

Merging Single-Atom-Dispersed Iron and Graphitic Carbon Nitride to a Joint Electronic System for High-Efficiency Photocatalytic Hydrogen Evolution

Wenyao Zhang, Qiong Peng, Lingling Shi, Qiushi Yao, Xin Wang, Aiping Yu,* Zhongwei Chen,* and Yongsheng Fu*

Scalable and sustainable solar hydrogen production via photocatalytic water splitting requires extremely active and stable light-harvesting semiconductors to fulfill the stringent requirements of suitable energy band position and rapid interfacial charge transfer process. Motivated by this point, increasing attention has been given to the development of photocatalysts comprising intimately interfaced photoabsorbers and cocatalysts. Herein, a simple one-step approach is reported to fabricate a high-efficiency photocatalytic system, in which single-site dispersed iron atoms are rationally integrated on the intrinsic structure of the porous crimped graphitic carbon nitride $(g-C_3N_4)$ polymer. A detailed analysis of the formation process shows that a stable complex is generated by spontaneously coordinating dicyandiamidine nitrate with iron ions in isopropanol, thus leading to a relatively complicated polycondensation reaction upon thermal treatment. The correlation of experimental and computational results confirms that optimized electronic structures of Fe@g-C₃N₄ with an appropriate d-band position and negatively shifting Fermi level can be achieved, which effectively gains the reducibility of electrons and creates more active sites for the photocatalytic reactions. As a result, the $Fe@g-C_3N_4$ exhibits a highlighted intramolecular synergistic effect, performing greatly enhanced solar-photon-driven activities, including excellent photocatalytic hydrogen evolution rate (3390 μ mol h⁻¹ g⁻¹, λ > 420 nm) and a reliable apparent quantum efficiency value of 6.89% at 420 nm.

Dr. W. Zhang, Q. Peng, L. Shi, Prof. X. Wang, Prof. Y. Fu Key Laboratory for Soft Chemistry and Functional Materials of Ministry of Education Nanjing University of Science and Technology Nanjing 210094, China E-mail: fuyongsheng0925@163.com, fuyongsheng@njust.edu.cn Dr. W. Zhang, Prof. A. Yu, Prof. Z. Chen Waterloo Institute for Nanotechnology University of Waterloo Waterloo, ON N2L3G1, Canada E-mail: aipingyu@uwaterloo.ca; zhwchen@uwaterloo.ca Dr. Q. Yao Department of Physics Southern University of Science and Technology Shenzhen 518055, China The ORCID identification number(s) for the author(s) of this article

can be found under https://doi.org/10.1002/smll.201905166.

DOI: 10.1002/smll.201905166

1. Introduction

The search for appropriate semiconductor materials as photocatalysts toward the production of green hydrogen (H₂) fuel from water using renewable solar energy is considered as one of the most considerable missions of material science.^[1-3] An optimal material should fulfill a series of stringent requirements, including great light-harvesting (i) property, (ii) suitable energy band position for water dissociation, and (iii) highly prominent charge separation and transfer under illumination.^[4,5] Retrospecting the past 40 years, numerous novel functional materials including inorganic semiconductors and molecular assemblies have been designed and developed as photocatalysts for the driving of hydrogen production reaction under visible light. Since the first report in 2009,^[3] graphitic carbon nitride (g-C₃N₄) increasingly stands out as the most typical of polymeric semiconductors. Tremendous attention is received in virtue of their attractive abilities of absorbing multiple photons, suitable band gaps, rational polaron mobilities, and, of greatest importance, diverse synthetic modularities

for adjusting their optical and electronic properties.^[6–8] Unfortunately, pure g-C₃N₄, without optimization of its structure and properties, suffer from the low efficiency of coupling multiple single-photon absorptions with multiple redox reaction equivalent generation, and show negligible activity toward photocatalytic hydrogen production. A series of factors have been manifested to improve photocatalytic efficiency.^[9–15] Among them, exquisite synthetic control and exhaustive understanding in the aspects of g-C₃N₄'s optical band gaps and band edges, highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) energy levels, the offset of the H₂O/H₂ redox potential and LUMO level, as well as interfacial wettabilities are critical to developing highly effective and efficient photocatalysts.

