Near-Field Drives Long-Lived Shallow Trapping of Polymeric C₃N₄ for Efficient Photocatalytic Hydrogen Evolution

Wenchao Wang, Xueqin Bai, Qing Ci, Lili Du,* Xingang Ren,* and David Lee Phillips*

Undesired photoelectronic dormancy through active species decay is adverse to photoactivity enhancement. An insufficient extrinsic driving force leads to ultrafast deep charge trapping and photoactive species depopulation in carbon nitride (g-C₃N₄). Excitation of shallow trapping in g-C₃N₄ with long-lived excited states opens up the possibility of pursuing high-efficiency photocatalysis. Herein, a near-field-assisted model is constructed consisting of an In₂O₃-cube/g-C₃N₄ heterojunction associated with ultrafast photodynamic coupling. This In₂O₃-cube-induced near-field assistance system provides catalytic “hot areas”, efficiently enhances the lifetimes of excited states and shallow trapping in g-C₃N₄ and this favors an increased active species density. Optical simulations combined with time-resolved transient absorption spectroscopy shows there is a built-in charge transfer and the active species lifetimes are longer in the In₂O₃-cube/g-C₃N₄ hybrid. Besides these properties, the estimated overpotential and interfacial kinetics of the In₂O₃-cube/g-C₃N₄ hybrid co-promotes the liquid phase reaction and also helps in boosting the photocatalytic performance. The photocatalytic results exhibit a tremendous improvement (34-fold) for visible-light-driven hydrogen production. Near-field-assisted long-lived active species and the influences of trap states is a novel finding for enhancing (g-C₃N₄)-based photocatalytic performance.

1. Introduction

Semiconductor-mediated artificial photosynthetic hydrogen generation from abundant water has been extensively surveyed to address meeting energy demand.[3] Traditionally, semiconductor-based photocatalysts suffer from two main issues in photocatalysis: 1) ultrafast charge carrier recombination rates and 2) low photon absorption efficiency.[2] An ingenious and successful strategy to accelerate charge carriers transfer rates was done by employing co-catalysts, as electron acceptors, mostly noble metals (Pt, Au, Ag, and Pd).[3] From an eco-friendly and economic viewpoint, 2D conjugated polymer graphitic carbon nitride (g-C₃N₄) has attracted considerable interest in visible-light-driven renewable energy production and environmental remediation since 2008.[3] The distinguishable function of multiple trap states of g-C₃N₄ to photocatalytic performance has been studied.[3] Generally, the insufficient extrinsic driving force leads to significant ultrafast deep charge trapping in g-C₃N₄, followed by the depopulation of a substantial amount of the photoactive species. Accelerating the free charge collection from the excited states (ES) and the shallow trap states (STS) plays an important role in photoactivity enhancement. Namely, the photoinduced free electrons can easily cool down and drop to deep trap states (DTS) that inevitably quench the photocatalytic proton reduction which presents a negative influence on solar-driven photo(electro)catalysis.[3] Hence, many strategies have been reported (such as employing vacancy engineering, using Z-scheme heterojunctions, and heteroatom doping) to tune photoelectron trapping by optimizing their internal photophysical behavior.[3] Recently, Tang et al. reported that N-defects associated with electron trap states can transform n-type g-C₃N₄ to photocatalytic performance. The TMDs have been made to link photocatalytic activity with the intrinsic and elusive trap states, but the understanding of the photocatalytic mechanism(s) is still not clear enough. Therefore, an in-depth investigation is urgently needed. To our knowledge, near-field assistance (NFA) to produce long-lived active species and influence the trap states’ behavior is a novel mechanism for enhancing (g-C₃N₄)-based photocatalytic performance by producing more photoactive species and catalytically relevant “hot sites”.

Transition metal-based oxides, phosphides, and sulfides have been regarded as economical alternatives to Pt-, Au-based photocatalysts for solar/electro-driven water-splitting.[9] Indium oxide (In₂O₃) with an indirect band gap of 2.8 eV and
excellent conductivity has been shown to be a high-efficiency co-catalyst for promoting photogenerated charge carriers’ separation/transfer with superior photoactivity. A lot of attention has been attracted to In$_2$O$_3$ and related composites in photocatalysis.[10] Zhao et al. demonstrated that a novel N-doped carbon-coated CuO-In$_2$O$_3$ p–n heterojunction could significantly reduce the Gibbs free energy of the intermediate adsorbed H*.[11] The special role of the In$_2$O$_3$-induced field enhancement effect promotes charge transfer occurrence and reduces the work function of the carbon nanotube.[12] Therefore, In$_2$O$_3$ can be one of the most attractive semiconductors for field emission because of its relatively low electron affinity and sputter resistance.[13] Searching for an effective In$_2$O$_3$-induced NFA strategy in the artificial photosynthetic energy conversion is very important.

