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## Excitonic $\text{Au}_4\text{Ru}_2(\text{PPh}_3)_2(\text{SC}_2\text{H}_4\text{Ph})_8$ cluster for light-driven dinitrogen fixation†

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The surface plasmon resonance of metal nanoparticles has been widely used to improve photochemical transformations by plasmon-induced charge transfer. However, it remains elusive for the molecular-like metal clusters with non-metallic or excitonic behavior to enable light harvesting including electron/hole pair production and separation. Here we report a paradigm for solar energy conversion on an atomically precise  $\text{Au}_4\text{Ru}_2$  cluster supported on  $\text{TiO}_2$  with oxygen vacancies, in which the electron–hole pairs can be directly generated from the excited  $\text{Au}_4\text{Ru}_2$  cluster and the  $\text{TiO}_2$  support, and the photogenerated electrons can transfer to the Ru atoms. Importantly, the Ru atoms in the  $\text{Au}_4\text{Ru}_2$  cluster are capable of injecting the electrons into adsorbed  $\text{N}_2$  to activate  $\text{N}_2$  molecules. The cooperative effect in the supported  $\text{Au}_4\text{Ru}_2$  catalyst efficiently boosts the photocatalytic activity for  $\text{N}_2$  fixation in comparison with homogold ( $\text{Au}_n$ ) clusters.

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## Introduction

Atomically precise metal clusters with exact formulas, molecular purity, and total structures have gathered momentum in recent years, owing to their unique physical and chemical properties.<sup>1–6</sup> The metal clusters in the quantum size regime possess discrete electron energy levels and show non-metallic or excitonic behaviours,<sup>7</sup> which are totally different from the larger metallic-state nanoparticles exhibiting a distinct surface plasmon resonance.<sup>8,9</sup> Significant advances in chemical synthesis of the clusters provide an exciting opportunity to unveil previously unknown or inaccessible insights into the applications in optics, catalysis, and biochemistry.<sup>10,11</sup> Especially the cluster-based heterogeneous catalysts have exhibited new catalytic properties in many chemical reactions compared to the plasmonic metal nanoparticles.<sup>12,13</sup> Furthermore, the precise relation of the properties with atomic-level structures not only reveals the origin of metal catalysis, but also promotes the exploration of important chemical processes with these clusters as well-defined, highly efficient catalysts.<sup>14,15</sup>

One important chemical process is the reduction of dinitrogen to ammonia, which is an essential chemical and energy carrier.<sup>16</sup> However, high temperature and pressure are necessary to drive the reaction of  $\text{N}_2$  with  $\text{H}_2$  to  $\text{NH}_3$ , due to the strong nonpolar triple bond in  $\text{N}_2$  and its high activation barrier.<sup>17</sup> Many efforts have been made to develop less energy-consuming alternatives that can overcome the kinetic limitation of  $\text{NH}_3$  production.<sup>18–21</sup> Inspired by nitrogenase enzymes that can fix nitrogen under ambient conditions, nanostructured metal catalysts are springing up to enable  $\text{N}_2$  fixation with the help of photosynthesis.<sup>22–25</sup> Despite the important advances in homogeneous complex systems, construction of heterogeneous metal sites for  $\text{N}_2$  fixation is currently still challenging. Considering that atomically precise metal clusters can bridge the gap between homogeneous and heterogeneous catalysts, we speculate whether metal clusters with excitonic behaviour can convert  $\text{N}_2$  into ammonia under mild conditions, that is, whether these clusters are capable of generating hot electrons driven by solar light, ensuring the charge separation, and then donating electrons into  $\text{N}_2$ . If this scenario is feasible, it can not only unravel the mystery of non-plasmon-induced solar energy conversion but also offer fundamental insights into exact, heterogeneous metal sites to govern the  $\text{N}_2$  transformation at the unprecedented level of atomic precision.

Since no example of  $\text{N}_2$  conversion on atomically precise metal clusters has been documented, a series of ligand-protected  $\text{Au}_n$  ( $n$  = gold atom number) clusters with different atomic structures were first screened to catalyse the  $\text{N}_2$  conversion under light irradiation. As shown in Fig. 1, these  $\text{Au}_n$  clusters failed to give a convincing activity for photocatalytic reaction of  $\text{N}_2$  fixation, mainly because the  $\text{N}_2$  molecule cannot

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Fig. 1 The photocatalytic activity of the ligand-protected  $Au_n$  clusters supported on  $TiO_2$ -Ov for  $N_2$  reduction. The inset shows the atomic structures of the  $Au_n$  clusters, which can only physisorb  $N_2$  molecule with distance between  $N_2$  and Au sites larger than 3.2 Å. The C, N, S, Au, P and Cl are shown in gray, blue, yellow, orange, green and violet colors, respectively. H atoms are omitted for clarity.

coordinate to clusters and be activated on the gold sites of the  $Au_n$  clusters, according to our density functional theory (DFT) calculations (inset of Fig. 1). We next turned our attention to the bimetal clusters. Since Ru is recognized as a suitable candidate for  $N_2$  fixation,<sup>24</sup> we sought to explore the wet chemical synthesis of atomically precise Au–Ru clusters.

