

9-15-2023

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Jinqiang Zhang

Xiaojie Tan

Lei Shi

Haijun Chen

Yazi Liu

See next page for additional authors

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[10.1016/j.apcatb.2023.122781](https://doi.org/10.1016/j.apcatb.2023.122781)

Zhang, J., Tan, X., Shi, L., Chen, H., Liu, Y., Wang, S., ... & Wang, S. (2023). Tandem internal electric fields in intralayer/interlayer carbon nitride homojunction with a directed flow of photo-excited electrons for photocatalysis. *Applied Catalysis B: Environmental*, 333, Article 122781. <https://doi.org/10.1016/j.apcatb.2023.122781>

This Journal Article is posted at Research Online.

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Authors

Jinjiang Zhang, Xiaojie Tan, Lei Shi, Haijun Chen, Yazhi Liu, Shuaijun Wang, Xiaoguang Duan, Mingbo Wu, Hongqi Sun, and Shaobin Wang



Tandem internal electric fields in intralayer/interlayer carbon nitride homojunction with a directed flow of photo-excited electrons for photocatalysis

Jinqiang Zhang^a, Xiaojie Tan^b, Lei Shi^c, Haijun Chen^{d,*}, Yazi Liu^e, Shuaijun Wang^f, Xiaoguang Duan^a, Mingbo Wu^b, Hongqi Sun^{f,*}, Shaobin Wang^{a,*}

^a School of Chemical Engineering, The University of Adelaide, North Terrace, Adelaide, SA 5005, Australia

^b State Key Laboratory of Heavy Oil Processing, Institute of New Energy, College of Chemical Engineering, China University of Petroleum (East China), Qingdao 266580, China

^c College of Materials Science and Engineering, Nanjing Forestry University, Nanjing 210037, China

^d Jiangsu Key laboratory of Process Enhancement and New Energy Equipment Technology, School of Mechanical and Power Engineering, Nanjing Tech University, Nanjing 211816, Jiangsu, China

^e School of Environment, Nanjing Normal University, Jiangsu Engineering Lab of Water and Soil Eco-Remediation, Nanjing 210023, China

^f School of Science, Edith Cowan University, 270 Joondalup Drive, Joondalup, WA 6027, Australia

ARTICLE INFO

Keywords:

Integrated carbon nitride homojunction
Tandem internal electrical field
Directed charge flow
Maximum photocatalysis
Hydrogen production

ABSTRACT

Photocatalytic hydrogen production is a green technology while significantly impeded by the sluggish and uncontrolled charge dynamics for less electron accumulation on catalyst surface. Herein, we proposed an effective strategy of epitaxial growth of a van der Waals (VDW) homojunction on an intralayer homojunction of carbon nitride for a controlled charge flow. Experimental and simulation collectively disclosed a tandem internal electric field (IEF) in the integrated hybrid, stringing a lateral IEF along the intralayer homojunction with a vertical IEF within the VDW homojunction. The planar IEF dominates laterally dispersive movement of charge carriers for their efficient separations and mobilities, meanwhile the vertical IEF induces an oriented accumulation of the dispersive hot electrons to the catalyst surface for intensified hydrogen reduction. The tandem IEF renders the hydrogen evolution rate at 3.5-fold higher than in-planar homojunction, and 6.3 times higher than g-C₃N₄ benchmark. This work realizes charge-directing dynamics for robust photocatalysis.

1. Introduction

Photocatalytic water splitting reaction has demonstrated its high feasibility to generate green hydrogen without carbon emissions [1,2]. Considering the highest energy density by weight, industrialization of green hydrogen production will significantly tackle the challenges in global energy crisis and environmental deterioration, thereby achieving the goal of carbon neutrality [3,4]. Cheap photocatalysts with high visible light harvesting and robust reduction capabilities are highly desired to realize the scaling production of green hydrogen [4–6]. Polymeric carbon nitride is a prevailing metal-free photocatalyst in water splitting reaction. The superiorities of visible light response, easy to be synthesized and stable in a wide pH range render carbon nitride based photocatalysts appealing in photocatalytic water splitting in the past decade. Nevertheless, the light harvesting efficiency and

photocatalytic throughputs of state-of-the-art carbon nitride photocatalysts are still far from meeting the requirements for practical applications [7–12].

Photocatalytic hydrogen production is a chain process involving the generation of hot electrons and their effective and directional outputs on catalyst surface for hydrogen reduction [13]. There are two resistances in carbon nitride toward impeding charge movements: one is the strong Coulomb force within a plane, and the other is the high energy barrier between interlayer stacking [14–19]. The former resistance always leads to a fast charge recombination, while the latter results in an easy dissipation or cooling of hot carriers during their transportation. While multifarious modification strategies, including a new concept of volume photocatalysis, have been proposed to improve the photocatalytic efficiency [20,21], the dynamics of photo-excited charge carriers in carbon nitride, including their separations, migrations and outputs, intrinsically

* Corresponding authors.

E-mail addresses: chenhj@njtech.edu.cn (H. Chen), h.sun@ecu.edu.au (H. Sun), shaobin.wang@adelaide.edu.au (S. Wang).

<https://doi.org/10.1016/j.apcatb.2023.122781>

Received 29 January 2023; Received in revised form 7 April 2023; Accepted 18 April 2023

Available online 20 April 2023

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determining the photocatalytic activities, remain sluggish and orderless due to the insufficient intralayer and interlayer driving forces in the catalyst.

An internal electric field (IEF) of a semiconductor based photocatalyst is a backstage manipulator to pose inherent driving forces on charge carriers and determines their dynamics and behaviors after excitations [22–26]. Its effect is becoming more prominent and has been recently brought to the forefront of photocatalysis. Unfortunately, IEFs are negligible in pristine carbon nitride due to the laterally symmetric unit cells and vertically periodic interlayer stacking, which reduce separation rate of charge carriers and their assembling on catalyst surface [27]. Fabrication of intralayer heterojunctions is an effective route to break the lateral symmetry of carbon nitride. For instance, doping with heteroatoms or creation of vacancy can enlarge the IEF along carbon nitride in plane for an enhanced photocatalysis. Besides, considerable works have been reported on fabrication of interlayer heterojunctions, including oriented heterojunction, to pose vertical IEFs on electron-hole pairs to accelerate their separations at the intimate contact [24,28–31]. However, subsequent accumulation of hot electrons on catalyst surface is of equal importance to the fast separation of charge carriers for photocatalytic hydrogen reduction, which has been overlooked.

Herein, we developed a three-dimensional carbon nitride homojunction (tandem-C₃N₄) by the integration of a carbon nitride van der Waals (VDW) homojunction on a carbon nitride intralayer homojunction (intra-C₃N₄). Characterizations disclosed that the shallow layers of tandem-C₃N₄ are carbon doped intra-C₃N₄, while the bulk remains as intra-C₃N₄, thus both the intralayer and interlayer symmetries of carbon nitride are broken. Experimental and computation simulation collaboratively revealed a tandem IEF comprising of a lateral and a vertical IEF in tandem-C₃N₄. Lateral IEF dominated the rapidly planar separation and movement of charge carriers, while the extra longitudinal IEF essentially directs the accumulation of more hot electrons on the catalyst surface, accomplishing a three-dimensional modulation of charge dynamics in a directed way. Accompanied with the short vertical diffusion pathway of hot electrons within the shallow layers of the VDW carbon nitride homojunction, a much higher photocatalytic hydrogen production was achieved, exhibiting 3.5-fold higher than in-planar homojunction and 6.3 times higher than g-C₃N₄.

2. Experimental section

2.1. Catalyst preparation

For fabrication of an intralayer carbon nitride homojunction with a lateral IEF, 5 g of melamine and 0.5 g of sodium nitrate were fully dissolved and mixed in ultrapure water. Then, the solution was dried at 100 °C and the obtained powder was placed in a vacuum oven (60 °C) overnight. After that, the precursor was ground and put into a muffle furnace. A heat treatment of the precursor was performed at 550 °C for 4 h with a ramping rate of 2.3 °C min⁻¹. After cooling down to room temperature, the powder was successively washed by hot water and ethanol for several times and subsequently dried at 60 °C overnight to obtain a final product (named as intra-C₃N₄). For comparison, pristine g-C₃N₄ was prepared similarly without the addition of sodium nitrate.