In this work, an In$_2$O$_3$-cube decorated polymeric ultrathin g-C$_3$N$_4$ (PUCN) photocatalyst is engineered by a direct solvothermal method. The synergistic effect of NFA and ultrafast photodynamic coupling explicitly boost the high-frequency occurrence of the long-lived shallow trapping and excited states in PUCN. By taking the In$_2$O$_3$-cube/PUCN system as a prototypical model, we propose that size-dependent electromagnetic field distribution helps to minimize electron trapping into DTS and thus greatly improves photoactivity. Finite-difference time-domain (FDTD) simulations combined with femtosecond/nanosecond transient absorption spectroscopy (fs/ns-TAS) measurements help to determine a clearer picture of the photophysical process and how NFA influences these at the microscopic level. The expansion of shallow trapping (175.0–210.0 ps) and a half-cut lifetime of deep trapping (73.2–85.2 ns) play important roles in the observed photocatalytic enhancement. A detailed photoelectrochemical analysis demonstrates there is a high photocurrent density and a low overpotential for the In$_2$O$_3$-cube/PUCN system toward eliminating reaction rate limiting in the liquid phase which helps lead to superior photocatalytic water splitting. The over 34-fold hydrogen evolution reaction (HER) enhancement observed is much more accessible for the development of systems that may be able to meet industrial requirements in the future. This work reveals and highlights an ingenious synergism engineering strategy between NFA and the ultrafast internal kinetics that favors and maximizes photoactivity for solar-to-hydrogen production.

2. Results and Discussion

2.1. Materials Characterizations

A facile solvothermal method is demonstrated step wisely in Figure 1a for the synthesis of the In$_2$O$_3$-cube/PUCN composites. First, the commercial dicyandiamide was employed as the C, N-precursor to fabricate the polymeric bulk g-C$_3$N$_4$ (PBCN) through high-temperature self-assembly. And then, a certain amount of InCl$_3$, 4H$_2$O and as-prepared PBCN are mixed and suspended in water under vigorous sonication, followed by the hydrothermal treatment. The morphology was detected by field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM), respectively. As shown in Figure 1b, PBCN exhibits a multilayer and wrinkle shape after molecular self-assembly of dicyandiamide. Importantly, compared with PBCN, the hydrothermal exfoliation resulted in a thin and loose shape for the PUCN system as presented in Figure 1c. Notably, Figure 1e shows the In$_2$O$_3$-cube is well dispersed on the surface of PUCN. The pure In$_2$O$_3$-cube was prepared without the addition of PUCN. Figure 1d reveals the cubic shape of In$_2$O$_3$ with a diameter of ≈200 nm. Similarly, the TEM images further demonstrate the complex structure of PBCN (Figure 1f) and a clean and transparent surface of PUCN (Figure 1g), respectively. Moreover, the N$_2$ adsorption/desorption isotherms exhibited a smaller surface area (20.7 cm$^2$ g$^{-1}$), pore volume (0.21 cc g$^{-1}$), and size (3.53 nm) for PBCN than that for PUCN (Figure S4 and Table S1, Supporting Information), suggesting the successful exfoliation of ultrathin carbon nitride. However, owing to the smallest BET surface area of the In$_2$O$_3$-cube (15.22 cm$^3$ g$^{-1}$), 5.0 wt% In$_2$O$_3$-cube/PUCN composite showed a slight decline (33.47 cm$^3$ g$^{-1}$). As shown in Figure 1h,i, PUCN is thoroughly surrounded by the uniformly crystallized In$_2$O$_3$-cubes with a smaller size (≈20–100 nm), corresponding to the confined growth of In$_2$O$_3$ by PUCN. As expected, the TEM image of the pure In$_2$O$_3$-cube further confirms the cubic shape and longer diameter than that of the In$_2$O$_3$-cubes in the 5.0 wt% In$_2$O$_3$-cube/PUCN composite (Figure 1j,k).

