potential photocatalyst and a good chemosensor. The photocatalytic performance of the fabricated ternary nanocomposite was tested with the photodegradation of rhodamine B (RhB) dye in the aqueous phase under visible light. The electrochemical sensing activity of the prepared ternary nanocomposite was investigated by cyclic voltammetry (CV) against acetone. The probable mechanism of dye degradation and sensing of acetone were discussed. The fabricated composite is expected to show high photocatalytic and sensing property. The stability and sensitivity of the prepared composite were also investigated.

2. RESULTS AND DISCUSSION

2.1. Fourier Transform Infrared Spectroscopy. Fourier transform infrared spectroscopy (FTIR) was used to identify the characteristic functional groups in the as-prepared nanocomposites. The samples are dried and mixed with KBr to form pellets, which were then analyzed by FTIR. The FTIR spectrum of the prepared samples is displayed in Figure 1. The characteristic broad peaks around 3400–3500 cm−1 depict O–H stretching of the water molecule. The peaks around 400–600 cm−1 arise because of M–O and O–M–O (M = Ni, Zn, Ag) vibrations.56 The characteristic peak for Ni–O and Zn–O metal–oxygen vibrations arises at 432 and 490 cm−1, respectively.

The peaks in the wavenumber range of 1000–1250 cm−1 are attributed to S–O vibrations and are clearly seen in AZN nanocomposites. The peaks around 1186–1224 and 1018–1095 cm−1 correspond to asymmetric valence vibrations and symmetric valence vibrations of the S–O bond, respectively.57,58 The characteristic band for Ag–S vibration occurs at a wavenumber (237 cm−1) much lower than M–O vibrations.59,60

2.2. XRD Analysis. The XRD patterns of pure ZnO, pure NiO, pure Ag2S, NZ, and AZN nanocomposites with different weight percentages of Ag2S are depicted in Figure 2. The XRD peaks of pure NiO with 2θ values of 37.0°, 43.1°, and 62.7°, corresponding to the crystal planes (111), (200), and (220), respectively.
respectively, are in good agreement with the face-centered cubic structure of NiO (COD 4329325). It is clear from the figure that no peaks of Ni(OH)₂ are observed, suggesting complete decomposition of Ni(OH)₂ into NiO.⁶¹

The diffraction peaks of ZnO centered at 2θ values of 31.9°, 34.5°, 36.3°, 47.6°, 56.8°, 62.9°, 68.0°, and 69.1° with the crystal planes (100), (002), (101), (102), (110), (103), (200), and (112), respectively, are consistent with the hexagonal crystal planes (100), (002), (101), (102), (110), (103), (200), and (112), respectively, are consistent with the hexagonal structure of ZnO (COD 9011662).

The NZ nanocomposite exhibits the coexistence of peaks from both NiO and ZnO. Compared with the NZ nanostructure of ZnO (COD 9011662).

The crystallite size of the prepared samples was elucidated from the Scherrer formula shown in eq 1

\[ D = \frac{k\lambda}{\beta \cos \theta} \]  

where \( k \) is a constant equal to 0.9, \( D \) is the crystallite size, \( \lambda \) is the wavelength of X-ray equal to 1.5406 Å, \( \beta \) is the full width at half-maximum, and \( \theta \) is the Bragg angle.

As evident from Table 1, the average crystallite size of the AZN catalyst decreases with increase in the amount of Ag₂S up to 8%, suggesting high dispersion of Ag₂S in the nanocomposite.

Table 1. Average Particle Size of Pure and Composite Samples

| Prepared Samples | Peak Chosen (2θ) | Average Particle Size (nm) |
|------------------|------------------|---------------------------|
| ZnO              | 36.303           | 48.8                      |
| NiO              | 43.326           | 24.3                      |
| Ag₂S             | 34.406           | 28.1                      |
| NZ               | 36.303           | 31.7                      |
| AZN-6            | 36.303           | 30.5                      |
| AZN-8            | 36.303           | 29.4                      |

2.3. Optical Properties. The UV-diffuse reflectance spectra (DRS) curves of ZnO, NiO, NZ, and AZN-8 are presented in Figure 3. The optical absorbance shown by ZnO and NiO lies below 400 nm that depicts absorption in the ultraviolet region. With the formation of a binary metal oxide (NZ), the absorbance was slightly shifted toward longer wavelength. However, upon introduction of Ag₂S, the composite showed greater absorption and the absorbance edge was shifted to the visible region (red shift). This suggests that grafting of Ag₂S on the surface of the binary metal oxide improved the absorption properties of the AZN nanocomposite and might be the reason for better catalytic activity of AZN photocatalysts under UV-visible light.

