

Supporting information

Modulating photoelectrochemical water splitting performance *via* the construction of Type-II heterojunction between g-C₃N₄ and BiOI

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1. Experimental section

1.1. Chemicals and reagents

Chemicals such as melamine ($C_3H_6N_6$ – Alfa Aesar), bismuth nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$ - SRL), potassium iodide (KI - Merck), ammonium sulfate ($(NH_4)_2SO_4$ - Fischer Scientific), and ethylene glycol ($(CH_2OH)_2$ - SRL), Nafion (Alfa Aesar) were purchased as analytical grade and used as received.

1.2. Characterization instruments

The diffuse reflectance spectra for the prepared hybrid materials were analyzed using $BaSO_4$ as a reference in Cary 500 Scan UV–visible spectrophotometer equipped with a diffuse reflectance accessory. The FT-IR spectra were carried out using Bruker (Model: TENSOR 27), Germany Optik GmbH, Fourier-transform infrared spectrophotometer. The crystalline nature of the samples was analyzed using a Bruker AXS D8 Advance X-ray diffractometer with ($\lambda = 1.54178 \text{ \AA}$) Cu $K\alpha$ radiation. Photoluminescence spectra were recorded using a Perkin Elmer fluorescence spectrophotometer. The surface composition and oxidation state of the elements were investigated by ($K\alpha$ -1253.6 eV) XPS with Mg as X-ray source (MULTILAB 2000, Thermo Scientific, X-ray Photoelectron Spectrometer). High-resolution transmission electron microscopic image and elemental mapping in high angle annular dark field in scanning TEM (HAADF - STEM) mode were carried out with FEI Tecnai F20 Super-Twin. The STEM and elemental mapping were performed in HAADF mode. A bath type ultrasonic cleaner with ultrasonic power and ultrasonic frequency of 100 W and 50 Hz, used for the sonication process for the synthesis of BiOI and g- C_3N_4 /BiOI hybrid material.

1.3. Photoelectrochemical studies

Photoelectrochemical experiments were carried out using a three-electrode system with an electrochemical workstation Autolab (ECO CHEMIE PGSTAT302 BV TYPE serial no.AUT72831) for LSV, CA analysis and OriGalys (OrigaMaster 5 software) used for EIS analysis. The ORIEL LCS-100 solar simulator (Newport, USA) with AM 1.5 AG (100 mW cm⁻²) filter was employed as a light source. The platinum wire and Ag/AgCl with saturated KCl were employed as counter electrode, reference electrodes, and the working electrode consist with fabricated materials on FTO (Fluorine doped Tin Oxide) glass.

A 50 mg of prepared material mixed in 500 µL of Nafion:ethanol (2:1 ratio) solution stirred for 18 h and 30 µL of the suspension coated on 1 cm² of FTO plate by drop-cast method. The photoelectrodes were calcinated at 450 °C for 1 h and cooled to room temperature.

The photocurrent response by linear sweep voltammetry, chronoamperometry, and electrochemical impedance spectroscopy (EIS) were performed at room temperature. The measured potentials from Ag/AgCl reference electrode could be converted to the reversible hydrogen electrode (RHE) using Eqn. (S1).

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \text{ pH} + E^{\circ}_{\text{Ag/AgCl}} \quad \text{---- (1)}$$

Where, E_{RHE} = Potential at reversible hydrogen electrode, $E_{\text{Ag/AgCl}}$ is the experimentally measured potential, $E^{\circ}_{\text{Ag/AgCl}} = 0.1976 \text{ V}$ at 25° C, pH of the electrolyte 0.5 M (Na₂SO₃ + NaHCO₃).

1.4. Synthesis of g-C₃N₄

The g-C₃N₄ synthesized by pyrolysis method in which, melamine and ammonium sulfate (1:1) was mixed and ground for an hour with mortar and pestle to get homogeneous mixture ³⁸.