To this end, enormous progress has been made by modifying g-C₃N₄ with processes such as morphology control, π -conjugated copolymerization, donor-acceptor incorporation, structural engineering, and heteroatoms doping. For instance, Guo et al.^[16] fabricated a phosphorus-doped hexagonal tubular g-C₃N₄ that presented a high photocatalytic hydrogen production rate. These unique tubular structures of g-C₃N₄ significantly enhance the light-scattering abilities and gain their active sites; moreover, the incorporation of phosphorus elements is capable of narrowing band gaps and increasing electric conductivities. Yu et al.^[9] reported a nitrogen-defective g-C₃N₄, which notably redshifts the absorption edge of g-C₃N₄. Depending on the introduced concentration of the nitrogen vacancies, the chemical composition, optical response, and photocatalytic properties could be optimized to some extent. Zhang et al.^[6] constructed the internal triazine-heptazine donor-acceptor heterostructures to tailor the structure of polymeric g-C₃N₄ and accelerate photocatalytic activity. Nonetheless, most of the pure g-C₃N₄ materials are still restricted by their moderate exciton splitting and slow surface redox reactions, because covalent g-C₃N₄, cognate to the other polymeric semiconductors usually possess high exciton binding energies and slow interfacial reaction kinetics.

Fabricating heterojunction has been witnessed to be an effective way of facilitating charge separation and surface redox reaction.^[17–19] A feasible method is considered the further introduction of cocatalysts. Transition metals and their compounds are used as the typical cocatalysts, which in principle provides a straightforward pathway to manipulate H⁺ reduction rate in the reaction solution owing to their strong electron capture ability.^[18,20-22] Meanwhile, the inherent periodic cavities and high level of nitrogen content in g-C₃N₄ give rise to the possibility of firmly anchoring and homogeneously distributing metal nanoparticles or even single-site metal atoms. Recently, single-site Pd atom has been successfully anchored and stabilized on mesoporous $g-C_3N_4$. It is found that the sp²-bonded nitrogen atoms at the cavity's edge, which act as the coordination sites for metal ions, induce effective polarized charges on the metal to further facilitate the surface redox reactions. These atoms also result in strong covalent metal-nitrogen bonds so as to prohibit metal drifting and aggregating.^[23,24] Although all these findings demonstrate that g-C₃N₄ could serve as an ideal single-site metal-atom host, the methods of metal introduction and the types and amounts of metal incorporated need to be fastidious depending on each case. Consequently, it is still a great challenge to derive synthesis-property relations for the improved development and design of single-atom-modified heterophotocatalysts.

In this work, we report a strategy for the simultaneous introduction of single-site iron atoms and functionalization of marginal amino groups into the g-C₃N₄ network, which induces a super high solar-photon-driven hydrogen production. A single molecular source of dicyandiamide was converted into dicyandiamidine nitrate under the assistance of nitrate acid, which was then spontaneously coordinated with iron ions to form a stable complex serving as the reactive comonomer. The strongly adaptive coordination environment of dicyandiamidine nitrate with iron ions leads to a relatively complicated polycondensation process. Here the porous crimple g-C₃N₄ rationally integrates with the highly dispersed single-site iron atoms (Fe@g-C₃N₄). Experiments and density function theory (DFT) calculations demonstrated that the Fe@g-C₃N₄ shows two unique and critical features for the photocatalytic hydrogen production, with respect to bulk g-C3N4 and other kinds of polymeric semiconductors. First, the iron atoms significantly optimized the electron/band structures of g-C₃N₄, resulting in extended light absorption ranges for effectively light harvesting, and upshifted conduction bands for strengthened reducibilities and increased separation efficiency toward photoexcited electron hole pairs. Second, and most importantly, g-C₃N₄ can influence the electronic structure of iron by shifting its d-orbital position toward the Fermi level; this not only provides far more accessible active sites for H₂ absorption, but also efficiently accelerates the interfacial charge transfer process. As a consequence, the Fe@g-C₃N₄ shows a highlighted intramolecular synergistic effect, performing greatly enhanced solar-photon-driven activities, including an excellent photocatalytic hydrogen production rate (3390 μ mol h⁻¹ g⁻¹, λ > 420 nm) and a reliable apparent quantum efficiency (AQE) value of 6.89% at 420 nm.

