Supplementary Information (SI) for Nanoscale Advances.

Developing a crystalline n-AgBr/p-NiO binary heterojunction for photocatalytic degradation of organic contaminants accompanied mineralization, adsorption, and antimicrobial study

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2. Experimental

2.1. Chemicals required

Nickel (II) Nitrate Hexahydrate [$Ni(NO_3)_2.6H_2O$] was bought from Sisco Research Laboratories India Pvt. Ltd. The Potassium Bromide (KBr) and Potassium dichromate ($K_2Cr_2O_7$) was obtained from Thermo Fisher Scientific, India Pvt. Ltd. Whereas, Silver Nitrate and Rhodamine B (RhB), Bisphenol A (BPA) and 1,5-diphenylcarbazide (DPC) were acquired from Sigma Aldrich. Other compounds like terephthalic acid, isopropyl alcohol (IPA), disodium ethylenediaminetetraacetate (EDTA-2Na), and benzoquinone (BQ) were procured from Merck. All the chemicals were used without additional purification. The solutions of organic compounds were made in freshly prepared double distilled water.

2.2. Synthesis of pure NiO

A solution of Nickel (II) Nitrate Hexahydrate [$Ni(NO_3)_2.6H_2O$] (0.1 M) was prepared in water (140 ml) and an aqueous solution of NaOH (1 M) was added dropwise with stirring to give a greenish precipitate product. The pH of the solution was maintained at 10 and it was further stirred for 8 h at room temperature to complete the growth of precipitate. The precipitate was filtered and washed several times with water, and then dried overnight at 80 °C. The synthesized material was then heated at 400 °C for two hours.

2.3. Synthesis of pure AgBr

The preparation of AgBr NPs involved dissolving $AgNO_3$ (1.7 g) in distilled water (50 mL) and stirring it quickly in the dark for 30 minutes. A KBr solution (50 ml, 1.19 g) was added dropwise to the AgBr solution under stirring in the dark to produce a light yellow precipitate and stored for 2 h under gentle stirring. The AgBr product was processed by filtration as a light yellow precipitate, washing with water, and drying overnight at 70 °C.

2.4. Synthesis of AgBr-NiO nanocomposite

The AgBr-NiO nanocomposite was synthesized by deposition-precipitation method under ambient conditions. The prepared NiO (1 g) was suspended in 100 ml water, stirring and sonication for 1 hour, followed by adding a 100 ml solution of KBr (0.05 M) slowly with stirring for 30 minutes. Then, 100 ml of the solution of prepared $AgNO_3$ (0.05 M) was added to the above mixture under a magnetic stirrer in the dark and kept for 12 h. The obtained mixture was filtered, washed with water, and dried at 80° C overnight. The product was labeled as 0.05 AgBr-NiO. Synthesis of the other prepared samples of 0.1 AgBr-NiO and 0.15 AgBr-NiO was achieved by altering the molar ratio of samples (0.1 and 0.15 M) under similar conditions.

2.5. Materials characterization

All the prepared materials were characterized by using standard analytical techniques, including X-ray beam diffractometer (XRD), Fourier Transform infrared spectroscopy (FTIR), Diffuse reflectance spectroscopy (UV-vis DRS), and Scanning electron microscope (SEM). The synthesized samples phase structure was monitored on an X-ray beam diffractometer (Smart Lab S. E.) using graphite monochromatic radiation [Cu Kα radiation (1.540 Å)], with a voltage of 30 kV and a 15 mA current at an output speed of 10^{o}/min in the range of 5-80^{o} at the value of 2θ. The FTIR of all the synthesized materials was recorded on Perkin Elmer Spectrum 2 with a KBr disc as reference. For a better understanding of the optical properties of samples, UV-vis diffuse reflectance spectrophotometer (DRS, Perkin Elmer Lambda 35) was used. The SEM study was conducted with the JEOL JSM-6510L instrument to know the morphology of prepared samples. The EDX analysis was carried out to detect the elements present in the synthesized material and mapping images of the samples were made on an energy-dispersive X-ray detector (EDX) equipped with a microscope (JEOL-JSM-6510). A transmission electron microscope (TEM) was employed to investigate further the internal morphology of the samples using the JEOL-JEM 2100 instrument operating at 120 keV. Fluorescence Spectrometer (Perkin Elmer LS 55) was used to measure the photoluminescence spectra of the synthesized materials. A JOEL (JES-FA200) ESR spectrometer has been utilized to analyze the EPR signals of radical spin trapped by DMPO (5,5-dimethyl-1-pyrroline N-oxide). The electrochemical experiments were conducted in a three-electrode beaker cell with an Ag/AgCl reference electrode, a platinum wire counter electrode, and 0.5 N Na_2SO_4 aqueous electrolyte. The CHI660E electrochemical workstation (CHI Instruments, USA) was used to determine the electrochemical performance of the samples. The catalyst ink was prepared with 5 mg of sample in 90 μL Milli-Q water, 100 μL of isopropyl alcohol (IPA), and 10 μL of Nafion.