In this work, we successfully synthesized a new  $Au_4Ru_2$  cluster protected by thiolate and triphenylphosphine ligands (namely,  $Au_4Ru_2(PPh_3)_2(SC_2H_4Ph)_8$ ) and solved its crystal structure. Excitingly, the  $Au_4Ru_2$  cluster supported on  $TiO_2$  with oxygen vacancies (hereafter denoted as  $TiO_2$ -Ov) exhibited a drastic increase in the photocatalytic activity for  $N_2$  reduction compared to the supported  $Au_n$  catalysts. Furthermore, we explicitly demonstrated the cooperative mechanism within the  $Au_4Ru_2/TiO_2$ -Ov catalyst for achieving light-driven  $N_2$  fixation.

## Results and discussion

The crystal structure of the  $Au_4Ru_2(PPh_3)_2(SC_2H_4Ph)_8$  cluster is shown in Fig. 2A. This cluster resembles a distorted hexahedron, in which four Au atoms are located at the midpoints of four side edges, two Ru atoms reside on the centres of the top and the bottom planes, and eight S atoms are fixed at the vertexes. The two apex Ru atoms are coordinated by two  $PPh_3$  with the average Ru–P bond length of 2.204 Å. Four S atoms binding to a Ru atom are within the same plane as indicated by the average S–Ru–S angle of 90°. The average S–Au–S angle is 172.9°, where S–Au bond distances are 2.310 and 2.318 Å, respectively. The Au–Au distances fall in a very narrow range of 3.045–3.144 Å, which are shorter than the sum of van der Waals radii of two Au atoms (3.32 Å), suggesting the presence of  $d^{10}$ – $d^{10}$  metallophilic contact within the  $Au_4Ru_2$  cluster.<sup>26</sup> Electro-spray ionization mass spectrometry (ESI-MS) further confirmed

the formula of the cluster, where the  $m/z$  2745 peak was assigned to  $[Au_4Ru_2(PPh_3)_2(SC_2H_4Ph)_8 + Cs]^+$  adduct supported by the agreement between experimental and simulated isotopic patterns (Fig. 2B). Thermogravimetric analysis further confirmed that the  $Au_4Ru_2$  cluster was highly pure (Fig. S1†).

UV-vis absorption spectrum of the  $Au_4Ru_2$  cluster shows two prominent peaks at 349 and 640 nm and one weak peak at 453 nm (Fig. 2C), corresponding to excitation energies of 3.55, 1.94 and 2.74 eV (Fig. 2D), respectively. Accordingly, the optical gap is determined to be 1.33 eV based on the photon-energy scale spectrum, which is basically consistent with the computed gap of 1.25 eV between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) from our DFT calculations (Fig. 2E). As revealed by the computed electronic density of states (DOS) in Fig. 2E, the emergence of discrete electronic states and a moderate HOMO–LUMO gap for the  $Au_4Ru_2$  cluster indicates single electron excitations, that is an exciton.<sup>7</sup> Importantly, the projected DOS shows that the low-lying unoccupied states (LUMO and LUMO+1) are mostly localized on the Ru atoms, suggesting that the excited carriers in the  $Au_4Ru_2$  cluster will be on the Ru atoms, which may act as reaction centers and utilize the excess electrons for  $N_2$  activation.

With the newly synthesized cluster, we explored the proposed light-driven  $N_2$  fixation using  $Au_4Ru_2$  as a heterogeneous catalyst. As shown in Fig. 3A, the  $Au_4Ru_2/TiO_2$ -Ov catalyst gave rise to an ammonia production rate of 44.5  $\mu\text{mol g}^{-1} \text{h}^{-1}$  under full spectrum illumination, which exhibited over 3-fold increase in photocatalytic activity compared to the  $Au_n/TiO_2$ -Ov and pure  $TiO_2$ -Ov catalysts. As much, the  $Au_4Ru_2/TiO_2$ -Ov catalyst resulted in a 4-time higher activity than  $TiO_2$ -Ov in visible light-driven  $N_2$  reduction (Fig. 3A), suggesting a strong synergistic effect between  $Au_4Ru_2$  and  $TiO_2$ -Ov. Time-dependent photocatalytic ammonia production over the  $Au_4Ru_2$  catalysts revealed that, not only the ammonia concentration increased linearly with the irradiation time in the visible light region (Fig. 3B), but also the  $Au_4Ru_2$  loaded on the  $TiO_2$  support without abundant oxygen vacancies gave a much lower activity driven by either UV-vis or visible light (Fig. 3A and B). In fact, both  $TiO_2$ -Ov and  $TiO_2$  substrates were in anatase phase (Fig. S2A†). The difference in the two  $TiO_2$  samples was that the former contained oxygen vacancies, but the latter not, which was confirmed by electron paramagnetic resonance (EPR).  $TiO_2$ -Ov showed a characteristic EPR signal at approximately  $g = 1.998$ , suggesting the presence of oxygen vacancies,<sup>27</sup> whereas no EPR signal was observed on the other  $TiO_2$  sample (Fig. S2B†). It can be conjectured that the abundant oxygen vacancies in  $TiO_2$  facilitate the photochemical reaction of  $N_2$  reduction.<sup>17</sup>

DFT calculations demonstrated that  $TiO_2$  with oxygen vacancies can efficiently promote the photolysis of water to produce hydrogen as the proton source of ammonia (Fig. S3†). The anatase  $TiO_2(101)$  surfaces with an oxygen vacancy on the surface ( $TiO_2\text{-Ov}_1$ ) and subsurface ( $TiO_2\text{-Ov}_2$ ), have low kinetic barriers ( $\Delta E_a$ ) of 0.09 and 0.02 eV for water dissociation, respectively, compared to 0.23 eV for the perfect  $TiO_2(101)$  surface (Fig. 3C). Moreover, they all provide moderate binding

