Fabrication of AgNi Nano-alloy-Decorated ZnO Nanocomposites as an Efficient and Novel Hybrid Catalyst to Degrade Noxious Organic Pollutants

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ABSTRACT: Contamination through industrial effluents is a major threat to the environment. Degradation of organic pollutants remains a major challenge, and semiconductor-based catalysis is reported to be a viable solution. Recently, AgNi bimetallic alloy nanoparticles attracted great attention with superior properties. We report the synthesis of AgNi nano-alloy particles immobilized over the surface of ZnO hexagonal rods through an in situ chemical co-reduction process to develop a novel AgNi@ZnO nanocomposite for catalytic applications. The crystal structure, phase purity, morphology, particle size, and other properties of the as-synthesized AgNi@ZnO nanocomposite were scrutinized using powder X-ray diffraction, scanning electron microscopy, Raman spectroscopy, energy-dispersive X-ray analysis, multipoint Brunauer−Emmett−Teller, and transmission electron microscopy. The composite exhibits excellent catalytic activity toward the reduction of nitroarenes and environment polluting organic dyes. The synthesized nanocomposite shows enhanced catalytic activity with an incredible reaction rate constant, noticeable low degradation time, and greater stability. The catalyst is easily recyclable and exhibits consecutive catalytic cycle usage.

1. INTRODUCTION
The rapid growth of industrialization results in increased discharge of harmful effluents that leads to serious intimidation to the ecosystem and also to the human health.1−4 As a consequence, the polluted water discharged in larger quantities is considered as one of the foremost challenges for pollution control. The massive amount of effluents from the industrial discharge contains various hazardous compounds including nitroarenes and organic dyes. However, nitroarenes are considered to be important compounds due to their use in production of anilines, pharmaceuticals, agrochemicals, dyes, explosives, and so forth.5 These aromatic nitro compounds are used as important precursors in the fabrication of several analgesics and anti-pyretic drugs like paracetamol, acetaminophen, phenacetin, and acetonilide.6−8 Although, concurrently, these aromatic nitro compounds are a major source of water contaminants and are found to be environmentally hazardous materials that cause severe health threats to human, animal, and aquatic lives.9 4-Nitrophenol has been reported as a prospective carcinogen, mutagen, and teratogen; therefore, several aromatic nitro compounds have been counted in environmental legislation.9−11 On the other hand, in the industrial synthesis of several important products, the reduction of nitroarenes to the corresponding amine derivatives is a very crucial process. The aminophenols are utilized as the paint for wood and the dyeing medium for fur and feathers in dye industries.12 Aminophenol compounds are also used as a photographic developer, an anticorrosion lubricating medium in fuels for two-cycle engines, and a corrosion inhibitor in paints.13 Therefore, in order to make the environment safe by reducing the water pollutants and to meet the demand of 4-aminophenol (4-AP), the scientific community is continuously working for the catalytic reduction of 4-nitrophenol.14−16

Recently, the semiconducting material ZnO having a wide band gap (3.37 eV) has earned a lot of attention as it exhibits various application domains such as fascinating optical, luminescence, chemical, electrical, and biological properties.15,16 ZnO nanoparticles exhibit an extensive series of promising applications in photodetectors, antibacterial treatment, catalysis, transparent transistors, UV-light emitters, fabrication of gas sensors, solar cells, piezoelectric transducers, short-wavelength optoelectronic devices (LED and lasers), and so forth.17,18 Various methods and techniques including thermal evaporation,19,21 hydrothermal synthesis,23,24 electro-
deposition, vapor phase transport process, thermal annealing method, pyrolysis, laser ablation, sol–gel process, electro-spinning, and chemical vapor deposition have been employed to synthesize the ZnO nanoparticles with varied morphology. Among the reported methods of ZnO rod synthesis, a hydrothermal method has been utilized to fabricate ZnO rods in the present study. Hydrothermal synthesis is one of the most extensively used nanostructure synthesis methods. It is basically a solution reaction-based approach. Hydrothermal synthesis can be controlled by controlling different parameters like temperature, concentrations of different precursors, and stabilizing agents to get the desired product.

