

Laser flash photolysis study of Nb₂O₅/g-C₃N₄ heterostructures as efficient photocatalyst for molecular H₂ evolution

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ABSTRACT

Improvements of visible light activity, slow recombination rate, stability, and efficiency are major challenges facing photocatalyst technologies today. Utilizing heterostructures of g-C₃N₄ (bandgap ~2.7eV) with Nb₂O₅ (bandgap ~3.4eV) as an alternative materials for the first time, we tried to overcome such challenges in this work. Heterostructures of Nb₂O₅/g-C₃N₄ have been synthesized via hydrothermal technique. And then a time-resolved laser flash photolysis of those heterostructures has been analyzed, focusing on seeking how to improve photocatalytic efficiency for molecular hydrogen (H₂) evolution. The transient absorption spectra and the lifetime of charge carriers at different wavelengths have been observed for Nb₂O₅/g-C₃N₄, where g-C₃N₄ was used for a control. The role of hole scavenger (methanol) has also been investigated for the purpose of boosting charge trapping and H₂ evolution. The long lifetime of Nb₂O₅/g-C₃N₄ heterostructures (6.54165 μs) compared to g-C₃N₄ (3.1651897 μs) has successfully supported the increased H₂ evolution of 75 mmol/h.g. An enhancement in the rate of H₂ evolution (160 mmol/h.g) in the presence of methanol has been confirmed. This study not only deepens our understanding of the role of scavenger, but also enables a rigorous quantification of the recombination rate crucial for photocatalytic applications in relation with efficient H₂ production.

1. Introduction

Photocatalysis is one of the most intriguing energy conversion processes that employ renewable and eco-friendly solar energy to generate ideal fuels and resolve the problem of photocatalytic degradation [1,2]. Hence, photocatalysis has gained a growing interest in connection with its applicability in solar energy conversion including water-splitting, photocatalytic H₂ production, photoreduction of CO₂, photodegradation of organic contaminants, and organic photosynthesis [3–6]. For photocatalytic H₂ reactions, few metal oxides have been explored but due to their large band gaps and inappropriate band potentials, they are usually not ideal for H₂

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generation or other photocatalytic applications. Some other oxides, such as CuO and Cu₂O, have favourable band gaps but have not been preferred because of their less chemical stability and less light absorption in visible region [7–9]. On account of this, scientists are trying to engineer photocatalysts which are cost-effective, efficient, and chemically stable, as well as possessing suitable band potentials [9].

Graphitic carbon nitride (g-C₃N₄), a n-type polymer semiconductor, has earned significant importance because of its visible bandgap of 2.7 eV, non-toxicity, adaptable electronic properties, and chemical stability [10–12]. Yet, a fast recombination rate of charge-carriers has limited its use as a bare photocatalyst. This issue has been addressed by preparing its heterojunctions with metal-oxides/metal-sulfides/metal nitrates, e.g., g-C₃N₄/ZnO, g-C₃N₄/TiO₂, g-C₃N₄/WS₂, etc. However, these heterostructures are not really ideal mainly due to expensive and complex fabrication processes [12–15].

On the other hand, niobium pentoxide (Nb₂O₅) has been proven as one of the favourite materials for heterostructures preparation with g-C₃N₄. It belongs to n-type semiconductors with a bandgap between 3.1 and 3.4 eV, suitable for photocatalytic reactions and energy storage [15,16]. Moreover, it exhibits highly acidic properties and water-tolerant characteristics required for photo-electrochemical devices and photocatalysis. To make this material active on visible light with a high efficiency, its heterostructures such as Nb₂O₅/ZnO, and Nb₂O₅/Cu₂O [17–19] have been considered in previous works. Along this line, we prepared Nb₂O₅/g-C₃N₄ heterostructures which exhibit high efficiency for molecular H₂ generation.

Herein, a hydrothermal synthetic method was used in synthesizing Nb₂O₅/g-C₃N₄ heterostructures. Compared to bare Nb₂O₅ and g-C₃N₄, the heterostructure of Nb₂O₅/g-C₃N₄ can produce high molecular H₂, which is 75 mmol/h.g without methanol and 160 mmol/h.g with methanol. This efficient photocatalytic performance is owing to appropriate interfacial contact, which promotes the rapid photogeneration of electron-hole pairs at the Nb₂O₅/g-C₃N₄. The laser flash photolysis (LFP) technique was used as an extension to observe the trapping and lifetime of charge carriers to increase the generation of molecular H₂. The investigation of Nb₂O₅/g-C₃N₄ LFP has not been carried out so far to the best of our knowledge.

In the LFP technique, Nb₂O₅/g-C₃N₄ was excited by a nanosecond pulsed laser for the photogeneration of active species, i.e., electron-hole pairs were monitored through transient absorption spectra. The utilization of laser pulses in this field initiated the development of transient species in flash photolysis experiments. And this is typically followed by a change in the original optical characteristics of the tested material, which was recognized by using a flash lamp. Trapping of charge carriers was observed in the presence and absence of a-holes scavenger. Trapped-hole peaks are often seen at lower wavelengths ranging from 420 to 450 nm, whereas trapped electron peaks are usually found at higher wavelengths ranging from 700 to 760 nm. However, no substantial peak could be detected on the transient spectra between 400 and 600 nm [20]. A significant increase of hole trapping was observed in the presence of a-holes scavenger, while the range of electron trapping remains the same. Additionally, a unified model equation is used to explain the decay curves of the observed transient absorption signal. Then the lifetime of Nb₂O₅/g-C₃N₄ was calculated and compared with that of g-C₃N₄ to show its usefulness for photocatalysts associated with the molecular H₂ evolution.

2. Experimental setup

Hydrothermal synthesis was used to prepare Nb₂O₅ and Nb₂O₅/g-C₃N₄ heterostructures, while a conventional method was employed for g-C₃N₄ preparation as reported in our previous work [1].

2.1. Preparation of Nb₂O₅

Nb₂O₅ has been synthesized through the oxidant-peroxo route. 0.5 ml of HNO₃ was diluted by 20 ml of deionized water, followed by adding 1 g of NbCl₅ during continuous stirring. The solution became milky white containing a few white and colourless precipitates at the bottom. Then 20 ml of H₂O₂ was added drop-wise which gradually changed the color of the solution to yellow, indicating the formation of niobium peroxo-complex (NPC): [Nb(O₂)₄]³⁻. The prepared solution was transferred into an autoclave and was kept in the oven for 24 h at 200 °C. After cooling down naturally, the prepared powder was separated through centrifugation for 30 min and thoroughly washed with deionized water. The obtained product was dried in a drying oven at 90 °C for 12 h. Afterwards, the Nb₂O₅ powder was annealed at 200 °C for 2 h.

