Beyond the Thermal Equilibrium Limit of Ammonia Synthesis with Dual Temperature Zone Catalyst Powered by Solar Light

Plasmonic local heating effect of Fe nanonecklace endowed TiO$_{2-x}$H$_y$/Fe catalyst of hot-zone Fe and cool-zone TiO$_{2-x}$H$_y$, which were responsible for tandem N$_2$ activation and NH$_3$ assembly, respectively. With such dual temperature zones and the tandem kinetic mechanism, light-driven TiO$_{2-x}$H$_y$/Fe nanonecklace achieved highly efficient ammonia synthesis with NH$_3$ yield beyond the thermodynamic equilibrium limit of thermocatalytic ammonia synthesis.
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SUMMARY

Artificial ammonia synthesis (Haber-Bosch process) is a prototypical exothermic reaction of maximum catalytic yield restricted by the unbreakable equilibrium law. This is because bottlenecked N_2 dissociation necessitates high temperature, but high temperature reversely shifts the thermal equilibrium toward NH_3 decomposition. To surmount this equilibrium limit, here, we propose a new scenario of dual-temperature-zone catalysis. Powered by sunlight, the apparent temperature of TiO_2-xHy/Fe hybrid reaches 495°C with a local temperature difference up to 137°C between the hot zone (Fe) and “cooling” zone (TiO_2-xHy) owing to the plasmonic local heating effect. The hot Fe bearing hot carriers efficiently dissociates N_2, while working-in-tandem TiO_2-xHy well accommodates spilled-over N from Fe via successive hydrogenation, prominently mitigating the reverse equilibrium shift and thus delivering record NH_3 concentrations of 1,939 (1 atm) and 19,620 ppm (10 atm) at 495°C, 1.55 and 1.57 times the theoretical equilibrium limits of 1,249 and 12,459 ppm, respectively.

INTRODUCTION

Ammonia synthesis from nitrogen reduction constitutes the key step of nitrogen cycle, being vital to all the living beings on Earth. Artificially, it relies on the well-established energy-intensive Haber-Bosch process via N_2 + 3H_2 = 2NH_3 (350°C–550°C, 150–250 atm; ΔH° = −92.44 kJ mol⁻¹). This reaction is kinetically favored at gradually increased temperatures (from 350°C to 550°C) for higher speed but the increase of temperature would reversely shift this prototypical exothermal reaction toward the direction of NH_3 decomposition and thus severely lowers the outlet NH_3 concentration. Governed by the contradicting temperatures desirable for kinetics and thermodynamics, NH_3 generation of thermocatalysis are limited to no more than the low equilibrium concentrations (Scheme 1A). Realization of higher NH_3 yields, especially the equilibrium-beyond ones, which in turn reduces the applied pressure and energy consumption, is highly desired but remains unexplored.

Intuitively, an ideal scenario for surmounting the above-mentioned equilibrium law is to spatially confine the “in-tandem” N_2 dissociation and N-hydrogenation onto a local high-temperature zone (center I) and a local low-temperature zone (center II), respectively. This is because among the elemental steps of ammonia synthesis involving the dissociative activation of reactants (*N_2 → 2*N, *H_2 → 2*H) and the subsequent N-hydrogenation (*NH_z₋₁ + *H ⇄ *NH_z; z = 1, 2, and 3), high temperature is kinetically necessitated usually by the rate-limiting nitrogen activation, while...
the low-temperature NH₃ generation is kinetically feasible and thermodynamically desirable. Unfortunately, neat thermocatalysis is not able to engender precise non-uniform heat distribution onto constituent catalytic centers.

Herein, by altering the traditional thermal heating way into solar-powered one, we report a plasmonic-based dual-temperature-zone catalysis (DTZC; high-temperature N₂ activation and low-temperature NH₃ formation) for highly efficient ammonia synthesis. The three theoretical bases of our DTZC are as follows. First, nanostructured metals with localized surface plasmon resonance effect, including ammonia synthesis metals Fe and Ru, can concentrate the diffused solar flux to generate heat in a small volume (local heating: up to 600°C at present), workable for sufficient N₂ dissociation as the center I. Second, a "cooling" zone is easy to be constructed when a well-arranged center II of low thermal conductivity is coupled to the "plasmonic-heated" center I (Schemes 1B and 1C). Third, separating the elemental steps of a reaction into two spatially separated active sites is common in natural metalloenzymes and multi-component heterocatalysts, specifically for the state-of-the-art ammonia synthesis catalysts, such as Co₃Mo₃N₂, electrides supported Ru, TM(N)-alkali or alkaline earth metal hydride (TM = V, Cr, Mn, Fe, Co, and Ni) and BaTiO₂₋₋½H₂O supported Ru, Fe, and Co catalysts. By means of such a catalyst design, we could also potentially take advantage of the plasmonic molecular activation engendered by hot carriers, which was reported to decrease the activation energy, to kinetically reduce the energy barrier of ammonia synthesis. To implement our scenario, we first select Fe with a nanonecklace microstructure as the possible center I and the high-temperature zone. Among diverse potential center II candidates, which are usually metal hydrides, hydrogenated titanium oxides (TiO₂₋₋½H₂) appear as a promising candidate because of its chemical stability, earth abundance, hydrogen storage capability, and, more importantly, a low thermal conductivity (0.18 W/mK; Supplemental Information) far below that of Fe (80 W/mK) and close to that of air (0.026 W/mK), desirable as the possible center II and the low-temperature zone.

Scheme 1. “Equilibrium-Beyond” Solar Ammonia Synthesis Scheme
(A) Thermal equilibrium of ammonia synthesis on Fe surface. 
(B) Reaction scheme of the dual-temperature-zone solar ammonia synthesis. Under illumination, plasmonic heating of metallic Fe nanonecklace induces local temperature difference (LTD), rendering N₂ activation on high-temperature Fe (red; zone I) and NH₃ generation on low-temperature TiO₂₋₋½H₂ (blue; zone II). 
(C) The feasible analysis of acquiring “equilibrium-beyond” reactivity.
RESULTS

Guided by the above theoretical design, we prepared TiO$_2$-xHy/Fe nanocomposite (TiO$_2$-H$_y$/Fe) via a facile in situ reduction strategy (Figure S1). Typically, hydrogenated titanium oxide (TiO$_2$-H$_y$) nanoparticles were first prepared via the reduction and hydrogenation of TiO$_2$ by NaBH$_4$. Low-temperature (100 K) high-resolution electron paramagnetic resonance (EPR) spectra demonstrated TiO$_2$-H$_y$ contained oxygen vacancies ($g = 2.001$), Ti$^{3+}$ ($1.925 \leq g \leq 1.990$), and oxygen vacancy incorporated H atoms (multiplet across $g = 2.001$ with a hyperfine splitting constant $a_H = 7.7$ gauss; Figure S2A).$^{17}$ Presence of Ti-based hydrides was further evidenced by a distinct Ti-H peak with a chemical shift of 1.60 ppm in the H-NMR spectra of TiO$_2$-H$_y$ (Figure S2B),$^{40}$ being generated by the occupation of atomic-hydrogen on oxygen vacancies. Subsequently, TiO$_2$-H$_y$/Fe was synthesized via reducing FeCl$_3$ in the presence of uniformly dispersed TiO$_2$-H$_y$ nanoparticles. By regulating the reduction time, as well as the concentration of reductant (NaBH$_4$), Fe nanospheres could self-assemble into nanonecklace structure in a controlled manner (Figures 1A and S1). Scanning electron microscopy (SEM) images, X-ray diffraction (XRD) pattern, surface enhanced Raman scattering (SERS) spectra, and elemental-mapping of scanning transmission electron microscopy (STEM) revealed the uniform anchoring of TiO$_2$-H$_y$ nanoparticles onto Fe nanonecklaces (Figures 1B–1H and S2–S6). Rather through weak physical adhesion, TiO$_2$-H$_y$ was strongly bound to Fe nanonecklace through lattice interaction mediated by a protective amorphous transition iron oxide (Fe$_2$O$_3$-$\delta$) layer (Figure 1I). This strong lattice interaction was believed to establish via the "adsorption and in situ reduction" interaction between the reducible metal ions and the reducible sites (such as oxygen vacancies) of oxides during the catalyst preparation.$^{41,42}$

We then conducted solar-powered catalytic NH$_3$ synthesis on TiO$_2$-xHy/Fe nanocomposite in a transparent quartz reactor under a continuous N$_2$-H$_2$ flow. Steady-state NH$_3$ concentrations, the corresponding light intensities, and the photothermal temperatures were simultaneously recorded to assess the catalyst performances (Figure S7). Under ambient pressure and light intensities of 5,002–10,242 mW/cm$^2$ corresponding to temperatures of catalysts from 270°C to 550°C, neither TiO$_2$ nor TiO$_2$-H$_y$ were catalytically active for ammonia synthesis, while the NH$_3$ concentration of reference catalysts, including Fe nanonecklaces, TiO$_2$/Fe, and a superior commercial-wüüstite-based Haber-Bosch Fe catalyst at low temperatures and low pressures, were no more than 175 ppm. Interestingly, a qualitative jump of NH$_3$ concentration was witnessed when “inert” TiO$_2$-H$_y$ was anchored onto Fe nanonecklaces. When TiO$_2$-xHy/Fe was light heated to 495°C at 10,242 mW/cm$^2$, it delivered a 1939 ppm NH$_3$ concentration, an order of magnitude (>22 times) higher than that of commercial-wüüstite-based Haber-Bosch Fe catalyst (Figures 1J–1L, S8, and S9; Table S1). As thermodynamic equilibrium limit of ammonia synthesis at 495°C and 1 atm is 1,249 ppm, this is a breakthrough to first exceed equilibrium-defined maximum NH$_3$ concentration by merely adding the assistant catalytic center and the low-temperature zone (TiO$_2$-xHy). This high reactivity of TiO$_2$-xHy/Fe could maintain at least for 15 h without significant decrease under continuous illumination because of TiO$_2$-xHy anchoring promoted Fe-structure stability, while increased or dropped sharply when the light was turned on or off with reproducibility for five times, respectively (Figures 1M and S8–S10).