Recently, various methods have been employed to enhance the catalytic activity of ZnO. In this regard, the inorganic solid support nanomaterials have been studied as highly potential candidates for diverse usage such as energy production, catalysis, sensing, and so forth. The heterogeneous materials provide a higher surface area to adsorb the reacting species on their surface that leads to an increased rate of reaction. The incorporation of metal nanoparticles into semiconductors as a heterogeneous catalyst based on inorganic solid support material has been reported as a promising method to improve the catalytic activity. These metal-doped semiconductors exhibit improved catalytic activity due to the strong catalytic and electron-transporting ability of a metal, high surface areas, possibility to functionalize with active groups, and high thermal stability of inorganic solid support materials. Moreover, incorporation of ZnO with metals and non-metals such as Fe, Ag, Au, Pd, B, S, and N has been reported as a better catalyst. In recent years, bimetallic alloy nanoparticles have gained a lot of interest because of their excellent and distinctive catalytic, optical, magnetic, and electronic properties. These bimetallic alloy nanoparticles exhibit potential applications in diverse domains such as organic synthesis, catalysis, oxygen reduction reactions, antibacterial activity, fuel cell catalysis and magnetic recording, and so forth. An excellent improvement in the specific physical and chemical properties of bimetallic alloy particles could be observed because of the synergistic effect. When two different metals are mixed together, a synergistic effect is produced. This synergistic effect can enhance their properties including catalytic efficiency. The strong metal–metal interaction alters the bonding between the reactants and the surface of the catalyst, which results in the extra stability of the transition state on the bimetallic alloy nanoparticles as compared to the interaction on a single-metal surface, and hence, AgNi alloy has an advantage against single Ag metal in catalysis. Recently, AgNi alloy nanoparticles attracted great attention as they are the new member of the bimetallic alloy nanoparticle family and possess inimitable kinds of synthesis and theoretical calculations.

However, there has been no report on AgNi alloy nanoparticle-decorated ZnO rods, and AgNi@ZnO is a novel material. Moreover, in most of the reports, the metal particles were incorporated using a solution-state process.

Herein, we report the immobilization of AgNi alloy nanoparticles on the surface of ZnO rods using an in situ chemical co-reduction method, and the synthesized material has been further utilized in the catalytic reduction of nitroarenes and organic dyes. A homogeneous distribution of AgNi alloy nanoparticles on the ZnO surface has been obtained. The synthesized AgNi@ZnO catalyst exhibits a high surface area. The catalytic nitroarene reduction and dye degradation studies revealed that the catalyst exhibits outstanding catalytic efficiency and reusability for several catalytic cycles with minimal loss in its catalytic activity. In addition, the synthesized catalyst is cost-effective, eco-friendly, recyclable, and easy to synthesize.

2. RESULTS AND DISCUSSION

2.1. Characterization of the AgNi Nano-alloy-Decorated ZnO Nanocomposite.

2.1.1. Powder X-ray Diffraction Analysis. The crystallographic structure, composition, and phase purity of the as-synthesized ZnO and the bimetallic alloy nanoparticle-decorated ZnO nanocomposite were analyzed by the powder X-ray diffraction (XRD) technique. Figure 1 illustrates the powder XRD patterns of Ag, Ni, ZnO, and AgNi@ZnO.
solution with the dissolution of Ni atoms in the Ag crystal lattice and hence confirmed the presence of Ag and Ni atoms in the resulting alloy nanoparticles.\textsuperscript{69–71} The phase purity of the synthesized material can be validated by the absence of any other peak.

2.1.2. Scanning Electron Microscopy Analysis. The morphology of ZnO and AgNi@ZnO was scrutinized by scanning electron microscopy (SEM). It is observed that ZnO has hexagonal rod-shaped morphology. The average size of the hexagonal rod is $9.12 \mu m$ (length) and $0.46 \mu m$ (diameter) with smooth surfaces as represented in Figure 2A. Figure 2B shows the ZnO hexagonal rods decorated with AgNi alloy nanoparticles (AgNi@ZnO).

2.1.3. Energy dispersive X-ray and Elemental Mapping Analysis. Energy dispersive X-ray (EDAX) analysis was used to study the elemental composition of the synthesized materials. The sharp peaks represented in Figure S1 confirmed the presence of respective constituent elements. Figure S1 shows the peaks for the entire elemental composition, that is, Ag, Ni, Zn, and O in the AgNi@ZnO nanocomposite, which confirms the successful immobilization of AgNi alloy nanoparticles on the surface of ZnO hexagonal rods. Furthermore, the elemental mapping of the AgNi@ZnO nanocomposite was performed to confirm the uniform immobilization of hybrid nano-alloy particles on the composite. Figure S2 shows the elemental mapping images of Ag, Ni, Zn, and O.

