Spatiotemporal Coupling Dual-photocatalytic Integration in Atomic- hybridized Co0.5Fe0.5In2S4 Nanoflowers for High Efficiency Nitrogen Reduction

Qifan Wu  
Nanjing University

Gang Zhou  
Nanjing University

Tao Li  
Hohai University

Jun Guo  
Nanjing University of Posts and Telecommunications

Lizhe Liu  
Nanjing University

Article

Keywords: Co0.5Fe0.5In2S4 ultrathin nanoflowers, hydrogen evolution reaction, N2 reduction reaction

DOI: https://doi.org/10.21203/rs.3.rs-41091/v1

License: This work is licensed under a Creative Commons Attribution 4.0 International License. Read Full License
Abstract

The photocatalytic reduction of N2 to NH3 under mild conditions using low-cost solar is an attractive alternative to replace the energy-intensive Haber-Bosh process, but which is typically hampered by poor binding of N2 to catalysts and high activation energy of intermediates. In particular time window, catalyst hydrogenation directly induced by photocatalytic water splitting can provide an alternation pathway to overcome limitations in conventional N2 reduction reaction (NRR). Herein, we propose a spatiotemporal coupling strategy in Co0.5Fe0.5In2S4 ultrathin nanoowers to integrate hydrogen evolution reaction (HER) and NRR together, in which the photo-excited carrier life time is intentionally extended to match six-electron NRR process; meanwhile hydrogen evolution rate is limited to generate a transient hydrogenation on catalytic surface for accelerating N2 adsorption and activation. This spatiotemporal coupling design can easily drive N2 to *N2H2 and far away from conventional stagewise activation of N≡N triplet bonds. As a result, the photocatalytic performance of N2 reduction is about 85.8 μmol g-1 h-1 without sacrificial agent. Our findings provide a new paradigm for integrating dual photocatalytic reduction, bringing a transient hydrogenation and free nitrogen directly to reactants without requiring N2 molecular adsorption to the catalyst.

Introduction

Different from industrial Haber-Bosh process requiring at high temperature (400-500 °C) and pressures (200-300 atm)\textsuperscript{1-3}, the photocatalytic nitrogen reduction reaction (NRR) is a sustainable approach that can produce ammonia from air and water when powered by renewable solar energy\textsuperscript{4,5}. Therefore, photocatalytic NRR method can overcome drawbacks of Haber-Bosh process, such as huge energy consumption, enormous greenhouse gas emissions, process complexity and extreme synthetic condition\textsuperscript{6-8}. From a reaction kinetic point of view, the formation of NH\textsubscript{3}, which requires six electrons, is more difficult than that the two-electron hydrogen evolution reaction (HER)\textsuperscript{9,10}. Consequently, a lot of semiconductor photocatalysts\textsuperscript{11-13} have been designed to regulate photoelectron kinetic process and rate-limiting step, but still suffer from low energy conversion efficiency and unsatisfactory ammonia yield.

Essentially, a typical photocatalytic reaction primarily depends on electron-hole separation, N\textsubscript{2} adsorption and activation at reactive sites\textsuperscript{14,15}. The first step is closely related to the reaction kinetics rate (in temporal dimension)\textsuperscript{16-18}, while two latter steps mainly depend the rate-limiting energy levels of the reactive intermediates (in spatial dimension)\textsuperscript{19,20}. In principle, the breakthrough in N\textsubscript{2} reduction efficiency should be simultaneously considered from the regulation of reaction pathway and the enhancement of carrier separation. Recently, some reports disclose that surface hydrogenation can drive NRR on catalysts with weak N\textsubscript{2}-binding strength at low potentials\textsuperscript{5,21}, lightening the idea of directly integrating NRR onto HER together. Supposing that the H*-covered active sites induced by HER enable N\textsubscript{2} to be activated and directly reduced into *N\textsubscript{2}H\textsubscript{2} to overcome relatively high energy barriers at N≡N triplet bond activation, we
will realize a dual photocatalytic integration strategy for steering the reaction kinetic pathway and boosting NH₃ production efficiency.

In order to realize this idea, the catalyst designs must be considered from temporal and spatial requirements simultaneously. (1) The catalyst’s HER activity is neither too high (H* converting H₂) nor too low (cannot generate H*), meanwhile the NRR activity should be as excellent as possible. (2) The photoexcited carrier life time should be long enough to satisfy the temporal requirement of relatively slow six-electron NRR reaction process. Therefore, it is better for designing atomic-hybridized catalysts, which not only provides a feasibility in steering reaction activity of NRR and HER in spatial dimensional but also benefits for implanting trapping sites to capture photoexcited electrons or holes, hence prolonging carrier life time. In other words, the dual-photocatalytic intermediates directly determine whether or how fast a given reaction pathway will occur.

Results

With conventional metal oxide or sulfide photocatalysts, the surface active site tends to bond weakly with adsorbed N₂ through hybridization between the 2p and 3d orbital (top panel of Fig. 1a), which leads to a series of reactive intermediates. However, compared with the highly stable N≡N triplet bonds, the relatively weak M-N bonds (where M represents the metal site) needs much more energy to satisfy NH₃ production. One can imagine that if N₂ could be simultaneously affected by metal sites and passivated H*, this would give rise to a more stable configuration of M-HN-NH-M intermediates and high NRR efficiency (middle panel of Fig. 1a), owing to integration reaction between surface hydrogenation in HER and N₂ activation in NRR. Interestingly, it becomes difficult once again to break N≡N triplet bond to form NH₃, supposing that passivated H* from HER is released as H₂ (bottom panel of Fig. 1a). Therefore, the rate-limiting activation energy barrier in NRR may be significantly decreased through a conversion in reaction pathway, after considering dual photocatalytic integration.