Integrated carbon nitride homojunction with tandem lateral and vertical IEFs was synthesized by an epitaxial growth method in a self-designed furnace. The obtained intra-C₃N₄ sample was placed in a sample holder where methane gas can go through the catalyst bed. Then, the furnace was successively purged with Ar and a mixture gas of CH₄ and Ar (a ratio of 1:1 and flow rate of 10 mL/min). The furnace was heated up to 500 °C for 2 h at a ramping rate of 2.3 °C min⁻¹. The obtained product was named as tandem-C₃N₄.

2.2. Characterizations

The crystal structures of the prepared samples were analyzed by X-ray diffraction (XRD, X'Pert PRO MPD, Holland). A Micromeritics Tristar 3000 was employed to obtain N₂ adsorption-desorption isotherms under –196 °C. A Talos F200X and a Hitachi SU8010 were used to capture transmission electron microscopy (TEM, and high resolution TEM, HRTEM) and scanning electron microscopy (SEM) images, respectively. A Bruker ADVANCEIII 500 MHz equipment was employed to collect solid-state ¹³C NMR spectra. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet Nexus 670 spectrometer. Diffused reflectance spectra and photoluminescence spectra were collected on a TU-1901 spectrometer with BaSO₄ as a reflectance standard and a Hitachi F-4600 luminescence spectrophotometer, respectively. Time-resolved decay spectra were acquired on a FLS1000. A Kratos Axis Ultra DLD system under ultrahigh vacuum condition was used for X-ray photoelectron spectroscopy (XPS), and the results were calibrated with C 1 s reference signal (284.6 eV). A Bruker EMS-plus instrument was adopted to record solid electron paramagnetic resonance (EPR) results, which were analyzed with a Bruker Xeon software. An CEL-SPS1000 (Beijing China Education AuLight Co. Ltd., China) was used to perform surface photovoltage spectroscopy (SPV) measurements. Z potential was determined using a Malvern Zetasizer Nano ZS90 and the dispersion solution was adjusted to a pH of 7, which closely mimics the environment of the catalysts in a photocatalytic water splitting reaction.

2.3. Performance evaluation

Photocatalytic water splitting for H₂ was performed in a LabSolar-III AG reaction cell (Beijing PerfectLight Co.) equipped with a 300 W Xe-lamp (CEL-HXF300, Beijing Cel Sci-tech Co., Ltd.). A visible-light long-pass filter was used as the visible light source. In the reaction, 50 mg photocatalyst was put in 50 mL aqueous solution with 0.8 mL of H₂PtCl₆·(H₂O)₆ (3.0 wt%), and 5 mL of triethanolamine. Prior to light irradiation, the reactor was evacuated for 30 min to thoroughly remove air inside. The reaction temperature was kept at 6 °C. H₂ was finally determined by an online gas chromatograph (GC7920, Techcomp) equipped with a 5 Å molecular sieve column and a thermal conduction detector (TCD).

2.4. Electrochemical measurements

The electrochemical measurements of the prepared samples were performed on a CHI 760E electrochemical workstation (CH Instruments, Shanghai, China) with a three-electrode framework including a working electrode, an Ag/AgCl reference electrode, and a platinum counter electrode. The working electrodes were prepared using Indium Tin Oxide (ITO) glasses decorated with the prepared samples. Specifically, a slurry was prepared by mixing photocatalyst (10 mg) with 20 μL Nafion in 1 mL of ethanol solution, and then was dispersed onto the ITO (2 cm × 5 cm). After naturally dried, the electrode was put into an oven at 80 °C for 2 h. Na₂SO₄ solution (0.1 M) was used as the electrolyte. A 300 W Xenon lamp was used as the visible light source. For the tests of electrochemical impedance spectroscopy (EIS), the frequency ranged from 100 kHz to 10 mHz with the perturbation signal of 10 mV.

2.5. Computational methods

First-principles density functional theory (DFT) calculations were performed using Vienna Ab initio Simulation Package (VASP) with the projector augmented wave (PAW) method. The exchange-functional was treated by the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) functional. HSE06 hybrid functional was used for more accurate calculations of electronic structure. The energy cutoff was set at 500 eV for the plane wave basis expansion and the force on each atom was set less than 0.02 eV/Å for convergence criterion of

geometry relaxation. The Monkhorst-Pack K-mesh was applied for the Brillouin-zone integration in the calculation, with the K-point separation of 0.04 \AA^{-1} . A convergence energy threshold of 10^{-5} eV was set in the self-consistent calculations.

3. Results and discussion

The processes to integrate tandem- C_3N_4 are shown in Fig. 1a. Pristine carbon nitride ($\text{g-C}_3\text{N}_4$) with centrosymmetric and periodical tri-triazine rings was synthesized by direct calcination of melamine at $550 \text{ }^\circ\text{C}$ (left model in Fig. 1a). To break up the lateral symmetry, we added NaNO_3 salt during the polymerization of carbon nitride to make

damage to the triazine ring, acquiring an intralayer homojunction (intra- C_3N_4 , middle model in Fig. 1a). Then an extra longitudinal VDW homojunction was created on intra- C_3N_4 by further calcination under methane atmosphere. The carbon radicals from methane pyrolysis replaced nitrogen atoms on the shallow layers of intra- C_3N_4 to further break up the longitudinal symmetry. As the bulk structure of intra- C_3N_4 homojunction maintained, a tandem carbon nitride homojunction (tandem- C_3N_4 , right model in Fig. 1a) was obtained, which was comprised of a lateral carbon nitride intralayer homojunction and a vertical carbon nitride VDW homojunction.

XRD patterns were collected to study the crystalline structure of the different types of carbon nitride homojunctions (Fig. 1b). Two obvious