Regarding pressure dependence of industrial ammonia synthesis, we also carried out solar ammonia synthesis under high pressure and found the NH$_3$ concentrations of TiO$_2$-xHy/Fe increased to 9,886 ppm under 5 atm and 19,620 ppm under 10 atm at 495°C, respectively. Surprisingly, all these NH$_3$ concentrations of TiO$_2$-xHy/Fe under
different pressures were respectively 1.55, 1.57, and 1.57 times the thermodynamic equilibrium limits (1,249 ppm at 1 atm, 6,308 ppm at 5 atm, and 12,459 ppm at 10 atm; 495°C), which was never achieved by thermocatalysis (Figures 1N and S11).

When altering the driven force of solar light into thermal heating, the NH₃ concentration of TiO₂-xHy/Fe decreased by more than 2/3 (560 ppm versus 1,939 ppm) at the same temperature of 495°C. Meanwhile, the apparent activation energy (E_a) of...
Ammonia synthesis on TiO$_2$-xH$_y$/Fe increased to 57 kJ mol$^{-1}$ under thermal heating compared with 47 kJ mol$^{-1}$ of solar catalysis, both of which were significantly lower than that (77 kJ mol$^{-1}$) of commercial Fe catalyst, indicating that the TiO$_2$-xH$_y$/Fe-based ammonia synthesis is far beyond Fe catalysis (Figures 1L and S12).

Obviously, the fact that equilibrium law appeared “broken” by DTZC was closely related to the TiO$_2$-xH$_y$ domains anchored on Fe nanonecklaces and the light. According to our design, TiO$_2$-xH$_y$ zone (center II) was “cool” enough to mitigate the overall reverse equilibrium shift toward NH$_3$ decomposition if it could accommodate dissociated N atoms from “hot” zone Fe necklaces (center I) for successive hydrogenation. This non-uniform temperature distribution within TiO$_2$-xH$_y$/Fe was theoretically revealed by the finite difference time domain (FDTD) simulation as follows (Figures 2A–2H). As for the freestanding Fe nanosphere ($d = 120$ nm), it triggered surface plasmon resonance in the UV (365 nm) and visible (vis) (510 nm) region with respective extinction cross-section of 5.2 and 7.5, indicating the excellent

![Figure 2. LTD Generation of Illuminated TiO$_2$-xH$_y$/Fe](Figure2.png)

(A) The light adsorption mechanism of Fe nanonecklaces via plasmon hybridization.
(B) Near field intensities of Fe nanosphere and nanonecklace normalized to incident field ($|E/E_0|^2$) at corresponding resonant wavelengths, two resonant peaks for Fe nanosphere (360 and 510 nm) and full-range resonant for Fe nanonecklace (selected four wavelengths: 300, 726, 1,221, and 2,500 nm).
(C) Enhancement in electric field intensity ($|E/E_0|^2$).
(D) Heat power volume density ($Q_1$), and (E) steady-state non-equilibrium temperature distribution and proposed dual-temperature-zone ammonia synthesis of TiO$_2$-xH$_y$/Fe at incident $\lambda = 726$ nm.
(F) Dependence of calculated normalized extinction spectra ($C_{ext}/C_{geo}$) of Fe nanonecklace on the number $N$ of nanosphere (radius = 60 nm). $C_{ext}$ and $C_{geo}$ are the extinction cross-section and geometry cross-section of the nanostructures, respectively.
(G) Diffuse reflectance spectra of Fe nanonecklace and titanium oxides.
(H) LTDs between Fe ($d = 120, 240, \text{and } 360$ nm) and TiO$_2$-xH$_y$ under light intensities from 5,400 to 10,200 mW/cm$^2$, obtained after calibrating the FDTD-simulated temperature with the experimentally measured counterpart.

See also Figures S13 and S14.
UV-vis-plasmon property of Fe (Figure 2B). Intriguingly, close proximity of Fe nanospheres, when gradually assembled to form a nanonecklace, induced a gradual broadening and redshift of the plasmon resonant wavelengths toward the infrared regime in the extinction spectra (Figures 2B and 2F). This nanonecklace-triggered plasmon hybridization effect\textsuperscript{35,36} extended the plasmon resonant wavelengths of Fe without significantly decreasing the extinction cross-section (from 5.2/7.5 to 5.1), endowing the Fe nanonecklace with pronounced light adsorption throughout the solar spectrum region from 300 to 2,500 nm (Figures 2B, 2F, and 2G). After Fe nanonecklace was densely packed by small TiO$_{2-x}$H$_{y}$ domains (25 nm), the local electric field enhancement of Fe nanonecklace maintained at $\lambda_{C24}^{\text{6}}$ at wavelength of 726 nm (Figure 2C). This light flux concentration and localized electromagnetic field enhancement of Fe plasmonics would drive the carriers oscillating inside the Fe, and then the energy gained by carriers turned into heat in Fe ($Q_1$):\textsuperscript{12,14,44}

$$Q_1 = 0.5 \epsilon_0 \omega \text{Im}(\epsilon_r)|E|^2, \quad (\text{Equation 1})$$

where $\epsilon_0$ is permittivity of vacuum, $\omega$ is angular frequency of the incident light, $\epsilon_r$ is the relative permittivity of Fe, and $E$ is surface plasmon resonant induced electromagnetic field. As shown in Figure 2D, $Q_1$ was as high as $\sim 6 \times 10^{19}$ W/m$^3$, suggesting that Fe nanonecklaces served as a nanoheater under illumination to diffuse heat to the surrounding medium. Because of heat dissipation to surrounding reaction gas during the heat transfer, the steady-state temperatures of surrounding materials (including subsurface Fe and shady TiO$_{2-x}$H$_{y}$) were not homogeneous but proportional to $I_0/(r \cdot k)$, where $I_0$ is the light intensity, $r$ is the distance to the center of Fe nanonecklace, and $k$ is the thermal conductivity of the surrounding material,\textsuperscript{12} resulting in the formation of “hot” Fe ($T_{Fe}$) and “cool” TiO$_{2-x}$H$_{y}$ ($T_{Ti}$). This local temperature difference (LTD; $T_{Fe} - T_{Ti}$) could be quantified by solving the heat transfer equation as follows:\textsuperscript{12,14,44}

$$C_s \rho (\partial T/\partial t) + \nabla(-k \nabla T) = Q_2, \quad (\text{Equation 2})$$

where $T$ is the time- and space-dependent temperature of the plasmonic nanostructure, $C_s$, $\rho$, and $k$ are the respective specific heat capacity, density, and thermal conductivity of materials. $Q_2$ is heat source per unit volume. Because we focused on the steady-state heat transfer, the calculation could be simplified by setting $Q_1 = Q_2$ and the time derivative of temperature equaled zero, respectively.\textsuperscript{44} As shown in Figure S12E, the Fe nanonecklace was instantly heated up to 550°C upon irradiation with 10,200 mW/cm$^2$ at 726 nm. At a distance of 25 nm from the Fe nanonecklace surface, the temperature of TiO$_{2-x}$H$_{y}$ dropped down to 413°C. Utilizing such a calculation method and further considering the size effect of Fe nanonecklace, which originated from inhomogeneous size distribution of Fe nanospheres and high-temperature Fe-Fe partial aggregation, the maximum LTDs between Fe and TiO$_{2-x}$H$_{y}$ were identified as 79°C–137°C for $d_{Fe_a} = 120$ nm (major in the catalyst), 69°C–120°C for $d_{Fe_a} = 240$ nm (two Fe nanospheres aggregation) and 63–109°C for $d_{Fe_a} = 360$ nm (three Fe nanospheres aggregation) with input light intensities from 5,004 to 10,260 mW/cm$^2$, respectively (Figures 2E, 2H, S13, and S14).

To further verify the LTD between Fe and TiO$_{2-x}$H$_{y}$, we designed a FT-IR experiments of temperature programmed adonitol transformation (TP-FT-IR; Figures 3A and S15). Here, adonitol, a polyhydroxyl molecule with a high boiling point and strong coordination ability to catalyst surfaces, was used as a molecular temperature probe because of its temperature-dependent dehydration to corresponding ether (2R-OH $\rightarrow$ R-O-R + H$_2$O$_{g}$). In the dark, adonitol-to-ether transformation on TiO$_{2-x}$H$_{y}$/Fe was initiated at
312°C (Figures 3B and 3C). As expected, when solar light of 10,260 mW/cm² was added, the onset temperature for adonitol dehydration was notably lowered to 257°C, confirming that the local temperature of plasmonic Fe nanonecklaces (T_{Fe}) was estimated to be 55°C higher than the apparent temperature of TiO$_2$-xHy/Fe (T_{Ti-Fe}). Furthermore, this difference between T_{Fe} and T_{Ti-Fe} was largely decreased to 27°C, 22°C, and 4°C when the plasmonic-heating effect was attenuated under weaker solar light intensity of 7,920, 6,363 and 5,004 mW/cm², respectively (Figures 3D–3H and S16).

