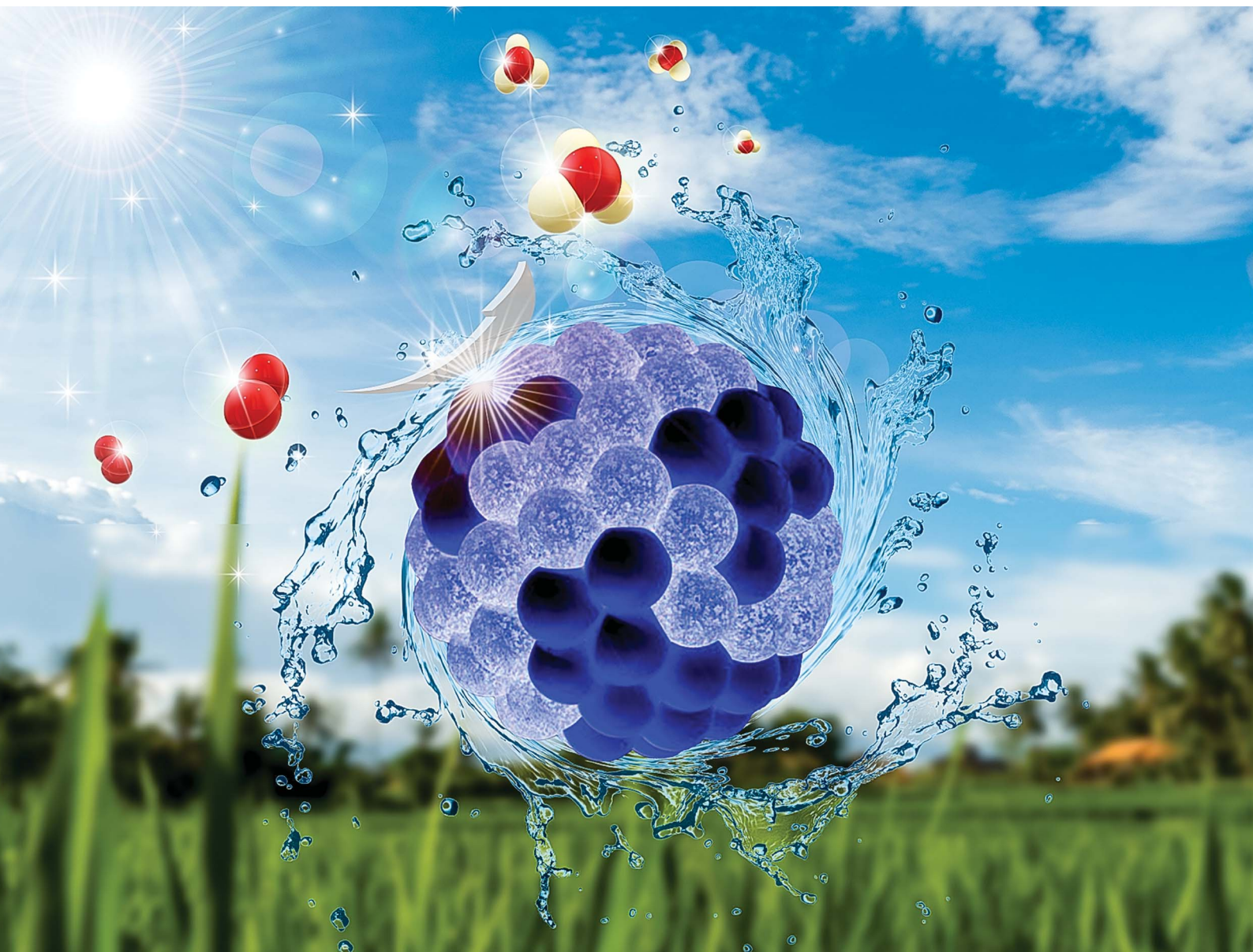


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Phase-selective active sites on ordered/disordered titanium dioxide enable exceptional photocatalytic ammonia synthesis

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# Phase-selective active sites on ordered/disordered titanium dioxide enable exceptional photocatalytic ammonia synthesis†

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Photocatalytic N<sub>2</sub> fixation to NH<sub>3</sub> *via* defect creation on TiO<sub>2</sub> to activate ultra-stable N≡N has drawn enormous scientific attention, but poor selectivity and low yield rate are the major bottlenecks. Additionally, whether N<sub>2</sub> preferentially adsorbs on phase-selective defect sites on TiO<sub>2</sub> in correlation with appropriate band alignment has yet to be explored. Herein, theoretical predictions reveal that the defect sites on disordered anatase (A<sub>d</sub>) preferentially exhibit higher N<sub>2</sub> adsorption ability with a reduced energy barrier for a potential-determining-step (\*N<sub>2</sub> to NNH\*) than the disordered rutile (R<sub>d</sub>) phase of TiO<sub>2</sub>. Motivated by theoretical simulations, we synthesize a phase-selective disordered-anatase/ordered-rutile TiO<sub>2</sub> photocatalyst (Na-A<sub>d</sub>/R<sub>o</sub>) by sodium-amine treatment of P25-TiO<sub>2</sub> under ambient conditions, which exhibits an efficient NH<sub>3</sub> formation rate of 432 μmol g<sup>-1</sup> h<sup>-1</sup>, which is superior to that of any other defect-rich disordered TiO<sub>2</sub> under solar illumination with a high apparent quantum efficiency of 13.6% at 340 nm. The multi-synergistic effects including selective N<sub>2</sub> chemisorption on the defect sites of Na-A<sub>d</sub> with enhanced visible-light absorption, suitable band alignment, and rapid interfacial charge separation with R<sub>o</sub> enable substantially enhanced N<sub>2</sub> fixation.

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## 1. Introduction

Ammonia (NH<sub>3</sub>) is not only the most important industrial chemical but also the most promising carbon-free energy alternative due to its high hydrogen density (17.8 wt%).<sup>1</sup> Industrial NH<sub>3</sub> production has heavily relied on the traditional Haber–Bosch process (150–350 atm, 350–550 °C), which consumes ~2% of the global energy supply and accounts for 1.6% of total global CO<sub>2</sub> emissions.<sup>2,3</sup> To circumvent these issues, an alternative N<sub>2</sub> fixation method operating under milder reaction conditions is necessary, and in response to this, electrocatalytic and photocatalytic N<sub>2</sub> reduction reactions (NRRs) have emerged as promising choices as they can be performed under green and sustainable conditions.<sup>4–9</sup>

However, the reduction of N<sub>2</sub> to NH<sub>3</sub> under ambient conditions is extremely difficult due to the inherent nature of the N≡N (bond dissociation energy: 940.95 kJ mol<sup>-1</sup>) along with additional thermodynamically challenging multistep processes. Although recent progress in the photocatalytic NRR demonstrated that N<sub>2</sub> fixation can be promoted using various semiconductors including two-dimensional materials such as Mxenes,<sup>10</sup> TiO<sub>2</sub> nanosheets,<sup>11</sup> Au/end-CeO<sub>2</sub>,<sup>12</sup> Bi<sub>5</sub>O<sub>7</sub>X (X = Cl, Br, I) nanotubes,<sup>13,14</sup> and single atoms anchored on various supports,<sup>15,16</sup> the selectivity and NH<sub>3</sub> yield rate for most of them are far from satisfactory. The two main reasons for the poor photocatalytic NRR are (i) poor interfacial charge transfer (CT) due to the high recombination rate of photo-generated holes and electrons and (ii) weak N<sub>2</sub> adsorption ability.<sup>9</sup> Therefore, a novel strategy to design photocatalysts with efficient charge separation and high N<sub>2</sub> adsorption ability is urgently needed to improve the performance of the photocatalytic NRR.

More recently, defect engineering of photocatalysts has received immense attention as it offers unsaturated sites for N<sub>2</sub> chemisorption, further weakening the N≡N and lowering the activation energy barrier for the NRR.<sup>17</sup> For instance, Hirakawa *et al.* reported that introducing oxygen vacancies (O<sub>v</sub>) on commercial JRC-TIO-6 (rutile phase, R) can boost the photocatalytic NRR with a solar-to-chemical conversion (SCC) efficiency of 0.02%.<sup>18</sup> Zhao *et al.* elucidated that O<sub>v</sub> along with lattice strain rich ultrathin anatase (A) nanosheets obtained *via* a facile copper-doping strategy exhibited strong chemisorption and activation of N<sub>2</sub> and water, resulting in high rates of NH<sub>3</sub>

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evolution under visible-light irradiation.<sup>11</sup> However, the defect sites introduced additionally act as the recombination centers of the photogenerated carriers and limit the efficiency of the reported photocatalysts. Therefore, despite such significant efforts on the defect engineering of the TiO<sub>2</sub> surface, the lack of fundamental understanding of the nature of phase-selective defect sites, high recombination rate, poor visible-light harvesting ability, harsh defect-engineering procedure, and insufficient chemisorption/activation of N≡N severely hamper the photocatalytic NRR kinetics. In addition, one important issue remained unanswered “Whether N<sub>2</sub> chemisorption happens at all the O<sub>v</sub> sites, or it is specific to a particular phase of P25-TiO<sub>2</sub> (A: 75% and R: 25%) in correlation with appropriate band alignment for activating N<sub>2</sub> and subsequent conversion to NH<sub>3</sub>” deserves to be further investigated.