2.2. Preparation of heterostructures of Nb₂O₅/g-C₃N₄

The preparation route of g-C₃N₄ has been provided in the supporting information. 0.04 g of g-C₃N₄ was added to the prepared NPC solution for heterostructures. The obtained solution was placed in a suitable autoclave and heated for 24 h at 200 °C in an oven. After cooling down, the powder was separated from the liquid by centrifugation for 10 min, followed by drying in the oven. This approach was employed to make heterostructures with g-C₃N₄. The schematic illustration of the whole synthesis has been provided in the supporting information for clarification.

2.3. Incident photon-to-current efficiency (IPCE)

IPCE measurements can give an important insight into the contribution of photocatalysts in the conversion of incident photons into charge carriers. In this experiment, the light powder at each photo energy is measured and calculated to the IPCE value from the photocurrent according to equation (1).

$$IPCE = \frac{J \times 1240}{P_{\text{mono}} \times \lambda} \quad (1)$$

Where J is the photocurrent density ($\text{mA}\cdot\text{cm}^{-2}$), P_{mono} is the light power density ($\text{mW}\cdot\text{cm}^{-2}$) at λ . λ - wavelength of illuminating monochromatic photons.

2.4. Laser flash photolysis (LFP)

Nitrogen was purged on each sample for 25 min to remove air. The mixture of $\text{Nb}_2\text{O}_5/\text{g-C}_3\text{N}_4$ was excited by an excimer Laser (LPX200) provided by Lambda physic and the pulse duration was 20 ns. The excitation wavelength for the first sample was 680 nm and for the second sample 700 nm, whereas its laser energy per pulse was 2–10 mJ. The illumination area of the laser beam and analyzing light from the sample was $0.6 \times 0.196 \text{ cm}^2$. The change of reflectance was monitored through the LFP spectrometer LKS 80 from Applied Photophysics. Xenon arc lamp 150W was used as a light source. When the light was fallen on the $\text{Nb}_2\text{O}_5/\text{g-C}_3\text{N}_4$ sample, then the photogenerated charge carriers were produced. The reflected light was collected by the monochromator before it was sent to the photomultiplier detector (Hamamatsu R928 photomultiplier) to produce current. This change of reflectance is then recorded by the oscilloscope. The oscilloscope captured the transient with better sensitivity by adjusting the input voltage. The best part of the diffuse reflectance LFP technique is that the results obtained can be directly compared with the results of the photocatalytic experiments, although powdered samples are used in both processes. Experimental conditions for various time scales are provided in Table 1.

2.5. Photocatalytic molecular hydrogen (H_2) formation

The molecular hydrogen (H_2) evolution process was conducted using the prepared photocatalysts in the presence of a scavenger and without a scavenger. Methanol was used as a hole scavenger. In a typical experiment, 0.02 g of the prepared photocatalysts were mixed with 40 ml of deionized water. With the addition of methanol, a suspension containing 10 vol% of a-holes scavenger were obtained. The prepared solutions were degassed with Ar for 30 min and then stirred for a further 25 min. The photoreactor was then put under a solar-simulating Xenon light source (1000 W, 1.5 G) for 8 h. A homemade cooling system was used to keep the temperature constant. A gas chromatograph was used to measure the evolved H_2 after every 1 h.

2.6. Material characterizations

The as-synthesized materials XRD data was recorded by a Bruker (D8 Advance) analyzer using $\text{Cu K}\alpha$ ($\alpha = 0.15406 \text{ nm}$) radiation. The morphologies were analyzed using scanning electron microscopy (JEOL JSM-6700F, JEOL, Tokyo, Japan) equipped with a Lower Secondary Electron Image (LEI) detector. Additionally, the samples were characterised by transmission electron microscopy (TEM) using a 200 kV FEI TecnaiG2 F20 microscope. Micrographs were obtained in two modes: bright field (BF) and selected area electron diffraction (SAED). The UV–vis absorption spectrum was measured using a Varian Cary. Shimadzu 8A (Shimadzu, Kyoto, Japan) gas chromatograph equipped with a TCD detector and a 5 Å molecular sieve packed column; Ar as the carrier gas was used.

3. Results and discussion

3.1. Structural and morphological analysis

Structural analysis was conducted by XRD for $\text{g-C}_3\text{N}_4$, Nb_2O_5 before annealing (BA) and after annealing (AA) and $\text{Nb}_2\text{O}_5/\text{g-C}_3\text{N}_4$ as shown in Fig. 1. Their corresponding Miller indices were also provided in Fig. 1. XRD measurements for Nb_2O_5 -BA exhibited a combination of niobic acid and amorphous Nb_2O_5 , therefore, slight distortion from the original crystalline structure was observed. While after annealing at 200°C , the peaks were well-matched with Nb_2O_5 orthorhombic phase (T- Nb_2O_5): ICDD#30–0873 ($a = 6.17 \text{ \AA}$, $b = 29.97 \text{ \AA}$ and $c = 3.93 \text{ \AA}$). The lattice constants were calculated by using equation (2) and were found in good agreement with the T- Nb_2O_5 ($a = 5.96 \text{ \AA}$, $b = 29.26 \text{ \AA}$ and $c = 3.89 \text{ \AA}$) except 'a' was found smaller. This change possibly be due to changed morphology.

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad (2)$$

XRD of $\text{g-C}_3\text{N}_4$ shows two peaks observed at 13.25° and 27.8° that can be indexed as (100) and (002), respectively. The (100)

Table 1
Experimental conditions for LFP.

