# Nitrogen doping of indium oxide for enhanced photocatalytic reduction of CO<sub>2</sub> to methanol

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#### Abstract

Herein, the nitrogen-doped indium oxide (N-In<sub>2</sub>O<sub>3</sub>) photocatalyst was confirmed to be highly active and stable for photocatalytic reduction of CO<sub>2</sub> to methanol in an aqueous solution at ambient conditions. The efficiency of N-In<sub>2</sub>O<sub>3</sub> in producing methanol can be flexibly improved by tuning the nitrogen doping content. The highest formation rate of methanol reaches to 394  $\mu$ mol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>, with a methanol selectivity of 63%, at a nitrogen doping content of 3.74%. Nitrogen doping generates mid-gap energy states and reduces the bandgap of In<sub>2</sub>O<sub>3</sub>, thus boosting photon absorption and electron-hole separation. Nitrogen doping creates more oxygen vacancies on In<sub>2</sub>O<sub>3</sub>, thus forming more active sites for CO<sub>2</sub> adsorption and conversion. Nitrogen doping also enhances the activity of the surface frustrated Lewis pairs (SFLPs), which further promotes CO<sub>2</sub> adsorption and activation. The multiple-role of nitrogen doping results in the highly active and stable photocatalytic reduction of CO<sub>2</sub> to methanol.

Keywords: nitrogen doping; In<sub>2</sub>O<sub>3</sub>; CO<sub>2</sub>; methanol; photocatalytic reduction

#### 1. Introduction

Climate change originated from  $CO_2$  accumulation in the atmosphere has become the most urgent global issue [1-6]. Solar-driven photocatalytic reduction of  $CO_2$  is one of the most promising strategies to solve the  $CO_2$ -related issue, as it utilizes green and sustainable solar energy to reduce  $CO_2$  emission whilst converting  $CO_2$  into valuable fuels and chemicals, *e.g.* methanol (CH<sub>3</sub>OH) [7-9], carbon monoxide (CO) [10-13], and methane (CH<sub>4</sub>) [14-17]. Fabricating efficient photocatalysts for the photocatalytic reduction of  $CO_2$  has thereby become a hot topic.

As an n-type semiconductor, In<sub>2</sub>O<sub>3</sub> has been widely applied for photocatalytic conversions [18-26]. The narrow bandgap (~2.8 eV), high conductivity, good stability and photo-corrosion resistance make In<sub>2</sub>O<sub>3</sub> be a promising alternative to popular photocatalysts like TiO<sub>2</sub>. In<sub>2</sub>O<sub>3</sub> is efficient in adsorbing and activating CO<sub>2</sub>, benefitted from its oxygen vacancies and abundant hydroxyl groups. The positions of conduction band (CB) and valence band (VB) of In<sub>2</sub>O<sub>3</sub> have been proved to meet the reduction potentials for driving the photocatalytic reduction of CO<sub>2</sub>. However, pristine In<sub>2</sub>O<sub>3</sub> shows poor activity for photocatalytic reduction of CO<sub>2</sub> under ambient conditions, suffering from the rapid recombination of the photogenerated electrons and holes as well as the uncontrolled reactions of radicals [18]. The pristine In<sub>2</sub>O<sub>3</sub> is in a pale-yellow colour, and can only respond to the ultraviolet light region, which accounts for only 7% of sunlight. Tuning the surface property and crystal structure of In<sub>2</sub>O<sub>3</sub> has been considered to be an efficient strategy to improve the efficiency of In<sub>2</sub>O<sub>3</sub> in the photocatalytic reduction of CO<sub>2</sub>. For example, creating more oxygen vacancies on In2O3 to fabricate In2O3-x changes the colour of the material into black, and the light absorption is thus extended to the visible light region, which accounts for about 43% of sunlight [19]. In addition, the black In<sub>2</sub>O<sub>3-x</sub> also shows a stronger ability in separating the photogenerated electron-hole pairs as well as adsorbing and activating CO<sub>2</sub>, as compared with pristine In<sub>2</sub>O<sub>3</sub>, due to the more oxygen vacancies [19]. Black In<sub>2</sub>O<sub>3-x</sub>/In<sub>2</sub>O<sub>3</sub> composite with amorphous non-stoichiometric In<sub>2</sub>O<sub>3-x</sub> on a core of crystalline