FESEM and TEM images of all of the as-synthesized photocatalysts imply that there is a linear increase of the edge length (EL, ≈25–230 nm) from 1.0 to 20.0 wt% (Figures S5 and S7, Supporting Information). From the TEM image of the 5.0% In$_2$O$_3$-cube/PUCN, the intimately interface between PUCN and the In$_2$O$_3$-cubes could be observed as shown in Figure 2a. More importantly, the adjacent lattice fingers of the In$_2$O$_3$-cubes could be recorded as ≈0.29 and 0.41 nm from the high-resolution TEM analysis analysis (Figure 2b) and may be assigned to the (222) (200) and (211) facets of the In$_2$O$_3$ phase, respectively. Figure 2c presents the selected area electron diffraction (SAED) results and illustrates two diffraction short arcs which could be indexed to the (200) and (211) facets of the In$_2$O$_3$ phase, respectively. Figure 2d presents the selected area electron diffraction (SAED) results and illustrates two diffraction short arcs which could be indexed to the (200) and (211) facets of the In$_2$O$_3$ phase, respectively. The energy dispersive X-ray (EDX) characterization was carried out to investigate the elemental composition of the 5.0% In$_2$O$_3$-cube/PUCN hybrid, as shown in Figure 2e. The homogeneous distribution of the individual elements (C, N, In, and O) indicates that the uniform dispersion of In$_2$O$_3$-cubes on the PUCN surface. Also, the dense response of C, N, and the cube-like profile of the In, O elements indicate a layer and cubic structure for PUCN and In$_2$O$_3$, respectively. The crystallinity and phase structures of PUCN, In$_2$O$_3$-cube, 5.0% In$_2$O$_3$-cube/PUCN, 20.0% In$_2$O$_3$-cube/PUCN were all investigated by X-ray diffraction (XRD) measurements (Figure 2e). The two 2θ peaks around 13.1° and 27.3° are indexed to the characteristic g-C$_3$N$_4$ peaks (shown by the triangles in the figure) which are ascribed to the intralayer tri-s-triazine (100) and periodic stacking (002).[13] The blue profile of the XRD results indicates that the six 2θ peaks (shown by the asterisks in the figure) match well with the cubic In$_2$O$_3$ (JCPDS PDF 89–4595) and this is in agreement with the (211), (222), (411), (431), (440), and (611) crystal planes of cubic In$_2$O$_3$.[14] Figure S6 shows a slight shift of the periodic stacking (002) to a smaller 2θ degree, suggesting there is an increasing disturbance and a looser packing of the graphitic-like structure caused by the In$_2$O$_3$-cubes.[17] The UV–vis diffuse reflectance spectra (DRS) of
PUCN and 5.0 wt% In$_2$O$_3$-cube/PUCN are given in Figure S8a, Supporting Information. Compared with PUCN, the 5.0 wt% In$_2$O$_3$-cube/PUCN system shows a slight extension in the visible light area ($\lambda \geq 400$ nm). Due to the formation of robust heterojunctions, a clear blue-shift of the Tauc plot of $(\alpha h\nu)^{1/2}$ is observed and the calculated bandgap energies ($E_g$) are 2.95, and 2.87 eV for PUCN and 5.0 wt% In$_2$O$_3$-cube/PUCN, respectively (Figure S8b, Supporting Information).

X-ray photoelectron spectroscopy (XPS) was carried out to further identify the chemical composition and electronic structures (Figure 2g–k). As shown in Figure 2g, PUCN mainly presents C, N, and a small amount of O, respectively. Importantly, the full survey XPS spectra of the 5.0 wt% In$_2$O$_3$-cube/PUCN system demonstrates the presence of C, N, In, and O, which can be assigned to the successful anchoring of the In$_2$O$_3$-cubes on the PUCN surface. In the high-resolution C 1s spectra (Figure 2h), the two predominant peaks at about 285.1 and 288.1 eV are ascribed to the sp2 hybridized carbon in the s-triazine ring (N–C=N) and the C–C skeleton.[18] Both the N 1s spectrum of PUCN and the 5.0 wt% In$_2$O$_3$-cube/PUCN system have three typical peaks around 398.7, 399.8, and 400.9 eV that can be assigned to the pyridinic N (N–C=N), pyrrolic N (C–N–C), and graphitic N (N–C$_3$) structures respectively (Figure 2i).[19] The binding energies of In 3d centered at 445.4 and 453.0 eV (Figure 2j) agree well with the In$^{3+}$ of In$_2$O$_3$ nanocrystals although these energy values are somewhat higher than those of previous reports.[20] Also, the O 1s peaks at 530.7, 531.5, and 532.3 eV can be indexed to the lattice oxygen (O$^{2-}$), oxygen-deficient, and oxygen species (O$^-$, or O$^{2-}$) in In$_2$O$_3$ (Figure 2k).[21] Compared with the pure In$_2$O$_3$, a slight blue binding energy shift ($\Delta E = 0.3$ eV) is observed at both of the In 3d (445.1 and 452.7 eV) and O 1s (530.4, 531.2, and 532.0 eV) regions in the In$_2$O$_3$-cube/PUCN hybrid system which reveals the presence of intimated electronic interactions between g-C$_3$N$_4$ and In$_2$O$_3$. This robust junction can be regarded as the built-in charge and energy transfer channel for boosting photocatalytic performance. Figure 2f illustrates the FT-IR spectra of PUCN, In$_2$O$_3$-cubes, and In$_2$O$_3$-cube/PUCN composites, respectively. Compared to PUCN, both of the In$_2$O$_3$-cube/PUCN samples exhibit an apparent peak around 500 cm$^{-1}$ that can be assigned to In-O vibrations.[22] The stretching modes (1200–1700 cm$^{-1}$) of CN heterocycles are also observed which contains characteristic absorption peaks of the triazine unit.[23]
2.2. Photocatalytic Performance Associated with FDTD Simulation