TOTAL TIME ACQUIRED	10 μs	20 μs
Laser Frequency	2 Hz	8 Hz
Terminal Resistance	40 Ω	5 k Ω
Excitation source (Xenon Lamp)	Pulsed	Non-pulsed
Average Shots	12 shots	200 shots
Time Resolution	100 ps/point	100 ns/point
Laser Energy Per Pulse	2–10 mJ	2–10 mJ

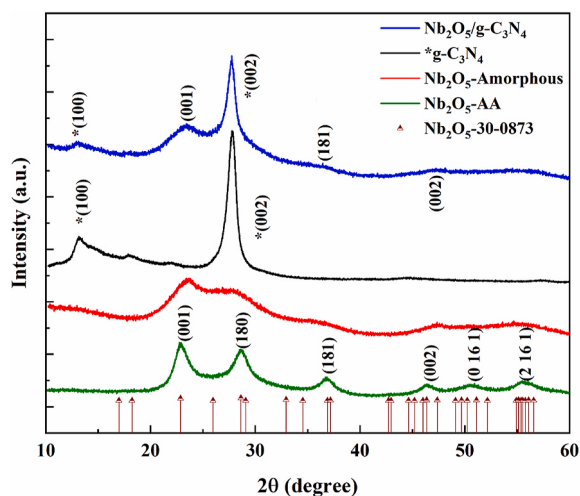


Fig. 1. XRD patterns of g-C₃N₄, Nb₂O₅-BA, Nb₂O₅-AA, Nb₂O₅/g-C₃N₄ heterostructures and reference pattern of Nb₂O₅-30-0873.

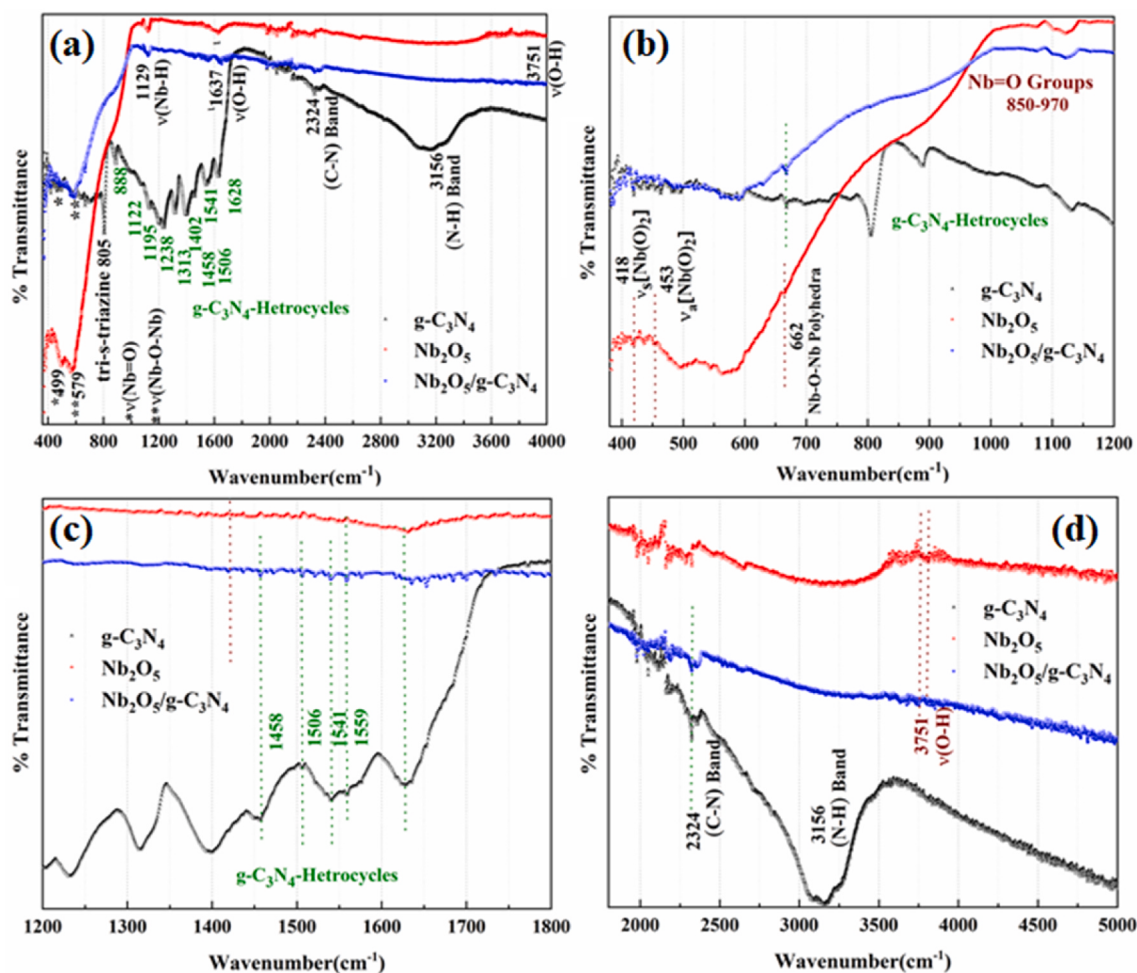


Fig. 2. FTIR spectra of g-C₃N₄, Nb₂O₅ and Nb₂O₅/g-C₃N₄ heterostructures (a) Full Scan, (b) 400-1200 cm⁻¹, (c) 1200-1800 cm⁻¹ and (d) 1800-5000 cm⁻¹.

diffraction plane corresponds to the characteristic interplanar system and the (002) plane corresponds to inter-layer structural packing. XRD pattern of Nb₂O₅ exhibited mild and broad diffraction peaks indicating its amorphous behaviour. In comparison to pure Nb₂O₅ and g-C₃N₄, Nb₂O₅/g-C₃N₄ composites showed a combination of both characteristic peaks. High characteristic peak of g-C₃N₄ (002), suggesting a major pairing between g-C₃N₄ and Nb₂O₅. Energy-dispersive X-ray spectroscopy (EDX) analysis of the Nb₂O₅/g-C₃N₄ heterostructures is given in Figure S1 (a-b) of the supplementary material, which confirmed the existence of the elements Nb, C, O, and N for the prepared sample. Moreover, it confirmed the Nb₂O₅ formation for amorphous. EDX measurements revealed that Nb₂O₅ agglomerates interact strongly with g-C₃N₄.