stoichiometric In<sub>2</sub>O<sub>3</sub> has a broader light absorption, from the ultraviolet region to the visible region, and improves electron-hole separation, thus enhancing the photocatalytic reduction of CO<sub>2</sub> [20-22]. Doping In<sub>2</sub>O<sub>3</sub> by metal or non-metal elements (*e.g.* N and C) can also improve light absorption, electron-hole separation and CO<sub>2</sub> adsorption, thus enhancing photocatalytic reduction of CO<sub>2</sub> [18,23-25]. Wang *et al.* [26] found that the main product was methane in the photocatalytic reduction of CO<sub>2</sub> on Pt-decorated In<sub>2</sub>O<sub>3</sub> nanorods. The In<sub>2</sub>O<sub>3</sub> nanorods promoted light absorption and electron-hole separation, while the supported Pt nanoparticles provided active sites to generate hydrogen atoms for reducing CO<sub>2</sub> into methane. However, how to exactly control the amounts of doped elements on In<sub>2</sub>O<sub>3</sub> is a long-term objective for the studies on the photocatalytic reduction of CO<sub>2</sub>. Excessive doped elements induce fast electron-hole recombination, thus reducing photoreduction efficiency.

On the other hand, as the heterogeneous hydrogenation of  $CO_2$  [27], tuning the product selectivity of photocatalytic reduction of  $CO_2$  is still a challenge. It is very important not only for the potential applications but also for the fundamental understanding on the structureperformance relationship of photocatalysts. Herein, we efficiently tune the product selectivity of photocatalytic reduction of  $CO_2$  from CO evolution to methanol formation by doping nitrogen on  $In_2O_3$ . We confirm that nitrogen doping endows the N-In<sub>2</sub>O<sub>3</sub> with enhanced light absorption capacity, superior charge separation efficiency, improved photocatalytic activity and significantly increased methanol yield. The methanol formation rate can be efficiently improved by tuning nitrogen doping content, which enables the controllable photocatalytic production of methanol.

# 2. Experimental and calculation methods

# 2.1. Photocatalysts preparation

In this work, a discharge-enhanced nitrogen doping *via* dielectric barrier discharge (DBD) plasma was employed for the preparation of N-In<sub>2</sub>O<sub>3</sub> photocatalysts. This kind of plasma has

been commercially applied for ozone generation, polymer treatment and others. Plasma is the fourth form of matter. Different from solid, liquid and gas, plasma is a collection of molecules, free radicals, excited species, ions, photons and electrons [28]. It is normally generated by partial ionization or dissociation of gas molecules between two electrodes under some high voltages. DBD contains one or two electrodes covered by the dielectric barrier, which plays an important role in the stabilization of the discharge. It can be operated at atmospheric pressure and as low as room temperature. However, its electron energy is very high with average electron temperature ranged from 10,000 to 100,000 K (1-10 eV) [28]. DBD is also highly effective and efficient for the nitrogen doping of catalysts [29,30].

The DBD reactor applied here is shown in Fig. S1. To dope nitrogen onto  $In_2O_3$ , the pristine  $In_2O_3$  was firstly placed in the discharge chamber. A gas mixture of NH<sub>3</sub> and argon was running into the discharge chamber, with a flowrate of 20 mL min<sup>-1</sup>, at atmospheric pressure. Finally, DBD was initiated for nitrogen doping. During the discharge-enhanced doping, NH<sub>3</sub> was ionized and dissociated into energetic nitrogen and hydrogen species, causing the doping of nitrogen into  $In_2O_3$ . The temperature during the doping was ~150 °C, according to the measurement by the infrared imaging (Icron 100PHT). More details of the operation of the DBD setup have been given in our previous works [31,32]. The experimental study shows the time of the discharge-enhanced nitrogen doping has a significant effect, and there is an optimum time (10 min) for nitrogen doping. In the following discussions, the pristine  $In_2O_3$  is denoted as M1, while the photocatalysts with nitrogen doping times of 2, 5, 10, 20, 30 and 40 min are assigned as M2, M3, M4, M5, M6 and M7, respectively. Fig. S2 shows the photos of M1-M7.

