

Support information

Fabrication of binary g-C₃N₄ /UU-200 composites with enhanced visible-light-driven photocatalytic performance toward organic pollutant eliminations

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Text S1. Materials

Melamine ($C_3H_6N_6$, 99.0%) was purchased from HiMedia Laboratories Pvt. Ltd. (India). Thiourea (CH_4N_2S , 99.8%) was obtained from Prolabo (France). 1,3,5-benzenetricarboxylic acid (H_3BTC , $C_9H_6O_6$, 95.0%), bismuth (III) nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$, $\geq 98.0\%$), rhodamine b (RhB, $C_{28}H_{31}ClN_2O_3$, $\geq 95.0\%$), tetracycline hydrochloride (TCH, $C_{22}H_{24}N_2O_8 \cdot HCl$, $\geq 95.0\%$), *tert*-butanol (TBA, $C_4H_{10}O$, $\geq 99.5\%$), and 1,4-benzoquinone (BQ, $C_6H_4O_2$, $\geq 99.0\%$) were purchased from Sigma-Aldrich (USA). Methanol (MeOH, CH_4O , $\geq 99.5\%$), N,N-dimethylformamide (DMF, C_3H_7NO , 99.0%), ammonium chloride (NH_4Cl , $\geq 99.5\%$), potassium dichromate ($K_2Cr_2O_7$, $\geq 99.8\%$), and sodium oxalate ($Na_2C_2O_4$, $\geq 99.8\%$) were obtained from Xilong Scientific Co., Ltd. (China). All the used commercial reagents and solvents were received without further purification.

Text S2. Synthesis of UU-200

The UU-200 was obtained by a solvothermal method according to the previous reports in the literatures ^{1,2} with minor modifications. Typically, bismuth (III) nitrate pentahydrate (0.150 g, 0.303 mmol) and 1,3,5-benzenetricarboxylic acid (1.340 g, 6.060 mmol) were dissolved in the mixture of N,N-dimethylformamide (30 mL) and methanol (30 mL). Then the obtained clear solution was transferred into a Teflon liner with a capacity 100 mL. After that, it was sealed in a stainless-steel autoclave. The autoclave was put into an oven and heated at 120 °C for 24 h, then naturally cooled to room temperature. The resultant suspension was centrifuged and purified with DMF and MeOH three times to remove the remaining H_3BTC molecules and the occluded DMF molecules in channels. The white UU-200 powder was collected by centrifugation and dried in a vacuum oven at 80 °C for 12 h to obtain the final products.

Text S3. Synthesis of g- C_3N_4

The bare g- C_3N_4 was synthesized according to literature ³ and made some improvements. In a typical synthesis procedure, 2.5 g of melamine, 2.5 g of thiourea, and 5 g of ammonium chloride were mixed and ground for 30 minutes in a ceramic mortar. Then the solid white mixture was transferred into a ceramic crucible with a cover and calcined at 550 °C for 3 h (heating rate of 5 °C min^{-1}) under an air atmosphere. After cooling naturally to room temperature, the yellow g- C_3N_4 powder was formed.

Text S4. Characterization

We used X-ray diffractometer (D8 Advance, Bruker, USA) and Fourier transform infrared spectrometer (EQUINOX 55, Bruker, USA) to investigate the X-ray diffraction (XRD) patterns and Fourier transform-infrared (FT-IR) spectra of photocatalysts, respectively. Optical properties, including UV–visible diffuse reflectance spectra (UV–vis DRS) and photoluminescence (PL) spectra of photocatalysts, were obtained using Cary 4000 UV–visible spectrophotometer (Agilent, USA) and Cary Eclipse Fluorescence Spectrophotometer (Varian, Australia, $\lambda_{\text{excitation}} = 355 \text{ nm}$), respectively. The morphology of the samples was studied using scanning electron microscopy (SEM, JEOL JSM 7401F, USA). Transmission electron microscopy (TEM) was measured using an HT7800 microscope (Hitachi Hightech, Japan) with acceleration voltage of 120 kV. X-ray photoelectron spectroscopy (XPS) measurements were conducted with a VG Multilab 2000 spectrometer (Thermo Scientific, UK). The ultra violet photoemission spectroscopy (UPS) were measured using X-ray photoelectron spectrometer (AXIS SUPRA, KRATOS Analytical Ltd.) with He I photon source of 21.22 eV. The nitrogen adsorption-desorption isotherms were recorded by means of the accelerated surface area porosimetry system (TriStar 3000 V6.07, Micromeritics instrument corporation, USA). The specific surface area values were determined using the Brunauer–Emmett–Teller (BET) method. Pore size distribution and pore volume of photocatalysts were determined using the Barrett–Joyner–Halenda (BJH) method.