Herein, we first investigated the N<sub>2</sub> fixation activity of single-phase ordered (R<sub>o</sub>, A<sub>o</sub>) and disordered (R<sub>d</sub>, A<sub>d</sub>) TiO<sub>2</sub> by theoretical calculations, which suggested that creating O<sub>v</sub> on the anatase phase of TiO<sub>2</sub> (A<sub>d</sub>) is conducive for N<sub>2</sub> adsorption, significantly reducing the energy barrier of the potential-determining step (PDS: \*N<sub>2</sub> to NNH\*), boosting the intrinsic NRR over the rutile phase (R<sub>d</sub>). Encouraged by theoretical predictions, we developed a facile strategy to synthesize a phase-selective A<sub>d</sub>/R<sub>o</sub> heterostructure by alkali metal (Na) amine treatment of P25-TiO<sub>2</sub> (Na-A<sub>d</sub>/R<sub>o</sub>) under ambient conditions, which exhibits an efficient adsorption/desorption kinetics of N<sub>2</sub>/NH<sub>3</sub> specifically on the Na-A<sub>d</sub> phase and faster hole transport through the heterointerface region of the R<sub>o</sub> phase hindering charge recombination, significantly facilitating water oxidation to produce necessary protons for efficient N<sub>2</sub> fixation. The novel Na-A<sub>d</sub>/R<sub>o</sub> without any co-catalyst possesses a superior NH<sub>3</sub> formation rate (432 μmol g<sup>-1</sup> h<sup>-1</sup>), which is ~125 and 5.5 times

higher than that of bare TiO<sub>2</sub> and Na-A<sub>d</sub>, respectively under solar illumination, exhibiting one of the superior NRR performances with a high selectivity of 97.6%. Theoretical simulations clearly revealed that high intrinsic N<sub>2</sub> chemisorption ability with the reduced energy barrier for PDS selectively originated from defect sites on Na-A<sub>d</sub> rather than R<sub>o</sub> and Li-R<sub>d</sub> (Li-EDA treated R<sub>o</sub>) along with a suitable band alignment promoting the NRR over hydrogen (H<sub>2</sub>) generation on Na-A<sub>d</sub>/R<sub>o</sub>. The multi-synergistic effects induced by phase-selective defect sites on Na-A<sub>d</sub>/R<sub>o</sub>, increased visible light absorption, and enhanced interfacial charge separation are found to be the key factors for higher photocatalytic activity.

## 2. Results and discussion

### 2.1 Theoretical calculation predictions

To understand the nature of phase-selective defect sites, density functional theory (DFT) calculations were first conducted to study the intrinsic N<sub>2</sub> adsorption ability on the specific phase of ordered (R<sub>o</sub>, A<sub>o</sub>) and defect-rich disordered (Li-R<sub>d</sub>, Na-A<sub>d</sub>) TiO<sub>2</sub> samples. The optimized atomic models with adsorbed N<sub>2</sub> molecules on Li-R<sub>d</sub>, Na-A<sub>d</sub>, R<sub>o</sub>, and A<sub>o</sub> are presented in Fig. 1a–d. The computed N<sub>2</sub> adsorption energy ( $E_{\text{ads}}$ ) values on R<sub>o</sub> and A<sub>o</sub> are close to 0 eV, indicating that the adsorption/activation of N<sub>2</sub> in the absence of defect-sites on A<sub>o</sub> and R<sub>o</sub> hardly takes place at room temperature (Fig. 1e). In contrast, N<sub>2</sub> can readily adsorb on Na-A<sub>d</sub> with an  $E_{\text{ads}}$  of -0.21 eV (thermodynamically favorable), while N<sub>2</sub> adsorption on Li-R<sub>d</sub> is an endothermic process ( $E_{\text{ads}}$ : +0.61 eV), suggesting that the defect sites on the A<sub>d</sub> phase of TiO<sub>2</sub> selectively prefer N<sub>2</sub> chemisorption over the R<sub>d</sub> phase. Furthermore, we examined the Gibbs free energy diagrams of the NRR along the alternating pathway on Na-A<sub>d</sub> and Li-R<sub>d</sub>

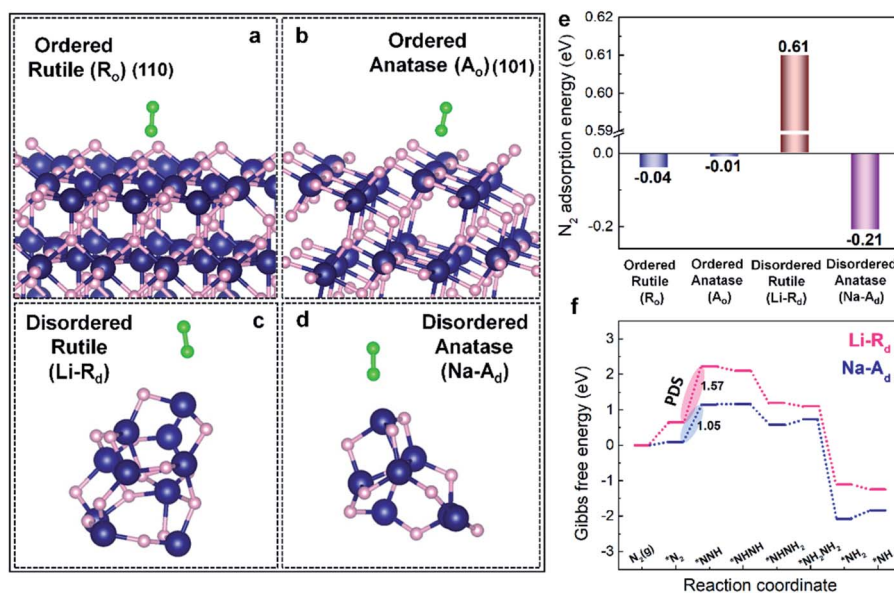


Fig. 1 DFT calculations of N<sub>2</sub> adsorption on ordered/disordered TiO<sub>2</sub> and the reaction pathway. (a–d) Optimized atomic models with N<sub>2</sub> molecules on R<sub>o</sub>, A<sub>o</sub>, Li-R<sub>d</sub>, and Na-A<sub>d</sub>. (e) N<sub>2</sub> adsorption energy on R<sub>o</sub>, A<sub>o</sub>, Li-R<sub>d</sub>, and Na-A<sub>d</sub> atomic models. (f) Gibbs free energy ( $\Delta G$ ) profiles of N<sub>2</sub> fixation over Li-R<sub>d</sub> and Na-A<sub>d</sub> along the alternating pathway. Navy, pink, light green balls represent titanium, oxygen, and nitrogen, respectively.



(Fig. 1f). Similar to the  $E_{\text{ads}}$  trend, the first hydrogenation step (PDS:  $^*N_2$  to  $NNH^*$ ) on  $Na-A_d$  is energetically more favorable than that on  $Li-R_d$ , boosting  $NH_3$  synthesis for the former. In a nutshell, DFT calculations certify that phase-selective defect sites on the  $A_d$  phase of  $TiO_2$  ( $Na-A_d$ ) show higher  $N_2$  adsorption ability with superior intrinsic NRR activity over defect sites on the  $R_d$  phases of  $TiO_2$  ( $Li-R_d$ ).

## 2.2 Synthesis and structural analysis of ordered/disordered $TiO_2$ photocatalysts

Motivated by the theoretical predictions, a series of selectively ordered/disordered phases of  $P25-TiO_2$  were synthesized by

alkali-metal amine treatment also known as “dissolving-metal reduction” following our previous reports with slight modifications,<sup>19,20</sup> as it is an effective strategy to create  $O_v$  on the specific phase of  $TiO_2$ . Using lithium and the sodium ethylenediamine complex (Li, Na-EDA) with different reduction abilities of the solvated electrons can selectively create defect sites ( $Ti^{3+}$  adjacent to  $O_v$ ) on  $R_o$  and  $A_o$  phases, respectively, to generate  $Li-R_d$  and  $Na-A_d$ , under mild conditions. The X-ray diffraction (XRD) (Fig. S1†) peaks indicate a gradual decrease in the specific phase of  $P25-TiO_2$  with the reaction time (1, 3, and 7 days) by Li/Na-EDA treatments. Fig. 2a reveals that either the  $R_o$  or  $A_o$  phase in mixed-phase  $P25-TiO_2$  nearly disappeared

