Direct Z-Scheme AgBr/β-MnO₂ Photocatalysts for Highly Efficient Photocatalytic and Anticancer Activity

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1. INTRODUCTION

Highlights

- A highly efficient visible light-responsive photocatalyst, AgBr/β-MnO₂ nanocomposite, has been synthesized.
- The synthesized material was fully characterized using standard analytical techniques.
- The photocatalyst showed enhanced activity toward degradation of organic pollutants (dyes and drugs) and anticancer activity against A549 cancer cell lines.

Water is the most imperative part of our daily life and is used extensively for drinking, industrial purposes, public hygiene, energy, and agriculture. The rapid growth of the world population and the development of industries result in a vehement increase in environmental contamination by producing industrial effluents and waste materials. These toxic materials in the water system harm the ecological system and human health.⁴⁻⁵ Many industries use organic dyes for paint, leather, textiles, and other items. Ultimately, these colors are released into the environment, which is the primary source of raising the rate of contamination and declining water quality.⁶⁻⁸ Many dyes and pigments are produced annually in the entire world. Additionally, around 2,000,000 tons of industrial effluents are discharged daily into worldwide water.⁹,¹⁰ Although these dyes are chemically resistant and carcinogenic, they are still excessively used for different purposes, such as paint, cosmetics, textiles, food, pharmaceuticals, and pulp industries, which are considered the main source of organic dyes.⁸,¹⁰⁻¹¹ Removal of dyes from water systems is extremely desirable for a healthy environment.¹² Generally, organic pollutants and toxic contaminants are stable and hard to remove or degrade by traditional biochemical treatment. Recently, various technologies have been proposed for the remediation of pollutants, such as adsorption, oxidation process, photocatalysis, ion exchange process, metal–organic framework (MOF), and biodegradation.¹²⁻¹⁷ Qiu et al. studied...
the advantages and properties of biochar-based catalysts and their applications in the photocatalytic removal of organic contaminants. Among them, photocatalysis is considered a green and facile suitable technology for treating contaminated water. The synthesis of high-performance heterogeneous photocatalysis has become one of the most popular research areas, as this method is eco-friendly, low-cost, and highly effective. In addition, this method may lead to the degradation of organic/inorganic contaminants into harmless components. Metal oxide semiconductors based on photocatalysts have shown a promising capacity for the decomposition of organic contaminants. Recently, various metal oxide-based semiconductors, such as BiOCl, SnO₂, CeO₂, NiO₂, TiO₂, and MnO₂, have attracted wide attention due to their good stability and low toxicity. Moreover, reported various modified routes for the synthesis of BiOCl and used them in the photocatalysis of organic contaminants. Furthermore, these materials have better chemical properties and suitable band gaps to stimulate the organic reaction under UV/visible solar irradiation. Among different semiconductors, manganese dioxide (MnO₂) is considered a popular and most active photocatalyst for the oxidation of contaminants due to its high chemical stability, simple synthesis, low cost, environmental compatibility, low toxicity, and high adsorption. They have a narrow band gap as well as numerous morphology variations over a wide range of temperatures up to 1200 °C. Unfortunately, MnO₂, due to a narrow band gap, offers low activity under visible light. Therefore, the photocatalytic activity of MnO₂ under visible light can be improved by combining it with other semiconductors. In addition, low electron transfer and quick recombination of photogenerated electron–hole restricted the photocatalytic efficiency of MnO₂. Hence, research has offered the best way to enhance the use of MnO₂ in photocatalysis by rising the lifetime of charge carriers. Wu et al. synthesized the nanostructures of α-MnO₂/MnO₂ through catalytic oxidation via a potential-transformation synthesis process. Zhang et al. reported the synthesis of the Cu₂BrO₄/MnO₂ composite for removal of lomefloxacin, cefotin, and tetracycline with the loading of 0.3 g L⁻¹ of catalyst at pH 11 and offered excellent percent rate degradation up to 93.6% within 40 min. The nanocomposite 2D/2D g-C₃N₄/MnO₂ fabricated by Xia et al. studied the decolorization of dye and proposed a direct Z-scheme. Wen et al. investigated the photocatalytic degradation of Congo red, melamine blue, and rhodamine B in visible light with composite core–shell nanospheres of CS@MnO₂. The photocatalyst CS@MnO₂ established an excellent performance for decolorizing cationic and anionic dyes. Bao et al. reported the coupling of α-MnO₂ with h-MnO₃ for photocatalysis and as a supercapacitor. Besides, silver bromide (AgBr) is also considered a visible light p-type semiconductor having a low band gap (E_g = 2.69 eV) and is used in the photocatalytic reaction and antibacterial test.