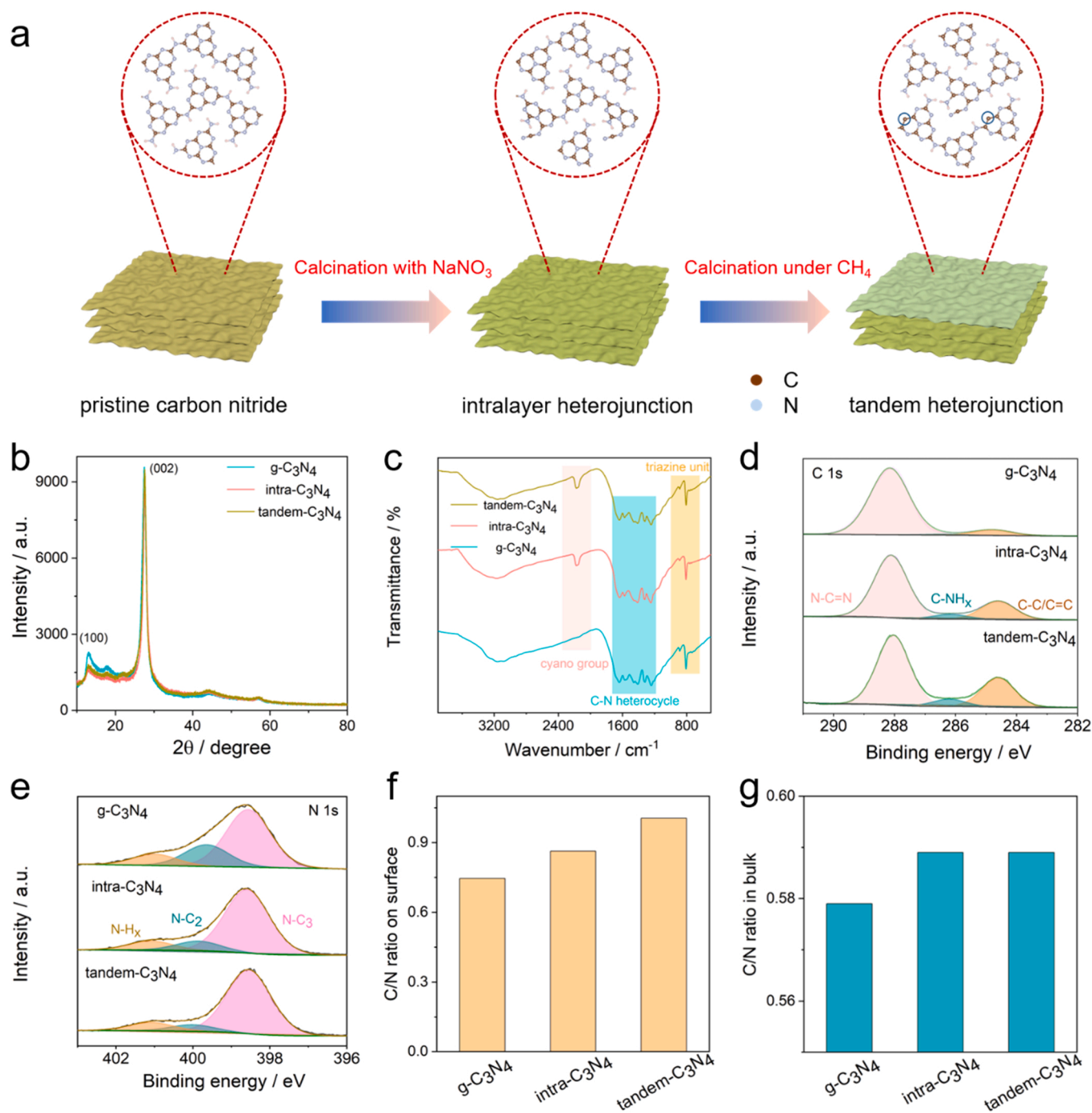


Fig. 1. Catalyst synthesis and characterizations. (a) Schematic illustration for integration of intralayer and VDW homojunctions in a tandem carbon nitride homojunction. Compositional information of $\text{g-C}_3\text{N}_4$, intra- C_3N_4 and tandem- C_3N_4 , including (b) XRD patterns, (c) FT-IR spectra, high resolution XPS C 1 s (d) and N 1 s (e) spectra, (f) C/N ratio on surface determined by XPS tests and (g) C/N ratio in bulk revealed from element analysis (EA).

characteristic peaks at 13.0 and 27.4° can be observed on pristine carbon nitride. The former peak is ascribed to the (100) diffraction of laterally periodic tri-s-triazine units, while the latter one is attributed to the (002) vertical stacking diffraction of the graphitic structure [32–34]. Compared with pristine g-C₃N₄, the intensity for the (100) peak of intra-C₃N₄ and tandem-C₃N₄ apparently decreased but the (002) peak kept unchanged. This means that the planar triazine structure of g-C₃N₄ was destroyed after calcination of melamine with NaNO₃ and the damaged triazine structure failed to be recovered after further calcination of intra-C₃N₄ under methane [6]. Meanwhile, neither NaNO₃ nor methane failed to break the interlayer van der Waals interaction of g-C₃N₄ during the calcination. This is consistent with the observations of the unchanged bulk morphology of intra-C₃N₄ and tandem-C₃N₄ from TEM images (Fig. S1). As such, the symmetric and periodical unit cells within the intralayer structure of g-C₃N₄ were destroyed in intra-C₃N₄ and tandem-C₃N₄, but their thickness of cross section remained.

Fourier transform infrared (FT-IR) spectroscopy was then employed to investigate the molecular structure of intra-C₃N₄ and tandem-C₃N₄ (Fig. 1c). Absorption bands at 810, 1200–1750 and 3000–3700 cm⁻¹ can be clearly seen in all the three samples, which are corresponded to the breathing mode of triazine units, stretching mode of N-containing heterocycles, and the N-H stretch of marginal amino groups, respectively, indicating the main C-N frameworks maintain (unit cell of C₃N₄, Fig. S2a) after the fabrication of lateral and vertical homojunctions [35]. The result is also supported by the two evident ¹³C NMR peaks of C=N carbon atoms at 165 ppm and C-NH₂ carbon atom at 155 ppm in intra-C₃N₄ and tandem-C₃N₄ samples (Fig. S3) [36]. Noticeably, an obvious peak emerged at 2170 cm⁻¹ on intra-C₃N₄ (Fig. 1c), which is assigned to the asymmetric stretching vibration of cyano groups [37]. The intriguing result suggested that the triazine ring in the carbon nitride framework was opened after calcination with sodium salt, leaving nitrogen vacancies in the unit cell (unit cell of N_v-C₃N₄, Fig. S2b). It should be noted that further calcination of intra-C₃N₄ under methane failed to recover the melon structure. This well matched with the similar (100) peak between intra-C₃N₄ and tandem-C₃N₄ in their XRD profiles, confirming that the intralayer homojunction exists in both the samples.

We then use X-ray photoelectron spectroscopy (XPS) to study the surface composition of the as-prepared samples (Fig. S4 and Table S1). C1s spectra are deconvoluted into three peaks at around 284.6, 285.7 and 288.1 eV, which are assigned to the C=C bonding, sp²-hybridized C bonded to the amino group (C-NH₂), and sp²-hybridized C bonded to N inside the triazine rings (N-C=N), respectively (Fig. 1d) [33]. Compared with g-C₃N₄, the C-NH₂ peak of intra-C₃N₄ at 286.0 eV was intensified and upshifted. As the binding energy of cyano group is similar to amino group, the intensified and upshifted peak at 286.0 eV proves the creation of the cyano group in intra-C₃N₄ sample, indicating the damage of triazine rings [37].

N 1s spectra are fitted to the peaks at 398.6, 399.7 and 400.9 eV, which are attributed to the tertiary N (N-(C)₃), sp²-hybridized N (C-N=C), and amino group (-N-H), respectively (Fig. 1e) [38]. Compared with g-C₃N₄, the N-C₂ peak on intra-C₃N₄ was obviously upshifted and weakened (Table S2). This again proves the damaged triazine structure when calcination of melamine with NaNO₃. A further upshift and decrease of N-C₂ peak can be observed after calcination under methane gas, suggesting that some N atoms were replaced by the carbon atoms from decomposed methane molecules to form C=C bonding. Meanwhile, D and G bands assigning to defect carbon and graphitic carbon, respectively, fail to be found on tandem-C₃N₄ from Raman spectra (Fig. S5), indicating that C-doped carbon nitride intralayer homojunction (unit cell of C-N_v-C₃N₄, Fig. S2c), rather than carbon material was formed in tandem-C₃N₄.

We further compared the element contents in the bulk structure of the three samples (determined by element analysis) with those on catalyst surface (revealed from XPS) [39]. As displayed in Fig. 1f-g and Table S3-4, the C/N ratio of g-C₃N₄ surface within shallow layers

gradually increased after NaNO₃ and subsequent methane treatments. The overall C/N ratio of intra-C₃N₄ measured by element analysis also increased compared with g-C₃N₄, illustrating that the nitrogen vacancies were created throughout the whole structure of intra-C₃N₄. While the bulk carbon content after calcination under methane is almost the same as intra-C₃N₄. The results indicate that substitution of nitrogen by carbon atom occurs only on the top layers of intra-C₃N₄, thereby forming an extra carbon nitride van der Waals homojunction in tandem-C₃N₄. Therefore, an intralayer homojunction exists in intra-C₃N₄, and an additional van der Waals homojunction is formed in tandem-C₃N₄.