#### 2.2. Characterization

X-ray diffraction (XRD) analyses were performed on a Rigaku D/MAX-2500 diffractometer with a scan speed of 4° min<sup>-1</sup> over the 2 $\theta$  range of 10-90°. The diffractometer was equipped with a Cu K $\alpha$  radiation source ( $\lambda = 1.54056$  Å). The diffraction patterns were compared with the data from the Joint Committee on Powder Standards (JCPDS) database to identify the crystalline phase of the catalysts. High-resolution transmission electron microscopy (HRTEM) analyses were carried out on a JEM-F200 microscope with an accelerating voltage of 200 kV. Before the test, each catalyst was dispersed in ethanol and ultrasonicated for 30 min. The upper suspension was dripped on an ultra-thin carbon film to dry naturally. The element mapping patterns were characterized *via* energy-dispersive X-ray spectroscopy (EDS) using JEM-F200. X-ray photoelectron spectroscopy (XPS) analyses were performed on an ESCA 2000 X-ray photoelectron spectrophotometer (VG Scientific, monochromated Mg K $\alpha$  X-ray). The results of the XPS depth profile were collected by a Thermo Fisher Scientific K-Alpha+ spectrometer equipped with an Al K $\alpha$  X-ray. The Ar<sup>+</sup> sputtering speed was ca. 0.1 nm s<sup>-1</sup> with Ta<sub>2</sub>O<sub>3</sub> as standard material. The binding energies were calibrated by the C 1*s* peak at 284.8 eV.

 $N_2$  adsorption-desorption isotherms were determined on a Micromeritics TriStar II 3020 instrument at 77 K. The Brunauer-Emmett-Teller (BET) model was used to calculate the specific surface area of the catalyst. All the catalysts were outgassed at 150 °C for 6 h before the test. The ultraviolet-visible diffuse reflectance spectroscopy (UV-vis-DRS) observations were done at room temperature on a UV-2600 ultraviolet-visible spectrophotometer (Shimadzu Corporation) equipped with an integrating sphere. Photoluminescence (PL) spectra were measured on an FSL-1000 (Edinburgh Instruments) system at room temperature, using a 325 nm laser as the excitation source. The time-resolved fluorescence decay spectra were recorded with 440 nm as the emission center. The average fluorescence lifetime ( $\tau_{avg}$ ) was calculated by fitting the single exponential function. Photocurrents were measured on an electrochemical workstation (CHI760E, CH Instrument, Inc.) at room temperature.

 $CO_2$  temperature-programmed desorption ( $CO_2$ -TPD) profiles were obtained on a Micromeritics Autochem II 2920 chemisorption analyzer equipped with a Hiden HPR-20 EGA mass spectrometer (MS). 300 mg catalyst was placed in a U-shaped quartz tube, which was heated to 200 °C at 10 °C min<sup>-1</sup> in a helium atmosphere and kept for 60 min. Then the catalyst

was cooled to 50 °C in flowing helium naturally.  $CO_2$  was adsorbed at 50 °C for 2 h. After purging with flowing helium for 1 hour to remove the physically absorbed  $CO_2$ , the catalyst was heated to 700 °C at 10 °C min<sup>-1</sup> for the temperature-programmed desorption. The signal collected by the mass spectrometer at m/z = 44 and 28 represented  $CO_2$  and CO, respectively. *In situ* diffuse reflectance infrared Fourier-transform spectroscopy (DRIFT) analyses were performed on a PerkinElmer Spectrum 3 FTIR spectrometer. Before measurement, the catalyst was purged with Ar at 50 °C for 1 hour and cooled down to room temperature subsequently. The catalyst was then exposed to the  $CO_2$  stream (20 ml min<sup>-1</sup>, 50 vol%) for 20 min.

#### 2.3. Density functional theory (DFT) calculation method

All periodic DFT calculations were performed using the Vienna ab initio simulation package (VASP 5.4.4), a periodic DFT code with projector augmented wave (PAW) potentials [33]. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional was applied to describe the electronic exchange-correlation energy [34]. The 4*d*, 5*s* and 5*p* states of In were treated explicitly as valence states within the scalar-relativistic PAW approach [35]. A plane wave basis with a cutoff energy of 400 eV and a Monkhorst-Pack mesh with a grid of  $(3 \times 3 \times 1)$  *k*-points were applied. Both the conjugate gradient algorithm and the quasi-Newton method were used in the structural optimization until the forces on all unconstrained atoms were less than 0.03 eV Å<sup>-1</sup>. The cubic In<sub>2</sub>O<sub>3</sub>(111) facet was modelled by a periodic supercell slab with three atomic layers, which contained 72 O and 48 In atoms and was separated by a vacuum height of 12 Å in the *z*-direction to eliminate the unphysical interactions between the periodic surface slabs. During the calculations, the bottom layer of atoms was fixed, while the rest of the surface layer atoms were allowed to relax.