The optical band gaps of NZ and AZN were determined by eq 2 given by Butler.

\[ h\nu \alpha = (A\nu - E_g)^{n/2} \]  

On transforming eq 2 to the Kubelka–Munk function form, the expression becomes

\[ h\nu F(R) = (A\nu - E_g)^{n/2} \]  

where \( F(R) \) is the Kubelka–Munk function, \( \nu \) is the frequency, \( E_g \) is the band gap energy, and \( A \) is the proportionality constant. The value of \( n \) depends upon the type of transition \( (n = 1 \) for direct and indirect transitions, respectively). Herein, we plotted \( (F(R) \times h\nu)^{1/2} \) versus \( h\nu \) for both NZ and AZN, and the optical band gaps were calculated to be 3.0 and 2.399 eV, respectively.

2.4. Microscopic Studies. The surface nanostructures of the prepared samples were studied with the help of scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), and transmission electron microscopy (TEM). The typical SEM micrographs of NZ and AZN nanocomposites at different magnifications are shown in Figure 4a,b. It is clear from Figure 4b that the particles of the NZ nanocomposite show uniform size, high porosity, and perfect hollow nanospheres. The porous nature of the nanocomposite is highly desirable for better photocatalytic activity.⁶³ After impregnation of Ag₂S into the NZ binary oxide, the morphology of nanocomposites changed and is clearly depicted in Figure 4c,d. The Ag₂S nanoparticles are randomly scattered on the surface of NZ, providing more surface area and greater reactive sites and subsequently enhancing its activity. The surface becomes irregular and the particle size
decreases after coupling of Ag2S into the binary metal oxide. This shows concurrence and nanocomposite formation between NZ and Ag2S.

The elemental composition of NZ and AZN nanocomposites was determined by EDS analysis, and the spectrum is shown in Figure 4e,f. The EDS spectrum of NZ shows the presence of Ni, Zn, and oxygen (Figure 4e), whereas the EDS spectrum of AZN shows, in addition to Ni, Zn, and oxygen, that Ag and sulfur are also present (Figure 4f). To further confirm the dispersion of Ag2S in the host matrix, the EDS elemental mapping of the AZN-8 nanocomposite was performed. It can be depicted from Figure 5d that Ag (Figure 5d) and S (Figure 5b) are highly dispersed in the AZN-8 nanocomposite.

The morphological characterization was further investigated by TEM analysis. The TEM images of the NZ nanocomposite (Figure 6a,b) depict the perfect spherical (NiO) and hexagonal (ZnO) shapes of the particles. Moreover, the shape of the AZN nanocomposite (Figure 6c,d) shows the irregular distribution of Ag2S nanoparticles on the surface of NZ. The rough surface of NZ decorated with Ag2S is clearly visible, which dictates the nanocomposite formation and improves its activity.

2.5. Electrochemical Surface Area Measurement. The surface area of the synthesized nanocomposites (NZ and AZN) was calculated by electrochemical double-layer capacitance (EDLC, Cdl)64,65. For the measurement of the active surface area, CV was performed in the non-faradaic potential range of 0.1−0.2 V with varying scan rates (10−80 mV s−1) (Figure 7a). The linear slope of the plot (capacitive currents vs scan rates) was used to represent the surface area and is equal to twice the double-layer capacitance (Cdl). The Cdl is supposed to be linearly proportional to active sites, and the number of active sites often scales to the surface area of the catalyst. The electrochemical surface areas of NZ and AZN-8 nanocomposites were found to be 0.000723 and 0.007452 F cm−2, respectively (Figure 7b). The high surface area of AZN-8 nanocomposites, which is almost 10 times more than that of NZ, is consistent with experimental inferences. The greater the surface area of the catalyst, the greater the active sites and the better the catalytic activity will be.66 Thus, AZN-8 nanocomposites are expected to show better photocatalytic and electroanalytic activity because of high electrochemical active surface area.

3. APPLICATIONS

3.1. Photodegradation of Textile Dye. The photocatalytic activity of the prepared catalysts was assessed for decolorization and degradation of organic textile dye, RhB, in aqueous media and in the presence of visible light. Before irradiation, adsorption test was performed in dark to ensure an adsorption−desorption phenomenon. For this, the experiment was carried out in dark for 30 min, and it was found that the concentration of the dye remains unchanged, suggesting insignificant adsorption. The photocatalytic performances of the NZ and AZN nanocomposites with different Ag2S contents under visible light radiation are presented in Figure 8. As depicted from Figure 8c, even after 120 min exposure of visible light without a catalyst, the concentration of the dye remains unaltered, confirming the significance of the photocatalyst in degrading the dye molecule. The degradation efficiency of the NZ nanocomposite was limited because of the poor absorption in the visible region due to higher band gap. The AZN nanocomposites showed enhanced degradation of dye molecules in comparison to NZ. The enhanced photocatalytic performance shown by AZN can be attributed to better absorption in visible light, large surface area, and the separation of photoinduced electron−hole pairs. As the photocatalytic reaction is a surface reaction, the surface properties greatly influence the catalytic efficiency. Also, ternary nanocomposites having three different junctions possess more than one pathway for the generation of electron−hole pairs and their subsequent separation.67