2.1.4. TEM and HRTEM Study. In addition, TEM measurement was carried out to examine the thorough insights into morphology and particle size of ZnO and AgNi@ZnO nanocomposites. The obtained images further confirmed that the morphology of ZnO is a hexagonal rod (Figure 2C) as supported by the SEM analysis. After decorating the AgNi alloy nanoparticles, it is clear that AgNi alloy nanoparticles are finely immobilized on the surface of ZnO hexagonal rods, which is supportive in enhancing the catalytic activity (Figure 2D). Figure 2E shows the lattice fringes in HRTEM, which further reveals more discernible microstructure information, in order to get a precise information of the junction between ZnO and AgNi alloy nanoparticles. The calculated fringe spacing ($d$-spacing) for ZnO (0.27 nm) corresponds to the (200) plane of the hexagonal structure (inset Figure 2E-a). On the other hand, the interplanar distance for AgNi alloy nanoparticles calculated from lattice fringes was 0.23 and 0.24 nm that are consistent with the (111) plane of AgNi alloy nanoparticles (inset Figure 2E-b).\textsuperscript{67} The TEM/HRTEM investigations are consistent with the powder XRD patterns and SEM results.

2.1.5. Raman Spectroscopy Analysis. The vibrational properties of the synthesized materials were studied by utilizing the Raman spectra. Figure S3 represents the Raman spectra of ZnO and AgNi@ZnO nanocomposites. The Raman shift at 437 cm$^{-1}$ resembles to the E$_2$ mode of the wurtzite structure from the P6$_3$mc symmetry group. The stronger intensity and narrow line width of the peak corresponding to the E$_2$ mode indicate the good crystalline property of the synthesized material. The spectroscopic peak at 585 cm$^{-1}$ could be allocated to the E$_1$ (LO) mode and represents structural defects in ZnO. A peak at 380 cm$^{-1}$ corresponds to...
A$_1$ (TO)-mode frequency. The spectroscopic peaks centered at 330 and 1147 cm$^{-1}$ correspond to multi-phonon scattering. The Raman peaks corresponding to ZnO in the AgNi@ZnO nanocomposite are found to be broad and of low intensity because of the higher scattering and interaction of AgNi alloy nanoparticles with ZnO.

2.1.6. Brunauer–Emmett–Teller Analysis. It is well known that the surface area of a catalyst is the key factor that affects its catalytic performance. Figure 3A,B represents the nitrogen adsorption–desorption isotherms for ZnO and AgNi@ZnO nanocomposites, respectively. It is evident that the isotherms obtained for both ZnO and AgNi@ZnO nanocomposites are of type IV, according to the Brunauer–Dening–Dening–Teller (BDDT) classification. Both the isotherms exhibit the area of the hysteresis loop, which shows the existence of mesoporous nature of the synthesized materials. Furthermore, adsorption–desorption isotherms show increased porous nature of the composite AgNi@ZnO that further increases the surface area (Figure 3B). Pore size distribution curves are shown in the insets of the figure. The multipoint Brunauer–Emmett–Teller (BET) surface area, pore volume, and pore radius of the synthesized samples are shown in Table 1. It could be observed that the surface area of AgNi@ZnO is appreciably higher as compared to ZnO, because of the increased porosity. Figure 3B shows a different nature of the isotherm (in terms of adsorbed volume), indicating the increased porosity of the composite. This higher surface area and porosity make the AgNi@ZnO nanocomposite a better option for catalytic applications.

2.1.7. Thermogravimetric Analysis. Figure S4 shows the thermogravimetric analysis (TGA) curve for ZnO and AgNi@ZnO nanocomposites. The total weight loss in the case of the ZnO sample was found to be 2.33% that can be attributed to the removal of adsorbed moisture from the surface of the sample. For the AgNi@ZnO nanocomposite, a total of 9.22% weight loss was observed in the temperature range of 25–800°C. The first step of weight loss, that is, 1.42%, was observed between 25 and 150°C, representing the elimination of physically adsorbed water molecules. Furthermore, weight loss in the temperature range of 200–400°C was 5.49%, which could be attributed to the conversion of zinc hydroxide. The third step of weight loss (i.e. 2.31%) was observed in the 400–800°C range, which corresponds to the leftover ZnO nanoparticles formed by organic degradation. This study reveals that all the nitrate reactants utilized in the synthesis of AgNi@ZnO were completely consumed and converted to AgNi@ZnO as reported earlier. In addition, the synthesized materials are highly stable up to 800°C temperature.