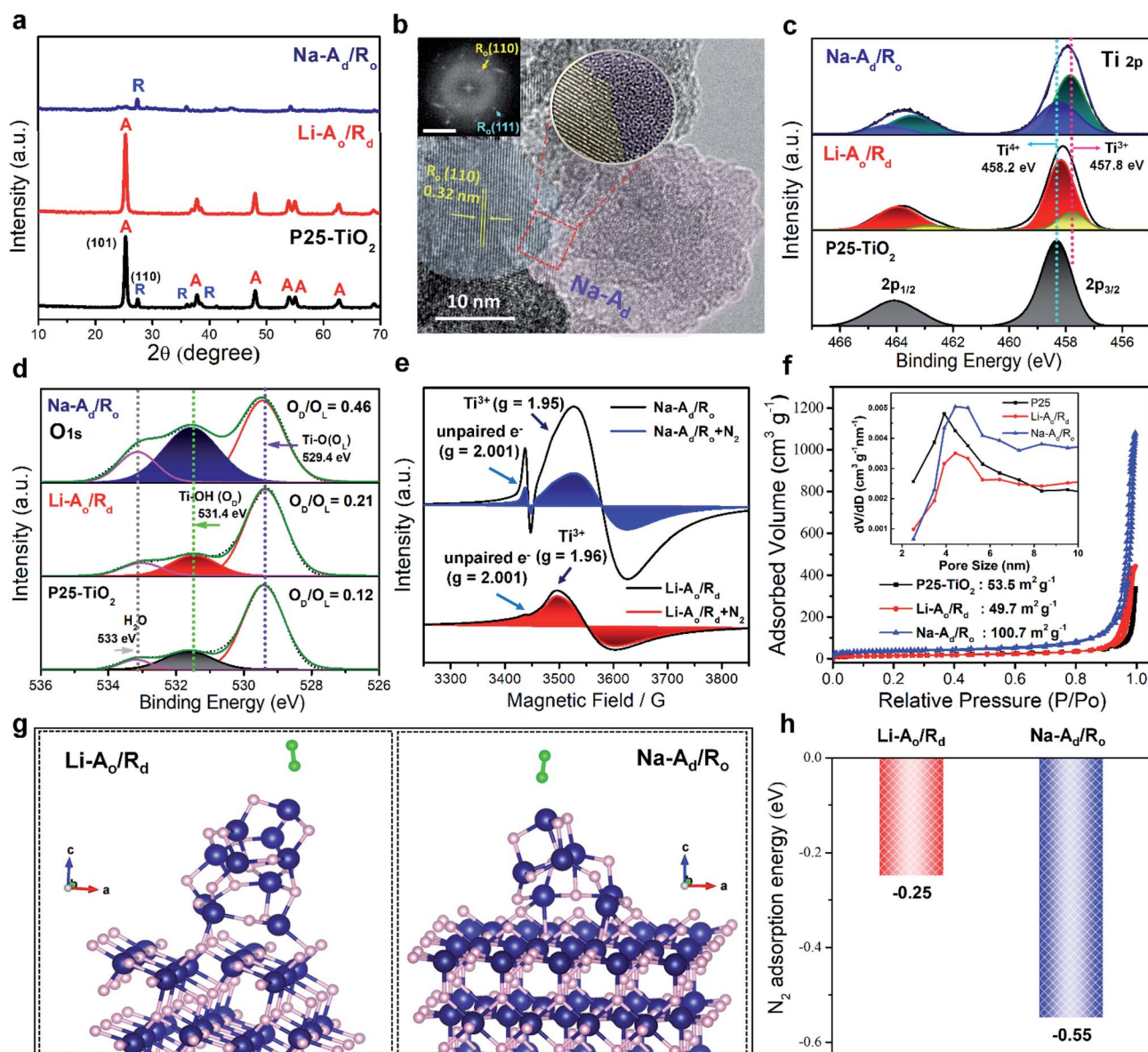


Fig. 2 Structural characterization and simulation for  $N_2$  adsorption on  $P25-TiO_2$ ,  $Li-A_o/R_d$ , and  $Na-A_d/R_o$ . (a) The powder X-ray diffraction spectra (XRD). (b) HR-TEM image of  $Na-A_d/R_o$  (inset scale bar:  $5\text{ nm}^{-1}$ ). XPS spectra of (c) Ti 2p and (d) O 1s. (e) Electron paramagnetic resonance (EPR) spectra of  $Li-A_o/R_d$  and  $Na-A_d/R_o$  before and after  $N_2$  saturation at 77 K. (f)  $N_2$  adsorption–desorption isotherms of  $P25-TiO_2$ ,  $Li-A_o/R_d$  and  $Na-A_d/R_o$  (inset, corresponding pore-size distribution). (g) Optimized atomic models with  $N_2$  molecules on  $Li-A_o/R_d$  and  $Na-A_d/R_o$ . (h)  $N_2$  adsorption energy of  $Li-A_o/R_d$  and  $Na-A_d/R_o$ . Navy, pink, light green balls represent titanium, oxygen, and nitrogen, respectively.



after 7 days of treatment, denoted as Li-A<sub>o</sub>/R<sub>d</sub> and Na-A<sub>d</sub>/R<sub>o</sub>, respectively, which is additionally supported by Raman spectra (Fig. S2†). The high-resolution transmission electron microscopy (HRTEM) image with the selected area electron diffraction (SAED) pattern of Na-A<sub>d</sub>/R<sub>o</sub> revealed the formation of a distinct heterointerface between the crystalline phase of R<sub>o</sub> and disordered phase of Na-A<sub>d</sub> along with uniform distribution of Ti and O as confirmed by EDX mapping (Fig. 2b and S3†). The ordered lattice fringes with a spacing of 3.6 Å and 2.1 Å can be assigned to the A<sub>o</sub>(101) and R<sub>o</sub>(111) plane (Fig. S4a and b†), respectively, along with each disordered phase starting from the surface to the core after 5 days of treatment, further confirming the random distribution of atoms in the disordered phase by HADDF-STEM (Fig. S4c–f†). Thus, our phase-selective disordered method successfully introduces defect sites on the specific phase of the TiO<sub>2</sub> surface, which could selectively capture inert N<sub>2</sub> and boost the NRR.

To investigate the chemical composition and valence states of the elements over the selectively reduced TiO<sub>2</sub> catalysts, high-resolution X-ray photoelectron spectroscopy (XPS) was employed. Compared to P25-TiO<sub>2</sub>, the binding energy (BE) of the Ti 2p doublet peaks at 458.2 and 463.9 eV consistent with the typical characteristic peaks of Ti 2p<sub>1/2</sub> and Ti 2p<sub>3/2</sub> for Ti<sup>4+</sup> showed a negative shift to lower BE for Li-A<sub>o</sub>/R<sub>d</sub> and Na-A<sub>d</sub>/R<sub>o</sub>, attributed to the appearance of a low-valence Ti<sup>3+</sup> at 457.8 and 462.8 eV on the surface (Fig. 2c).<sup>21</sup> The removal of lattice oxygen left excessive electrons trapped by the adjacent Ti<sup>4+</sup> species, generating Ti<sup>3+</sup> sites or unpaired electrons, which could behave as an active center for surface adsorption of key N<sub>2</sub> adsorbates. The O 1s XPS spectra exhibit three peaks at 529.4, 531.4, and 533 eV, attributed to the TiO<sub>2</sub> lattice oxygen (Ti–O, O<sub>L</sub>), surface hydroxyl group (Ti–OH, defective oxygen: O<sub>D</sub>) originating from the reaction between chemisorbed water and the oxygen vacancy of disordered TiO<sub>2</sub>, and adsorbed H<sub>2</sub>O molecule, respectively (Fig. 2d). In Fig. S5a–d,† there is a gradual increase of Ti<sup>3+</sup> sites with a simultaneous increase of O<sub>D</sub>/O<sub>L</sub> ratio for Li-A<sub>o</sub>/R<sub>d</sub> (0.21) and Na-A<sub>d</sub>/R<sub>o</sub> (0.46) as a function of reaction time, confirming the generation of Ti<sup>3+</sup> with oxygen vacancies during alkali-metal amine treatment.<sup>22</sup> Furthermore, the absence of all possible impurities like EDA (ethylenediamine), alkali ions (Na<sup>+</sup>), and chloride (Cl<sup>−</sup>) in the samples which may cause exaggerated and erroneous NH<sub>3</sub> yield was confirmed by N 1s, Na 1s, and Cl 2p XPS spectra, respectively, (Fig. S5e–h†).<sup>23</sup> We further quantified the amount of Ti<sup>3+</sup> on Li-A<sub>o</sub>/R<sub>d</sub>, Na-A<sub>d</sub>/R<sub>o</sub>, Li-R<sub>d</sub>, and Na-A<sub>d</sub> by XPS peak deconvolution and CO<sub>2</sub> temperature-programmed desorption (CO<sub>2</sub>-TPD) measurements, as summarized in Table 1. Atomic percentages of Ti<sup>3+</sup>/Ti<sup>4+</sup> over the samples in the Ti 2p orbitals of XPS were calculated (Fig. S6†). CO<sub>2</sub>-TPD was also investigated to monitor surface defects (Ti<sup>3+</sup>) existing in disordered structures (Fig. S7 and Table S1†). CO<sub>2</sub>-TPD analysis between 150 and 500 °C resulted in two ranges: one range between 170 and 204 °C attributed to CO<sub>2</sub> molecules bound to a regular five-coordinate Ti<sup>4+</sup> site in the ordered TiO<sub>2</sub> and the other over 280 °C corresponds to CO<sub>2</sub> molecules bound to defective Ti<sup>3+</sup> species in the disordered structure, indicating Ti<sup>3+</sup> species bonded CO<sub>2</sub> more strongly than the regular five-coordinate Ti<sup>4+</sup> sites.<sup>24</sup> From the above results, it was found

that the surface defects (Ti<sup>3+</sup>) with oxygen vacancies on phase-selective disordered TiO<sub>2</sub> were successfully created by Li/Na-EDA treatment while P25-TiO<sub>2</sub> had a few defect sites.