The effect of Ag2S grafting on the NZ nanocomposite for the degradation of RhB molecules is depicted in Figure 8b. It is clearly evidenced that Ag2S loading had a pronounced effect on photocatalytic activity. Initially, with increase of Ag2S content, the photodegradation activity of the nanocomposite increases, but after grafting a certain amount, the activity decreases. The decrease in the activity has been due to agglomeration of
nanoparticles and fast recombination rate of photogenerated electron–hole pairs. The RhB degradation efficiencies of NZ and AZN nanocomposites with Ag₂S percentages of 2, 4, 6, 8, and 10% are shown in Figure 8d. Among all photocatalysts, the optimal photocatalytic activity was shown by AZN-8 with a 95% degradation efficiency in 120 min. It is evident from Figure 8d that the efficiency of RhB degradation for the AZN-8 (95%) nanocomposite is about 2.1 times higher than the NZ (45%) nanocomposite. The degradation of RhB over AZN-8 can be visualized from Figure 8a, which displays the absorption spectral changes of RhB at 554 nm. It can be seen from Figure 8a that the absorption of the dye decreases remarkably with time, followed by a slight shift of absorption maxima toward lower wavelength (blue shift), which shows the gradual destruction and de-ethylation of RhB into its metabolites.

The absorption spectral changes of RhB over the NZ nanocomposite can be seen from the Supporting Information (Figure S1). As the concentration of Ag₂S is increased, the RhB degradation efficiency is increased, suggesting the prominent role of Ag₂S in the photocatalytic activity. The enhanced activity of AZN nanocomposites is due to shift of absorption to longer wavelength on grafting Ag₂S, which increased visible light absorption. The absorption spectra of RhB over AZN-10 and AZN-6 nanocomposites are shown in the Supporting Information (Figure S2).

To study the kinetics of the reaction, the Langmuir–Hinshelwood pseudo-first-order model was tested

$$\ln(\frac{C_0}{C_t}) = K_{app}t$$

where $K_{app}$ is the pseudo-first-order rate constant, $C_0$ is the initial concentration, and $C_t$ is the concentration of the dye after time $t$. The value of $K_{app}$ can be obtained from the first-order linear fit curves (Figure 8c). The apparent rate constants $K_{app}$ (min⁻¹) for various nanocomposite photocatalysts are given in Table 2. It is clear from Table 2 that the rate constant for the AZN-8 nanocomposite photocatalyst is 0.0302 min⁻¹, which is about 6 times higher than the NZ (0.0051 min⁻¹) nanocomposite. This shows that the AZN-8 nanocomposite shows enhanced photocatalytic activity, which may be due to efficient charge separation and strong light absorption.

Figure 5. EDS elemental mapping of the AZN-8 nanocomposite [(a) O, (b) S, (c) Ni, (d) Ag, (e) Zn].

Figure 6. TEM images of NZ (a,b) and AZN-8 (c,d) nanocomposites.

Figure 7. (a) Cyclic voltammograms of AZN-8 at different scan rates (10–80 mV s⁻¹) and (b) capacitive current as a function of scan rate for NZ and AZN-8 nanocomposites.
3.1.1. Mechanism of Photodegradation. To evaluate the mechanism of photodegradation of the dye, the relative position of the valence band (VB) and the conduction band (CB) of ZnO, NiO, and Ag₂S must be known. The approximate energies of VB of ZnO, NiO, and Ag₂S can be investigated by the formula shown below:

\[ E_{\text{VB}} = X - E_C^0 + 0.5E_g \]  

(5)

where \( E_g \) is the forbidden gap energy, \( E_C^0 \) symbolizes the energy of free electron on hydrogen scale (4.5 eV), and \( X \) is the electronegativity of the material expressed in terms of geometric mean of electronegativity of constituent atoms. 

The \( E_{\text{VB}} \) values for ZnO, NiO, and Ag₂S were calculated to be 3.0, 1.95, and 1.1 eV, respectively. The apparent positions of the CB of ZnO, NiO, and Ag₂S were calculated from the equation below

\[ E_{\text{CB}} = E_{\text{VB}} - E_g \]  

(6)

From the equation, the \( E_{\text{CB}} \) values of ZnO, NiO, and Ag₂S were calculated to be \(-0.2\), \(-1.34\), and 0 eV, respectively.