2. Results and Discussions

Evidences of the conversion of dicyandiamide into dicyandiamidine nitrate are first given by the Fourier-transform infrared (FT-IR) spectra and solid-state NMR spectra. As shown in Figure S1a, Supporting Information, the pure dicyandiamide $(C_2H_4N_4)$ possesses characteristic peaks centered at 2155 and 2203 cm⁻¹, attributed to the typical stretching vibrations of C≡N. After being processed with concentrated HNO₃ at 40 °C for 120 min, the absorption peaks of C≡N disappeared, while five new characteristic peaks raised: These changes correspond to O-H stretching vibrations (3444 cm) of HNO₃, C=O stretching vibrations (1726 cm) of primary amide (-CONH₂), N-O stretching vibrations of HNO₃ (1139 cm), and N-H wagging vibrations (703 cm) of -CONH2 respectively, as a result of the hydrolysis reaction of dicyandiamide to yield dicyandiamidine nitrate. NMR spectroscopy is conducted to further confirm the molecular structure of hydrolysate. The chemical shift at 6.6 ppm of dicyandiamide in Figure S1b, Supporting Information, is assigned to H in the amine group. For the hydrolysate, there are three distinct signals with the peak area of 1:4:2. The chemical shifts centered at 9.6 and 8.1 ppm correspond to the H in the HNO3 and amine group, respectively. The resonance at 7.2 ppm arises from the H in amide. On the basis of the above results of FT-IR and ¹H NMR spectra, it could be carefully concluded that the hydrolysate of dicyandiamide is dicyandiamidine nitrate under given experimental conditions.

The formation mechanism of single iron-embedded g- C_3N_4 composite was then studied via thermogravimetry-differential scanning calorimeter analysis (TG-DSC), FT-IR spectra, and X-ray diffraction (XRD) pattern. Four rapid mass losses can be observed in Figure S2a, Supporting Information, in the ranges of 200–250, 270–310, 380–430, and 470–560 °C along with four endothermic peaks located at 210, 300, 413, and 545 °C, respectively. This indicates that there are at least five reaction steps in the complicated formation process of Fe@g-C₃N₄. At the beginning, according to the template reaction as illustrated in **Figure 1**a(i), isopropanol was added to allow the coordination reactions of Fe²⁺ with dicyandiamidine nitrate. The preparation of the complex was done under nitrogen atmosphere in order to avoid the air oxidation of the complex. After being dried,

www.advancedsciencenews.com





Figure 1. a) Proposed reaction process for forming the catalyst. b) Proposed $Fe@g-C_3N_4$ structure and c) DFT calculated electronic properties of the $Fe@g-C_3N_4$. The red, blue, gray, and white spheres denote Fe, N, C, and H atoms, respectively.

the complex is quite stable to oxidation, in agreement with previous reports.^[25,26] Figure S2b, Supporting Information, shows the FT-IR spectra of dicyandiamidine nitrate at different calcination temperatures. It could be noticed that a new characteristic peak of the triazine ring located at 760 cm appeared in the temperature range of 200–250 °C, corresponding to the first step of mass loss, while the characteristic peaks of HNO₃ (O–H and N–O stretching vibrations) disappeared, indicative that HNO₃ removal and intermolecular cyclization reactions took place to produce 6-amino-1,3,5-triazine-2,4(1*H*,3*H*)-dione (reaction [ii] in Figure 1a). Meanwhile, the guanidine, as a by-product of the dicyandiamidine nitrate cyclization reaction, can be polymerized to form melamine by eliminating

NH₃ from adjacent amino groups in the temperature range of 270–310 °C (the second step of mass loss) as described in reaction (iii).^[27] It has been reported that melamine could interact with cyanuric acid via three hydrogen bonds to form perfect melamine-cyanuric acid supramolecular compounds.^[28,29] A similar result is observed in this study (reaction [iv] in Figure 1a): supramolecular compound with free NH₂ can be generated by using up to two hydrogen bonds between 6-amino-1,3,5-triazine-2,4(1*H*,3*H*)-dione and melamine in the temperature range of 300–400 °C. Moreover, XRD patterns of dicyandiamidine nitrate treated at 350 °C can further confirm the generation of supramolecular compounds (Figure S3, Supporting Information). The diffraction peaks at 10.66°,



Figure 2. a) Typical FE-SEM image, b,c) TEM image, d) HAADF-STEM of the Fe@g-C₃N₄ composite, e) STEM image of the Fe@g-C₃N₄ composite, and f) the corresponding elemental mapping of C, N, Fe, and O element.

18.13°, and 21.74° correspond to (100), (110), and (200) peaks of the supramolecular compound respectively, confirming the existence of in-plane repeating unit structure. The peak at 28.1° may be assigned to graphite-like (002) lattice planes.^[10,30] When the calcined temperature is raised over 400 °C, typical FT-IR stretching vibration modes and XRD diffraction patterns of g-C₃N₄ can be observed, demonstrating that the supramolecular compound together with the Fe complex is completely converted into the final iron-embedded g-C₃N₄. During the formation process, the Fe complex is able to participate in the formation of supramolecular, which played a crucial role in the engineering and construction of iron ions-modified precursors. The subsequent pyrolysis could achieve in-situ polymerization, where the confinement effect of robust coordinate trap bonds guarantees the atomic introduction of single-site iron atoms. XRD patterns, presented in Figure S4, Supporting Information, clearly demonstrated that iron ions are effectively embedded in the intrinsic structure of g-C₃N₄. By virtue of that, there is no signal associating with iron species, including iron, iron chlorides, iron nitrides, iron carbides, and iron oxides. Besides, the carbonyl and amino groups on the supramolecular compound can be decomposed to produce ammonia and hightemperature steam, thus producing resultant abundant bubbles that can be used as the porous templates, accounting for the porosity of Fe@g-C₃N₄ and large specific surface areas. Meanwhile, free amino groups on the supramolecular compound could result in the unique crimped structure of Fe@g-C₃N₄.