To better understand this fundamental mechanism, a crystal-field theory to describe the molecular orbital energy diagram is proposed in Fig. 1b. For transition metal catalysts, their reaction activity strongly depends on the combination of empty and occupied 3d orbitals. To realize the molecular chemisorption, the metal sites need to empty 3d orbitals to accept the lone-pair electrons of N₂. On the contrary, to enhance the activity of N-M bonds, the metal atoms should have separate 3d electrons that can donate into the antibonding orbital to weak the N≡N triplet bond. Generally speaking, “acceptance-donation” of electrons is the essential interaction between the metal site and N₂. When N₂ adsorbs onto the hydrogenated Fe sites, the relevant adsorbate molecules interact with vertically oriented e_g-like orbitals, which allows for stronger
overlap with t_{2g}-like states (right panel of Fig. 1b). Therefore, the hydrogenated Fe atom can serve as an active center for driving the “acceptance-donation” process, resulting in an efficient reduction of N\textsubscript{2}.

Co\textsubscript{0.5}Fe\textsubscript{0.5}In\textsubscript{2}S\textsubscript{4} is an earth-abundant and non-toxic quaternary sulfide\textsuperscript{27} that has desirable electron-hole separation and controllable catalytic activity in HER and NRR, which suggests it should be capable of integrating reaction pathway. After the analysis about electronic features and its chemical structure, we reasoned that it should be a promising candidate to integrate HER and NRR by manipulating catalytic activity of reactive site and life time of photo-generated carrier simultaneously. Therefore, we initially fabricated Co\textsubscript{0.5}Fe\textsubscript{0.5}In\textsubscript{2}S\textsubscript{4} ultrathin nanoflowers by a citric-assisted solvothermal procedure with cobaltous nitrate, iron 2,4-pentanedionate, indium chloride and thioacetamide as the Co, Fe, In and S sources, respectively. The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images in Fig. 2a display that the Co\textsubscript{0.5}Fe\textsubscript{0.5}In\textsubscript{2}S\textsubscript{4} nanoflowers are vertically aligned with three-dimensional porous textures, indicating distinguished capture of sunlight. The atomic force microscopy (AFM) in Fig. 2b discloses that the exfoliated self-assembly nanosheet is of 8 nm in thickness and 0.5 µm in width. The high-resolution TEM (HR-TEM) images in Fig. 2c and selected diffraction pattern in the inset confirm that the Co\textsubscript{0.5}Fe\textsubscript{0.5}In\textsubscript{2}S\textsubscript{4} nanoflowers have a typical polycrystalline structure, with a resolved 0.32 nm lattice fringe corresponding to (311) planes. The corresponding element mapping in bottom panel confirms the uniform distribution of Co, Fe, In and S elements, and their atomic ratio was found to 0.5:0.5:2.1:3.9 associated with energy-dispersive spectroscopy (Supplementary Fig. 1). As a comparison, the X-ray diffraction (XRD) patterns of ternary FeIn\textsubscript{2}S\textsubscript{4} and CoIn\textsubscript{2}S\textsubscript{4} sample are also provided, which matches well with JCPDS card No. 80–0609 and No.65-7271. Remarkably, the XRD pattern of Co\textsubscript{0.5}Fe\textsubscript{0.5}In\textsubscript{2}S\textsubscript{4} sample has similar fingerprint to cubic CoIn\textsubscript{2}S\textsubscript{4} phase, showing that expected Fe implantation cannot change the original crystal structure. The slight difference in XRD fingerprint can be attributed to the alloy-induced changes in geometrical structure factor.

X-ray absorption fine structure (XAFS) was conducted to investigate the atomic-hybridized influence towards the electronic structure. The energies of X-ray absorption near edge structure (XANES) for Fe K-edges and Co K-edges in CoIn\textsubscript{2}S\textsubscript{4}, FeIn\textsubscript{2}S\textsubscript{4}, Co\textsubscript{0.5}Fe\textsubscript{0.5}In\textsubscript{2}S\textsubscript{4} are positively shifted compared with those of Fe/Co foils (Fig. 3a and b), showing the oxidized states of Fe/Co. The XANES spectra of Co and Fe in Co\textsubscript{0.5}Fe\textsubscript{0.5}In\textsubscript{2}S\textsubscript{4} display similar patterns to CoIn\textsubscript{2}S\textsubscript{4} and FeIn\textsubscript{2}S\textsubscript{4}, but the peak intensities and positions are slightly changed due to the difference in radial charge distribution for Co-3\textit{d} and Fe-3\textit{d} atomic orbitals (Supplementary Fig. 2). Fourier transform analysis of the corresponding K-edge extended EXANES was then used to verify their distinct local structures. As displayed in Fig. 3c, the Fourier transform spectrum of FeIn\textsubscript{2}S\textsubscript{4} centred at 1.79 Å corresponds to the nearest Fe-S coordination, which also occurs at Co\textsubscript{0.5}Fe\textsubscript{0.5}In\textsubscript{2}S\textsubscript{4} sample. However, the Fe-S peak intensity obtained from Co\textsubscript{0.5}Fe\textsubscript{0.5}In\textsubscript{2}S\textsubscript{4} is weak and this peak position shifts to a large bond length (~ 1.81 Å). A similar change associated with the Co-S coordination is also observed in Fig. 3d. The aforementioned difference suggests that the Co-S and Fe-S shell in Co\textsubscript{0.5}Fe\textsubscript{0.5}In\textsubscript{2}S\textsubscript{4} is distorted comparing to pristine CoIn\textsubscript{2}S\textsubscript{4} and FeIn\textsubscript{2}S\textsubscript{4} and its structural homogeneity is changed by hybridization of atomic orbitals. Moreover, the curve fitting of coordination
environment was conducted using IFEFFIT software package to acquire the quantitative structural parameters\textsuperscript{28}, and the corresponding results (Supplementary Fig. 3) are listed in Supplementary Table 1. It was found that the coordination numbers of CoIn\textsubscript{2}S\textsubscript{4} (Co: 4.6 ± 0.7), FeIn\textsubscript{2}S\textsubscript{4} (Fe: 3.7 ± 0.5) and Co\textsubscript{0.5}Fe\textsubscript{0.5}In\textsubscript{2}S\textsubscript{4} (Co: 4.1 ± 0.5; Fe: 3.6 ± 0.7) are very similar, indicating that they have consistent space symmetry. Compared to Co\textsubscript{0.5}Fe\textsubscript{0.5}In\textsubscript{2}S\textsubscript{4}, the Fe-S bond length of FeIn\textsubscript{2}S\textsubscript{4} is reduced by 0.02 Å, while the Co-S bond length of CoIn\textsubscript{2}S\textsubscript{4} was increased by 0.02 Å. This indicates that the Fe and Co atoms are equivalently distributed in Co\textsubscript{0.5}Fe\textsubscript{0.5}In\textsubscript{2}S\textsubscript{4} structure. However, the electronegativity difference between Fe (1.83) and Co (1.88) make their chemical state display a discrepancy, due to different valence electron ability in transferring to surrounding sulfur site, which can be reflected by XPS analysis in Supplementary Fig. 4. As a result, the valence state of Fe and Co ion lineally depend on alloy compositions (Supplementary Fig. 2), implying that nonequilibrium charge site is fabricated to regulate photo-excited carrier life time. This is because that the carrier transfer on the catalyst surface strongly depends on atomic-hybridized-induced electrostatic potential difference\textsuperscript{29}.