The possible mechanism of the RhB dye degradation over the AZN-8 photocatalyst under visible light irradiation has been given in Figure 9. Upon irradiation of the photocatalyst, the migration of photogenerated charge carriers will occur on the interface of NiO and ZnO. Doping of Ag₂S to NiO–ZnO nanocomposites reduces the band gaps of both NiO and ZnO by shifting the Fermi level of both NiO and ZnO to the visible region. Upon visible light irradiation, the electron from the VB is excited and drifts over the CB. The CB edge potential of NiO is high enough to transfer its electron to the CB of ZnO and Ag₂S, but the CB edge potential of Ag₂S is not enough to produce superoxide (\( \cdot \text{O}_2^- \)) radicals; however, the CB potential of ZnO through the oxidation produces \( \cdot \text{O}_2^- \) radicals by the reaction with the electrons and the atmospheric oxygen. At the same instant, the holes \( h^+ \) generated in the VB of NiO and ZnO will move from the higher positive value to the lower positive value and will go to the VB of Ag₂S. The holes in the VB of Ag₂S will react with the H₂O molecules and produce hydroxide (\( \cdot \text{OH} \)) radicals, and the electron in the CB of ZnO produces \( \cdot \text{O}_2^- \) radicals. The incorporation of Ag₂S into the matrix thus helps to minimize the recombination of photo-initiated reactive species by enhancing the rate of transfer of the electron through the LSPR effect. Therefore, the reactive oxygen species (ROS) generated during the reaction attacked and degraded the complex dye molecules into simpler ones. The photodegradation of the dye molecules under the controlled condition was checked by monitoring the concentration of the aliquots taken out from the photoreaction at regular intervals of time.

The following reactions were involved in the photodegradation process 

\[ \text{NiO/ZnO/Ag}_2\text{S} + h\nu \rightarrow e^-/h^+ (\text{Ag}_2\text{S}) + e^-/h^+ (\text{NiO/ZnO}) \]  

(7)

\[ \text{e}^- + \text{O}_2 \rightarrow \cdot \text{O}_2^- \]  

(8)

\[ \text{h}^+ + \text{H}_2\text{O} \rightarrow \cdot \text{OH} \]  

(9)

\[ \cdot \text{OH}/\cdot \text{O}_2^-/h^+/e^- + \text{dye molecules} \rightarrow \text{degraded product} \]  

(10)

Table 2. Apparent Rate Constant of Different Photocatalysts Obtained from Linear Fit Data

| Catalyst | \( K_{\text{app}} \) (min\(^{-1}\)) |
|----------|-----------------|
| NZ       | 0.0051          |
| AZN-2    | 0.0075          |
| AZN-4    | 0.0103          |
| AZN-6    | 0.0119          |
| AZN-8    | 0.0302          |
| AZN-10   | 0.0192          |
3.1.2. Fluorescence Emission Spectra. In order to examine the recombination rate of photoinduced charge carriers, photoluminescence (PL) spectra were measured. PL spectra have a strong correlation with photocatalytic activity as the spectra originate due to the recombination of charge carriers in semiconductors. The PL intensity is inversely related to photocatalytic activity, that is, higher PL intensity means faster recombination of electron−hole pairs and lower photocatalytic activity and vice versa. The PL spectra of samples at an excitation wavelength of 640 nm are depicted in Figure 10. It can be seen from the figure that the PL intensity of ZnO and NiO is higher because of fast recombination rate, whereas the lower PL intensity was observed for NZ, which is lowered further on adding different contents of Ag2S, owing to separation of charge carriers and better photocatalytic activity. The lower PL intensity is shown by the AZN-8 nanocomposite, which shows better photocatalytic activity among all prepared photocatalysts.

3.1.3. Role of Reactive Species. ROS plays a crucial role in the photodegradation of dye molecules. During the photooxidation reaction, various reactive species are generated including a superoxide radical anion (\(\cdot O_2^-\)), a hydroxyl radical (OH\(^•\)), holes (h\(^+\)), electrons (e\(^−\)), and \(H_2O_2\). The generation of reactive species and subsequently their role depend upon the light source used. To investigate the dominant reactive species involved in the photodegradation of RhB, ROS scavenging experiments with different scavengers over the AZN-8 nanocomposite under visible light were performed. The effect of different scavengers is determined in terms of decrease of the first-order rate constant (\(K_{app}\)) and is depicted in Figure 11. Isopropyl alcohol (IPA) was added to the reaction system to quench (OH\(^•\)) radicals, sodium nitrate was added to quench electrons, whereas ammonium oxalate (AO) and benzoquinone (BQ) were added as hole (h\(^+\)) and superoxide radical anion (\(O_2\cdot^-\)) scavengers, respectively. It is evident from the figure that addition of scavengers had a profound effect on the rate of RhB degradation showing a
substantial decrease. The rate of decrease of RhB degradation with AO was slightly less than IPA, sodium nitrate, and BQ, whereas IPA shows the maximum decrease in the rate of RhB degradation, followed by BQ and sodium nitrate. These results suggest that all the four reactive species are involved in dye degradation, but \( \text{OH}^\bullet \) radicals are the main reactive species in RhB degradation over the AZN-8 catalyst under visible light irradiation. The spectral change of RhB over the AZN-8 nanocomposite in the presence of IPA is shown in the Supporting Information (Figure S3).