The N<sub>2</sub> adsorption capacity is one of the key factors impacting NH<sub>3</sub> synthesis. The N<sub>2</sub> physisorption ability of defect sites on Na-A<sub>d</sub>/R<sub>o</sub> and Li-A<sub>o</sub>/R<sub>d</sub> compared to P25-TiO<sub>2</sub> was firstly investigated by electron paramagnetic resonance (EPR) analysis. Each catalyst (20 mg) was separately placed in a quartz EPR tube and analyzed at 77 K before and after N<sub>2</sub> (99.999%) gas saturation (20 torr) (Fig. 2e). Commercial TiO<sub>2</sub> with Ti<sup>4+</sup> sites are diamagnetic (3d<sup>0</sup>, S = 0) in nature whereas defective TiO<sub>2</sub> contains paramagnetic Ti<sup>3+</sup> centers (3d<sup>1</sup>, S = 1/2) also known as “spin-active defects” generated due to oxygen vacancies.<sup>25</sup> Both Na-A<sub>d</sub>/R<sub>o</sub> and Li-A<sub>o</sub>/R<sub>d</sub> show distinctive EPR signals of paramagnetic Ti<sup>3+</sup> (g = 1.96) and unpaired electrons (g = 2.001) trapped in the oxygen vacancies while P25-TiO<sub>2</sub> showed a negligible EPR signal (Fig. S8†). The Na-A<sub>d</sub>/R<sub>o</sub> exhibits a much higher number and signature of spin active Ti<sup>3+</sup> sites compared to Li-A<sub>o</sub>/R<sub>d</sub>, suggesting a high density of electron spin polarization arising from the spin active Ti<sup>3+</sup> centers on Na-A<sub>d</sub>/R<sub>o</sub>. Especially, these spin active Ti<sup>3+</sup> centers containing unpaired electrons in Na-A<sub>d</sub> can effectively interact with the N<sub>2</sub> adsorbates expected to be effective for N<sub>2</sub> fixation, which is corroborated by the significantly quenched EPR signal of Na-A<sub>d</sub>/R<sub>o</sub> after N<sub>2</sub> saturation (Fig. 2e). Additionally, the BET specific surface area of all samples was examined by N<sub>2</sub> adsorption–desorption measurements in Fig. 2f, which revealed that the P25-TiO<sub>2</sub>, Li-A<sub>o</sub>/R<sub>d</sub>, and Na-A<sub>d</sub>/R<sub>o</sub> are mesoporous in nature with an average pore distribution in the range of 3.5 to 4.5 nm. The specific surface area for Na-A<sub>d</sub>/R<sub>o</sub> (100.67 m<sup>2</sup> g<sup>−1</sup>) is much higher than that of Li-A<sub>o</sub>/R<sub>d</sub> (49.7 m<sup>2</sup> g<sup>−1</sup>) with a slightly larger average pore size compared to P25-TiO<sub>2</sub>, implying higher N<sub>2</sub> adsorption with better mass transport, suitable for enhancing N<sub>2</sub> fixation. Interestingly, the Na-A<sub>d</sub> (143.74 m<sup>2</sup> g<sup>−1</sup>) exhibited a much higher surface area than Li-R<sub>d</sub> (14.508 m<sup>2</sup> g<sup>−1</sup>) even with abundant Ti<sup>3+</sup> species in both cases, indicating high intrinsic N<sub>2</sub> adsorption ability of the defect sites on Na-A<sub>d</sub>, consistent with the calculated N<sub>2</sub> adsorption energy (Fig. 1e and S9†). To further understand the chemisorption ability of surface defects on Na/Li-TiO<sub>2</sub> samples compared to P25-TiO<sub>2</sub>, N<sub>2</sub>/NH<sub>3</sub>-TPD measurements were then employed (Fig. S10 and Table S2†).<sup>26,27</sup> The area of N<sub>2</sub> desorption follows the order of Na-A<sub>d</sub> > Na-A<sub>d</sub>/R<sub>o</sub> > Li-A<sub>o</sub>/R<sub>d</sub> ~ Li-R<sub>d</sub> > P25-TiO<sub>2</sub>, indicating that Na-A<sub>d</sub> and Na-A<sub>d</sub>/R<sub>o</sub> have higher and stronger N<sub>2</sub> adsorption capacities than Li-R<sub>d</sub> and Li-A<sub>o</sub>/R<sub>d</sub>. Meanwhile, NH<sub>3</sub>-TPD was evaluated to monitor the NH<sub>3</sub> desorption from the catalysts.<sup>27</sup> Most of the NH<sub>3</sub> desorbed on Na-A<sub>d</sub>/R<sub>o</sub> and Na-A<sub>d</sub> relatively at a low temperature (100–194 °C), which indicates its weak adsorption on defect sites compared to Li-A<sub>o</sub>/R<sub>d</sub> and Li-R<sub>d</sub>, implying much faster reaction kinetics and mass diffusion for the former. Likewise, the optimized N<sub>2</sub>-E<sub>ad</sub> of Na-A<sub>d</sub> on Na-A<sub>d</sub>/R<sub>o</sub> (−0.55 eV) exhibits more negative values than that of Li-R<sub>d</sub> on Li-A<sub>o</sub>/R<sub>d</sub> (−0.25 eV) as calculated by DFT (Fig. 2g and h) and AIMD simulations (Movies S1–S6†),<sup>28–32</sup> suggesting that N<sub>2</sub> adsorption is favorable on the defect sites of Na-A<sub>d</sub> over Li-R<sub>d</sub> in the heterostructure, further verifying our above-mentioned claims. Note that we also considered the N<sub>2</sub>-E<sub>ad</sub> at the interface between Na-A<sub>d</sub> and R<sub>o</sub>,



Table 1 Summary of photoactivity and selectivity of various phase-selective ordered/disordered TiO<sub>2</sub> samples for photocatalytic N<sub>2</sub> fixation

| Sample                            | Surface area <sup>a</sup> (m <sup>2</sup> g <sup>-1</sup> ) | E <sub>g</sub> <sup>b</sup> (eV) | Quantity of Ti <sup>3+</sup> <sup>c</sup> (%/mmol g <sup>-1</sup> ) | k <sub>H<sub>2</sub></sub> <sup>d</sup> (μmol g <sup>-1</sup> h <sup>-1</sup> ) | k <sub>NH<sub>3</sub></sub> <sup>e</sup> (μmol g <sup>-1</sup> h <sup>-1</sup> ) | Selectivity of N <sub>2</sub> reduction <sup>f</sup> (%) | Selectivity of H <sub>2</sub> evolution <sup>g</sup> (%) | NH <sub>3</sub> yield per BET <sup>h</sup> (μmol h <sup>-1</sup> m <sup>-2</sup> g) |
|-----------------------------------|---|----------------------------------|---|---|--|--|--|---|
| P25-TiO <sub>2</sub>              | 53.5  | 3.12                             | 2.6/0.1   | 18.3  | 3.4  | 21.8   | 78.2   | 3.2   |
| Li-A <sub>o</sub> /R <sub>d</sub> | 49.7  | 2.84                             | 21.8/0.4  | 213   | 23   | 14.0   | 86.0   | 23.1  |
| Na-A <sub>d</sub> /R <sub>o</sub> | 100.7   | 2.65                             | 62.1/0.6  | 15.7  | 432  | 97.6   | 2.4  | 214.5   |
| Na-A <sub>d</sub>                 | 143.7   | 2.66                             | 73.4/NA   | Trace   | 77.1   | NA   | NA   | 26.8  |
| Li-R <sub>d</sub>                 | 14.5  | 2.75                             | 74.8/NA   | Trace   | 4.2  | NA   | NA   | 14.5  |

<sup>a</sup> Determined by Brunauer–Emmett–Teller (BET) for N<sub>2</sub> adsorption/desorption isotherms. <sup>b</sup> Determined by a plot of the Kubelka–Munk function versus the energy of light absorbed. <sup>c</sup> Quantification of Ti<sup>3+</sup> concentration over all samples measured by XPS (%) and CO<sub>2</sub>-TPD (mmol g<sup>-1</sup>).

<sup>d</sup> The H<sub>2</sub> production rate (k<sub>H<sub>2</sub></sub>) during the N<sub>2</sub> reduction reaction under solar light under closed conditions. All the H<sub>2</sub> gas was detected by syringe using GC-TCD. <sup>e</sup> The NH<sub>3</sub> production rate (k<sub>NH<sub>3</sub></sub>) during the N<sub>2</sub> reduction reaction under solar light determined by cation exchange chromatography (IC). <sup>f</sup> Selectivity for N<sub>2</sub> reduction (%) = 3k<sub>NH<sub>3</sub></sub>/R<sub>c</sub> × 100%. Electron consumption rate for the reduced products (μmol g<sup>-1</sup> h<sup>-1</sup>), R<sub>c</sub> = 2k<sub>H<sub>2</sub></sub> + 3k<sub>NH<sub>3</sub></sub>. <sup>g</sup> Selectivity for H<sub>2</sub> evolution (%) = 2k<sub>H<sub>2</sub></sub>/R<sub>c</sub> × 100%. <sup>h</sup> NH<sub>3</sub> yield per BET surface area = k<sub>NH<sub>3</sub></sub> × 50 mg/BET.

showing that N<sub>2</sub> hardly adsorbs during the relaxation process (Fig. S11†). These results concluded that N<sub>2</sub> molecules selectively adsorb on the surface defects of the Na-A<sub>d</sub> phase, neither on the Li-R<sub>d</sub> phase nor at the heterointerface.

### 2.3 Photocatalytic N<sub>2</sub> reduction activity and durability over ordered/disordered TiO<sub>2</sub> samples

To confirm the effect of phase-selective defect sites on N<sub>2</sub> fixation, we assessed the efficacy of Na-A<sub>d</sub>/R<sub>o</sub> and other catalysts for

