Supporting Information

Amplified photocatalytic performance of UiO-66-NH_2/BiOI@α-Bi_2O_3 ternary heterojunctions towards Congo red degradation and H_2O_2 production

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Total no. of Text sections: 2 (S1, S2)

Total no. of References: 5 (S1, S2, S3, S4, S5, S6)

Total no. of Figures: 2 (Figure S1, S2, S3)

S1. Experimental

S1.1 Materials

Analytical-grade chemicals were utilised to synthesize pristine and composite samples and conduct photocatalytic tests without further purification. Zirconium Chloride ($ZrCl_4$), 2-amino terephthalic acid (2-ATP), N, N-dimethylformamide (DMF), bismuth (III) nitrate pentahydrate [$Bi(NO_3)_3.5H_2O$], potassium Iodide (KI), ethylene glycol (ELG), hydrochloric acid (HCl), ethanol, and Congo red (CR) were used in the present study.

S1.2 Synthesis of α-Bi_2O_3

Fabrication of BR was performed to identify its presence in the fabricated ternary composite. Its synthesis process was performed by a simple solid-state route[S1]. A crucible containing a certain amount of Bi $(NO_3)_3.5H_2O$ was heated in a muffle furnace at 500 °C for 6 hours. The collected sample was then pulverized into fine powder to obtain BR.

S1.3 Material Characterisation

FE-SEM (JEOL JSM-7610FPlus) and HR-TEM (JEM 2100F JEOL) were used to study the morphology of the prepared samples. The chemical valence states of the catalyst surface were examined using Phi Ulvac X-ray photoelectron spectroscopy (XPS). The specific surface area of the prepared samples was determined through N_2 adsorption isotherms using a BET surface area analyzer (Nova 800). XRD (Rigaku Miniflex Japan) was used to investigate the structure and phase purity using wavelength λ = 1.54 Å of Cu Kα. JASCO FT/IR-4600 Type A

spectrophotometer was used to record the FTIR Spectra over a wavenumber range of 4000–400 cm^{-1}.

S1.4 Optical and electrochemical measurements

UV–Vis diffuse reflectance spectra (DRS) of the synthesised catalysts were recorded by a JASCO V-750 spectrophotometer to assess their optical absorption properties. Photoluminescence (PL) spectra were measured on a JASCO FP-8300 spectrofluorometer to evaluate charge carriers' recombination behaviour. Photoelectrochemical studies of the synthesized samples were conducted using an IVIUM nSTAT electrochemical analyser under illumination from a 300 W xenon lamp. A 0.1 M aqueous solution of sodium sulphate (Na_2SO_4, pH = 6.8) was used as the electrolyte. A three-electrode system was utilised, with an Ag/AgCl electrode functioning as the reference electrode, a platinum (Pt) electrode as the counter electrode, and a photocatalyst-coated fluorine-doped tin oxide (FTO) electrode as the working electrode for all electrochemical measurements.

S1.5 Photocatalytic CR degradation efficiency evaluation

A photochemical reactor (5D-FLEXI) was used to evaluate the photocatalytic activity of the synthesised catalysts by CR degradation under the interaction of visible light. Typically, 0.5 gL^{-1} of prepared photocatalyst was mixed in 50 ml of 50 ppm CR. The mixture was subsequently stirred in the dark for 30 minutes to establish adsorption-desorption equilibrium. Immediately afterward, the solution was exposed to visible light for 60 minutes under constant stirring. After 60 minutes, the catalysts were isolated from the solution through centrifugation, and the concentration of CR was determined by a UV-vis spectrophotometer (SYSTRONICS 2202) at a 495 nm wavelength. In order to achieve optimised photocatalytic reaction conditions for maximum degradation efficiency, experiments were conducted by varying catalyst dose

from 0.25 gL^{-1} to 1.0 gL^{-1}, CR concentration (25- 100 ppm), and pH (2.0-9.0). The performance of the fabricated photocatalysts was determined by Eq. 1.

$$\text{Degradation efficiency (\%)} = \left(\frac{C_0 - C_t}{C_0}\right) \times 100 \quad \ldots\ldots\ldots\ldots\ldots \quad (1)$$

Where C_t and C_o are represented as the concentration at time t, and the initial concentration of CR, respectively.

S1.6 Photocatalytic H_2O_2 production experiment

A measured amount of the synthesised photocatalyst (25 mg) was dispersed in 50 ml of an ethanol/water mixture solution prepared with a 1:9 w/w ratio. To attain adsorption-desorption equilibrium, the solution was stirred for 30 minutes in the dark under an oxygen-purged environment. Following this, the photocatalytic H_2O_2 production experiment was conducted under visible light for 1 hour. UV-Vis spectrophotometer (SYSTRONICS 2202) with absorbance at 350 nm was used to quantify liberated H_2O_2 through the iodometric method[S2].