### 3.1.4. Recyclability and Stability of the Catalyst.

The reusability and stability of the catalyst are an important factor to determine the reliability of the catalyst for the potential application. To evaluate the stability and durability of the AZN-8 catalyst, cyclic experiments were performed. After each cycle, the photocatalyst was collected by centrifugation and then washed with deionized (DI) water and ethanol repeatedly. As evidenced from Figure 12, after six recycling runs, the efficiency of RhB degradation of the catalyst is maintained at 85%, suggesting only 10% decrease in the efficiency of the catalyst. The slight decrease in the degradation capability of AZN-8 catalysts indicates the high stability and recyclable nature of the catalyst. The decrease in the efficiency of the photocatalyst may be due to weight loss during the washing of the photocatalyst (Table 3).

#### 3.2. Electrochemical Sensing of Acetone Using Cyclic Voltammetry.

Acetone has vast industrial applications and is a commonly used solvent in multiple areas. Because it is colorless and highly volatile, exposure to even parts per million level might cause serious problems such as headache, allergy, fatigue, and narcosis in human beings.\(^{77}\) For patients suffering from diabetes mellitus, sensing of acetone is important to examine the sugar level.\(^{77}\) According to the breath diagnosis report, a healthy human should contain 0.8 ppm and a diabetic patient contains higher than 1.8 ppm of acetone.\(^{77}\) Therefore, a facile and reliable method is needed to quantify traces of acetone present in a particular environment and also in human breath. For this purpose, electrochemical sensing of acetone

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**Table 3. Comparison of Photocatalytic Performance with the Reported Photocatalyst**

| material used           | synthetic route            | light used     | dye degradation | % removal (%) | literature |
|-------------------------|----------------------------|----------------|-----------------|---------------|------------|
| NiO–ZnO heterojunction  | hydrothermal method        | UV–visible     | rhodamine B     | 83            | 73         |
| NiO/CNF/ZnO composite   | chemical vapor deposition  | UV–visible     | rhodamine B     | 78            | 74         |
| NiO–ZnO core–shell heterostructure | electrochemical deposition | UV–visible     | rhodamine B     | 94            | 75         |
| NiO–ZnO–Ag composite    | precipitation method       | UV–visible     | methylene blue  | 94            | 76         |
| Ag\(_2\)S/NiO–ZnO nanocomposite | homogeneous precipitation method | visible light | rhodamine B     | 95            | present work |

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**Scheme 1. Pictorial Representation of GCE (WE) and Possible Mechanism of Acetone Sensing over Pasted GCE**
using surface-coated electrodes [glassy carbon electrode (GCE)] is a promising method over conventional electrochemical methods in terms of sensitivity, reproducibility, and stability. CV proved to be a reliable technique for studying solvent sensing ability of nanomaterials. In the method of quantification, the target analyte is either oxidized or reduced upon application of certain potential, which can be monitored by the corresponding change in current.

The electrocatalytic properties of the NZ and AZN-8 nanocomposites toward acetone detection were examined in 0.1 M phosphate-buffered saline (PBS) buffer at room temperature using CV. The assembly of the working electrode (GCE) and the plausible mechanism of acetone detection are demonstrated pictorially in Scheme 1.

The comparative analysis of electrochemical activity of bare GCE electrode and modified electrode with NZ (NZ/GCE/binder) and AZN-8 (AZN-8/GCE/binder) toward detection of acetone was carried out. Figure 13 represents the cyclic voltammograms of differently modified electrodes toward 0.2 M acetone in 0.1 M PBS at a scan rate of 30 mV s⁻¹. Figure 13a depicts the response of bare GCE electrode with and without acetone. As seen in Figure 13a, bare GCE electrode shows negligible response toward acetone, and no redox peaks were observed. In the case of NZ/GCE (Figure 13b), the modified electrode shows limited response toward acetone, which can be attributed to poor electrocatalytic property and slow electrode kinetics. In contrast, the AZN-8-modified electrode shows better response with acetone (Figure 13c), and a pair of distinctive redox peaks appears upon addition of acetone. The appearance of characteristic anodic and cathodic peaks may be ascribed to the synergistic effect of the NZ nanocomposite and the grafted Ag₂S nanoparticles, which generates more catalytic sites and increases electron transfer.

The variation of redox current with acetone in the concentration range of 10 mmol L⁻¹ to 0.5 mol L⁻¹ for the AZN-8 nanocomposite is shown in Figure 14a. With successive addition of acetone in the buffer system, characteristic anodic peaks with amplified current at around 0.2 V potential are observed. At a fixed potential, the variation of anodic peak current with the concentration of acetone was found to be linear. The analytical characteristics of the AZN-8 nanocomposite were calculated from a linear calibration curve (Figure 14b). From the curve, regression coefficient (r² = 0.9848), sensitivity (4.0764 μA mmol L⁻¹ cm⁻²), and limit of detection (LOD: 0.06 mmol L⁻¹) were calculated at the S/N ratio of 3.