The photocatalytic water splitting performance of the catalysts were probed under visible light excitation (λ ≥ 400 nm) by using triethanolamine (TEOA) as the sacrificial agent. Figure 3a shows the H₂ generation rate of PUCN, In₂O₃-cubes, and In₂O₃-cube/PUCN samples, respectively. Compared to the In₂O₃-cube/PUCN system, the pristine PUCN displays extremely low photocatalytic activity under visible-light exposure (only 55.42 μmol h⁻¹ g⁻¹). As expected, the H₂ evolution reaction (HER) is enormously...
improved after In$_2$O$_3$-cube decoration and the maximal rate can be as high as 1917 µmol h$^{-1}$ g$^{-1}$ in the 5.0 wt% In$_2$O$_3$-cube/PUCN system which is up to 34 times greater than that of PUCN. With respect to the tiny difference in the UV–vis DRS results (Figure S8, Supporting Information), the HER improvement appears not to be mainly caused by photon absorption. Steady-state photoluminescence spectroscopy was used to gain insights into the internal photo-physical and chemical behavior (Figure 3c). For PUCN and 5.0 wt% In$_2$O$_3$-cube/PUCN, the signal around 445 nm can be ascribed to the photoinduced emission. Generally, the ultrafast decay of the excited states demonstrates that there is a short-lived active charge with inevitable emission which is adverse to photocatalytic performance. Notably, the 5.0 wt% In$_2$O$_3$-cube/PUCN system shows a great inhibition of the excited states decay suggesting there is a high density of active species and effective interfacial charge transfer in this system. No appreciable H$_2$ production from the pristine In$_2$O$_3$-cubes was observed under visible light irradiation ($\lambda \geq 400$ nm) and this may be due to the low quantum yield and the negative effect of their big size (few catalytic sites and small surface area, etc.). The control experiment explicitly illustrates that the positive influence of the hydrothermal time (~5–20 h) for the H$_2$ production observed (Figure S9a, Supporting Information). In contrast, the photoactivity decreases from 1917 to 973 µmol h$^{-1}$ g$^{-1}$ when further hydrothermal time is used up to 30 h. We propose that the size effect of the In$_2$O$_3$-cubes plays a significant role in the photoactivity enhancement due to the lower efficiency of the charge separation, the presence of fewer catalytic sites, and a weaker near field (Figure 3d–h).

To further examine the NFA of the In$_2$O$_3$-cubes, the electromagnetic field distributions of various sized In$_2$O$_3$-cubes were simulated by using the FDTD method (Figure 3d–h). The 400 nm laser is simplified by using a plane wave along the z-axis which irradiates vertically to the x–y plane of the islands in our model. The simulation results demonstrate the occurrence of the intense electromagnetic field at the nearby In$_2$O$_3$-cubes. The highly localized electromagnetic field focused around the tip regions (e.g., the “hot spots”) of the In$_2$O$_3$-cubes in the PUCN substrate thereby result in the enhancement of the light–matter interaction. The promotion of the local electromagnetic field density appears to originate from the locally accumulated free photoelectron around the tips of the cubes to provide robust photocatalytic sites. Consistent with the photoactivities measurements, the In$_2$O$_3$-cubes exhibit an enhancement of the electromagnetic field with different cube sizes under perpendicular polarization that favors strengthening the free photoelectron density and enhancing the built-in charge transfer. This size effect has a significant influence on the electromagnetic field distribution, near-field enhancement ($|\mathbf{E}|/|\mathbf{E}_0|$), and also the photocatalytic performance improvement; the electromagnetic field intensity grows with increasing edge length (EL) from 25 to 60 nm, followed by a decline in the 120 and 250 nm samples (Figure 3d–h), in agreement with the observed photoactivities. Moreover, compared with other samples, the EL-60 nm sample shows more active “hot edges” with higher active surface area (Figure 3f), offering an idea of the extrinsic driving force to speed up the free-electron generation and immigration. In summary, the strongest “hot spots/edges”, and the biggest
active surface area co-determine the strongest light–matter interaction and the highest photocatalytic performance. To better clarify the significant role of Pt nanoparticles (NPs) in photocatalytic reduction reaction, the near-field distribution of Pt NPs and Pt NPs/In$_2$O$_3$-cube are simulated by using FDTD method. Compared to Pt NPs and In$_2$O$_3$-cube, Pt NPs/In$_2$O$_3$-cube hybrid demonstrates an apparent enhancement of near-field intensity range in the tip and edge area, respectively, as shown in Figure S13, Supporting Information. Pt NPs not only act as an important role in near-field enhancement, but also for accelerating electron transfer and enhancing the efficiency of proton reduction. The photostability of PUCN and the 5.0 wt% In$_2$O$_3$-cube/PUCN system were investigated under visible light irradiation (λ ≥ 400 nm). As displayed in Figure 3b, both samples revealed a stable linear increase at every cycle period, and the performance of the 5.0 wt% In$_2$O$_3$-cube/system gradually declines and remains 65% after five cycles within a 15 h period corresponding to the consumption of TEOA (sacrificial agent). To further monitor the photoactivity recovery, 2.0 mL fresh TEOA was added into the bath solution at the beginning of the sixth run (Figure 3b). The rising hydrogen evolution suggests that there is high photostability of the In$_2$O$_3$-cube/PUCN system with the continuous function of the near-field. On the other hand, Figure S10, Supporting information displays the morphology of the 5.0 wt% In$_2$O$_3$-cube/PUCN system after the photostability measurements. Cubic In$_2$O$_3$ and ultrathin g-C$_3$N$_4$ are observed, demonstrating the stable nanostructures of this photocatalyst. The excellent catalytic activity and stability provide a unique chance for potential development to help meet highly efficient industrial demands. To verify the influence of the various sacrificial agents on the photocatalytic H$_2$ evolution reaction, the photocatalytic performance of the 5.0 wt% In$_2$O$_3$-cube/PUCN sample was carried out in ascorbic acid, methanol, and Na$_2$S/Na$_2$SO$_3$ aqueous solution, respectively (Figure S9b, Supporting Information). The highest HER was obtained using the TEOA as an electron donor. Additionally, the HER performance of different g-C$_3$N$_4$-based photocatalysts are summarized as listed in Table S2, Supporting Information. The In$_2$O$_3$-cube/PUCN system displays the highest photocatalytic activity compared to other reported similar (g-C$_3$N$_4$)-based photocatalysts. The photocatalytic hydrogen evolution performance and apparent quantum yield (AQY) of photocatalysts were detected under specific visible light wavelength (λ = 420 nm), as summarized in Table S3, Supporting Information. 5.0 wt% In$_2$O$_3$-cube/PUCN (Pt NPs as co-catalyst) exhibits a higher AQY (7.73%) than that of Pt NPs/PUCN (1.07%) at the same condition. In addition, due to the restricted excitation efficiency of In$_2$O$_3$, no appreciable gas production from the Pt NPs/In$_2$O$_3$-cube sample under 420 nm irradiation.