The electron and band structures of the Fe@g-C₃N₄ composite were first theoretically evaluated by DFT computation. Figure 1b shows the optimized geometry structure of Fe@g-C₃N₄. Although the band gap maybe is a little underestimated,^[31,32] this Fe@g-C₃N₄ presents such an idealized structure, which corresponds well with the following observation: an effectively

reduced bandgap for efficiently harvesting visible light, a flat band structure, and suitable LUMO energy levels for hydrogen evolution. Further examination of the d-band center based on the PDOS analysis was figured subsequently (Figure 1c), determining that of -1.94 eV for Fe@g-C₃N₄. Such a high d-band position leads to a d-center closer to the Fermi level, which is of electronic origin, therefore leading to a relatively enhanced reactivity.

Then we selected Fe@g-C₃N₄-1 composite, obtained by pyrolysis of 1 mg ferrous nitrate with 2 g supramolecular precursor, as a representative model to investigate their morphology and chemical composition in detail. As shown in Figure 2, the typical field emission scanning electron microscopy (FE-SEM) image of $Fe@g-C_3N_4-1$ reveals a porous crimped morphology with numerous ripples and wrinkles in the layers. This makes the resulting Fe@g-C3N4-1 possess a large specific surface area of 60.14 m² g⁻¹, with a porosity structure (average pore size of 9.16 nm and pore volume of 0.255 cm³ g⁻¹) (Figure S5, Supporting Information), which can provide rich absorption sites and a large catalytic interface. Moreover, the transmission electron microscope (TEM) imaging in Figure 2b has clearly demonstrated that the Fe@g-C₃N₄-1 is entirely composed of uniform ultrathin nanosheets, and the ordered parallel lattices with the inter-planar distance of 0.33 nm can be noticed in Figure 2c, in accordance with the XRD results. Importantly, no significant clusters or nanoparticles can be found. To elucidate the form of the Fe atoms, we also carried out aberration-corrected high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) measurements (Figure 2d) with sub-angstrom resolution. In comparison with that of C and N atoms, Fe atoms exhibit much higher electron density, so that in Figure 2d, the single-site Fe atoms can be easily recognized due to the highly intense and

www.advancedsciencenews.com

DVANCED



Figure 3. XPS analysis of the Fe@g-C₃N₄-1 architectures. a) The XPS survey spectrum of Fe@g-C₃N₄-1 and pure g-C₃N₄. High-resolution b) C 1s, c) N 1s, and d) Fe 2p XPS spectra of Fe@g-C₃N₄-1 and pure g-C₃N₄, respectively.

bright dots (highlighted with white circles). The phenomenon of only isolated bright dots observing indicates that iron species existed exclusively in the form of a single-atomic site. The corresponding energy dispersive X-ray (EDX) mapping analysis indicates that the signals of Fe, C, and N are completely superimposed on each other, at least on the nanoscale, suggesting that Fe might be boned with C or N. (Figure 2e,f).