The IEFs in the different types of carbon nitride homojunctions were theoretically studied. Single layer models of C₃N₄, N_v-C₃N₄ and C-N_v-C₃N₄ were built to represent the different components in intralayer and VDW carbon nitride homojunctions (Fig. S2). The bandgaps for C₃N₄, N_v-C₃N₄ and C-N_v-C₃N₄ were calculated to be 3.65, 3.17 and 2.52 eV, respectively (Fig. 2a), suggesting that the creation of nitrogen vacancy and carbon doping are both effective pathways to improve the light absorption. Combined with the calculated conduction (CB) and valence bands (VB), the band structures of these three models are presented in Fig. 2b. Meanwhile, the work functions for the three models were acquired (Fig. 2c-e). In the intra-C₃N₄, the work functions for C₃N₄ and N_v-C₃N₄ unit cells were estimated to be 6.57 and 6.45 eV, respectively. As thus, when N_v-C₃N₄ and C₃N₄ unit cells are laterally combined, the electrons will flow from N_v-C₃N₄ to C₃N₄ unit cells until their Fermi levels are equilibrated, leaving positive charges on C₃N₄ unit cells. Consequently, an internal electric field would be created in intra-C₃N₄, horizontally directing from C₃N₄ to N_v-C₃N₄ (Fig. S6). Repulsion of electrons in N_v-C₃N₄ by the internal electric field leads to increases on potential energy and upwards on bands bend. Conversely, decreases on potential energy and the downwards on bands bend occur in the C₃N₄. Therefore, the photogenerated electrons at the CB of C₃N₄ are likely to transfer through the interface to recombine with the holes at the VB of N_v-C₃N₄, suggesting a S-scheme charge-transfer process in intra-C₃N₄ (Fig. 2f) [40].

In the same way, as the work function of N_v-C₃N₄ is calculated to be higher than that of C-N_v-C₃N₄, another vertical IEF is created within the VDW carbon nitride homojunction, directing from the top layer of C-N_v-C₃N₄ to N_v-C₃N₄ (Fig. S7). Combined with the proposed band structures of C-N_v-C₃N₄ and N_v-C₃N₄, another S-scheme charge-transfer process is inferred in tandem-C₃N₄ that photo-excited electrons on the CB of N_v-C₃N₄ traverse through the interlayer to the VB of C-N_v-C₃N₄ to recombine with the holes, leaving hot electrons on the C-N_v-C₃N₄ part (Fig. 2g). On this occasion, the lateral and vertical electrostatic potentials for the three samples were calculated to compare the planar and interlayer energy barriers on charge carriers (Fig. S8). Two layers of the melon sheets were modelled, with a typical VDW distance of 3 Å interlayer separation (Fig. S9). It can be clearly seen that the vertical energy barrier is much higher than the lateral one, meaning that a lateral charge transferring is preferred to a vertical traversing [33]. As such, the photo-excited electrons at the CB of C₃N₄ prefer to migrate to the VB of N_v-C₃N₄ under the lateral IEF, and the hot electrons at the CB of N_v-C₃N₄ transfer to the VB of C-N_v-C₃N₄ under the vertical IEF (Fig. 2h). As the results, a series of directed IEF is confirmed in the tandem-C₃N₄.

The directed IEF in the tandem-C₃N₄ can be vividly observed by the highest occupied molecular orbital (HOMO) and the lowest unoccupied orbital (LUMO), which provide a pertinent description of the electron orbital configurations at the intralayer contact and interlayer VDW interactions (Fig. 3). The orbitals in both the HOMO and LUMO of benchmark g-C₃N₄ are symmetric horizontally and vertically. This indicates low intensity of lateral and vertical IEFs in g-C₃N₄ due to the uniform distribution of electrons. After the construction of intralayer homojunction in intra-C₃N₄, the orbitals in both the HOMO and LUMO are non-symmetric within the in-plane. This configuration confirms a lateral IEF in intra-C₃N₄ due to the non-symmetric concentration of electrons [41]. Further, an interlayer IEF failed to be observed on g-C₃N₄ and intra-C₃N₄ because of the similar distribution between the two

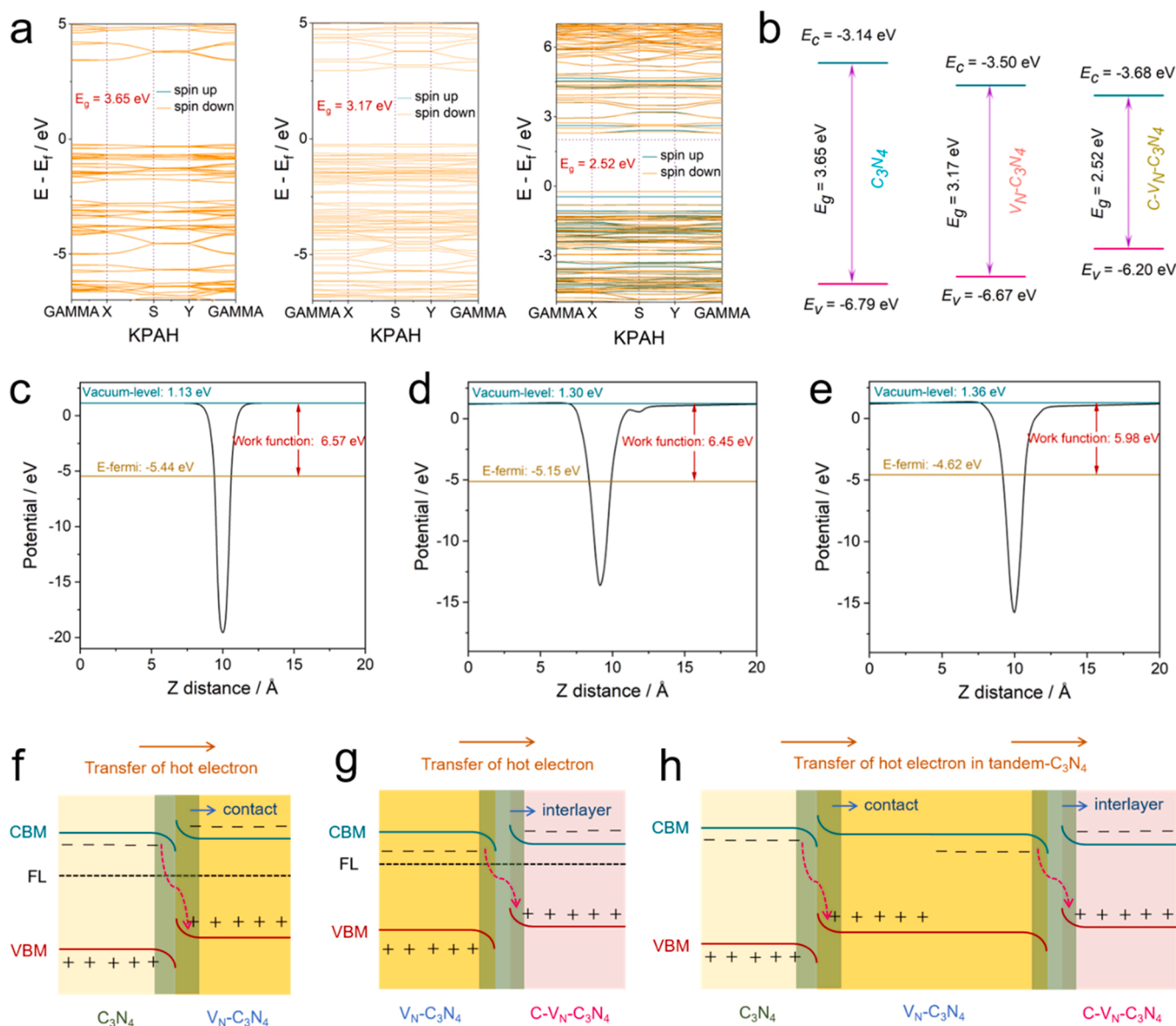


Fig. 2. IEF studies in different carbon nitride homojunctions. (a) Calculated bandgap. (b) Band structure. (c-e) Work function for C_3N_4 , $V_N-C_3N_4$ and $C-V_N-C_3N_4$. (f) S-scheme photo-induced electron transfer in intra- C_3N_4 under light irradiation. (g) S-scheme photo-induced electron transfer in VDW homojunction under light irradiation. (h) A series of directed IEF in tandem- C_3N_4 with transfer direction of photo-excited hot electron under light irradiation.

layers. For tandem- C_3N_4 , very interesting details are demonstrated. A same non-symmetric distribution of orbitals as intra- C_3N_4 is observed within the in-plane. In the meantime, the distributions of orbitals within the bottom layer ($N_V-C_3N_4$) and the top layer ($C-N_V-C_3N_4$) are also totally different. This indicates that a vertical IEF at the VDW junction co-exists with a lateral IEF, proving the series-directed IEF in tandem- C_3N_4 .