Text S4. Trapping test

Hydroxyl radicals ($\bullet\text{OH}$), active electrons (e^-), active holes (h^+), and superoxide radicals ($\text{O}_2\bullet^-$) are the main oxidative species in the photocatalytic process. The role of these attacking species in the organic pollutant degradation was determined through active species trapping experiments using *tert*-butanol, potassium dichromate, sodium oxalate, and 1,4-benzoquinone as scavengers for $\bullet\text{OH}$, e^- , h^+ and $\text{O}_2\bullet^-$ radical anions, respectively. These scavenger agents were added to a suspension solution before the beginning of the photocatalytic operation. The concentration of scavenger agents added was $2 \times 10^{-4} \text{ M}$.

Text S5. Recycling test

To examine the stability and recyclability of the 40% g- C_3N_4 /UU-200 photocatalyst, 40% g- C_3N_4 /UU-200 used in the photocatalytic reaction was recovered repeatedly used for four cycles. The cyclic runs for 60% UU-200/40% g- C_3N_4 photocatalyst was carried out by collecting the

photocatalyst through centrifugation, washed with water and ethanol three times, dried at 80 °C for 12 h, and then reused for the next run.

Text S6. Electrochemical test

Electrochemical impedance spectroscopy (EIS) measurements were carried out at room temperature using a PGSTAT-128N Autolab electrochemical system (Metrohm, Utrecht, The Netherlands). An Ag/AgCl electrode, a platinum (Pt) wire, and a modified glassy carbon electrode (GCE) were used as the pseudo-reference electrode, counter electrode, and working electrode, respectively. The tests were recorded in a frequency range of 0.1 Hz–10 kHz and 5 mV of amplitude. The electrochemical reaction was performed in 0.1 M KCl aqueous solution containing 5 mM $\text{Fe}(\text{CN})_6^{3-}$ and 10 mM KCl ratio (1:1) as the electrolyte. UU-200, g- C_3N_4 , and g- C_3N_4 /UU-200 electrodes were prepared by suspending 10 mg of the photocatalyst in 1 mL of ethanol and then dispersing 4 μL of this suspension onto the electrode GCE for EIS analysis. The EIS was measured at room temperature ⁴.

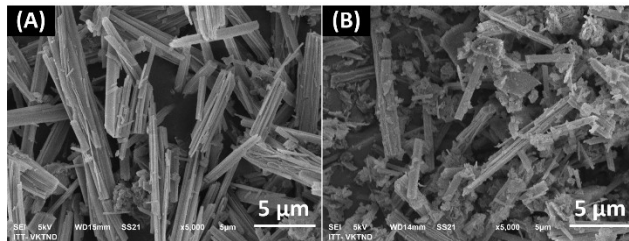


Fig. S1. SEM images of 20% g-C₃N₄/UU-200 (A) and 60% g-C₃N₄/UU-200 (B) samples

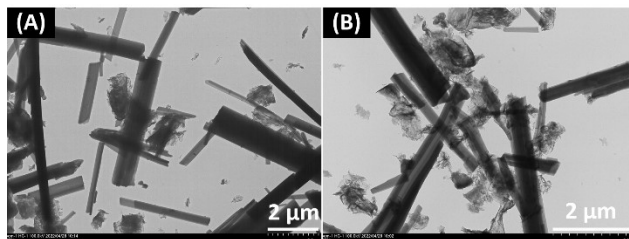


Fig. S2. TEM images of 20% g-C₃N₄/UU-200 (A) and 60% g-C₃N₄/UU-200 (B) samples

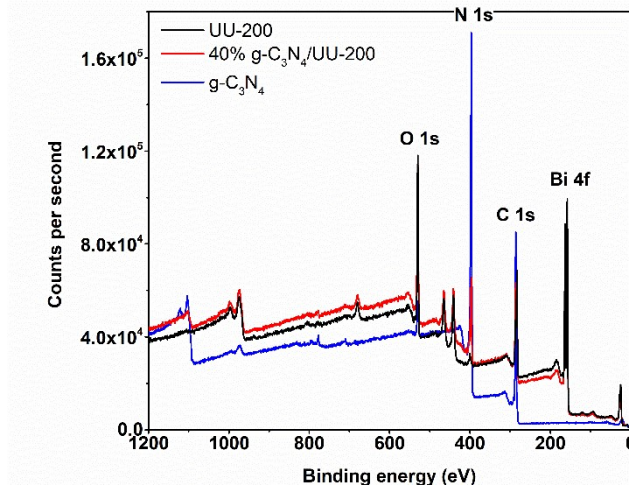


Fig. S3. XP survey spectra of UU-200, 40% g-C₃N₄/UU-200 and g-C₃N₄.

