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## Plasmon-enabled N<sub>2</sub> photofixation on partially reduced Ti<sub>3</sub>C<sub>2</sub> MXene†

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Benefiting from the superior conductivity, rich surface chemistry and tunable bandgap, Ti<sub>3</sub>C<sub>2</sub> 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 N<sub>2</sub> fixation. However, the realization of N<sub>2</sub> photofixation with Ti<sub>3</sub>C<sub>2</sub> 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 Ti<sub>3</sub>C<sub>2</sub>, and demonstrate its efficient N<sub>2</sub> photofixation in pure water under ambient conditions. The abundant low-valence Ti (Ti<sup>(4-x)+</sup>) sites in partially reduced Ti<sub>3</sub>C<sub>2</sub> (r-Ti<sub>3</sub>C<sub>2</sub>) produced by surface engineering through H<sub>2</sub> thermal reduction effectively capture and activate N<sub>2</sub>, while Au nanospheres offer plasmonic hot electrons to reduce the activated N<sub>2</sub> into NH<sub>3</sub>. The Ti<sup>(4-x)+</sup> active sites and plasmon-generated hot electrons work in tandem to endow r-Ti<sub>3</sub>C<sub>2</sub>/Au with remarkably enhanced N<sub>2</sub> photofixation activity. Importantly, r-Ti<sub>3</sub>C<sub>2</sub>/Au exhibits ultrahigh selectivity without the occurrence of competing H<sub>2</sub> 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 N<sub>2</sub> occupies ~78 vol% of the atmosphere, its efficient utilization by organisms is greatly hindered because of the strong N≡N bond (945 kJ mol<sup>-1</sup>).<sup>1,2</sup> Atmospheric N<sub>2</sub> is continuously fixed into biologically usable forms of nitrogen, such as NH<sub>3</sub> and NO<sub>3</sub><sup>-</sup>. At the same time, the fixed forms of nitrogen are also continuously converted back to N<sub>2</sub> in nature, constituting a giant nitrogen cycle (Fig. S1†).<sup>3</sup> In this cycle, synthesized NH<sub>3</sub> 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).<sup>4,5</sup> In addition, the obtained H<sub>2</sub> and O<sub>2</sub> 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 NH<sub>3</sub> synthesis is a critical step in the cycle. Traditionally, NH<sub>3</sub> 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 CO<sub>2</sub> emission.<sup>6,7</sup> 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 NH<sub>3</sub> production.

Nitrogen photofixation offers an approach for achieving the energy-saving and environmentally friendly NH<sub>3</sub> synthesis under ambient conditions with renewable solar energy as the driving force.<sup>8–10</sup> In N<sub>2</sub> photofixation, H<sub>2</sub> is replaced by H<sub>2</sub>O as a reducing agent. N<sub>2</sub> and 3H<sub>2</sub>O are converted to 2NH<sub>3</sub> and 1.5O<sub>2</sub>.<sup>11–17</sup> The key is to design an efficient photocatalyst. Two-dimensional (2D) photocatalysts exhibit unique merits in solar-to-chemical energy conversion.<sup>18–22</sup> MXenes, a family of 2D layered transition metal carbides, nitrides or carbonitrides, have aroused much interest since the first report in 2011.<sup>23</sup> 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.<sup>24–26</sup> Ti<sub>3</sub>C<sub>2</sub>, the first reported MXene, possesses several unique characteristics.<sup>24,25</sup> (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;

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(iv) excellent surface hydrophilicity improves the interfacial connection with other materials, facilitating the formation of heterostructures.  $\text{Ti}_3\text{C}_2$  has therefore become a research hotspot in photocatalysis.<sup>27–30</sup> Theoretical calculations have shown that  $\text{Ti}_3\text{C}_2$  presents valid  $\text{N}_2$ -philicity and the ability to chemisorb and activate  $\text{N}_2$ , suggesting that  $\text{Ti}_3\text{C}_2$  can be a promising material for  $\text{N}_2$  capture and reduction.<sup>31</sup> Unfortunately, the extremely low Fermi level and metallic nature of  $\text{Ti}_3\text{C}_2$  make it a superior electron acceptor, resulting in a poor separation efficiency of photogenerated electrons and holes.<sup>32,33</sup> In addition, the narrow bandgap of  $\text{Ti}_3\text{C}_2$  makes  $\text{N}_2$  photoreduction difficult.<sup>34</sup> As a result, it has remained challenging to realize  $\text{N}_2$  photofixation solely with  $\text{Ti}_3\text{C}_2$ .

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.<sup>18,35</sup> 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  $\text{NH}_3$  synthesis.<sup>18,36–38</sup> The plasmon-intensified electric field can promote the photogeneration of charge carriers in semiconductors.<sup>39,40</sup> As a result, combining plasmonic metal nanoparticles with 2D MXenes is expected to be a feasible strategy for constructing efficient photocatalysts for  $\text{NH}_3$  production.

Herein, we report on the construction of a Au nanosphere-embedded, partially reduced, and layered  $\text{Ti}_3\text{C}_2$  ( $\text{r-Ti}_3\text{C}_2$ ) photocatalyst with a unique sandwich-like architecture for efficient  $\text{N}_2$  photofixation under ambient conditions.  $\text{r-Ti}_3\text{C}_2$  shows an expanded layer spacing and exposes many low-valence Ti sites ( $\text{Ti}^{(4-x)^+}$ ) on the edge and basal planes, which serve as active sites for  $\text{N}_2$  activation. The unique sandwich-like, Au nanosphere-embedded  $\text{r-Ti}_3\text{C}_2$  not only provides a large number of  $\text{Ti}^{(4-x)^+}$  active sites but also brings a high contact area between Au nanospheres and  $\text{r-Ti}_3\text{C}_2$ , 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  $\text{r-Ti}_3\text{C}_2$  layers, benefiting 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  $\text{r-Ti}_3\text{C}_2$  and thereby reduce  $\text{Ti}^{(4-x)^+}$  site-activated  $\text{N}_2$  into  $\text{NH}_3$ . The charge carrier recombination is largely suppressed because the electrons and holes are located in  $\text{r-Ti}_3\text{C}_2$  and the Au nanospheres, respectively. The photocatalysts exhibit a superior activity for  $\text{N}_2$  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  $\text{N}_2$  fixation.

## Results and discussion

### Materials synthesis and characterization

The Au nanosphere-embedded, partially reduced, and layered  $\text{Ti}_3\text{C}_2$  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  $\text{Ti}_3\text{AlC}_2$  particles (Fig. S2†) were etched by HF to produce layered  $\text{Ti}_3\text{C}_2$  with abundant O, OH and F terminations. During etching, some carbon atoms were replaced by oxygen atoms in the lattice of  $\text{Ti}_3\text{C}_2$ .<sup>41</sup> Second,  $\text{Ti}_3\text{C}_2$  was then thermally treated in a  $\text{N}_2/\text{H}_2$  atmosphere to alter its surface chemistry and generate oxygen vacancies (OVs) through  $\text{H}_2$  reduction. Third, the Au nanospheres were driven by  $\text{H}_2\text{O}$  and gradually interlaminated in layered  $\text{r-Ti}_3\text{C}_2$ , resulting in a unique sandwich-like structure.

Scanning electron microscopy (SEM) imaging (Fig. 1b) reveals the accordion-like multilayered structure of  $\text{Ti}_3\text{C}_2$ , suggesting the successful etching of the Al layers. The layered texture is well kept in  $\text{r-Ti}_3\text{C}_2$  (Fig. 1c), indicating that the  $\text{H}_2$  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  $12.8 \pm 0.7$  nm (Fig. S4†). In the low-magnification SEM images of  $\text{Ti}_3\text{C}_2/\text{Au}$  and  $\text{r-Ti}_3\text{C}_2/\text{Au}$  (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  $\text{Ti}_3\text{AlC}_2$  (Fig. S6a†) reveals a strong and typical diffraction pattern of the pure  $\text{Ti}_3\text{AlC}_2$  phase (JCPDS no. 52-0875). After HF treatment, the strong (002) peak exhibits a downshift from  $9.55^\circ$  to  $9.05^\circ$ , 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  $\text{Ti}_3\text{C}_2$ . In addition, the disappearance of the intense peak at  $2\theta = 39.08^\circ$  in  $\text{Ti}_3\text{AlC}_2$  after HF etching verifies the removal of the Al layers.<sup>42</sup> Taken together, these results confirm the successful synthesis of  $\text{Ti}_3\text{C}_2$  MXene. After  $\text{H}_2$  reduction,  $\text{r-Ti}_3\text{C}_2$  displays a similar XRD pattern to  $\text{Ti}_3\text{C}_2$  (Fig. 1g), except an additional (006) diffraction peak at  $2\theta = 28.5^\circ$  (Fig. S6b†), reflecting a better-organized multilayered structure with more opened  $\text{Ti}_3\text{C}_2$  layers.<sup>43</sup> The XRD patterns also reveal the coexistence of the cubic Au phase (JCPDS no. 01-1172) and  $\text{Ti}_3\text{C}_2$  in  $\text{Ti}_3\text{C}_2/\text{Au}$  and  $\text{r-Ti}_3\text{C}_2/\text{Au}$  (Fig. 1g). Compared to  $\text{Ti}_3\text{C}_2$ , the (002) peak shows clear and different shifts among  $\text{r-Ti}_3\text{C}_2$ ,  $\text{Ti}_3\text{C}_2/\text{Au}$  and  $\text{r-Ti}_3\text{C}_2/\text{Au}$  (Fig. 1h). A slight shift of the (002) peak to a higher angle of  $9.12^\circ$  for  $\text{r-Ti}_3\text{C}_2$  corresponds to a *c*-LP decrease from  $19.48$  Å to  $19.25$  Å, signifying a reduced interlayer spacing of  $0.96$  nm in  $\text{r-Ti}_3\text{C}_2$ . The small *c*-LP change of  $\text{r-Ti}_3\text{C}_2$  can be ascribed to the elimination of  $\text{H}_2\text{O}$  molecules interlaminated between the  $\text{Ti}_3\text{C}_2$  layers or surface reactions during  $\text{H}_2$  reduction.<sup>23,44</sup> The (002) peak shifts down to  $2\theta = 8.95^\circ$  for sandwich-like  $\text{Ti}_3\text{C}_2/\text{Au}$  and  $\text{r-Ti}_3\text{C}_2/\text{Au}$ , 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  $\text{Ti}_3\text{C}_2$  and  $\text{r-Ti}_3\text{C}_2$  segments.<sup>45</sup> Each segment contains multiple  $\text{Ti}_3\text{C}_2$  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  $\text{Ti}_3\text{AlC}_2$  (Fig. S7†), four major peaks appearing at