The effect of IEF in intra- C_3N_4 and tandem- C_3N_4 on the behaviors of photo-excited charge carriers was then experimentally studied. Steady-state fluorescence spectroscopy is employed to compare the separation rate of photo-excited charge carriers on the prepared samples (PL, Fig. 4a), and a high peak intensity suggests a rapid recombination rate of the charge carriers. As such, compared with g- C_3N_4 , the separation efficiency of charge carriers after the creation of lateral IEF in intra- C_3N_4 is dramatically enhanced. However, we cannot see further enhancement on charge separation efficiency after assembling the IEF in tandem- C_3N_4 . The same trend can be observed from in situ light irradiation electron paramagnetic resonance (EPR) spectra (Fig. 4b) in which the concentration of photoexcited hot electrons can be estimated by the difference of integrated areas of the EPR signals under light irradiation

and in dark (Fig. S10) [42]. The concentrations of CB^- in intra- C_3N_4 and tandem- C_3N_4 are almost the same, and are apparently higher than that of g- C_3N_4 . These results mean that more hot carriers can be excited driven by lateral IEF forces and the extra vertical electric field in tandem- C_3N_4 fails to generate more hot carriers.

On this occasion, the movement of hot carriers after their generations toward separations was investigated. First, the lifetimes of hot electrons in intra- C_3N_4 and tandem- C_3N_4 were measured (Fig. 4c). Compared with the lifetime of 3.5 ns for intra- C_3N_4 , the lifetime of hot electrons in tandem- C_3N_4 turned a bit longer, indicating that the photo-induced hot electrons can move longer, actuated by the series-directed IEF. Besides, the electric impedance of different samples that can affect the movements of hot carriers was tested (Fig. 4d). The impedances of intra- C_3N_4 and tandem- C_3N_4 are almost identical, which are much lower than that of g- C_3N_4 , suggesting the separated hot carriers can be easier to be transported in both homojunctions.

The effect of series-directed IEF in tandem- C_3N_4 on the transferring orientation of photo-induced charge carriers was also studied. We first used surface photovoltage (SPV) spectra to observe the accumulation

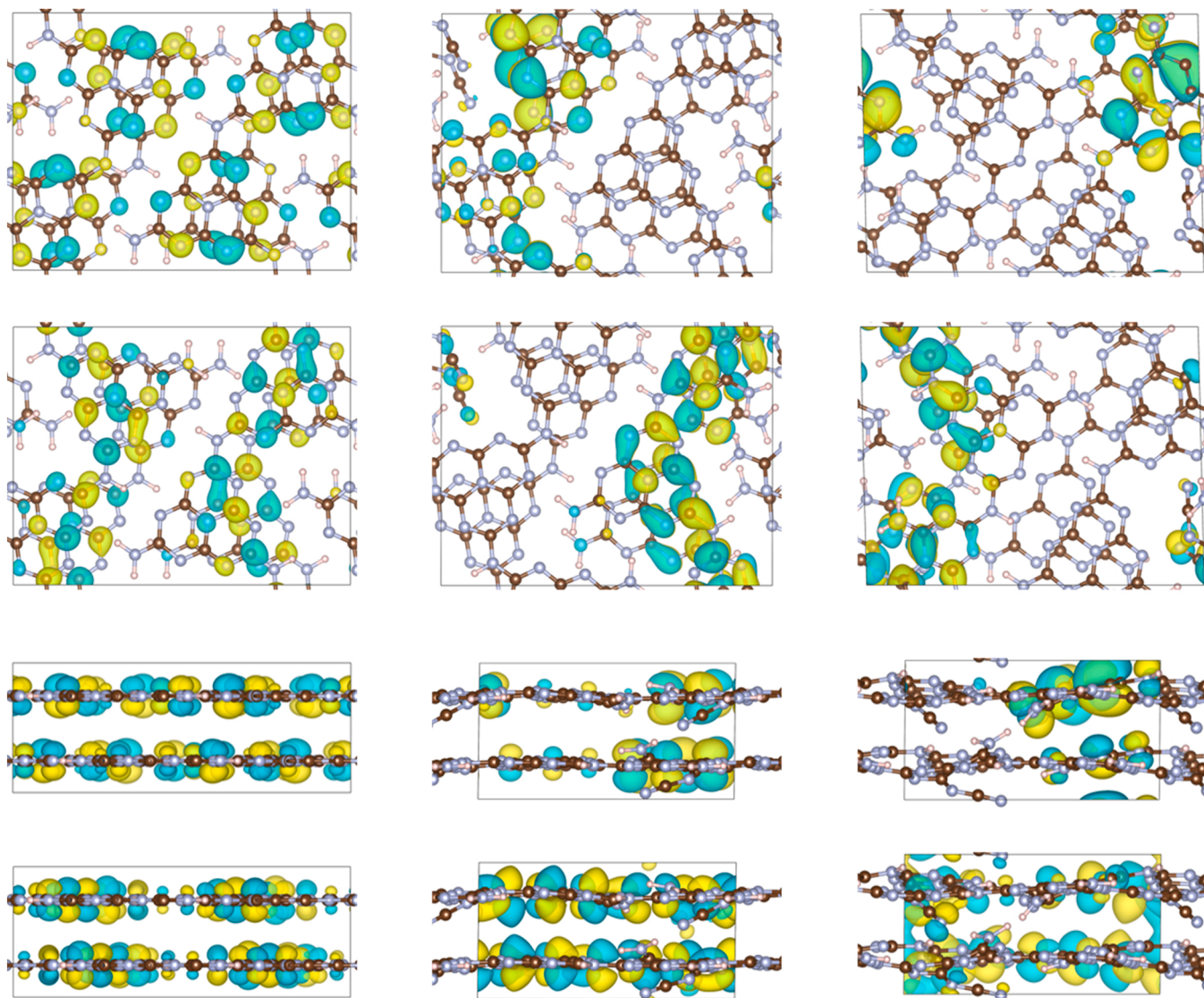


Fig. 3. DFT simulations. Front view of HOMO (first line) and LUMO (second line) of $g\text{-C}_3\text{N}_4$ (left), $\text{intra-C}_3\text{N}_4$ (middle) and $\text{tandem-C}_3\text{N}_4$ (right), and side view of HOMO (third line) and LUMO (last line) of $g\text{-C}_3\text{N}_4$ (left), $\text{intra-C}_3\text{N}_4$ (middle) and $\text{tandem-C}_3\text{N}_4$ (right).

region of hot electrons in different samples (Fig. 4e). A weak peak can be found on pristine carbon nitride, confirming the low separation rate of charge carriers in the symmetric and periodic unit cells. After the fabrication of a lateral electric field in $\text{intra-C}_3\text{N}_4$, the charge dynamics was significantly improved as revealed by the sharp peak in SPV spectra. However, as evidenced by the very positive signal in SPV spectra (Fig. 4e), the activated hot electrons in $\text{intra-C}_3\text{N}_4$ prefer to transfer in the bulk structure rather than to the catalyst surface [43,44]. This is attributed to the negligible vertical IEF in $\text{intra-C}_3\text{N}_4$ and the negative Zeta potential on the surface. After further creation of a vertical IEF between the interlayer of VDW homojunction in $\text{tandem-C}_3\text{N}_4$, the signal turned much lower. As the charge separation rate after the creation of vertical IEF was barely affected, the weakened peak intensity means that more hot electrons are gathered on the catalyst surface once separated. Furthermore, we also observed the accumulation region of hot electrons by a photo-deposition experiment, where methanol was used as the hole scavenger so that Pt^{4+} was reduced to Pt by the photoexcited hot electrons [45]. The TEM images of catalysts after photo-deposition are displayed (Fig. 4f-g). More and larger Pt nanoparticles are deposited on $\text{tandem-C}_3\text{N}_4$ than those on $\text{intra-C}_3\text{N}_4$, reflecting that the extra vertical IEF in $\text{tandem-C}_3\text{N}_4$ drives more hot electrons to accumulate on the catalyst surface for Pt reduction.