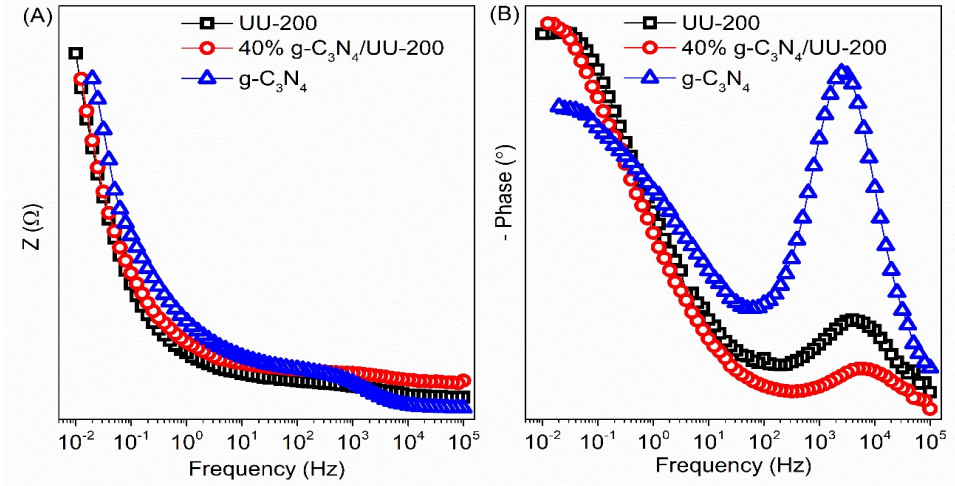


Fig. S4. Impedance diagrams (Bode plots): (A) Z versus frequency and (B) phase angle versus frequency of UU-200, 40% $g\text{-C}_3\text{N}_4/\text{UU-200}$ and $g\text{-C}_3\text{N}_4$.

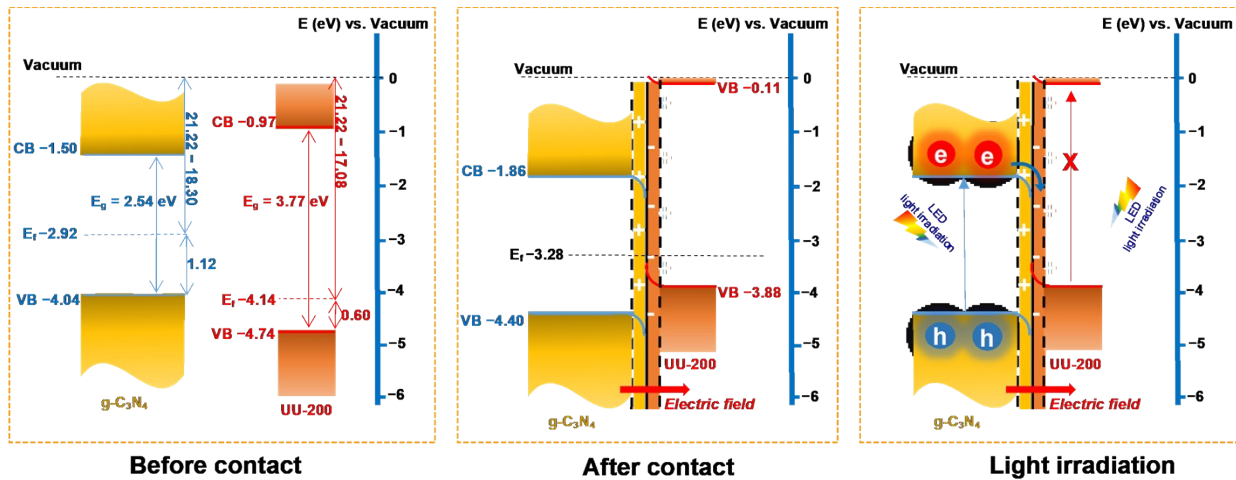


Fig. S5. Schematic illustration of $g\text{-C}_3\text{N}_4/\text{UU-200}$ heterojunction with staggered band configuration: (A) before contact, (B) after contact, (C) photogenerated charge carrier transfer process in $g\text{-C}_3\text{N}_4/\text{UU-200}$ heterojunction.