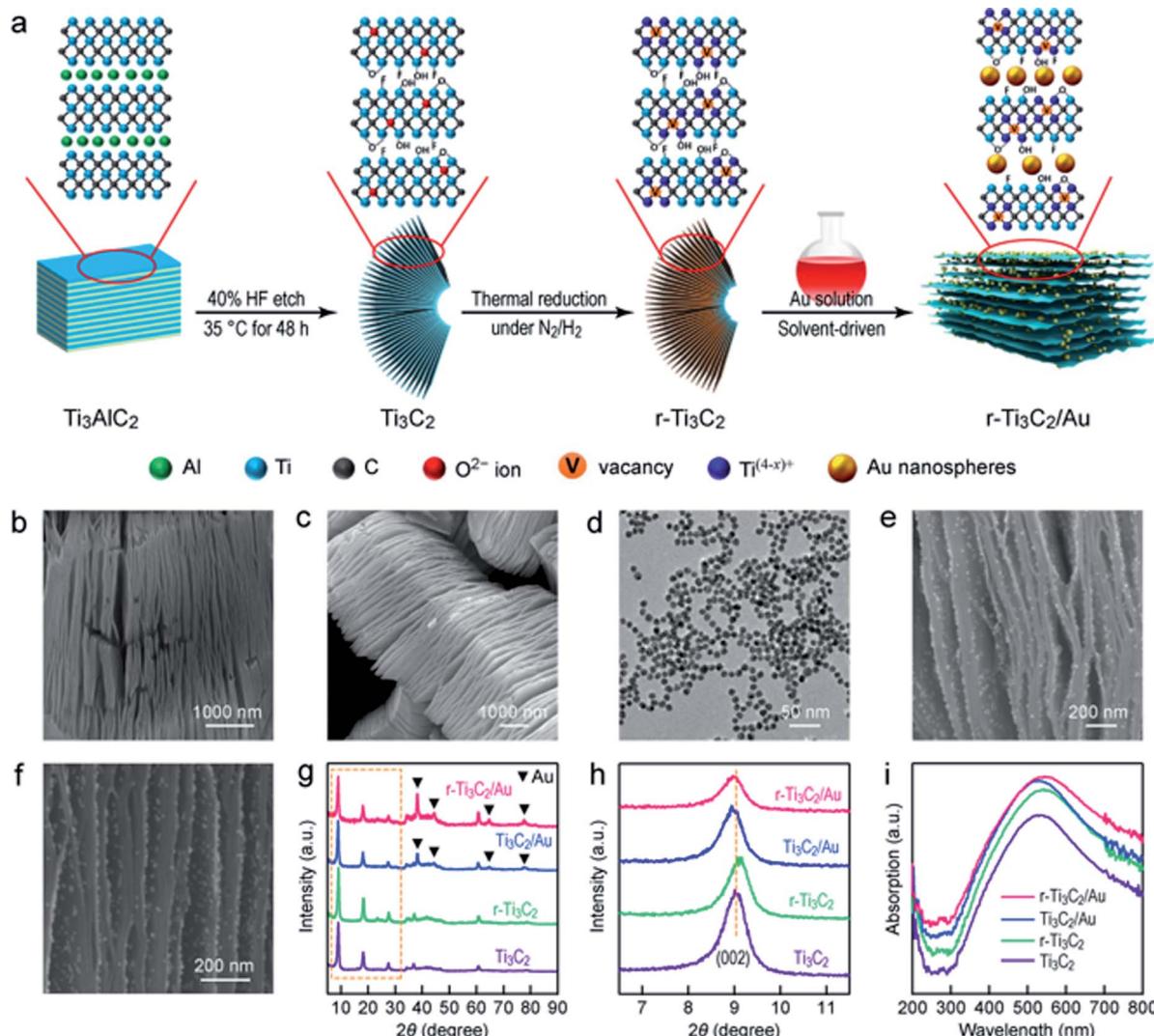


Fig. 1 Synthesis of the sandwich-like r-Ti<sub>3</sub>C<sub>2</sub>/Au nanostructure. (a) Schematic illustrating the synthesis process. The Ti<sub>3</sub>C<sub>2</sub> layer and Au nanosphere components are not drawn on the same size scale. (b) SEM image of Ti<sub>3</sub>C<sub>2</sub>. (c) SEM image of r-Ti<sub>3</sub>C<sub>2</sub>. (d) TEM image of the Au nanospheres. (e) SEM image of Ti<sub>3</sub>C<sub>2</sub>/Au. (f) SEM image of r-Ti<sub>3</sub>C<sub>2</sub>/Au. (g) XRD patterns of Ti<sub>3</sub>C<sub>2</sub>, r-Ti<sub>3</sub>C<sub>2</sub>, Ti<sub>3</sub>C<sub>2</sub>/Au and r-Ti<sub>3</sub>C<sub>2</sub>/Au. (h) XRD peaks of Ti<sub>3</sub>C<sub>2</sub>, r-Ti<sub>3</sub>C<sub>2</sub>, Ti<sub>3</sub>C<sub>2</sub>/Au and r-Ti<sub>3</sub>C<sub>2</sub>/Au for the (002) lattice planes. (i) Absorption spectra of Ti<sub>3</sub>C<sub>2</sub>, r-Ti<sub>3</sub>C<sub>2</sub>, Ti<sub>3</sub>C<sub>2</sub>/Au and r-Ti<sub>3</sub>C<sub>2</sub>/Au.

145, 260, 410 and 605 cm<sup>-1</sup> are the characteristic Raman bands of Ti<sub>3</sub>AlC<sub>2</sub>. They arise from the  $\omega_1$ ,  $\omega_2$ ,  $\omega_3$  and  $\omega_4$  Raman-active vibrational modes.<sup>46,47</sup> Ti<sub>3</sub>C<sub>2</sub> and r-Ti<sub>3</sub>C<sub>2</sub> show similar Raman peaks, with a highly intensified peak at 153 cm<sup>-1</sup>, along with three weak peaks at 260, 428 and 610 cm<sup>-1</sup>. All the four peaks can be ascribed to the Raman-active vibrational modes of Ti-C,<sup>48,49</sup> suggesting the successful etching of the Al atoms and the preservation of the Ti<sub>3</sub>C<sub>2</sub> layers. In addition, two broad bands observed at 1350 and 1610 cm<sup>-1</sup> for Ti<sub>3</sub>C<sub>2</sub> and r-Ti<sub>3</sub>C<sub>2</sub> 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<sub>3</sub>C<sub>2</sub> reveal the existence of more disordered carbon after H<sub>2</sub> reduction, suggesting the formation of more oxygen defects in the carbon layers of r-Ti<sub>3</sub>C<sub>2</sub>.<sup>50</sup> Such oxygen defects can bring more active sites for N<sub>2</sub> adsorption on the surface of r-Ti<sub>3</sub>C<sub>2</sub>.

Ti<sub>3</sub>C<sub>2</sub> shows clear absorption in the spectral region of 300–800 nm with a maximum at ~520 nm (Fig. 1i). r-Ti<sub>3</sub>C<sub>2</sub> also exhibits a broad absorption band in the region of 300–800 nm, but the absorption maximum exhibits a slight redshift. This phenomenon is probably caused by the changes in the surface chemistry and terminal groups of r-Ti<sub>3</sub>C<sub>2</sub>, resulting in a changed bandgap.<sup>51</sup> Despite the broad light absorption, very few charge carriers can be photogenerated and separated in Ti<sub>3</sub>C<sub>2</sub> and r-Ti<sub>3</sub>C<sub>2</sub>.<sup>32–34</sup> On the other hand, the efficient photo-thermal conversion of Ti<sub>3</sub>C<sub>2</sub> MXene can facilitate surface catalytic reactions through the conversion of light to heat to activate the supported catalyst.<sup>52</sup> Unlike common plasmonic Au/semiconductor hybrid photocatalysts,<sup>36,53</sup> the absorption peak from the LSPR band of the Au nanospheres cannot be clearly observed in Ti<sub>3</sub>C<sub>2</sub>/Au or r-Ti<sub>3</sub>C<sub>2</sub>/Au. This result is likely caused by the spectral overlap between the LSPR of the Au nanospheres and the strong broad absorption of Ti<sub>3</sub>C<sub>2</sub> 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  $N_2$  atmosphere (Fig. S8†). A smaller semicircle in the obtained Nyquist plot implies a better charge transfer capability at the electrode–electrolyte interface. r-Ti<sub>3</sub>C<sub>2</sub>/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-Ti<sub>3</sub>C<sub>2</sub>/Au. Though the metallic Ti<sub>3</sub>C<sub>2</sub> 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.<sup>32</sup>

### Nitrogen photofixation

The photocatalytic  $N_2$  fixation experiments were performed in  $N_2$ -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  $NH_4^+$  concentrations over different photocatalysts under white light illumination. The Au nanospheres were found to be inactive for  $N_2$  photofixation under both white and visible light.  $NH_4^+$  was hardly detected over Ti<sub>3</sub>C<sub>2</sub>. The  $NH_4^+$  concentration reached 10.7 and 18.3  $\mu\text{mol L}^{-1}$  in 6 h over r-Ti<sub>3</sub>C<sub>2</sub> and Ti<sub>3</sub>C<sub>2</sub>/Au, respectively. The  $N_2$  photofixation activity of the r-Ti<sub>3</sub>C<sub>2</sub>/Au catalyst was greatly boosted to 216.8  $\mu\text{mol L}^{-1}$  in 6 h. Under visible light ( $\lambda > 400$  nm), the produced  $NH_4^+$  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  $NH_4^+$  generation rate over r-Ti<sub>3</sub>C<sub>2</sub>/Au is 22.6 (12.4)  $\mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$  under white light (visible light) illumination, which is 5.8 (5.9) and 10.2 (10.3) times those of Ti<sub>3</sub>C<sub>2</sub>/Au and r-Ti<sub>3</sub>C<sub>2</sub>, respectively.