S2. Factors affecting CR photodegradation

S2.1 Effect of pH

The photocatalytic degradation of CR was investigated using the synthesized samples at pH 2, 5, 7, and 9, as displayed in **Figure S2(a)**. It was observed that the percentage photodegradation was decreased under both acidic and alkaline conditions, suggesting that extreme pH levels negatively influence photocatalytic performance[S3]. UN, BM, and BBUN-4 demonstrated maximum CR degradation of 62.7%, 57.2%, and 97.25%, respectively, at pH 7. This finding emphasizes the potential of BBUN-4 for efficient CR removal in real-world water treatment applications, particularly under environmentally relevant conditions.

S2.2 Concentration of CR

CR solution concentration was varied from 25 ppm to 100 ppm to investigate the performance of UN, BM, and BBUN-4 photocatalysts. It was observed from **Figure S2(b)** that the CR degradation rate decreased upon raising the initial concentration. It might be attributed to the fact that the increased availability of dye molecules leads to the saturation of surface-active sites on the photocatalyst at higher CR concentrations. This hinders the interaction of light with the catalyst's surface, thereby reducing the overall degradation efficiency[S4]. Among the investigated samples, BBUN-4 demonstrated superior performance, achieving degradation efficiencies of 97.5%, 97.25%, 88.4%, and 76.3% for 25, 50, 75, and 100 ppm CR concentrations, respectively. The enhanced photodegradation of CR over BBUN-4 may be ascribed to its enormous surface area, which can accumulate large amounts of CR molecules through numerous surface-active sites. Interestingly, only a minimal difference in degradation efficiencies was observed between 25 ppm and 50 ppm CR concentrations. Based on this finding, subsequent studies were carried out by using a 50 ppm CR solution for further optimization and evaluation.

S2.3 Effect of catalyst dose

The dosage of the catalyst is a crucial parameter to adjudicate a photocatalytic system for its potential application in the real-world water environment. The photocatalytic efficiency of UN, BM, and BBUN-4 for the degradation of CR was determined at 0.25 g/L, 0.5 g/L, 0.75 g/L, and 1 g/L doses. The results illustrated in **Figure S2(c)** revealed that the degradation rate was increased first from 0.25 g/L to 0.5 g/L, followed by a sharp decline with further rising the dose. This decrease can be attributed to excessive catalyst concentrations causing photon reflection or scattering, thereby reducing their light absorption ability and their subsequent

activity. Additionally, higher catalyst dosages can lead to particle agglomeration, wherein particles cluster together, resulting in a reduced surface area, which renders fewer active sites available for the catalytic reaction[S5]. As observed from the figure, BBUN-4 displayed superior performance compared to UN and BM. It achieved the highest degradation efficiencies of 78.6%, 97.25%, 81.9%, and 68.7% for dosages of 0.25 g/L, 0.5 g/L, 0.75 g/L, and 1 g/L, respectively. Since maximum photodegradation of CR was achieved at 0.5 g/L, it was considered the optimal dosage for the photocatalytic CR degradation in the present system.

S2.3 Reusability and stability

The photocatalytic cycling experiments were performed to evaluate the reusability of BBUN-4. The catalyst was tested for four consecutive cycles of Congo Red degradation, and the results were shown in **Figure S2(d)**. It was evident from the figure that BBUN-4 exhibited 89% of CR degradation after the fourth cycle. This efficiency was approximately 8% less than that observed for the first run. The obtained result confirmed that the synthesised BBUN-4 can practically be used in the photocatalytic degradation of Congo red. The XRD patterns of BBUN-4 after the four consecutive cycles of reuse was compared with that of the fresh one and was presented in **Figure S3(a)**. Despite the attenuation of diffraction peak intensities after the cycling experiments, the peak position remains unchanged, indicating that the crystalline phase composition is preserved. As presented in **Figure S3(b)**, the FTIR spectra of the used catalyst exhibited the preservation of all characteristic peaks. A slight broadening and enhancement in the intensity of the O-H stretching region is noticeable, which can be associated with the adsorbed water molecules resulting from the degradation of CR dye[S6]. These results demonstrated that the catalyst maintains its structural integrity upon repeated use, underscoring its suitability for practical applications.