2. EXPERIMENTAL DETAILS

2.1. Synthesis of Pure AgBr Nanoparticles. 1.7 g of AgNO₃ was dissolved in 50 mL of distilled water under vigorous stirring for 30 min in the dark to form a solution (A). At the same time, 1.19 g of KBr was prepared in 50 mL of distilled water and labeled as solution (B). Solution (B) was added dropwise to solution (A) under stirring to give a yellow precipitate. The mixed solution was kept under continuous stirring for 1 h in the dark for complete precipitation of AgBr. The product was filtered, washed with water, and dried at 120 °C for 12 h.

2.2. Synthesis of Pure β-MnO₂ Nanorods. β-MnO₂ was synthesized by stirring a mixture of 1.69 g of manganese sulfate monohydrate (MnSO₄·H₂O) and 2.28 g of ammonium persulfate ((NH₄)₂S₂O₈) in 80 mL of water. The dissolved mixture was transferred into an autoclave (100 mL) and heated at 140 °C overnight. The obtained product was filtered, washed several times with water and ethanol, and then dried at 70 °C overnight.

2.3. Synthesis of the AgBr/β-MnO₂ Nanocomposite. 0.2 g of as-synthesized β-MnO₂ was suspended in 50 mL of water through stirring and sonicating for 45 min. To this mixture, 50 mL of 0.1 M aqueous solution of AgBr was added through stirring in the dark for 30 min. Later on, 50 mL of KBr (0.1 M) was added dropwise to the above mixture and stirred for 80 min for complete precipitation. The obtained product was filtered, washed thoroughly with water, and dried at 80 °C overnight. The product was designated as 0.1 AgBr/β-MnO₂. For comparison, a similar procedure was adopted for the preparation of other prepared nanocomposite materials with 0.2 and 0.3 M AgBr onto β-MnO₂, and the obtained samples were named 0.2 AgBr/β-MnO₂ and 0.3 AgBr/β-MnO₂, respectively.

3. RESULTS AND DISCUSSION

3.1. Structural Study. The crystal structures of as-prepared samples (β-MnO₂ and AgBr) including AgBr/β-MnO₂ nanocomposites with the varying molar ratio of AgBr are presented in Figure 1. As can be seen from the obtained results, different diffraction peaks located at 28.63, 37.30, 40.84, 42.81, 56.60, 59.36, 65.87, 67.43, and 72.36° correspond to the (110), (101), (200), (111), (211), (220), (002), (310), and (301) tetragonal phases of pure photocatalyst β-MnO₂. The AgBr diffraction peaks centered at 26.68, 31.0, 44.4, 52.69, 55.04, 64.2, and 73.36° were attributed to (111), (200), (220), (311), (222), (400), and (420) crystal planes of hexagonal AgBr.

The AgBr/β-MnO₂ nano-
composites have the same diffraction peaks as those of AgBr. At the same time, the diffraction peaks of $\beta$-MnO$_2$ are so weak that they are difficult to observe in AgBr/$\beta$-MnO$_2$ nanocomposites compared with AgBr, which may be due to the small amount of $\beta$-MnO$_2$ in the nanocomposite materials, and its existence was later confirmed by the EDS. According to the above results, the prepared nanocomposite photocatalyst is AgBr/$\beta$-MnO$_2$.