As Co\textsubscript{0.5}Fe\textsubscript{0.5}In\textsubscript{2}S\textsubscript{4} surface shown in Fig. 3e, the first layer has a lower electrostatic potential than the second one due to the asymmetric charge density for Fe and Co site (as shown in the right panel), leading to an instinct dipole moment for generating a built-in electric field between two adjacent atomic layers (marked by Δδ). Interestingly, this electrostatic potential difference cannot occur at pristine CoIn\textsubscript{2}S\textsubscript{4} and FeIn\textsubscript{2}S\textsubscript{4} surface, showing that the electronic state can be regulated by Co-Fe alloy strategy. The electrostatic potential difference as a function of alloy composition in bottom of Fig. 3f disclose that alloys with 0.5:0.5 Fe/Co ratio display the optimal performance, which can be intuitively reflected by Bader charge analysis shown in the inset.

Subsequently, we experimentally confirm the atomic-hybridized contribution to extend carrier life time using a transient absorption technology. The orbital-resolved band of Co\textsubscript{0.5}Fe\textsubscript{0.5}In\textsubscript{2}S\textsubscript{4} in Fig. 4a displays an indirect semiconductor characteristic, similar with that of CoIn\textsubscript{2}S\textsubscript{4} and FeIn\textsubscript{2}S\textsubscript{4} in Supplementary Fig. 5. Interestingly, we find that the valence bands at G point are mainly contributed by Fe-\textit{d} orbitals, meanwhile the bands of Co-\textit{d} orbitals appear at deep level energy. This multi-level system provides a feasibility in regulating photo-excited carrier dynamics, as the discussion about electrostatic potential difference in Fig. 3e and f. In order to confirm this assertion, for a probe photon from 1.20 to 1.65 eV and a time delay of 0.00 to 2.00 ps, a three-dimensional picture of reflective transient absorption (TA) spectroscopic measurement with a pump fluence of 400 µJ/cm\textsuperscript{2} at 1.40 eV is conducted and shown in Fig. 4b. The most typical fingerprint in Co\textsubscript{0.5}Fe\textsubscript{0.5}In\textsubscript{2}S\textsubscript{4} is the strong negative TA within the first 500 fs, which is located around 1.42 eV. To better understand this physical origin, the TA dynamics for a time delay as long as 8.00 ps at 1.34, 1.36, 1.44 and 1.66 eV are acquired as a comparison in Fig. 4c. Noticeably, an oscillation appear at 1.44 eV, and the signal reverts to positive at 0.69 ps and then reach a positive maximum at 0.85 ps. It is interesting to note that the TA signals remain negative at 1.66 eV, meanwhile it keeps positive at 1.34 and 1.36 eV over the whole dynamics.
For better understanding, we aligned the total density of state (TDOS) of \( \text{Co}_{0.5}\text{Fe}_{0.5}\text{In}_{2}\text{S}_{4} \) with the electronic transitions disclosed by the TA spectra, as displayed in the left panel of Fig. 4d. The black open circle curve is a fit using multiple Gaussian functions, which are designated by the different shaded area and named as bands \( D_0, D_1, E_0, E_1 \), respectively. Associated band analysis in Fig. 4a, the ground-state bands only can be attributed to the band \( D_1 \) (Fe-3\text{d} at G point) instead of band \( D_0 \) that originates from Fe-3\text{d} orbital at L point. The lowest excited state is located at the lower edge of band \( E_0 \). This assignment can be confirmed by the optical transition moment \( \rho^2 \), in which the transition probability at G point from band \( D_1 \) to \( E_0 \) becomes dominant, as indicated by the bottom panel of Fig. 4a. Associated with these energy levels, we conclude the possible electronic transitions involved in the pump-probe process in the right panel of Fig. 4d. Therefore, the TA signal includes bleaching of the ground-state absorption at \( D_1 \), absorption by exactions at \( E_0 \), two-photon absorption (2PA) through absorbing one pump and one probe photon from the ground state \( D_1 \) and absorption by excitation at higher-lying excited state \( E_1 \). Then the oscillatory feature in the TA dynamics at 1.42 eV (Fig. 4e) can be explained due to existence of higher-lying \( E_1 \) state. This is because that bleaching of ground state absorption (negative signal) plays a decisive role in the TA dynamics at the arrival of the pump pulses, in which single-photon excitation (1PE) and two-photon excitation (2PE) pump the \( D_1 \) electron to populate \( E_1 \) and \( E_0 \), respectively. Subsequently, after considering the probe contribution, the exciton absorption at \( E_1 \) and \( E_0 \) state (allowed electronic transition in \( \text{I. and II. process} \) plays a dominant role, which leads to a positive TA signal. When this exciton absorption survives other competitive bleaching dynamics, the TA signal exhibit a turn from falling to rising dynamics at 0.44 ps and finally becomes positive signal at 0.69 ps. Because of the shorter life time of higher-lying metastable \( E_1 \) state, the long-lived bleaching dynamics dominate the electronic transition process again (\text{III.}), converging towards a negative TA signal after 1.87 ps.