2.2. Catalytic Activity. In order to investigate the catalytic performance of the as-synthesized nanocomposite, the nanocomposite was utilized as a heterogeneous catalyst in the reduction reaction of nitroarenes that results in the corresponding amine products. In addition, the catalytic activity of the as-synthesized catalyst was also tested by degrading various noxious organic dyes.

Table 1. Summary of the BET Surface Area, Pore Volume, and Pore Radius of ZnO Hexagonal Rods and AgNi@ZnO Nanocomposites

| sample       | multipoint BET surface area ($10^3$, m$^2$/g) | pore volume (cc/g) | pore radius (Å) |
|--------------|-----------------------------------------------|--------------------|-----------------|
| ZnO          | 6.37                                          | 11.7               | 16.98           |
| AgNi@ ZnO    | 8.40                                          | 15.07              | 17.15           |

![Figure 4](https://doi.org/10.1021/acsomega.1c05266)

**Figure 4.** UV–vis absorption spectra for the reduction of (A) 4-nitrophenol, (B) 2-nitrophenol, and (C) 2-nitroaniline in the presence of the AgNi@ZnO nanocomposite as a catalyst. (D) Plot of ln(C$_t$/C$_0$) against reduction time showing first-order kinetics for the performed reduction reaction.
2.2.1. Catalytic Reduction of 4-Nitrophenol. To examine the catalytic performance of the AgNi@ZnO nanocomposite, the catalytic reduction reaction of 4-nitrophenol to 4-AP using NaBH₄ was performed. The progress of the reduction reaction was observed and easily examined via UV–vis absorption spectroscopy. The aqueous solution of 4-nitrophenol was observed to be light yellow-colored and absorbed at 400 nm. When an aqueous solution of NaBH₄ was added to the 4-nitrophenol solution, an absorption peak was observed at 400 nm and the color changed from light yellow to dark yellow. Due to a change in the alkalinity (pH) of the mixture, the color was changed and thus resulted in 4-nitrophenolate ion (C₆H₄NO₃⁻) formation. This peak intensity at 400 nm remains unchanged even after 40 min, which indicates that in the absence of a catalyst, the reduction process does not take place. This can be attributed to a high kinetic barrier among commonly repelling negative ions of 4-nitrophenolate (C₆H₄NO₃⁻) and borohydride (BH₄⁻) ions. With the addition of 100 μL of AgNi@ZnO as a catalyst, the absorption peak intensity decreases expeditiously over a while resulting in the formation of a new peak observed at 309 nm for the corresponding amine. The absorption peak at 400 nm vanished utterly after 120 s, indicating the completion of the reduction reaction. After the complete reduction of 4-nitrophenol, the reaction mixture turned from yellow to colorless. Figure 4A shows the absorption spectra of 4-nitrophenol against reduction time, where the absorption peak at 400 nm vanished in 30 s. In the absorption spectra, absorption peaks at 240 and 305 nm can be observed, which attribute to the formation of the resulting amine derivative, that is, 4-aminophenol. In addition, the catalytic performance of the synthesized catalyst, that is, AgNi@ZnO was compared with a few of the catalysts that are reported for the reduction of 4-nitrophenol, and the results are shown in Table 2. In the process of reduction, the concentration of NaBH₄ taken is 0.2 M, which is far higher than that of nitroarenes (0.2 mM), and it remained nearly constant during the course of the reaction. Therefore, the reactions are supposed to be following the first-order kinetics, and hence, the efficiency of the AgNi@ZnO catalyst is calculated using the first-order kinetics. The value of the rate constant can be determined easily from the linear plot of (C₀/Cₜ) against reduction time, where C₀ and Cₜ denote the value of concentrations at time t and 0, respectively. The value of the rate constant could be calculated from the slope determined from the linear plot. By normalizing the rate constant, the activity parameter was calculated as $K = k/m$, where $k$ is the rate constant and $m$ denotes the catalyst amount.