On the basis of TP-FTIR result, we further carried out SERS mapping to directly visualize the spatially distributed non-homogeneous temperature between Fe and TiO$_2$-xHy via a modified method recently developed by Hu et al.,$^{45}$ with using adonitol as a molecular temperature probe. We utilized the 780 nm laser with a long duration time to trigger the Fe-plasmonic heating and Raman scattering simultaneously (Figure 3A). Because the inhomogeneous distribution of TiO$_2$-xHy within the catalyst (Figures 1G and S9D), the TiO$_2$-xHy-rich area and the Fe (Fe$_2$O$_3$)-rich area were distinguished by the Raman scattering mapping as shown in Figures 3I and 3J, respectively. Meanwhile, the map of catalyst surface coated adonitol was also obtained with low intensity at high-temperature area and vice versa (Figure 3K). Obviously, adonitol-rich area overlapped with the TiO$_2$-xHy-rich area but almost departed from the Fe-rich area, suggesting the high temperature of Fe-rich area and low temperature of TiO$_2$-xHy-rich area. Furthermore, according to relative signal intensity of TiO$_2$-xHy/adonitol and Fe$_2$O$_3$/adenitol plotted against temperature, the spatial temperature difference was identified as ~129°C between “hot” Fe and “cool” TiO$_2$-xHy (Figures 3L and S17). These
experimentally measured temperature differences, including the \((T_{Fe} - T_{Ti-Fe})\) measured by TP-FTIR and the \((T_{Fe} - T_{Ti})\) measured by SERS mapping, were in consistent with the simulated or calculated ones (Figures 1K, 3M, S18, and S19), strongly supporting the dual temperature zone between “hot” Fe and “cool” TiO\(_2\)\(_{x}H_y\) nanoparticles under illumination.

To explore whether Fe and TiO\(_2\)\(_{x}H_y\) could enable “in-tandem” nitrogen activation and N-hydrogenation, respectively, we employed catalyst structure-based density functional theory (DFT) calculations to gain mechanistic details of ammonia synthesis on TiO\(_2\)\(_{x}H_y/Fe\). The knowledge about Haber-Bosch Fe catalyst suggested that surface C\(_7\) site (one Fe atom with 7 nearest neighbors) of bcc Fe(0), generated via *in situ* high-temperature reduction of iron oxides by hydrogen, was the active center, and thus, Fe-based ammonia synthesis was highly \(111\) facet-dependent because of its highest C\(_7\)-site concentration among all the possibly exposed facets.\(^ {46-48}\) Regarding our similar reaction temperature and gas to Haber-Bosch process, we proposed the C\(_7\) site on \(111\) facet was also the major active center on Fe within TiO\(_2\)\(_{x}H_y/Fe\) during photothermal ammonia synthesis (Figure 4A). To support this point of view, we characterized the reacted TiO\(_2\)\(_{x}H_y/Fe\) under strictly anaerobic conditions. The Fourier transform Fe K-edge extended X-ray absorption fine structure (EXAFS) \((k)^2\) of the reacted sample revealed that the Fe-O bond (1.486 Å) diminished after reaction and only the Fe-Fe bond (2.177 Å) could be identified, suggesting the Fe\(_2O_3\) shell on Fe nanoncklace was reduced to Fe(0) by H\(_2\), forming a TiO\(_2\)\(_{x}H_y/Fe(0)\) hybrid *in situ* (Figure 4B). Subsequently, to confirm the *in situ* formation of C\(_7\) site on Fe(0), we utilized the method developed by Dumesic et al.\(^ {49}\) to examine TiO\(_2\)\(_{x}H_y/Fe\) treated by H\(_2\) (Ar-3H\(_2\)) and reaction gas (N\(_2\)-3H\(_2\)) via Mössbauer spectroscopy, respectively. As expected, for the Mössbauer spectra of TiO\(_2\)\(_{x}H_y/Fe(0)\) samples, the full width at half maximum (FWHM; obtained via Lorentzian fit; Supplemental Information) of the \(\alpha\)-Fe(0) peaks decreased from 0.286 mm s\(^{-1}\) (left) and 0.292 mm s\(^{-1}\) (right) to 0.277 mm s\(^{-1}\) (left) and 0.279 mm s\(^{-1}\) (right) after altering the reduction gas from Ar-3H\(_2\) to N\(_2\)-3H\(_2\), reflecting a decrease of surface magnetic anisotropy of Fe(0), which was typical for nitrogen adsorption induced surface reconstruction to form C\(_7\) site revealed by such a comparison (Figure 4C; Table S2). Based on above discussion and results, a model of periodic Fe (111) surface\(^ {48,50}\) partially covered with a Ti-O layer of hydrogen atom(s) on its oxygen vacancy,\(^ {51}\) was built to simulate the TiO\(_2\)\(_{x}H_y/Fe\) catalyst under working condition (Figures S20 and S21). SEM and transmission electron microscopy (TEM) images of reacted TiO\(_2\)\(_{x}H_y/Fe\), indicative of TiO\(_2\)\(_{x}H_y/Fe\) nanoparticles densely anchoring on Fe nanoncklaces surface, and corresponding topological structure analysis also confirmed such a Fe (111)-TiO\(_2\)\(_{x}H_y\) model was perfect to represent the real catalyst *in situ* (Figures 4D–4F, S9D, and S22).

Nitrogen dissociation on Fe sites within TiO\(_2\)\(_{x}H_y/Fe\) (Fe-Ti-H) was highly exothermic (\(-2.94\) eV) and possessed an activation barrier (TS) of only 0.59 eV, thus being thermodynamically and kinetically favorable. After being compensated by the released energy from its former step (\(-0.45\) eV), the activation barrier was reduced to a value as small as 0.14 eV, close to that (0.05 eV) on freestanding Fe (111) surface. In contrast, nitrogen activation on Ti sites of TiO\(_2\)\(_{x}H_y\) (Ti-H) or TiO\(_2\)\(_{x}H_y/Fe\) (Ti-Fe-H) were implausible because of the prohibited (activation) energies of 2.73 and 4.35 eV required for *N\(_2\) dissociation (*N\(_2\) \(\rightarrow\) 2*N; * represented the adsorbed state; Figures 4G and S23), respectively. Oxygen vacancy (OV), as reported to be a nitrogen associative activation site in water-involved photocatalysis, was not able to dissociate *N\(_2\) in our photothermal ammonia synthesis, regarding the prohibited energies of 2.56 eV for OV in TiO\(_2\)\(_{x}\), 3.10 eV for OV in TiO\(_2\)\(_{x}/Fe\) and 2.70 eV for OV in Fe\(_2O_3\).
*N2 dissociation on the interface of OV-Fe (111) was theoretically possible, but not as the major activation pathway, because its energy barrier of 1.24 eV was much higher than those (0.59 eV or 0.14 eV and 0.05 eV) on Fe (Figures S23 and S24).

The subsequent step, i.e., *N-hydrogenation to ammonia, was believed to dominantly occur on TiO2-xHy because of the readily reaction between metal hydride ions (Ti-H in TiO2-xHy) and *N [17, 30, 52, 53] which was involved with a preliminary N spillover process. N spillover from Fe to Fe-TiO2-xHy interface (Ti-H-Fe-*N → Ti-H-N-Fe) was feasible with a slightly endothermic step of 0.38 eV for *N transfer on Fe and free energy change of -0.15 eV (exothermic) for *N transfer from Fe to OV. Even in the absence of H2, spillover N could be quickly captured by the OV incorporated H atom(s) in TiO2-xHy (y = 1, 2, and 3) and transformed into NH3 species in a highly exothermic manner (Figures 4G and S25), more easily than the well-known “up-hill” N-hydrogenation on pure Fe surface. Finally, when the NH3 was fabricated on the OV of TiO2-xHy (Ti-NH3-Fe; orange line), it could be readily desorbed from surface with an energy barrier of 1.56 eV (obtained from the adsorption energy of...
NH₃ on hydrogenated OV of pure TiO₂₋ₓHₓ as NH₃ was proposed to be finally desorbed on the cool TiO₂₋ₓHₓ zone; Figure 4G). Interestingly, besides direct desorption, NH₃ could also immigrate on TiO₂₋ₓHₓ to a certain distance from the Fe-Ti interface via a path of “OV → Ti → OV” with a comparable activation energy of 1.28 eV (Figure S26). Similar atom transfer on TiO₂ of different sites via “OV → Ti → OV” path was reported recently for hydrogen atoms with an effective immigration distance of more than 1 μm, which, on the other hand, supported the feasibility of NH₃ transfer to lower temperature zone (with a distance only up to 25 nm from the Fe-Ti interface as proposed in our model) on TiO₂₋ₓHₓ/Fe for high-equilibrium desorption. In addition, the consumed H atom(s) on OV could be restored in TiO₂₋ₓHₓ by H₂ dosing, as the OV of TiO₂₋ₓHₓ (Ti) could accept spillover H atoms from Fe via easy H₂ dissociation (TS = 0.67 eV; E = 0.47 eV) and transfer (TS = 0.66 or 0.92 eV; E = 0.85 eV). Such a H₂ transfer to TiO₂₋ₓHₓ could reduce the occupation of active sites on Fe and thus facilitated nitrogen activation. Furthermore, OV of TiO₂₋ₓHₓ could also directly dissociate H₂ by itself to recycle the hydride ion(s) on OV (TS = 0.64 eV; E = 1.07 eV; Figures 4H and S27). Therefore, along with sufficient N₂ dissociation on Fe, TiO₂₋ₓHₓ was theoretically the N-hydrogenation center owing to its prominent reversible hydrogen storage capability.