Figure 14. (a) CVs of AZN-8/GCE with different acetone concentrations and (b) calibration curve depicting the relationship between the acetone concentration and oxidation peak current values.

The influence of scan rates on the redox peak currents of the AZN-8 nanocomposite has been examined in the range of 5−100 mV s⁻¹. It has been observed that both the cathodic peak current and anodic peak current vary linearly with scan rates (Figure 15). The proportional rise in redox peak currents with the scan rate suggests that the electrode reaction is a surface-controlled electrochemical reaction. Moreover, the optimization of pH was done in several buffer systems (pH = 4.5−8.5), and it was found that the fabricated sensor was more active at pH 7.5.

In the electrochemical sensing experiment, the current grows gradually with the enrichment of buffer solution with the target acetone.
plausible mechanism suggests that O2 and acetone are system, which accounts for enhancement of the current. The oxidation of acetone, the electrons are released into the bu therefore, the oxidation reaction is enhanced. During the system, the surface coverage of the electrode increases, and concentration of acetone is successively increased in the bu the oxidation reaction was limited. As the electrode (AZN-8/GCE/binder) was slightly occupied, and

Figure 15. CVs of AZN-8/GCE in 0.2 M PBS buffer at scan rates of 5−100 mV s−1 (from inner to outer); the inset shows the plots of redox peak currents vs scan rate.

analyte (acetone). Initially, the surface of the modified electrode (AZN-8/GCE/binder) was slightly occupied, and the oxidation reaction of acetone was limited. As the concentration of acetone is successively increased in the buffer system, the surface coverage of the electrode increases, and hence, the oxidation reaction is enhanced. During the oxidation of acetone, the electrons are released into the buffer system, which accounts for enhancement of the current. The plausible mechanism suggests that O2 and acetone are adsorbed onto the coated electrode surface, resulting in the release of electrons, hydrogen, and carbon dioxide as depicted in reactions 11 and 12.79

\[
\text{CH}_3\text{COCH}_3 + 4\text{O}^- \rightarrow \text{CH}_2\text{COOH} + \text{CO}_2 + \text{H}_2\text{O} + 4\text{e}^- \\
\text{CH}_3\text{COOH} + 7\text{O}^- \rightarrow 3\text{CO}_2 + 3\text{H}_2\text{O} + 7\text{e}^-
\]

(11)

(12)

The proposed mechanism clearly shows that oxidation of acetone produces electrons; hence, the acetone detection mechanism of the fabricated AZN-8/GCE/binder sensors is simple. Moreover, the proposed acetone sensor is easy to fabricate, inert in chemical systems, economical, and stable in air. Thus, the cost-effective synthesis combined with excellent photocatalytic and sensing performance is a promising strategy to remediate environment under optimum conditions (Table 4).

### 3.3. Practical Implications of Study

Photocatalytic oxidation of organic pollutants and simultaneous oxidation of VOCs and volatile inorganic compounds in both gas phase and solvent phase have received considerable attention from the scientific society. Photocatalysis has the signature of promising applications in environmental systems. Numerous applications of photocatalysis have achieved commercial maturity but have not yet penetrated mass markets. Industrial applications have impacted the construction sector, aerospace industries, automotive, medical sector, and food industry. Although photocatalysis is at the forefront of research, it is yet to attain commercialization; only a few small-scale or large-scale photocatalytic industries have been set up. However, these applications validate the utilization of photocatalysis as a beneficial technology for the environment, human health, and social structure.

The major challenge which should be dealt with is the commercialization of photocatalytic technology; it should be utilized in commercial applications. The second challenge deals with the efforts and techniques, which should be adopted to fabricate a potential photocatalyst that can be efficient, pragmatic, and useful. The third and the more realistic challenge is to increase the quantum efficiency of photocatalytic systems.

In addition to this, chemical sensing by nanostructures is an eco-friendly and cost-effective approach to detect and quantify the hazardous volatile chemicals from the environment. This approach has gained more compatibility as compared to enzymatic sensors because of reliability and economic approach. Lower detection limit and higher sensitivity are highly desirable for proper functioning of chemical sensors.

The future prospects envisage the utilization and optimization of photocatalysis for bringing sustainability in environmental processes and biocompatibility. The fabrication of capable nanocomposites with excellent photocatalytic activity and remarkable electronic and biological properties can be beneficial for humankind.