### 3.2. FT-IR Analysis

FTIR spectroscopy was used to confirm the structural properties of the bare $\beta$-MnO$_2$, AgBr, and nanocomposites AgBr/$\beta$-MnO$_2$ with the varying molar ratio of AgBr, and their results are shown in Figure 2. The FTIR spectrum of AgBr shows absorption peaks at 3442 and 1617 cm$^{-1}$, corresponding to stretching and bending vibrations of the H−O bond in AgBr$_x$ octahedral units. The oxygen symmetry stretching modes of Mo−O appear at 1095 cm$^{-1}$.$^7,29$ The FTIR spectrum of AgBr shows absorption peaks at 3442 and 1617 cm$^{-1}$, which are caused by H$_2$O molecules (H−O stretching and bending vibration) adsorbed on the surface of AgBr.$^8$ The typical characteristic peaks of AgBr and $\beta$-MnO$_2$ are observed in AgBr/$\beta$-MnO$_2$ nanocomposites and combined spectra are shown, which means that there was a covalent bond formed between the $\beta$-MnO$_2$ and AgBr nanoparticles in the AgBr/$\beta$-MnO$_2$ system as a result of the nanocomposite formation.

### 3.3. SEM Analysis

The surface morphology and microstructure of $\beta$-MnO$_2$, AgBr, and 0.2 AgBr/$\beta$-MnO$_2$ nanocomposites were investigated by SEM analysis at different magnifications, and the obtained images are shown in Figure 3.

As displayed in (Figure 3a,b), the bare $\beta$-MnO$_2$ demonstrated nanorod-shaped morphology. While Figure 3c,d showed smooth spherical-like particles in pure AgBr, the SEM images of AgBr/$\beta$-MnO$_2$ nanocomposites (Figure 3e–f) showed that the majority of AgBr NPs are deposited on the surface of $\beta$-MnO$_2$, which possesses a rod with a sphere-like structure. It is interesting to note that AgBr particles were found to be smaller in the nanocomposite compared to bare AgBr particles. This phenomenon implies that the $\beta$-MnO$_2$ can significantly inhibit the growth of AgBr particles. The SEM analysis confirmed that the AgBr particles coupled with $\beta$-MnO$_2$ nanorods to form binary AgBr/$\beta$-MnO$_2$ hybrid heterostructures.

### 3.4. Energy Dispersion Spectra (EDS) and Elemental Mapping Analysis

The EDX analysis was carried out to determine the elemental composition of $\beta$-MnO$_2$, AgBr, and 0.2 AgBr/$\beta$-MnO$_2$ nanocomposites. The EDX confirms the existence of two elements (Mn and O) in the pure $\beta$-MnO$_2$ (Figure 4a), while the bare AgBr clearly shows two absorption peaks related to Ag and Br elements (Figure 4b). Figure 4c displays the EDX spectrum of the 0.2 AgBr/$\beta$-MnO$_2$ nanocomposite’s existence in all the elements (Mn, Ag, Br, and O), and the absorption peaks corresponding to these elements, which indicate the co-existence of AgBr and $\beta$-MnO$_2$. To further investigate the elemental dispersion in the sample, EDS elemental mapping was performed, and the results are shown in Figure S1. The pure $\beta$-MnO$_2$ shows uniformly distributed elements on the surface of a sample, while AgBr shows the non-uniform distribution of elements, as displayed in Figure S1a-b and Figure S1c,d, respectively. In addition, Figure S1e–h shows the elemental mapping of 0.2
AgBr/β-MnO₂ nanocomposites, confirming that (Ag, Br, Mn, and O) elements are homogeneously distributed and the heterojunction nanocomposite is effectively created.

3.5. TEM Analysis. The internal morphology and crystal structure of β-MnO₂, AgBr, and 0.2 AgBr/β-MnO₂ nanocomposites were further investigated by TEM analysis, and the representative morphology is shown in Figure 5. Figure 5a displays the TEM image of β-MnO₂, which confirmed the nanorod-shaped structure of the as-synthesized β-MnO₂. Figure 5b illustrates the spherical shape of the AgBr sample. Figure 5c shows the TEM image of 0.2 AgBr/β-MnO₂ nanocomposites, revealing the AgBr nanosphere’s dispersion on the surface of β-MnO₂ nanorods and suggesting that the AgBr nanospheres have grown directly on the surface of β-MnO₂ nanorods. It is worth noting that the TEM images of β-MnO₂, AgBr, and 0.2 AgBr/β-MnO₂ nanocomposites found structural morphologies that were similar to the SEM images in Figure 3.