We further analyzed surface nitrogen species via FTIR and X-ray photoelectron spectroscopy (XPS) to correlate the above theoretical scheme with our experimental results. First, the surface N-H groups on Fe and TiO₂₋ₓHₓ/Fe after solar ammonia synthesis were measured via attenuated total reflectance-infrared (ATR-IR). Interestingly, distinct N-H bands appeared on TiO₂₋ₓHₓ/Fe at wavelength of 3,438 and 3,365 cm⁻¹, while no obvious peaks could be identified on pure TiO₂₋ₓHₓ or Fe. According to the DFT calculation, these species was assigned to Ti-NH₂, suggesting that TiO₂₋ₓHₓ was the preferential center for N-hydrogenation within TiO₂₋ₓHₓ/Fe (Figures 5A and S28). To further confirm this point of view, we in situ monitored the surface -NH₂ change in the presence of ¹⁵N-labeled N₂ by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and found that at room temperature, exposure of TiO₂₋ₓHₓ/Fe to a H₂-free N₂ atmosphere resulted in end-on N₂ adsorption on Fe (ν(N₂, doublet): 2,223 and 2,255 cm⁻¹), and cleavage of N≡N triple bond to yield TiO₂₋ₓHₓ adsorbed NH₂ νas: 3,170 cm⁻¹ (−NH₁₂), 3,272, 3,340, 3,393, and 3,443 cm⁻¹ (−NH₃), δas(NH₂): 1,593 cm⁻¹, δ₁(NH₃): 1,297 cm⁻¹),17,55 solidly supporting the hydrogenation of nitrogen by “metal hydride” of Ti-H on OV [TiO₂₋ₓHₓ + z*N/ (TiO₂₋ₓHₓ-z)-NH₂], consistent with the recent reports of nitrogen protonation by hydrides.53,56,57 When used isotope-labeled ¹⁵N₂ (98.5%), we observed all the expected isotopic frequency shifts (ν(¹⁵N₂): 2,137 and 2,168 cm⁻¹; νas(¹⁵NH₂): 3,135, 3,224, and 3,307 cm⁻¹; δas(¹⁵NH₂): 1,529 cm⁻¹; δ₁(¹⁵NH₃): 1,247 cm⁻¹) (Figures 5B and S29), confirming the assignment of above nitrogen species. After solar light was introduced (Figures 5C and 5D), original ν(¹⁵N₂) on Fe rapidly decreased and red shifted because of N-N triple bond dissociation and elongation, respectively. This suggested that the photon additionally promoted N₂ activation beyond the Fe d-orbitals induced orbital activation (electron density donation from d-occupied → *π upon N₂ adsorption), possibly through many ways, along the main reaction pathway (Figures 5E and 5F). First, hot electrons could be initially generated via the excitation of plasmonic Fe nanonecklaces and then injected to unoccupied orbitals of N₂ (Figure 5G), via (1) indirect charge transfer from d-occupied of Fe → unoccupied *π/d-π of N₂ because the energy of hot electrons with 0.5–4.1 eV above Fermi level (as evidenced by the UV-vis-NIR plasmonic resonant in Figures 2B, 2C, and 2F) and the acceptor levels of the unoccupied *π/d-π of N₂ (0–5 eV above Fermi level) could meet the resonant conditions for such a charge transfer, and/or (2) direct charge transfer from d-*π-occupied of N₂ → unoccupied...
because the energy gap for HOMO-(L)UMO of adsorbed N$_2$ was mostly within the range of photon energy of sunlight. This plasmonic activation induced by electronic transition, in terms of the Franck-Condon diagram, could be depicted as the ground state to negatively charged excited state (N$_2$$^-$) molecular N$_2$ (Figure 5H). The transient N$_2$$^-$ (usually with short lifetime in ps level), when its deposited energy could not overcome the activation barrier of N-N triple bond dissociation, returned to ground state in terms of potential energy surface (PES) but usually located to vibrationally excited state (blue arrow), of which was embodied by the redshift of N-N vibration bands in DRIFTS spectra. Direct vibrational transitions induced by photon excitation (green arrow), on the other hand, could result in the same vibrational energy increase of Fe-$^*$N$_2$. While those N$_2$$^-$ surpassed the activation energy would dissociate to $^*$N (orange arrow), which was consistent with the reduced intensity of N-N vibration bands in DRIFTS spectra, and transfer the electron back to Fe nanonecklace surface to maintain the electric neutrality. Second, the photon-driven plasmonic local heating effect of Fe could also excite its phonon mode for N$_2$ activation (Figure 5I). Besides, an alternative mechanism such as the semiconductor (titanium oxide) excitation coupled Fe-plasmonic excitation might be possible, according to the theoretic basis of photothermal Sabatier reaction. When readily excited by sunlight from UV to NIR, titanium oxide generated e$^-$-h$^+$ pair to migrate to the surface for initiating h$^+$ involved H$_2$ oxidation (h$^+$ + H$_2$ → H$_2^+$), while the e$^-$ might surpass the Schottky barrier (between metal and semiconductor) to activate N$_2$ and H$_2$ on Fe surface.
(e⁻ + H₂ + N₂ → H⁺ + N₂⁺ + H + N), in conjunction with hot electrons. If following the tandem mechanism of intermediate spillover to titanium oxide, the catalyst could assemble the NH₃ with H, N, and hydride on OV and maintain the electric neutrality via H⁺ + H⁻ = H₂ (Figure 5J). In our system, the largely inhibited e⁻-h⁺ separation efficiency of TiO₂ₓHₓ and possible competing hot electron transfer to conduction band of TiO₂ₓHₓ may need to be considered (Figures 5J and S30; Supplemental Information). However, this mechanism was very interesting as the electron transfer in different phases would facilitate the charge carrier separation for extended lifetime. Overall, these charge, vibration, and/or phonon excitations could reduce the energy barrier of rate-limiting nitrogen activation and thus the net reaction, which was supported by the apparent activation energy decrease from 57 kJ/mol of thermocatalysis to 47 kJ/mol of photothermal catalysis for ammonia synthesis (Figure 1L). Concurrent with the ν(¹⁵N₂) decrease, ¹⁵NH₁⁻² groups were then gradually hydrogenated to ¹⁵NH₃ by the incorporated H atom(s) of TiO₂ₓHₓ along with increasing irradiation time (Figure 5D). XPS analysis also unfolded that major nitrogen-related species was Ti-bonded N³⁻ (398.3 eV), rather than Fe-bonded N³⁻ (395.7 eV) on TiO₂ₓHₓ/Fe catalyst, confirming the NH₃ formation on TiO₂ₓHₓ (Figures 5K and S28). These Ti-bonded surface N³⁻ species could be easily hydrogenated and then desorbed from the surface after N₂-free H₂ treatment at 495°C, with NH₃ product detected in the outlet gas and N³⁻ species on TiO₂ₓHₓ/Fe sample prominently decreased (Figure S31). These results suggested that the bonded N³⁻ species were catalytic intermediates, instead of stable nitrides for active sites blocking, during the photothermal ammonia synthesis. The corresponding overall turnover number (TON) of atomic H was ~30 on Ti within TiO₂ₓHₓ/Fe (495°C, 1 atm, 15 h), an order of magnitude higher than the maximum coordination capability of Ti to atomic H within TiO₂ₓHₓ (Figure S32), suggesting the recycle of incorporated H atoms on OV after the generated NH₃ was desorbed.

We finally carried out thermodynamic studies to further understand how this TiO₂ₓHₓ/Fe-based dual-temperature-zone catalysis fundamentally promoted the reactivity surpassing thermocatalysis. When increasing the LTD between Fe and TiO₂ₓHₓ by re-introducing light into the thermocatalysis at 495°C, the NH₃ concentrations increased gradually with light intensities and finally approaching to equilibrium-beyond one powered by solely light without additional thermal heating, rendering a monotonic increase along with the light-induced LTD degrees (Figures 6A and 6B). Obviously, LTD elevated the equilibrium limit of ammonia synthesis. We then plotted the thermodynamic equilibrium limits at the two temperatures, hot Fe and cool TiO₂ₓHₓ, in the presence of LTD (using the maximum simulated value of 137°C). Under photothermal ammonia synthesis, if both N₂ activation and NH₃ formation occurred on hot Fe without the involvement of TiO₂ₓHₓ, the equilibrium limit for NH₃ at 495°C would be as low as 758 ppm (T_fe = 547°C) and thus could not result in the 1,939 ppm NH₃ generation, suggesting an additional reaction pathway besides the Fe-solo catalysis on Fe/TiO₂ₓHₓ. If this additional pathway proceeded via the “working-in-tandem” kinetics on Fe and TiO₂ₓHₓ as we proposed in this study, a prominently enhanced equilibrium limit of 3,294 ppm (T_TI = 415°C) would be achieved, approximately 2.7 times the counterpart (1,249 ppm) of thermal catalysis. Only in this way, the NH₃ concentration of 1,939 ppm in our photothermal system was thermodynamically plausible (Figure 6C).

DISCUSSION

Our dual-temperature-zone ammonia synthesis using earth-abundant TiO₂ₓHₓ/Fe catalyst is thermodynamically and kinetically more favorable than thermocatalysis,
and the solar-to-ammonia efficiencies ($\eta_{STA}$) of TiO$_2$–H$_2$/Fe are $3.9 \times 10^{-4}\%$ (1 atm) and $9.2 \times 10^{-3}\%$ (10 atm), 13 and 313 times the base load for the practical use of solar nitrogen fixation ($2.9 \times 10^{-5}\%$), respectively.$^{67}$ If hydrogen gas applied for NH$_3$ synthesis, which is primarily supplied by methane steam reforming at present, can alternatively be sustained through cutting-edge photocatalytic or photovoltaic or electrolytic technologies, the dream of “green” ammonia synthesis may come true.$^{68,69}$ One remaining challenge for this solar ammonia synthesis lies in concentrating the solar light, which, fortunately, has been industrially established and already applied into solar-thermal-electricity technology. The reached temperature is often above 500°C, high enough to meet the temperature criteria (300°C–550°C) of ammonia synthesis.

EXPERIMENTAL PROCEDURES

Solar Ammonia Synthesis

Solar ammonia synthesis was conducted in a designed continuous-flow reactor, which consisted of a plate quartz reaction cell (ambient pressure; cross-sectional area: ~7 cm$^2$) or a quartz-lined steel autoclave embedded with a sapphire window (high pressure; cross-sectional area: ~3 cm$^2$; PerfectLight Inc.) on its top. Typically, 0.2–0.5 g catalyst was placed in the reactor; then, the extra pure (99.99995%) mixture of reaction gas (N$_2$:H$_2$ = 1:3; 480 mL/h) flowed over the catalysts under light irradiation (Xe lamp; PerfectLight Inc.). The input light intensity was pre-measured using an optical power meter (PerfectLight Inc.), and the apparent temperatures of the catalysts were $in situ$ monitored using a thermocouple. The generated NH$_3$ was collected by bubbling the outlet gaseous stream through a 0.05 M H$_2$SO$_4$ solution; then, the steady-state activities were obtained by checking the ammonia content in the solution via (1) cation chromatography (Thermo, USA), (2) Nessler’s reagent, and (3) measuring the pH of the H$_2$SO$_4$ solution before and after the gas bubbling. The difference in pH, converted into reacted proton, was in good agreement with the amount of NH$_3$ produced according to cation chromatography and Nessler’s reagent methods.
The NH₃ yields under different light intensities were recorded under steady states after successively increasing the input power of Xe lamp. Typically, the catalysts were first photothermally heated at 5,004 mW/cm² (corresponding to ~300°C) on stream for 2 h to diminish the possible interference of nitrogen impurity to the detection of catalytic NH₃ yields and then irradiated at seven different light intensities (5,004, 5,670, 6,363, 6,948, 7,920, 9,000, and 10,242 mW/cm²) successively. After each increase of the input light intensity, the ammonia yield would first undergo a transient increase and then decrease with time, which was usually within 30 min after the temperature of the catalyst reached to a constant value, and finally reach to a steady value within the subsequent 1 h that was recorded as the steady-state reactivity.

