Plasmon-enabled N₂ photofixation on partially reduced Ti₃C₂ MXene†

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Benefiting from the superior conductivity, rich surface chemistry and tunable bandgap, Ti₃C₂ MXene has become a frontier cocatalyst material for boosting the efficiency of semiconductor photocatalysts. It has been theoretically predicted to be an ideal material for N₂ fixation. However, the realization of N₂ photofixation with Ti₃C₂ as a host photocatalyst has so far remained experimentally challenging. Herein, we report on a sandwich-like plasmon- and an MXene-based photocatalyst made of Au nanospheres and layered Ti₃C₂, and demonstrate its efficient N₂ photofixation in pure water under ambient conditions. The abundant low-valence Ti (Ti⁴⁺) sites in partially reduced Ti₃C₂ (r-Ti₃C₂) produced by surface engineering through H₂ thermal reduction effectively capture and activate N₂, while Au nanospheres offer plasmonic hot electrons to reduce the activated N₂ into NH₃. The Ti(4⁺) active sites and plasmon-generated hot electrons work in tandem to endow r-Ti₃C₂/Au with remarkably enhanced N₂ photofixation activity. Importantly, r-Ti₃C₂/Au exhibits ultra-high selectivity without the occurrence of competing H₂ evolution. This work opens up a promising route for the rational design of efficient MXene-based photocatalysts.

Introduction

Nitrogen is a requisite nutrient for all organisms on the Earth. Although N₂ occupies 78 vol% of the atmosphere, its efficient utilization by organisms is greatly hindered because of the strong N≡N bond (945 kJ mol⁻¹). Atmospheric N₂ is continuously fixed into biologically usable forms of nitrogen, such as NH₃ and NO₃⁻. At the same time, the fixed forms of nitrogen are also continuously converted back to N₂ in nature, constituting a giant nitrogen cycle (Fig. S1†). In this cycle, synthesized NH₃ not only is used as an indispensable chemical feedstock but also can act as a potential hydrogen carrier owing to its high hydrogen density (17.6 wt%) and low liquefying pressure (∼8 atm). In addition, the obtained H₂ and O₂ can be utilized in fuel cells. As a result, the realization of such a nitrogen cycle will be meaningful in developing sustainable clean energy and relieving environmental pollution. The NH₃ synthesis is a critical step in the cycle. Traditionally, NH₃ is produced through the industrial Haber–Bosch process. However, this process requires high temperatures (>300 °C) and high pressures (>100 atm) with a massive energy consumption and a huge amount of CO₂ emission. Because of the energy input and carbon footprint, it is highly desired to explore a promising artificial nitrogen fixation strategy under benign conditions for a sustainable, green and safe NH₃ production.

Nitrogen photofixation offers an approach for achieving the energy-saving and environmentally friendly NH₃ synthesis under ambient conditions with renewable solar energy as the driving force. In N₂ photofixation, H₂ is replaced by H₂O as a reducing agent. N₂ and 3H₂O are converted to 2NH₃ and 1.5O₂. The key is to design an efficient photocatalyst. Two-dimensional (2D) photocatalysts exhibit unique merits in solar-to-chemical energy conversion. MXenes, a family of 2D layered transition metal carbides, nitrides or carbonitrides, have aroused much interest since the first report in 2011. Benefiting from the metallic conductivity, abundant surface terminal groups, large surface-to-volume ratio, excellent hydrophilic and ion transport properties, MXenes have been explored in diverse fields. Ti₃C₂, the first reported MXene, possesses several unique characteristics: (i) Its high conductivity enables excellent charge transfer kinetics, favoring the rapid migration and efficient separation of photogenerated electrons and holes; (ii) abundant exposed metal sites offer many active sites for catalysis; (iii) adjustable terminal groups (OH, O, F, etc.) bring a tunable bandgap and optical absorption, enabling facile regulation of the photocatalytic performance;
Plasmonic metal nanoparticles possess extraordinary optical properties that arise from localized surface plasmon resonance (LSPR) and offer a powerful means for boosting the photocatalytic activity. LSPR-enhanced photocatalysis mainly relies on the extension of light absorption to the long-wavelength range and the enhancement of the local electric field. Plasmonic hot electrons can drive reduction reactions and improve photocatalytic NH3 synthesis. The plasmon-intensified electric field can promote the photogeneration of charge carriers in semiconductors. As a result, combining plasmonic metal nanoparticles with 2D MXenes is expected to be a feasible strategy for constructing efficient photocatalysts for NH3 production.