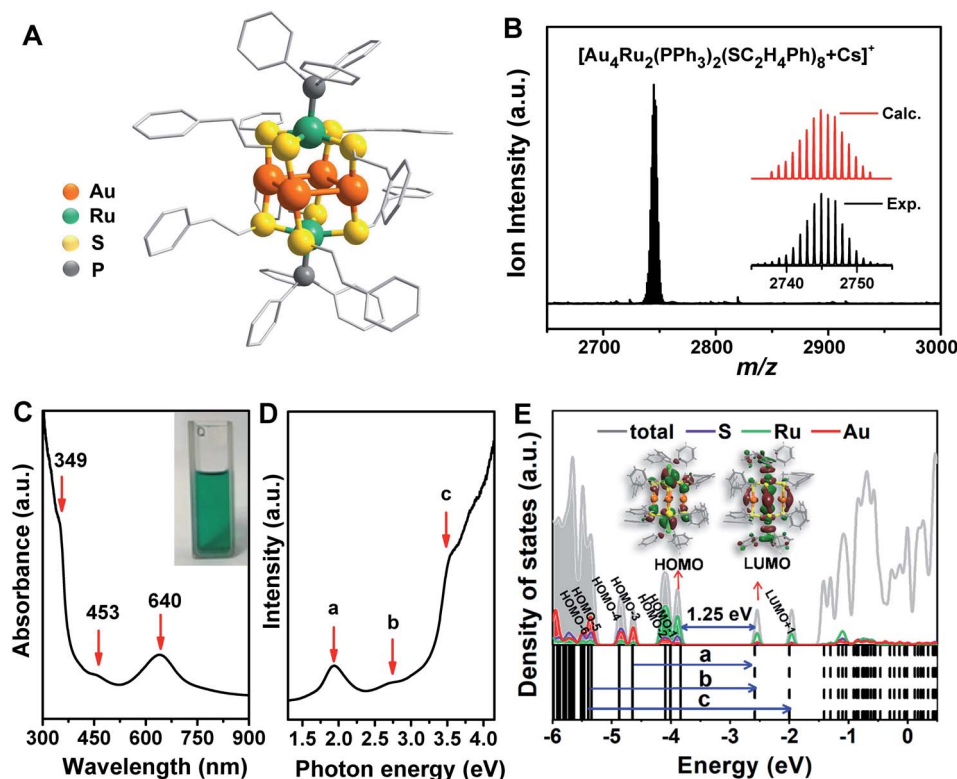


Fig. 2 (A) Atomic structure (H atoms are omitted for clarity) and (B) ESI-MS profile of  $\text{Au}_4\text{Ru}_2(\text{PPh}_3)_2(\text{SC}_2\text{H}_4\text{Ph})_8$ . (C) UV-vis spectrum of  $\text{Au}_4\text{Ru}_2(\text{PPh}_3)_2(\text{SC}_2\text{H}_4\text{Ph})_8$ . (D) UV-vis spectrum plotted on the photon energy scale. (E) Kohn-Sham orbitals (bottom panel) and density of states (top panel) of  $\text{Au}_4\text{Ru}_2(\text{PPh}_3)_2(\text{SC}_2\text{H}_4\text{Ph})_8$  from DFT calculations and the corresponding charge density distributions of HOMO and LUMO (insets).

strength with H atoms (binding energy  $\Delta E_{\text{H}} = 0.14\text{--}0.43$  eV relative to the energy of  $\text{H}_2$  molecule), which is beneficial for protons transfer from  $\text{TiO}_2$  to  $\text{Au}_4\text{Ru}_2$ . Photocatalytic  $\text{N}_2$  fixation on the  $\text{Au}_4\text{Ru}_2/\text{TiO}_2\text{-Ov}$  catalyst in  $\text{CH}_3\text{CN}$  solvent did not produce ammonia, again corroborating the origin of protons in ammonia from water splitting. For comparison, the  $\text{Au}_4\text{Ru}_2$  cluster supported on  $\text{SiO}_2$  gave a low ammonia production rate of  $2.4 \mu\text{mol g}^{-1} \text{h}^{-1}$ , implying the key role of  $\text{TiO}_2\text{-Ov}$  in water splitting.

Furthermore, the action spectrum for  $\text{NH}_3$  formation on the  $\text{Au}_4\text{Ru}_2/\text{TiO}_2\text{-Ov}$  catalyst was determined under monochromatic light irradiation at wavelengths of 334, 420, 520, 600, and 700 nm. The trend of apparent quantum efficiencies (AQEs) well matched that of the optical absorption spectrum of the  $\text{Au}_4\text{Ru}_2/\text{TiO}_2\text{-Ov}$  (Fig. 3D). This proved that the photocatalytic  $\text{N}_2$  fixation originated from the light absorption by the  $\text{Au}_4\text{Ru}_2$  cluster. In addition, the catalytic activity decreased slightly with multiple cycles (Fig. S4†), mainly due to the partial detachment of  $\text{Au}_4\text{Ru}_2$  from  $\text{TiO}_2\text{-Ov}$  ( $\sim 8$  wt% metal loss detected by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis). The diffuse reflectance optical spectra (DRS) of the  $\text{Au}_4\text{Ru}_2/\text{TiO}_2\text{-Ov}$  sample did not significantly change after the reaction (Fig. S5A and B†) and transmission electron microscopy (TEM) studies showed that the spent catalyst had no obvious aggregation (Fig. S5C and D†), suggesting that the  $\text{Au}_4\text{Ru}_2$  cluster was robust throughout the reaction.