Further structural information and detailed coordinate environment of the Fe@g-C3N4-1 architecture can be obtained by X-ray photoelectron spectroscopy (XPS). As presented in Figure 3a, the survey scan spectra of the Fe@g-C₃N₄-1 directly visualizes the coexistence of Fe, C, N, and O components without any other impurities. Additionally, the Fe, C, N, and O contents of Fe@g-C₃N₄-1 are determined to be 0.5, 45.9, 49.1, and 4.5 at%, respectively, consistent with the elemental mapping and EDX results. The high-resolution C 1s spectrum of Fe@g-C₃N₄-1 (Figure 3b) is resolved into two components at the binding energy of 284.6 and 288.1 eV, ascribing to C-C bond from adventitious hydrocarbon in the XPS instrument, and sp²-bonded C (N–C=N) in the g-C₃N₄ framework. An evident change in the main peak in C 1s is examined for Fe@g-C₃N₄-1 and pure g-C₃N₄. We attribute this shift to the incorporation of the iron species, adjusting the charge density difference of delocalized π electron on g-C₃N₄. The high-resolution N 1s spectrum of Fe@g-C₃N₄-1 (Figure 3c) validates the presence of three types of N functionalities in this complex. These include pyridinic N at 398.2 eV, pyrrolic N at 399.6 eV, and graphitic N at 400.8 eV. Importantly, in comparison with that of pure g-C₃N₄, all of these nitrogen signals in Fe@g-C₃N₄-1 negatively shift toward low binding energies. This phenomenon derives from the strong interactions between Fe and g-C₃N₄ support, where the nitrogen in tri-s-triazine hetero ring is able to donate their lone pair electrons to the more electrophilic iron neighbors, which results in the observation of spontaneous charge transfer, well consistent with the DFT computation results in Figure 1. In addition, the high-resolution Fe 2p spectrum of Fe 2p_{3/2} shows a distinctive peak for Fe²⁺ species (Figure 3d), as illustrated by the binding energy of 710.6 eV and the presence of a satellite peak, further confirming that the Fe²⁺ strongly coordinates with nitrogen atoms, in agreement with the formation scheme in Figure 1.

On the other hand, the optical and band structures of the Fe@g-C₃N₄-1 materials compared with pure g-C₃N₄ were analyzed via UV–vis absorbance spectra and XPS valence band spectra (VBXPS). A typical absorption behavior of graphitic carbon nitride can be observed in the spectra of Fe@g-C₃N₄-1 in **Figure 4**a, which suggests that the introduction of iron species does not change the basic 2D conjugated backbone structures of g-C₃N₄. For all the modified Fe@g-C₃N₄, the redshift of the absorption edges toward low energy can be noticed, and importantly, the more the iron incorporates, the lower the absorption edges are (Figure S6, Supporting Information). This phenomenon is derived from the alteration of the electronic band structure of g-C₃N₄ because of π -electron delocalization. The



www.small-journal.com



Figure 4. a) UV-vis absorbance spectra of pure $g-C_3N_4$ and $Fe@g-C_3N_4-1$. b) XPS valence band spectra of pure $g-C_3N_4$ and $Fe@g-C_3N_4-1$. c) HOMO and LUMO positions determined by UV-vis and VBXPS analysis. d) Time course of H_2 production from water with different catalysts under visible light irradiation. e) Cycling measurements of H_2 generation of $Fe@g-C_3N_4-1$. f) Wavelength-dependent AQY of H_2 evolution over $Fe@g-C_3N_4-1$ (right axis) and UV-vis light absorption spectra (left axis).

bandgap values of Fe@g-C₃N₄-1 deduced from Figure 4a were calculated to be 2.61 eV-narrower than that of pure g-C₃N₄ of 2.76 eV. Further alterations in the electronic properties are shown in VBXPS of both Fe@g-C₃N₄-1 and pure g-C₃N₄ (Figure 4b), where the valence band (VB) energy of Fe@g-C₃N₄-1 and pure g-C₃N₄ was calculated to be 1.8 and 2.2 eV, respectively. A combination of the VB energies with the bandgap values allows us to determine the energy levels of the corresponding HOMO and LUMO positions. As seen from Figure 4c, the conduction band (CB) energy for Fe@g-C₃N₄-1 and pure g-C₃N₄ are both negative to the reduction potential of a proton (thermodynamically at 0 eV), demonstrating that photogenerated electrons are able to meet the basic requirements for hydrogen production under illumination at an appropriate wavelength of visible light. Additionally, the CB energies are more negative than that of pure g-C₃N₄, thus leading to a stronger reducing capability which will be discussed in the following theoretical section.

To evaluate the photoactivities of the Fe@g-C₃N₄ catalysts in comparison with the bulk and pure g-C₃N₄, we first monitored their hydrogen production performance under visible light illumination (Figure 4d). The platinum was employed as cocatalyst and the reaction solution was water/triethanolamine (TEOA) solution. As presented, bulk g-C₃N₄ possesses an average hydrogen evolution rate of 9.3 µmol h⁻¹ and no hydrogen can be detected in the dark test. The pure g-C₃N₄ obtained by our supramolecular way exhibits an enhanced photocatalytic activity of 40.4 µmol h⁻¹, indicating that a porous crimped structure is beneficial for hydrogen evolution. Meanwhile, the incorporation of iron atoms further improves their photocatalytic