The obtained mixture was transferred into alumina crucible and pyrolysis for 550 °C by 4 h at 2 °C/min.

1.5. Synthesis of g-C₃N₄/BiOI hybrid material

The g-C₃N₄/BiOI hybrid material was prepared by ultrasonically assisted hydrothermal synthesis as follow (Scheme 1). A desired amount of g-C₃N₄ and 0.25 M of Bi(NO)₃.5H₂O were mixed with water under constant stirring for 15 min and it was dissolved in 20 mL EG by ultrasonication with 1 h (solution A). Meanwhile, 0.25 M of KI mixed in water and ethylene glycol and it was sonicated for 1 h. Then, it was poured into solution A with drop-wise under continuous stirring for 1 h to attain a homogenous solution. After that, a 80 mL of resultant solution was taken into a Teflon lined autoclave (stainless steel) and heated at 150 °C at 24 h. After reached the room temperature, the solution was centrifuged and washed with de-ionized water followed by ethanol and dried overnight at 60 °C. BiOI microspheres were synthesized with the similar procedure without the addition of g-C₃N₄.

1.6 Flat-band potential measurements

The flat-band potential could be calculated by the Poisson's equation:

$$\frac{1}{C^2} = \frac{2}{\epsilon\epsilon^{\circ}A2ND} \left(V - V_{fb} - \frac{kbT}{e} \right) \quad \text{----- (2)}$$

Where, C, A, N_D, V, T, k_b, e, ε^o and v_{fb} represents the interfacial capacitance, area, number of donors, applied voltage, absolute temperature, Boltzmann's constant, electronic charge, permittivity of free space and flat band potential, respectively.

The charge transfer mechanism in g-C₃N₄/BiOI was proposed based on conduction band (CB) and valance band (VB) potential level of g-C₃N₄ and BiOI using Eqn. (3) and (4)

$$E_{VB} = \chi - E^e + 0.5E_g \quad \text{---- (3)}$$

$$E_{CB} = E_{VB} - E_g \quad \text{---- (4)}$$

Where χ , E^e , E_{CB} , E_{VB} , and E_g represents the absolute Mulliken's electronegativity, free electrons energy in hydrogen scale (4.50 eV) calculated conduction band edge, valence band position and energy of band gap, respectively.