To directly visualize the  $\text{N}_2$  conversion on the  $\text{Au}_4\text{Ru}_2/\text{TiO}_2\text{-Ov}$  catalyst, *in situ* infrared Fourier transform (DRIFT) spectroscopy was utilized to monitor the time-dependent change of the functional nitrogenous intermediates on the surface of  $\text{Au}_4\text{Ru}_2/\text{TiO}_2\text{-Ov}$ . No signal change was observed in the DRIFT spectra within 30 min of incident light exposure in the absence of water (Fig. S6†), suggesting that the H atoms in ammonia indeed came from water. After water was introduced into the reaction cell, several absorption peaks appeared gradually with the irradiation time (Fig. 3E). The broad band at  $3590 \text{ cm}^{-1}$  is assigned to the  $\nu(\text{N-H})$  stretching vibration, and the two absorption bands at  $1705$  and  $1559 \text{ cm}^{-1}$  are attributed to the  $\sigma(\text{N-H})$  bending vibration.<sup>25,28</sup> Besides, the bands at  $1405$  and  $2912 \text{ cm}^{-1}$  assigned to the  $\text{NH}_4^+$  deforming vibration became stronger gradually with the irradiation time.<sup>29,30</sup> The result validated that the  $\text{Au}_4\text{Ru}_2/\text{TiO}_2\text{-Ov}$  catalyst can convert  $\text{N}_2$  into ammonia under the light irradiation.

Considering that the  $\text{Au}_4\text{Ru}_2$  cluster contained thiolate and  $\text{PPh}_3$  ligands, it is natural to ask whether the ligands can affect the catalytic conversion of  $\text{N}_2$ . To address this, the comparison experiments were conducted, where a series of  $\text{Au}_4\text{Ru}_2$  clusters protected by different ligands were prepared (Fig. S7†). As shown in Fig. 3F, the  $\text{Au}_4\text{Ru}_2$  clusters with different ligands showed no drastic difference in the photocatalytic performance for  $\text{N}_2$  reduction, manifesting that the catalytic reaction was mainly determined by metal sites, rather than the ligands. Furthermore, when all the ligands in  $\text{Au}_4\text{Ru}_2$  were removed *via*





Fig. 3 (A) The photocatalytic performances of the  $\text{Au}_4\text{Ru}_2/\text{TiO}_2\text{-Ov}$ ,  $\text{Au}_4\text{Ru}_2/\text{TiO}_2$ ,  $\text{TiO}_2\text{-Ov}$  and  $\text{TiO}_2$  catalysts for  $\text{N}_2$  reduction. (B) Time-dependent photocatalytic ammonia production over the  $\text{Au}_4\text{Ru}_2/\text{TiO}_2\text{-Ov}$ ,  $\text{Au}_4\text{Ru}_2/\text{TiO}_2$ ,  $\text{TiO}_2\text{-Ov}$  and  $\text{TiO}_2$  catalysts. (C) Reaction energy diagrams of water dissociation on the anatase  $\text{TiO}_2(101)$  surface without defect ( $\text{TiO}_2$ ) and with an oxygen vacancy per supercell on surface ( $\text{TiO}_2\text{-Ov}_1$ ) and subsurface ( $\text{TiO}_2\text{-Ov}_2$ ), respectively.  $\Delta E$  is relative to the energy of each substrate plus a free water molecule. Insets are the structures of water adsorption (top) and dissociation into  $^*\text{H}$  and  $^*\text{OH}$  species adsorbed on  $\text{TiO}_2\text{-Ov}_1$  (bottom), and the transition state (middle). The H, O and Ti are shown in cyan, red and yellow. (D) UV-DRS and quantum efficiency of  $\text{Au}_4\text{Ru}_2/\text{TiO}_2\text{-Ov}$  for  $\text{NH}_4^+$  evolution by photocatalytic  $\text{N}_2$  reduction under monochromatic light of different wavelengths. (E) *In situ* FTIR spectra of the photocatalytic  $\text{N}_2$  reduction over  $\text{Au}_4\text{Ru}_2/\text{TiO}_2\text{-Ov}$  during full spectrum illumination in the presence of  $\text{N}_2$  and water. (F) Performances of the  $\text{Au}_4\text{Ru}_2$  clusters protected by different ligands for photocatalytic  $\text{N}_2$  reduction.

the thermal treatment, the  $\text{Au}_4\text{Ru}_2$  clusters crashed into large nanoparticles and hence lost the activity for  $\text{N}_2$  fixation (Fig. S8†).