2.6. Trapping experiment

The trapping experiments were performed to know the key reactive species involved in the degradation process using the most active catalyst. In this study, irradiation of an aqueous solution of RhB was carried out using different scavengers such as isopropyl alcohol (2 mM), benzoquinone (2 mM), and EDTA-2Na (2 mM) in the presence of 0.15 AgBr-NiO nanocomposite to capture the hydroxyl radicals, superoxide radicals, and holes, respectively. The reaction conditions were kept similar to those used for photodegradation reactions, where the catalyst was added after the addition of scavengers into the model pollutant solution. On a quantitative basis, the hydroxyl radical was estimated by the terephthalic acid photoluminescence (TA-PL) process. In a typical procedure, 220 mg of the photocatalyst was taken in 220 mL aqueous solution containing (TA (5×10^{-4} M) and NaOH (2×10^{-3} M). Upon excitation at 300 nm, the hydroxyl radicals generated may react with terephthalic acid to give a fluorescent adduct (2-hydroxy- terephthalic acid), which was monitored spectrofluorimetrically.

2.7. Evaluation of photocatalytic study

All photocatalytic tests were carried out in a photoreactor made of Pyrex glass. During the experiment, eco-friendly light radiation (visible light radiation, $\lambda \geq 400$, halogen lamp (500W)) was used under continuous bubbling of atmospheric oxygen, and the photocatalytic reaction was adjusted at 25 °C temperature by circulating cold water. The degradation of organic compounds, RhB & BPA and photocatalytic reduction of Cr(VI) were studied by making an aqueous in distilled water.

In the photocatalytic experiment, 200 mg of the required catalyst was suspended in a 200 mL solution of pollutant, then sonicated and agitated for 30 min to scatter the catalyst particles into the solution and to ensure the adsorption-desorption equilibrium.

The samples were collected at various time intervals and centrifuged (6000 rpm) to remove the photocatalyst and monitored spectrophotometrically and the Cr(VI) were analyzed through DPC method [1–3]. With the use of the following equation, the degradation efficiency (D.E.) of all compounds under investigation was calculated (Eq. S1).

$$\text{D.E. (\%)} = (C_0 - C_t)/C_0 \times 100 \qquad \text{(S1)}$$

Where, C_0 is the sample's initial concentration before being exposed to light, and C_t is the concentration at the end of irradiation.

2.8 Adsorption studies

The adsorption experiments for the removal RhB adsorbate on the NiO-AgBr adsorbent were performed using Erlenmeyer flask of borosil glass. At 303 k, the adsorbate under investigation at various concentrations range (2.5-20 mgL^{-1}) kept in the flask and then the adsorbate molecule with different dosages (0.5-2.5 gL^{-1}) were added and this heterogeneous solution were properly shaken on the flask shaker instrument (160 rpm). The pH was adjusted through the diluted solution of HCl and NaOH in the range of pH 3-11. After the adsorption process, the solution was filtered out and its absorbance value were measured through UV-Vis spectrophotometer to determine the concentration of RhB at 553 nm. The percentage removal efficiency (R.E.) and adsorption capacity at equilibrium (q_e, mg/g) were measured by following Eq. S2&3 [4].

$$R.E. (\%) = (C_0-C_e)/C_0 \times 100 \tag{S2}$$

$$q_e = \frac{(C_0 - C_e).V}{M} \tag{S3}$$

Where q_e, C_0, and C_e denote RhB's adsorption capacity (mg/g), initial, and equilibrium concentrations (mg/L), respectively. M and V represent the mass of 0.15AgBr-NiO (g) and the volume of solution (L), respectively.