2.3. Photoelectrochemical Measurements

The solar-driven interfacial electrochemical properties were investigated by using a simple photoelectrochemical cell (Figure 4a). As shown in Figure 4b, the results for the 5.0 wt% In$_2$O$_3$-cube/PUCN system implies a rapid and continuous photoresponse with a photogenerated current density (ΔI) of 0.68 µA cm$^{-2}$ at about a 0.5 V bias (vs SCE) upon each repeated 20 s on–off cycle under visible light irradiation (λ ≥ 400 nm).
The extremely high photocurrent density observed compared to those of PUCN and the In$_2$O$_3$-cubes separately illustrates the effective inhibition of the charge carriers recombination caused by the NFA effect. The charge transmission efficiency and the water-splitting kinetics of PUCN, In$_2$O$_3$-cube, and the 5.0 wt% In$_2$O$_3$-cube/PUCN system photoanodes were evaluated by electrochemical impedance spectroscopy (EIS) and polarization curves, respectively (Figure 4c,d). In general, the smaller diameters of the Nyquist plots usually imply there is a lower charge-transfer resistance in the bath solution. Figure 4c shows the smallest semicircle of the Nyquist plots in the 5.0 wt% In$_2$O$_3$-cube/PUCN system than those of the pure PUCN and In$_2$O$_3$-cubes separately, indicating the efficient charge transfer kinetics and conductivity that favor photogenerated electron–hole pairs separation and the superior photocatalytic performance.[27] The polarization profiles were gained from LSV measurements under dark and visible light exposure (Figure 4d). It is notable that compared to the results for PUCN and In$_2$O$_3$-cubes separately, the highest photocurrent density was found in the 5.0 wt% In$_2$O$_3$-cube/PUCN hybrid system that supplies a strong driving force and kinetics for photocatalytic water splitting. For instance, due to the influence of the NFA effect, the 5.0 wt% In$_2$O$_3$-cube/PUCN system shows improved performance compared with the PUCN and In$_2$O$_3$-cubes separately under visible light excitation with the overpotential at 0.2 mA cm$^{-2}$ decreasing to 1275 mV for the In$_2$O$_3$-cubes and to 1248 mV for PUCN but to 1147 mV for the 5.0 wt% In$_2$O$_3$-cube/PUCN system. Additionally, all of these photoanodes exhibit a higher overpotential in the dark (Figure 4e). By plotting the overpotential ($\eta$) against log current (log J), the reaction kinetic of HER can be estimated. Tafel plots illustrate Tafel slopes of 37.1, 82.9, and 43.5 mV dec$^{-1}$ for the In$_2$O$_3$-cubes, PUCN, and the 5.0 wt% In$_2$O$_3$-cube/PUCN system, respectively. The overpotential ($\eta$, mV) is the significant factor for evaluating the degree of difficulty for water splitting. As shown in Figure 4f, the 5.0 wt% In$_2$O$_3$-cube/PUCN system displays a clear decay in the overpotential values at current densities of 200 and 300 mA cm$^{-2}$. The smallest $\eta$ and the fastest internal kinetics of the 5.0 wt% In$_2$O$_3$-cube/PUCN system co-determine the highest photocatalytic HER performance.[28]