The energy of substitution ( $\Delta E_{sub}$ ) was calculated according to Equation (1).

$$\Delta E_{\rm sub} = E_{\rm N-slab} - E_{\rm O-slab} - xE_{\rm N-atom} + xE_{\rm O-atom} \tag{1}$$

where  $E_{\text{N-slab}}$  and  $E_{\text{O-slab}}$  represented the total energy of N-In<sub>2</sub>O<sub>3</sub>(111) and In<sub>2</sub>O<sub>3</sub>(111) slab models, respectively.  $E_{\text{N-atom}}$  and  $E_{\text{O-atom}}$  represented the energy of nitrogen and oxygen atoms in the vacuum, respectively.

The energy of adsorption ( $\Delta E_{ads}$ ) was defined as Equation (2).

$$\Delta E_{\rm ads} = E_{\rm M/N-slab} - E_{\rm N-slab} - E_{\rm M} \tag{2}$$

where  $E_{M/N-slab}$ ,  $E_{N-slab}$ , and  $E_M$  represented the total energy of N-In<sub>2</sub>O<sub>3</sub>(111) slab model with the adsorbate, the clean N-In<sub>2</sub>O<sub>3</sub>(111) slab model, and the free molecule, respectively.

### 2.4. Photocatalytic performance

Photocatalytic reduction of CO<sub>2</sub> with H<sub>2</sub>O was performed in a closed gas circulationevacuation reactor. 100 mg photocatalyst was firstly dispersed in an aqueous solution (100 mL) containing triethanolamine (TEOA) (10 vol%) which served as a sacrificial reagent. The reactor was then evacuated and refilled with CO<sub>2</sub> three times to remove the air inside. Finally, the reactor was filled with CO<sub>2</sub> until the pressure reached 1.01 bar. During the photoreduction, the reactor was irradiated by a Xe-lamp (300 W) under vigorous stirring. The temperature of the reactor was kept at 25 °C by using cooling water. The effluent was analyzed by gas chromatography (Agilent 7890A) with a thermal conductivity detector (TCD) and a flame ionization detector (FID). To determine the source of the carbon in the products, isotopic experiments were carried out under identical reaction conditions. The products were analyzed by gas chromatography-mass spectrometry (GC-MS).

# 3. Results



**Fig. 1.** Morphology and structure of photocatalysts. (a) HRTEM image of M1. (b) HRTEM image of M4. (c) Element mapping patterns of M4. (d) XRD patterns of M1-M7. (e) N 1*s* and (f) O 1*s* XPS spectra of M1-M7.

In the HRTEM images (Figs. 1a and 1b), M1 and M4 exhibit well-defined lattice fringes with an inter-planar distance of 0.293 nm, which correspond to the (222) facet of cubic In<sub>2</sub>O<sub>3</sub>. As reflected by the elemental mapping patterns (Fig. 1c), in addition to In and O, N is uniformly distributed on the surface of M4. N<sub>2</sub> adsorption-desorption measurements suggest that the specific surface area of M4 (90.5 m<sup>2</sup>/g) is close to that of M1 (103.1 m<sup>2</sup>/g). The XRD patterns of M2-M7 are similar to that of pristine  $In_2O_3$  (M1), except that the peak attributed to the (222) facet of M4 and M5 shifts to a lower  $2\theta$  direction (Fig. 1d). This shift could be resulted from the doping of nitrogen into the lattice of In<sub>2</sub>O<sub>3</sub>. The covalent radius of N (0.71 Å) is larger than that of O (0.63 Å). [36] Doping of N into the lattices of In<sub>2</sub>O<sub>3</sub> causes the substitution of lattice O atoms by N. The larger covalent radius of N induces the shift of the XRD peaks to the lower  $2\theta$  direction. Fig. 1e shows the N 1s XPS spectra of M1-M7. The N 1s XPS peak at ca. 400.3 eV can be seen for M2-M7. This confirms the doping of N on M2-M7. According to the XPS spectra, the nitrogen doping content on M2-M7 is calculated to be 1.50%, 1.67%, 3.74%, 2.50%, 1.65% and 1.45%, respectively. Therefore, M4 shows the highest nitrogen doping content (3.74%). Evidently, increasing the discharge-enhanced doping time from 0 to 10 min increases the nitrogen doping content on N-In<sub>2</sub>O<sub>3</sub>. However, further increasing the discharge time from 10 to 40 min reduces the nitrogen doping content. In addition, doping N into the lattice of In<sub>2</sub>O<sub>3</sub> creates oxygen vacancies on In<sub>2</sub>O<sub>3</sub>. This makes the content of oxygen vacancies on N-In<sub>2</sub>O<sub>3</sub> higher than that on pristine In<sub>2</sub>O<sub>3</sub>, as reflected by the O 1s XPS spectra (Figs. 1f and S3).