2.2.2. Catalytic Reduction of 2-Nitrophenol. By applying a similar procedure, the catalytic activity of the synthesized catalyst for the reduction of 2-nitrophenol was determined. In the UV–vis spectra of 2-nitrophenol, the initial absorption peak was observed at 415 nm and the intensity decreases with the addition of the catalyst. Figure 4B shows that the absorption peak at 415 nm disappeared completely after 60 s and a fresh peak started appearing at 290 nm. This new peak that appeared at 290 nm indicates the formation of the resulting amine derivative, that is, 2-aminophenol. In addition, the dark yellow-colored reaction mixture of 2-nitrophenol became colorless after the complete reduction.

2.2.3. Catalytic Reduction of 2-Nitroaniline. In addition to 4-nitrophenol and 2-nitrophenol, the study of the catalytic activity of the AgNi@ZnO catalyst for the reduction of 2-nitroaniline was also carried out. Figure 4C represents the absorption spectra for the catalytic reduction of 2-nitroaniline with NaBH₄ in the presence of a catalyst (0.3 mg). 2-Nitroaniline exhibits a peak at 381 nm, which starts decreasing subsequently with the addition of the AgNi@ZnO catalyst and vanishes in 30 s. In the absorption spectra, absorption peaks at 240 and 305 nm can be observed, which attribute to the formation of the resulting amine derivative, that is, o-phenylenediamine. The rate of reaction and the activity parameter were determined similarly as discussed for the reduction of 4-nitrophenol (Tables 3 and 4).

### Table 2. Summary of the Catalytic Performance of the AgNi@ZnO Catalyst Compared with Few Previously Reported Catalysts for the Reduction of 4-Nitrophenol

| entry | catalyst | catalyst amount (mg) | rate constant ($k$, 10⁵ s⁻¹) | activity parameter ($K$, s⁻¹ g⁻¹) | reference |
|-------|----------|----------------------|-----------------------------|--------------------------------|-----------|
| 1     | ZnO      | 5                    | 0.43                        | 0.086                         | 78        |
| 2     | Ag/ZnO   | 4                    | 3.97                        | 0.992                         | 79        |
| 3     | RGO-Ni₂ZnO | 6                   | 1.553 ± 0.063              | 0.258                         | 80        |
| 4     | Pd@g-C₃N₄ | 0.2                 | 4.21                        | 21.05                         | 77        |
| 5     | cSiO₂@DFNSAg | 0.2           | 10.93                       | 54.65                         | 81        |
| 6     | Ag NP/C  | 1                    | 1.69                        | 1.69                          | 82        |
| 7     | Pd/Au@g-C₃N₄ | 0.25              | 13.1                        | 52.4                          | 83        |
| 8     | AgNi@ZnO | 0.3                  | 14.24                       | 47.46                         | This work |

| dye              | reduction time (s) | rate constant ($k$, s⁻¹) | correlation coefficient ($R^2$) | activity parameter ($K$, s⁻¹ g⁻¹) |
|------------------|--------------------|--------------------------|-------------------------------|---------------------------------|
| rhodamine B      | 90                 | 0.0138                   | 0.997                         | 45.86                           |
| methyl orange    | 60                 | 0.0105                   | 0.994                         | 35.03                           |
| methylene blue   | 60                 | 0.0900                   | 0.966                         | 300.06                          |

2.2.4. Study of Catalytic Degradation of Organic Dyes. Several organic dyes like rhodamine B, methyl orange, methylene blue, methyl red, and so forth are commonly utilized as coloring agents in textile industries. The release of these organic dyes into the ecosystem has become a conspicuous source of water pollution, leading the harmful effects on aquatic life. Before discharging into the aquatic environment, these organic dyes should be degraded to a non-

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hazardous level to protect the environment. In this study, we
have utilized rhodamine B, methylene blue, and methyl orange
dyes to investigate the archetypal degradation reaction of the
AgNi@ZnO catalyst. The degradation reaction of these dyes
was investigated by the addition of the AgNi@ZnO catalyst to
the aqueous dye solution containing NaBH4. The kinetics of
the degradation reaction was scrutinized by measuring
absorbance against degradation time on a UV−vis spectrom-
eter.