performances, especially for the Fe@g-C₃N₄-1 photocatalyst, which presents an optimal activity of 169.5 μ mol h⁻¹, giving a fourfold higher than that of pure g-C₃N₄ and 18-fold higher that of bulk g-C₃N₄. We attribute this enhancement to the promotion of interfacial charge carriers transport via the well established iron-g-C₃N₄ heterojunction. After that, the hydrogen evolution reaction processed a total of 16 h of reactions accompanying intermittent degassing at every 4 h (Figure 4e). It is found that a total amount of 2.1 mmol H₂ is collected upon the continuous reactions, and the activities show no conspicuous deterioration, suggestive of the reliable stability of Fe@g-C₃N₄-1 catalyst against photocorrosion. Figure 4f illuminates the wavelength dependence of the AQE values for hydrogen evolution of the Fe@g-C₃N₄-1 catalyst, evidencing the same tendency with the UV-vis absorbance spectra. The Fe@g-C₃N₄-1 catalyst shows extremely high AQE in a range of 400-450 nm. The AQE value at 420 nm is evaluated to be about 6.89%, which is extensively enhanced compared with the typical bulk g-C₃N₄.

This prominent activity of Fe@g-C₃N₄-1 originates mainly from its unique structural features as well as synergistic effects. First, the optimization of the band and electron structure of Fe@g-C₃N₄-1 significantly improves the efficiency toward anchoring, migration, and transport of the photogenerated charge carriers, that is considered as the key parameter in terms of determining the photocatalytic performance. This point was then studied by the room temperature photoluminescence (PL) spectra (**Figure 5**a). Upon excitation at 370 nm, the Fe@g-C₃N₄-1 originated a PL response in 400–550 nm, with the main emission peak centered at 445 nm, while it is www.advancedsciencenews.com

Ś

www.small-journal.com



Figure 5. a) Photoluminescence spectra (370 nm excitation at room temperature), b) the photoelectrochemical responses of bulk g-C₃N₄, pure g-C₃N₄, and Fe@g-C₃N₄-1 under visible light illumination. c) EPR spectra of pure g-C₃N₄ and Fe@g-C₃N₄-1. d) H₂ adsorption geometry on pure g-C₃N₄. e) H₂ adsorption geometry on Fe@g-C₃N₄-1. f) Schematic representation of the charge transfer mechanism on Fe@g-C₃N₄-1 system.

459 nm for pure g-C₃N₄, slightly blue-shifting by 14 nm. Furthermore, the PL intensities for Fe@g-C₃N₄-1 decreased almost half to that of pure g-C₃N₄, proving that the energetically unfavorable charge recombination is substantially inhibited, thus facilitating the charge separation. Further evidence to this point was obtained by electron paramagnetic resonance (EPR) spectra in Figure 5c. Taking pure g-C₃N₄ as a reference, it is evident that a strengthened EPR signal at g = 2.0031 observed in Fe@g-C₃N₄-1, attributing to the unpaired electrons on the carbon atoms in aromatic rings.^[33] The introduction of iron atoms is able to serve as the bridging sites, redistributing the electrons to the neighbor carbon atoms via the delocalized π -conjugated networks of polymeric carbon nitride.

Second, the interfacial charge transport process in Fe@g-C₃N₄-1 was greatly boosted due to the Fe atoms, which not only offers an instant transient light, but also guarantees a high transfer efficiency of the photoexcited electron hole pairs. Figure 5b shows a comparison of the photocurrent–time curves for bulk g-C₃N₄, pure g-C₃N₄, and Fe@g-C₃N₄-1 with typical on-off cycles under visible light illumination. A remarkably raised photocurrent response for Fe@g-C₃N₄-1 can be noted, which is nearly three times higher than that of the pure g-C₃N₄ and 30 times that of the bulk g-C₃N₄, strongly demonstrating the promotion of the mobility of the photoexcited charge carriers. Furthermore, the analysis of electrochemical impedance spectroscopy (EIS) suggests that the Fe@g-C₃N₄-1 exhibits a lower charge transfer resistance of 63.6 k Ω in contrast to that of pure g-C₃N₄ (69.8 k Ω) and bulk g-C₃N₄ (89.5 k Ω) (Figure S7, Table S2, Supporting Information). Such a phenomenon favors the transfer process of photoexcited electrons to the protons in the electrolyte, thus, in turn, accelerates the charge separation and increases the photocatalytic performance.

Third, the incorporation of iron atoms significantly strengthens the feasibility of H_2 activation, which greatly gains the accessible catalytically active sites for the photocatalytic reactions. Theoretical illustration in Figure 5d demonstrates weak adsorption of H_2 on pure g-C₃N₄, ruling out the possibilities of further activation. Significantly, after the introduction of the iron atoms, the coordinated metal site turns out to be the active center with a strong adsorption energy of 0.06 eV (Figure 5e), profiting from the availability of electrons spinning in *d*-orbital for being donated into the H–H antibonding, which potentially realizes the activation of H–H bond. The H₂ activation is the initial and one of the important processes during the photocatalytic H₂ production, that is, the Fe@g-C₃N₄-1 exhibits enough accessible and highly active catalytic performance.