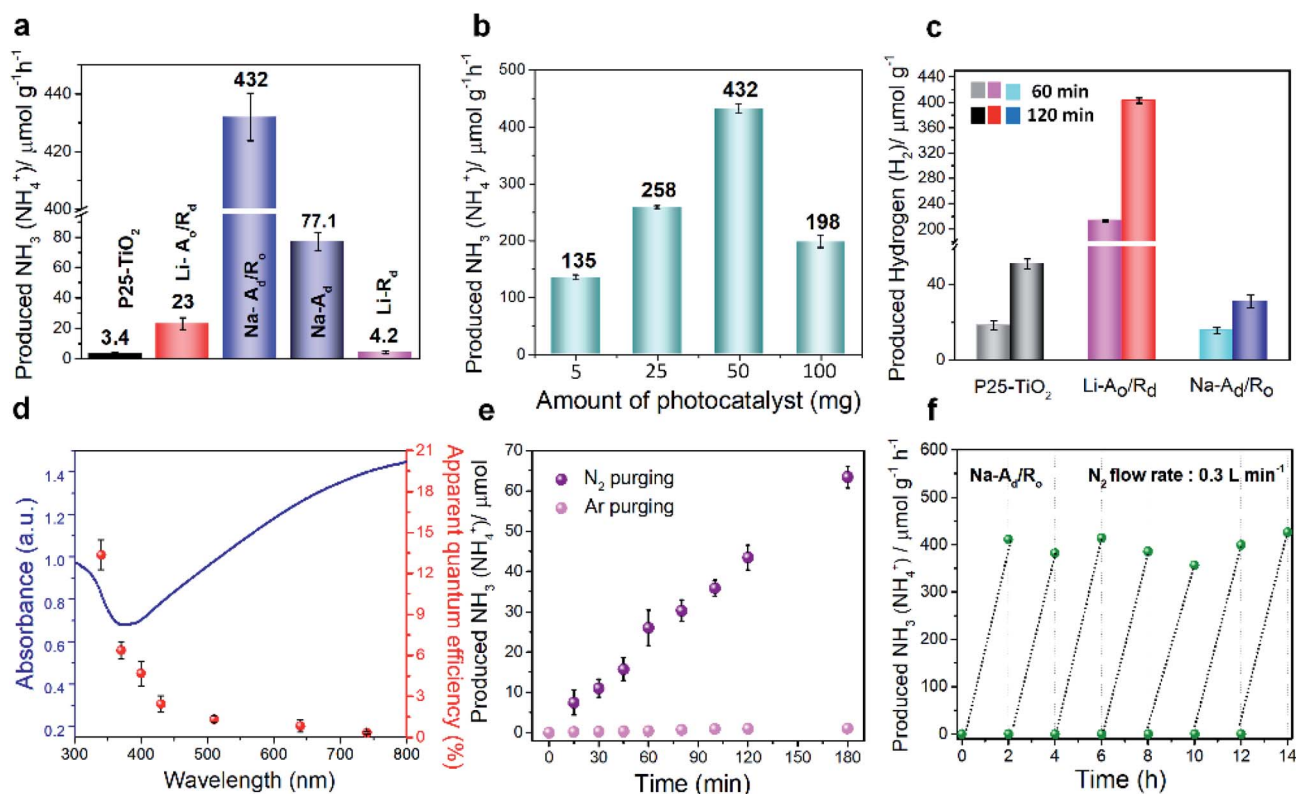


Fig. 3 Photocatalytic N<sub>2</sub> fixation activities of various ordered/disordered TiO<sub>2</sub> samples. (a) The rate of produced NH<sub>3</sub> (NH<sub>4</sub><sup>+</sup>) over P25-TiO<sub>2</sub>, Li-A<sub>o</sub>/R<sub>d</sub>, Na-A<sub>o</sub>/R<sub>o</sub>, Li-R<sub>d</sub> and Na-A<sub>o</sub> in N<sub>2</sub> saturated water with IPA (14%) as the hole/hydroxyl radical scavenger under solar illumination. (b) The rate of produced NH<sub>3</sub> (NH<sub>4</sub><sup>+</sup>) for Na-A<sub>o</sub>/R<sub>o</sub> at various amounts of the catalyst for photocatalytic N<sub>2</sub> reduction. (c) The rate of produced H<sub>2</sub> over P25-TiO<sub>2</sub>, Li-A<sub>o</sub>/R<sub>d</sub> and Na-A<sub>o</sub>/R<sub>o</sub> in N<sub>2</sub> saturated-water with IPA (14%) as the hole scavenger under solar illumination. (d) UV-vis diffuse reflectance spectrum (UV-DRS, left axis) and calculated apparent quantum efficiency (AQE, right axis) for N<sub>2</sub> fixation over Na-A<sub>o</sub>/R<sub>o</sub> under monochromatic light irradiation. (e) Time-dependent rates of produced NH<sub>3</sub> (NH<sub>4</sub><sup>+</sup>) for Na-A<sub>o</sub>/R<sub>o</sub> under N<sub>2</sub> and Ar gas purging. (f) Cycling test of photocatalytic N<sub>2</sub> fixation over Na-A<sub>o</sub>/R<sub>o</sub>.



the photocatalytic NRR, as schematically illustrated in Fig. S12†. Generally, the catalyst needs to be well-dispersed in a mixture containing 50 mL of N<sub>2</sub>-saturated water and 7 mL of isopropyl alcohol (IPA) as the hole and hydroxyl radical scavenger under 1 sun illumination with continuous N<sub>2</sub> gas flow (99.999%, flow rate: 0.3 L min<sup>-1</sup>, cc). One can see that the 7 day treated Na-A<sub>d</sub>/R<sub>o</sub> exhibits the highest rate of NH<sub>4</sub><sup>+</sup> production (432 μmol g<sup>-1</sup> h<sup>-1</sup>) with a high NRR selectivity of 97.6%, followed by Na-A<sub>d</sub> (77.1 μmol g<sup>-1</sup> h<sup>-1</sup>), Li-A<sub>o</sub>/R<sub>d</sub> (23 μmol g<sup>-1</sup> h<sup>-1</sup>), Li-R<sub>d</sub> (4.2 μmol g<sup>-1</sup> h<sup>-1</sup>) and P25-TiO<sub>2</sub> (3.4 μmol g<sup>-1</sup> h<sup>-1</sup>), benefitted by excellent N<sub>2</sub> adsorption ability of the Na-A<sub>d</sub> phase, as measured by ion chromatography (IC) (Fig. 3a and Table S3†). The Na-A<sub>d</sub>/R<sub>o</sub> showed the highest NH<sub>3</sub> yield at an optimum amount of 50 mg, while the NH<sub>3</sub> yield rate gradually decreased at a higher amount due to the poor penetration of photons and hindered mass diffusion (Fig. 3b).<sup>33</sup> It is interesting to note that in the absence of IPA, Na-A<sub>d</sub>/R<sub>o</sub> also showed a reasonable NH<sub>3</sub> production rate of 327 μmol g<sup>-1</sup> h<sup>-1</sup> along with oxygen (O<sub>2</sub>) generation as confirmed by GC-TCD (Fig. S13a and b†), with a stoichiometric ratio of NH<sub>3</sub> to O<sub>2</sub> (2 : 1.5), N<sub>2</sub> + 3H<sub>2</sub>O → 2NH<sub>3</sub> + 3/2O<sub>2</sub>, suggesting that the photogenerated holes are efficiently consumed *via* the water oxidation process. The NH<sub>3</sub> yield rate and apparent quantum efficiency (AQE) for Na-A<sub>d</sub>/R<sub>o</sub> can be comparable and superior to most of the reported photocatalysts with/without hole scavengers under solar light irradiation (Table S4†). Additionally, photocatalytic nitrate (NO<sub>3</sub><sup>-</sup>) reduction activity was evaluated; since N=O bonds have relatively lower dissociation energy (204 kJ mol<sup>-1</sup>) than N≡N bonds (945 kJ mol<sup>-1</sup>),<sup>34</sup> Na-A<sub>d</sub>/R<sub>o</sub> exhibits the highest NO<sub>3</sub><sup>-</sup> reduction activity under sunlight and 100 W LED light compared to Li-A<sub>o</sub>/R<sub>d</sub> and P25-TiO<sub>2</sub>, confirming the superior intrinsic activity for the former (Fig. S13c†). Furthermore, high NRR activity for Na-A<sub>d</sub>/R<sub>o</sub> over other catalysts was supported by the indophenol-blue method as an alternative analytical method, which can be used to ensure the produced NH<sub>4</sub><sup>+</sup>, as our solution is neutral or slightly basic before and the after reaction, as detected with a pH meter (Fig. S14a-c†).<sup>35</sup> To evaluate the effect of different ratios of Na-A<sub>d</sub> and R<sub>o</sub> phases on the NRR performance, we synthesized two different ratios of Na-A<sub>d</sub>/R<sub>o</sub> (90 : 10 and 50 : 50) and compared their NRR performance with main Na-A<sub>d</sub>/R<sub>o</sub> (75 : 25) (Fig. S14d†). As revealed in Fig. S14d,† Na-A<sub>d</sub>/R<sub>o</sub> (75 : 25) exhibited the highest NH<sub>3</sub> yield compared to other control ratios (90 : 10 and 50 : 50). Additionally, we conducted a blank experiment in the absence of any catalysts under the same conditions, which resulted in a non-traceable amount of NH<sub>3</sub> as confirmed by IC and the indophenol blue method, revealing that the photocatalytic NRR is the sole reason for a high rate of NH<sub>3</sub> production rather than any possible contamination from air or other impurities (Fig. S14d†). For the control experiment, we synthesized a heterostructure containing 75% of Li-R<sub>d</sub> and 25% of A<sub>o</sub> and performed the NRR under the same conditions. However, its NH<sub>3</sub> yield (4.8 μmol g<sup>-1</sup> h<sup>-1</sup>) quantified by IC was negligible because of poor N<sub>2</sub> adsorption ability on the abundant Li-R<sub>d</sub> phase. The superior intrinsic N<sub>2</sub> adsorption ability of Na-A<sub>d</sub> over Li-R<sub>d</sub> was further corroborated by the BET specific surface area-normalized NH<sub>3</sub> yield (Table 1), which strongly

reinforces the significance of phase-selective active sites for N<sub>2</sub> fixation.