Figures and captions

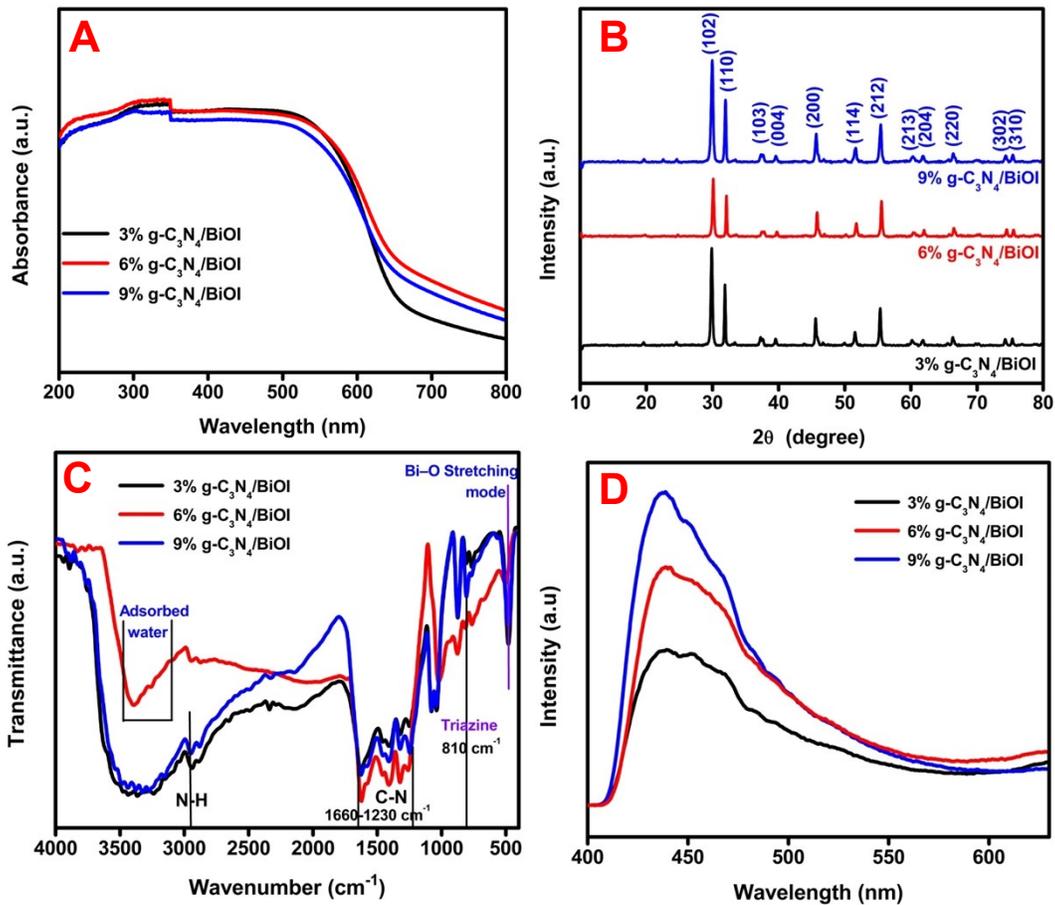


Figure S1. (A) DRS, (B) XRD pattern, (C) FT-IR and (D) PL spectra obtained for 3, 6 and 9% g-C₃N₄/BiOI hybrid materials