On the basis of the above results mentioned in the preceding paragraph, a tentative mechanism for this photocatalytic system is proposed. As illustrated in Figure 5f, Fe@g-C₃N₄-1 possesses a typical Schottky contact between the signal-site iron atoms and g-C₃N₄, which generates a negative shift of the Fermi level of Fe till an equilibrium of Fe and g-C₃N₄ (work function: $\Phi_{Fe} = 4.5 \text{ eV}$, $\Phi_{g:C_3N_4} = 4.3 \text{ eV}$), suggesting an enhancement of catalytic activities of Fe@g-C₃N₄-1 compared with pure iron nanoparticles. Upon visible light illumination, electrons in the VB of

SCIENCE NEWS _____ www.advancedsciencenews.com

DVANCED

 $g-C_3N_4$ were excited to the CB, subsequently rapid transferring to the Fe atoms that possess strong abilities in storing electrons. With the continuous increase of electron density around Fe atoms, the Fermi level of Fe is further shifting negatively to be balanced with that of CB of $g-C_3N_4$, where electrons have extremely strengthened reducibilities.^[34] Subsequently, the captured electrons are then transferred to the catalyst/electrolyte interface to drive the hydrogen evolution reactions.

3. Conclusion

To summarize, the modification of carbon nitride structures by functionalizing with amino groups in the edges and atomically anchoring iron ions within the structure was developed. A detailed analysis of the formation process shows that a stable complex was achieved by spontaneously coordinating dicyandiamidine nitrate with iron ions, thus leading to a relatively complicated polycondensation to form the porous crimple microstructure of Fe@g-C₃N₄. The strongly adaptive coordination environment ensures the rational integration of g-C₂N₄ with the well-dispersed singlesite iron atoms. Theoretical evaluation and experimental validation identified that the introduction of single-site iron atoms on g-C₃N₄ is critical in optimizing the electron and band structures and accelerating the interfacial charge transfer processes. The negative shift of the Fermi level in Fe@g-C3N4 system caused by the induced charge transfer effects effectively gains the reducibility of electron and creates more active sites for the photocatalytic reactions. As a result, the Fe@g-C₃N₄ exhibits an excellent photocatalytic hydrogen production rate (3390 μ mol h⁻¹ g⁻¹, λ > 420 nm) and reliable AQE at a value of 6.89% at 420 nm.

Supporting Information

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

Acknowledgements

This work was supported by National Natural Science Foundation of China (Grant Nos. 51772156 and 51872144), Natural Science Foundation of Jiangsu Province (Grant Nos. BK20180019 and BK20171423), China Postdoctoral Science Foundation (No. 2018M640489), the Fundamental Research Funds for the Central Universities (Nos. 30917015102, 30918014103), PAPD of Jiangsu, the Natural Sciences and Engineering Research Council of Canada (NSERC), and the Ontario government for the Ontario Early Research Award Program.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

d-band position, graphitic carbon nitride, photocatalytic hydrogen evolution, single-atom catalysis, synergistic active centers