We now discuss the mechanism that  $\text{Au}_4\text{Ru}_2/\text{TiO}_2\text{-Ov}$  can achieve an extraordinary activity for photocatalytic  $\text{N}_2$  reduction, but  $\text{Au}_n/\text{TiO}_2\text{-Ov}$  and  $\text{TiO}_2\text{-Ov}$  cannot. Mott-Schottky (M-S)

plots were first collected to provide the flat band potentials of  $\text{Au}_4\text{Ru}_2$  and  $\text{TiO}_2\text{-Ov}$ . The obtained tangent positive slopes indicated that both  $\text{Au}_4\text{Ru}_2$  and  $\text{TiO}_2\text{-Ov}$  were likely n-type semiconductors (Fig. 4A). The flat band potentials of  $\text{Au}_4\text{Ru}_2$  and  $\text{TiO}_2\text{-Ov}$  versus the saturated  $\text{Ag}/\text{AgCl}$  were  $-0.18$  and  $-0.38$  V, respectively. Based on the UV-DRS and M-S



measurements, the band alignments of  $\text{Au}_4\text{Ru}_2$  and  $\text{TiO}_2\text{-Ov}$  were shown in Fig. 4B. From the thermodynamic point of view, photogenerated electron carriers can transfer from  $\text{TiO}_2\text{-Ov}$  to  $\text{Au}_4\text{Ru}_2$ , while the  $\text{Au}_4\text{Ru}_2$  cluster was more capable of light-driven  $\text{N}_2$  reduction than the  $\text{TiO}_2\text{-Ov}$  substrate.

The charge carrier kinetics of the  $\text{Au}_4\text{Ru}_2$  cluster with  $\text{N}_2$ , including separation, transfer and recombination, was investigated by room temperature steady-state and time-resolved photoluminescence (PL) spectroscopy. As shown in Fig. S9,<sup>†</sup> when the Ar atmosphere was changed to the  $\text{N}_2$  atmosphere, the steady-state PL spectrum of  $\text{Au}_4\text{Ru}_2/\text{TiO}_2\text{-Ov}$  was significantly quenched, which was related to the non-radiative transfer of the photoexcited electrons from  $\text{Au}_4\text{Ru}_2$  to the  $\pi^*$  antibonding orbitals of  $\text{N}_2$  adsorbed on the cluster.<sup>30</sup> The time-resolved PL spectroscopy studies (Fig. 4C) showed that the average decay

time ( $\tau = 14.40$  ns) of  $\text{Au}_4\text{Ru}_2/\text{TiO}_2\text{-Ov}$  was longer than that of  $\text{TiO}_2\text{-Ov}$  ( $\tau = 5.26$  ns). The prolonged lifetime of the photo-generated electrons illustrated that  $\text{Au}_4\text{Ru}_2$  supported on  $\text{TiO}_2\text{-Ov}$  can reduce the charge recombination, thereby possess highly effective separation of electron-hole pairs.<sup>31</sup>

We argued that the high efficiency of  $\text{N}_2$  fixation on the  $\text{Au}_4\text{Ru}_2/\text{TiO}_2\text{-Ov}$  catalyst was acquired by a synergic effect between  $\text{Au}_4\text{Ru}_2$  and  $\text{TiO}_2\text{-Ov}$ . To confirm this, transient photocurrent responses were conducted on the  $\text{Au}_4\text{Ru}_2/\text{TiO}_2\text{-Ov}$ ,  $\text{TiO}_2\text{-Ov}$ , and two reference systems ( $\text{Au}_{24}/\text{TiO}_2\text{-Ov}$  and  $\text{Au}_{25}/\text{TiO}_2\text{-Ov}$ ) under the Ar and  $\text{N}_2$  atmospheres with light (Fig. 4D), respectively. Compared to  $\text{TiO}_2\text{-Ov}$ , the photocurrents of  $\text{Au}_{24}/\text{TiO}_2\text{-Ov}$  and  $\text{Au}_{25}/\text{TiO}_2\text{-Ov}$  were enhanced under the Ar atmosphere, suggesting that the  $\text{Au}_n$  clusters also can serve as trapping sites for the photogenerated electrons.<sup>30</sup> However, the