The exciton behavior of \( E_1 \) also can be confirmed by the dynamics of pump fluence dependence, as shown in Fig. 4 f. For a delay of 1.10 ps, owing to the existence of metastable state \( E_1 \), the relative TA intensity is increased with third-order dependence on the pump fluence. This process includes exciton absorption at \( E_0 \) and \( E_1 \) state, which can be defined as \( \Delta I \propto A_1 I_p I_d - B_1 I_p^2 I_d - C_1 I_p I_d^2 \). Here \( I_p, I_d \) denote the intensities of pump and probe pulses. When higher-lying metastable state \( E_1 \) disappears at 2.80 ps, the relation between pump fluence and TA signal is changed as \( \Delta I \propto A_2 I_p I_d - B_2 I_p^2 I_d \). As a critical criterion, compared to \( \text{CoIn}_2\text{S}_4 \) and \( \text{FeIn}_2\text{S}_4 \), the \( \text{Co}_{0.5}\text{Fe}_{0.5}\text{In}_2\text{S}_4 \) sample in Supplementary Fig. 6 displays a typical three-stage evolution dynamic behavior and the photo-excited carrier life time is also obviously extended by atomic-hybridized-generated higher-lying metastable state.

The photocatalytic NRR performances of different samples were conducted to test our proposed dual-photocatalytic integration, and detailed descriptions about experimental measurement and conditions are provided in the Methods. As shown in Fig. 5a, the pristine \( \text{CoIn}_2\text{S}_4 \) and \( \text{FeIn}_2\text{S}_4 \) display \( \text{NH}_3 \) evolution rates of 21.8 \( \mu \text{mol g}^{-1} \text{h}^{-1} \) and 38.3 \( \mu \text{mol g}^{-1} \text{h}^{-1} \), which is obviously higher than that of commercial TiO\(_2\). Their photolysis yields are monotonically increased with photolysis time. Remarkably, average \( \text{NH}_3 \).
evolution rate of Co$_{0.5}$Fe$_{0.5}$In$_2$S$_4$ is enhanced to 85.8 µmol g$^{-1}$ h$^{-1}$, 3.9 (2.2) times higher than that of pristine CoIn$_2$S$_4$ and FeIn$_2$S$_4$ (Supplementary Figs. 7–10). Meanwhile, the apparent quantum efficiency (AQE) of Co$_{0.5}$Fe$_{0.5}$In$_2$S$_4$ was estimated to be 1.65% at 350 nm, 1.09% at 400 nm and 0.12% at 450 nm (Supplementary Fig. 11). After four successive photocatalytic cycles over 12 hours in Supplementary Fig. 12, the Co$_{0.5}$Fe$_{0.5}$In$_2$S$_4$ also keeps excellent structural stability and photocatalytic performance. Compared to other photocatalysts under similar conditions as a potential application, the Co$_{0.5}$Fe$_{0.5}$In$_2$S$_4$ catalyst exhibits a state-of-the-art N$_2$ reduction performance, as shown in Supplementary Table 2. In addition, a series of isotopic labelling and verified experiments are also conducted in Supplementary Figs. 13–14, which indicates that the evolved NH$_3$ indeed originates from the photoreduction of N$_2$. Notably, the high selectivity of Co$_{0.5}$Fe$_{0.5}$In$_2$S$_4$ for N$_2$ photoreduction into ammonia also can be verified, because no apparent hydrazine was detected in the product solutions (Supplementary Fig. 15).

To confirm the photocatalytic integration between HER and NRR, we conducted in situ Raman spectroscopy to detect the reaction intermediates in the N$_2$ reduction process. After light irradiation, a new Raman peak at 1028.53 cm$^{-1}$ for Co$_{0.5}$Fe$_{0.5}$In$_2$S$_4$ in water solution and Ar atmosphere is detected, and this peak subsequently disappear after removing light source. Naturally, this peak only can be attributed to passivated H* group on metal site due to H$_2$O splitting, which also can be confirmed by the pH-dependent Raman behavior, as shown in Supplementary Fig. 16. When N$_2$ is introduced into this reaction process, the Raman intensity at 1028.53 cm$^{-1}$ is depressed accordingly, while a stronger Raman peak is detected at 960.39 cm$^{-1}$. This Raman behavior can be assigned to symmetric stretching vibration of *N$_2$H$_2$ group on Co$_{0.5}$Fe$_{0.5}$In$_2$S$_4$ surface$^{30–33}$, which well coincides with the calculated results of 975.73 cm$^{-1}$. This interdependent spectral behavior indicates passivated H* group is a crucial intermediate during N$_2$ reduction to NH$_3$. In other words, dual photocatalytic integration from HER to NRR is realized and this strategy leads to an excellent NH$_3$ evolution efficiency.