**STA Efficiency**

$$\eta_{\text{STA}} = 0.5 \ E_a \times \frac{r}{w_{\text{solar}}} \quad \text{(Equation 3)}$$

where $E_a$ is the apparent activation energy of ammonia synthesis (47 kJ/mol), 0.5 represents the energy required by each mole of NH₃, $r$ is the ammonia flux ($r_{\text{atm}} = 166.7$ nmol-N/m²/s, and $r_{\text{O atm}} = 3916.7$ nmol-N/m²/s for TiO₂-xH₂/Fe, the average global nitrogen flux is the base load of $f_{\text{g}} = 12.5$ nmol-N/m²/s)² and $w_{\text{solar}}$ is the solar flux in the whole 200–2,500 nm region (1 kJ/m²/s for sunlight of AM 1.5G).

**In Situ FT-IR Measurements**

DRIFTS measurements were recorded by Nicolet iS50 spectrometer (Thermo, USA) with a liquid nitrogen cooled MCT detector in a designed reaction cell. 32 spectra were co-added with a resolution of 4 cm⁻¹. Powder samples after reaction were pressed to disks (~0.05 g, with a radius of 0.35 cm), subsequently heated to 400°C and maintained for 1 h to remove adsorbed water and organic contaminants at a vacuum level of $8 \times 10^{-7}$ mbar with continuous vacuum pumping, and then treated with H₂ pulse (3.4 kPa) for several times. Next, the samples were evacuated for 1 h at 400°C to remove Fe surface adsorbed hydrogen atoms ($E_{\text{Fe-H}} = 60–65$ kcal/mol; H adatoms desorbed quickly above 200°C) and subsequently cooled down to room temperature in vacuum for the subsequent N₂ exposure. After the N₂ (6.7 kPa) exposure, a steady-state spectrum of nitrogen adsorption was obtained, then light was turned on to in situ investigate the light-facilitated nitrogen activation.

**SUPPLEMENTAL INFORMATION**

Supplemental Information can be found online at https://doi.org/10.1016/j.chempr.2019.07.021.

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AUTHOR CONTRIBUTIONS

L.Z. and J.Z. supervised the project. C.M. designed and carried out the study. C.M., J.W., Y.Z., and S.W. conducted the experiments. H.G. and S.L. measured optical constants of the material. C.M. performed DFT calculation and FDTD simulation. G.Q., J.X., and F.D. performed EPR simulation and analysis. C.M., L.Z., H.L., and J.Z. co-wrote the manuscript. All authors discussed the results and commented on the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests. L.Z. and C.M. have applied for a US patent, which has been granted (no. 10,112,841), and a provisional Chinese patent related to this work.

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REFERENCES AND NOTES


Supplemental Information

Beyond the Thermal Equilibrium Limit of Ammonia Synthesis with Dual Temperature Zone Catalyst Powered by Solar Light

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Content:

Materials and Methods

Figure S1-S32

Table S1 and S2
Materials and Methods

Chemicals and apparatus

FeCl$_3$•6H$_2$O, NaBH$_4$ and ethanol were obtained from Sinopharm chemical reagent Co., Ltd. TiO$_2$ (Degussa P25) was used as received. $^{15}$N$_2$ gas (98.5%) and adonitol were obtained from Shanghai Aladdin Bio-Chem Technology Co., LTD. The Xe lamp (PLS-SXE300), optical power meter and the high-pressure ammonia synthesis apparatus were obtained from PerfectLight Inc.

Synthesis of Fe nanonecklaces

The Fe nanonecklaces were synthesized via reaction between FeCl$_3$ and NaBH$_4$, a modified method from our previous report.$^1$ Typically, 0.25 g of FeCl$_3$•6H$_2$O and 0.5 g of NaBH$_4$ were dissolved in 200 mL and 80 mL deionized water, respectively. Then the NaBH$_4$ solution was added into the FeCl$_3$ solution dropwise, with a rate of 4 mL/min. Plenty H$_2$ bubbles were generated upon the addition of NaBH$_4$ into the FeCl$_3$ solution, accompanying by black precipitates emerging and migrating with the bubbles. These black precipitates were collected, washed with 1) consecutive deionized water and ethanol for several times, then 2) 0.05 M ammonia solution to remove residual Cl$,^-$ followed by 3) consecutive deionized water and ethanol for several times to remove the residual ions via suction filtration using the Büchner funnel, and finally dried at extra pure (99.99995%) nitrogen atmosphere under infrared lamp ($T_{Fe}$ $\approx$ 90 °C) for later use.

Synthesis of TiO$_{2-x}$H$_y$

The TiO$_{2-x}$H$_y$ was prepared from TiO$_2$ (Degussa P25) using a modified solid NaBH$_4$ reduction and fast cooling method from our previous method.$^{17}$ Briefly, 1 g of TiO$_2$ was thoroughly ground (in an
agate mortar; additional pressure: 83-166 kPa; 20 min) with 2 g of NaBH₄ to form a white mixture, then the mixture was transferred to a 10 mL crucible with cap, followed by heating to 420 °C for 0.5 h in a muffle furnace. Subsequently, the crucible was taken out to air from the furnace (420 °C) for fast cooling. The resulting black powders were the mixture of TiO₂₋ₓHy, NaBH₄ and the decomposition products of NaBH₄, and they could react vigorously with water (with sparks) to generate plenty H₂ bubbles (while the white mixture of TiO₂ and NaBH₄ before calcination react sluggishly with H₂O generating a few H₂ bubbles). To obtain the pure TiO₂₋ₓHy, the black powders should be washed with deionized water and ethanol for many times until no bubbles were generated.

Synthesis of titanium oxides anchored Fe nanonecklaces

These catalysts were synthesized via reaction between FeCl₃ and NaBH₄ in the presence of titanium oxides (TiO₂ or TiO₂₋ₓHy). Typically, 0.25 g of FeCl₃•6H₂O and 0.5 g of NaBH₄ were dissolved in 200 mL and 80 mL deionized water, respectively, then certain amount of titanium oxides were dispersed into the NaBH₄ solution under ultrasonic stirring. Specifically, for the synthesis of TiO₂₋ₓHy/Fe, the black powders obtained after the solid reduction of TiO₂ by NaBH₄ under 420 °C, which were the mixture of TiO₂₋ₓHy and decomposition products of NaBH₄, instead of the pure TiO₂₋ₓHy samples, were added into the NaBH₄ solution. Subsequently, the black NaBH₄-titanium oxides solution was added into the FeCl₃ solution dropwise, with a rate of 4 mL/min, to obtain black precipitates. At last, these black precipitates were treated with similar post-procedures used in the synthesis of Fe nanonecklaces. Tuning the dosage of TiO₂₋ₓHy-containing mixture (TiO₂₋ₓHy and decomposition products of NaBH₄) from 0.3 g, 0.6 g, 1.2 g to 2.4 g, the resulting TiO₂₋ₓHy/Fe
samples demonstrated the Ti/Fe ratio from 0.12, 0.27, 0.54 to 2.15, respectively, suggesting that only 10-30% of TiO$_2$-H$_y$ particles were anchored onto the surface of Fe nanonecklaces and the resting free-standing particles were removed during the washing and suction filtering. For the synthesis of TiO$_2$/Fe, 0.2 g TiO$_2$ was used and the resulting sample demonstrated a Ti/Fe ratio of 0.35.

Materials characterization

Thermal conductivity measurement

The thermal conductivity of TiO$_{2-x}$H$_y$ was measured by a hot disk thermal constant analyzer (Hot Disk TPS 2500S, Hot Disk AB Company, Sweden) with a flat sensor, which is made of a spiral nickel wire probe insulated between two layers of Kapton. The sensor acted as the heat source and temperature monitor simultaneously, which was placed between the two flattened TiO$_{2-x}$H$_y$ specimens to form a sandwich structure and then measured the thermal conductivity using a transient plane source technique. The measured thermal conductivity of TiO$_{2-x}$H$_y$ was 0.18 W/mK (at a probe depth of 2.25 mm).

Optical constants ($n, k$ value) measurement

At first, the TiO$_{2-x}$H$_y$ film with thickness of ~120 nm was manufactured by spin-coating the TiO$_{2-x}$H$_y$-ethanol solution on the monocrystalline silicon wafer. Subsequently, dual rotating-compensator Mueller matrix ellipsometer (ME-L ellipsometer, Wuhan Eoptics Technology Co., Wuhan, China) was used to collect the ellipsometric data of the thin film samples at the reflection measurement mode with the incident angle set at 65°. At last, the optical constants,
including the refractive index $n$ and the extinction coefficient $k$, were determined by performing a model-based fitting analysis on the measured ellipsometric spectral data.

The powder X-ray diffraction (XRD) characterizations

The XRD patterns were recorded on a Rigaku D/MAX-RB diffractometer with monochromatized Cu Kα radiation ($\lambda = 0.15418$ nm) with a scan rate of ~2.04 degrees/min ($2\theta$).