To confirm the origin of the NH<sub>3</sub> generated from the supplied N<sub>2</sub> gas, <sup>15</sup>N<sub>2</sub> (98 atom%, <sup>15</sup>N) isotope labeling experiments were carefully performed for 50 min at 8 sccm controlled by the mass flow control (MFC) system (Fig. S15†). Double coupling of <sup>15</sup>NH<sub>4</sub><sup>+</sup> and triple coupling of <sup>14</sup>NH<sub>4</sub><sup>+</sup> are identified by <sup>1</sup>H nuclear magnetic resonance (<sup>1</sup>H NMR), signifying that the N<sub>2</sub> gas is the only source of NH<sub>3</sub>, further supported by mass spectra,<sup>18</sup> EDS analysis of Na-A<sub>d</sub>/R<sub>o</sub> and additional control NRR experiments under Ar-saturated solution (Fig. S15c and S16†).<sup>23,36</sup> Importantly, some reported papers claimed that oxygen vacancies introduced on catalysts could behave as active sites for water dissociation and boost HER activity.<sup>22,37-39</sup> Hence, it is necessary to examine the HER activity and selectivity over disordered catalysts in a closed system under the same conditions for the NRR (Fig. 3c and Table 1). Interestingly, the Na-A<sub>d</sub>/R<sub>o</sub> (H<sub>2</sub> yield rate: 15.7 μmol g<sup>-1</sup> h<sup>-1</sup>) exhibits poor HER activity compared to Li-A<sub>o</sub>/R<sub>d</sub> (H<sub>2</sub> yield rate: 213 μmol g<sup>-1</sup> h<sup>-1</sup>), which may be attributed to the high surface coverage of N<sub>2</sub> molecules on the defect sites of Na-A<sub>d</sub> rather than the proton (H<sup>+</sup>), but an opposite trend to O<sub>v</sub> defective sites on Li-R<sub>d</sub>, as revealed by experimental analysis and theoretical calculations. Additionally, hydrazine (N<sub>2</sub>H<sub>4</sub>) and nitrate acid (HNO<sub>3</sub>) are possible by-products that can be detected by the Watt and Chrisps method and IC, respectively, and negligible N<sub>2</sub>H<sub>4</sub> and a trace amount of NO<sub>3</sub><sup>-</sup> (0.17 μmol g<sup>-1</sup> h<sup>-1</sup>) were detected during the NRR, suggesting high selectivity of NH<sub>3</sub> synthesis for Na-A<sub>d</sub>/R<sub>o</sub> (Fig. S17, S18 and Table S5†).<sup>40</sup> To confirm the effect of trace NO<sub>3</sub><sup>-</sup> produced during the reaction on the total yield of NH<sub>3</sub> for Na-A<sub>d</sub>/R<sub>o</sub>, twice the amount of trace NO<sub>3</sub><sup>-</sup> (0.34 μmol g<sup>-1</sup> h<sup>-1</sup>) was added into the catalyst dispersed solution and examined under solar light for 2 h under the same NRR conditions. The NH<sub>3</sub> yield of only 0.357 ppm (1.05 μmol h<sup>-1</sup> g<sup>-1</sup>) detected by IC was well within the error range. Therefore, the influence of trace NO<sub>3</sub><sup>-</sup> on the total yield of NH<sub>3</sub> was negligible. In Fig. 3d, the wavelength-dependent quantum efficiency (QE) experiment for N<sub>2</sub> fixation on Na-A<sub>d</sub>/R<sub>o</sub> under monochromatic light irradiation closely fits the absorption spectrum, showing approximately 13.6%, 6.4%, 4.7%, 2.4%, 1.3%, 0.8% and 0.3% at 340, 370, 400, 430, 510, 640 and 740 nm, respectively. However, the apparent QE of Na-A<sub>d</sub>/R<sub>o</sub> over 500 nm is inconsistent with the visible light absorption distribution in the ultraviolet-visible spectrum. Creating oxygen defects on disordered TiO<sub>2</sub> can harvest visible light, however, the excited electrons which are located at deep trap states are unable to be utilized for the NRR because they cannot be excited and migrated thermally to the CB as well as their states are located well below the N<sub>2</sub>/NH<sub>3</sub> redox potential, which makes them inactive for N<sub>2</sub> fixation.<sup>41</sup> Although these trap sites are inactive for N<sub>2</sub> fixation, they are the main sites for enhancing the N<sub>2</sub> adsorption on the surface of the Na-A<sub>d</sub> accelerating NRR process.

Besides superior activity, the durability of the catalyst is another crucial parameter for practical applications. The cycling tests for Na-A<sub>d</sub>/R<sub>o</sub> were conducted for 3 h under 1 sun illumination with continuous N<sub>2</sub> gas supply showing linearly produced NH<sub>4</sub><sup>+</sup>, quantified by IC (Fig. 3e) and the indophenol-



blue method (Fig. S19<sup>†</sup>). Moreover, the rate of NH<sub>3</sub> yield for Na-A<sub>d</sub>/R<sub>o</sub> remained constant for 7 consecutive cycles (Fig. 3f), suggesting its excellent stability towards the NRR. After stability tests, careful examination of XPS, XRD, and TEM characterization on Na-A<sub>d</sub>/R<sub>o</sub> phases shows no distinct changes over surface Ti<sup>3+</sup> and the amorphous structure of the Na-A<sub>d</sub> junction with the crystalline R<sub>o</sub> phase, indicating the robustness of Na-A<sub>d</sub>/R<sub>o</sub> towards the photocatalytic NRR, however, a slight decrease of the O<sub>v</sub> sites was observed probably due to water molecules or reactants/intermediates after stability tests (Fig. S20<sup>†</sup>). From the results, we found that the photocatalytic NRR showed a close relationship with a specific type of phase-selective absorption site for N<sub>2</sub> fixation rather than all possible surface defects sites. Although sufficient defect sites on Li-R<sub>d</sub> and Li-A<sub>o</sub>/R<sub>d</sub> were present, poor intrinsic N<sub>2</sub> adsorption ability and favorable HER kinetics significantly hamper the formation of NH<sub>3</sub> and its selectivity (Table 1).<sup>16</sup>

#### 2.4 Optical and charge transfer (CT) properties and band alignment over ordered/disordered TiO<sub>2</sub> samples

To develop an in-depth mechanistic understanding of the outstanding NRR performance of Na-A<sub>d</sub>/R<sub>o</sub> over the other catalysts, the electronic band position was determined based on the Tauc plots, UPS, and valence-band XPS spectra (VB-XPS) (Fig. 4a–e and S21<sup>†</sup>).<sup>42</sup> It is known that a heterointerface between two different phases is an important factor leading to rapid interfacial CT and modulation of the energy band alignment.<sup>19</sup> The secondary-electron cut-off energy for Na-A<sub>d</sub> and R<sub>o</sub> was measured by UPS as 16.40 and 16.3 eV, respectively (Fig. 4a), and the Fermi level ( $E_f$ ) was then estimated to be  $-0.04$  and  $0.06$  eV (*vs.* NHE, pH = 7), respectively. The VB positions with respect to  $E_f$  were determined by VB-XPS as 2.10 and 1.86 eV, respectively (Fig. 4b). To further obtain the conduction-band position ( $E_{CB}$ ) of Na-A<sub>d</sub> and R<sub>o</sub>, the energy bandgap ( $E_g$ ) was also obtained by linear extrapolation of the Tauc plots ( $\alpha h\nu$ )<sup>1/2</sup> *vs.*  $h\nu$ , obtaining indirect bandgap energies of 2.49 and 3.04 eV, respectively (Fig. 4c). Consequently, the  $E_{CB}$  of Na-A<sub>d</sub> and R<sub>o</sub> can be further determined as  $-0.39$  and  $-1.18$  eV, respectively (*vs.* NHE, pH = 7) (Fig. 4d). In general, the energy band at the interface of two different semiconductors would be rearranged by a band alignment through contacts until  $E_f$  is aligned at the same level. The possible electronic band structure of Na-A<sub>d</sub>/R<sub>o</sub> (Fig. 4d) is finally depicted after rearrangement. For Na-A<sub>d</sub>, both CB and VB potentials are downshifted while those for R<sub>o</sub> are upshifted, which is a type-II band structure, indicating that the CB potential of Na-A<sub>d</sub> ( $-0.39$  eV) is suitable for N<sub>2</sub>/NH<sub>3</sub> and the VB potential of R<sub>o</sub> (1.81 eV) is much closer for the water oxidation reaction.<sup>43</sup> Combined with a suitable band-alignment and enhanced visible-light absorption, possible interfacial charge separation at the heterointerface where electrons on Na-A<sub>d</sub> are consumed to activate the adsorbed N<sub>2</sub> molecules and holes on R<sub>o</sub> oxidize the water molecules in the meantime (Fig. 4d) corroborates the superior NRR selectivity of Na-A<sub>d</sub>/R<sub>o</sub>. Additionally, we also delineated the possible electronic band structure of Li-A<sub>o</sub>/R<sub>d</sub> and P25-TiO<sub>2</sub> (Fig. S21<sup>†</sup>). Interestingly, we found that the CB potential of Li-A<sub>o</sub>/R<sub>d</sub> and P25-TiO<sub>2</sub> is placed

nearby HER potentials with low N<sub>2</sub> adsorption, resulting in poor NRR selectivity (14%) and high HER kinetics (86%) for Li-A<sub>o</sub>/R<sub>d</sub>.