To verify the nitrogen and proton sources of the produced  $NH_3$ , control experiments were carried out with r-Ti<sub>3</sub>C<sub>2</sub>/Au (Fig. S11†).  $NH_4^+$  was not detected when  $N_2$  or  $H_2O$  was replaced with Ar or aprotic acetonitrile, suggesting that the nitrogen and proton sources for the  $NH_4^+$  formation are from  $N_2$  and  $H_2O$ , respectively. In addition,  $NH_4^+$  cannot be generated in dark, suggesting that light is an essential driving force for  $N_2$  photofixation. To further corroborate the origin of the produced  $NH_3$ , an isotope labeling experiment was performed using <sup>14</sup>N<sub>2</sub> and <sup>15</sup>N<sub>2</sub> as the nitrogen sources. The obtained <sup>14</sup>NH<sub>4</sub>Cl and <sup>15</sup>NH<sub>4</sub>Cl were measured by <sup>1</sup>H nuclear magnetic resonance (NMR) spectroscopy (Fig. 3a). The triplet and doublet peaks corresponding to <sup>14</sup>NH<sub>4</sub><sup>+</sup> and <sup>15</sup>NH<sub>4</sub><sup>+</sup> can be clearly observed in the <sup>1</sup>H NMR spectra of the photocatalytic reaction solutions when <sup>14</sup>N<sub>2</sub> and <sup>15</sup>N<sub>2</sub> were used as the feed gas, respectively. This result verifies that the produced  $NH_4^+$  indeed originated from  $N_2$  photofixation. Moreover, the evolution of  $O_2$  was also detected during the  $N_2$  photofixation process in a sealed reactor (Fig. S12a†). To assess whether  $O_2$  was produced during the  $N_2$  photofixation reaction catalyzed by r-Ti<sub>3</sub>C<sub>2</sub>/Au, the reactor was

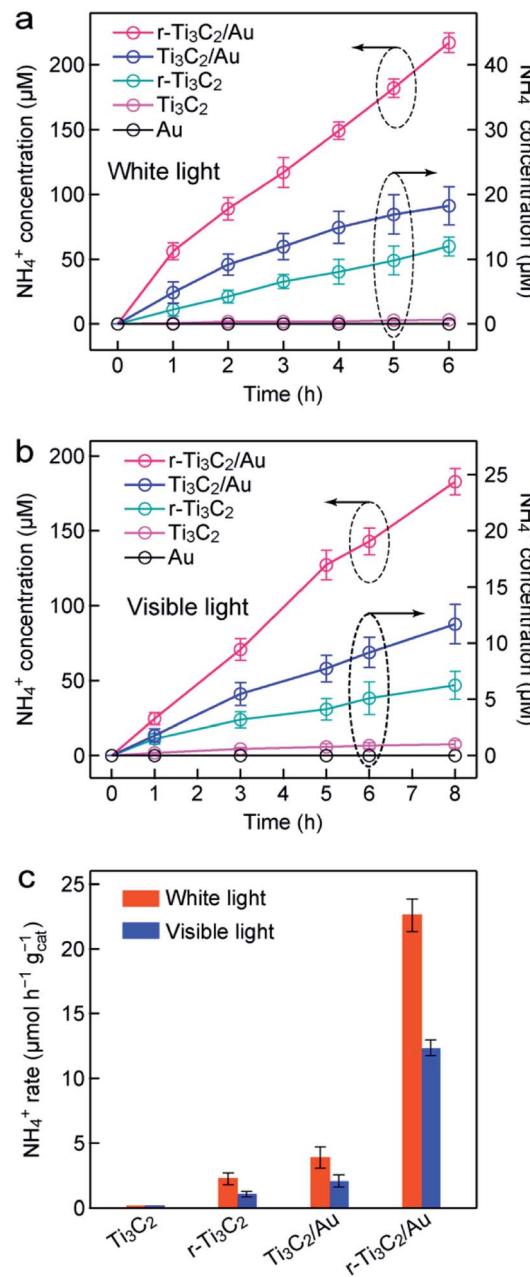
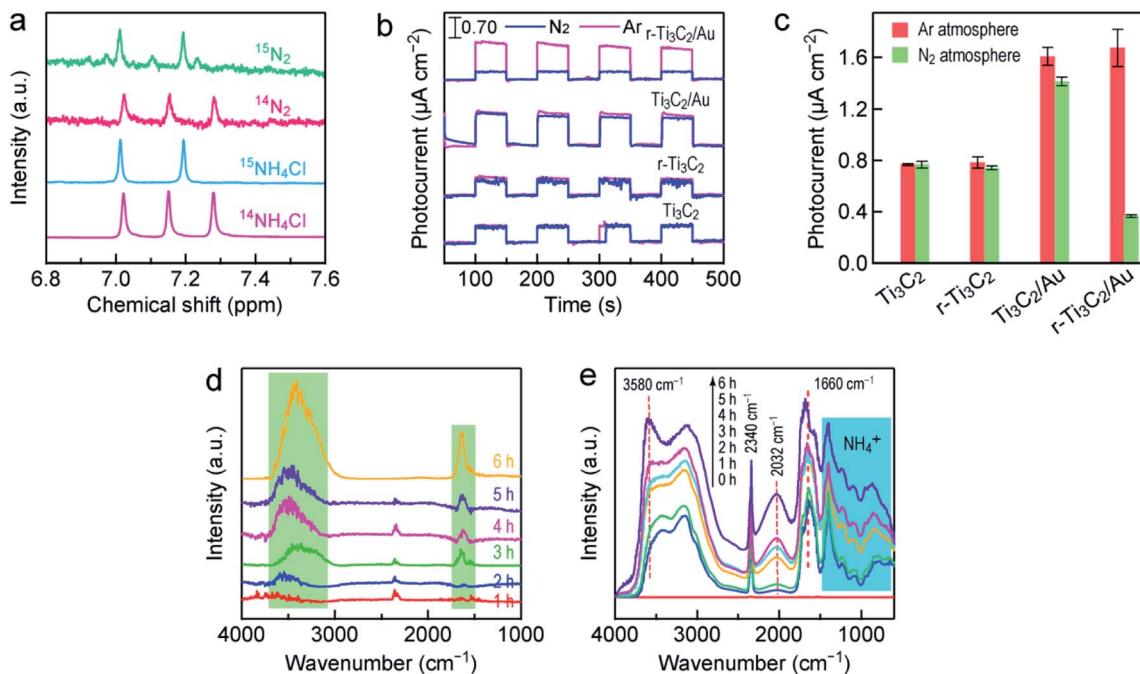


Fig. 2  $N_2$  photofixation over Au, Ti<sub>3</sub>C<sub>2</sub>, r-Ti<sub>3</sub>C<sub>2</sub>, Ti<sub>3</sub>C<sub>2</sub>/Au, and r-Ti<sub>3</sub>C<sub>2</sub>/Au. (a) Time courses of the ammonia concentrations measured under white light illumination. (b) Time courses of the ammonia concentrations measured under visible light illumination ( $\lambda > 400$  nm). (c) Ammonia production rates under white light and visible light. The rates for the Au nanospheres are not drawn because the Au nanospheres exhibit no activity for  $N_2$  photofixation.

evacuated, bubbled with  $N_2$ , and then sealed. Upon illumination for 1 h under white light,  $O_2$  was detected. The generated  $O_2$  should result from the oxidization of  $H_2O$  by the hot holes in the Au nanospheres.<sup>54</sup> Its amount is about three fourths that of  $NH_4^+$  (Fig. S12b†), close to the stoichiometric ratio of 3 : 4 according to the reaction  $N_2 + 3H_2O \rightarrow 2NH_3 + 1.5O_2$ , proving that  $NH_3$  is generated by coupling the activated  $N_2$  with the protons from  $H_2O$ . Importantly,  $H_2$  was not detected during the





**Fig. 3** Understanding the photocatalytic  $\text{N}_2$  fixation process. (a)  $^1\text{H}$  NMR spectra of the solutions after the  $\text{N}_2$  fixation reaction over r-Ti<sub>3</sub>C<sub>2</sub>/Au in  $^{15}\text{N}_2$  and  $^{14}\text{N}_2$  atmospheres. The bottom two spectra were taken from the standard  $^{15}\text{NH}_4\text{Cl}$  and  $^{14}\text{NH}_4\text{Cl}$  solutions. (b) Photocurrent responses of the different catalysts recorded in Ar and  $\text{N}_2$  atmospheres, with the white light illumination switched on and off repeatedly. (c) Photocurrent densities of the different catalysts in Ar and  $\text{N}_2$  atmospheres under white light illumination. (d) *In situ* DRIFT spectra recorded as a function of time during the  $\text{N}_2$  photofixation reaction over r-Ti<sub>3</sub>C<sub>2</sub>/Au in the Ar atmosphere. (e) *In situ* DRIFT spectra recorded as a function of time during the  $\text{N}_2$  photofixation reaction over r-Ti<sub>3</sub>C<sub>2</sub>/Au in the  $\text{N}_2$  atmosphere.