Besides, the abilities of light harvesting and mass transfer after fabrication of lateral and vertical IEFs were studied. $g\text{-C}_3\text{N}_4$ has been revealed to be a visible light responsive photocatalyst (Fig. 5a), however, it is impeded by the weak absorption in the visible light region. After the creation of nitrogen vacancy in $\text{intra-C}_3\text{N}_4$, the absorption of visible light was improved, with the bandgap narrowed from 2.66 eV for $g\text{-C}_3\text{N}_4$ to 2.62 eV for $\text{intra-C}_3\text{N}_4$ (Fig. S11 and Table S5). A further enhancement is realized on $\text{tandem-C}_3\text{N}_4$ with a long absorption tail extending throughout the whole visible light region. The corresponding bandgap is further decreased to 2.58 eV. The trend in the decreasing bandgap is in a qualitative agreement with the DFT simulation, in which the calculated bandgaps are 3.40, 2.70 and 2.34 eV for $g\text{-C}_3\text{N}_4$, $\text{intra-C}_3\text{N}_4$ and $\text{tandem-C}_3\text{N}_4$, respectively (Fig. 5b). From the conduction band determined by Mott-Schottky plots (Fig. S12) and valence band measured by XPS VB spectra (Fig. S13), the band structures of all the three samples were obtained and presented in Fig. S14. The CB and VB positions are gradually dropped down after the fabrication of lateral IEF in $\text{intra-C}_3\text{N}_4$ and further construction of vertical IEF in $\text{tandem-C}_3\text{N}_4$. The variations from the measurements are consistent with those from DFT calculation, confirming the reliability of both the experimental and simulation results.

The capability of the prepared samples on mass transfer was also

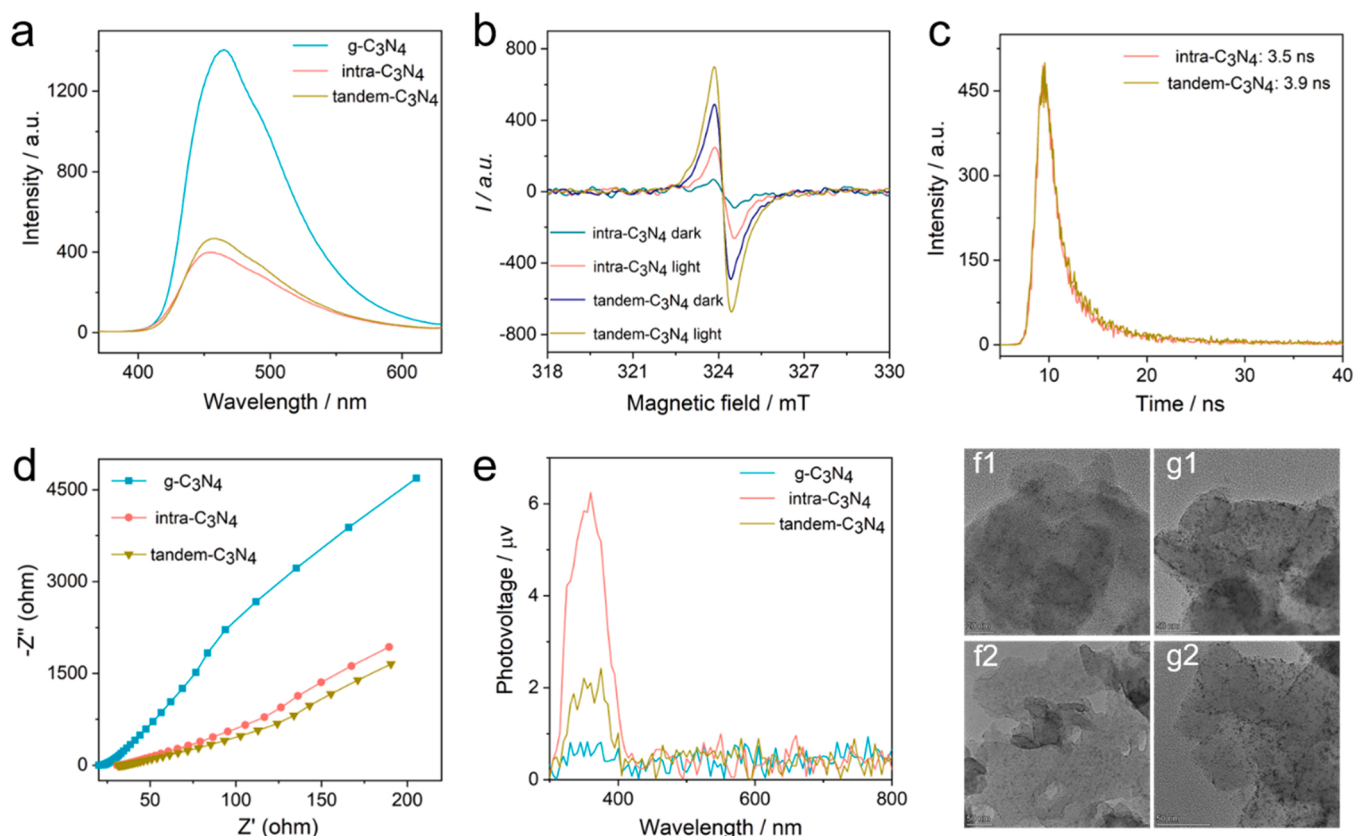


Fig. 4. Charge dynamics for different types of carbon nitride photocatalysts. (a) Separation of charge carriers investigated by a steady-state fluorescence spectrometer. (b) Excitation of charge carriers revealed by in situ light irradiation EPR spectra. (c) Lifetime of photoexcited electrons measured by a transient state fluorescence spectrometer. (d) Movement of hot carriers tested by EIS spectra. (e) Direction of movement of hot carriers determined by surface photovoltage spectra. (f-g) Accumulation of photo-excited hot electrons in intra-C₃N₄ and tandem-C₃N₄ reflected from the amount and size of photo deposited Pt nanoparticles.

assessed. All the three samples show mesoporous nanostructures, which are proven by the same type of IV isotherm with H3 hysteresis in the nitrogen adsorption-desorption isotherms (Fig. S15a). The surface areas of intra-C₃N₄ and tandem-C₃N₄ samples slightly dropped compared with that of g-C₃N₄ (Table S5). The pore size distribution of all catalysts is also similar (Fig. S15b). We also measured the contact angles of the prepared samples with water (Fig. 5c). The samples exhibited good hydrophilicity and the contact angles of intra-C₃N₄ and tandem-C₃N₄ turned slightly larger than that of g-C₃N₄. A larger contact angle would prejudice the mass transfer in photocatalytic water splitting process. Zeta potential of all the prepared samples was collected to clarify the surface charge of homojunctions (Fig. 5d). All of them exhibited negative surface potential, which is beneficial for H⁺ adsorption. Compared with g-C₃N₄, the surface charge of intra-C₃N₄ and tandem-C₃N₄ turned less negative, ascribing to the creations of cyano groups and C=C bonding, respectively.

The photocatalytic performances of these three catalysts were evaluated in water splitting reaction to green hydrogen (Fig. 5e). Pristine g-C₃N₄ exhibits a low hydrogen evolution rate of 129.5 μmol/h/g, attributing to the weak light absorption and sluggish charge carriers. While a slight improvement on hydrogen evolution rate to 231.5 μmol/h/g was achieved after the formation of intralayer carbon nitride homojunction in intra-C₃N₄. A remarkable enhancement on hydrogen production was realized on the integrated three-dimensional homojunction of tandem-C₃N₄, with a H₂ production rate of 815 μmol/h/g, which is 6.3 or 3.5 folds higher than those of g-C₃N₄ and intra-C₃N₄, respectively. The performance outperforms reported carbon nitride based photocatalysts (Table S6), indicating the significance of a tandem electric field in tandem-C₃N₄. Moreover, the special structure of tandem-C₃N₄ exhibited an excellent photostability, without an obvious decay in

hydrogen evolution rate after 4 cycles (Fig. S16) [46]. Besides, photocurrent measurements further verified the photocatalytic performance in water splitting reaction (Fig. 5f). Compared with g-C₃N₄, a slight and a sharp increase of the photocurrents can be observed on intra-C₃N₄ and tandem-C₃N₄, respectively. The trend is consistent with that of photocatalytic activity, proving the remarkably enhanced photocatalytic activity after assembling the series-directed IEF in tandem-C₃N₄.