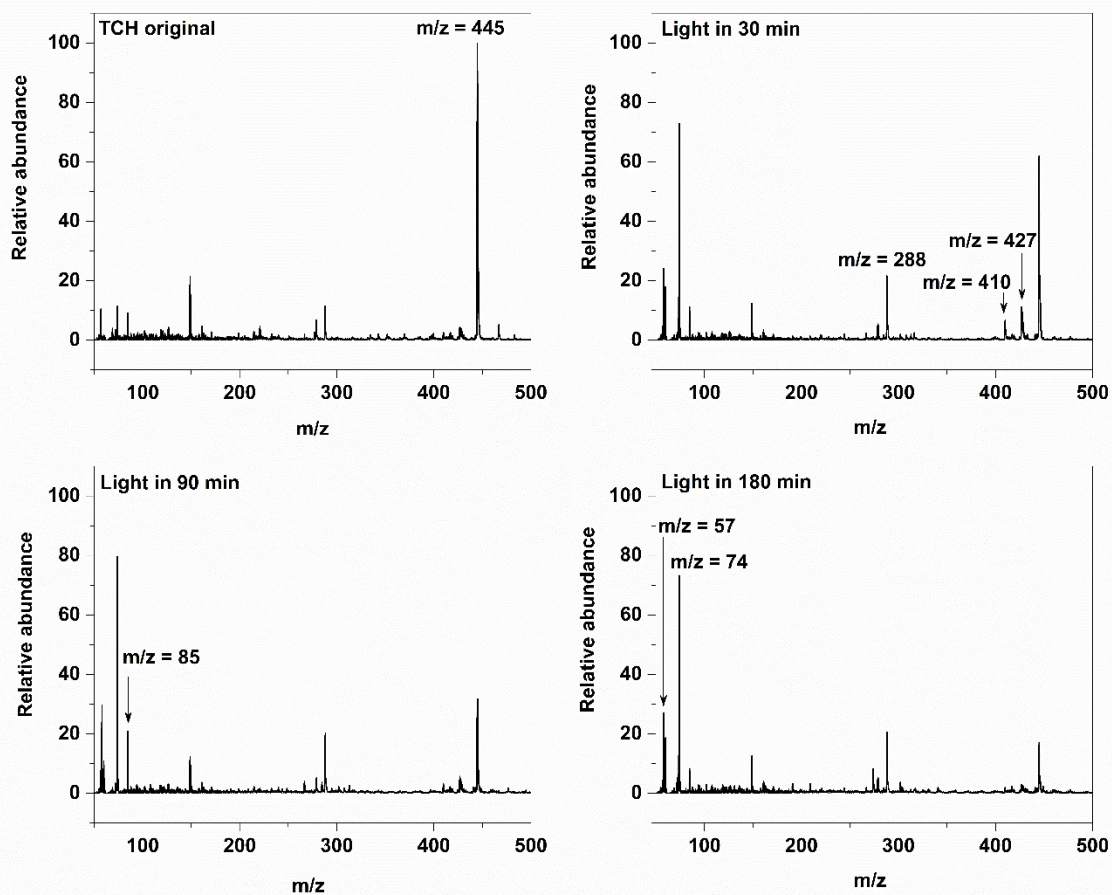


Fig. S6. Principal by-products of TCH degradation detected by LC-MS

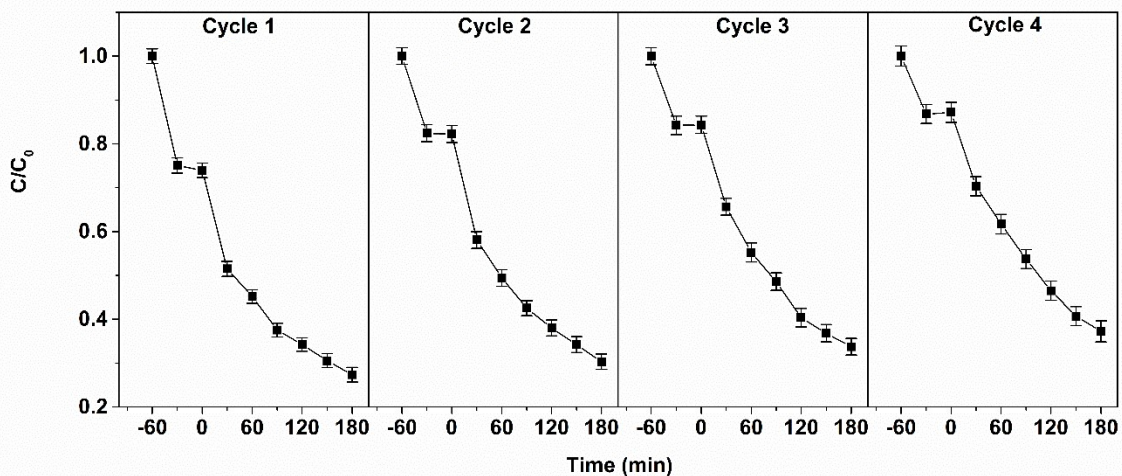


Fig. S7. Photocatalytic recycle degradation of TCH over 60% g-C₃N₄/UU-200 photocatalyst. Conditions: [catalyst] = 10 mg, [TC] = 5 mg L⁻¹, V = 100 mL, Light source: White light LED (4 × 10 W), [scavenger] = 2 × 10⁻⁴ mg L⁻¹.

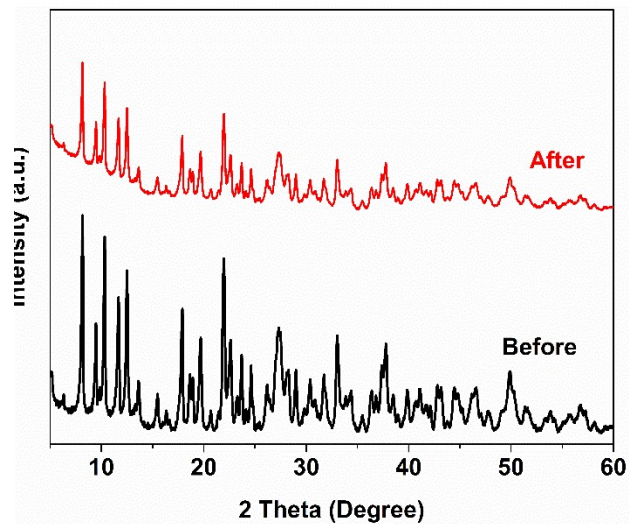