$\text{N}_2$  photofixation process (Fig. S12a†), suggesting the absence of the competing hydrogen evolution reaction. r-Ti<sub>3</sub>C<sub>2</sub>/Au is therefore a highly selective photocatalyst for  $\text{N}_2$  fixation.

To reveal the mechanism of the photocatalytic  $\text{N}_2$  fixation, photocurrent tests were first performed under white light illumination in both  $\text{N}_2$  and Ar atmospheres (Fig. 3b). For Ti<sub>3</sub>C<sub>2</sub>, the photocurrent densities measured in Ar and  $\text{N}_2$  are nearly the same and reach  $\sim 0.76 \mu\text{A cm}^{-2}$  (Fig. 3c). The photocurrent density of r-Ti<sub>3</sub>C<sub>2</sub> is similar to that of Ti<sub>3</sub>C<sub>2</sub>, and the photocurrent in  $\text{N}_2$  shows a slight reduction. In the presence of the Au nanospheres, the photocurrents of Ti<sub>3</sub>C<sub>2</sub>/Au and r-Ti<sub>3</sub>C<sub>2</sub>/Au are enhanced in Ar because of the LSPR effect, and both reach  $\sim 1.65 \mu\text{A cm}^{-2}$ . There is a small decrease of  $\sim 0.15 \mu\text{A cm}^{-2}$  in the photocurrent density of Ti<sub>3</sub>C<sub>2</sub>/Au when the Ar atmosphere changed to  $\text{N}_2$ , which means a slight electron consumption for the reduction of  $\text{N}_2$  molecules. Remarkably, the photocurrent density of r-Ti<sub>3</sub>C<sub>2</sub>/Au in  $\text{N}_2$  is only one fifth of that in Ar, suggesting that the four fifth difference in photocurrent is consumed to reduce  $\text{N}_2$  molecules. As a result, r-Ti<sub>3</sub>C<sub>2</sub>/Au displays a remarkable  $\text{N}_2$  photofixation activity (Fig. 2). To look into the reaction process of adsorbed  $\text{H}_2\text{O}$  and  $\text{N}_2$  and prove the activation and reduction of  $\text{N}_2$  on the surface of r-Ti<sub>3</sub>C<sub>2</sub>/Au, *in situ* diffuse-reflectance infrared Fourier transform spectroscopy (DRIFTS) was employed to monitor the  $\text{N}_2$  photofixation process. To record the DRIFTS spectra, r-Ti<sub>3</sub>C<sub>2</sub>/Au was exposed to water vapor-saturated  $\text{N}_2$  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  $3580 \text{ cm}^{-1}$ , corresponding to the characteristic bending modes of adsorbed  $\text{H}_2\text{O}$  molecules,<sup>36</sup> 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  $\text{NH}_3$  truly originated from  $\text{N}_2$  molecules. The time-dependent DRIFTS spectra recorded after the injection of  $\text{N}_2$  under white light reveal that several absorption peaks gradually appear as the illumination time was prolonged from 0 to 6 h. The signal at  $2340 \text{ cm}^{-1}$  can be ascribed to strongly chemisorbed  $\text{N}_2$  molecules.<sup>55</sup> The absorption band at  $2032 \text{ cm}^{-1}$  is believed to arise from the Ti-N=N complex formed through  $\text{N}_2$  binding to the Ti<sup>3+</sup> sites.<sup>56</sup> The absorption band at  $\sim 3160 \text{ cm}^{-1}$  corresponds to the adsorbed ammonia.<sup>9,37</sup> Furthermore, the characteristic absorption band at  $1410 \text{ cm}^{-1}$  assigned to the NH<sub>4</sub><sup>+</sup> deformation vibration is intensified with increasing illumination time.<sup>37,57</sup> These DRIFTS results provide strong evidence that  $\text{N}_2$  molecules can be adsorbed, activated and further reduced to form NH<sub>4</sub><sup>+</sup> under light illumination.

To further understand the photocatalytic  $\text{N}_2$  fixation performance of r-Ti<sub>3</sub>C<sub>2</sub>/Au, the effect of the Au nanosphere amount in r-Ti<sub>3</sub>C<sub>2</sub>/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-Ti<sub>3</sub>C<sub>2</sub> 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

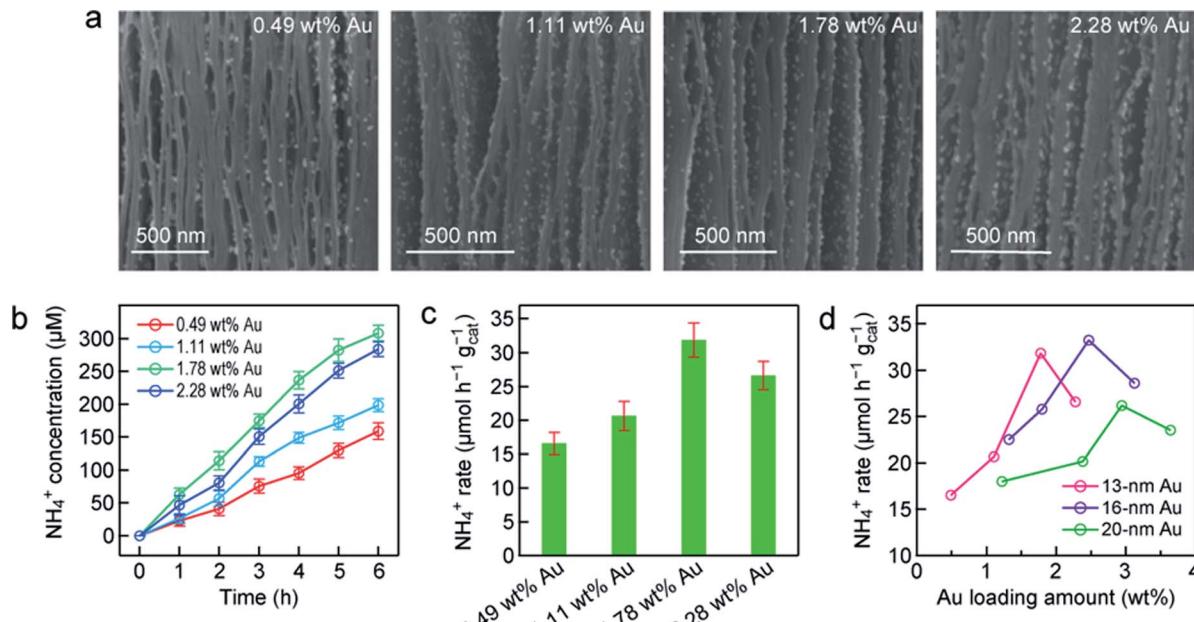


Fig. 4 Nitrogen photofixation over different r-Ti<sub>3</sub>C<sub>2</sub>/Au samples. (a) SEM images of r-Ti<sub>3</sub>C<sub>2</sub>/Au containing the 13 nm-sized Au nanospheres at different amounts indicated in the images. (b) Time courses of the ammonia concentrations measured under white light for the samples shown in (a). (c) Ammonia production rates under white light for the samples shown in (a). (d) Photocatalytic ammonia production rates as a function of the loaded Au amount for r-Ti<sub>3</sub>C<sub>2</sub>/Au containing the differently sized Au nanospheres.

amount of Au and r-Ti<sub>3</sub>C<sub>2</sub>, 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 NH<sub>4</sub><sup>+</sup> concentrations catalyzed by the Au/r-Ti<sub>3</sub>C<sub>2</sub> 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 NH<sub>4</sub><sup>+</sup> amount steadily increases within the same reaction time. The r-Ti<sub>3</sub>C<sub>2</sub>/Au sample with the Au amount of 1.78 wt% gives the highest amount of the produced NH<sub>4</sub><sup>+</sup>, whose concentration reaches 307.8 μmol L<sup>-1</sup> in 6 h. However, when the embedded Au amount is further increased to 2.28 wt%, the generated NH<sub>4</sub><sup>+</sup> concentration is clearly reduced. Similarly, the normalized NH<sub>4</sub><sup>+</sup> production rate first increases with the Au amount, reaches the highest value of 31.8 μmol h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup> at the loaded Au amount of 1.78 wt%, and then decreases (Fig. 4c). To further explore the relationship between the N<sub>2</sub> photofixation activity and the LSPR effect of the Au nanospheres, r-Ti<sub>3</sub>C<sub>2</sub>/Au with different Au nanosphere sizes and amounts were prepared. The uniform Au nanospheres with average sizes of 16.1 ± 0.8 (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 NH<sub>4</sub><sup>+</sup> production. Fig. 4d summarizes the relationship between the NH<sub>4</sub><sup>+</sup> generation rate and the loaded Au nanosphere size and amount. For the same Au size, the NH<sub>4</sub><sup>+</sup> production rates show a nearly volcano-shaped dependence on the embedded Au amount. An optimal N<sub>2</sub> 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 N<sub>2</sub> 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-Ti<sub>3</sub>C<sub>2</sub> for N<sub>2</sub> adsorption by the excessive Au nanospheres. The N<sub>2</sub> photofixation rates for the r-Ti<sub>3</sub>C<sub>2</sub>/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 N<sub>2</sub> photofixation. The optimal sample was found to be r-Ti<sub>3</sub>C<sub>2</sub>/Au containing the 16 nm-sized Au nanospheres at 2.45 wt%. This sample gives a NH<sub>4</sub><sup>+</sup> production rate of 33.8 μmol h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>.