We summarized the physicochemical, optical and electrochemical properties of the different samples in Table 1 to clarify the contributing factors in intra-C₃N₄ and tandem-C₃N₄ to the improved photocatalytic performances. We cannot see much improvements on mass transfer and light harvesting after the fabrication of lateral IEF and tandem IEF in intra-C₃N₄ and tandem-C₃N₄. These two factors on the enhanced photocatalytic hydrogen evolution are thus excluded. Therefore, the enhanced photocatalytic activity in water splitting reaction is attributed to the modification of charge dynamics. Compared with g-C₃N₄, it can be clearly inferred that the sharply improved charge dynamics (including separation and mobility) of intra-C₃N₄ by the lateral driving force contributes to the increased photocatalytic hydrogen evolution rate. However, compared with intra-C₃N₄, we fail to see a further enhancement on the separation and movement of charge carriers after the formation of series-directed IEF in tandem-C₃N₄. But, more hot electrons can be detected on the surface of tandem-C₃N₄ under light irradiation. Therefore, it can be concluded that the vertical IEF in the tandem-C₃N₄ mainly dominates the orientated assembly of photo-generated hot electrons on the surface of the tandem-C₃N₄, which is much beneficial for hydrogen production.

To clearly elucidate the contributions of lateral and vertical IEFs in the tandem-C₃N₄ to the enhanced photocatalytic performances, we calculated the electrostatic potentials and charge density difference to

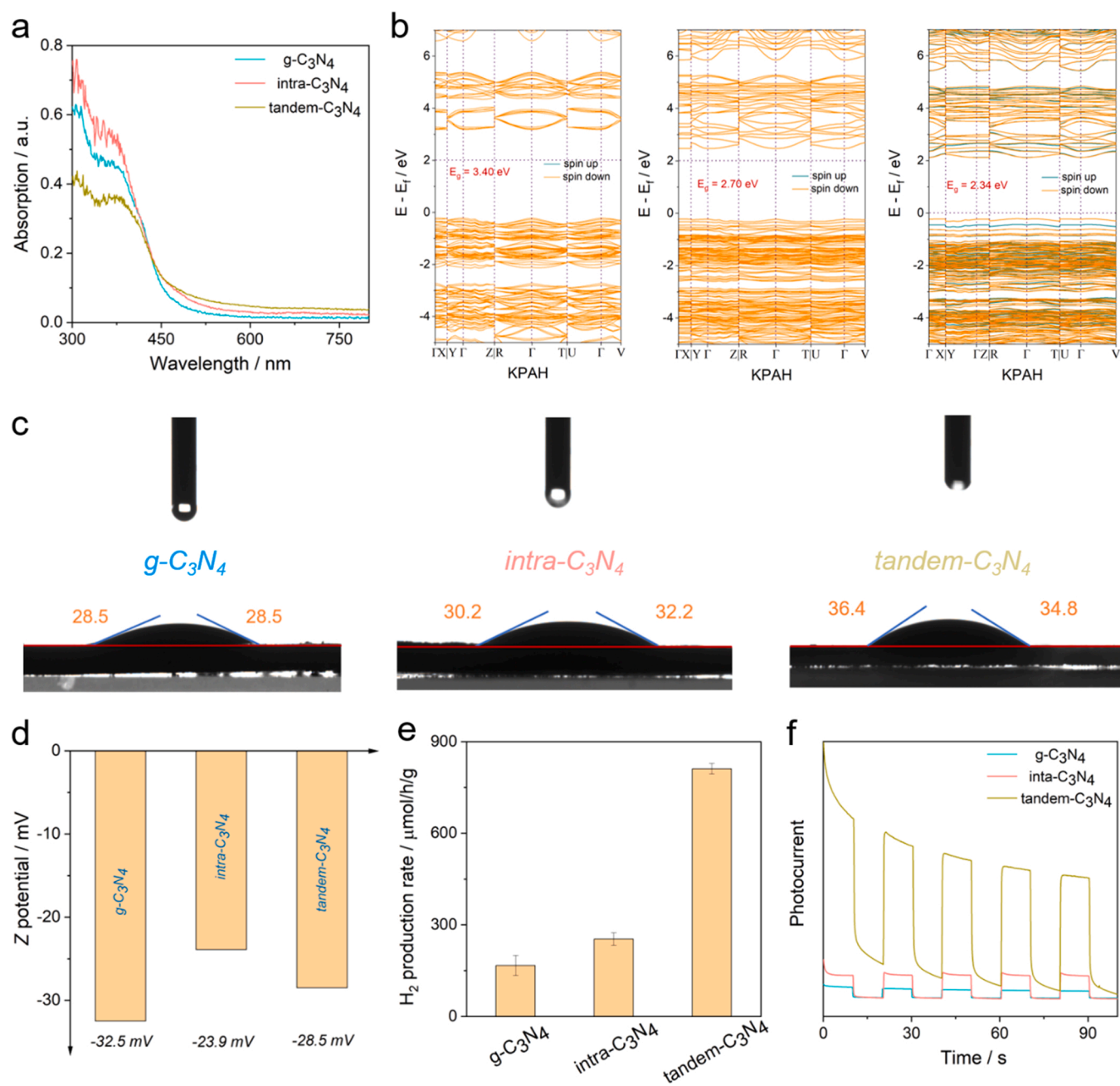


Fig. 5. Physicochemical properties and photocatalytic performances of different samples. (a) UV-Vis spectra. (b) Calculated bandgap energies of different samples by DFT simulation. (c) Contact angles. (d) Zeta potentials. (e) Photocatalytic performances in hydrogen evolution from water. (f) Photocurrent tests for different types of carbon nitride homojunction.

Table 1

Physicochemical, optical and electrochemical properties of different samples in the three typical processes of photocatalysis.

Sample	Mass transfer		Light harvesting	Charge dynamics			
	Contact angle	BET		PL	EPR	Lifetime	EIS
g-C ₃ N ₄	28.6°	8.2 m ² /g	2.66 eV	high intensity	low		high
intra-C ₃ N ₄	31.2°	6.2 m ² /g	2.62 eV	low intensity	almost the same concentration	3.5 ns	low
tandem-C ₃ N ₄	35.6°	6.7 m ² /g	2.56 eV			3.9 ns	

quantify the resistance and IEF force, respectively, on photo-excited hot electrons in the three samples (Fig. 6a-f). The interlayer electrostatic potentials in the three samples are much higher than that within in-plane (Fig. 6g-h). The higher interlayer energy barrier compels photo-induced charge carriers to prefer moving along carbon nitride in-plane

to traversing through the interlayer. As such, in-plane charge transport dominates the overall charge dynamics in carbon nitride materials [33].