The FTIR spectra of g-C₃N₄, Nb₂O₅ and Nb₂O₅/g-C₃N₄ were shown in Fig. 2. The spectrum of pure g-C₃N₄ presented all bands described in the literature [21–23] with intensive bands at 808 cm^{−1}, 886 cm^{−1} and in the range of 1122–1632 cm^{−1}, which are assigned to out-of-plane bending vibration of heptazine rings, deformation mode of N–H bonds and stretching modes of C–N heterocycles, respectively. These are also known as g-C₃N₄ heterocycles which has been marked in Fig. 2(a). The spectrum of pure Nb₂O₅ presented the symmetric stretching mode of Nb–O polyhedral (NbO₆, NbO₇, and NbO₈), stretching of Nb=O groups, symmetric stretching ν_s [Nb(O)₂] and the asymmetric stretching ν_a [Nb(O)₂], indicating the presence of a small amount of coordinated peroxide on the Nb(V) ions [1]. The vibration of OH groups ν (O–H) of adsorbed water was also observed. Details are provided in Table 2. The FTIR spectra of the Nb₂O₅/g-C₃N₄ heterostructures exhibited characteristic peaks of both phases as marked in Fig. 2(b–d) (see Table 3).

SEM images of as-synthesized Nb₂O₅ and the Nb₂O₅/g-C₃N₄ heterostructures are presented in Fig. 3(a–b), respectively. The SEM image of g-C₃N₄ is provided in Fig. S2 of the supporting information. The hierarchical nanospheres of Nb₂O₅ and Nb₂O₅/g-C₃N₄ heterostructures could be observed. A TEM analysis of Nb₂O₅/g-C₃N₄ was performed as shown in Fig. 3(c–d). Lattice fringes were found for Nb₂O₅ and g-C₃N₄ as shown in the HRTEM image of Fig. 3(d). SAED pattern has also been provided in Fig. 3(c-inset). The BET surface areas of Nb₂O₅, g-C₃N₄, Nb₂O₅/g-C₃N₄ before annealing and Nb₂O₅/g-C₃N₄ after annealing at 200 °C have been provided in Table S1. The specific surface area (SSA) decreased after heterostructure formation with g-C₃N₄. Annealing processes further reduce the SSA which indicates a decrease in the surface defects.

3.2. UV–vis and IPCE spectroscopy

Bandgap energies and corresponding absorption spectra of g-C₃N₄, Nb₂O₅, and Nb₂O₅/g-C₃N₄ were shown in Fig. 4. The bandgap energies were estimated by the absorption coefficient (inset) of Tauc's plot as shown in Fig. 4 (a). g-C₃N₄ and Nb₂O₅ possess indirect transition band gaps, i.e., 2.56 eV and 3.1 eV, respectively. In addition, the bandgap of Nb₂O₅/g-C₃N₄ heterostructures was red-shifted to 2.52 eV. The observed band gap helped to increase the photocatalytic efficiency of the prepared heterostructures.

IPCE (Incident Photon to Current Conversion Efficiency) spectra of as-prepared electrodes were measured in electrolyte without any sacrificial reagents and conducted with a standard two electrodes in a short circuit. The corresponding IPCE spectra of bare Nb₂O₅, g-C₃N₄, Nb₂O₅/g-C₃N₄ and FTO are presented in Fig. 4 (b). Nb₂O₅/g-C₃N₄ exhibited the highest IPCE values along the scanned wavelength in the UV region in comparison to Nb₂O₅ and g-C₃N₄. The reduced recombination rate of photoinduced electrons and holes provides a meaningful contribution to an increment of IPCE for the Nb₂O₅/g-C₃N₄ electrode. Its photoactivity is also observed in the visible light region from 400 nm to 450 nm, which IPCE value is higher than that of Nb₂O₅. These results indicated that the introduction of g-C₃N₄ not only highly enhances the photoelectric conversion ability of Nb₂O₅/g-C₃N₄ in the UV light region, but also extends its light capture into the visible light region.

3.3. Charge carriers trapping in Nb₂O₅/g-C₃N₄

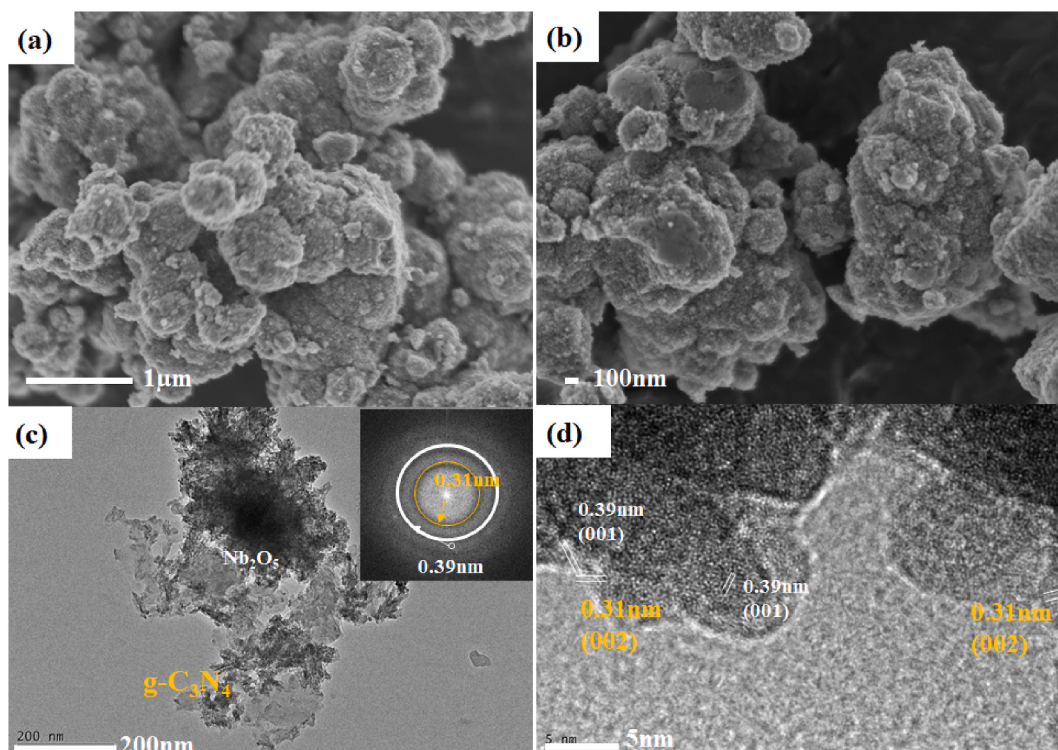
Nb₂O₅/g-C₃N₄ bandgap is 2.52 eV and by IPCE spectra the maximum was observed at 350 nm, therefore, the irradiated laser pulse of λ_{ex} = 320 nm was used. The transient absorption spectra of Nb₂O₅/g-C₃N₄ were observed for different wavelengths ranging between 400 and 800 nm against ΔJ . The experiment was performed under inert conditions (N₂ environment) and the recombination of pure charge carrier kinetics was observed with and without a hole-scavenger (methanol). After a full spectrum scan ranging from 400 to 850 nm two different values of time was used to investigate charges in the transient spectra, as shown in Fig. 5. Without methanol, the transient absorption has shown a random pattern as shown in Fig. 5(a). With methanol, the transient absorption strongly increases at 680 nm and 720 nm, while decreasing at 425 nm as shown in Fig. 5 (b). This strategy employed that the trapped holes have transient absorption peaks around 420–450 nm and peaks of trapped electrons ranging from 700 to 760 nm at higher wavelengths. Therefore, we further observed the transient absorption spectra at 680 nm and 720 nm to calculate the lifetime of electrons which are possibly taking part in the increased photocatalytic efficiency for H₂ generation.