Au nanospheres capped with different molecules were next employed to study their assembly with r-Ti<sub>3</sub>C<sub>2</sub> and in turn their effect on N<sub>2</sub> 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-Ti<sub>3</sub>C<sub>2</sub> layers (Fig. 5a). The resultant sample is therefore denoted r-Ti<sub>3</sub>C<sub>2</sub>/edge-Au. The CTAB-capped Au nanospheres are positively charged with a zeta potential of +34.2 mV, and the layered r-Ti<sub>3</sub>C<sub>2</sub> 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-Ti<sub>3</sub>C<sub>2</sub>. It also implies that

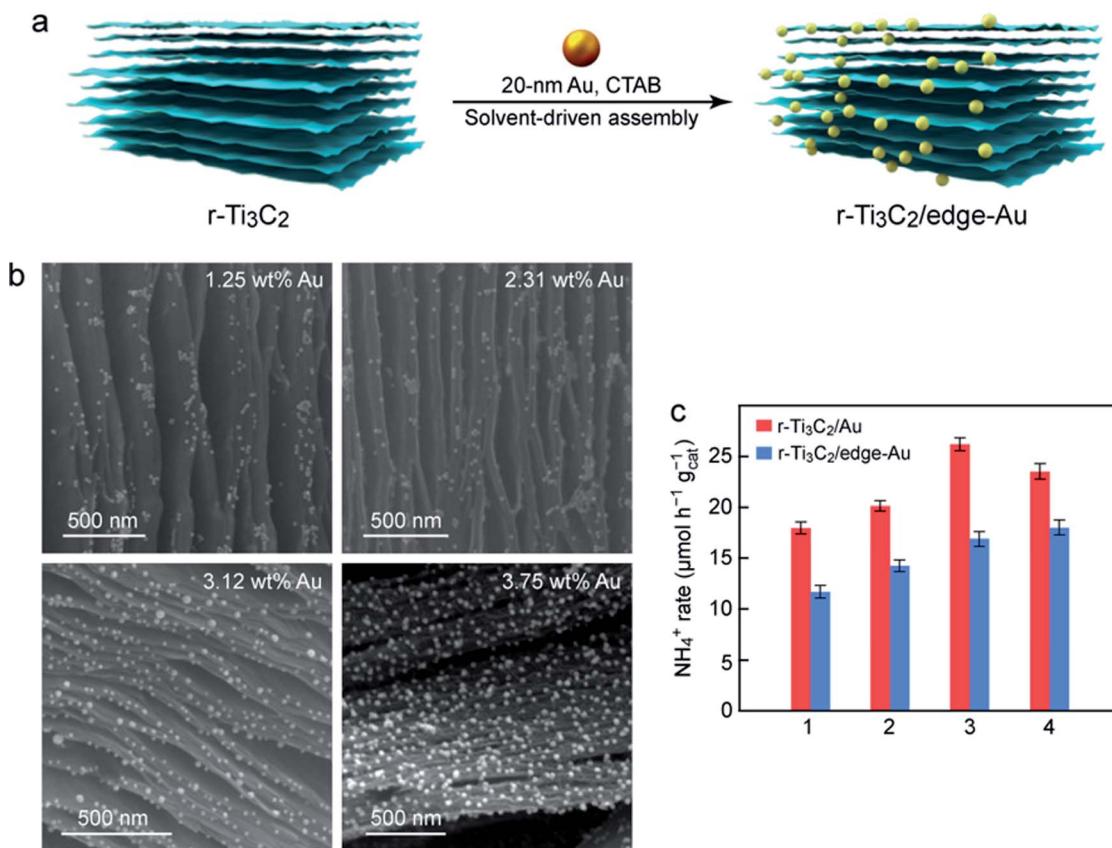


Fig. 5 Characterization and N<sub>2</sub> photofixation of r-Ti<sub>3</sub>C<sub>2</sub>/edge-Au. (a) Schematic illustrating the synthesis process of r-Ti<sub>3</sub>C<sub>2</sub>/edge-Au. (b) SEM images of r-Ti<sub>3</sub>C<sub>2</sub>/edge-Au with different loaded Au amounts. (c) Comparison of the ammonia production rates over the sandwich-like r-Ti<sub>3</sub>C<sub>2</sub>/Au and the r-Ti<sub>3</sub>C<sub>2</sub>/edge-Au catalysts under white light illumination. The sizes of the Au nanospheres in both catalysts are ~20 nm. The loaded Au amounts in both catalysts are nearly the same in each group from 1 to 4.

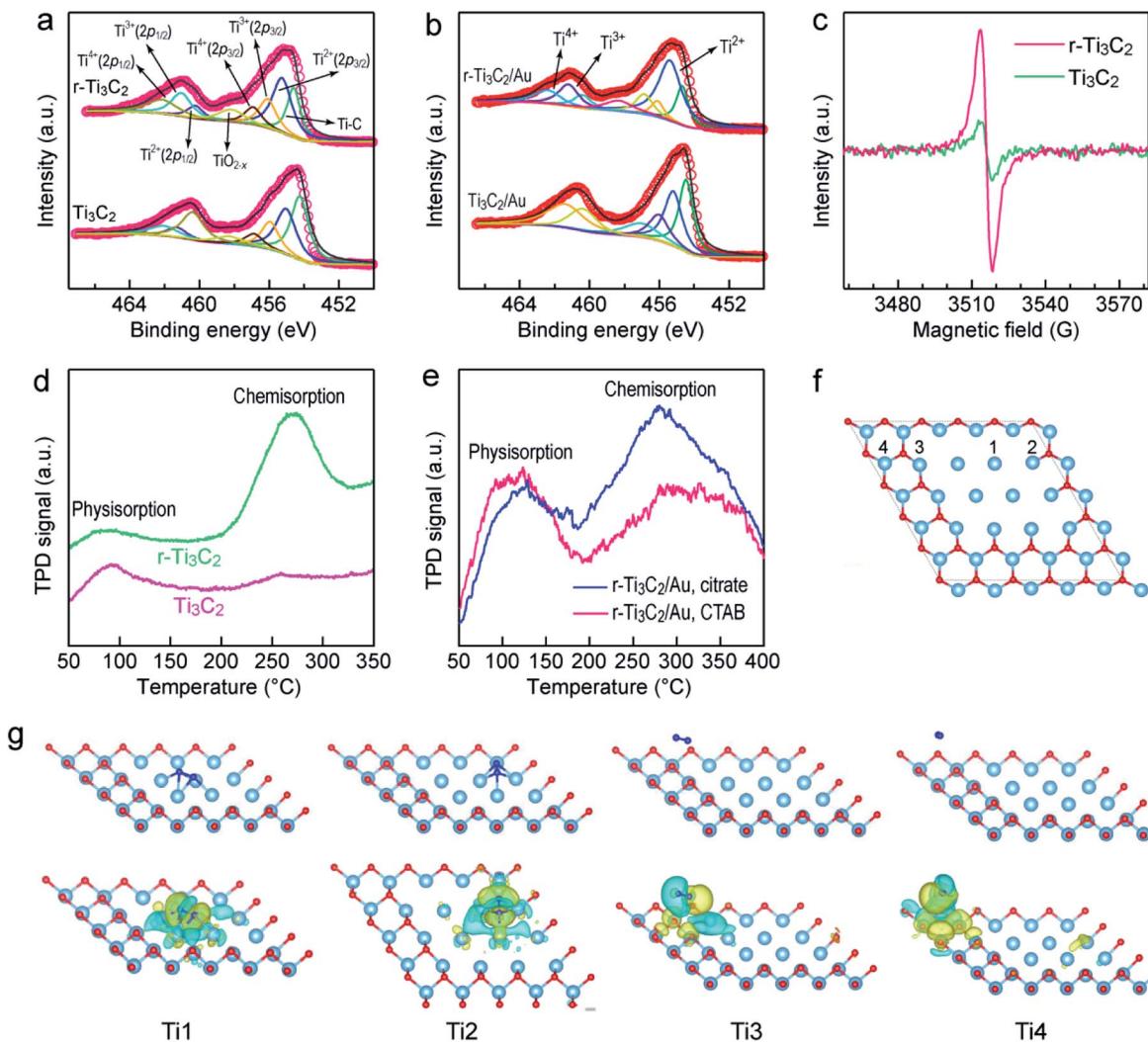
the electrostatic attraction force is stronger than the solvent-driven force. In contrast, the citrate-capped Au nanospheres cannot be adsorbed onto the edges of r-Ti<sub>3</sub>C<sub>2</sub> due to electrostatic repulsion. They are driven into the interlayers of r-Ti<sub>3</sub>C<sub>2</sub> by the solvent, producing the sandwich-like nanostructure. The SEM images (Fig. 5b) of r-Ti<sub>3</sub>C<sub>2</sub>/edge-Au reveal that the Au nanospheres are distributed along the edges of the layered r-Ti<sub>3</sub>C<sub>2</sub> without clear aggregation, even when the Au amount is increased from 1.25 to 3.75 wt%. The N<sub>2</sub> photofixation activity of r-Ti<sub>3</sub>C<sub>2</sub>/edge-Au increases with increasing Au amounts (Fig. S18†). The photocatalytic N<sub>2</sub> fixation performances of r-Ti<sub>3</sub>C<sub>2</sub>/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<sub>4</sub><sup>+</sup> production rate are seen for the r-Ti<sub>3</sub>C<sub>2</sub>/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<sub>3</sub>C<sub>2</sub>. The large distance increases the probability for electrons to get lost during their transport.