Herein, we report on the construction of a Au nanosphere-embedded, partially reduced, and layered Ti3C2 (r-Ti3C2) photocatalyst with a unique sandwich-like architecture for efficient N2 photofixation under ambient conditions. r-Ti3C2 shows an expanded layer spacing and exposes many low-valence Ti sites (Ti$^{4+}$-LP) on the edge and basal planes, which serve as active sites for N2 activation. The unique sandwich-like, Au nanosphere-embedded r-Ti3C2 not only provides a large number of Ti$^{4+}$-LP active sites but also brings a high contact area between Au nanospheres and r-Ti3C2, improving the probability of excited charge carriers to interact with the reaction solution. Moreover, the embedding of Au nanospheres hinders the self-stacking of the r-Ti3C2 layers, benefitting the exposure of the active sites and boosting the effective utilization of the active sites and charge carriers. The hot electrons photoexcited on the plasmonic Au nanospheres inject into r-Ti3C2 and thereby reduce Ti$^{4+}$-LP site-activated N2 into NH3. The charge carrier recombination is largely suppressed because the electrons and holes are located in r-Ti3C2 and the Au nanospheres, respectively. The photocatalysts exhibit a superior activity for N2 photofixation in pure water at ambient temperature and pressure. Our strategy opens up new opportunities for designing MXene/plasmonic metal nanostructures to achieve efficient photo-driven NH3 fixation.

Results and discussion

Materials synthesis and characterization

The Au nanosphere-embedded, partially reduced, and layered Ti3C2 with a unique sandwich-like architecture was prepared by a solvent-driven approach (Fig. 1a; see Experimental in the ESI†). First, the Al layers in layered Ti3AlC2 particles (Fig. S2†) were etched by HF to produce layered Ti3C2 with abundant O, OH and F terminations. During etching, some carbon atoms were replaced by oxygen atoms in the lattice of Ti3C2. Second, Ti3C2 was then thermally treated in a N2/H2 atmosphere to alter its surface chemistry and generate oxygen vacancies (OVs) through H2 reduction. Third, the Au nanospheres were driven by H2O and gradually interlaminated in layered r-Ti3C2, resulting in a unique sandwich-like structure.