### 4. CONCLUSIONS

In summary, ternary AZN nanocomposites with different weight ratios of Ag2S were successfully synthesized by a simple homogeneous precipitation method. The detailed morphological characterizations demonstrate the porous nature and high surface area of the nanocomposite. In contrast to NZ, the AZN nanocomposite showed enhanced photocatalytic performance, indicating strong visible light-harvesting and efficient charge separation characteristics. Among all nanocomposites formed, AZN-8 exhibits optimal photocatalytic activity with the RhB degradation efficiency of 95% in 120 min under visible light irradiation. The prominent species involved in photocatalysis was found to be hydroxyl and superoxide radicals. Recycling experiments proved the stability and reliability of the nanocomposite. Moreover, the electrochemical and electroanalytical results revealed that the prepared nanocomposite exhibits remarkable activity toward detection of acetone. The fabricated nanocomposite sensor showed excellent activity in terms of high sensitivity and lower detection limit. The notable enhancement in photocatalytic and sensing activity can be ascribed to the impregnation of Ag2S into the NZ nanostructure, which due to the LSPR effect enhances the visible light absorption, suppresses the charge carrier recombination, and increases the electronic properties.

### Table 4. Comparison of Nanocomposite Sensor Performance with Various Reported Sensors

| sensing material/chemical sensor | LOD     | sensitivity (μA mM⁻¹ cm⁻²) | linearity (r²) | literature |
|----------------------------------|---------|-----------------------------|----------------|------------|
| ZnO nanoparticles                | 1.18 μM | 0.14                        |                | 82         |
| ZnO/CO3O4 nanorods               | 14.7 μM | 3.58                        | 0.9684         | 83         |
| Ag2O microflowers                | 0.11 μM | 1.60                        | 0.9462         | 79         |
| lead foil electrode              | 50.0 ppm| 2.07                        | 0.9780         | 84         |
| Ag2S/AgO−ZnO nanocomposites      | 0.06 mmol L⁻¹ | 4.07                  | 0.9848         | present work |

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5. EXPERIMENTAL SECTION

5.1. Chemicals and Materials. All chemicals were of analytical grade and used without further purification. The chemicals used are as follows: zinc nitrate [Zn(NO$_3$)$_2$]·6H$_2$O, nickel nitrate [Ni(NO$_3$)$_2$·6H$_2$O], sodium hydroxide (NaOH), silver nitrate [Ag(NO$_3$)$_2$], sodium sulfide (Na$_2$S·6H$_2$O), RhB, acetone, methanol, glucose, terephthalic acid, AO, BQ, IPA, acetic acid, and chitosan. All chemicals were purchased from Sigma-Aldrich (India). DI water was used throughout the experimental study.

5.2. Synthesis of NiO, ZnO, and NiO–ZnO (NZ) Nanocomposites. NiO, ZnO, and NiO–ZnO nanocomposites were synthesized by a homogeneous precipitation method.$^{61}$ In a typical procedure for preparing ZnO nanoparticles, 0.05 M Zn(NO$_3$)$_2$·6H$_2$O was magnetically stirred in 250 mL of distilled water for 25 min at 70°C on a hot plate. A white precipitate appears on adding 40 mL of 2.0 M NaOH solution. The resulting solution was ultrasonicated for 5 min to attain adsorption–desorption equilibrium. After ultrasonication, the calculated amount of Na$_2$S·6H$_2$O was added, and the precipitate was harvested via filtration.

For synthesizing NiO–ZnO binary oxide, equal quantities of nickel and zinc precursors were dissolved in 250 mL of water. The resulting solution was ultrasonicated for 5 h. A similar procedure was followed thereafter to prepare NiO–ZnO (NZ) binary oxide nanocomposites. All prepared samples were calcined at 500°C for 3 h.

5.3. Synthesis of Ag$_2$S/NiO–ZnO Ternary Nanocomposites. The grafting of Ag$_2$S on the surface of NiO–ZnO binary oxide was carried out by using a solution of Ag$_2$S on the surface of binary metal oxide nanocomposites at room temperature. For that, 1 g of NiO–ZnO mixed oxide nanoparticles and different weight percentages of AgNO$_3$ were dispersed in 60 mL of ethanol and ultrasonicated for 40 min. After ultrasonication, the calculated amount of Na$_2$S was added to the suspension while stirring. The resulting suspension was stirred continuously for 8 h. The precipitate thus obtained was collected with filtration, washed repeatedly with distilled water and absolute ethanol, and then dried at 80°C for 10 h. Different weight ratios of Ag$_2$S to NiO–ZnO were synthesized and labeled as 2% Ag$_2$S/NiO–ZnO (AZN-2), 4% Ag$_2$S/NiO–ZnO (AZN-4), 6% Ag$_2$S/NiO–ZnO (AZN-6), 8% Ag$_2$S/NiO–ZnO (AZN-8), and 10% Ag$_2$S/NiO–ZnO (AZN-10).