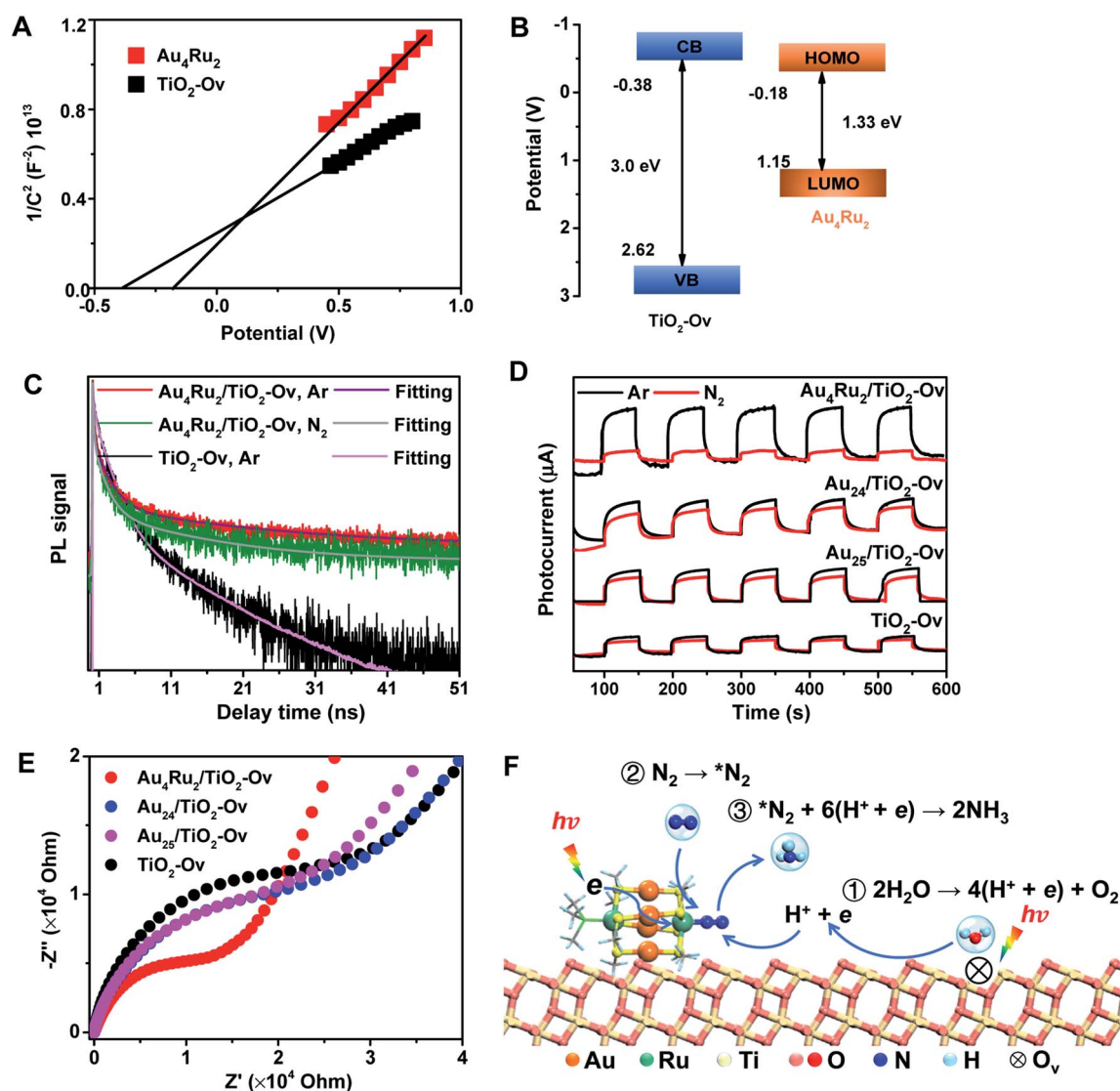


Fig. 4 (A) Mott-Schottky plots of  $\text{Au}_4\text{Ru}_2$  and  $\text{TiO}_2\text{-Ov}$  (potential V vs. Ag/AgCl at pH 6.4). (B) Schematic diagram of band alignment (potential V vs. Ag/AgCl at pH 6.4). VB means valence band, and CB denotes conduction band. (C) Time-resolved PL spectra of the  $\text{Au}_4\text{Ru}_2/\text{TiO}_2\text{-Ov}$  and  $\text{TiO}_2\text{-Ov}$  under Ar and  $\text{N}_2$  atmospheres, respectively. (D) Photocurrent responses of  $\text{Au}_4\text{Ru}_2/\text{TiO}_2\text{-Ov}$ ,  $\text{Au}_{24}/\text{TiO}_2\text{-Ov}$ ,  $\text{Au}_{25}/\text{TiO}_2\text{-Ov}$  and  $\text{TiO}_2\text{-Ov}$  under Ar and  $\text{N}_2$  atmospheres, respectively. (E) Electrochemical impedance spectra of  $\text{Au}_4\text{Ru}_2/\text{TiO}_2\text{-Ov}$ ,  $\text{Au}_{24}/\text{TiO}_2\text{-Ov}$ ,  $\text{Au}_{25}/\text{TiO}_2\text{-Ov}$  and  $\text{TiO}_2\text{-Ov}$  in the presence of 300 W xenon lamp. (F) Proposed mechanism for the photocatalytic  $\text{N}_2$  reduction on the  $\text{Au}_4\text{Ru}_2/\text{TiO}_2\text{-Ov}$  catalyst.