2.9. In vitro antibacterial studies

Agar-well diffusion method was used to test the antimicrobial activity of all synthesized different samples as displayed by Gonelimali et al [5]. Gram-positive test bacteria, *Micrococcus luteus* and *Staphylococcus aureus,* were grown in nutrient broth (peptone, 5 g/L, sodium chloride, 5 g/L, meat extract, 1.5 g/L, and yeast extract, 1.5 g/L). 0.1 ml of fresh bacterial culture was pipetted into a sterile petri dish with 40 ml of nutrient agar (Peptone-5 g/L, Sodium chloride-5 g/L, meat extract-1.5 g/L, yeast extract-1.5 g/L, Agar-20 g/L). The cultures were spread all over the petri dish containing nutrient agar. Five wells were cut using a sterile cork borer (6 mm in diameter) and sealed with 0.7% soft agar. Then, 150 µl of each test sample at different concentrations

(10,000 ppm, 1,000 ppm, 750 ppm, 500 ppm, and 250 ppm) were added to each well. The plates were placed into an incubator for incubation at 37 °C in the presence of fluorescent light. After incubation for 18 hours, the diameters of the growth inhibition zone were measured in mm (millimeters) using the antibiotic zone scale.

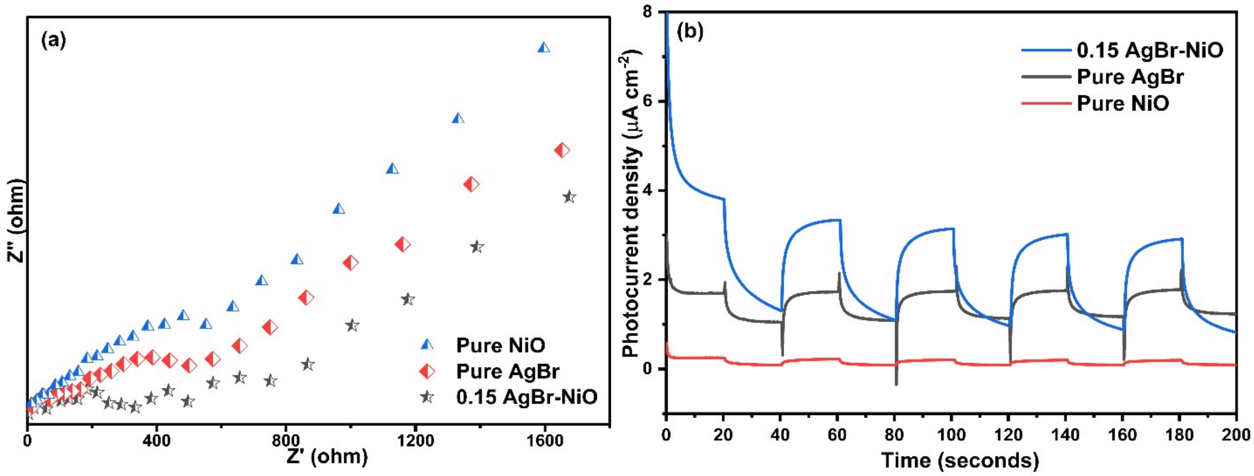
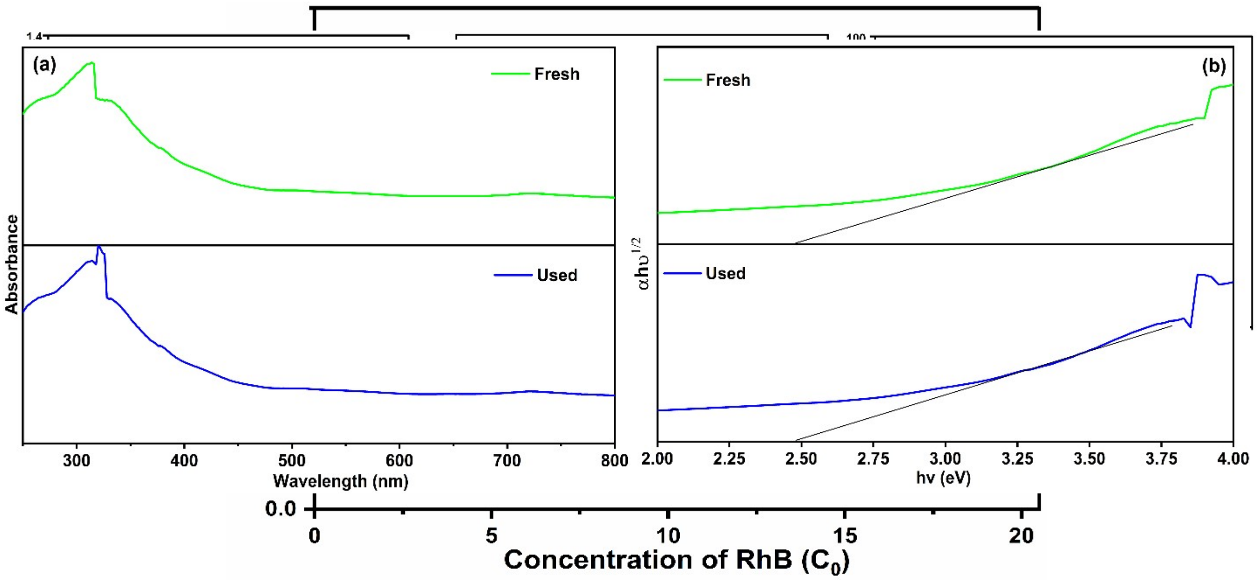