In order to further understand the interfacial charge carrier dynamics, photoluminescence (PL) spectra of P25-TiO<sub>2</sub>, Na-A<sub>d</sub>, and Na-A<sub>d</sub>/R<sub>o</sub> were examined (Fig. 4e). All catalysts exhibit a distinct PL peak centered approximately at 506 nm upon excitation by a 375 nm laser. After defect formation, the PL intensity of Na-A<sub>d</sub> is quenched at 550 nm corresponding to defect states attributed to Ti<sup>3+</sup> on oxygen vacancies and further quenched for Na-A<sub>d</sub>/R<sub>o</sub>. This PL quenching behavior corresponds to facile CT between Na-A<sub>d</sub> and R<sub>o</sub> at the interface. We then used TRPL spectroscopy to probe charge carrier dynamics over Na-A<sub>d</sub> and Na-A<sub>d</sub>/R<sub>o</sub> films by electrophoretic deposition (10 V, 15 s each on the ITO substrate, inset) in Fig. 4f. The light intensity decay curves through two relaxation pathways can be fitted with an exponential equation as shown below:<sup>44</sup>

$$f(t) = A_0 + A_1(\exp(-t/\tau_1) + A_2(\exp(-t/\tau_2))), \quad (1)$$

where  $A_0$  is a constant for the baseline offset,  $\tau_1$  is fast decay time responsible for exciton recombination with the involvement of surface states or electron transfer, and  $\tau_2$  is slow decay time correlated with the indirect recombination of self-trapped excitons with trapped electrons.  $A_1$  and  $A_2$  are the corresponding decay amplitudes. The obtained parameters of the TRPL data are listed in Table S6.<sup>†</sup> For both Na-A<sub>d</sub> and Na-A<sub>d</sub>/R<sub>o</sub>, the increased amplitude of short-lived excited species ( $A_1$ ) and decreased amplitude of long-lived excited species ( $A_2$ ) as compared to P25-TiO<sub>2</sub> are observed, especially the  $A_2$  for Na-A<sub>d</sub>/R<sub>o</sub> dramatically decreased with R<sub>o</sub> incorporation, indicating the appearance of additional non-radiative recombination pathways from the electronic interaction *via* the heterojunction, further verifying the proposed mechanism of interfacial CT by type-II band alignment. The intensity-average PL lifetime ( $\tau_{av}$ ) was also calculated for better comparison. The  $\tau_{av}$  of Na-A<sub>d</sub>/R<sub>o</sub> (184.3 ps) is shorter than that of Na-A<sub>d</sub> (359.2 ps), indicating outstanding interfacial CT properties which contribute to superior NRR kinetics with an appropriate CB band position. Moreover, photocurrent and electrochemical impedance spectroscopy (EIS) measurements under solar light illumination are ascribed to photoinduced electrons transferring to the electrode (Fig. 4g and S22<sup>†</sup>).<sup>14</sup> The increase in photocurrent response and the decrease in CT resistance ( $R_{CT}$ ) for Na-A<sub>d</sub>/R<sub>o</sub> compared to Na-A<sub>d</sub> indicated that photogenerated charge carriers are well separated at the heterojunction (Table S7<sup>†</sup>), consistent with TRPL analysis. We can further explicate the enhanced charge separation in correlation with NRR activity for Na-A<sub>d</sub>/R<sub>o</sub> by BET specific surface area-normalized NH<sub>3</sub> yield compared to Na-A<sub>d</sub> (Table 1).

#### 2.5 Proposed mechanistic pathway for N<sub>2</sub> fixation

To identify the time-dependent change of N-related functional groups in the early stages of the photocatalytic NRR, *in situ* diffuse reflectance infrared Fourier transform (*in situ* DRIFT) measurements were conducted (Fig. S23<sup>†</sup>).<sup>11,14,45</sup> To exclude the background spectra of adsorbed gas and impurities, the sample was fully dried at 333 K in a vacuum oven overnight, and then





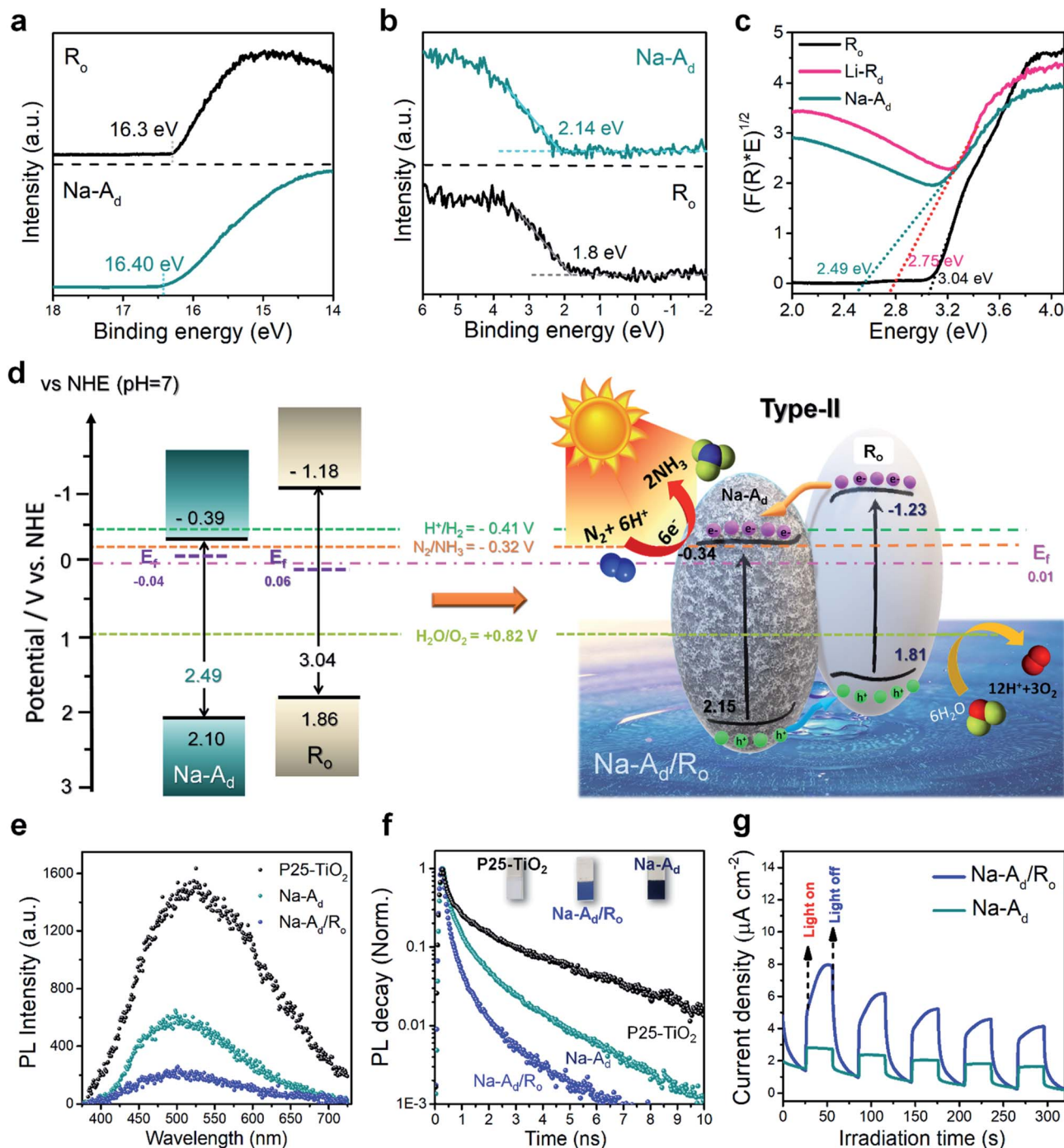


Fig. 4 Spectroscopic analysis for possible charge carrier dynamics and the corresponding energy level diagram depicting the photochemical reaction. (a) UPS spectra and (b) valence band XPS edge spectra of  $R_0$  and  $Na-A_d$ . (c) Kubelka–Munk function versus the photon energy graphs and calculated bandgap of  $R_0$ ,  $Li-R_d$ , and  $Na-A_d$ . (d) Estimation of energy band structures of  $Na-A_d$ ,  $R_0$ , and  $Na-A_d/R_0$ . (e) Photoluminescence (PL) spectra ( $\lambda_{ex} = 375$  nm;  $\lambda_{em} = 506$  nm) and (f) time-resolved photoluminescence (TRPL) of  $P25-TiO_2$ ,  $Na-A_d$  and  $Na-A_d/R_0$ . The scatter points were fitted using a biexponential decay. (g) Transient photocurrent response of  $Na-A_d/R_0$  and  $Na-A_d$ .

was placed into a DRIFT specimen chamber. Several absorption bands gradually increase under 1 sun irradiation from 0 to 60 min in the range of  $1100-1700$   $cm^{-1}$  (Fig. 5a). The FT-IR spectra of N-related functional groups represent six bands:  $1123$ ,  $1289$ ,  $1329$ ,  $1425$ ,  $1551$ , and  $1660$   $cm^{-1}$ . The interference from  $CO_2$  and  $H_2O$  from the air was removed by a background

calibration. The bands at  $1123$  and  $1660$   $cm^{-1}$  can be assigned to N–N stretching in chemisorbed  $N_2H_y$  species on catalysts. Two weak bands at  $1329$  and  $1551$   $cm^{-1}$  are characteristic of adsorbed  $NH_3$  and sharp bands at  $1289$  and  $1425$   $cm^{-1}$  can be assigned to adsorbed  $NH_4^+$  ( $-NH_2$  wagging and H–N–H bending of adsorbed  $N_2H_y$  species, respectively), which are intensified