Fig. S8. XRD patterns of 40% g-C₃N₄/UU-200 before and after photocatalytic reaction

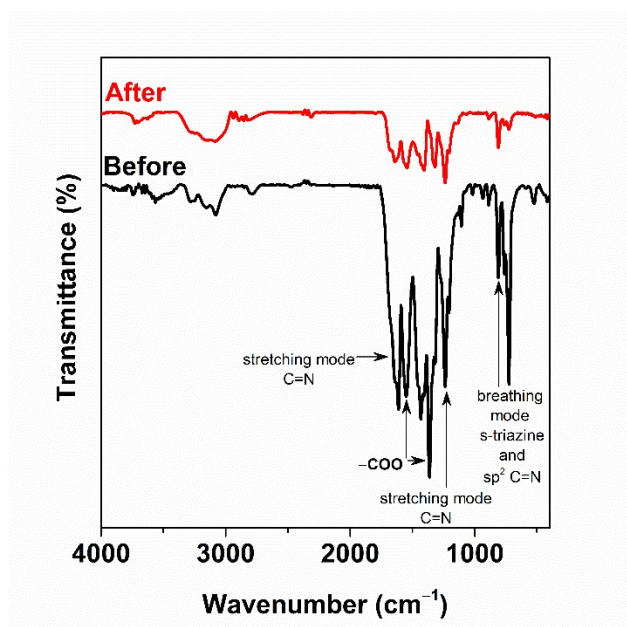


Fig. S9. FTIR spectra of 40% g-C₃N₄/UU-200 before and after photocatalytic reaction

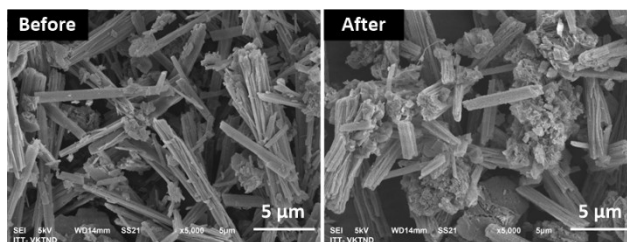


Fig. S10. SEM images of 40% g-C₃N₄/UU-200 before and after photocatalytic reaction

References

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