The synthesis of 0.2 AgBr/β-MnO₂ heterojunctions has been confirmed by the foregoing discussions.
3.6. Optical Studies. The UV−vis diffuse reflectance analysis was used to investigate the optical properties of the generated β-MnO₂, AgBr, and AgBr/β-MnO₂ nanocomposites with different molar ratios of AgBr, and the results are shown in Figure 6a. The absorption edge for AgBr was found to be around 469 nm, while the UV spectrum for β-MnO₂ nanorods showed a broad absorption band in the region of 520 to 800 nm with a peak at 595 nm, which is attributed to the d−d transition of Mn ions. On the other hand, AgBr/β-MnO₂ composites with different AgBr molar ratios showed a wide absorption peak from 562 to 800 nm with the absorption edge at 600−635 nm. The results indicate that the absorption of the AgBr/β-MnO₂ nanocomposite increased with the loading of AgBr on β-MnO₂ materials, which was ascribed to the formation of Ag nanoparticles, which may be beneficial for light absorption and enhanced performance. The band gap energies of β-MnO₂, AgBr, and AgBr/β-MnO₂ nanocomposites were determined by eq 1.

\[
\alpha h\nu = A(h\nu - E_g)^{3/2} 
\]

Where the absorption coefficient, Planck's constant, light frequency, and band gap energy are denoted by \(\alpha\), \(h\), \(\nu\), and \(E_g\), respectively. For β-MnO₂, AgBr, and AgBr/β-MnO₂ nanocomposites with varying molar ratios of AgBr, the value of \(n\) is 1/2, 5, 68, 69 According to the plots of \((\alpha h\nu)^{3/2}\) versus \(h\nu\) (Figure 6b), the calculated values of \(E_g\) for β-MnO₂, AgBr, 0.1 AgBr/β-MnO₂, 0.2 AgBr/β-MnO₂, and 0.3 AgBr/β-MnO₂ were 1.33, 2.64, 1.30, 1.26, and 1.17 eV respectively.

3.7. Photoluminescence Study (PL). PL spectroscopy was used to assess the recombination rate of photogenerated \((e^-/h^+)\) pairs in the synthesized samples. In general, fast \(e^-\) and \(h^+\) recombination results in a higher PL signal, while lower recombination of \(e^-\) and \(h^+\) results in a lower PL signal. Figure 7 shows the PL spectra of β-MnO₂, AgBr, and AgBr/β-MnO₂ nanocomposites with various molar ratios of AgBr at an excitation of 350 nm. All synthesized samples produced emission peaks at about 680 nm; however, the 0.2 AgBr/β-MnO₂ sample showed the weakest emission signal, implying that the heterojunction between AgBr and β-MnO₂ could inhibit their recombination rate of photogenerated charge carriers and effectively enhance photocatalytic activity.

3.8. Electrochemical Impedance Spectroscopy (EIS) Analysis. Photocatalytic performance is influenced by the efficiency of charge separation of the photogenerated electron−hole pair, and EIS analysis gives the details of this parameter. In general, the lower charge transfer resistance and higher charge transfer impact are represented by the smaller arc radius. Figure 8 shows the Nyquist impedance spectra of β-MnO₂, AgBr, 0.1 AgBr/β-MnO₂, 0.2 AgBr/β-MnO₂, and 0.3 AgBr/β-MnO₂ photocatalysts. Among all samples, the EIS of 0.2 AgBr/β-MnO₂ exhibits the lowest semicircle diameter, signifying the lowest charge transfer resistance and the best transfer efficiency of the photoexcited charge carriers. In addition, the EIS analyses further confirm the formation of AgBr/β-MnO₂ heterostructures, enhanced \((e^-/h^+)\) separation, and interface charge transfer properties.
3.9. Photocatalytic Degradation Study. To test the photocatalytic activity of all the produced catalysts, they were used to study the photo-decolorization of dyes (RhB and MB) in an aqueous solution under a visible light source in the presence of atmospheric air. All photochemical tests were carried out after 30 min of agitation of the aqueous dye solution in the presence of a photocatalyst to equilibrate adsorption−desorption. The UV−vis absorption spectra of an irradiated aqueous solution of MB and RhB at different time intervals in the presence of 0.2 AgBr/β-MnO₂ nanocomposites are shown in Figures 9a and 10a. The absorption intensity diminishes as illumination time increases, leading to a 97% degradation of MB in 12 min and 98.9% of RhB in 9 min, respectively.