For g-C₃N₄, the electrostatic potentials within the in-plane and between the interlayer are all maximum, while its lateral and vertical electron transferring amounts are all minimum among the three

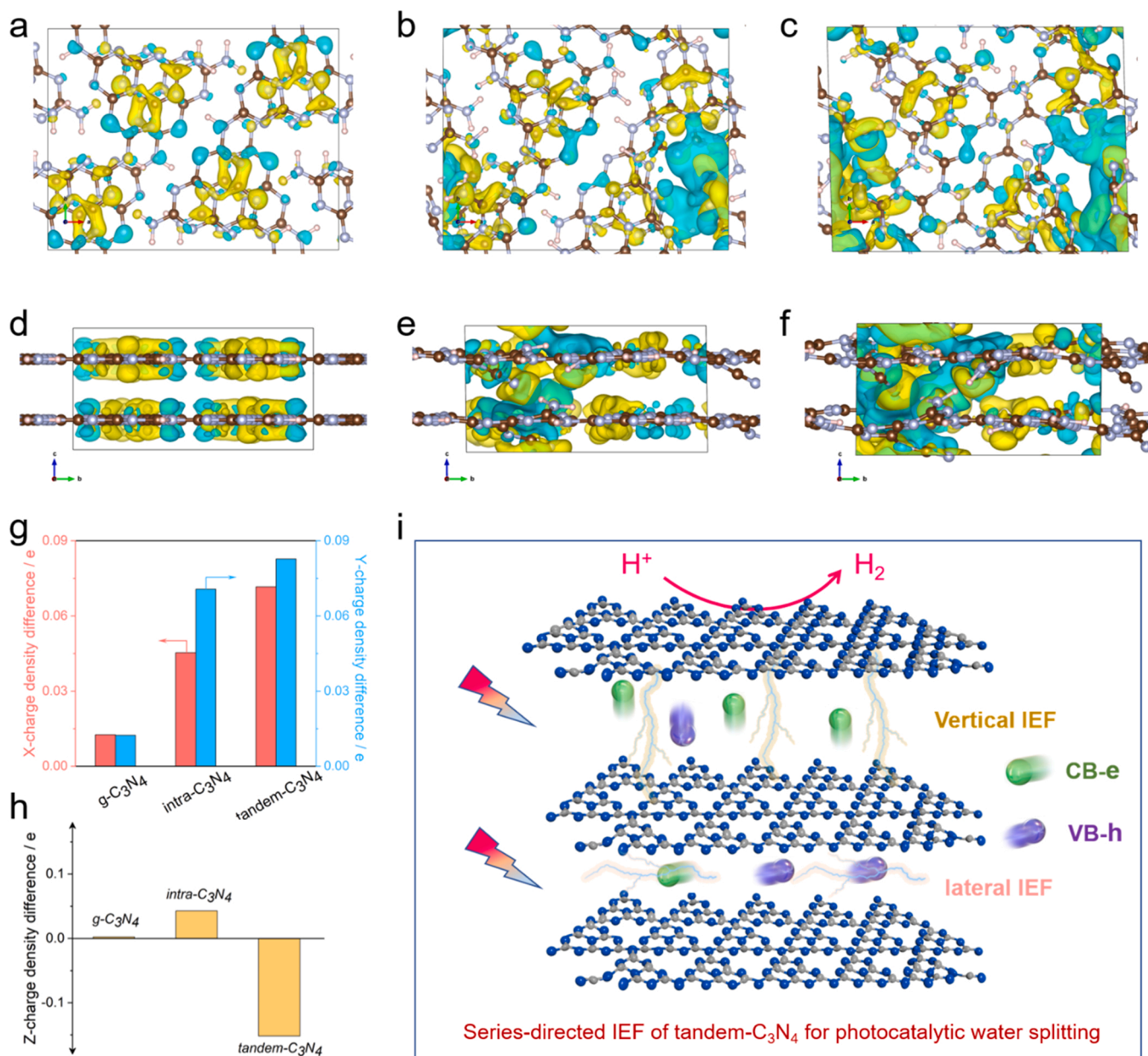


Fig. 6. Contributions of lateral and vertical IEF to photocatalysis. Charge density difference for in-plane of (a) g-C₃N₄, (b) intra-C₃N₄ and (c) tandem-C₃N₄. Charge density difference for interlayer of (d) g-C₃N₄, (e) intra-C₃N₄ and (f) tandem-C₃N₄. Quantitative results are shown in (g) in-plane and (h) interlayer. (i) Reaction mechanism of series-directed IEFs in tandem-C₃N₄ for photocatalytic water splitting.

samples. This means that the highest energy barriers and lowest IEF forces among the three samples exist along the in-plane and interlayer of g-C₃N₄. Therefore, the resultant sluggish charge dynamics finally leads to a low photocatalytic hydrogen production rate in g-C₃N₄.

By contrast, the lateral resistance in intra-C₃N₄ experiences a significant decrease, and the lateral IEF force is enlarged. As thus, the pockets of charge carriers along the in-plane of intra-C₃N₄ are quickly isolated and a dramatic enhancement on the overall charge dynamics is acquired in intra-C₃N₄. In the meantime, the interlayer traversing resistance of intra-C₃N₄ decreased and the vertical driving force on hot electrons of intra-C₃N₄ increased, indicating that the amount of charge carriers crossing layers is increased. However, the longitudinal movement of hot electrons directs from the surface of intra-C₃N₄ to the bulk, resulting in a longer diffusion path for the hot electrons before they involved into hydrogen reduction process [46]. The long diffusion path of hot electrons would easily lead to the decay of the hot electrons and

the very limited enhancement of intra-C₃N₄ in photocatalytic hydrogen reduction reaction on the surface [14].

After the fabrication of series-directed IEF in tandem-C₃N₄, the lateral electrostatic potentials and IEF force are not further increased as the structure of lateral homojunction in tandem-C₃N₄ is the same as intra-C₃N₄. So, compared with intra-C₃N₄, we cannot see a further enhancement on the charge dynamics in tandem-C₃N₄. Conversely, a smaller vertical electrostatic potential and a larger vertical IEF can be seen after the creation of VDW homojunction on the foundation of intra-C₃N₄. Meanwhile, the vertical IEF in tandem-C₃N₄ directs from the top layers to the lower layers. More energetic hot electrons would transfer across a short diffusion pathway (shallow surface layers of tandem-C₃N₄), accumulate on the surface of tandem-C₃N₄ and participate into hydrogen reduction, resulting in a much higher H₂ production. Therefore, tandem-C₃N₄ is integrated by an intralayer homojunction and a VDW homojunction, inducing a lateral IEF and a vertical IEF,

respectively, for a series-directed IEF (Fig. 6i). A lateral IEF contributes to a highly uneven orbital distributions and promotes overall charge dynamics within tandem-C₃N₄ in plane, while a vertical electric field in the VDW homojunction dominates less on the improvement of charge dynamics but can drive more hot electrons to traverse a short diffusion pathway to the catalyst surface. Compared with the performance enhancement from lateral IEF boosted charge dynamics, a higher surface electron concentration by vertical IEF plays a determining role in the performance enhancement of tandem-C₃N₄.

4. Conclusions

We have developed a strategy and employed different techniques to break the intralayer and interlayer symmetries in pristine carbon nitride for integration of a lateral carbon nitride homojunction with a vertical VDW carbon nitride homojunction into a tandem-C₃N₄. Theoretical calculations revealed a lateral S-scheme and a vertical S-scheme transfer of photo-excited charge carriers in the intralayer and VDW homojunctions, respectively, realizing a three-dimensional modulation of charge separation and directed movement of photoelectrons. Experiments and DFT calculations collectively confirm that the lateral driving force in intralayer homojunction accelerates the separation and movement of charge carriers, while the additional vertical driving force in VDW homojunction enables more hot electrons to accumulate on the surface of the photocatalyst for reduction reaction. The vertical electric field plays the dominant role in the enhancement of photocatalytic hydrogen production. This work discloses the contributions of lateral and vertical electric fields to photocatalytic activities and blazes a trail to design and synthesize effective photocatalysts for clean hydrogen production and other photocatalytic reactions.

CRedit authorship contribution statement

Jinqiang Zhang: Conceptualization, Methodology, Data curation, Writing – original draft. **Xiaojie Tan:** Software, Investigation. **Lei Shi:** Data curation. **Haijun Chen:** Resources, Funding acquisition, Supervision. **Yazi Liu:** Conceptualization, Resources. **Shuaijun Wang:** Methodology. **Xiaoguang Duan:** Methodology. **Mingbo Wu:** Resources, Conceptualization. **Hongqi Sun:** Funding acquisition, Data curation, Supervision. **Shaobin Wang:** Project administration, Funding acquisition, Writing – review & editing, Supervision.

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.

Data availability

Data will be made available on request.

Acknowledgements

The author (H. Sun) would like to thank the support from ECU Vice-Chancellor's Professorial Research Fellowship. This work is also partially supported by the Australian Research Council (DP170104264 and DP190103548). The support from the National Natural Science Foundation of China (51676096) is acknowledged.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.apcatb.2023.122781](https://doi.org/10.1016/j.apcatb.2023.122781).

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