Table 2
FTIR Vibrational Data of Nb₂O₅ and g-C₃N₄ [1,21–23].

Nb ₂ O ₅	418 cm ^{−1}	453 cm ^{−1}	499 cm ^{−1}	579 cm ^{−1}	850-970 cm ^{−1}	3751 cm ^{−1}
	ν_s [Nb(O) ₂]	ν_a [Nb(O) ₂]	ν (Nb=O)	ν (Nb–O–Nb)	ν (Nb=O)	ν (O–H)
g-C ₃ N ₄	805 cm ^{−1}	886, 1122-1632 cm ^{−1}		2324 cm ^{−1}		3156 cm ^{−1}
	Tri-s-triazine	g-C ₃ N ₄ heterocycles		C–N		N–H

Table 3Results of nonlinear second-order kinetic fit at 680 and 720 nm for Nb₂O₅/g-C₃N₄ after excitation with 2–10 mJ/cm².

Parameters	Wavelength 680 nm	Wavelength 720 nm
A	$1.42663 \times 10^{44} \pm 1.63283 \times 10^{45}$	$1.01592 \times 10^{45} \pm 2.61135 \times 10^{45}$
B	4.05706 ± 0.17132	0.64582 ± 0.01425
K	$-9.84014 \times 10^{13} \pm 6.76485 \times 10^{19}$	$2.7570910^{22} \pm -$
T	$-3.39871 \times 10^{14} \pm 2.34827 \times 10^{20}$	$2.6864 \times 10^{25} \pm -$

**Fig. 3.** SEM images of (a) Nb₂O₅ and (b) Nb₂O₅/g-C₃N₄, (c) TEM image (inset SAED patterns) and (d) HRTEM image of Nb₂O₅/g-C₃N₄ heterostructures.

3.4. Transient absorption kinetics and second-order fit on transient signals

To observe the transients in the oscilloscope, the Beer-Lambert law was applied by using equation (3). Herein, photogenerated species were detected by the fraction of transmitted light.

$$A = -\log\left(\frac{I_t}{I_0}\right) \quad (3)$$

Where I_0 is the incident intensity and I_t is the fraction of light measured after interaction with the powder sample. Fig. 6 represents the transient absorption kinetics at (a) 680 nm and (b) 700 nm in an N₂-methanol atmosphere for Nb₂O₅/g-C₃N₄ after 0.078 μs in the 10 μs measurements. The full transient signal can be seen in the inset of Fig. 6(a–b). In the beginning, there is a negative peak associated with scattering from UV lasers, which was used as the source of excitation. The 40 Ω terminal resistance enables a short period of rising and allows the signal to be easily detected after 0.078 μs. The 5 kΩ high resistance used for the 20 μs measurements eventually led to a much longer detector rise time. Before kinetic analysis, the first 0.08 μs of observations were removed as they did not reflect the transient signal.

The data point was reduced to 897 for the easy processing of the transient signal by removing 103 points. The sample reflecting changes was determined by equation (4).

$$\Delta J = 1 - 10^{-Abs} = \frac{I_0 - I}{I_0} \quad (4)$$

As predicted that LFP was used to observe the recombination of charge carriers corresponding to second-order kinetics [22]. Many

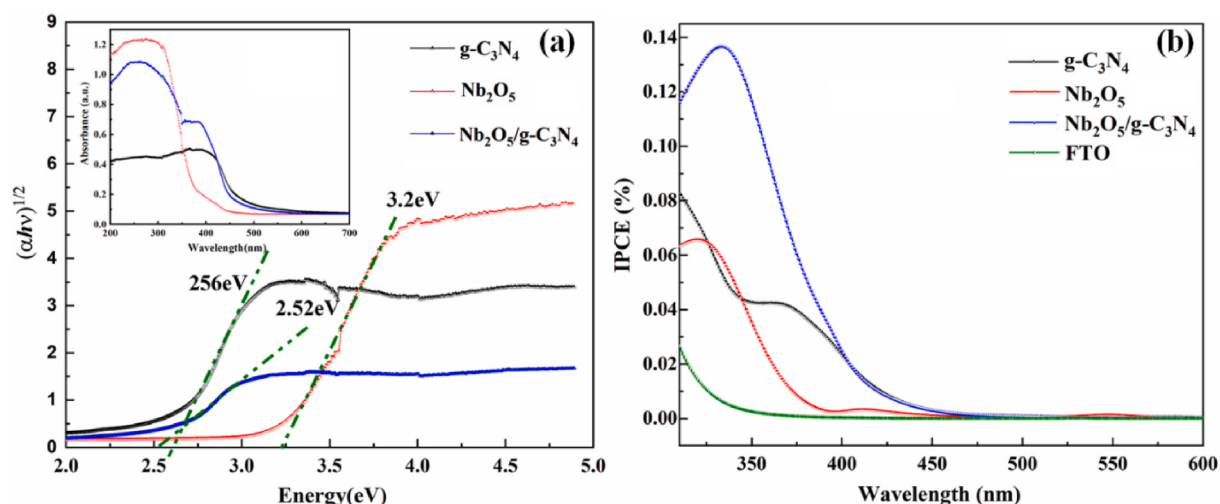


Fig. 4. (a) Tauc's plots for Nb_2O_5 , $\text{g-C}_3\text{N}_4$, and $\text{g-C}_3\text{N}_4/\text{Nb}_2\text{O}_5$ heterostructures obtained through UV-Vis-diffuse Absorption curves provided inset, (b) IPCE spectra of $\text{g-C}_3\text{N}_4$, bare Nb_2O_5 , $\text{Nb}_2\text{O}_5/\text{g-C}_3\text{N}_4$ and FTO in 0.2 M Na_2SO_4 electrolyte without any sacrificial reagents conducted with a standard two electrodes in a short circuit.