Scanning electron microscopy (SEM) imaging (Fig. 1b) reveals the accordion-like multilayered structure of Ti3C2, suggesting the successful etching of the Al layers. The layered texture is well kept in r-Ti3C2 (Fig. 1c), indicating that the H2 treatment does not deteriorate the original layered structure. The Au nanospheres dispersed in aqueous solutions exhibit an extinction peak at 518 nm (Fig. S3†). Their sizes are uniform (Fig. 1d), as revealed by transmission electron microscopy (TEM), with an average diameter of 12.8 ± 1.0 nm. In the low-magnification SEM images of Ti3C2/Au and r-Ti3C2/Au (Fig. S5†), a unique sandwich-like architecture is clearly observed. The Au nanospheres are interlaminated between the MXene layers and uniformly distributed on the basal planes. High-magnification SEM imaging further shows clearly that the Au nanospheres are uniformly interlaminated in the MXene layers (Fig. 1e and f). The X-ray diffraction (XRD) of Ti3AlC2 (Fig. S6a†) reveals a strong and typical diffraction pattern of the pure Ti3AlC2 phase (JCPDS no. 52-0875). After HF treatment, the strong (002) peak exhibits a downshift from 9.55° to 9.05°, which corresponds to a c-lattice parameter (c-LP) increase from 18.53 Å to 19.48 Å, implying an interlayer spacing of 0.98 nm in Ti3C2. In addition, the disappearance of the intense peak at 2θ = 39.08° in Ti3AlC2 after HF etching verifies the removal of the Al layers. Taken together, these results confirm the successful synthesis of Ti3C2 MXene. After H2 reduction, r-Ti3C2 displays a similar XRD pattern to Ti3C2 (Fig. 1g), except an additional (006) diffraction peak at 2θ = 28.5° (Fig. S6b†), reflecting a better-organized multilayered structure with more opened Ti3C2 layers. The XRD patterns also reveal the coexistence of the cubic Au phase (JCPDS no. 01-1172) and Ti3C2 in Ti3C2/Au and r-Ti3C2/Au (Fig. 1g). Compared to Ti3C2, the (002) peak shows clear and different shifts among r-Ti3C2, Ti3C2/Au and r-Ti3C2/Au (Fig. 1h). A slight shift of the (002) peak to a higher angle of 9.12° for r-Ti3C2 corresponds to a c-LP decrease from 19.48 Å to 19.25 Å, signifying a reduced interlayer spacing of 0.96 nm in r-Ti3C2. The small c-LP change of r-Ti3C2 can be ascribed to the elimination of H2O molecules interlaminated between the Ti3C2 layers or surface reactions during H2 reduction. The (002) peak shifts down to 2θ = 8.95° for sandwich-like Ti3C2/Au and r-Ti3C2/Au, which corresponds to a c-LP of 19.68 Å, indicative of an enlarged interlayer spacing of 1.00 nm. The increased interlayer spacing is probably caused by the intercalation of the Au nanospheres between the Ti3C2 and r-Ti3C2 segments. Each segment contains multiple Ti3C2 layers, but its overall thickness is greatly reduced in comparison with the sample before the intercalation of the Au nanospheres. In the Raman spectra of Ti3AlC2 (Fig. S7†), four major peaks appearing at
145, 260, 410 and 605 cm$^{-1}$ are the characteristic Raman bands of Ti$_3$AlC$_2$. They arise from the $\omega_1$, $\omega_2$, $\omega_3$ and $\omega_4$ Raman-active vibrational modes. Ti$_3$C$_2$ and r-Ti$_3$C$_2$ show similar Raman peaks, with a highly intensified peak at 153 cm$^{-1}$, along with three weak peaks at 260, 428 and 610 cm$^{-1}$. All the four peaks can be ascribed to the Raman-active vibrational modes of Ti–C,$^{46,47}$ suggesting the successful etching of the Al atoms and the preservation of the Ti$_3$C$_2$ layers. In addition, two broad bands observed at 1350 and 1610 cm$^{-1}$ for Ti$_3$C$_2$ and r-Ti$_3$C$_2$ correspond to the D- and G-bands of carbon, manifesting the existence of disordered carbon and ordered graphitic carbon, respectively. The larger peak intensities of the D- and G-bands in r-Ti$_3$C$_2$ reveal the existence of more disordered carbon, with a highly intensified peak at 153 cm$^{-1}$, indicating an enhanced conversion of light to heat to activate the supported catalyst. Unlike common plasmonic Au/semiconductor hybrid photocatalysts,$^{36,53}$ the absorption peak from the LSPR band of the Au nanospheres cannot be clearly observed in Ti$_3$C$_2$/Au or r-Ti$_3$C$_2$/Au. This result is likely caused by the spectral overlap between the LSPR of the Au nanospheres and the strong broad absorption of Ti$_3$C$_2$ MXene, which is...
reflected by the enhanced absorption in the region of 500–600 nm. The charge transport ability is another key factor in photocatalysis. Electrochemical impedance spectroscopy (EIS) measurements were conducted under white light illumination in a N2 atmosphere (Fig. S8†). A smaller semicircle in the obtained Nyquist plot implies a better charge transfer capability at the electrode–electrolyte interface. r-Ti3C2/Au exhibits the smallest arc radius, signifying a good charge transfer ability. The improved charge transfer ability can be attributed to the effective interfacial charge transfer in the sandwich-like r-Ti3C2/Au. Though the metallic Ti3C2 is difficult to photogenerate charge carriers, it can serve as an electron acceptor to capture the hot electrons generated by the plasmonic Au nanospheres owing to its superior electrical conductivity.32

Nitrogen photofixation

The photocatalytic N2 fixation experiments were performed in N2-saturated water under light illumination and ambient conditions in a quartz reactor (Fig. S9†). The produced ammonia amount was determined by Nessler's method, as shown by the calibration curve (Fig. S10†). Fig. 2a displays the time-dependent NH4+ concentrations over different photocatalysts under white light illumination. The Au nanospheres were found to be inactive for N2 photofixation under both white and visible light. NH4+ was hardly detected over Ti3C2. The NH4+ concentration reached 10.7 and 18.3 μmol L−1 in 6 h over r-Ti3C2 and Ti3C2/Au, respectively. The N2 photofixation activity of the r-Ti3C2/Au catalyst was greatly boosted to 216.8 μmol L−1 in 6 h. Under visible light (λ>400 nm), the produced NH4+ amounts of all catalysts decreased (Fig. 2b). The ammonia generation rates were normalized against the illumination time and the catalyst amount under both white and visible light (Fig. 2c). The NH4+ generation rate over r-Ti3C2/Au is 22.6 (12.4) μmol h−1 gcat−1 under white light (visible light) illumination, which is 5.8 (5.9) and 10.2 (10.3) times those of Ti3C2/Au and r-Ti3C2, respectively.