Received: September 10, 2019

- Revised: October 18, 2019
- Published online: November 14, 2019

- [1] J. Ran, G. Gao, F.-T. Li, T.-Y. Ma, A. Du, S.-Z. Qiao, Nat. Commun. 2017, 8, 13907.
- [2] A. Fujishima, K. Honda, Nature 1972, 238, 37.
- [3] X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen, M. Antonietti, *Nat. Mater.* 2009, *8*, 76.
- [4] G. Zhang, Z. A. Lan, X. Wang, Angew. Chem. Int. Ed. 2016, 55, 15712.
- [5] F. K. Kessler, Y. Zheng, D. Schwarz, C. Merschjann, W. Schnick, X. Wang, M. J. Bojdys, *Nat. Rev. Mater.* **2017**, *2*, 17030.
- [6] G. Zhang, L. Lin, G. Li, Y. Zhang, A. Savateev, X. Wang, M. Antonietti, Angew. Chem. Int. Ed. 2018, 57, 9372.
- [7] J. Xu, T. J. Brenner, L. Chabanne, D. Neher, M. Antonietti, M. Shalom, J. Am. Chem. Soc. 2014, 136, 13486.
- [8] M. Shalom, S. Gimenez, F. Schipper, I. Herraiz-Cardona, J. Bisquert, M. Antonietti, Angew. Chem. Int. Ed. 2014, 53, 3654.
- [9] H. Yu, R. Shi, Y. Zhao, T. Bian, Y. Zhao, C. Zhou, G. I. Waterhouse, L. Z. Wu, C. H. Tung, T. Zhang, *Adv. Mater.* 2017, *29*, 1605148.
- [10] S. Guo, Z. Deng, M. Li, B. Jiang, C. Tian, Q. Pan, H. Fu, Angew. Chem. Int. Ed. 2016, 55, 1830.
- [11] Q. Liang, Z. Li, Z. H. Huang, F. Kang, Q. H. Yang, Adv. Funct. Mater. 2015, 25, 6885.
- [12] H. Ou, L. Lin, Y. Zheng, P. Yang, Y. Fang, X. Wang, Adv. Mater. 2017, 29, 1700008.
- [13] Y. Kang, Y. Yang, L. C. Yin, X. Kang, L. Wang, G. Liu, H. M. Cheng, Adv. Mater. 2016, 28, 6471.
- [14] Y. Kang, Y. Yang, L. C. Yin, X. Kang, G. Liu, H. M. Cheng, Adv. Mater. 2015, 27, 4572.
- [15] G. Zhang, G. Li, Z. A. Lan, L. Lin, A. Savateev, T. Heil, S. Zafeiratos, X. Wang, M. Antonietti, Angew. Chem. Int. Ed. 2017, 56, 13445.
- [16] T. Y. Ma, J. Ran, S. Dai, M. Jaroniec, S. Z. Qiao, Angew. Chem. Int. Ed. 2015, 54, 4646.
- [17] M. Liu, Y. Chen, J. Su, J. Shi, X. Wang, L. Guo, Nat. Energy 2016, 1, 16151.
- [18] Y. H. Li, J. Xing, Z. J. Chen, Z. Li, F. Tian, L. R. Zheng, H. F. Wang, P. Hu, H. J. Zhao, H. G. Yang, *Nat. Commun.* **2013**, *4*, 2500.
- [19] S. S. K. Ma, T. Hisatomi, K. Maeda, Y. Moriya, K. Domen, J. Am. Chem. Soc. 2012, 134, 19993.
- [20] Q. Xiang, J. Yu, M. Jaroniec, J. Am. Chem. Soc. 2012, 134, 6575.
- [21] J. Ran, J. Zhang, J. Yu, M. Jaroniec, S. Z. Qiao, Chem. Soc. Rev. 2014, 43, 7787.
- [22] J. Yang, D. Wang, H. Han, C. Li, Acc. Chem. Res. 2013, 46, 1900.
- [23] Z. Chen, E. Vorobyeva, S. Mitchell, E. Fako, M. A. Ortuño, N. López, S. M. Collins, P. A. Midgley, S. Richard, G. Vilé, *Nat. Nanotechnol.* 2018, 13, 702.
- [24] G. Vilé, D. Albani, M. Nachtegaal, Z. Chen, D. Dontsova, M. Antonietti, N. López, J. Pérez-Ramírez, Angew. Chem. Int. Ed. 2015, 54, 11265.
- [25] A. Syamal, Z. Anorg. Allg. Chem. 1976, 419, 189.
- [26] R. Trimble, Anal. Chem. 1962, 34, 1633.
- [27] W. J. Ong, L. L. Tan, Y. H. Ng, S. T. Yong, S. P. Chai, Chem. Rev. 2016, 116, 7159.
- [28] Y.-S. Jun, E. Z. Lee, X. Wang, W. H. Hong, G. D. Stucky, A. Thomas, Adv. Funct. Mater. 2013, 23, 3661.
- [29] J. Sun, J. Xu, A. Grafmueller, X. Huang, C. Liedel, G. Algara-Siller, M. Willinger, C. Yang, Y. Fu, X. Wang, M. Shalom, *Appl. Catal. B* 2017, 205, 1.
- [30] Y. Guo, J. Li, Y. Yuan, L. Li, M. Zhang, C. Zhou, Z. Lin, Angew. Chem. Int. Ed. 2016, 55, 14693.
- [31] Q. Yao, Y. Liu, R. Lu, C. Xiao, K. Deng, E. Kan, RSC Adv. 2014, 4, 17478.
- [32] S. Lany, A. Zunger, Phys. Rev. B 2008, 78, 235104.
- [33] S. Cao, H. Chen, F. Jiang, X. Wang, Appl. Catal. B 2018, 224, 222.
- [34] Y. Fu, T. Huang, B. Jia, J. Zhu, X. Wang, Appl. Catal. B 2017, 202, 430.