To further evaluate the flat band potential and the carrier density of the samples, the Mott–Schottky plot was analyzed by fitting the $x$-axis intercept of the linear section (Figure S11, Supporting Information). The $E_{FB}$ values of the n-type PUCN, the In$_2$O$_3$-cubes, and the 5.0 wt% In$_2$O$_3$-cube/PUCN system were measured to be $-1.23$, $-0.64$, and $-1.16$ V versus SCE, assigning them to $-0.99$, $-0.40$, and $-0.92$ V versus NHE. The conduction band (CB) of the n-type semiconductor is about $-0.1$ to $-0.3$ eV (0.2 eV is set in this work) higher than $E_{FB}$.[29] Therefore, the CB of the pristine PUCN, the In$_2$O$_3$-cubes, and the 5.0 wt% In$_2$O$_3$-cube/PUCN hybrid are about $-0.79$, $-0.20$, and $-0.72$ eV. The $N_D$ values of PUCN and 5.0 wt% In$_2$O$_3$-cube/PUCN are calculated to be $2.14 \times 10^{20}$ and $3.63 \times 10^{20}$ cm$^{-3}$. The higher $N_D$ value of the 5.0 wt% In$_2$O$_3$-cube/PUCN system suggests that the faster carrier immigration kinetics and the higher free photoelectron density of the 5.0 wt% In$_2$O$_3$-cube/PUCN system favor the photocatalytic activity improvement under visible light irradiation. In$_2$O$_3$-cubes-induced NFA greatly enhanced the charge carrier density and separation. In summary, the synergistic effect between the electronic energy levels and the highly localized “hot spots” of the In$_2$O$_3$-cubes maximizes the transmission efficiency of the active free electrons.

### 2.4. Ultrafast Time-Resolved Spectroscopy

However, even though the theoretical calculation and electrochemical characterization results demonstrated that the efficient charge carriers transfer correlates with the high performance of the photoactivity in the 5.0 wt% In$_2$O$_3$-cube/PUCN hybrid, it is still necessary to figure out more details of the photocatalytic mechanism by using a more straightforward observation method. As shown in Figure 5, femtosecond time-resolved spectroscopy methods (like fs-TAS) can be used to study the intermediate species of PUCN and the 5.0 wt% In$_2$O$_3$-cube/PUCN system (excited at 400 nm; the time delays range from 500 fs to 2.5 ns in the data shown). Note that the fs-TAS features of the 5.0 wt% In$_2$O$_3$-cube/PUCN system mainly originate from the PUCN component, because no discernible peak for the In$_2$O$_3$-cubes was observed (Figure S12, Supporting Information). Besides, Figure S12b, Supporting Information implies the fs-TAS data of Pt NPs/In$_2$O$_3$-cube/PUCN, just as pure In$_2$O$_3$, no intermediate state was found in Pt NPs/In$_2$O$_3$-cube/PUCN system. The 3D contour plots and kinetics profiles of PUCN and the 5.0 wt% In$_2$O$_3$-cube/PUCN system are given in Figure 5. To date, both Schlenker and Luo reported that a deep understanding of the photoinduced intermediate species of g-C$_3$N$_4$ could be gained from fs-TAS measurements.[30] They ascribed the broad, negative profile (from 440 to 570 nm) to the ground state bleach (GSB). And, the broad, positive feature around 580–720 nm was attributed to an excited-state absorption (ESA). This positive absorption feature in the visible and near-infrared regions is primarily assigned to photogenerated electrons or holes or electron–hole pairs in the carbon nitride part of the system.[31] Compared to PUCN, the 5.0 wt% In$_2$O$_3$-cube/PUCN system shows a stronger and longer-lived absorption for its ESA.