To explore the nitrogen doping depth on N-In<sub>2</sub>O<sub>3</sub>, depth profile XPS analyses with Ar<sup>+-</sup> sputtering were conducted on M4. The depth profile XPS spectra are shown in Fig. S4 as a function of Ar<sup>+</sup>-sputtering time. Along with increasing the sputtering time from 0 to 120 s, the depth detected increases from 0 to about 12 nm below the surface of the initial photocatalyst. As shown in Fig. S4, the XPS peaks of N and O, assigned to oxygen vacancy, become weaker with the increasing sputtering time. No evident XPS peaks of N can be observed at the sputtering time longer than 120 s. Therefore, the doping depth of N on N-In<sub>2</sub>O<sub>3</sub> is less than 16 nm. This means the doped N atoms are located on the surface of N-In<sub>2</sub>O<sub>3</sub>.

The photocatalytic reduction of CO<sub>2</sub> with H<sub>2</sub>O is carried out in an aqueous solution with 10 vol% TEOA at 25 °C under light irradiation. TEOA serves as a sacrificial reagent for capturing the photogenerated holes, thus releasing more photogenerated electrons for reducing CO<sub>2</sub> with H<sub>2</sub>O. As illustrated in Figs. 2a and 2b, M1 has no photocatalytic activity. Doping N onto In<sub>2</sub>O<sub>3</sub> triggers the photocatalytic reduction of CO<sub>2</sub> with H<sub>2</sub>O efficiently (Figs. 2a and S3). During the photocatalytic reduction, CH<sub>3</sub>OH and CO are the two detectable carbon-containing products. The formation rates of other carbon-containing products like CH<sub>4</sub> are all less than 0.1 µmol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>, which can be ignorable. The ratios of CH<sub>3</sub>OH and CO in the measurable carboncontaining products are used to denote the selectivity of CH<sub>3</sub>OH and CO, respectively. Among all the N-In<sub>2</sub>O<sub>3</sub> photocatalysts, M4 is the most efficient for the photocatalytic reduction of CO<sub>2</sub> with H<sub>2</sub>O. On M4, the formation rate and selectivity of methanol are 394  $\mu$ mol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> and 63%, respectively, while those of CO are 230 µmol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> and 37%, respectively. The methanol and CO formation rates on M4 are much higher than those on other photocatalysts. The stability of M4 in the photocatalytic reduction of CO<sub>2</sub> with H<sub>2</sub>O is explored in five consecutive runs (Fig. 2c). After each run (6 h), the light is stopped, and the reactor is then evacuated and refilled with CO<sub>2</sub> of 1.01 bar, without washing the photocatalyst or adding fresh reaction solution. After five runs, the CH<sub>3</sub>OH and CO yields over M4 are almost unchanged, indicating the excellent stability of M4 for the photocatalytic reduction of CO<sub>2</sub>. Table S1 presents a comparison of the activity of M4 with the reported photocatalysts for the photocatalytic reduction of CO<sub>2</sub>. The efficiency of M4 for the photocatalytic reduction of CO<sub>2</sub> into methanol is higher than the reported photocatalysts.



**Fig. 2.** Photocatalytic performance of photocatalysts. (a)  $CH_3OH$  and CO formation rates on M1-M7. (b)  $CH_3OH$  and CO selectivities on M1-M7. (c) Stability of M4. (d) Mass spectroscopy signals observed during the photocatalytic reduction of  ${}^{13}CO_2$  with  $H_2O$  on M4.