Electron paramagnetic resonance (EPR) measurements

EPR spectra were conducted on a JEOL EMX EPR Spectrometer (Billerica, MA) with powder samples. The working frequency and power were 9153.202 MHz and 5.000 mW, and the center field was set at 326.000 mT with an accumulation number of 4 for each spectrum.

$^1$H nuclear magnetic resonance (NMR) measurements

$^1$H MAS NMR experiments were carried out at 9.39 T on a Bruker AVANCE III 400 WB spectrometer, using a 4 mm HX double-resonance probe. The resonance frequencies for $^1$H channel was 400.18 MHz. The dried and finely powdered samples were packed in the ZrO$_2$ rotor closed with Kel-F cap. Single-pulse excitation $^1$H MAS experiments were recorded for each sample after 32 scans by using a $\pi/2$ pulse width of 4.6 $\mu$s, a repetition time of 6 s, and a magic angle spinning rate of 12 kHz. The $^1$H chemical shift was referenced to adamantane ($C_{10}H_{16}$) at 1.91 ppm, as the second reference to tetramethylsilane (TMS).

Scanning transmission electron microscopy (STEM) characterizations
Electron microscopy characterizations were performed on a spherical aberration corrected transmission electron microscope operated at 200 kV (Titan™ G2 80-200, FEI, The Netherlands). The system is equipped with a FEI X-FEG high-brightness Schottky field emission source (brightness $1.8 \times 10^9$ A/cm$^2$ srad at 200 kV, beam current of 1300 pA in a 0.2 nm spot), high-angle annular dark-field (HAADF) and bright-field (BF) detectors, and the FEI ChemiSTEM system. HAADF images were acquired at a dwell time of 29.0 μs per pixel. XEDS analysis were achieved with the FEI ChemiSTEM system operated at a beam current of $\sim 0.8$ nA and a probe size of $\sim 0.2$ nm at 200 kV. Each spectrum image of 512 × 512 pixels was acquired over a 10 min duration. To minimize effects of specimen drift, a drift-correction mode was used during the acquisition of XEDS maps.

**The diffuse reflection spectra**

UV-Vis-NIR spectra of the samples were obtained using a UV-3600 plus spectrophotometer (Shimadzu, Japan) from 300 nm to 2500 nm with pressed powder samples.

**X-ray absorption spectroscopy (XAS) measurements**

The reacted TiO$_{2-x}$H$_x$/Fe samples were sealed with Kapton tape in glove box for XAS measurements. The extended X-ray absorption fine structure (EXAFS) spectra were recorded at the beamline 1W1B of Beijing Synchrotron Radiation Facility, Institute of High Energy Physics, Chinese Academy of Sciences. The spectra were processed using Athena (Demeter, 0.9.24) with standard procedures.
Mössbauer measurements

TiO$_2$-xH$_y$/Fe samples of the same batch were photothermally heated to 495 ºC (light intensity: 10242 mW/cm$^2$) for 5 h in N$_2$/3H$_2$ and Ar/3H$_2$ gas, respectively, then the reacted samples were sealed with Kapton tape in glove box for Mössbauer measurements, which were performed at room temperature using a conventional spectrometer (Germany, Wissel MS-500) in transmission geometry with constant acceleration mode. A $^{57}$Co(Rh) source with activity of 25 mCi was used. The velocity calibration was done with a room temperature α-Fe absorber. A velocity offset mode was adopted for high resolution, and the two outer most metallic-α-Fe(0) peaks (-5.31 mm s$^{-1}$ and 5.22 mm s$^{-1}$ at the traditional mode) were simultaneously scanned. The spectra were fitted by the software Recoil using Lorentzian Multiplet Analysis.$^3$

X-ray photoelectron spectroscopy (XPS) measurements

XPS data were obtained using a Thermo Scientific Escalab 250Xi. All binding energies were calibrated with C$_{1s}$ = 284.6 eV and all the spectra were smoothed with a Savitzky-Golay function for presentation.

FT-IR measurements

Temperature-programmed transformation of adonitol in an in-situ FT-IR reaction cell (TP-FT-IR) were conducted on Nicolet iS50 spectrometer (Thermo, USA). 32 spectra were co-added with a resolution of 4 cm$^{-1}$. Powder catalysts were ultrasonic dispersed into the adonitol-ethanol solution (catalyst : adonitol = 5 : 1; mol/mol), then evaporated and dried under vacuum at 40 °C in a rotary evaporator to obtain the catalyst-adonitol powder samples, which were pressed to disks to form
specimens (~0.05 g, with a radius of 0.35 cm). These specimens were placed in Harrick in-situ reaction cell of the FT-IR spectrometer, first illuminated with solar light of certain intensity to reach a steady state (steady temperature) and then thermally heated under a programmed temperature (heating rate: 10 K/min), purging with Ar (30 mL/min). During the process, the consecutive FT-IR spectra were auto-collected by the software of Macros\Basic and OMNIC, and the temperature programs were controlled by the software of Watlow EZ-ZONE CONFIGURATOR.

Attenuated total reflectance FT-IR measurements (ATR-IR) were taken on a Nicolet iS50 (Thermo, USA) with a liquid nitrogen cooled MCT detector. The ATR cell used was a Smart iTR single reflection cell equipped with a diamond internal reflection element (IRE) (refractive index \(n_{\text{diamond}} = 2.4\), incidence angle \(r = 42^\circ\)). Data collection and analysis were carried out with the OMNIC software package. In a typical measurement 64 scans were averaged with a 4 cm\(^{-1}\) resolution. All powder samples were clamped down onto the diamond crystal by means of a manually-tightened pressure tower.

Diffuse reflectance infrared Fourier transform spectra (DRIFTS) were recorded by Nicolet iS50 spectrometer (Thermo, USA) with a liquid nitrogen cooled MCT detector in a designed reaction cell. 32 spectra were co-added with a resolution of 4 cm\(^{-1}\). Powder samples after reaction were pressed to disks (~0.05 g, with a radius of 0.35 cm), subsequently heated to 400 °C and maintained for 1 h to remove adsorbed water and organic contaminants at a vacuum level of \(8 \times 10^{-7}\) mbar with continuous vacuum pumping, and then treated with H\(_2\) pulse (3.4 kPa) for several times. Next, the samples were evacuated for 1 h at 400 °C to remove Fe surface adsorbed hydrogen atoms (\(E_{\text{Fe-H}} = 60-65\) kcal/mol; H adatoms desorbed quickly above 200 °C)\(^7\) and subsequently cooled down to room temperature in vacuum for the subsequent N\(_2\) exposure. After the N\(_2\) (6.7 kPa) exposure, a
steady-state spectrum of nitrogen adsorption was obtained, then light was turned on to in-situ investigate the light facilitated nitrogen activation.

**Surface enhanced Raman scattering (SERS) characterizations**

Small amount of the powder sample was first placed on a monocrystalline silicon wafer with densely deposited Au film (50 nm in thickness; SERS substrate) to form specimens. Then the Raman spectra of these specimens were obtained using a confocal laser micro-Raman spectrometer (Thermo DXR Microscope, USA) with a 532 nm (power: 8 mW, acquisition time: 1 s).

For the temperature-sensing SERS, the catalyst was ultrasonic dispersed into the adonitol-ethanol solution (catalyst : adonitol = 5 : 1; mol/mol), then evaporated and dried under vacuum at 40 °C in a rotary evaporator to obtain the catalyst-adonitol powder sample. The obtained sample were re-dispersed in ethanol and dip-coated onto SERS substrate, dried under IR lamp with Ar purging to form specimen. The specimen was placed in Harrick in-situ reaction cell, first thermally heated under a programmed temperature (heating rate: 15 K/min) to obtain the temperature-relative intensity [Fe (296 cm⁻¹; Fe₂O₃-δ), TiO₂-xHy (158 cm⁻¹; TiO₂-xHy) and adonitol (1337 cm⁻¹; -OH and -CH₂)] relations with a purging with Ar (30 mL/min). A 780 nm laser was applied to trigger prominent Fe-plasmonic heating and to match the FDTD simulation (726 nm), despite the enhancement in Raman signal of the SERS substrate would be reduced in this way. The microscope objective is of 50× magnification with a numerical aperture of 0.5, resulting in a Raman spot size of about 1.9 μm. The laser power was 500 μW and the acquisition time was 10 s for the consecutive temperature-dependent SERS measurements to minimum the laser heating effect, while in the SERS mapping experiments, the laser, which was used to trigger Fe-plasmonic heating and
Raman scattering simultaneously, was tuned to a power as large as 15 mW and an acquisition time of 50 s.

**FDTD simulations**

Simulations were performed using the commercial software (Lumerical, Canada) of *FDTD Solutions* (8.15.736) for plasmonic near-field maps and *Device-Heat* (5.0.736) for temperature profiles. Typically, a plasmonic metal nanostructure absorbs light, triggering the collective oscillation of conduction electrons in the metal, and then delivers light-to-heat transformation as the Joule heat generated when light activated electrons pass through the metal with ohmic resistance. The optical absorption and generated plasmonic volume power intensity could be calculated by *FDTD Solutions* and was subsequently used as heat input for the temperature simulation by *Device-Heat*. Optical constants, $n$ and $k$, of Fe were taken from literature,$^\text{S4}$ while those of TiO$_{2-x}$H$_y$ were measured using a dual rotating-compensator Mueller matrix ellipsometer.