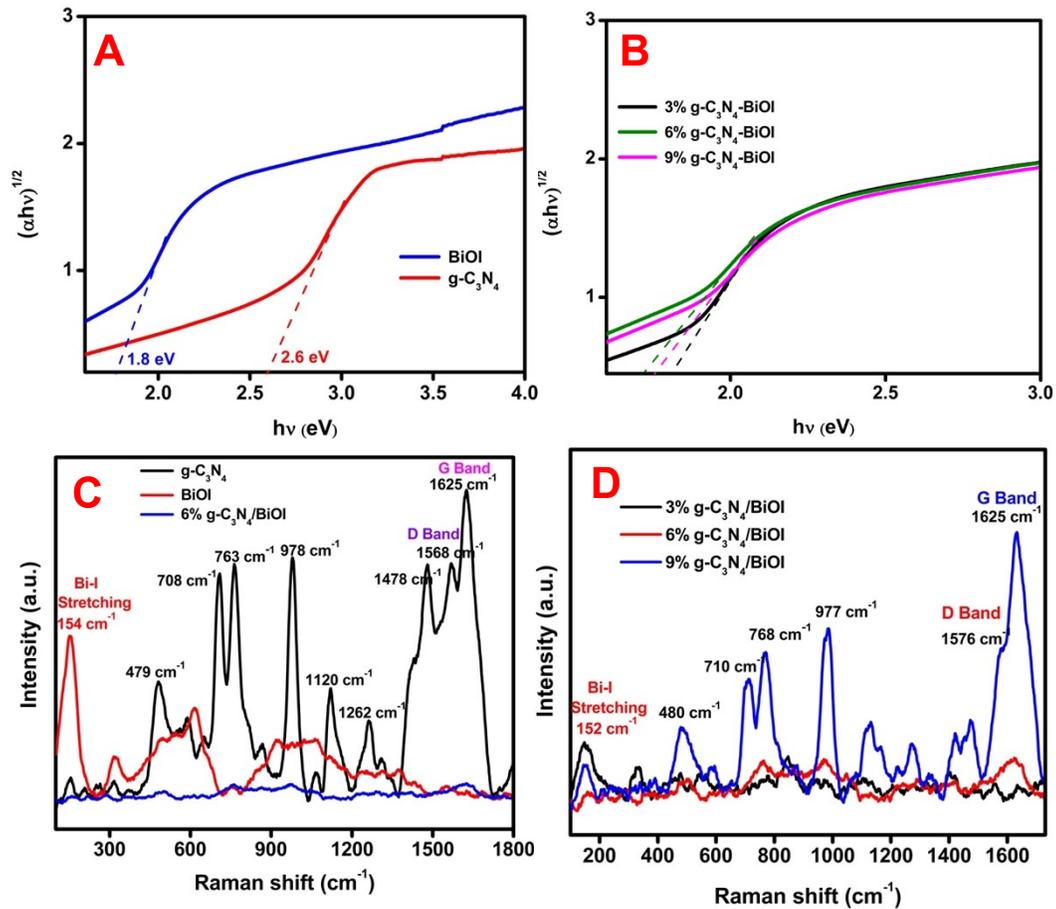


Figure S2. Tauc's plot obtained for (A) g-C₃N₄, BiOI and (B) 3, 6, 9% g-C₃N₄/BiOI hybrid materials, (C) Raman spectra obtained for g-C₃N₄, BiOI and 6% g-C₃N₄/BiOI hybrid and (D) Raman spectra obtained for 3, 6 and 9% g-C₃N₄/BiOI hybrid materials

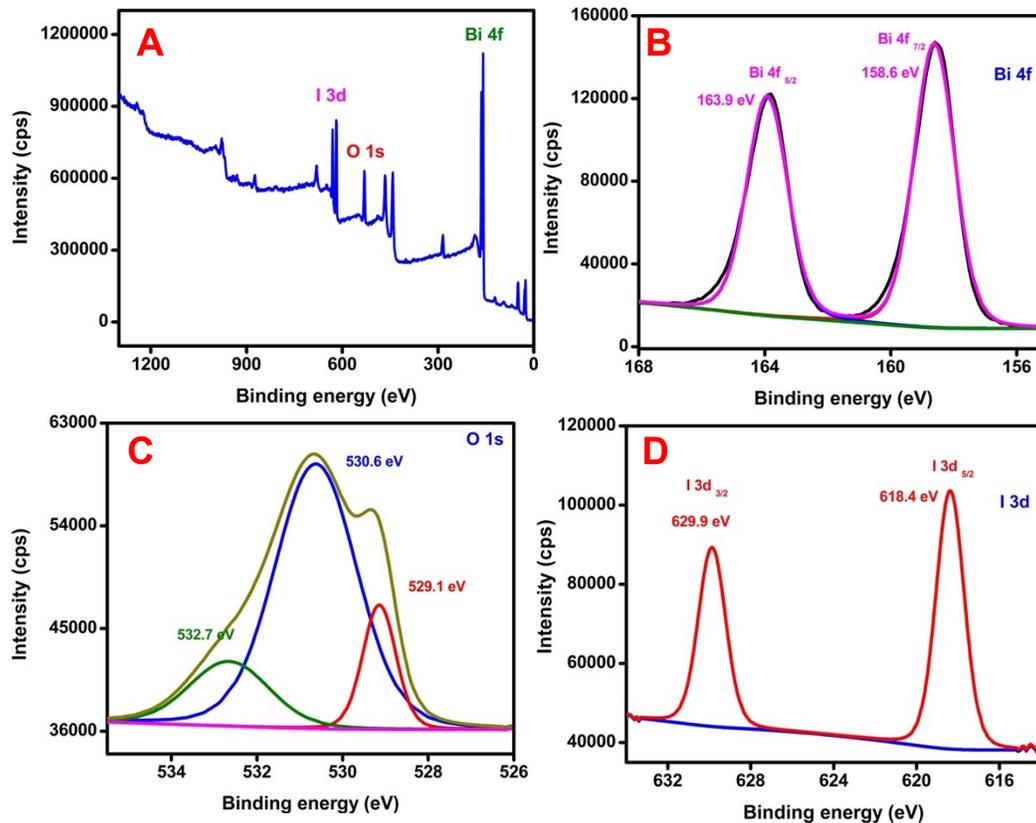


Figure S3. XPS spectra obtained for BiOI microspheres (A) Survey scan for BiOI, (B) Bi 4f, (C) O 1s and (D) I 3d core-level spectra.