### Active sites and N<sub>2</sub> photofixation mechanism

The active sites of Ti<sub>3</sub>C<sub>2</sub> MXene are vital for N<sub>2</sub> adsorption and activation and crucial for the utilization of Ti<sub>3</sub>C<sub>2</sub> MXene in N<sub>2</sub>

photofixation. X-ray photoelectron spectroscopy (XPS) was performed on Ti<sub>3</sub>C<sub>2</sub> and r-Ti<sub>3</sub>C<sub>2</sub> to examine the active sites (Fig. 6a and b). The peak at 454.6 eV for Ti<sub>3</sub>C<sub>2</sub> and r-Ti<sub>3</sub>C<sub>2</sub> can be assigned to the Ti-C bond. The peak appearing at 458.5 eV for both samples can be assigned to TiO<sub>2-x</sub>, which arises mainly from the Ti atoms surrounded by O<sup>2-</sup> ions in the lattice owing to the replacement of some carbon atoms by oxygen atoms during etching.<sup>37,50</sup> The peaks at 455.3 (460.2), 456.1(461.2) and 457.1 eV (462.3 eV) come from 2p<sub>3/2</sub> (2p<sub>1/2</sub>) of Ti<sup>2+</sup>, Ti<sup>3+</sup> and Ti<sup>4+</sup>, respectively. Compared to Ti<sub>3</sub>C<sub>2</sub>, r-Ti<sub>3</sub>C<sub>2</sub> exhibits an enhanced fraction of Ti<sup>3+</sup> with a diminished fraction of Ti<sup>4+</sup> (Table S1†), manifesting the partial reduction of Ti<sup>4+</sup> to the low-valence states of Ti<sup>3+</sup> or Ti<sup>2+</sup> through H<sub>2</sub> treatment. The low-valence state Ti<sup>3+</sup> has been known to be active for N<sub>2</sub> chemisorption. No clear changes were observed in the Ti 2p peaks for Ti<sub>3</sub>C<sub>2</sub>/Au and r-Ti<sub>3</sub>C<sub>2</sub>/Au, suggesting that the embedding of the Au nanospheres does not change the chemical state of Ti. The O 1s spectra of Ti<sub>3</sub>C<sub>2</sub> and r-Ti<sub>3</sub>C<sub>2</sub> can be fitted with two peaks at 529.4 and 531.2 eV (Fig. S19a†), which are, respectively, derived from Ti-O and Ti-OH. The decreased intensity ratio between Ti-OH and Ti-O for r-Ti<sub>3</sub>C<sub>2</sub> is attributed to the H<sub>2</sub> treatment. After the loading of the Au nanospheres, a new peak appears at ~532.3 eV (Fig. S19b†), suggesting the strong affinity between the Au nanospheres and the Ti<sub>3</sub>C<sub>2</sub> layers through the formation of Au-O-Ti.<sup>58</sup> The peaks at 83.7 and 87.3 eV in Ti<sub>3</sub>C<sub>2</sub>/Au and r-Ti<sub>3</sub>C<sub>2</sub>/Au





**Fig. 6** Adsorption and activation of N<sub>2</sub> molecules. (a) Ti 2p XPS spectra of Ti<sub>3</sub>C<sub>2</sub> and r-Ti<sub>3</sub>C<sub>2</sub>. (b) Ti 2p XPS spectra of Ti<sub>3</sub>C<sub>2</sub>/Au and r-Ti<sub>3</sub>C<sub>2</sub>/Au. (c) EPR spectra of Ti<sub>3</sub>C<sub>2</sub> and r-Ti<sub>3</sub>C<sub>2</sub>. (d) N<sub>2</sub> TPD profiles of Ti<sub>3</sub>C<sub>2</sub> and r-Ti<sub>3</sub>C<sub>2</sub>. (e) N<sub>2</sub> TPD profiles of r-Ti<sub>3</sub>C<sub>2</sub>/Au and r-Ti<sub>3</sub>C<sub>2</sub>/edge-Au. (f) Various Ti sites on r-Ti<sub>3</sub>C<sub>2</sub>. 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 N<sub>2</sub> molecule adsorbed at different Ti sites on the r-Ti<sub>3</sub>C<sub>2</sub> surface. Light blue balls: Ti; red balls: O; and dark blue balls: N. Yellow cloud: electron enrichment and cyan cloud: electron depletion.

(Fig. S19c†) arise, respectively, from Au 4f<sub>5/2</sub> and Au 4f<sub>7/2</sub>, further verifying the successful assembly of the Au nanospheres onto the Ti<sub>3</sub>C<sub>2</sub>/r-Ti<sub>3</sub>C<sub>2</sub> layers. Low-temperature electron paramagnetic resonance (EPR) spectra were measured to further confirm the existence of Ti<sup>3+</sup> and surface OVs (Fig. 6c). The EPR spectrum of Ti<sub>3</sub>C<sub>2</sub> shows a weak signal at  $g = 1.998$ , which originated from the delocalized electrons of the O<sup>2-</sup> ions in the lattice.<sup>11,59</sup> In comparison, r-Ti<sub>3</sub>C<sub>2</sub> displays a stronger EPR peak with  $g = 2.004$ , demonstrating the formation of OVs caused by the H<sub>2</sub> treatment and the existence of more Ti<sup>3+</sup> in r-Ti<sub>3</sub>C<sub>2</sub>.<sup>57</sup> Both XPS and EPR therefore reveal that r-Ti<sub>3</sub>C<sub>2</sub> possesses a number of Ti<sup>3+</sup> species and OVs in its framework, which can act as active sites for N<sub>2</sub> chemisorption. N<sub>2</sub> temperature-programmed desorption (TPD) further revealed the N<sub>2</sub> adsorption ability of different samples. Only one peak at  $\sim 100$  °C was detected for Ti<sub>3</sub>C<sub>2</sub> (Fig. 6d), which is caused by N<sub>2</sub> physisorption. In addition to the physisorption peak, r-Ti<sub>3</sub>C<sub>2</sub> presents a strong peak at

a higher temperature of  $\sim 250$ –300 °C, which should have originated from the chemisorption of N<sub>2</sub> molecules.<sup>60</sup> These results indicate that N<sub>2</sub> chemisorption occurs at the Ti<sup>3+</sup> sites on the r-Ti<sub>3</sub>C<sub>2</sub> framework through the electron donation from the OV-induced Ti<sup>3+</sup>, as further discussed below.

Density functional theory (DFT) calculations were performed to investigate the chemisorption and activation of N<sub>2</sub> molecules on different Ti sites of Ti<sub>3</sub>C<sub>2</sub> MXene (Fig. 6f). Upon adsorption of a N<sub>2</sub> molecule on the Ti1 site, the optimized N<sub>2</sub> coordination configuration shows that the N<sub>2</sub> 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 tripolymer and the other binds with the Ti-Ti dimer (Fig. 6g). When a N<sub>2</sub> molecule is adsorbed on the Ti2 site, the optimized coordination configuration is similar to that of N<sub>2</sub> 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

and Ti4 sites cannot adsorb N<sub>2</sub> molecules (Fig. 6g), which is probably caused by the weak interaction due to the strongly electronegative nature of the surface O-terminal groups.<sup>61</sup> To disclose the electron transfer between r-Ti<sub>3</sub>C<sub>2</sub> and the adsorbed N<sub>2</sub>, 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-Ti<sub>3</sub>C<sub>2</sub> to the N<sub>2</sub> molecule. The electron-enriched isosurface on the adsorbed N<sub>2</sub> molecule exhibits a  $\pi$ -orbital feature, indicating that the d-orbital electrons on the adjacent Ti atoms at the Ti1-site are transferred to the captured N<sub>2</sub> molecule. As electrons are injected into the N<sub>2</sub> molecule, the N≡N triple bond is considerably weakened with an elongated bond length. The triple bond lengths of the N<sub>2</sub> 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 N<sub>2</sub> molecule (Fig. S20a and b<sup>†</sup>). 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  $\sigma$ -orbital of the N<sub>2</sub> molecule to the adjacent Ti sites. Such phenomena of electron donation from N<sub>2</sub> to the metal and back-donation from the metal to N<sub>2</sub> also happen in M (transition metal)–N<sub>2</sub> complexes and have been discovered for many metals.<sup>1,62,63</sup> The strong activation of N<sub>2</sub> molecules through electron back-donation from transition metals with available d-orbital electrons plays a crucial role in boosting the photocatalytic N<sub>2</sub> fixation activity of the r-Ti<sub>3</sub>C<sub>2</sub> catalyst.

In order to better understand the N<sub>2</sub> chemisorption, we also performed DFT calculations to examine the adsorption energy

( $E_{ad}$ ) of N<sub>2</sub> at different sites on r-Ti<sub>3</sub>C<sub>2</sub> MXene (Fig. S20<sup>†</sup>). A comparison of the  $E_{ad}$  values of a N<sub>2</sub> molecule at the Ti1 site with different adsorption configurations reveals that the optimal N<sub>2</sub> coordination configuration mentioned above gives the largest  $E_{ad}$  value of -3.525 eV, meaning that N<sub>2</sub> activation can be spontaneously realized when it is adsorbed at the Ti1 site. A comparison of the  $E_{ad}$  values of N<sub>2</sub> at different sites (Fig. S20<sup>†</sup>) shows that Ti1 is the strongest active site for N<sub>2</sub> adsorption in r-Ti<sub>3</sub>C<sub>2</sub> MXene. In addition, the adjacent Ti1 sites can help to build the optimal coordination configuration for N<sub>2</sub> 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 N<sub>2</sub> molecule at the Ti1 site obtained in our calculations for Ti<sub>3</sub>C<sub>2</sub> MXene are very close to those obtained in previous works for Ti<sub>2</sub>C MXene.<sup>64,65</sup>

### Solar utilization efficiency and stability of r-Ti<sub>3</sub>C<sub>2</sub>/Au

To evaluate the light utilization efficiency, the wavelength-dependent apparent quantum efficiencies (AQE) of r-Ti<sub>3</sub>C<sub>2</sub>/Au were determined by measuring the amount of produced ammonia in pure water under monochromatic light illumination (Fig. 7a). The AQE spectrum of r-Ti<sub>3</sub>C<sub>2</sub>/Au matches well with its absorption spectrum, suggesting that the ammonia evolution is photo-driven. Specifically, the AQE value for r-Ti<sub>3</sub>C<sub>2</sub>/Au reaches 0.697% at 520 nm owing to the synergistic effect of the strong plasmonic light harvesting capability of the Au nanospheres and the N<sub>2</sub>-activation capability of r-Ti<sub>3</sub>C<sub>2</sub>. Such an AQE value is higher than those obtained in many previous works at