To verify the nitrogen and proton sources of the produced NH3, control experiments were carried out with r-Ti3C2/Au (Fig. S11†). NH4+ was not detected when N2 or H2O was replaced with Ar or aprotic acetonitrile, suggesting that the nitrogen and proton sources for the NH4+ formation are from N2 and H2O, respectively. In addition, NH4+ cannot be generated in dark, suggesting that light is an essential driving force for N2 photofixation. To further corroborate the origin of the produced NH3, an isotope labeling experiment was performed using 14N2 and 15N2 as the nitrogen sources. The obtained 14NH4Cl and 15NH4Cl were measured by 1H nuclear magnetic resonance (NMR) spectroscopy (Fig. 3a). The triplet and doublet peaks corresponding to 14NH4+ and 15NH4+ can be clearly observed in the 1H NMR spectra of the photocatalytic reaction solutions when 14N2 and 15N2 were used as the feed gas, respectively. This result verifies that the produced NH4+ indeed originated from N2 photofixation. Moreover, the evolution of O2 was also detected during the N2 photofixation process in a sealed reactor (Fig. S12a†). To assess whether O2 was produced during the N2 photofixation reaction catalyzed by r-Ti3C2/Au, the reactor was evacuated, bubbled with N2, and then sealed. Upon illumination for 1 h under white light, O2 was detected. The generated O2 should result from the oxidation of H2O by the hot holes in the Au nanospheres.34 Its amount is about three fourths that of NH4+ (Fig. S12b†), close to the stoichiometric ratio of 3:4 according to the reaction N2 + 3H2O → 2NH3 + 1.5O2, proving that NH3 is generated by coupling the activated N2 with the protons from H2O. Importantly, H2 was not detected during the
N₂ photofixation process (Fig. S12a†), suggesting the absence of the competing hydrogen evolution reaction. r-Ti₃C₂/Au is therefore a highly selective photocatalyst for N₂ photofixation.

To reveal the mechanism of the photocatalytic N₂ photofixation, photocurrent tests were first performed under white light illumination in both N₂ and Ar atmospheres (Fig. 3b). For Ti₃C₂, the photocurrent densities measured in Ar and N₂ are nearly the same and reach ~0.76 μA cm⁻² (Fig. 3c). The photocurrent density of r-Ti₃C₂ is similar to that of Ti₃C₂, and the photocurrent in N₂ shows a slight reduction. In the presence of the Au nanospheres, the photocurrents of Ti₃C₂/Au and r-Ti₃C₂/Au are enhanced in Ar because of the LSPR effect, and both reach ~1.65 μA cm⁻². There is a small decrease of ~0.15 μA cm⁻² in the photocurrent density of Ti₃C₂/Au when the Ar atmosphere changed to N₂, which means a slight electron consumption for the reduction of N₂ molecules. Remarkably, the photocurrent density of r-Ti₃C₂/Au in N₂ is only one fifth of that in Ar, suggesting that the four difference in photocurrent is consumed to reduce N₂ molecules. As a result, r-Ti₃C₂/Au displays a remarkable N₂ photofixation activity (Fig. 2). To look into the reaction process of adsorbed H₂O and N₂ and prove the activation and reduction of N₂ on the surface of r-Ti₃C₂/Au, in situ diffuse-reflectance infrared Fourier transform spectroscopy (DRIFTS) was employed to monitor the N₂ photofixation process. To record the DRIFT spectra, r-Ti₃C₂/Au was exposed to water vapor-saturated N₂ under white light illumination, which allows for the investigation of the time-dependent change of the molecular species adsorbed on the catalyst. In the control experiment performed in an Ar atmosphere, two clear absorption peaks at 1660 and 3580 cm⁻¹, corresponding to the characteristic bending modes of adsorbed H₂O molecules, were observed. Their intensities were enhanced as the reaction time was prolonged (Fig. 3d). No absorption bands related to the N-containing species were detected, which further indicates that the nitrogen in NH₃ truly originated from N₂ molecules. The time-dependent DRIFT spectra recorded after the injection of N₂ under white light reveal that several absorption peaks gradually appear as the illumination time was prolonged from 0 to 6 h. The signal at 2340 cm⁻¹ can be ascribed to strongly chemisorbed N₂ molecules. The absorption band at 3160 cm⁻¹ corresponds to the adsorbed ammonia. Furthermore, the characteristic absorption band at 1410 cm⁻¹ assigned to the NH₄⁺ deformation vibration is intensified with increasing illumination time. These DRIFTS results provide strong evidence that N₂ molecules can be adsorbed, activated and further reduced to form NH₄⁺ under light illumination.