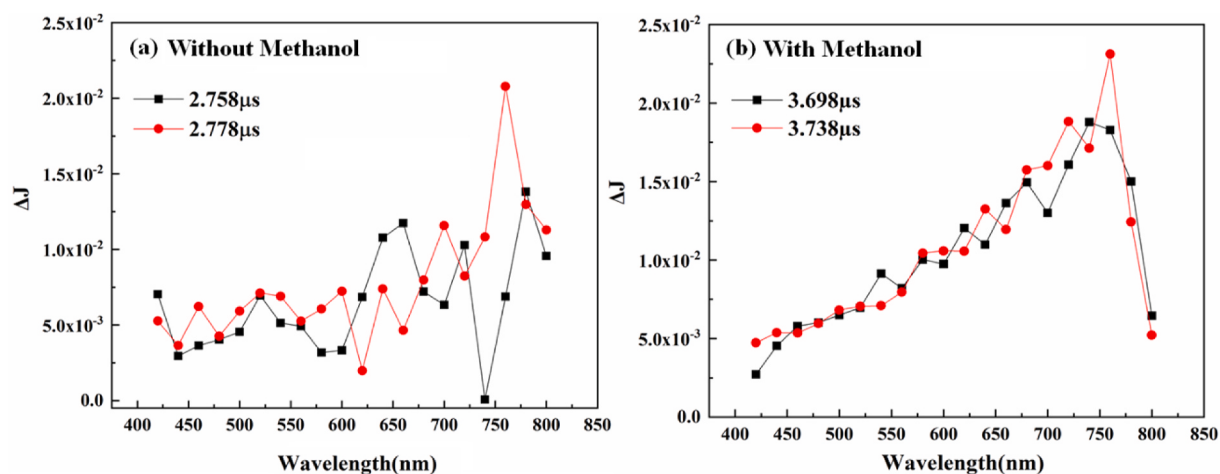


Fig. 5. Transient absorption spectra of the $\text{Nb}_2\text{O}_5/\text{g-C}_3\text{N}_4$ composite were measured at different times for wavelengths ranging from 400 to 850 nm ($\lambda_{\text{ex}} = 320$ nm) (a) without methanol and (b) with methanol.

scientists worked on this kinetics, but Tamaki et al. [23] are the ones who provided the detailed kinetic analysis regarding second-order processes. However, they focused only on signals ranging from picosecond (ps) to nanosecond (ns). In the present work, a second-order kinetic fit was used, and the signal ranges have been taken from μs -ns. A second-order fit function that we have used is provided in equation (5) [24]. The fitted model has been shown in Fig. 6(c-d).

$$Y = \frac{t \times A}{k \times A \times X + 1} + B \quad (5)$$

Where Y is the second-order adsorption, A is the altitude at which transient signals are detected, k is the recombination constant, B is the residual signal after fitting, X is the varying parameter used for fitting and t is the time taken by the curve of decay (μs -fs). By using the above equation, charge carrier signals were fitted with the obtained parameters by taking three different percentage change values (ΔJ %) at 680 nm and 720 nm. This model explains the enhanced performance of the composite material in photocatalytic hydrogen production experiments.

3.5. Calculation for lifetime

Table 4 presents the comparison of the lifetimes of $\text{g-C}_3\text{N}_4$ and $\text{Nb}_2\text{O}_5/\text{g-C}_3\text{N}_4$. To calculate the average lifetime of $\text{Nb}_2\text{O}_5/\text{g-C}_3\text{N}_4$,