To understand the origin of the CH<sub>3</sub>OH and CO formed on M4, three control experiments are carried out, including (i) CO<sub>2</sub> reduction with H<sub>2</sub>O using M4 in the absence of light; (ii) CO<sub>2</sub> reduction with H<sub>2</sub>O using light without M4; (iii) reduction of H<sub>2</sub>O without CO<sub>2</sub> over M4 with light. Neither CH<sub>3</sub>OH nor CO is detected in the control experiments, implying that CH<sub>3</sub>OH and CO are produced from the photocatalytic reduction of CO<sub>2</sub> with H<sub>2</sub>O on M4. An isotopic experiment with <sup>13</sup>CO<sub>2</sub> and H<sub>2</sub>O as the reactants of the photocatalytic reduction is also carried out to further determine the origin of CH<sub>3</sub>OH and CO. In the isotopic experiment, m/z signals of H, H<sub>2</sub>, <sup>13</sup>CH, <sup>13</sup>CH<sub>2</sub>, <sup>13</sup>CH<sub>3</sub>, OH, H<sub>2</sub>O, <sup>13</sup>CH, <sup>13</sup>CH<sub>0</sub>, <sup>13</sup>CH<sub>3</sub>OH and <sup>13</sup>CO<sub>2</sub>

are visible with no species containing  $^{12}$ C, revealing that CH<sub>3</sub>OH and CO are originated from CO<sub>2</sub> (Fig. 2d).

During the photocatalytic reduction of CO<sub>2</sub> with H<sub>2</sub>O, the H<sub>2</sub> evolution is the main competitive reaction for CO<sub>2</sub> reduction, as it consumes H and photogenerated electrons, which are the key species for reducing CO<sub>2</sub>. During the photocatalytic H<sub>2</sub>O splitting in the absence of CO<sub>2</sub>, the H<sub>2</sub> evolution rate on M1, M2, M3, M4, M5, M6 and M7 is 90, 974, 1108, 1954, 1424, 1038 and 906  $\mu$ mol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>, respectively (Fig. S5). As such, M4 has a higher activity to splitting H<sub>2</sub>O than other photocatalysts. Furthermore, TEOA serves as a sacrificial reagent for capturing the photogenerated holes and the O atoms from H<sub>2</sub>O splitting. Thus, there is no O<sub>2</sub> evolution observed in the absence of CO<sub>2</sub> (Fig. S6). In the photocatalytic reduction of CO<sub>2</sub> with H<sub>2</sub>O, the evolution rate of H<sub>2</sub> on M1, M2, M3, M4, M5, M6 and M7 is 86, 862, 826, 494, 624, 848 and 892  $\mu$ mol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>, respectively (Fig. S5). In addition to H<sub>2</sub>, a small amount of O<sub>2</sub> is detected in the presence of CO<sub>2</sub> (Fig. S6). This is due to the combination of O atoms from H<sub>2</sub>O splitting. During the photocatalytic reduction of CO<sub>2</sub> with H<sub>2</sub>O, part of H from H<sub>2</sub>O splitting is consumed by CO<sub>2</sub> reduction, thus decreasing the H<sub>2</sub> evolution rate as compared with those in the reactions without CO<sub>2</sub>. As reflected by the H<sub>2</sub> evolution rate, M4 could have a higher ability in suppressing the combination of H atoms to form H<sub>2</sub>. DFT studies demonstrate that the H<sub>2</sub> generation energy of N-In<sub>2</sub>O<sub>3</sub> becomes higher with the increasing nitrogen doping content (Fig. S7). Nitrogen doping can effectively suppress the combination of H atoms. Therefore, the higher nitrogen doping content on M4 than those on other photocatalysts is the origin for the higher ability of M4 in suppressing the H combination. The suppressed H combination makes more H atoms available for the photocatalytic reduction of CO<sub>2</sub>.

### 4. Discussions

It is well known that photon absorption, separation of the photogenerated electron-hole pairs and CO<sub>2</sub> adsorption/activation are key steps in the photocatalytic reduction of CO<sub>2</sub>. The process of photon absorption and electron-hole separation is closely related to the intrinsic properties of the photocatalyst, while the CO<sub>2</sub> adsorption/activation process is highly dependent on the surface of the photocatalyst.