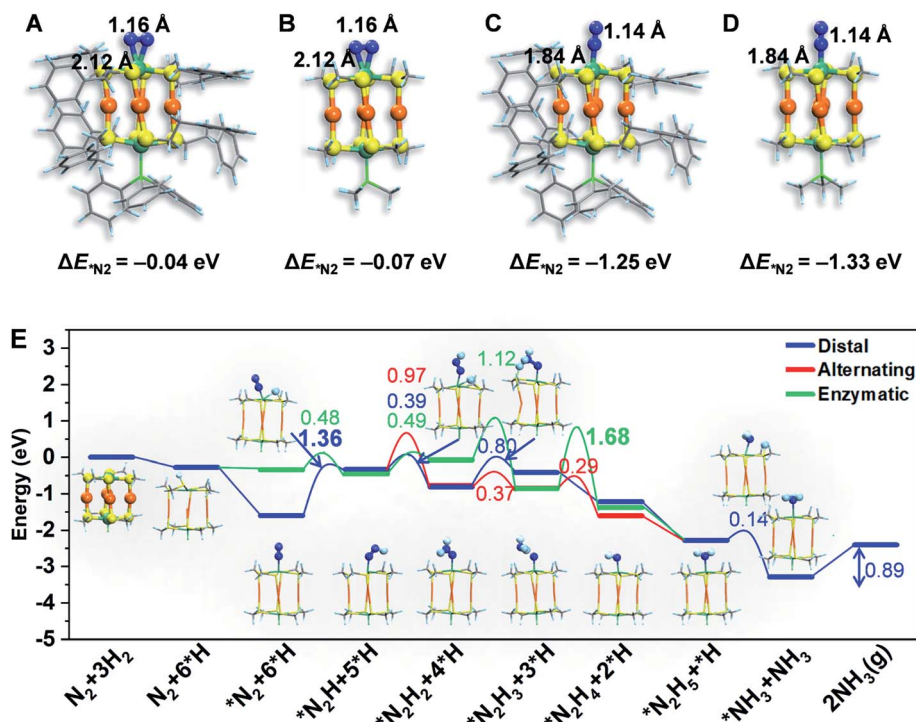


Fig. 5 The atomic structures of  $\text{N}_2$  molecule adsorption via (A and B) end-on and (C and D) side-on patterns on the  $\text{Au}_4\text{Ru}_2(\text{SC}_2\text{H}_4\text{Ph})_8\text{PPh}_3$  and  $\text{Au}_4\text{Ru}_2(\text{SCH}_3)_8\text{P}(\text{CH}_3)_3$ . The H, C, N, S, Au and Ru are shown in light blue, gray, blue, yellow, orange and blackish green colors, respectively. The adsorption energy of a  $\text{N}_2$  molecule is shown for each system, revealing that simplifying the ligands of  $-\text{PPh}_3$  and  $-\text{SC}_2\text{H}_4\text{Ph}$  by  $-\text{P}(\text{CH}_3)_3$  and  $-\text{SCH}_3$ , respectively, has a minor effect on the binding properties of the cluster with  $\text{N}_2$ . (E) The colors numbers indicate the kinetic barriers of  $\text{N}_2$  fixation on the  $\text{Au}_4\text{Ru}_2$  cluster, and the barriers of rate-limiting step are bolded. The atomic structures of reaction intermediates are displayed as insets. The H, C, N, S, Au and Ru are shown in light blue, gray, blue, yellow, orange and green colors, respectively.

transient photocurrent responses of  $\text{TiO}_2\text{-Ov}$ ,  $\text{Au}_{24}/\text{TiO}_2$  and  $\text{Au}_{25}/\text{TiO}_2\text{-Ov}$  samples under  $\text{N}_2$  atmosphere were similar to those under Ar atmosphere, indicating that the interfacial electron transfer in the three samples was not interfered by surrounding  $\text{N}_2$ . It partially accounted for the catalytic performance of the  $\text{Au}_n/\text{TiO}_2\text{-Ov}$  catalysts shown in Fig. 1 that the  $\text{Au}_n/\text{TiO}_2\text{-Ov}$  catalysts did not significantly enhance the photoactivity of  $\text{N}_2$  reduction in comparison with the  $\text{TiO}_2\text{-Ov}$ . Notably, the photocurrent of the  $\text{Au}_4\text{Ru}_2/\text{TiO}_2\text{-Ov}$  sample under the  $\text{N}_2$  atmosphere was only a quarter of that under the Ar atmosphere (Fig. 4D), in which the quenching of the other three-quarters of photocurrent was possibly due to the electrons consumed by the adsorbed  $\text{N}_2$  molecules.

Moreover, electrochemical impedance spectroscopy (EIS) was measured to investigate the interfacial charge-transfer properties of the above four samples under illumination. As shown in Fig. 4E, the semicircular diameters of  $\text{Au}_{24}/\text{TiO}_2\text{-Ov}$  and  $\text{Au}_{25}/\text{TiO}_2\text{-Ov}$  measured under light irradiation were slightly smaller than that of  $\text{TiO}_2\text{-Ov}$ , indicating that the  $\text{Au}_n$  clusters had an inherent ability of electron transport, but this ability was not extraordinary. Notably, the impedance of  $\text{Au}_4\text{Ru}_2/\text{TiO}_2\text{-Ov}$  was the smallest among the four samples, providing a solid evidence that there existed a fast transfer of the interfacial charges between  $\text{Au}_4\text{Ru}_2$  and  $\text{TiO}_2\text{-Ov}$ .<sup>32</sup> The charge transfer resistance on the  $\text{Au}_4\text{Ru}_2/\text{TiO}_2\text{-Ov}$  sample without illumination was also investigated (Fig. S10†). It was found that the

impedance of  $\text{Au}_4\text{Ru}_2/\text{TiO}_2\text{-Ov}$  in the absence of light was much higher than that in the presence of light. Therefore, these observations supplied a clue that the  $\text{Au}_n$  clusters were able to generate the electrons under the light irradiation, but lacked the ability to activate  $\text{N}_2$ , and thus the Ru atoms in  $\text{Au}_4\text{Ru}_2$  should be crucial for  $\text{N}_2$  binding and activation. To further elucidate the critical contribution of the Ru atoms in the  $\text{Au}_4\text{Ru}_2$  cluster to the activation of the inert  $\text{N}\equiv\text{N}$  triple bond, the two Ru atoms of  $\text{Au}_4\text{Ru}_2$  were replaced by the two Pd atoms (Fig. S11A†), that is,  $\text{Au}_4\text{Pd}_2$ . No increase in the photocatalytic reduction of  $\text{N}_2$  on the  $\text{Au}_4\text{Pd}_2/\text{TiO}_2\text{-Ov}$  was observed when compared to the  $\text{Au}_n/\text{TiO}_2\text{-Ov}$  (Fig. S11B†). The result definitely confirmed that the Ru atoms in the  $\text{Au}_4\text{Ru}_2$  cluster indeed can provide unique reaction sites for the  $\text{N}\equiv\text{N}$  cleavage by strong coordination.