References

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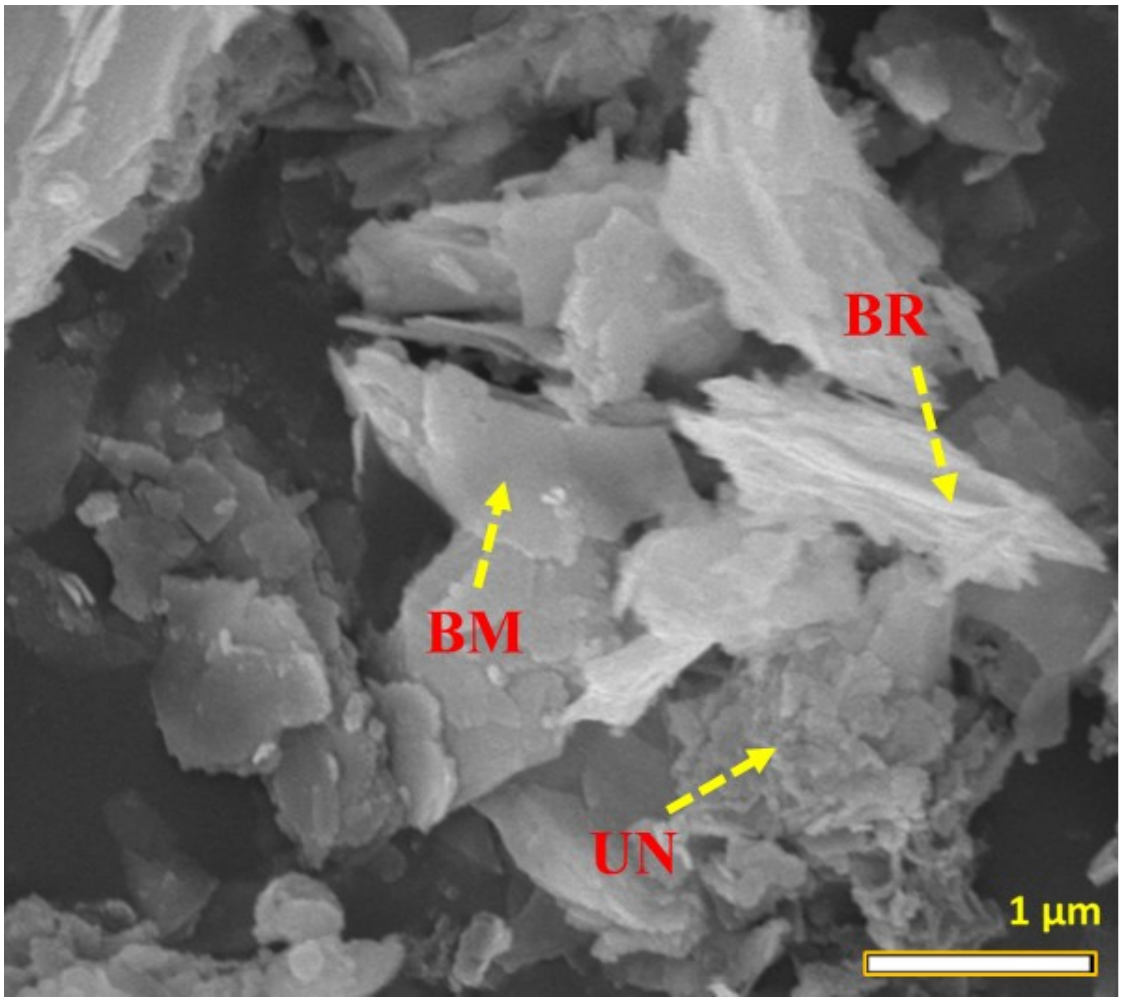

Figure S1. Field emission scanning electron microscopy (FE-SEM) images of BBUN-5.