Initially, the rhodamine B dye was used to study the catalytic
degradation activity of the AgNi@ZnO catalyst. Rhodamine B
shows an absorption peak at 554 nm. Figure 5A shows the
UV−vis spectra for the degradation of 2 mL of rhodamine B
(0.02 mM) with the addition of 100 μL of aqueous solution of the
AgNi@ZnO catalyst (0.3 mg mL−1). The absorption
peak progressively decreased and completely vanished within
90 s in presence of NaBH4 and the as-synthesized catalyst.
ZnO hexagonal rods without the immobilization of AgNi alloy
nanoparticles were also used to degrade the rhodamine B, but
the reduction reaction did not proceed even after 40 min,
indicating the necessity of bimetal alloy nanoparticles to
proceed the reaction (Figure S5). Similarly, the methyl orange
and methylene blue dyes were degraded to study the catalytic
performance of the synthesized catalyst. Figure 5B shows the
absorption spectra of methyl orange in the presence of NaBH4
and the catalyst. From the spectrum, we can observe the
absorption peak for an aqueous solution of methyl orange at
464 nm that vanished gradually in 60 s after the addition of
catalyst. On the other hand, the characteristic peak for an
aqueous solution of methylene blue containing NaBH4 was

Figure 5. UV−vis absorption spectra for the degradation of (A) rhodamine B, (B) methyl orange, and (C) methylene blue in the presence of the
AgNi@ZnO catalyst. (D) Plot of ln(Ct/C0) against degradation time showing first-order kinetics for the performed degradation reaction.

Figure 6. UV−vis absorption spectra of reduction of (A) rhodamine B with various concentrations of the catalyst (100−25 μL) and (B) 4-
nitrophenol with various concentrations of the catalyst (100−25 μL).
observed at 663 nm, which disappeared completely within 30 s after the addition of the synthesized catalyst. The absorption peak (663 nm) started decreasing rapidly when the catalyst was added and finally disappeared within 60 s (Figure 5C). After the completion of the reaction, the reaction mixture of all the three dyes was found to be colorless, indicating the complete degradation of dyes into water, carbon dioxide, and other side products.86–88

The rate constant in the case of dyes was determined similarly as in the reduction of nitroarenes (Figure 5D).

2.2.5. Effect of Different Catalyst Amounts on the Catalytic Efficiency of the Synthesized Catalyst. The effect of various amounts of the catalyst was investigated by utilizing the 4-nitrophenol reduction and the rhodamine B degradation reactions. Figure 6A represents the absorbance against time spectra for rhodamine B at different catalytic amounts while the other parameters were kept constant. Different concentrations were chosen for the dye and nitro compounds to bring the absorbance to the comparable scale and to avoid the concentration-dependent deviation. When dye concentration was 2.0 × 10⁻⁴ M, the measured absorbance was very high, instead a lower concentration, 2.0 × 10⁻⁵ M, for rhodamine B dye was used. It could be observed that by changing the concentration of the catalyst (aqueous solution of AgNi@ZnO) from 100 to 50 μL and then to 25 μL, the reduction time was increased from 90, 135, and 315 s, respectively. We compared the results in the form of reaction time, which is inversely proportional to the rate of reaction. It was observed that the rate of reaction in the case of rhodamine B increases with the increase in catalyst concentration. Similarly, 4-nitrophenol was also investigated by varying the concentration of the catalyst from 100 to 50 μL and then to 25 μL (an aqueous solution of the AgNi@ZnO catalyst), for which the reaction time was 120, 155, and 180 s, respectively (Figure 6B). An intense decrease in the reaction time with the increase in catalyst amount could be attributed to the increased active catalytic sites, which facilitates the massive transportation of 4-nitrophenolate ions on the surface of the AgNi@ZnO catalyst for the efficient catalytic activity. The results including the rate constant values, reaction time, and the activity parameter for the 4-nitrophenol reduction and rhodamine B degradation with various catalyst amounts are summarized in Table S1.