Figures 9b and 10b depict the change in concentration against illumination time for the degradation of MB and RhB under comparable conditions with and without photocatalysts. The figure shows that in the absence of catalysts, dye degradation is negligible, implying that they are extremely stable and cannot be decolorized by direct photolysis. It was also discovered that in the presence of 0.2 AgBr/β-MnO₂, both
suspension is illuminated over 0.2 AgBr/UV vis absorption spectra of paracetamol in an aqueous solution was studied under similar reaction conditions. The change in the degradation of a colorless compound such as paracetamol Table 1. Pseudo Zero-, First-, and Second-Order Rate Constants, and the Corresponding R² Values for all the Synthesized Photocatalysts

| sample          | zero-order (kapp) (ppm min⁻¹) | R²        | first-order (kapp) (min⁻¹) | R²        | second-order (kapp) (ppm min⁻¹) | R²        |
|-----------------|--------------------------------|-----------|---------------------------|-----------|-------------------------------|-----------|
| blank           | -0.0114                        | 0.8499    | 0.0                       | 0.0       | 0.0033                        | 0.8211    |
| β-MnO₂          | -0.019                         | 0.9658    | 0.01345                   | 0.77624   | 0.0066                        | 0.95526   |
| AgBr            | -0.110                         | 0.9438    | 0.0658                    | 0.92791   | 0.08741                       | 0.9582    |
| 0.1 AgBr/β-MnO₂ | -0.1664                        | 0.7849    | 0.2463                    | 0.9881    | 0.80305                       | 0.94765   |
| 0.3 AgBr/β-MnO₂ | -0.1621                        | 0.7911    | 0.3233                    | 0.98816   | 0.4539                        | 0.98726   |
| 0.2 AgBr/β-MnO₂ | -0.1736                        | 0.7027    | 0.4964                    | 0.99782   | 2.4057                        | 0.86581   |

dyes degraded more effectively than in the presence of any other produced catalysts.

To distinguish between direct and indirect photocatalysis, the degradation of a colorless compound such as paracetamol was studied under similar reaction conditions. The change in UV–vis absorption spectra of paracetamol in an aqueous suspension is illuminated over 0.2 AgBr/β-MnO₂ nanocomposites under visible light irradiation as shown in Figure 11a. The results show that the optical intensity diminishes with increasing illumination time, showing 80% degradation after 180 min.

In addition, Figure 11b shows the change in paracetamol concentration as a function of irradiation time with and without various catalysts. Without a catalyst, the photo-decomposition of paracetamol is mostly negligible, indicating that paracetamol is stable under direct photolysis. Furthermore, the 0.2 AgBr/β-MnO₂ nanocomposite was found to degrade paracetamol faster than any other photocatalyst.

3.10. HPLC Measurement. The photocatalytic degradation of paracetamol by the synthesized catalyst (0.2 AgBr/β-MnO₂) in the presence of visible light was also carried out by HPLC to analyze the by-products formed during the photo-oxidation reaction. The starting material peak, which occurs at a retention time of R₂ = 7.5 min, continuously drops with illumination time and is eliminated within 180 min, as shown in Figure S2. Furthermore, no by-products are detected as observed in the HPLC spectra.