To gain atomistic insight into the photochemical  $\text{N}_2$  reduction on the  $\text{Au}_4\text{Ru}_2/\text{TiO}_2\text{-Ov}$  catalyst, we performed DFT calculations to determine the active sites and reaction pathways. Our calculations show that the Au atoms do not have any activity for  $\text{N}_2$  fixation, but  $\text{N}_2$  can be adsorbed onto the Ru atom in the side-on or end-on configuration, with adsorption energies of  $-0.07$  eV and  $-1.33$  eV and Ru–N bond length of 2.14 Å and 1.84 Å, respectively (Fig. 5A–D). The N–N bond is elongated to 1.14–1.16 Å compared to 1.13 Å for the gaseous  $\text{N}_2$  molecule, which manifests that  $\text{N}_2$  is activated on the Ru site of the  $\text{Au}_4\text{Ru}_2$  cluster. Moreover, we examined the structure of

$\text{Au}_4\text{Ru}_2(\text{SCH}_3)_8(\text{P}(\text{CH}_3)_3)_2$  cluster supported on the anatase  $\text{TiO}_2(101)$  surface (Fig. S12†), which exhibits a weak interfacial interaction with a distance of 2.57 Å between the cluster and substrate and a binding energy of only  $-0.28$  eV per Au(Ru) atom. Therefore, the presence of substrate should not affect the adsorption properties of the  $\text{Au}_4\text{Ru}_2$  cluster with  $\text{N}_2$ . Hereafter, we considered  $\text{N}_2$ -to- $\text{NH}_3$  conversion on the  $\text{Au}_4\text{Ru}_2$  cluster without support of the substrate.

Ammonia synthesis on the  $\text{Au}_4\text{Ru}_2$  cluster can proceed through three pathways, *i.e.* distal, alternating and enzymatic mechanisms (Fig. 5E).<sup>24,33</sup> For the former two paths, the  $\text{N}_2$  molecule strongly binds with the underlying Ru atom in the end-on configuration. Protonation of the chemisorbed  $^*\text{N}_2$  species to form a  $^*\text{NNH}$  intermediate is endothermic and has a kinetic barrier of 1.36 eV, which is the rate-limiting step of  $\text{N}_2$ -to- $\text{NH}_3$  conversion. The following reaction steps are exothermic involving barriers below 0.97 eV or even barrierless. For the enzymatic mechanism, the adsorption strength of  $^*\text{N}_2$  species on Ru is relatively weak. The reaction proceeds almost down-hill in energy. Reaction from  $^*\text{N}_2$  to form a  $^*\text{HN-NH}$  species is favorable with a kinetic barrier of only 0.48 eV. Protonation of  $^*\text{H}_2\text{N-NH}$  leads to the breaking of N-N bond and generation of two  $^*\text{H}_2\text{N}$  species, which requires the largest barrier of 1.68 eV during the whole reaction. Finally, desorption of  $^*\text{NH}_3$  has to overcome a moderate energy barrier of 0.89 eV. In brief, our DFT calculations suggest that the synergistic effect of the  $\text{Au}_4\text{Ru}_2/\text{TiO}_2\text{-Ov}$  catalyst stems from the cooperation between cluster and substrate during the catalytic reaction (Fig. 4F): the Ru atom in the  $\text{Au}_4\text{Ru}_2$  cluster serves as the active site for  $\text{N}_2$  fixation and ammonia synthesis through the distal or alternating pathways; the anatase  $\text{TiO}_2(101)$  substrate plays important roles in water splitting to generate hydrogen protons that transfer to the cluster for the  $\text{N}_2$ -to- $\text{NH}_3$  reaction.

## Conclusions

In conclusion, we have synthesized an excitonic  $\text{Au}_4\text{Ru}_2$  cluster, which enables light harvesting including electron/hole pair production and separation. The experimental studies combined with theoretical calculations demonstrate that the cooperative effect between  $\text{Au}_4\text{Ru}_2$  cluster and  $\text{TiO}_2$  substrate with oxygen vacancies leads to an extraordinary activity for light-driven  $\text{N}_2$  reduction. The electron-hole pairs can be generated from the excited  $\text{Au}_4\text{Ru}_2$  cluster; the heterojunction between  $\text{Au}_4\text{Ru}_2$  cluster and the  $\text{TiO}_2\text{-Ov}$  substrate also facilitates photocarriers separation; the photoelectrons transfer to the Ru atoms of the cluster; meanwhile,  $\text{TiO}_2\text{-Ov}$  induces water splitting to produce hydrogen protons for  $\text{N}_2$  fixation and conversion on the Ru atoms. Certainly, this work provides deep insights into non-plasmon-induced charge transfer from atomically precise metal clusters and develops a feasible strategy to enable highly efficient solar energy utilization *via* pursuing heterogeneous catalysts with atomic precision.

## Conflicts of interest

No conflicts of interest.

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