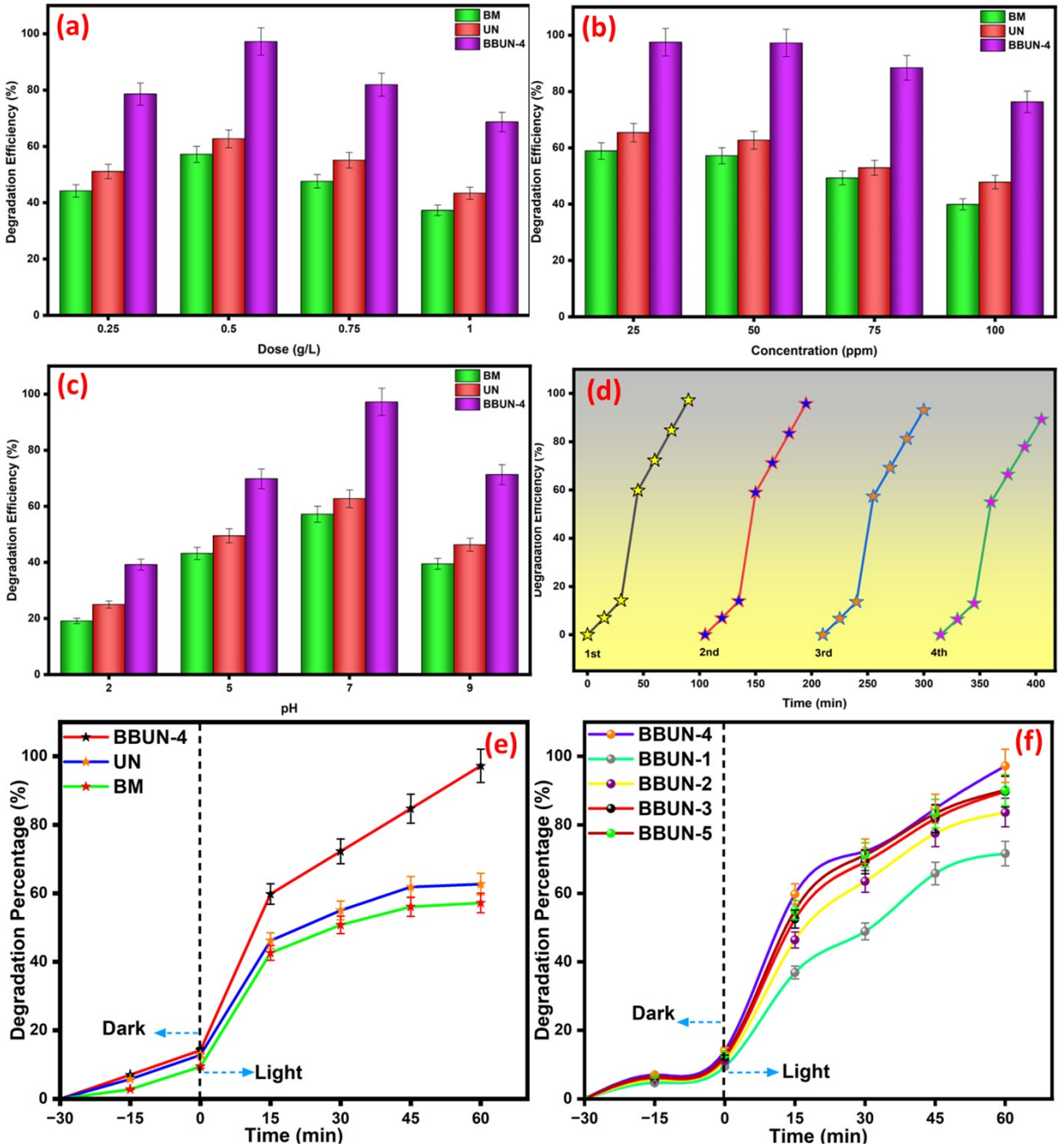

Figure S2. Effect of **(a)** pH, **(b)** CR concentration, **(c)** Catalyst dose on CR degradation performance of UN, BM, and BBUN-4, **(d)** reusability test of BBUN-4 catalyst for four consecutive cycles, **(e)** photocatalytic CR degradation efficiency plots of UN, BM, and BBUN-4, and **(f)** BBUN-1, BBUN-2, BBUN-3, BBUN-4, and BBUN-5 heterojunctions.

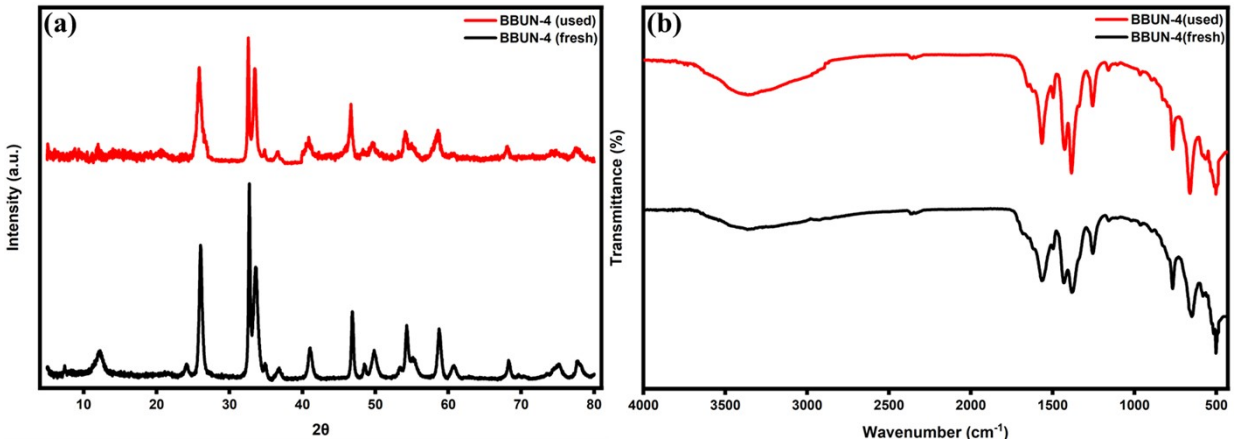

Figure S3. (a) XRD patterns, and **(b)** FTIR spectra of BBUN-4 composite before and after use of four consecutive cycles.