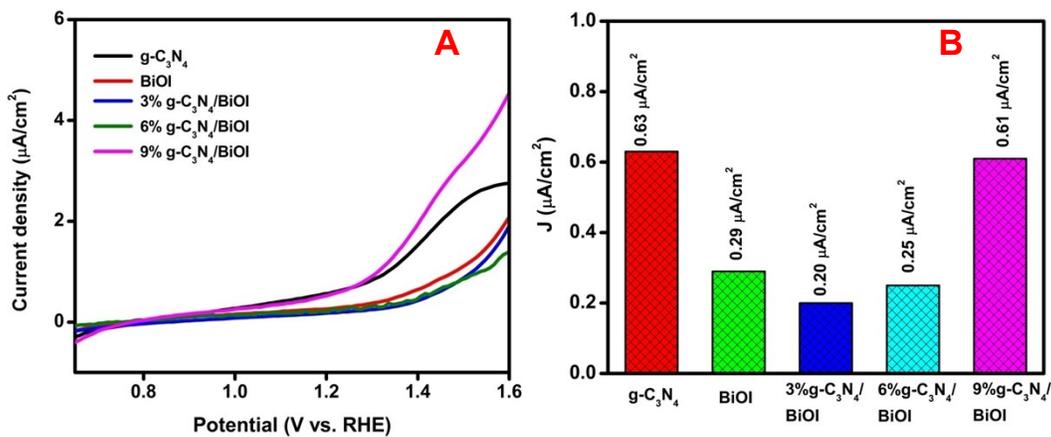


Figure S4. (A) Linear sweep voltammograms obtained for g-C₃N₄, BiOI, 3, 6 and 9% g-C₃N₄/BiOI under light illumination of 100 mW cm⁻² (AM 1.5G) at a scan rate of 10 mV s⁻¹ in 0.5 M Na₂SO₄ and (B) Photocurrent density of different photoanode materials under light illumination of 100 mW cm⁻² (AM 1.5 G) at a scan rate of 10 mV s⁻¹ in 0.5 M Na₂SO₄