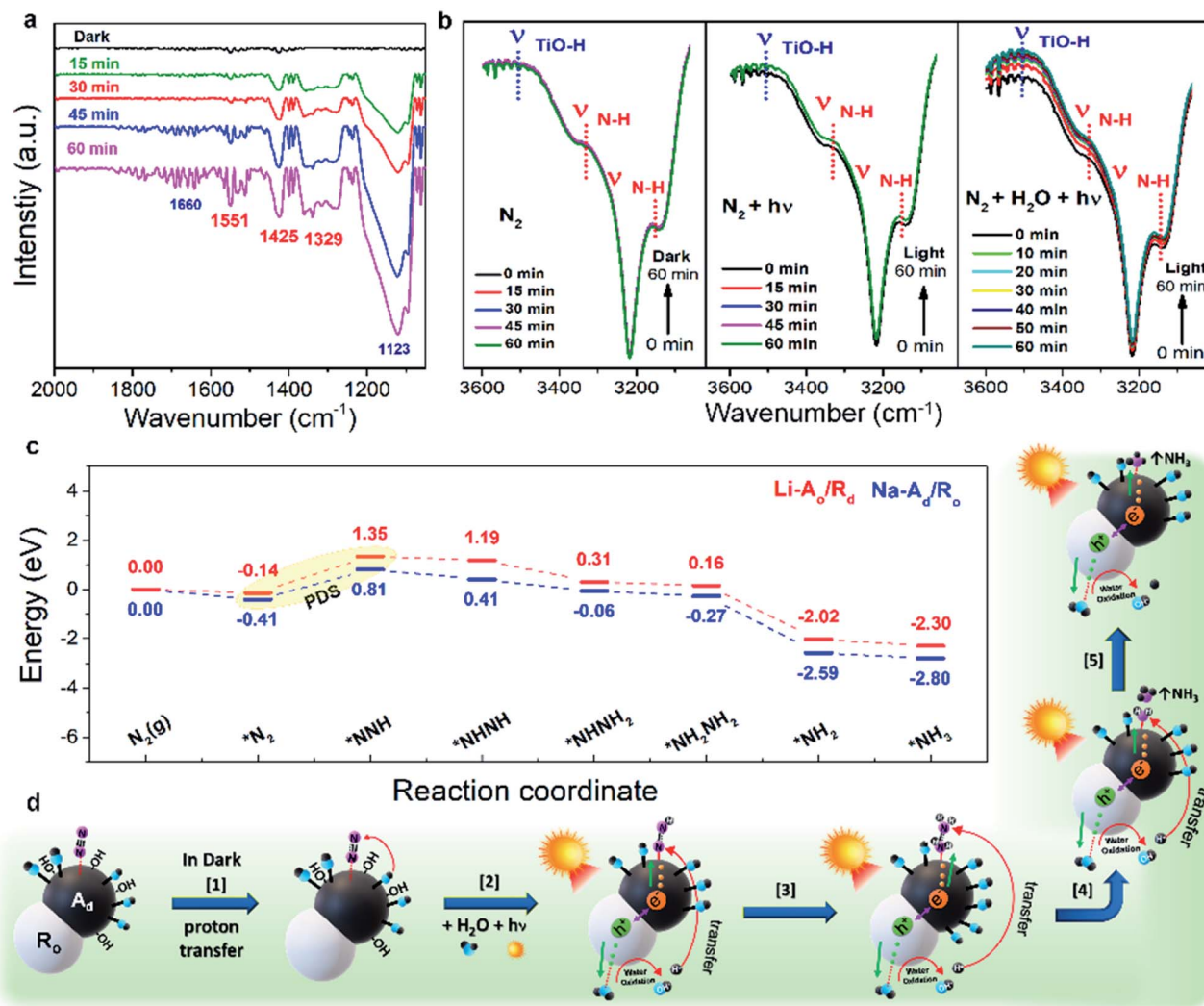


Fig. 5 Proposed mechanistic pathway for  $N_2$  fixation. (a) Fourier Transform Infrared (FT-IR) spectra during the  $N_2$  reduction reaction in the presence of water and  $N_2$  under solar illumination for 60 min. (b) Time-dependent change of *in situ* Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectra of  $Na-A_d/R_o$  after  $N_2$  adsorption in the dark for 60 min and then sunlight irradiation for 60 min and then water vapor supply for 60 min simultaneously (from left to right) under ambient conditions. (c) Gibbs free energy diagram of the  $N_2$  reduction reaction on  $Na-A_d/R_o$  and  $Li-A_o/R_d$ . (d) Schematic illustration of the alternating pathway during the photocatalytic  $N_2$  fixation on  $Na-A_d/R_o$ .

with the increase of reaction time. Absorption bands in the range of  $3100\text{--}3600\text{ cm}^{-1}$  for  $Na-A_d/R_o$  and  $Na-A_d$  are shown in Fig. 5b and S24.† The intensity of peaks at  $3150$  and  $3334\text{ cm}^{-1}$  attributed to an N–H stretching mode ( $\nu_{N-H}$ ) gradually increases, followed by the increased peaks at  $3527\text{ cm}^{-1}$  assigned to the O–H stretching ( $\nu_{TiO-H}$ ) mode after water supply.<sup>46</sup> As a result, *in situ* measurements elucidate that inert  $N\equiv N$  is efficiently activated on phase-selective defect sites on  $Na-A_d/R_o$  under 1 sun irradiation, leading to the subsequent  $N\equiv N$  cleavage to  $NH_3$  or  $NH_4^+$  at the last step.

To gain further insight into the NRR mechanism of phase-selective defect sites over  $Li-A_o/R_d(110)$  and  $Na-A_d/R_o(101)$ , the DFT calculations were carried out as shown in Fig. 5c. After successful  $*N_2$  adsorption, the Gibbs free energy for the first hydrogenation step is significant as a potential determining step (PDS). One can see that the PDS ( $*N_2$  to  $N-NH^*$ ) on  $Na-A_d/R_o$

$R_o(101)$  was indeed favored by a lower energy barrier ( $1.22\text{ eV}$ ), in comparison to  $1.49\text{ eV}$  for  $Li-A_o/R_d$ , indicating that  $Na-A_d/R_o$  possesses better NRR intrinsic activity than  $Li-A_o/R_d$ . Note that the alternating pathway is the thermodynamically favorable process compared to the distal pathway after the PDS (Fig. S25†). Subsequent  $N-NH^*$  hydrogenation to  $NH-NH^*$  requires a low energy barrier for  $Na-A_d/R_o$  compared to  $Li-A_o/R_d$ , which is thermodynamically more feasible during the NRR. Corresponding visual images of different steps involved in the DFT calculation for both  $Na-A_d/R_o$  and  $Li-A_o/R_d$  are presented in Fig. S26.† Based on *in situ* DRIFT and theoretical calculations, we deduced a possible NRR pathway on  $Na-A_d/R_o$  in Fig. 5d and additionally, and listed the chemical equations (Discussion S1†). The photo-driven  $NH_3$  synthesis proceeds through the activation of  $N_2$  by the supply of multiple exciton transfer using photons as a driving force. At first, there is a proton-coupled



electron transfer step (Step 1) where the N<sub>2</sub> adsorbed on Ti<sup>3+</sup> species in Na-A<sub>d</sub> (\*N≡N) interact with H atoms of the adjacent Ti<sup>3+</sup>-OH, resulting in the appearance of an N-H stretching vibration ( $\nu_{\text{N-H}}$ ) band. After 1 sun irradiation and water supply (Step 2), protons (H<sup>+</sup>) from the oxidized water *via* photo-generated holes (h<sup>+</sup>) at the VB of R<sub>o</sub> and electrons (e<sup>-</sup>) at the CB of Na-A<sub>d</sub> generate the adsorbed chemical species (\*N=NH) as follows: \*N≡N + H<sup>+</sup> + e<sup>-</sup> → \*N=NH. Consequently, transferring four e<sup>-</sup> and H<sup>+</sup> to \*NH<sub>2</sub>-NH<sub>2</sub> (Step 3) on Na-A<sub>d</sub> produces free-NH<sub>3</sub> (Step 4), and the remaining \*NH<sub>2</sub> is hydrogenated and regenerates the Ti<sup>3+</sup> sites after NH<sub>3</sub> desorbed from the catalysts for the next N<sub>2</sub> adsorbates (Step 5). This ideal alternating pathway on Na-A<sub>d</sub>/R<sub>o</sub> which involves the one-by-one addition of H atoms and electrons to simultaneously break down the N≡N bond can efficiently produce NH<sub>3</sub>.<sup>47</sup>

### 3. Conclusions

In summary, superior NRR activity with high selectivity was achieved by phase-selective defect sites on mixed-phase commercial P25-TiO<sub>2</sub>. Our DFT simulations revealed that defect sites on the disordered Na-A<sub>d</sub> phase exhibit higher N<sub>2</sub> adsorption ability and better intrinsic NRR activity than those on the disordered Li-R<sub>d</sub> phase. Consistently, the experimental findings confirmed highly selective N<sub>2</sub> affinity on defect sites on Na-A<sub>d</sub> over Li-R<sub>d</sub>. Moreover, Na-A<sub>d</sub> can harvest the visible-range spectrum ascribed to the bandgap reduced by Ti<sup>3+</sup> sites on oxygen vacancies. Upon integration with the R<sub>o</sub> phase, a suitable CB band position for the NRR over the HER and rapid interfacial charge separation at the heterointerface for Na-A<sub>d</sub>/R<sub>o</sub> facilitate the desired intermediates (\*N=NH) *via* subsequent hydrogenation steps along with a thermodynamically favorable process verified by charge dynamics and band structure analysis combined with DFT simulations. As a result, noble-metal free Na-A<sub>d</sub>/R<sub>o</sub> achieved a superior NH<sub>3</sub> formation rate of 432 μmol g<sup>-1</sup> h<sup>-1</sup>, which is ~125 times higher than that of bare TiO<sub>2</sub> (3.4 μmol g<sup>-1</sup> h<sup>-1</sup>) under simulated AM 1.5G light irradiation at room temperature with a high AQE of 13.6%, suppressing H<sub>2</sub> generation. This finding highlights a promising approach to demonstrate the importance of phase-selective active sites with a suitable band position to develop a novel photocatalyst for future energy-related applications.

### Data availability

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

### Author contributions

J. S., X. L. and A. K. equally contributed to this work. J. S. and Y. H. conceived and designed the experiments. J. S. and Y. H. carried out the synthesis of the materials and photocatalytic NRR. X. L. conducted the DFT calculation. A. K., J. Y. and Y. D. K. supported the data analysis and supported *in situ* measurements. E. L. conducted the PL measurements. H. L. supervised the project. J. S., A. K., and H. L. wrote the paper. All authors

discussed the results and commented on the manuscript. All authors have given approval to the final version of the manuscript.

### Conflicts of interest

The authors declare no competing financial interest.

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