To further understand the photocatalytic N₂ fixation performance of r-Ti₃C₂/Au, the effect of the Au nanosphere amount in r-Ti₃C₂/Au was systematically investigated. The amount of embedded Au nanospheres was determined by inductively coupled plasma mass spectrometry (ICP-MS; Fig. S13†). Fig. 4a shows the high-magnification SEM images of the Au/r-Ti₃C₂ samples that were embedded with the 12.8 nm-sized Au nanospheres at 0.49, 1.11, 1.78 and 2.28 wt% relative to the total...
amount of Au and r-Ti3C2, respectively. The unique sandwich-like architecture is observable for all samples. The Au nanospheres are uniformly distributed on the basal planes even when the loaded Au amount is increased to 1.78 wt%. As the embedded Au amount is increased to 2.28 wt%, aggregation occurs. The NH4+ concentrations catalyzed by the Au/r-Ti3C2 samples with different Au amounts increase with the illumination time under white light (Fig. 4b). When the embedded Au amount is increased from 0.49 to 1.78 wt%, the produced NH4+ amount steadily increases within the same reaction time. The r-Ti3C2/Au sample with the Au amount of 1.78 wt% gives the highest amount of the produced NH4+, whose concentration reaches 307.8 μmol L⁻¹ in 6 h. However, when the embedded Au amount is further increased to 2.28 wt%, the generated NH4+ concentration is clearly reduced. Similarly, the normalized NH4+ production rate first increases with the Au amount, reaches the highest value of 31.8 μmol h⁻¹ gcat⁻¹ at the loaded Au amount of 1.78 wt%, and then decreases (Fig. 4c). To further explore the relationship between the N2 photofixation activity and the LSPR effect of the Au nanospheres, r-Ti3C2/Au with different Au nanosphere sizes and amounts were prepared. The uniform Au nanospheres with average sizes of 16.1 ± 0.8 nm (Fig. S14†) and 21.0 ± 0.8 nm (Fig. S15†) were synthesized. The unique sandwich-like structure with the uniform distribution of the Au nanospheres in the interlayers was obtained. Similarly, a high Au amount results in a reduction in the NH4+ production. Fig. 4d summarizes the relationship between the NH4+ generation rate and the loaded Au nanosphere size and amount. For the same Au size, the NH4+ production rates show a nearly volcano-shaped dependence on the embedded Au amount. An optimal N2 photofixation performance is achieved at a particular Au amount, which increases with the Au nanosphere diameter. The optimal Au amount for each size can be attributed to the enhanced LSPR effect with increasing amounts of Au nanospheres. The decrease in the N2 photofixation rate at a higher Au amount should be caused by the aggregation of the Au nanospheres and/or the blocking of the active sites on r-Ti3C2 for N2 adsorption by the excessive Au nanospheres. The N2 photofixation rates for the r-Ti3C2/Au samples containing the 20 nm-sized Au nanospheres are generally smaller than those of the samples containing the 13 nm- and 16 nm-sized Au nanospheres. This is probably because the number of Au nanospheres plays a more important role than the absorption cross-section for the LSPR effect in N2 photofixation. The optimal sample was found to be r-Ti3C2/Au containing the 16 nm-sized Au nanospheres at 2.45 wt%. This sample gives a NH4+ production rate of 33.8 μmol h⁻¹ gcat⁻¹.

Au nanospheres capped with different molecules were next employed to study their assembly with r-Ti3C2 and in turn their effect on N2 photofixation. Au nanospheres coated with cetyltrimethylammonium bromide (CTAB) were chosen. They exhibit good dispersibility and uniform sizes with an average diameter of 19.8 ± 0.7 nm (Fig. S16†). The CTAB-capped Au nanospheres were found to predominantly assemble onto the edges of the r-Ti3C2 layers (Fig. 5a). The resultant sample is therefore denoted r-Ti3C2/edge-Au. The CTAB-capped Au nanospheres are positively charged with a zeta potential of +34.2 mV, and the layered r-Ti3C2 sample is negatively charged with a zeta potential of −28.8 mV (Fig. S17†). The two components can therefore spontaneously assemble together through electrostatic attraction during solvent evaporation. The assembly results in an intimate contact between the Au nanospheres and the edges of r-Ti3C2. It also implies that...
the electrostatic attraction force is stronger than the solvent-driven force. In contrast, the citrate-capped Au nanospheres cannot be adsorbed onto the edges of r-Ti$_3$C$_2$ due to electrostatic repulsion. They are driven into the interlayers of r-Ti$_3$C$_2$ by the solvent, producing the sandwich-like nanostructure. The SEM images (Fig. 5b) of r-Ti$_3$C$_2$/edge-Au reveal that the Au nanospheres are distributed along the edges of the layered r-Ti$_3$C$_2$ without clear aggregation, even when the Au amount is increased from 1.25 to 3.75 wt%. The N$_2$ photofixation activity of r-Ti$_3$C$_2$/edge-Au increases with increasing Au amounts (Fig. S18†). The photocatalytic N$_2$ photofixation performances of r-Ti$_3$C$_2$/Au with the Au nanospheres located at different positions are compared under the identical nanosphere diameter of ~20 nm and the close amounts of Au (Fig. 5c). Considerable reductions in the NH$_4^+$ production rate are seen for the r-Ti$_3$C$_2$/edge-Au catalysts. The reductions are probably caused by the relatively large average distance from the edge-positioned Au nanospheres, which act as the electron sources, to the active sites on the layers of r-Ti$_3$C$_2$. The large distance increases the probability for electrons to get lost during their transport.