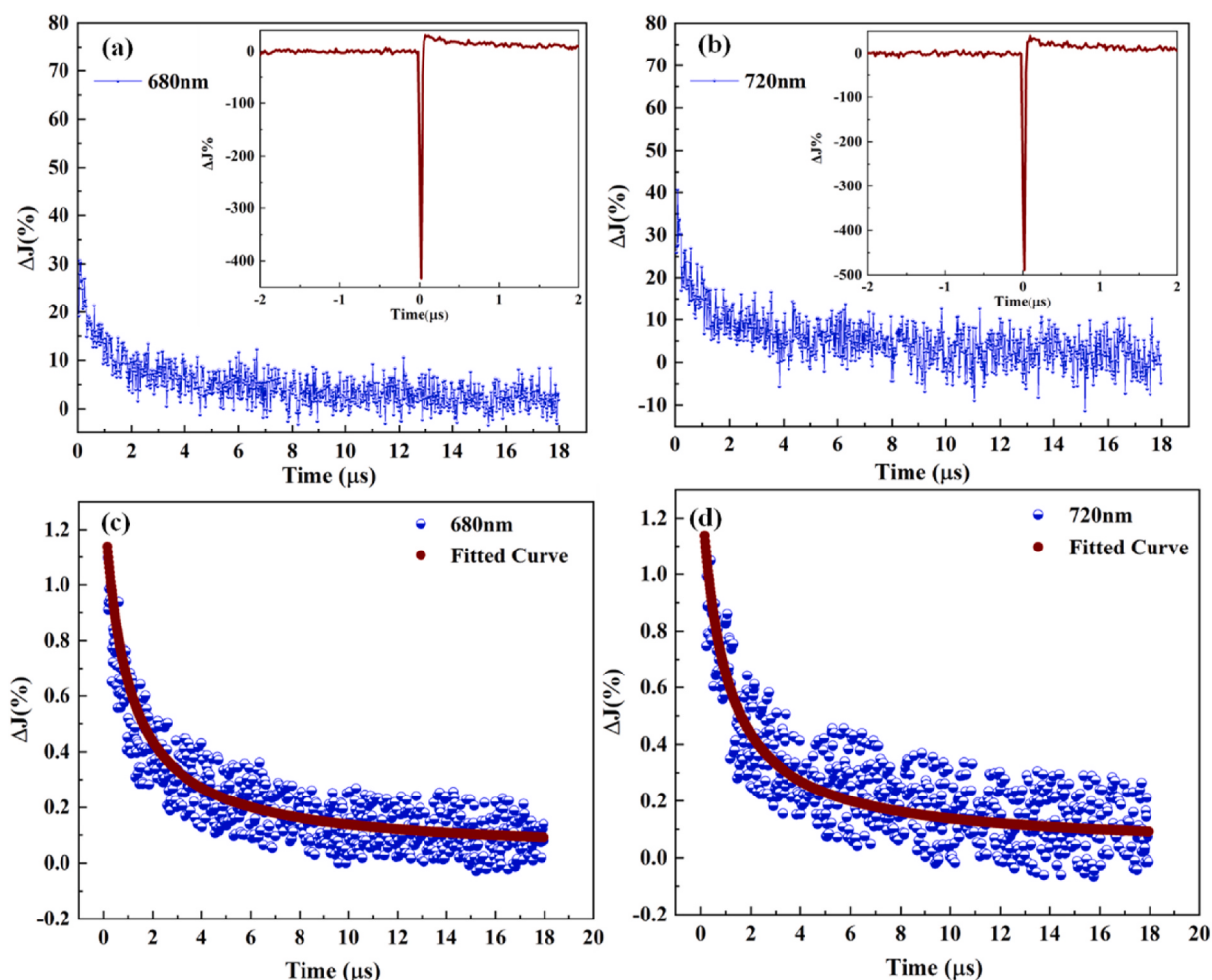


Fig. 6. Reflectance transition of Nb₂O₅/g-C₃N₄ at (a) 680 nm and (b) 700 nm after laser excitation ($\lambda_{\text{ex}} = 320$ nm); Modified percentage reflectance of Nb₂O₅/g-C₃N₄ after excitation with 2–10 mJ/cm² at (c) 680 nm and (d) 720 nm and laser excitation ($\lambda_{\text{ex}} = 320$ nm).

we have calculated the lifetime of g-C₃N₄. After plotting the values, we plotted a graph between these values and then integrated this graph by clicking on the analysis, mathematics and then integrated the function. After performing all these steps correctly, we finally generated the area $A_1 = 3.79384980 \times 10^{-10}$ which was taken in the numerator of equation (5). Then we plotted another graph by doing the same process as mentioned above and calculated the area $A_2 = 1.1986165 \times 10^{-06}$ which was taken in the denominator of equation (5). By dividing A_1 by A_2 , the average lifetime of the decay curve was calculated as 3.1651897 μ s. Similarly, the average lifetime of Nb₂O₅/g-C₃N₄ was calculated as 6.54165 μ s by using the $A_1 = 3.88509 \times 10^{-13}$, $A_2 = 5.939 \times 10^{-08}$.

3.6. Photocatalytic evolution of molecular H₂

Detailed research was conducted to determine the effect of various factors on the rate of molecular hydrogen evolution. Initially, photocatalytic production of molecular H₂ for P25, g-C₃N₄, Nb₂O₅, and Nb₂O₅/g-C₃N₄ was performed with and without methanol. Fig. 7(a–b) exhibits the evolved H₂, while Fig. 7(c–d) the overall comparison and total rate of H₂ evolution with and without methanol. Heterostructures prepared with and without methanol show a higher molecular H₂ than P25, g-C₃N₄, and Nb₂O₅. An increase in the H₂ production rate in the presence of methanol is evidence of efficient interfacial charge separation. Nb₂O₅/g-C₃N₄ heterostructures generated the highest hydrogen production rate (22.75 mmol/h g) due to their wide surface area and suitable band positions. Thus,

Table 4

Comparison of lifetimes of g-C₃N₄ and Nb₂O₅/g-C₃N₄.

Material	A ₁	A ₂	Average Lifetime
g-C ₃ N ₄	$3.79384980 \times 10^{-10}$	$1.1986165 \times 10^{-06}$	3.1651897 μ s
Nb ₂ O ₅ /g-C ₃ N ₄	3.88509×10^{-13}	5.939×10^{-08}	6.54165 μ s