2.2.6. Recyclability Test. In order to study the stability of the AgNi@ZnO catalyst, a reusability test was carried out, for which the reduction of 4-nitrophenol and rhodamine B degradation was utilized as an archetypal reaction. When the reaction was completed, the catalyst was recovered from the reaction mixture with the help of centrifugation and washed thoroughly using distilled water followed by drying. The recovered catalyst was used up to five repeated catalytic cycles. We observed a minor increase in the time to complete the reduction/degradation reaction that might be due to the reduced/blockaded catalytic sites on the surface of catalyst. Figure 7 shows the reduction time for successive cycles, and it can be observed that for the last cycle, the reaction was completed in 150 and 135 s for 4-nitrophenol and rhodamine B, respectively. To check the stability of the catalyst after five catalytic cycles, a powder XRD study was performed. In the PXRD patterns of the used catalyst, all the corresponding peaks for the AgNi@ZnO nanocomposite were there and there was no extra peak observed (Figure S6), indicating that even after five cycles, the catalyst is stable.

2.3. Plausible Reaction Mechanism for the Reduction of Nitroarenes. The catalytic reaction mechanism for the reduction of nitroarenes has been proposed. Scheme 1 shows the plausible mechanism for the reduction of 4-nitrophenol that is based on the Langmuir–Hinshelwood (L–H) model. In the first step, adsorption of both the reactants, BH₄⁻ and 4-nitrophenol, takes place on the surface of the AgNi@ZnO catalyst via electrostatic interaction and/or Van der Waals force. As a result, the reaction of BH₄⁻ and 4-nitrophenol, the corresponding 4-nitrophenolate ion is formed that can be simply observed by the color change from light yellow to dark yellow. In the next step, BH₄⁻ transfers the hydrogen to AgNi@ZnO that results in a reaction which gives the formation of unstable intermediates, that is, 4-nitrosophenol and 4-hydroxylaminophenol. Furthermore, the reduction of 4-hydroxylaminophenol results in 4-AP formation, which is a slow process and considered as the rate-determining step. Subsequently, in the last step, desorption of 4-AP from the surface of the catalyst takes place. This desorption of the product occurs from the surface of the catalyst to provide the free active site for the new catalytic cycle. In addition, an adsorption–desorption equilibrium exists in each step of the catalytic cycle.79,85,90 The other nitro compounds (2-nitrophenol and 2-nitroaniline) and the organic dyes were reduced in a similar way. The AgNi@ZnO catalyst enhances the electron transfer from reducing BH₄⁻ to the nitroarenes and organic dyes, which results in the excellent catalytic activity of the catalyst.

3. CONCLUSIONS

In summary, the AgNi@ZnO nanocomposite was successfully synthesized by decorating AgNi nano-alloy on the surface of ZnO hexagonal rods via utilizing a chemical co-reduction method. The AgNi alloy nanoparticles were homogeneously dispersed on ZnO hexagonal rods. In addition, the synthesized nanocomposite showed excellent catalytic activity for the reduction of nitroarenes. Similarly, the nanocomposite showed overwhelming catalytic activity toward the degradation of dyes with remarkably high rate constants and activity parameters. The higher surface area and porosity of the AgNi@ZnO nanocomposite resulted in the excellent catalytic performance. The novel AgNi@ZnO nanocomposite is easy to synthesize, excellently active, reusable, cost-effective, and ecofriendly, which makes it potential candidates for several useful applications in industries.
4. EXPERIMENTAL SECTION

4.1. Materials. Zinc nitrate (98%), sodium hydroxide (98%), nickel nitrate (98%), rhodamine B, methyl orange, methylene blue, 4-nitrophenol (99%), 2-nitrophenol (98%), and 2-nitroaniline (98%) were purchased from Alfa Aesar, and silver nitrate (>99.5%) was bought from Merck. These materials were utilized as precursors without further purification. Deionized water was used for the preparation of solutions and in all the experiments.

4.2. Synthesis of ZnO Rods. ZnO hexagonal rods were synthesized using the hydrothermal method.24 Primarily, an alkaline solution (2 M) was prepared by dissolving sodium hydroxide in 30 mL of distilled water, and then, zinc nitrate (6 mmol) solution was added to this alkaline solution followed by vigorous stirring. Subsequently, the reaction mixture was poured into a Teflon beaker (50 mL) and then sealed in a stainless-steel autoclave. The sealed Teflon-lined autoclave was kept in a muffle furnace at 100 °C for 5 h. Finally, the obtained product was washed multiple times with deionized water followed by ethanol and then dried in an oven at 65 °C.