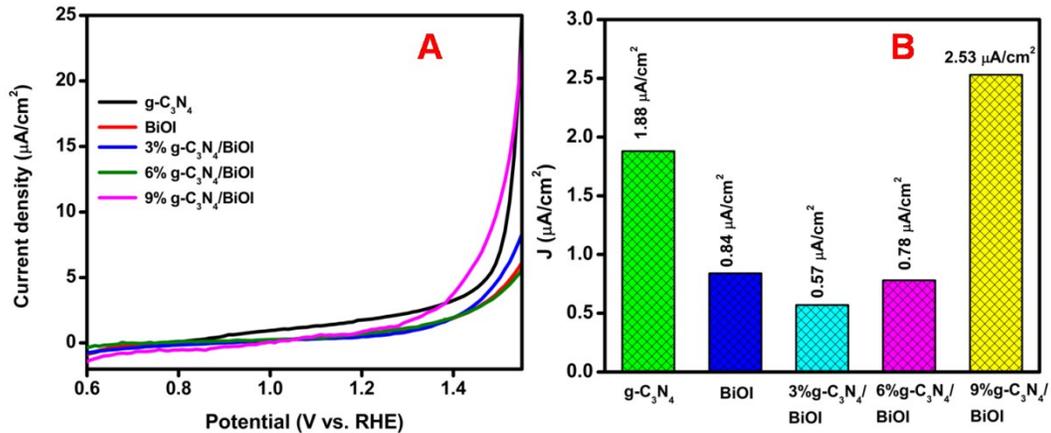


Figure S5. (A) Linear sweep voltammograms obtained for $\text{g-C}_3\text{N}_4$, BiOI, 3, 6 and 9% $\text{g-C}_3\text{N}_4/\text{BiOI}$ under light illumination of 100 mW cm^{-2} (AM 1.5G) at a scan rate of 10 mV s^{-1} in 1 M KOH and (B) Photocurrent density of different photoanode materials under light illumination of 100 mW cm^{-2} (AM 1.5 G) at a scan rate of 10 mV s^{-1} in 1 M KOH

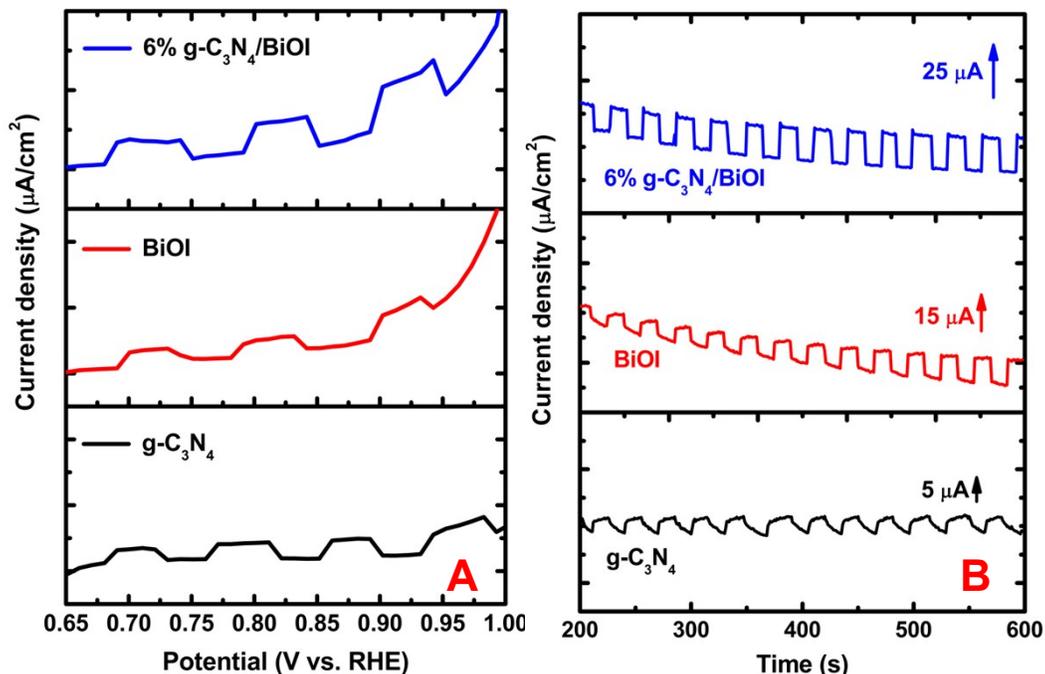


Figure S6. (A) Linear sweep voltammograms obtained for $\text{g-C}_3\text{N}_4$, BiOI, 6% $\text{g-C}_3\text{N}_4/\text{BiOI}$ hybrid materials under the chopped condition and (B) Chronoamperometric J - T curves obtained for $\text{g-C}_3\text{N}_4$, BiOI, 6% $\text{g-C}_3\text{N}_4/\text{BiOI}$ hybrid materials at 1.23 V vs. RHE

Table S1. EIS Nyquist plot fitting parameters obtained for different photoanodes

Photoanode	R_s (kΩ)	R_{ct} (kΩ)
g-C ₃ N ₄	0.045	22.2
BiOI	0.051	37.2
6% g-C ₃ N ₄ /BiOI	0.038	18.7