Fig. S1 EIS Nyquist plot (a) and Photocurrent responses (b) of pure NiO, pure AgBr, and 0.15 AgBr-NiO.
Fig. S2 Change in absorbance of DPC-Cr(VI) complex after irradiation with 0.15 AgBr-NiO (a), decrease in concentration of complex in presence of pure, composite and absence of photocatalyst (b), and effect of different scavengers on the photocatalytic reduction (c).
Fig. S3 UV-Vis DRS spectra (a) and corresponding Tauc plot (b) of 0.15 AgBr-NiO before and after the photodegradation experiment.

Table S1. The Langmuir separation factor (R_L) of the 0.15 AgBr-NiO for the absorption of RhB

RhB Initial concentration	R_L value
C_0 (mg L^{-1})	



2.5	0.7573
5	0.6094
10	0.4488
15	0.3411
20	0.2806

Fig. S4 Plot of R_L vs C_0 representing the decrease in separation factor with variation in initial concentrations of RhB.

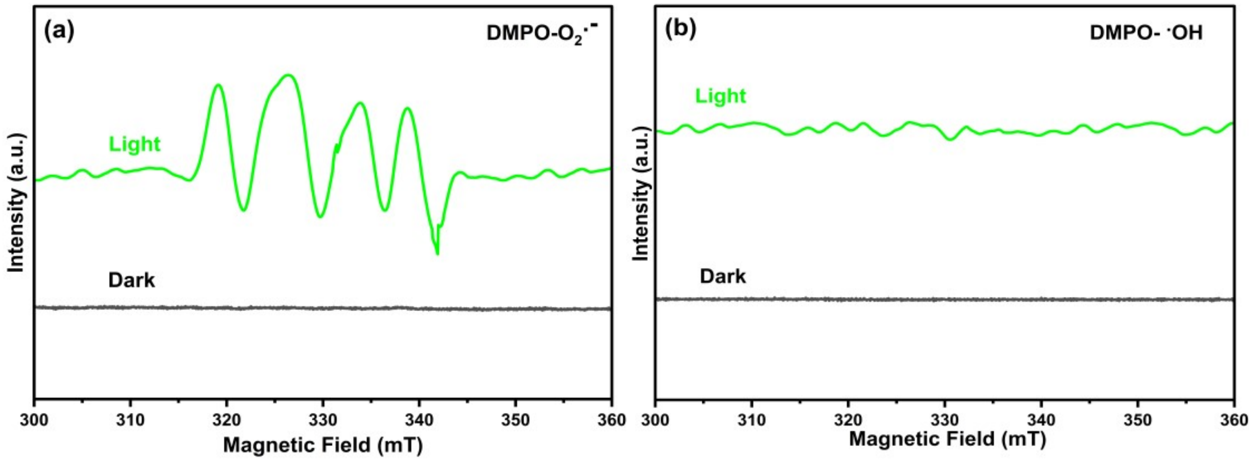


Fig. S5 ESR signals of DMPO-$O_2^{\bullet-}$ (a) and DMPO-$^{\bullet}OH$ (b) adducts in 0.15 AgBr-NiO composite.