To detect the underlying physical mechanism, Fig. 5c shows the H* free energy ($\Delta G_{H}$) (left axis) and N$_2$H$_2$ dissociation energy (right axis) as a function of charge-transfer energy (energy difference between occupied metal 3d and unoccupied N 2p-band center or H 1 s-band center, top panel in Fig. 5c) for different metal site of (001) surface in different alloy compositions. The charge-transfer energy is strongly dependent of type of metal site and its coordination environment, displaying a linear dependence relation with catalytic activity. The Co, Fe, Co(1), Co(2), Fe(1), Fe(2), In-Co, In-Fe, In-CoFe represents different reactive sites for HER and CoFe, Fe(1&2), Co(1&2) represents different reactive sites for NRR, details shown in Supplementary Fig. 17. The calculation discloses that Co and Fe site (marked by grey Co and Fe) at Co$_{0.5}$Fe$_{0.5}$In$_2$S$_4$ surface have smaller $\Delta G_{H}$ than corresponding In site (marked by grey In-CoFe), indicating the HER prefers to occur at Co and Fe site. Additionally, the HER activity of Co$_{0.5}$Fe$_{0.5}$In$_2$S$_4$ is obvious excellent than that of CoIn$_2$S$_4$ (Co(1), Co(2) and In-Co) and FeIn$_2$S$_4$ (Fe(1), Fe(2) and In-Fe). It is generally accepted that the $\Delta G_{H}$ can be used to evaluate the HER activity. The optimal value of $\Delta G_{H}$ is zero$^{34}$, where hydrogen is bound neither too strongly nor too weakly. The negative $\Delta G_{H}$ (-0.10 eV) in
Co$_{0.5}$Fe$_{0.5}$In$_2$S$_4$ implies a not outstanding HER performance due to an existence of rate-limiting potential. From another perspective, this not excellent HER performance provides a feasibility for integrating following NRR, which can be confirmed by changes in hydrogen production in N$_2$ and Ar atmosphere (Supplementary Fig. 18). The detailed reaction pathway for NRR is shown in Supplementary Fig. 19 and the N$_2$H$_2$ dissociation energy (rate-limiting step) is extracted and described as a function of charge-transfer energy in Fig. 5c. The formation of metal-nitrogen bond has a mixed ionic-covalent character because of the energetic similarity (covalency) and spatial overlap (hybridization) between metal 3$d$ orbitals and N 2$p$ states, which plays a critical role in NRR. In alloying design, replacing the Co site with a more electronegative Fe atom to form Co$_{0.5}$Fe$_{0.5}$In$_2$S$_4$, the enhancing valence state of Fe site (Supplementary Fig. 2) increases the Fe-N covalency and hybridization, resulting in a lower N$_2$H$_2$ dissociation energy (marked by red CoFe). From the understanding of reaction pathway in Supplementary Fig. 19, the integration of HER and NRR is a good choice to enhance the photocatalytic performance.

In order to further confirm this dual-photocatalytic integration, the in situ Mössbauer spectrum of Co$_{0.5}$Fe$_{0.5}$In$_2$S$_4$ (Fig. 5d) was conducted in different experimental condition. The isomer shift (IS=-0.08) and quadrupole splitting (QS = 0.54) with light irradiation in water solution under Ar environment is obviously different from that in the dark (IS=-0.06 and QS = 0.61). This can be understood that the unpaired valence electrons in the π-symmetry (e$_{2g}$) Fe 3$d$-orbitals is filled by residual H* group induced by HER, which make the spin magnetic moment become smaller (Fig. 5e), leading to an influence on the Zeeman splitting. When a certain amount of nitrogen is introduced, the isomer shift and quadrupole splitting are furthered changed as IS=-0.06 and QS = 0.60. This is due to the fact that the intermediate onto the Fe and Co site is replaced by *NH$_2$ group and their spin configurations are changed subsequently due to the orbital hybridization of Fe-N and Co-N bonds (Fig. 5e). The changes in Mössbauer spectra successfully confirm the photocatalytic integration between HER and NRR.

**Discussion**

In summary, we have demonstrated that the photocatalytic HER and NRR can be integrated together in Co$_{0.5}$Fe$_{0.5}$In$_2$S$_4$ nanoflowers through regulating the photo-excited carrier life time and metal site catalytic activity simultaneously. This dual photocatalytic integration strategy can enhance their intrinsic catalytic activity through a conversion in reaction pathway, producing an excellent NH$_3$ evolution efficiency of 84.5 μmolg$^{-1}$h$^{-1}$. More importantly, different from complex nanostructure, our work offers a new insight for enhancing NRR performance through an integration of dual photocatalytic reaction.