5.4. Characterization. The characterization of the prepared samples was done with several analytical techniques. The functional group analysis was performed with a Fourier transform infrared spectrometer (PerkinElmer) in the range of 400–4000 cm$^{-1}$. The crystallinity and phase identification of the samples were analyzed by powder X-ray diffraction (Shimadzu 6100) with Cu Ka radiation (1.5418 Å) in the scan range 20°–80° (2θ). Band gap analysis of samples was done by UV–vis DR spectral analysis using a UV–vis NIR spectrometer (PerkinElmer). Morphological characterizations and elemental composition were done with SEM (JEOL, JSM6510LV) fitted with an energy-dispersive X-ray detector and TEM (JEOL, JEM 2100). The electrochemical surface areas of the catalysts were investigated by EDLC ($C_d$). PL spectra were recorded by a Shimadzu fluorospectrometer at 640 nm excitation wavelength.

5.5. Photocatalytic Test Procedure. Photocatalytic performance of as-prepared nanocomposites was checked in a quartz photoreactor against aqueous solution of organic dyes (RhB). The assembly of the photoreactor consists of an inner and outer chamber with a water circulating jacket for maintaining temperature and an opening for bubbling molecular oxygen. The inner chamber consists of a halogen lamp (500 W, 9500 lumens) used for irradiation. The decolorization/photodegradation of the organic dye was assessed in the outer chamber. The catalyst dosage was optimized by taking different amounts of the prepared catalyst. Before irradiation, appropriate amount of dye solution (1 mM) with 1 mg mL$^{-1}$ catalyst dosage was magnetically stirred for 30 min to attain adsorption–desorption equilibrium. After irradiation, dye aliquots were taken at 5 min intervals, centrifuged, and analyzed in a UV–vis spectrophotometer to measure the maximum absorbance at 554 nm. The degradation potentiality was deduced by using eq 13:

\[
\text{Degradation efficiency} = \frac{C_0 - C_i}{C_0} \times 100
\]

where $C_0$ is the starting concentration of the dye and $C_i$ is the concentration of the dye at a particular time.

The effect of reactive species was also assessed by adding calculated quantity of scavengers in the reaction system to elucidate the possible mechanism of photodegradation. The photostability of the catalyst was also evaluated by performing recycling experiment.

5.6. Sensor Fabrication and Sensing Activity. Electrochemical and electroanalytical measurements of samples were done with CV (Autolab, PGSTAT204). A three-electrode assembly was employed for electroanalytical measurements comprising an Ag/AgCl electrode as the reference electrode, modified GCE as the working electrode, and platinum wire as the counter electrode. The pictorial representation of a three-electrode assembly is shown in the Supporting Information (Figure S4). The prepared ternary nanocomposite (Ag$_2$S/NiO–ZnO) was pasted on the surface of GCE (0.5 mm diameter) using a conventional conducting binder. The electrolytic solution used was 0.1 M PBS within the pH range of 7.0–7.5, and the experiment was carried out at room temperature (25 °C).

Sensing performance of the fabricated sensor (Ag$_2$S/NiO–ZnO/GCE/binder) was evaluated with acetone. The concentration of acetone was varied from 10 mmol L$^{-1}$ to 0.5 mol L$^{-1}$, and the corresponding $I$–$V$ plots were drawn. A calibration plot was drawn between current and concentration, whose slope was used for the evaluation of sensitivity and detection limit of sensing films.

The conventional binder was prepared by taking 1 mL of IPA and DI water and 2.6 mg of nanocomposites. The prepared suspension was converted into a binder by adding appropriate quantities of chitosan and glacial acetic acid.
10 and AZN-6 nanocomposites, spectral changes of RhB over AZN-8 in the presence of IPA, and pictorial representation showing a three-electrode assembly used in the experiment (PDF)

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**Notes**
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**ABBREVIATIONS**

| Abbreviation | Description |
|--------------|-------------|
| AOP          | advanced oxidation process |
| XRD          | X-ray diffraction |
| EDS          | energy-dispersive X-ray spectroscopy |
| UV-DRS       | Ultraviolet-diffuse reflectance spectra |
| FTIR         | Fourier transform infrared spectroscopy |
| AZN-2        | 2% Ag2S/NiO-ZnO |
| AZN-4        | 4% Ag2S/NiO-ZnO |
| AZN-6        | 6% Ag2S/NiO-ZnO |
| AZN-8        | 8% Ag2S/NiO-ZnO |
| AZN-10       | 10% Ag2S/NiO-ZnO |
| NZ           | NiO-ZnO |
| GCE          | glassy carbon electrode |
| PBS          | phosphate-buffered saline |
| CV           | cyclic voltammmograms |
| IPA          | isopropl alcohol |
| AO           | ammonium oxalate |
| PL           | photoluminescence |
| Rhb          | rhodamine B |
| ROS          | reactive oxygen species |
| SEM          | scanning electron microscopy |
| TEM          | transmission electron microscopy |
| CB           | conduction band |
| VB           | valence band |

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