Active sites and N$_2$ photofixation mechanism

The active sites of Ti$_3$C$_2$ MXene are vital for N$_2$ adsorption and activation and crucial for the utilization of Ti$_3$C$_2$ MXene in N$_2$ photofixation. X-ray photoelectron spectroscopy (XPS) was performed on Ti$_3$C$_2$ and r-Ti$_3$C$_2$ to examine the active sites (Fig. 6a and b). The peak at 454.6 eV for Ti$_3$C$_2$ and r-Ti$_3$C$_2$ can be assigned to the Ti–C bond. The peak appearing at 458.5 eV for both samples can be assigned to TiO$_2$/C0x, which arises mainly from the Ti atoms surrounded by O2-/C0 ions in the lattice owing to the replacement of some carbon atoms by oxygen atoms during etching. The peaks at 455.3 (460.2), 456.1(461.2) and 457.1 eV (462.3 eV) come from 2p$_{3/2}$ (2p$_{1/2}$) of Ti$^{2+}$, Ti$^{3+}$ and Ti$^{4+}$, respectively. Compared to Ti$_3$C$_2$, r-Ti$_3$C$_2$ exhibits an enhanced fraction of Ti$^{3+}$ with a diminished fraction of Ti$^{4+}$ (Table S1†), manifesting the partial reduction of Ti$^{4+}$ to the low-valence states of Ti$^{3+}$ or Ti$^{2+}$ through H$_2$ treatment. The low-valence state Ti$^{3+}$ has been known to be active for N$_2$ chemisorption. No clear changes were observed in the Ti 2p peaks for Ti$_3$C$_2$/Au and r-Ti$_3$C$_2$/Au, suggesting that the embedding of the Au nanospheres does not change the chemical state of Ti. The O 1s spectra of Ti$_3$C$_2$ and r-Ti$_3$C$_2$ can be fitted with two peaks at 529.4 and 531.2 eV (Fig. S19af), which are, respectively, derived from Ti–O and Ti–OH. The decreased intensity ratio between Ti–OH and Ti–O for r-Ti$_3$C$_2$ is attributed to the H$_2$ treatment. After the loading of the Au nanospheres, a new peak appears at ~532.3 eV (Fig. S19bf), suggesting the strong affinity between the Au nanospheres and the Ti$_3$C$_2$ layers through the formation of Au–O–Ti. The peaks at 83.7 and 87.3 eV in Ti$_3$C$_2$/Au and r-Ti$_3$C$_2$/Au...
(Fig. S19c†) arise, respectively, from Au 4f5/2 and Au 4f7/2, further verifying the successful assembly of the Au nanospheres onto the Ti3C2/r-Ti3C2 layers. Low-temperature electron paramagnetic resonance (EPR) spectra were measured to further confirm the existence of Ti3+ and surface OVs (Fig. 6c). The EPR spectrum of Ti3C2 shows a weak signal at $g = 1.998$, which originated from the delocalized electrons of the O2/C0 ions in the lattice. In comparison, r-Ti3C2 displays a stronger EPR peak with $g = 2.004$, demonstrating the formation of OVs caused by the H2 treatment and the existence of more Ti3+ in r-Ti3C2. Both XPS and EPR therefore reveal that r-Ti3C2 possesses a number of Ti3+ species and OVs in its framework, which can act as active sites for N2 chemisorption. N2 temperature-programmed desorption (TPD) further revealed the N2 adsorption ability of different samples. Only one peak at ~100 °C was detected for Ti3C2 (Fig. 6d), which is caused by N2 physisorption. In addition to the physisorption peak, r-Ti3C2 presents a strong peak at a higher temperature of ~250–300 °C, which should have originated from the chemisorption of N2 molecules. These results indicate that N2 chemisorption occurs at the Ti3+ sites on the r-Ti3C2 framework through the electron donation from the OV-induced Ti3+, as further discussed below.