**DFT theoretical calculation**

All calculations were performed using the first-principles density of functional theory (DFT) calculations with the exchange-correlation energy function of GGA-RPBE.$^8$ The calculations were performed using the CASTEP package$^{55}$ in which the ultrasoft pseudopotentials or norm conserving pseudopotentials was employed for all the atoms with corresponding accuracy set as *coarse* or *ultrafine* (for the vibration calculation only). A (2×3) Fe (111) supercell with a slab thickness of six atoms and a vacuum thickness being larger than 13 Å was used for Fe model, whose spin was set as “polarized” and “used a formal spin as initial”. A (2×2) Anatase-TiO$_2$ (001) supercell with seven
Ti-O layers and a vacuum thickness being larger than 13 Å was used for TiO$_2$ model, TiO$_{2-x}$ model was obtained by subtracting a surface lattice oxygen, and TiO$_{2-x}$H$_y$ model was obtained by replacing a surface oxygen atom of TiO$_2$ model by hydrogen.$^{41}$ After considering the lattice match, TiO$_{2-x}$/Fe model and TiO$_{2-x}$H$_y$/Fe model were obtained by covering the surface of (2×3) Fe (111) with a layer of non-hydrogenated and hydrogenated Ti-O atoms (with oxygen vacancy), respectively. All the models were first fully relaxed via geometry optimization and then applied for the energy calculation. All the transitional state (TS) search were conducted via a complete LST/QST protocol (the max number of QST step was set at 20) with 20 fragments from the initial state to the final state.

The adsorption energies of adsorbates were defined as

$$E_{ad}(m) = E_{m-s} - E_s - E_m$$

where $m$ represents molecular adsorbate and $s$ represents the surface of Fe, TiO$_{2-x}$H$_y$ or TiO$_{2-x}$H$_y$/Fe.
Supplementary figures and texts.

Figure S1. Schematic synthesis of TiO$_{2-x}$H$_y$/Fe catalyst via the facile in-situ reduction method. The black and yellow colors represented the experimentally observed colors of solutions.

Figure S2. (A) Low temperature (100 K) EPR spectra of TiO$_{2-x}$H$_y$ (purple) and TiO$_2$ (dark grey), and simulated spectra of OV-Ti$^{3+}$-H (light grey) and OV-Ti$^{3+}$ (yellowish-brown). OV, oxygen vacancy within titanium oxide, $g = 2.001$; Ti$^{3+}$, coordinatively unsaturated Ti besides OV, $1.925 \leq g \leq 1.990$; OV-(Ti$^{3+}$)-H, oxygen vacancy with incorporated H atoms, the multiplet across $g = 2.001$ with a hyperfine splitting constant $a_H = 7.7$ gauss. The match of simulated OV-Ti$^{3+}$-H with experimental TiO$_{2-x}$H$_y$ spectra represented that one oxygen vacancy of TiO$_{2-x}$H$_y$ was coupled by eight equivalent H atoms. Given one oxygen vacancy was accompanied by two adjacent Ti$^{3+}$ (two equivalent Ti/e$^-$), this means one Ti$^{3+}$ was coupled with four equivalent H atoms, which might be
explained by a configuration of all four surface O atoms around Ti were abstracted to form oxygen
vacancies and thus the excess electron could be coupled with four equivalent H atoms. (B) $^1$H-NMR
spectra of TiO$_{2-x}$H$_y$ and TiO$_2$. TiO$_{2-x}$H$_y$ possessed more oxygen vacancies and additional Ti-H
species in comparison with that of TiO$_2$.\textsuperscript{40}

Figure S3. (A) XRD patterns and (B) surface-enhanced Raman scattering spectra of TiO$_2$, TiO$_{2-x}$H$_y$,
Fe nanonecklace and TiO$_{2-x}$H$_y$/Fe.

Figure S4. SEM images of TiO$_2$ (A) and TiO$_{2-x}$H$_y$ (B). No obvious change in morphology was
observed after the TiO$_2$ undergoing the reduction and hydrogenation to form TiO$_{2-x}$H$_y$, both of
which were consisted of nanoparticles with average diameter of 25 nm.
Figure S5. (A) HAADF image and (B) BF image of TiO$_{2-x}$H$_y$ nanoparticles anchored Fe nanonecklace. Arrows indicated the anchored TiO$_{2-x}$H$_y$ nanoparticles on the surface of Fe nanonecklace as the low Z-contrast between Ti (element 22) and Fe (element 26).

Figure S6. (A-C) STEM image of Fe nanonecklaces. Fe nanonecklaces displayed the typical Fe@Fe$_2$O$_{3-δ}$ core-shell structure without nanoparticles anchored on the surface (B and C).$^{S1}$
Figure S7. (A) Digital photo of the ambient-pressure device for photothermal temperature measurement as well as catalytic ammonia synthesis. (B) Schematic device. (C) The temperature versus time plots were recorded for samples of the same weight on irradiation by a Xe lamp with light intensity of 5004 mW/cm².

Figure S8. The dependence of initial reactivity to the Ti/Fe mole ratio within TiO$_{2-x}$H$_y$/Fe catalyst at 495 °C under illumination. Inset was the on-stream activity of TiO$_{2-x}$H$_y$/Fe catalyst with Ti : Fe of 0.27 : 1 and 0.12 : 1. The optimal catalyst with Ti/Fe of 0.27, which demonstrated both high NH$_3$ yield and satisfactory stability, was the TiO$_{2-x}$H$_y$/Fe catalyst as mentioned in the main text. The mole ratio (Ti/Fe) of different catalysts were determined by XPS analysis.
Figure S9. (A-D) SEM images of Fe nanonecklaces, TiO$_2$-xH$_y$/Fe, TiO$_2$/Fe and commercial Fe catalyst before (A, C, E and G) and after (B, D, F and H) the reaction under light intensity from 5004 mW/cm$^2$ to 10242 mW/cm$^2$, demonstrating the densely anchored TiO$_2$-xH$_y$ nanoparticles not only forming high-density spots with LTD, but also stabilizing Fe nanonecklaces during the high-temperature reaction.

Figure S10. SEM images of TiO$_2$-xH$_y$/Fe after (A) 2 h, (B) 4 h, (C) 6 h, (D) 8 h and (E)10 h photothermal reaction under 495 ºC. The nanonecklace structure of TiO$_2$-xH$_y$/Fe remained during reaction only with partially enlarged size of the constituting Fe nanospheres.
Figure S11. (A) Schematic illustration and (B) digital images of the continuous-flow high-pressure experimental laboratory rig applied within this work for the solar ammonia synthesis.

Figure S12. Arrhenius plots of TiO$_2$-xHy/Fe and commercial Fe catalysts in the temperature range 581-787 K under solar (photothermal) catalysis or thermal catalysis.
Figure S13. (A) Schematic models of \( \text{TiO}_2\cdot\text{H}_y \) nanoparticles anchored Fe nanonecklace for FDTD simulation. From “1 layer” (left), “2 layers” (middle) to “\( n \) layers” (right) model, the thickness of the support (Fe) was gradually increased to mimic the stacked powder catalyst (on quartz glass; \( \text{SiO}_2 \)) consist of Fe nanonecklaces in the practical conditions. Specifically, the morphology of support Fe in “\( n \) layers” model was simplified as rectangle because it did not interact with light but only transferred heat which was insensitive to morphology (nanonecklace or rectangle). (B) The \( n \), \( k \) value of \( \text{TiO}_2\cdot\text{H}_y \). Steady-state local temperature distribution of “1 layer” (C), “2 layers” (D) and “\( n \) layers” (E) model due to 726 nm light excitation of Fe/\( \text{TiO}_2\cdot\text{H}_y \). Apparently, the “\( n \) layers” model was close to the practical catalyst and the local temperature difference (LTD) between Fe and \( \text{TiO}_2\cdot\text{H}_y \) was approximately \( 1/4 \) of \( T_{\text{Fe}} \). Although the FDTD method would give a precise prediction of the relative temperature distribution in different regions of a nanostructure, to correlate the simulated temperature and practical temperature, a calibration of temperature between them was
usually needed. This was because a practical system suffered inevitable heat loss via means such as parasitic radiative losses and re-emissive losses, and usually resulted in much lower practical temperature that was up to several orders of magnitude less than the simulated temperature. (F) The LTD/T_{Fe} as a function of the thickness of support Fe (the total thickness of Fe-SiO_{2} support was set as 60 μm to simulate the practical conditions of TiO_{2-x}H_{y}/Fe supported on quartz glass). (G) Temperature calibration. The LTD was calibrated by three steps: 1) Calibrating the simulated photothermal temperature of Fe (T_{Fe}; Thickness of Fe support: 60 μm) with that measured experimentally via thermocouple to calculate the correction coefficients, 2) Calculating the simulated LTD between Fe and TiO_{2-x}H_{y} via \sim 1/4 T_{Fe} and calibrated via the correction coefficients, and 3) meanwhile comparing the calibrated LTD (simulated) with the differential photothermal temperature between pure Fe nanonecklaces and pure TiO_{2-x}H_{y} nanoparticles (T_{Fe} - T_{Ti}).

**Figure S14.** Size effect of Fe plasmonic heating. (A, B) Enhancement in electric field intensity (\mid E/E_{0} \mid^{2}), (C) calculated normalized extinction spectra (C_{ext}/C_{geo}) of Fe nanonecklace, (D, E) volume power density, and (F-H) temperature distribution on the diameter of constituting Fe nanosphere.
Figure S15. Experimental FT-IR and Raman spectra of TiO$_2$-xH$_{y}$/Fe surface adsorbed adonitol and the corresponding calculated spectra. The signal of 2934 cm$^{-1}$ was assigned to the stretching vibration of -CH, while 1421 cm$^{-1}$, 1337 cm$^{-1}$ and 1122 cm$^{-1}$ represented the (-CH + -OH) signals. Insets were the calculated configurations corresponding to different IR vibrations, with green arrows indicating the movements of atoms.

Figure S16. (A–D) Consecutive FT-IR spectra of the TiO$_2$-xH$_{y}$/Fe-adonitol plotted against the linear temperature program under illumination with light intensity of 5004 mW/cm$^2$ (A), 6363 mW/cm$^2$ (B), 7920 mW/cm$^2$ (C) and 10242 mW/cm$^2$ (D).
**Figure S17.** Consecutive SERS spectra of the TiO$_{2-x}$H$_y$/Fe-adonitol plotted against the linear temperature program.