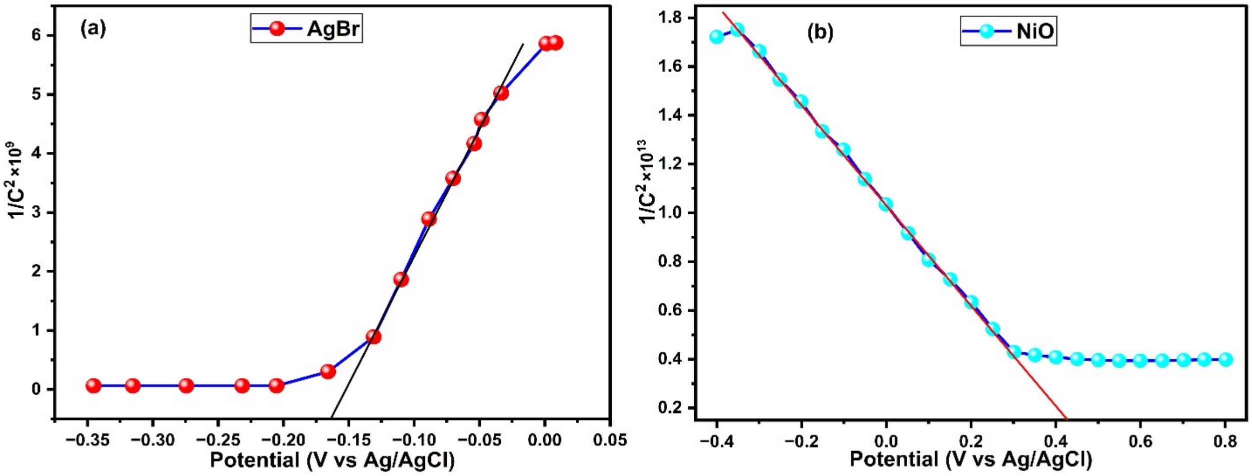


Fig. S6 Mott-Shottky plot of pristine AgBr **(a)** and pristine NiO **(b).**

Table S2 Comparison of photocatalytic performance of the prepared catalysts with the previously reported materials

Pollutants	Conc.	Photocatalyst	Cat. Dosage (g/L)	Light Source	Time (min)	Degradation Rate (%)	References
RhB BPA	10 ppm 30 ppm	NiO/AgBr	1	500W halogen lamp	11 120	97.6 85	**Present Work**
MB MO	40 ppm 40 ppm	ZnO/ZnS/AgBr	0.5	UVA irradiation (Philips TL 8W × 4)	40 40	99 81.7	6
MB RhB PCM	12 ppm 12 ppm 12 ppm	AgBr/β-MnO_2	1	500W halogen lamp	12 9 180	97 98.9 80	7
RhB	10 ppm	$AgBr/Ag_3PO_4$	1	300 W Xe lamp	12	83	8
RhB	0.01 mM	$TiO_2/Ag_2WO_4/AgBr$	1	50 W LED lamp	60	99.4	9
RhB CIP	0.01 mM 0.018 mM	Ag/AgBr@G	0.5 0.3	500W halogen lamp	10 120	94.8 99	10
RhB TC	0.01 mM 30 ppm	$Bi_2SiO_5/Ag/AgBr$	0.4	500W Xe lamp	30 150	97.2 ~80	11
MO RhB TC	0.01 mM	$TiO_{2-x}/BiOBr/AgBr$	1 0.5 1	50W LED lamp	120 15	97.7 99.4 90.8	12

AO7	20 ppm	*p*-BiOI/*p*-NiO	1	400W halogen lamp	180	97.5	[13]
Cr (VI)	20 ppm	NiO/TiO_2	1	100W Hg lamp	60	~95	[14]
MB PCM ASP	5ppm 2ppm 2ppm	NiO/Ag/TiO_2	1	400W halogen lamp	60 60 60	93.15 - -	[15]

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