**Methods**

**Preparation of ultrathin Co$_{0.5}$Fe$_{0.5}$In$_2$S$_4$ nanoflowers.** All chemicals were of analytical grade and used as received without further purification. In a typical process, 0.05 mmol cobaltous nitrate, 0.05 mmol iron 2,4-pentanedionate and 0.2 mmol indium chloride were dissolved into 35 mL of ethanol solvent and the solution was refluxed at 25 °C for about 2 h under continuous stirring to ensure adequate dispersion,
followed by further sonication for 30 min under the same conditions. Thereafter, 5 mL of thioacetamide ethanol solution (0.1 M) containing 1 mg of sodium citrate was injected into the flask using a syringe pump at a rate of 2.5 mL min\(^{-1}\) and the mixture was stirred under the high-purity argon (Ar 99.999\%) current protection for 1 h to form a homogeneous solution at 10 °C. Finally, the obtained suspension was transferred to 50 mL Teflon-lined stainless-steel autoclave and then heated in an oven at 180 °C for 16 h. After naturally cooling down to room temperature, the products were collected by using centrifugation at 8000 rpm for 15 min and washed several times with deionized water and absolute ethanol to remove the residues of organic solvent, and freeze-dried in a vacuum overnight. The annealed process was employed to improve the purity and crystallization of the Co\(_{0.5}\)In\(_{0.5}\)In\(_2\)S\(_4\) nanoflowers. Typically, the Co\(_{0.5}\)In\(_{0.5}\)In\(_2\)S\(_4\) nanoflowers were placed in a ceramic boat, which was inserted into the middle of a horizontal quartz tubular reactor. The quartz tubular reactor was purged with 500 sccm (standard cubic centimeters per minute) high-purity argon for 2 h before heating. With a heating rate at 10 °C min\(^{-1}\), the furnace was heated to 300 °C for 1 h. The Ar gas flow rate was set at 150 sccm during the heating process to avoid oxidation. For comparison, pure CoIn\(_2\)S\(_4\) or FeIn\(_2\)S\(_4\) were synthesized by the same procedure except for the addition of the cobalt source or iron source.

**Photochemical NRR measurement.** The photocatalytic activities of the samples were evaluated under simulated solar light irradiation, using a Xe lamp with an AM 1.5 filter as the light source. The different samples with the same mass of 40 mg were used as catalysts dissolved into 100 mL aqueous solution without any sacrificial agent. The quartz reactor was equipped with a circulating water outer jacket in order to maintain at a temperature of 25 °C. The catalyst suspension was continuously stirred in the dark whilst high-purity N\(_2\) was bubbled through the suspension at a flow rate of 30 mL min\(^{-1}\) for 60 min to obtain a N\(_2\)-saturated aqueous suspension. Before the lamp was turned on, the suspension was continuously stirred for 10 min in the dark to achieve adsorption-desorption equilibrium between the catalyst, dissolved N\(_2\) and H\(_2\)O. The focused light power intensity on the reactor was uniformly calibrated to 100 mW cm\(^{-2}\). At regular intervals, 5 mL aliquots of the reaction solution were collected using a syringe, and then immediately centrifuged to remove the catalyst. The concentrations of NH\(_3\) products were determined by two colorimetrries using the indophenol blue method and Nessler’s reagent method. The absorption spectra of the colored complexes formed were recorded on a Shimadzu UV-1800 UV-Vis spectrometer, and the concentrations of NH\(_3\) determined using standard calibration curves of absorbance versus concentration for each complex.

**DFT calculation details.** Our calculations were performed on the density functional theory (DFT) as implemented in Vienna *ab initio* simulations package (VASP)\(^{35}\). The generalized gradient approximation (GGA) and Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional was adopted\(^{36}\). The integrations over the Brillouin zone were performed considering 10×10×10 uniform Monkhorst-Pack k-point grid for FeIn\(_2\)S\(_4\), CoIn\(_2\)S\(_4\) and Co\(_{0.5}\)Fe\(_{0.5}\)In\(_2\)S\(_4\) unit cell, respectively. In surface calculation, the Monkhorst-Pack k-point grid of 8×8×1 was adopted, and a vacuum space of 18 Å was considered to avoid the interaction between periodical images. The plane-wave energy cutoff of 480 eV was used to
expand the Koh-Sham wave functions and relaxation was carried out until all forces on the free ions converge to 0.01 eV/Å. The Gibbs free energy for all H\(_2\) and N\(_2\) reduction reaction on catalyst surface were defined as follows\(^{10,37}\): \(\Delta G = \Delta E_{ad} + \Delta E_{zpe} - T\Delta S + \Delta G_{pH}\), where \(\Delta E_{ad}\) and \(T\Delta S\) are the adsorption energy and the entropy difference between the adsorbed state and gas phase, respectively. \(\Delta E_{zpe}\) is zero-point energy between intermediates and gas phase.

**Declarations**

**Data availability**

The data described in this paper are available from the authors upon reasonable request.

**Acknowledgements**

This work was supported by National Basic Research Programs of China under Grants (Nos. 2018YFA0306004 and 2017YFA0303200), National Natural Science Foundation (Nos. 61964004, and 11874204), and Natural Science Foundation of Jiangsu Province (Nos. BK20171332 and SBK2020043594). This work was also supported by “Blue Project” in Jiangsu Province. This work was partially supported by the Fundamental Research Funds for the Central Universities (No. 0204-14380083) and high Performance Computing Centers of Nanjing University and Shenzhen.

**Author contributions**

G.Z performed the experiments and co-wrote this manuscript. Q.F.W and H.L prepared the samples and proofread the manuscript. J.H.G plotted the figures. L.Z.L analyzed the data, theoretical calculation and wrote the manuscript.

**Additional information**

Correspondence and requests for materials should be addressed to L.Z.L or X.L.W.

Supplementary information accompanies this paper at www.nature.com/naturecommunications.

**Competing interests**

The authors declare that they have no competing interests.

Reprints and permission information are available online at http://npg.nature.com/reprintsandpermissions/.