To better understand the relationship between shallow and deep trapping, the kinetics at 670 nm was investigated in Figure 5c,d. The kinetics fitting results of PUCN are summarized in Table 1 and show two of the three time constants with $\tau_1 = 170$ ps, and $\tau_2 = 175$ ps, which are due to the recombination of the free photogenerated electrons and the holes as well as the shallow charge trapping. Usually, the recombination of the free electrons and the holes is too fast to transfer the photogenerated electrons. Therefore, the transferred photogenerated electrons could be subsequently trapped by the shallow state where they could possess high mobility and driving force for photocatalytic H$_2$ evolution.[32] The 5.0 wt% In$_2$O$_3$-cube/PUCN system shows longer-lived species than that of pristine PUCN after irradiation as listed in Table 1. The kinetics for the In$_2$O$_3$-cube/PUCN system could be fitted by three time constants with $\tau_1 = 30.9$ ps, and $\tau_2 = 210$ ps, and $\tau_3 > 3$ ns. As discussed before, the 30.9 and 210 ps could be assigned to the recombination of the free photogenerated electrons and the holes and the shallow trapping states (STS). The slower decay of $\tau_3$ (recombination...
process) increases the possibility of the active electrons utilization and transfer to other electron acceptors. Additionally, the stronger NFA effect around the In\(_2\)O\(_3\)-cube directly causes the long-lived shallow electron trapping in the 5.0 wt% In\(_2\)O\(_3\)-cube/PUCN hybrid to help deliver the active electrons and resulting in efficient photocatalytic H\(_2\) production performance. A long-lived intermediate (\(\tau > 3\) ns) is ascribed to the charge trapping into deep states which leads to low photoactivity. These deeply trapped electrons have a time scale of about (nano- to micro-seconds) which is beyond the time delay range used for the fs-TAS. The \(\tau^*\) of PUCN and 5.0 wt% In\(_2\)O\(_3\)-cube/PUCN are estimated as 163.3 and 192.8 ps. The higher lifetime of the active electrons implies a higher active photoelectron density that will favor the photoactivity improvement under visible light irradiation. Therefore, the pronounced NFA effect of the In\(_2\)O\(_3\)-cubes would essentially account for this slower decay dynamics.

To further investigate DTS, nanosecond transient absorption kinetic analysis (ns-TAS) was carried out as shown in Figure 5d. The faster decay (85.2 ns) of the 5.0 wt% In\(_2\)O\(_3\)-cube/PUCN system than that of PUCN (173.2 ns) demonstrates an efficient restraint for the deep trapping of the active electrons in g-C\(_3\)N\(_4\). As discussed before, Figure 6 visually displays the whole photocatalytic mechanism from excitation to recombination, followed by shallow and deep charge trapping. In summary, due to the In\(_2\)O\(_3\)-cubes-induced NFA effect, the high efficiency of the interfacial charge transfer and the inhibition of the deep electron trapping that is found in PUCN. Meanwhile, the long-lived shallow trapping and the slower decay of the recombination allow more active electrons to possess high mobility and driving force for photocatalytic HER.

### 3. Conclusion

In summary, a near-field-assisted model has been constructed using an In\(_2\)O\(_3\)-cube/PUCN heterojunction system that can produce some long-lived shallow electron trapping. Time-resolved transient absorption spectroscopy combined with optical simulation results gave a deeper understanding of the photophysical and photochemical processes involved in this new system. The NFA of the In\(_2\)O\(_3\)-cubes helps favor a higher free photoelectron density and a faster charge carriers’ separation. Importantly, the sufficient extrinsic driving force guarantees some internal active species production and utilization, followed by an

| Photocatalysts          | \(A_1\) [%] | \(\tau_1\) [ps] | \(A_2\) [%] | \(\tau_2\) [ps] | \(A_3\) [%] | \(\tau_3\) [ps] | \(\tau^*\) [ps] |
|-------------------------|-------------|-----------------|-------------|-----------------|-------------|-----------------|-----------------|
| PUCN                    | 33.4        | 17.0            | 40.4        | 175.0           | 26.2        | >3000           | 163.3           |
| 5.0 wt% In\(_2\)O\(_3\)-cube/PUCN | 29.3        | 30.9            | 40.7        | 210.0           | 30.0        | >3000           | 192.8           |

Table 1. Exponential function fitted parameters of absorption decay for PUCN and 5.0 wt% In\(_2\)O\(_3\)-cube/PUCN at 670 nm.
interfacial free-electron transfer. The kinetics analysis from the fs/ns-TAS results clearly illustrates that there are longer shallow electron trapping and shorter deep electron trapping processes in the In$_2$O$_3$-cube/PUCN heterojunction system than in pristine PUCN. Both processes allow more active electrons to participate in the photocatalytic reaction before recombination. We prepared an In$_2$O$_3$-cube/PUCN photocatalyst that shows a 34-times improvement of the photocatalytic HER performance compared to pristine PUCN. The proposed synergistic effect of photophysics and photochemistry is important for maximizing the photoactivity in solar-to-hydrogen evolution.

4. Experimental Section

**Synthesis of Polymeric Bulk g-C$_3$N$_4$:** Bulk carbon nitride was synthesized by a thermal condensation approach. Typically, 5 g of dicyandiamide (99.0%, Aladdin) was treated at 923 K, with a heating rate of 10 K min$^{-1}$. A PBCN was obtained in the form of yellow powder.