4.3. Fabrication of the AgNi@ZnO Nanocomposite. The AgNi@ZnO nanocomposite was synthesized using a modified in situ chemical co-reduction method.91 ZnO (120 mg) was dispersed in 25% ethanol (90 mL) via ultrasonication; an equimolar amount (0.5 mmol) of Ni(NO₃)₂·6H₂O and AgNO₃ was dissolved in 30 mL of deionized water to obtain a molar ratio of 1:1.5 (AgNi/ZnO) and further added in a three-neck round-bottom flask containing the ZnO dispersion and was equipped with a condenser in addition to a magnetic stirrer having a temperature controller. The reaction mixture was magnetically stirred for 10 min in a N₂ atmosphere. Furthermore, 1 M NaBH₄ (24 mL) was added dropwise to the above reaction mixture in a N₂ atmosphere. The entire reaction setup was maintained at 105 °C and refluxed for 2.5 h. The obtained brown-coloured product was isolated using centrifugation and further washed with deionized water in addition to ethanol finally to wash the impurity present if any. The product was dried in an oven at 65 °C and preserved for further analysis.

4.4. Characterization. The crystal structure and phase purity of the synthesized samples were investigated using XRD technique (Bruker D8 ADVANCE X-ray diffractometer) with a radiation source of Cu Kα (λ = 1.5406 Å) at a scanning rate of 1° min⁻¹ and 0.02° s⁻¹ scanning speed. To examine the morphology and particle size of the synthesized materials, SEM was employed using a JEOL JSM-6610LV scanning electron microscope operated at an accelerating voltage of 20 kV. EDAX was used to determine the elemental compositions of the bimetallic alloy-decorated ZnO nanocomposite and investigated by using an energy dispersive spectrometer that was attached to a JEOL JSM-6610LV scanning electron microscope. To study the crystallinity, disorder and defects in the structure of the synthesized materials, Raman spectroscopy was used. For this, a Renishaw inVia Raman spectrometer with an Ar⁺-ion laser having 514.5 nm line along with 2.5 mW laser...
power was used. The obtained Raman spectra display a resolution of ∼0.5 cm⁻¹. TEM and HRTEM analysis was performed using an FEI-Technai-G20 with a LaB6 filament operating at 200 kV accelerating voltage. Sample preparation for TEM analysis was carried out by placing a drop of the synthesized sample that was dispersed in ethanol (25%) on a carbon-coated copper grid, and thereafter, the solvent was allowed to evaporate. A UV–vis spectrophotometer (Shimadzu UV-2450) was utilized to study the catalytic activity of the synthesized catalyst. A multipoint BET technique was used to measure the surface area, pore volume, and pore radius, and the analysis was carried out by using a Quantachrome Autosorb-1C TCD analyzer. In this analysis, nitrogen was used as an adsorptive gas, and the nitrogen adsorption–desorption isotherms were obtained. The thermal stability of the synthesized materials was examined by the TGA technique using a Shimadzu DTG-60 apparatus under the flowing nitrogen at a rate 50 cm³/min. The analysis was recorded in a temperature range of 25–800 °C at a heating rate of 10 °C/min.

4.5. Catalytic Study for the Reduction of Nitroarenes and Dye Degradation. In order to study the activity of the synthesized AgNi alloy nanoparticle-decorated ZnO nanocomposite (AgNi@ZnO) as an efficient, recyclable, and stable catalyst, the reductions of 4-nitrophenol, 2-nitrophenol, and 2-nitroaniline were selected as model reactions. Several composites with different molar ratios of AgNi over ZnO were optimized to check their catalytic efficiency. The composite with a molar ratio of AgNi/ZnO (1:1.5) showed the highest catalytic activity. The evaluation of the catalytic reduction reaction of 4-nitrophenol, 2-nitrophenol, and 2-nitroaniline was performed in a manner as stated here. In the process, an aqueous solution (2.5 mL) of nitroarenes (0.2 M) and 0.3 mL of NaBH₄ (0.2 M) were taken in a standard quartz cuvette cell having a path length of 1 cm with 3.5 mL volume. To this, a 0.2 mL aqueous solution of the consistently dispersed AgNi@ZnO (0.3 mg/mL) catalyst was added, and UV–vis absorption spectra were recorded instantly against the bare sample. For the measurement of 4-nitrophenol and degradation of rhodamine B with various concentrations of the catalyst, and powder XRD patterns of the reused AgNi@ZnO catalyst (PDF).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c05266.

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Notes

The authors declare no competing financial interest.

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