**References**

1. Honkala, K. et al. Ammonia synthesis from first-principles calculations. *Science* **307**, 555–558 (2005).
2. Pool, J. A., Lobkovsky, E. & Chirik, P. J. Hydrogenation and cleavage of dinitrogen to ammonia with a zirconium complex. *Nature* **427**, 527–530 (2004).

3. Montoya, J. H., Tsai, C., Vojvodic, A. & Nørskov, J. K. The challenge of electrochemical ammonia synthesis: a new perspective on the role of nitrogen scaling relations. *ChemSusChem* **8**, 2180–2186 (2015).

4. Brown, K. A. et al. Light-driven dinitrogen reduction catalyzed by a CdS: nitrogenase MoFe protein biohybrid. *Science* **352**, 448–450 (2016).

5. Zhu, D., Zhang, L., Ruther, R. E. & Hamers, R. J. Photo-illuminated diamond as a solid-state source of solvated electrons in water for nitrogen reduction. *Nat. Mater.* **12**, 836–841 (2013).

6. van Kessel, M. A. et al. Complete nitrification by a single microorganism. *Nature* **528**, 555–559 (2015).

7. Kitano, M. et al. Electride support boosts nitrogen dissociation over ruthenium catalyst and shifts the bottleneck in ammonia synthesis. *Nat. Commun.* **6**, 1–9 (2015).

8. Gruber, N. & Galloway, J. N. An Earth-system perspective of the global nitrogen cycle. *Nature* **451**, 293–296 (2008).

9. Zhang, S., Zhao, Y., Shi, R., Waterhouse, G. I. & Zhang, T. Photocatalytic ammonia synthesis: Recent progress and future. *EnergyChem* **1**, 100013 (2019).

10. Zhou, G. et al. Half-metallic carbon nitride nanosheets with micro grid mode resonance structure for efficient photocatalytic hydrogen evolution. *Nat. Commun.* **9**, 1–9 (2018).

11. Zhang, N. et al. Refining defect states in W$_{18}$O$_{49}$ by Mo doping: a strategy for tuning N$_2$ activation towards solar-driven nitrogen fixation. *J. Am. Chem. Soc.* **140**, 9434–9443 (2018).

12. Zhao, Y. et al. Tuning oxygen vacancies in ultrathin TiO$_2$ nanosheets to boost photocatalytic nitrogen fixation up to 700 nm. *Adv. Mater.* **31**, 1806482 (2019).

13. Di, J. et al. Defect-Tailoring Mediated Electron-Hole Separation in Single-Unit-Cell Bi$_3$O$_4$Br Nanosheets for Boosting Photocatalytic Hydrogen Evolution and Nitrogen Fixation. *Adv. Mater.* **31**, 1807576 (2019).

14. Song, Y. et al. A physical catalyst for the electrolysis of nitrogen to ammonia. *Sci. Adv.* **4**, e1700336 (2018).

15. Kuriyama, S. et al. Catalytic transformation of dinitrogen into ammonia and hydrazine by iron-dinitrogen complexes bearing pincer ligand. *Nat. Commun.* **7**, 1–9 (2016).

16. Xue, X. et al. Review on photocatalytic and electrocatalytic artificial nitrogen fixation for ammonia synthesis at mild conditions: Advances, challenges and perspectives. *Nano Res.* 1–21 (2019).

17. Li, C. et al. Promoted fixation of molecular nitrogen with surface oxygen vacancies on plasmon-enhanced TiO$_2$ photoelectrodes. *Angew. Chem. Int. Ed.* **57**, 5278–5282 (2018).

18. Xu, H. et al. Fabrication of In$_2$O$_3$/In$_2$S$_3$ microsphere heterostructures for efficient and stable photocatalytic nitrogen fixation. *Appl. Catal., B* **257**, 117932 (2019).
19. Ma, X.-L., Liu, J.-C., Xiao, H. & Li, J. Surface single-cluster catalyst for N\textsubscript{2}-to-NH\textsubscript{3} thermal conversion. *J. Am. Chem. Soc.* **140**, 46–49 (2018).

20. Ling, C., Niu, X., Li, Q., Du, A. & Wang, J. Metal-free single atom catalyst for N\textsubscript{2} fixation driven by visible light. *J. Am. Chem. Soc.* **140**, 14161–14168 (2018).

21. Ling, C. et al. New Mechanism for N\textsubscript{2} reduction: the essential role of surface hydrogenation. *J. Am. Chem. Soc.* **141**, 18264–18270 (2019).

22. Sultana, S., Mansingh, S. & Parida, K. Phosphide protected FeS\textsubscript{2} anchored oxygen defect oriented CeO\textsubscript{2}NS based ternary hybrid for electrocatalytic and photocatalytic N\textsubscript{2} reduction to NH\textsubscript{3}. *J. Mater. Chem. A* **7**, 9145–9153 (2019).

23. Foster, S. L. et al. Catalysts for nitrogen reduction to ammonia. *Nat. Catal.* **1**, 490–500 (2018).

24. Hinrichsen, S., Broda, H., Gradert, C., Söncksen, L. & Tuczek, F. Recent developments in synthetic nitrogen fixation. *Annu. Rep. Prog. Chem., Sect. A: Inorg. Chem.* **108**, 17–47 (2012).

25. Légaré, M.-A. et al. Nitrogen fixation and reduction at boron. *Science* **359**, 896–900 (2018).

26. Liu, J.-C. et al. Heterogeneous Fe\textsubscript{3} single-cluster catalyst for ammonia synthesis via an associative mechanism. *Nat. Commun.* **9**, 1610 (2018).