Density functional theory (DFT) calculations were performed to investigate the chemisorption and activation of N2 molecules on different Ti sites of Ti3C2 MXene (Fig. 6f). Upon adsorption of a N2 molecule on the Ti1 site, the optimized N2 coordination configuration shows that the N2 molecule is chemisorbed on a Ti–Ti tripolymer center through a dinuclear end-on coordination mode, in which one N atom binds with the Ti–Ti tri polymer and the other binds with the Ti–Ti dimer (Fig. 6g). When a N2 molecule is adsorbed on the Ti2 site, the optimized coordination configuration is similar to that of N2 coordinated to the Ti1 site, but the adjacent two Ti1 sites are combined to form a Ti1–Ti2 tripolymer and a Ti1–Ti2 dimer (Fig. 6g). The Ti3

Fig. 6 Adsorption and activation of N2 molecules. (a) Ti 2p XPS spectra of Ti3C2 and r-Ti3C2. (b) Ti 2p XPS spectra of Ti3C2/Au and r-Ti3C2/Au. (c) EPR spectra of Ti3C2 and r-Ti3C2. (d) N2 TPD profiles of Ti3C2 and r-Ti3C2. (e) N2 TPD profiles of r-Ti3C2/Au and r-Ti3C2/edge-Au. (f) Various Ti sites on r-Ti3C2. Only the top Ti layer terminated with a layer of O atoms is shown. (g) Adsorption configuration (top row) and charge density difference (bottom row) of a N2 molecule adsorbed at different Ti sites on the r-Ti3C2 surface. Light blue balls: Ti; red balls: O; and dark blue balls: N. Yellow cloud: electron enrichment and cyan cloud: electron depletion.
and Ti4 sites cannot adsorb N2 molecules (Fig. 6g), which is probably caused by the weak interaction due to the strongly electronegative nature of the surface O-terminal groups. To disclose the electron transfer between r-Ti3C2 and the adsorbed N2, the charge density difference was calculated (Fig. 6g, bottom row). A clear charge density difference is observed for the Ti1 and Ti2 sites, suggesting the occurrence of electron transfer from r-Ti3C2 to the N2 molecule. The electron-enriched isosurface on the adsorbed N2 molecule exhibits a π-orbital feature, indicating that the d-orbital electrons on the adjacent Ti atoms at the Ti1-site are transferred to the captured N2 molecule. As electrons are injected into the N2 molecule, the N≡N triple bond is considerably weakened with an elongated bond length. The triple bond lengths of the N2 molecules adsorbed at the Ti1 and Ti2 sites, respectively, increased to 1.351 and 1.345 Å, much longer than the value of 1.114 Å for a free N2 molecule (Fig. S20a and b†). In addition, a distinct reduction in the electron density between the two N atoms is also observed, implying that electrons are donated from the highest occupied σ-orbital of the N2 molecule to the adjacent Ti sites. Such phenomena of electron donation from N2 molecules at transition metals play a crucial role in boosting the photocatalytic N2 fixation activity of the r-Ti3C2 catalyst.

In order to better understand the N2 chemisorption, we also performed DFT calculations to examine the adsorption energy (E_{ad}) of N2 at different sites on r-Ti3C2 MXene (Fig. S20†). A comparison of the E_{ad} values of a N2 molecule at the Ti1 site with different adsorption configurations reveals that the optimal N2 coordination configuration mentioned above gives the largest E_{ad} value of −3.525 eV, meaning that N2 activation can be spontaneously realized when it is adsorbed at the Ti1 site. A comparison of the E_{ad} values of N2 at different sites (Fig. S20†) shows that Ti1 is the strongest active site for N2 adsorption in r-Ti3C2 MXene. In addition, the adjacent Ti1 sites can help to build the optimal coordination configuration for N2 activation. The more the Ti1 sites are involved, the higher the E_{ad} value is. Moreover, the Ti1 site does not bond with any O atoms. The bond length and adsorption energy of the N2 molecule at the Ti1 site obtained in our calculations for Ti3C2 MXene are very close to those obtained in previous works for Ti2C MXene.64,65