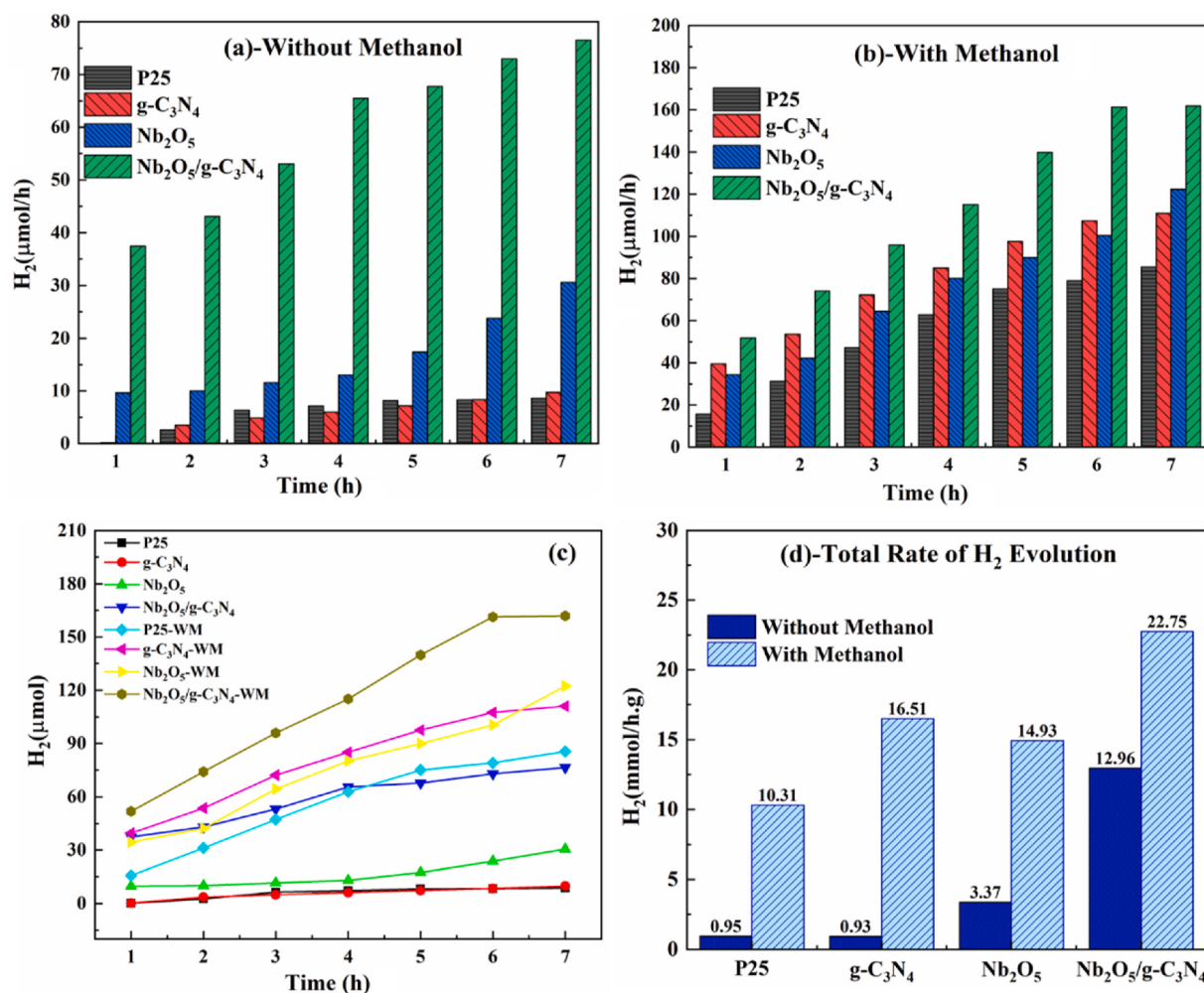


Fig. 7. Molecular H₂ evolution for P25, Nb₂O₅, g-C₃N₄, and Nb₂O₅/g-C₃N₄: (a) without methanol, (b) with methanol, (c) overall comparison, and (d) total rate with and without methanol.

Nb₂O₅/g-C₃N₄ heterostructures with enhanced photocatalytic activity were produced by loading g-C₃N₄ as an electron-hole separator. The current results of g-C₃N₄, Nb₂O₅, and Nb₂O₅/g-C₃N₄ were also compared with previous reports [13,21–24]. Our results showed a higher molecular H₂ rate, even without methanol.

3.7. Photocatalytic mechanism of g-C₃N₄/Nb₂O₅

Direct Z-scheme charge transfer favoured the band positions of Nb₂O₅ and g-C₃N₄. As shown in Fig. 8, under solar light electrons on the surface of the Nb₂O₅ conduction band (CB) moved to the g-C₃N₄ valence band (VB) and then recombined with holes. Electrons on the CB of g-C₃N₄ react with H⁺ to generate molecular H₂. The holes on the VB of Nb₂O₅ can undergo possible oxidation reactions. Compared to pure g-C₃N₄, the Nb₂O₅/g-C₃N₄ heterostructures exhibited higher photocatalytic activity for molecular hydrogen production due to the longer lifetime of photogenerated charges. These results indicated the generation of efficient heterojunctions between the g-C₃N₄ and Nb₂O₅ phases, which promoted charge carrier transfer and enhanced the lifetimes of the photogenerated charges. The proposed Z-Scheme photocatalysis mechanism has been provided in Fig. 8. The calculated band edges by Mott-Schottky analysis have been provided in Fig. S4.

4. Conclusions

Hydrothermal synthesis was employed to produce Z-scheme Nb₂O₅/g-C₃N₄ heterostructures, which reported the high molecular H₂ evolution with and without a hole scavenger as compared to pure g-C₃N₄ and Nb₂O₅. These heterostructures exhibited higher photocatalytic activity due to the longer lifetime of photogenerated charge carriers, where the lifetime was calculated through the Laser Transient Absorption Spectra. This study was conducted first time for Nb₂O₅/g-C₃N₄-prepared heterostructures.

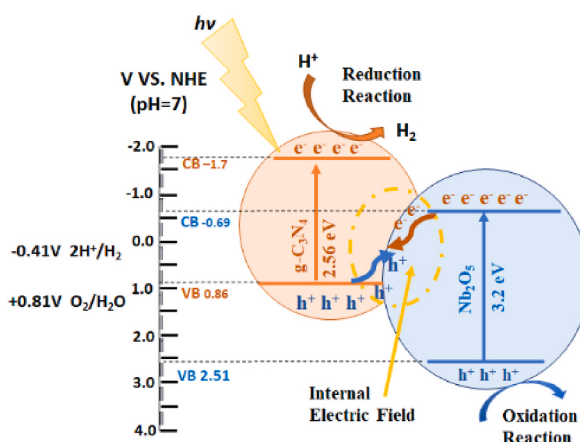


Fig. 8. Schematic illustration of the associated photocatalytic mechanism.

The contribution of hole scavenger for possible charge trapping and increased H_2 evolution was demonstrated. The laser flash photolysis study in this work showed that the hole and electron trapping occur in the wavelength ranges ~ 440 nm and ~ 750 nm in the absence of methanol. But, in the presence of methanol, hole trapping strongly increased whereas electron trapping remains the same. A second-order kinetic fit was applied to describe the recombination of charge carriers. Our model well predicts the charge carrier signal in $\text{Nb}_2\text{O}_5/\text{g-C}_3\text{N}_4$ that was seen in the nanosecond to microsecond time scale after being excited by a laser flash. Meanwhile average lifetimes of both $\text{g-C}_3\text{N}_4$ (~ 3.1651897 μs) and $\text{Nb}_2\text{O}_5/\text{g-C}_3\text{N}_4$ (~ 6.54165 μs) were shown, we observed a higher rate of molecular H_2 evolution for $\text{Nb}_2\text{O}_5/\text{g-C}_3\text{N}_4$ heterostructures.

Author contribution statement

Muhammad Umair Tariq: Analyzed and interpreted the data; Wrote the paper.
 Detlef Bahnemann: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data.
 Faryal Idrees: Conceived and designed the experiments; Performed the experiments; Wrote the paper.
 Saman Iqbal: Performed the experiments; Wrote the paper.
 Fauzia Iqbal: Contributed reagents, materials, analysis tools or data; Wrote the paper.
 Faheem K Butt: Performed the experiments; Analyzed and interpreted the data.
 Jeong Ryeol Choi: Contributed reagents, materials, analysis tools or data.
 Muhammad Bilal: Analyzed and interpreted the data.

Data availability statement

Data included in article/supp. material/referenced in article.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.heliyon.2023.e16772>.

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