27. Hou, W., Xiao, Y. & Han, G. An Interconnected Ternary MIn\textsubscript{2}S\textsubscript{4} (M = Fe, Co, Ni) Thiospinel Nanosheet Array: A Type of Efficient Platinum-Free Counter Electrode for Dye-Sensitized Solar Cells. *Angew. Chem. Int. Ed. Engl.* **56**, 9146–9150 (2017).

28. Ravel, B. & Newville, M. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. *J. Synchrotron Radiat.* **12**, 537–541 (2005).

29. Ju, L., Shang, J., Tang, X. & Kou, L. Tunable Photocatalytic Water Splitting by the Ferroelectric Switch in a 2D AgBiP\textsubscript{2}Se\textsubscript{6} Monolayer. *J. Am. Chem. Soc.* **142**, 1492–1500 (2020).

30. Saouma, C. T., Kinney, R. A., Hoffman, B. M. & Peters, J. C. Transformation of an [Fe(η\textsuperscript{2}-N\textsubscript{2}H\textsubscript{3})]\textsuperscript{+} Species to π-Delocalized [Fe\textsubscript{2}(µ-N\textsubscript{2}H\textsubscript{2})]\textsuperscript{2+/+} Complexes. *Angew. Chem. Int. Ed.* **50**, 3446–3449 (2011).

31. Smith, J. M. et al. Studies of low-coordinate iron dinitrogen complexes. *J. Am. Chem. Soc.* **128**, 756–769 (2006).

32. Liu, S. et al. Facilitating nitrogen accessibility to boron-rich covalent organic frameworks via electrochemical excitation for efficient nitrogen fixation. *Nat. Commun.* **10**, 1–9 (2019).

33. Shibahara, T. & Mori, M. Raman and infrared spectra of µ-O\textsuperscript{2} dicobalt (â€¢) complexes. *Bull. Chem. Soc. Jpn.* **51**, 1374–1379 (1978).

34. Zhou, G. et al. Photoinduced semiconductor-metal transition in ultrathin troilite FeS nanosheets to trigger efficient hydrogen evolution. *Nat. Commun.* **10**, 1–8 (2019).

35. Anisimov, V. I., Zaanen, J. & Andersen, O. K. Band theory and Mott insulators: Hubbard U instead of Stoner I. *Phys. Rev. B* **44**, 943 (1991).

36. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **77**, 3865 (1996).
Figure 1

Reaction mechanism design. a Manipulating the reaction pathway through a HER and NRR integration. b left panel: simplified schematic of N2 bonding to transition metals; middle panel: electronic configuration and relevant metal atomic orbitals; right panel: reaction mechanism after integrating HER and NRR.
Figure 2

Physical characterization. a FE-SEM image of Co0.5Fe0.5In2S4 nanoflowers. b Top panel: AFM topographical image of a Co0.5Fe0.5In2S4 nanosheet. Bottom panel: height profile of a Co0.5Fe0.5In2S4 nanosheet is marked by arrow line. c HR-TEM image of Co0.5Fe0.5In2S4 nanoflowers. Left inset: the SAED pattern; right inset: the enlarged image; EDS mapping in the bottom panel. d XRD patterns of FeIn$_2$S$_4$, CoIn$_2$S$_4$ and Co$_{0.5}$Fe$_{0.5}$In$_2$S$_4$ samples.
Figure 3

Electronic structure characterization. a The Fe-edge XANES of Co0.5Fe0.5In2S4, FeIn2S4 and Fe foil. b The Co-edge XANES of Co0.5Fe0.5In2S4, CoIn2S4 and Co foil. c The Fourier transforms of EXAFS spectra of Co0.5Fe0.5In2S4 and FeIn2S4 for Fe-edge. d The Fourier transforms of EXAFS spectra of Co0.5Fe0.5In2S4 and CoIn2S4 for Co-edge. e The electrostatic potential difference between the first and second atomic layer at Co0.5Fe0.5In2S4 (001) surface. Right panel: the corresponding charge density. f The electrostatic potential difference as a function of alloy composition. Inset: Bader charge analysis.
Figure 4

Photogenerated carrier dynamics and spectral characterization. a The orbital-resolved band structure of Co0.5Fe0.5In2S4. Bottom panel: the transition dipole moment between valance band and conduction band. b A three dimensional plot of the TA spectra at delays from 0.00 to 2.00 ps. c The TA dynamics at 1.34, 1.36, 1.44 and 1.66 eV for a time delay from 0.00 to 8.00 ps. d Alignment of the calculated TDOS with the transitions from the acquired TA spectra. e Detailed analysis of the oscillatory TA dynamics. f Plots of the measured TA amplitude at a delay of 1.10 ps (red circles) and 2.80 ps (blue circles) as a function of the pump fluence, together with fits to third-order \( Y = A1X - B1X^2 - C1X^3 \) and second-order \( Y = A2X - B2X^2 \) polynomials, respectively, with \( A1 = 4.06 \times 10^{-2}, B1 = 1.01 \times 10^{-5}, C1 = 2.04 \times 10^{-8}, A2 = 2.83 \times 10^{-3}, \) and \( B2 = 1.34 \times 10^{-9}. \)
Figure 5

N2 reduction reaction performance and in situ characterizations. a The NH3 yield of Co0.5Fe0.5In2S4, CoIn2S4, FeIn2S4 and commercial TiO2 with varied time. b In situ Raman measurement with/without light irradiation in Ar and N2 atmosphere. c Relationship of charge-transfer energy to relevant ΔGH and rate-determining N2 dissociation energy. d In situ Mössbauer spectrum of Co0.5Fe0.5In2S4 with/without light irradiation in Ar and N2 atmosphere. e The calculated spin density and magnetic moments for different intermediates onto Co0.5Fe0.5In2S4 surface.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- NCsup.docx