**Fabrication of In$_2$O$_3$-cube/Polymeric Ultrathin g-C$_3$N$_4$:** First, a certain amount of InCl$_3$·4H$_2$O ($\geq$99.0%, Macklin) and 0.1 g PBCN dissolved in 50 mL of deionized water at room temperature. Then, the mixture was exposed to ultrasound for 30 min. Subsequently, the suspension solution was transferred into a dried Teflon-lined autoclave and heated at 453 K for 20 h. The light yellow solid was collected by centrifugation and washed by H$_2$O and CH$_3$CH$_2$OH ($\geq$99.5%, Aladdin) several times, then dried at 323 K overnight. Specifically, by changing the added amount of InCl$_3$·4H$_2$O, In$_2$O$_3$ cubes and ultrathin g-C$_3$N$_4$ hybrids with different percentages of In$_2$O$_3$ cube were gained. The various wt% were investigated from 1.0 to 20.0 wt%. As a reference, the pure In$_2$O$_3$ cubes and PUCN samples were prepared by the same process without PBCN and InCl$_3$·4H$_2$O, respectively.

**Characterization:** XRD measurements were performed with a commercial instrument (Rigaku Smartlab with Cu K$_\alpha$ radiation) to obtain an analysis of the crystalline structure. FESEM was provided by model S-4800 Hitachi instrument and transmission electronic microscopy (TEM) images were achieved using Philips CM100 instruments. The UV–vis DRS were done by using a MC-2530 analyzer (BaSO$_4$ as a reference). N$_2$ adsorption-desorption experiments were carried out on a QDS-30 (QuantaChrome Instruments). Steady-state photoluminescence (PL) spectroscopy measurements were recorded by F-7000 Hitachi instrument. A Perkin-Elmer PHI 5000C instrument was employed to obtain XPS data. The Fourier transformation infrared (FT-IR) spectra were examined on an IRAffinity-1 spectrometer (Shimadzu).

**Photocatalytic H$_2$ evolution Performance:** Briefly, a 100 mL Pyrex flask was employed as the catalytic cell. And then, 10.0 mg photocatalyst was suspended into 50 mL TEOA (TEOA:H$_2$O = 1:9) and H$_2$PtCl$_6$·6H$_2$O (3.0 wt% Pt) solution. To ensure a nearly oxygen-free environment, the suspension was bubbled with Argon for 15 min before performing the photocatalytic reactions. The Xenon lamp light source (300 W, PerfectLight-SXE300) was equipped with a 400 nm cutoff filter and was positioned about 5.0 cm away from the catalytic cell (Figure S1, Supporting Information). The amount of generated hydrogen was detected by gas chromatography (GC-7800 BEIJINGPURIUI, China) instrument. The carrier gas used was argon.

**Photoelectrochemistry:** All of the electrochemical measurements were recorded using a commercial electrochemical station (CHI 760E, Chen Hua Instrument Co., Ltd., China). The Xenon lamp light source (300 W, PerfectLight-SXE300) in the visible region was obtained using a 400 nm cutoff filter, which was the same as used in the photoactivity test mentioned before. For the working electrode preparation, a photocatalyst (2.0 mg) and polyethylene glycol (100 mg) were mixed together, followed by spin coating onto a substrate (ITO glass) and heated at 473 K for 2 h. A suspension was obtained by mixing the as-synthesized material with ethanol. The counter electrode was the platinum foil and the reference electrode was the standard saturated calomel electrode (SCE). Na$_2$SO$_4$ (0.5 m) aqueous solution was used as the electrolyte. Different from photocatalytic activity measurement, none Pt nanoparticles were added in photoelectrochemical tests.

**Transient Absorption Spectroscopy Experiments:** fs-TAS measurements were collected with a femtosecond Ti/Sapphire regenerative amplifier laser system (Spitfire-Pro, Spectra-Physics Company), and an automated data acquisition transient absorption spectrometer (Ultrafast, Helios) was used to record transient absorption spectra of the photocatalysts.
The amplifier produced a 150 fs pulse at 800 nm (repetition rate at 1 kHz, average output energy was 2.5 W). In our experiments, the pump laser (400 nm) was obtained from the second harmonic generated from the 800 nm output from the Spitfire amplifier (~95.0% of the amplified output). The probe pulse (continuum white-light spectrum, 420 to 780 nm) was generated using the remaining 5.0% of the amplified 800 nm output, as shown in Figure S2, Supporting Information. Additionally, ns-TAS spectra were collected from a LP-920 laser system (Edinburgh Instruments). The Xenon lamp was the probe light source (450 W, model Xe900), which traversed the sample cell and the signal was recorded by an array detector (absorption mode) and a single detector (kinetic mode). The 355 nm pump laser pulse was generated by the third harmonic output of an Nd: YAG laser (Figure S3, Supporting Information). For the fs-TAS and the ns-TAS experiments, all of the as-prepared catalysts were dispersed in water. None Pt nanoparticles were added in transient absorption spectroscopy experiments.

Theoretical Simulations: The FDTD method was employed to study the electromagnetic field distributions. (FDTD Solutions 8.19.1584 Numerical Solutions, Inc.). In the simulations, a plane wave with a wavelength of 400 nm represents the laser source. The In$_2$O$_3$ cubes were simplified as a rectangle with edge lengths of 23, 40, 60, 120, and 250 nm, the substrate for the In$_2$O$_3$ cubes was PUCHN.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
Research data are not shared.

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