**Figure S18.** (A) The device based FDTD heat simulation that TiO$_{2-x}$H$_y$/Fe was placed on a rectangle iron with thickness of 60 μm. (B) The maximum temperature of Fe nanonecklace as a function of the thickness of support iron. The result demonstrated the maximum local temperature of Fe decreased with the increased thermal conductivity of support (such as increasing the thickness of Fe support) but the LTD/T$_{Fe}$ remained, supporting the much lower photo-induced apparent catalyst temperature of TiO$_{2-x}$H$_y$/Fe (T$_{Fe-Ti}$) during TP-FT-IR measurement.
Figure S19. SERS mapping coupled FDTD simulation for spatial temperature mapping of TiO$_{2-x}$H$_y$/Fe. (A) TiO$_{2-x}$H$_y$ SERS mapping and (B) corresponding inverse-color image. (C) Fe SERS mapping. (D) The mixing image of B and C. (E) Adonitol SERS mapping and (F) corresponding inverse-color image. (G) Large scale SEM image of reacted TiO$_{2-x}$H$_y$/Fe. (H) FDTD simulation analysis of the similar temperature of Fe nanospheres in the nanonecklace. The scale bars of A-G were set to the same. According to the comparison of D and F, the spatial LTD between Fe and TiO$_{2-x}$H$_y$ could be clearly identified with a resolution ~ 400 nm. This distance was within the range of several Fe nanospheres (2 for $d = 240$ nm and $d = 360$ nm, and 4 for $d = 120$ nm as evidenced by the SEM image), of which the temperatures were very close because the high thermal conductivity of Fe (80 W/mK), supporting the feasibility of SERS mapping to indicate LTD between vicinal TiO$_{2-x}$H$_y$ and Fe.
Figure S20. (A) Anatase TiO$_2$ of the {001} facet (side view), (B) the {111} facet of Fe (top view), and (C, D) the TiO$_2$/Fe model obtained from (001)-TiO$_2$ and (111)-Fe (C, top view; D, side view). The Fe (111) facet was adopted because it was widely accepted to be responsible for highly-reactive “ammonia iron” catalysts, and the anatase-TiO$_2$ (001) facet with oxygen vacancy incorporated H atom(s) was selected because of its rationality for hydrogenated TiO$_2$ according to Mao et al.’s DFT calculations, and also because of the lattice match between Fe (111) and the Ti-O (001) layer.

Figure S21. (A, B) Top view (A) and side view (B) of the fully relaxed model of TiO$_{2-x}$H$_y$/Fe ($y = 1$).
Figure S22. (A) The primitive cell of \( bcc \) Fe with the labeled \{111\} facet. (B) Topological structure analysis of Fe nanosphere with considerable percent of \{111\} facet exposed on the surface (labeled as yellow) of Fe nanosphere by considering the symmetry of its BravaisLattice property.
Table:

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<th>Cat. + ¹N₂</th>
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**Figure S23.** Nitrogen activation with corresponding N-N bond lengths on hydrogenated oxygen vacancy of TiO_{2-x}H_y (Ti-H), pure Fe (Fe), the Ti sites within TiO_{2-x}H_y/Fe (Ti-H-Fe), and oxygen vacancy of TiO_{2-x} (Ti-OV), TiO_{2-x}/Fe (Ti-OV-Fe) and interface of TiO_{2-x}/Fe (Ti-OV-Fe-interface). A full-path N₂ activation on Fe (111) was “free N₂ → γ (end-on adsorbed N₂) → δ (end-on adsorbed N₂) → α (side-on adsorbed N₂) → α’ (side-on adsorbed N₂) → β (2*N)”, here to simplify this well-documented process, we only calculated the most important “free N₂ → γ → α → α’ → β.”
(2*N)” steps which determined the entropy and TS position of the reaction.

**Figure S24.** Free energy diagram of nitrogen activation on oxygen vacancy of TiO$_{2-x}$ (Ti-OV), TiO$_{2-x}$/Fe (Ti-OV-Fe) and the interface of TiO$_{2-x}$/Fe (Ti-OV-Fe-interface) (A) and oxygen vacancy of Fe$_2$O$_3$ (B).

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**Figure S25.** Nitrogen hydrogenation process on Ti sites of TiO$_{2-x}$H$_y$/Fe with two (Fe-Ti-H$_2$) and three (Fe-Ti-H$_3$) hydrogen atoms on the oxygen vacancy of TiO$_{2-x}$H$_y$. 
**Figure S26.** Schematic and energy diagram of NH$_3$ immigration on the surface of TiO$_{2-x}$H$_y$ surface via a “OV-Ti-OV” pathway. The accessible activation energy of 1.28 eV indicated the favorable NH$_3$ transfer on TiO$_{2-x}$H$_y$ surface after being assembled on OV.

**Figure S27.** Energy diagram for H$_2$ dissociation on Fe or OV and *H transfer on Fe within TiO$_{2-x}$H$_y$/Fe catalyst. The energies for 2*H after H$_2$ dissociation and *H for initial immigration were aligned to the same.
**Figure S28.** (A) N1s XPS spectra of the commercial TiO2 (Degussa P25). Dots represented the raw data and the red line was the smoothed data using a Savitzky-Golay function. The N1s bonding energy of $N^{3-}$ impurities in well-crystalline TiO2 was much close to that in TiN (~397 eV), while that of O-deficient partially disordered TiO$_{2-x}$H$_{y}$ was slightly larger possibly because the significantly altered chemical environment between TiO2 and TiO$_{2-x}$H$_{y}$ and the decreased O fraction of TiO2 would shift the peak of N1s to lower binding energies.$^{65}$ (B) The origin analysis of N contaminants within TiO$_{2-x}$H$_{y}$ sample. (C) The fully relaxed model of NH$_{3}$ adsorbed on the oxygen vacancy (VO) of TiO$_{2-x}$H$_{y}$, and the corresponding (Ti)-N-H vibrations bands (IR) at 3372 and 3431 cm$^{-1}$.

**Figure S29.** Comparison of the N$_{2}$-adsorption spectra with the baseline to exclude the interference of baseline noise to the assignments of N-species (2282-2390 cm$^{-1}$: CO$_2$ vibration bands).
Figure S30. Photocurrent responses of the TiO$_2$ and TiO$_{2-x}$H$_y$ in 0.5 M Na$_2$SO$_4$ aqueous solutions under irradiation. The cell consists of a TiO$_2$ or TiO$_{2-x}$H$_y$ photoanode, Pt counter electrode and saturated calomel electrode (SCE) reference electrode. The electrolyte is 0.5 m Na$_2$SO$_4$ aqueous solution.

The inhibited charge separation of TiO$_{2-x}$H$_y$. The photon-to-electron transformation of amorphous TiO$_{2-x}$H$_y$, which possessed broad-spectrum light adsorption in the whole UV-Vis-NIR region of sunlight, was largely reduced compared with that of crystalline TiO$_2$ (two orders of magnitude; Figure S30). Many literatures in photocatalysis reported that amorphous TiO$_2$ demonstrated lower reactivity than that of crystalline anatase$^{6,7}$, and too much oxygen vacancy, especially the bulk one, could act as recombination center for charge carriers$^{8}$. These two factors, largely disordered lattice and too much bulk oxygen vacancies, might be the reason for the inhibited charge transfer and separation of TiO$_{2-x}$H$_y$. 

Figure S31. (A) NH₃ generation during the post-H₂ treatment of reacted TiO₂₋ₓHₓ/Fe at 495 °C under illumination via an on-stream reaction gas alteration from N₂/3H₂ to Ar/3H₂. (B) Comparison of N₁s XPS spectra of reacted TiO₂₋ₓHₓ/Fe and that after post-H₂ treatment. The Ti-N³⁻ peak almost disappeared and only the Ti-N₂ peak remained after the post-H₂ treatment, indicating the easy hydrogenation of adsorbed NHₓ on TiO₂₋ₓHₓ of TiO₂₋ₓHₓ/Fe.

Figure S32. (A) The estimate of surface-Ti density (The oxygen atoms in round circles represent the possible sites for crafting oxygen vacancies which are the active centers for ammonia generation), and (B) the overall number of reacted atomic H during the 15 h reaction. The 3 in the formula represents one molecular NH₃ originating from 3 atomic H atoms, and the above term is the number of obtained molecular NH₃, the below term is the number of surface Ti (3.3*10¹⁹;
calculated using a surface density method\textsuperscript{39}) within the TiO$_{2-x}$H$_y$/Fe catalyst. Obviously, the estimated surface Ti is a maximum of assumption because this represents an 8\% exposure of surface Ti which is too large for a 25 nm TiO$_{2-x}$H$_y$ nanoparticle with total Ti amount of merely 4.2*10\textsuperscript{20}, thus the calculated TON$_H$ is a minimum of assumption which strongly support the recycle of incorporated H atoms of TiO$_{2-x}$H$_y$. Among MH$_n$ (M: metal) compounds, TiH$_4$ is the only tetrahydride with laboratory data,\textsuperscript{310} so we conclude that the maximum coordinate capability of Ti to H atoms is 4, while this value would reduce to 3 for Ti of TiO$_{2-x}$H$_y$ because at least one coordinate site would be occupied by oxygen atom (assuming all the adjacent four in-plane O atoms of Ti are abstracted to form oxygen vacancies and only the subsurface O atom below the Ti atom remains, in fact, we experimentally found that only two H incorporated to a Ti according to the EPR result, so the coordinate capability of 3 H/Ti is a maximum of assumption).
Table S1. Comparison of the composition, surface area and morphology of several catalysts.

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¹Determined from the XPS results.
²Obtained from SEM images. The average size was determined by analyzing ~200 particles.
³The commercial industry Fe catalyst (Catalyst Co., Ltd., Zhejiang University of Technology) for ammonia synthesis was milled before use.
⁴The average particle size of commercial TiO₂ (P25) was 25 nm.

Table S2. Nitrogen adsorption induced surface construction to C₇ sites as revealed by the decrease in full width at half maximum (FWHM) of the α-Fe(0) two peaks in Mössbauer spectra.

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