### Solar utilization efficiency and stability of r-Ti3C2/Au

To evaluate the light utilization efficiency, the wavelength-dependent apparent quantum efficiencies (AQE) of r-Ti3C2/Au were determined by measuring the amount of produced ammonia in pure water under monochromatic light illumination (Fig. 7a). The AQE spectrum of r-Ti3C2/Au matches well with its absorption spectrum, suggesting that the ammonia evolution is photo-driven. Specifically, the AQE value for r-Ti3C2/Au reaches 0.697% at 520 nm owing to the synergistic effect of the strong plasmonic light harvesting capability of the Au nanoparticles and the N2-activation capability of r-Ti3C2. Such an AQE value is higher than those obtained in many previous works at...
this wavelength (Tables S2 and S3†). In addition, we also examined the N₂ photofixation activity of r-Ti₃C₂/Au under AM 1.5G solar light illumination in a sealed reactor filled with N₂. The NH₃ production rate was 21.26 μmol h⁻¹ gₐcatalyst⁻¹, and O₂ was also generated at a rate of 16.12 μmol h⁻¹ gₐcatalyst⁻¹ in this sealed system (Fig. S21†). The molar ratio of the produced NH₃ and O₂ is close to the theoretical stoichiometric ratio. Accordingly, the solar-to-ammonia conversion efficiency (SACE) was calculated to be 0.013%. The stability of r-Ti₃C₂/Au was evaluated by performing successive rounds of reaction under white and visible light illumination (Fig. 7b). Almost ~95% of the original ammonia generation activity was preserved after five successive cycles, indicative of the high stability of r-Ti₃C₂/Au. The unique sandwich-like structure with uniformly distributed Au nanospheres in the interlayers was well maintained in the used r-Ti₃C₂/Au catalyst (Fig. 7c). The slight decrease in the NH₃ production rate during the cycling tests is believed to be caused by the slight aggregation of the loaded Au nanospheres (Fig. 7c). A negligible amount of the leached Au was detected in the fifth cycle reaction solution by ICP-AES. The stability of r-Ti₃C₂/Au was further confirmed by the nearly unchanged XRD spectrum (Fig. 7d). The photocatalytic activity can be ascribed to the fact that electrons are constantly produced and transferred from the Au nanospheres to Ti₃C₂ under light illumination, which can inhibit the oxidation of Ti₃C₂.

Based on the above results, we propose a reaction mechanism for photocatalytic N₂ fixation with r-Ti₃C₂/Au under ambient conditions (Fig. 7e). Benefiting from the good hydrophilicity, the r-Ti₃C₂/Au photocatalyst can be stably and uniformly dispersed in water. r-Ti₃C₂ possesses numerous low-valence Ti₄⁺⁻ sites that are associated with OVs and generated through H₂ thermal reduction. They are active sites for capturing and activating N₂ molecules. Under light illumination, photogenerated hot electrons from the Au nanospheres are injected into r-Ti₃C₂, which subsequently reduce the activated N₂ at the Ti₄⁺⁻ sites. The hot holes remaining on the Au nanospheres are consumed through the oxidation of H₂O to produce O₂. The produced NH₃ is accumulated in the aqueous reaction solution.

**Conclusions**

We have demonstrated the potential of Ti₃C₂ MXene to photocatalytically fix N₂ in pure water under ambient conditions. Partially reduced layered Ti₃C₂ MXene is synthesized and integrated with Au nanospheres in a uniform sandwich-like structure through a controlled solvent-driven approach. r-Ti₃C₂ exposes abundant low-valence Ti sites, which act as active sites for capturing and activating N₂ molecules. The embedded Au nanospheres donate plasmonic hot electrons to reduce the activated N₂. Importantly, the unique sandwich-like architecture prevents the self-stacking of the Ti₃C₂ layers, which favors the exposure of the active sites for utilization. The abundant Ti₄⁺⁻ active sites and the LSPR effect work in tandem to endow r-Ti₃C₂/Au with a remarkably high N₂ photofixation activity. The design in this work not only broadens the photocatalytic applications of MXene in N₂ fixation as a host material but also opens up an avenue for the surface engineering of MXene with plasmonic nanoparticles to further explore the potential of MXene as a promising photocatalyst.

**Data availability**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Author contributions**

B. C. performed the experiments and wrote the manuscript. Y. Z. G assisted with the N₂ photofixation experiments. D. H. W. carried out the density functional theory calculations. L. L., B. C. Y. and J. F. W. designed the research work. J. F. W. revised the manuscript. All authors discussed the results and commented on the manuscript.

**Conflicts of interest**

There are no conflicts to declare.

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