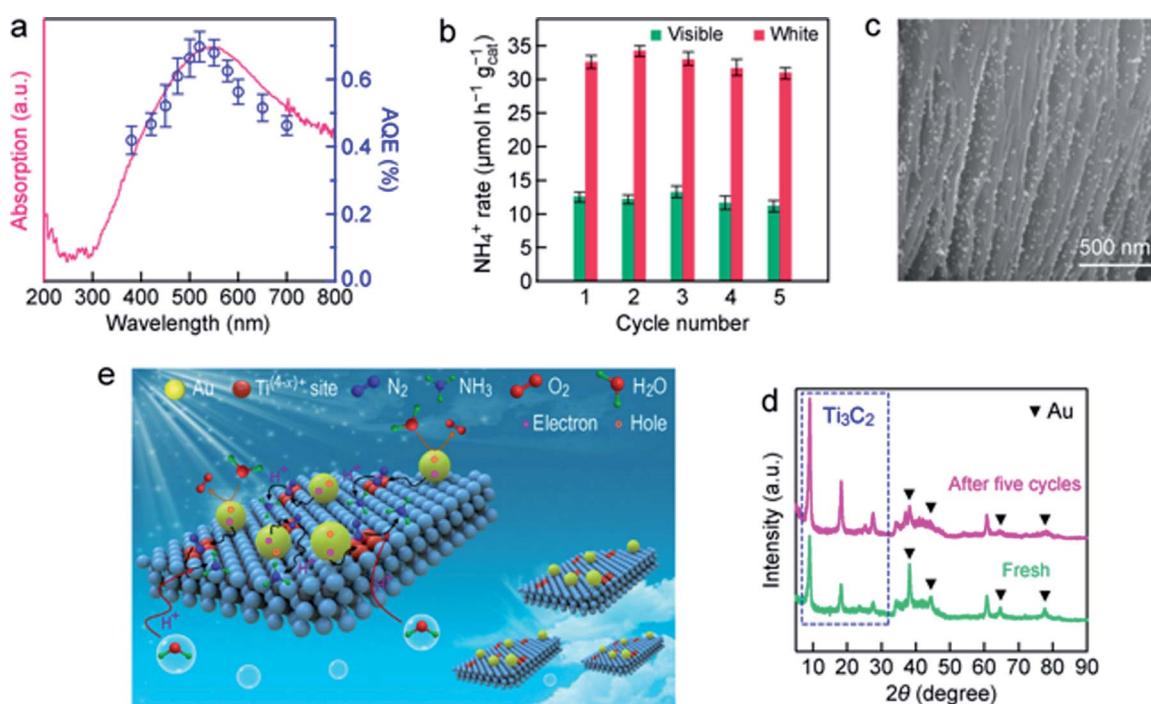


Fig. 7 AQEs and recyclability of r-Ti<sub>3</sub>C<sub>2</sub>/Au for N<sub>2</sub> photofixation. (a) AQE and absorption spectra. (b) Cyclic tests for N<sub>2</sub> photofixation under white and visible light. (c) SEM image of r-Ti<sub>3</sub>C<sub>2</sub>/Au after the fifth cycle of test. (d) XRD patterns of the fresh sample and those after the fifth cycle of test. (e) Artistic illustration of the proposed mechanism for photocatalytic N<sub>2</sub> fixation with r-Ti<sub>3</sub>C<sub>2</sub>/Au.



this wavelength (Tables S2 and S3†). In addition, we also examined the  $\text{N}_2$  photofixation activity of  $\text{r-Ti}_3\text{C}_2/\text{Au}$  under AM 1.5G solar light illumination in a sealed reactor filled with  $\text{N}_2$ . The  $\text{NH}_3$  production rate was  $21.26 \mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$ , and  $\text{O}_2$  was also generated at a rate of  $16.12 \mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$  in this sealed system (Fig. S21†). The molar ratio of the produced  $\text{NH}_3$  and  $\text{O}_2$  is close to the theoretical stoichiometric ratio. Accordingly, the solar-to-ammonia conversion efficiency (SACE) was calculated to be 0.013%. The stability of  $\text{r-Ti}_3\text{C}_2/\text{Au}$  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  $\text{r-Ti}_3\text{C}_2/\text{Au}$ . The unique sandwich-like structure with uniformly distributed Au nanospheres in the interlayers was well maintained in the used  $\text{r-Ti}_3\text{C}_2/\text{Au}$  catalyst (Fig. 7c). The slight decrease in the  $\text{NH}_3$  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  $\text{r-Ti}_3\text{C}_2/\text{Au}$  was further confirmed by the nearly unchanged XRD spectrum (Fig. 7d). The photocatalytic stability can be ascribed to the fact that electrons are constantly produced and transferred from the Au nanospheres to  $\text{Ti}_3\text{C}_2$  under light illumination, which can inhibit the oxidation of  $\text{Ti}_3\text{C}_2$ .

Based on the above results, we propose a reaction mechanism for photocatalytic  $\text{N}_2$  fixation with  $\text{r-Ti}_3\text{C}_2/\text{Au}$  under ambient conditions (Fig. 7e). Benefiting from the good hydrophilicity, the  $\text{r-Ti}_3\text{C}_2/\text{Au}$  photocatalyst can be stably and uniformly dispersed in water.  $\text{r-Ti}_3\text{C}_2$  possesses numerous low-valence  $\text{Ti}^{(4-x)+}$  sites that are associated with OVs and generated through  $\text{H}_2$  thermal reduction. They are active sites for capturing and activating  $\text{N}_2$  molecules. Under light illumination, photogenerated hot electrons from the Au nanospheres are injected into  $\text{r-Ti}_3\text{C}_2$ , which subsequently reduce the activated  $\text{N}_2$  at the  $\text{Ti}^{(4-x)+}$  sites. The hot holes remaining on the Au nanospheres are consumed through the oxidation of  $\text{H}_2\text{O}$  to produce  $\text{O}_2$ . The produced  $\text{NH}_3$  is accumulated in the aqueous reaction solution.

## Conclusions

We have demonstrated the potential of  $\text{Ti}_3\text{C}_2$  MXene to photocatalytically fix  $\text{N}_2$  in pure water under ambient conditions. Partially reduced layered  $\text{Ti}_3\text{C}_2$  MXene is synthesized and integrated with Au nanospheres in a uniform sandwich-like structure through a controlled solvent-driven approach.  $\text{r-Ti}_3\text{C}_2$  exposes abundant low-valence Ti sites, which act as active sites for capturing and activating  $\text{N}_2$  molecules. The embedded Au nanospheres donate plasmonic hot electrons to reduce the activated  $\text{N}_2$ . Importantly, the unique sandwich-like architecture prevents the self-stacking of the  $\text{Ti}_3\text{C}_2$  layers, which favors the exposure of the active sites for utilization. The abundant  $\text{Ti}^{(4-x)+}$  active sites and the LSPR effect work in tandem to endow  $\text{r-Ti}_3\text{C}_2/\text{Au}$  with a remarkably high  $\text{N}_2$  photofixation activity. The design in this work not only broadens the photocatalytic applications of MXene in  $\text{N}_2$  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. B. C. performed the experiments and wrote the manuscript. Y. Z. G. assisted with the  $\text{N}_2$  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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## Notes and references

- 1 H. P. Jia and E. A. Quadrelli, *Chem. Soc. Rev.*, 2014, **43**, 547.
- 2 C. J. M. Van der Ham, M. T. M. Koper and D. G. H. Hettterscheid, *Chem. Soc. Rev.*, 2014, **43**, 5183.
- 3 Y. M. Liu and T. J. Meyer, *Proc. Natl. Acad. Sci. U. S. A.*, 2019, **116**, 2794.
- 4 G. F. Chen, X. R. Cao, S. Q. Wu, X. Y. Zeng, L. X. Ding, M. Zhu and H. H. Wang, *J. Am. Chem. Soc.*, 2017, **139**, 9771.
- 5 A. Klerke, C. H. Christensen, J. K. Nørskov and T. Vegge, *J. Mater. Chem.*, 2008, **18**, 2304.
- 6 S. Licht, B. C. Cui, B. H. Wang, F. F. Li, J. Lau and S. Z. Liu, *Science*, 2014, **345**, 637.
- 7 D. Bao, Q. Zhang, F. L. Meng, H. X. Zhong, M. M. Shi, Y. Zhang, J. M. Yan, Q. Jiang and X. B. Zhang, *Adv. Mater.*, 2017, **29**, 1604799.
- 8 H. Li, C. L. Mao, H. Shang, Z. P. Yang, Z. H. Ai and L. Z. Zhang, *Nanoscale*, 2018, **10**, 15429.
- 9 H. Li, J. Shang, Z. H. Ai and L. Z. Zhang, *J. Am. Chem. Soc.*, 2015, **137**, 6393.
- 10 W. K. Wang, H. M. Zhang, S. B. Zhang, Y. Y. Liu, G. Z. Wang, C. H. Sun and H. J. Zhao, *Angew. Chem., Int. Ed.*, 2019, **58**, 16644.
- 11 H. Hirakawa, M. Hashimoto, Y. Shiraishi and T. Hirai, *J. Am. Chem. Soc.*, 2017, **139**, 10929.
- 12 G. N. Schrauzer and T. D. Guth, *J. Am. Chem. Soc.*, 1977, **99**, 7189.



13 C. M. Janet, S. Navaladian, B. Viswanathan, T. K. Varadarajan and R. P. Viswanath, *J. Phys. Chem. C*, 2010, **114**, 2622.

14 X. L. Xue, R. P. Chen, H. W. Chen, Y. Hu, Q. Q. Ding, Z. T. Liu, L. B. Ma, G. Y. Zhu, W. J. Zhang, Q. Yu, J. Liu, J. Ma and Z. Jin, *Nano Lett.*, 2018, **18**, 7372.