3.11. Kinetics of RhB Degradation. The kinetic models are essential for familiarizing yourself with the behavior of the photocatalytic activity. Herein, we have utilized three kinetic models to determine the kinetics of RhB decolorization with all produced catalysts. Eqs 2–4 expressed in terms of the decomposition rate with pseudo zero-, first-, and second-order kinetics.

\[
C_t = C_0 - k_1 t 
\]

\[
\ln(C_0/C_t) = k_2 t
\]

\[
\frac{1}{C_t} = \frac{1}{C_0} + k_3 t
\]

The concentrations of RhB before and after irradiation time t are C0 and Ct respectively, and k₀, k₁, and k₂ are the pseudo zero-, first-, and second-order rate constants. Figure 12a–c show the linear fit for the decolorization of RhB with bare AgBr, β-MnO₂, and various nanocomposites (AgBr/β-MnO₂) vs. irradiation time. The rate constant \(k_0\), \(k_1\), and \(k_2\) for the removal of RhB, corresponding to pure and nanocomposite materials determined from Figure 12, is shown in Table 1. The table displays the rate constant and the corresponding correlation coefficient \(R^2\) for AgBr, β-MnO₂, and nanocomposites (AgBr/β-MnO₂) with a varied molar ratio of AgBr (obtained from a linear fit of C₀, \(\ln(C_0/C_t)\), and \(1/C_t\) vs. irradiation time). In comparison to pure materials, all nanocomposite materials showed a better apparent rate constant. Due to more significant dye adsorption on the catalyst’s surface, the photocatalyst 0.2 AgBr/β-MnO₂ nanocomposite demonstrated the most significant rate constant within 9 min of irradiation duration. In addition, the results suggest that the first-order model showed a better fit than the zero- and second-order models for the photocatalytic decomposition of RhB dye.

3.13. Stability of the Photocatalyst. The recyclability of photocatalysts has always been an essential factor in determining their stability. As a result, for the degradation of...
RhB dye under comparable conditions, a four-cycle photostability test of 0.2 AgBr/β-MnO₂ was performed. The catalyst was collected after each irradiation, filtered, washed, dried, and reused for the next photoreaction experiment. Figure 13a shows the % degradation of RhB during each cycle of irradiation of an aqueous suspension for 9 min under similar conditions. A minimal decrease in photocatalytic efficacy was seen after four progressive runs, demonstrating the outstanding stability of the 0.2 AgBr/β-MnO₂ nanocomposite, which is essential from an application standpoint. In addition, the XRD study of 0.2 AgBr/β-MnO₂ before and after the photocatalytic experiment revealed no difference in the crystal structure of the catalyst (Figure 13b), showing outstanding stability of the produced material. The results clearly indicate that the photocatalyst is easily extracted and recycled for subsequent reactions with no perceptible efficiency loss.

3.14. In Vitro Cell Viability Studies Using the MTT Assay. The nanocomposite AgBr/β-MnO₂ (with a 0.2 M concentration of AgBr) performed better photodegradation activity and was chosen to evaluate the anticancer test. In vitro anticancer activity of 0.2 AgBr/β-MnO₂ was carried out on human lung cancer cell lines (A549). The viability of the cells was evaluated using an MTT assay by increasing the treatment concentration (25–200 μg/mL) of catalysts under dark and visible light conditions after 48 h. The detailed experimental procedure has been provided in the Supporting Information. The catalyst showed excellent anticancer activity under visible light and was found to inhibit A549 cell proliferation in a dose-dependent manner. Figure 14 indicates that there was no difference in the activity under dark and light conditions up to 100 μg/mL, but an enhancement in the activity was observed at higher concentrations under visible light treatment. For instance, cell viability at 200 μg/mL under dark treatment was approximately 45%, which was reduced to approximately 30% upon exposure to visible light. These observations could be attributed to the fact that photocatalysts increase ROS production, which leads to cell death. Furthermore, Figure 15 clearly shows a reduction in the typical morphology of A549 cells upon treatment with 0.2 AgBr/β-MnO₂.