15 C. K. Yao, R. Wang, Z. S. Wang, H. Lei, X. P. Dong and C. Z. He, *J. Mater. Chem. A*, 2019, **7**, 27547.

16 Q. X. Liu, L. H. Ai and J. Jiang, *J. Mater. Chem. A*, 2018, **6**, 4102.

17 Y. C. Hao, X. L. Dong, S. R. Zhai, H. C. Ma, X. Y. Wang and X. F. Zhang, *Chem.-Eur. J.*, 2016, **22**, 18722.

18 H. L. Jia, A. Du, H. Zhang, J. H. Yang, R. B. Jiang, J. F. Wang and C. Y. Zhang, *J. Am. Chem. Soc.*, 2019, **141**, 5083.

19 H. Diarmand-Khalilabad, A. Habibi-Yangjeh, D. Seifzadeh, S. Asadzadeh-Khaneghah and E. Vesali-Kermani, *Ceram. Int.*, 2019, **45**, 2542.

20 Y. F. Sun, S. Gao, F. C. Lei and Y. Xie, *Chem. Soc. Rev.*, 2015, **44**, 623.

21 Y. F. Sun, S. Gao, F. C. Lei, C. Xiao and Y. Xie, *Acc. Chem. Res.*, 2015, **48**, 3.

22 Q. Su, Y. Li, R. Hu, F. Song, S. Y. Liu, C. P. Guo, S. M. Zhu, W. B. Liu and J. Pan, *Adv. Sustainable Syst.*, 2020, **4**, 2000130.

23 M. Naguib, M. Kurtoglu, V. Presser, J. Lu, J. J. Niu, M. Heon, L. Hultman, Y. Gogotsi and M. W. Barsoum, *Adv. Mater.*, 2011, **23**, 4248.

24 M. Naguib, V. N. Mochalin, M. W. Barsoum and Y. Gogotsi, *Adv. Mater.*, 2014, **26**, 992.

25 B. Anasori, M. R. Lukatskaya and Y. Gogotsi, *Nat. Rev. Mater.*, 2017, **2**, 16098.

26 X. B. Hui, X. L. Ge, R. Z. Zhao, Z. Q. Li and L. W. Yin, *Adv. Funct. Mater.*, 2020, **30**, 2005190.

27 Z. Li and Y. Wu, *Small*, 2019, **15**, 1804736.

28 J. H. Peng, X. Z. Chen, W. J. Ong, X. J. Zhao and N. Li, *Chem.*, 2019, **5**, 18.

29 R. D. Tang, S. Xiong, D. X. Gong, Y. C. Deng, Y. C. Wang, L. Su, C. X. Ding, L. H. Yang and C. J. Liao, *ACS Appl. Mater. Interfaces*, 2020, **12**, 56663.

30 X. Li, Y. Bai, X. Shi, N. Su, G. Z. Nie, R. M. Zhang, H. B. Nie and L. Q. Ye, *Mater. Adv.*, 2021, **2**, 1570.

31 L. M. Azofra, N. Li, D. R. Macfarlane and C. H. Sun, *Energy Environ. Sci.*, 2016, **9**, 2545.

32 K. L. Huang, C. H. Li, H. Z. Li, G. M. Ren, L. Wang, W. T. Wang and X. C. Meng, *ACS Appl. Nano Mater.*, 2020, **3**, 9581.

33 L. F. Hong, R. T. Guo, Y. Yuan, X. Y. Ji, Z. S. Li, Z. D. Lin and W. G. Pan, *Mater. Today Energy*, 2020, **18**, 100521.

34 J. Z. Qin, X. Hu, X. Y. Li, Z. F. Yin, B. J. Liu and K. H. Lam, *Nano Energy*, 2019, **61**, 27.

35 J. H. Yang, Y. Z. Guo, W. Z. Lu, R. B. Jiang and J. F. Wang, *Adv. Mater.*, 2018, **30**, 1802227.

36 J. H. Yang, Y. Z. Guo, R. B. Jiang, F. Qin, H. Zhang, W. Z. Lu, J. F. Wang and J. C. Yu, *J. Am. Chem. Soc.*, 2018, **140**, 8497.

37 C. Y. Hu, X. Chen, J. B. Jin, Y. Han, S. M. Chen, H. X. Ju, J. Cai, Y. R. Qiu, C. Gao, C. M. Wang, Z. M. Qi, R. Long, L. Song, Z. Liu and Y. J. Xiong, *J. Am. Chem. Soc.*, 2019, **141**, 7807.

38 T. T. Hou, L. L. Chen, Y. Xin, W. K. Zhu, C. Y. Zhang, W. H. Zhang, S. Q. Liang and L. B. Wang, *ACS Energy Lett.*, 2020, **5**, 2444.

39 P. Zhang, T. Wang and J. L. Gong, *Adv. Mater.*, 2015, **27**, 5328.

40 J. H. Yang, H. Y. Bai, Y. Z. Guo, H. Zhang, R. B. Jiang, B. C. Yang, J. F. Wang and J. C. Yu, *Angew. Chem., Int. Ed.*, 2021, **60**, 927.

41 T. B. Limbu, B. Chitara, J. D. Orlando, M. Y. Garcia Cervantes, S. Kumari, Q. Li, Y. Tang and F. Yan, *J. Mater. Chem. C*, 2020, **8**, 4722.

42 Y. Y. Wen, T. E. Rufford, X. Z. Chen, N. Li, M. Q. Lyu, L. M. Dai and L. Z. Wang, *Nano Energy*, 2017, **38**, 368.

43 M. Ghidiu, S. Kota, J. Halim, A. W. Sherwood, N. Nedfors, J. Rosen, V. N. Mochalin and M. W. Barsoum, *Chem. Mater.*, 2017, **29**, 1099.

44 C. J. Zhao, Q. Wang, H. Zhang, S. Passerini and X. Z. Qian, *ACS Appl. Mater. Interfaces*, 2016, **8**, 15661.

45 G. D. Zou, Z. W. Zhang, J. X. Guo, B. Z. Liu, Q. R. Zhang, C. Fernandez and Q. M. Peng, *ACS Appl. Mater. Interfaces*, 2016, **8**, 22280.

46 J. X. Low, L. Y. Zhang, T. Tong, B. J. Shen and J. G. Yu, *J. Catal.*, 2018, **361**, 255.

47 A. A. Khan, M. Tahir and A. Bafaqueer, *Energy Fuels*, 2020, **34**, 9810.

48 R. B. Rakhi, B. Ahmed, M. N. Hedhili, D. H. Anjum and H. N. Alshareef, *Chem. Mater.*, 2015, **27**, 5314.

49 X. L. Li, X. W. Yin, M. K. Han, C. Q. Song, H. L. Xu, Z. X. Hou, L. T. Zhang and L. F. Cheng, *J. Mater. Chem. C*, 2017, **5**, 4068.

50 Y. Yoon, T. A. Le, A. P. Tiwari, I. Kim, M. W. Barsoum and H. Lee, *Nanoscale*, 2018, **10**, 22429.

51 H. Wang, Y. Wu, X. Z. Yuan, G. Zeng, J. Zhou, X. Wang and J. W. Chew, *Adv. Mater.*, 2018, **30**, 1704561.

52 R. Y. Li, L. B. Zhang, L. Shi and P. Wang, *ACS Nano*, 2017, **11**, 3752.

53 Y. Z. Guo, J. H. Yang, D. H. Wu, H. Y. Bai, Z. Yang, J. F. Wang and B. C. Yang, *J. Mater. Chem. A*, 2020, **8**, 16218.

54 S. Y. Moon, H. C. Song, E. H. Gwag, L. I. Nedrygailov, C. Lee, J. J. Kim, W. H. Doh and J. Y. Park, *Nanoscale*, 2018, **10**, 22180.

55 S. Y. Wang, X. Hai, X. Ding, K. Chang, Y. G. Xiang, X. G. Meng, Z. X. Yang, H. Chen and J. H. Ye, *Adv. Mater.*, 2017, **29**, 1701774.

56 J. Liu, M. S. Kelley, W. Q. Wu, A. Banerjee, A. P. Douvalis, J. S. Wu, Y. B. Zhang, G. C. Schatz and M. G. Kanatzidis, *Proc. Natl. Acad. Sci. U. S. A.*, 2016, **113**, 5530.

57 Y. X. Zhao, Y. F. Zhao, R. Shi, B. Wang, G. I. N. Waterhouse, L. Z. Wu, C. H. Tung and T. R. Zhang, *Adv. Mater.*, 2019, **31**, 1806482.

58 D. Liu, G. Zhang, Q. H. Ji, Y. Y. Zhang and J. H. Li, *ACS Appl. Mater. Interfaces*, 2019, **11**, 25758.

59 C. D. Lv, Y. M. Qian, C. S. Yan, Y. Ding, Y. Y. Liu, G. Chen and G. H. Yu, *Angew. Chem., Int. Ed.*, 2018, **57**, 10246.

60 X. M. Li, X. Sun, L. Zhang, S. M. Sun and W. Z. Wang, *J. Mater. Chem. A*, 2018, **6**, 3005.

61 L. R. Johnson, S. Sridhar, L. Zhang, K. D. Fredrickson, A. S. Raman, J. Jang, C. Leach, A. Padmanabhan,



C. C. Price, N. C. Frey, A. Raizada, V. Rajaraman, S. Saiprasad, X. Tang and A. Vojvodic, *ACS Catal.*, 2020, **10**, 253.

62 Y. Tanabe and Y. Nishibayashi, *Coord. Chem. Rev.*, 2013, **257**, 2551.

63 M. A. Legare, G. Belanger-Chabot, R. D. Dewhurst, E. Welz, I. Krummenacher, B. Engels and H. Braunschweig, *Science*, 2018, **359**, 896.

64 J. D. Gouveia, Á. Morales-García, F. Viñes, J. R. B. Gomes and F. Illas, *ACS Catal.*, 2020, **10**, 5049.

65 S. Li, G. Liu, Z. Liu, W. Hu and H. Deng, *J. Mater. Chem. A*, 2019, **7**, 19950.