3.15. Quenching Experiments and Photocatalytic Mechanisms. The purpose of the trapping studies was to find out the key active species involved in the photodegradation reaction. During RhB photodegradation, quenchers such as benzoquinone (BQ), isopropanol (IPA), and ethylenediaminetetraacetic acid disodium (EDTA-2Na) are used to capture O₂•−, •OH, and h⁺, respectively. Figure 16a demonstrates the effect of IPA, BQ, and EDTA-2Na on the photocatalytic decomposition of RhB in the presence of 0.2 AgBr/β-MnO₂ in an aqueous solution under visible light. The results imply that O₂•− and h⁺ were the primary active species. On the other hand, the introduction of isopropyl alcohol as an •OH scavenger did not affect the photodegradation of RhB.
The ESR study was conducted using 0.2 AgBr/β-MnO₂ composites to further demonstrate the formation of the main active substance during the degradation process, and the results obtained are shown in Figure 16b. As observed from the figure, no DMPO-•O₂⁻ signals are produced in the dark; however, DMPO-•O₂⁻ peaks can be seen under the influence of light (500 W lamp, 1–2 min irradiation). This result and the trapping experiment imply that •O₂⁻ is the primary active species.

In addition, the participation of •OH in the photocatalytic degradation process was investigated using the terephthalic acid photoluminescence probe method. The irradiation of terephthalic acid under an alkaline medium in the presence of a photocatalyst produces 2-hydroxy terephthalic acid at an excitation of 315 nm, giving a fluorescence peak at 425 nm. Figure 17 exposed the fluorescence spectrum during illumination of a 5 × 10⁻⁴ M basic terephthalic acid solution (λexc = 315 nm) with TiO₂ (a) and 0.2 AgBr/β-MnO₂ (b).

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The positions of band edges for the semiconductor were estimated using the electronegativity concept to investigate the charge transfer mechanism of the 0.2 AgBr/β-MnO₂ heterojunctions using the following equations:

\[ E_{VB} = \chi - E^* + 0.5 E_g \]  
\[ E_{CB} = E_{VB} - E_g \]

Where \( E_{CB} \) and \( E_{VB} \) are the CB and VB edge potentials, respectively, \( E^* \) is the free electron energy on the hydrogen scale (4.5 eV), \( \chi \) is the absolute electronegativity of the compound, and \( E_g \) is the semiconductor band gap. The absolute electronegativity was determined from the mean of the first ionization energy (eV) and electron affinity (eV). Thus, the calculated values of \( \chi \) for β-MnO₂ and AgBr were found to be 5.94 and 5.8 eV, respectively. By referring to eqs 5 and 6, the values of the VB and CB for β-MnO₂ are found to be 2.1 and 0.77 V, and those for AgBr are 2.62 and −0.02 V, respectively. The measured band gap energies (\( E_g \)) of β-MnO₂ and AgBr are 1.33 and 2.64 eV, respectively. Based on the aforementioned experimental findings, a potential Z-scheme photocatalytic mechanism for the excellent photocatalytic performance of the AgBr/β-MnO₂ nanocomposite has been proposed and is schematically represented in Schemes 1 and 2. It is well known that both β-MnO₂ and AgBr can absorb photons and create electron/hole pairs when exposed to light (Scheme 1). Because the CB of AgBr is more negative than that of β-MnO₂, photogenerated electrons can be transported from the CB of AgBr to the CB of the β-MnO₂ semiconductor. In addition, the valence band (VB) of β-MnO₂ (2.1 V) is lower.
than the VB of AgBr (2.62 V), and the photogenerated holes in the VB of AgBr can move to the VB of β-MnO$_2$; meanwhile, the VB potential of β-MnO$_2$ (2.1 V) is lower than the potentials of *OH/OH$^-$ (+2.38 V) and *OH/H$_2$O (+2.72 V). The photoinduced h$^+$ in the VB of β-MnO$_2$ cannot oxidize OH$^-$ or H$_2$O to *OH, which is in agreement with the fluorescence measurement that *OH remains undetected by using β-MnO$_2$/AgBr as the catalyst under light illumination, and the photoinduced h$^+$ in the VB of β-MnO$_2$ can directly oxidize the adsorbed organic compound to give harmless products. Moreover, the accumulated electron in the CB of β-MnO$_2$ could not react with O$_2$ to produce O$_2^{**}$ due to the redox potential of O$_2$/O$_2^{**}$ (−0.33 V vs. NHE) being more negative than the CB energy level of β-MnO$_2$ (0.77 V). This contradicted the results of the above-mentioned trapping studies, which showed that *O$_2$ was the dominant reactive species in the AgBr/β-MnO$_2$ system. As a result, the Z-scheme system would be closer to the actual photocatalytic mechanism. As shown in Scheme 2, the photogenerated electrons in the $E_{CB}$ of β-MnO$_2$ tend to transfer and recombine with the photogenerated holes in the $E_{VB}$ of AgBr due to the relative positions of the $E_{CB}$ and $E_{VB}$ resulting in efficient separation of electrons in the CB of β-MnO$_2$ and holes in the VB of AgBr.

The photoinduced electrons in the CB of AgBr could easily be shifted to the Fermi level of Ag nanoparticles. Interestingly, the photo-corrosion of AgBr at the interface between AgBr and β-MnO$_2$ under visible light irradiation results in the formation of metallic Ag nanoparticles. As the Fermi level of Ag $−0.4$ V (vs. NHE)$^{36,72}$ shifts from $−0.02$ V (vs. NHE) to an energy level greater than the usual redox potential of O$_2$/O$_2^{**}$ (−0.33 V vs. NHE), the transferred electrons on the surface of AgBr nanoparticles may then react with absorbed oxygen to produce *O$_2$ $^{56,73,75}$ which might further react directly with the compound to give the degradation products, whereas the holes in the VB of β-MnO$_2$ could directly oxidize the organic compound.

These results are consistent with the trapping experiment, which showed that adding IPA as an *OH scavenger did not affect the degradation process, while adding BQ/EDTA as *O$_2$ and h$^+$ drastically affects the degradation rate (Figure 16).

4. CONCLUSIONS

In conclusion, Z-scheme AgBr/β-MnO$_2$ nanocomposites were effectively produced using a simple in-situ precipitation process used in the photocatalytic decomposition of organic compounds in water using visible light (>420 nm). Different techniques were used to investigate the as-made photocatalyst’s structure, morphology, surface, and optical properties. Under visible light irradiation, the synthesized nanocomposite AgBr/β-MnO$_2$ showed better activity for the photodecomposition of MB, RhB, and paracetamol compared with pure AgBr and β-MnO$_2$. Of these, the nanocomposite AgBr/β-MnO$_2$ with 0.2 M AgBr onto β-MnO$_2$ showed the highest activity. Furthermore, radical trapping tests demonstrated the Z-scheme photodegradation of the compounds under investigation using the as-obtained AgBr/β-MnO$_2$ nanocomposite. Besides, the photo-corrosion of AgBr nanoparticles was significantly reduced due to the effective transfer of electrons between AgBr and β-MnO$_2$. This work may give more insights into the understanding of the mechanism for the degradation of organic compounds with AgBr/β-MnO$_2$ composites via Z-scheme heterostructure design. In addition, the visible light-mediated anticancer activity of AgBr/β-MnO$_2$ was carried out on A549 lung cancer cell lines. The MTT assay indicated higher anticancer activity (cell viability = 45%) upon irradiation compared to dark (cell viability = 45%) on treatment with 200 μg/mL of 0.2 AgBr/β-MnO$_2$. This may be due to the generation of a higher level of ROS in vitro over irradiated AgBr/β-MnO$_2$, leading to cell cytotoxicity. A more mechanistic investigation of its potential activity is currently underway in our laboratory. This approach offers several advantages such as the use of visible light, short reaction time, use of a smaller amount of the photocatalyst, high degradation efficiency, utilization of air as the oxidant, use as an anticancer agent, and ease of catalyst recycling without reduction in the degradation efficiency.

ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://doi.org/10.1021/acsomega.2c03260.
Details on the materials used for synthesizing the composite photocatalyst, techniques used for material characterization, experimental procedure for the photocatalytic test, trapping, and cell culture treatment, elemental mapping analysis, and HPLC results (PDF)

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors are grateful for the support from the SERB Project (CRG/2019/001370), DST, and UGC for DRS II, PURSE, and FIST to the Department of Chemistry at Aligarh Muslim University, Aligarh. M.Z.A.W. is thankful to ICCR for the financial assistance for his Ph.D. program.

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