**Fig. 3.** Electronic properties of photocatalysts. (a) UV-vis-DRS spectra and (b) Tauc plots of M1-M7. (c) Bandgap as a function of nitrogen doping content. (d) DFT-simulated DOS plots and band structure of pristine In<sub>2</sub>O<sub>3</sub> without N. (e) DFT-simulated DOS plots and band structure of N-In<sub>2</sub>O<sub>3</sub>. (f) Photocurrent-time profiles of M1-M7. (g) PL spectra of M1 and M4.

Fig. 3a shows the UV-vis-DRS spectra of M1-M7. The bandgaps of M1-M7 are obtained after the transformation by using the Tauc equation (Fig. 3b). As compared with pristine In<sub>2</sub>O<sub>3</sub> (M1), the bandgap of the N-In<sub>2</sub>O<sub>3</sub> photocatalysts becomes narrower distinctly (Fig. 3b). M4 has the narrowest bandgap among all the photocatalysts, with a bandgap of about 2.6 eV, which is about 0.2 eV smaller than that of M1. This reveals that the nitrogen doping content affects the bandgap of N-In<sub>2</sub>O<sub>3</sub>. As shown in Fig. 3c, there is a strong negative linear relationship between the nitrogen doping content and the bandgap of the photocatalyst, indicating that a higher nitrogen doping content leads to a narrower bandgap. To further understand the bandgap narrowing of N-In<sub>2</sub>O<sub>3</sub> photocatalysts in the presence of nitrogen dopants, DFT calculations are performed to investigate the electronic structure of N-In<sub>2</sub>O<sub>3</sub>. As revealed by the density of states (DOS) of pristine In<sub>2</sub>O<sub>3</sub> and N-In<sub>2</sub>O<sub>3</sub> in Figs. 3d and 3e, additional electronic states are created above the original valence band maximum (VBM) after nitrogen doping. This results in the reduction of the bandgap. The DOS of N-In<sub>2</sub>O<sub>3</sub> (Fig. 3e) indicates that the additional electronic states are mainly composed of N 2p orbitals, which are completely mixed with In 3d and O 2p orbitals in N-In<sub>2</sub>O<sub>3</sub>. The narrower bandgap is beneficial for enhancing the absorption of visible light, which is the main part of sunlight. This leads to the highest photocatalytic activity of M4 with the narrowest bandgap.

Photocurrents are measured to explore the ability of M1-M7 in separating the photogenerated electron-hole pairs (Fig. 3f). The photocurrent is originated from the transfer of the photogenerated electrons into the circuit for measuring the photocurrents. A higher photocurrent indicates that a more efficient electron-hole separation is achieved with more electrons transferred into the circuit. As demonstrated in Fig. 3f, the photocurrents of all N-In<sub>2</sub>O<sub>3</sub> photocatalysts are higher than that of pristine In<sub>2</sub>O<sub>3</sub> (M1). M4 exhibits the largest photocurrent intensity, which is about 3 times higher than that of M1, indicating the significantly improved electron-hole separation on M4 as compared with that on M1. The

higher electron-hole separation efficiency of M4 is further confirmed by the significantly decreased PL emission peak as compared with that of M1. As shown in Fig. 3g, the PL spectrum of M1 exhibits a strong green emission peak at ca. 440 nm, which is attributed to the recombination of the photogenerated electrons trapped in the conduction band and the photogenerated holes trapped in the valence band [23,37]. In contrast, the emission peak at ca. 440 nm is almost invisible in the PL spectrum of M4. As revealed by DFT calculations (Fig. 3e), the doped N creates an additional state above the original valence band. The additional state acts as hole traps to capture the holes, thus inhibiting the electron-hole recombination. The more efficient electron-hole separation on M4 is also demonstrated by the difference in fluorescence lifetime in Fig. S8. The nitrogen doping extends the fluorescence lifetime from 0.45 ns to 0.57 ns. The longer fluorescence lifetime implies a more efficient electron-hole separation on M4. The higher electron-hole separation efficiency is a reason for the enhanced photocatalytic activity of M4.

In order to compare the ability of M1 and M4 in CO<sub>2</sub> adsorption, CO<sub>2</sub>-TPD experiments are performed. As shown in Fig. 4a, the CO<sub>2</sub>-TPD signal of M1 and M4 can be divided into three main regions. In region I, a strong CO<sub>2</sub> desorption peak is observed for M1 and M4 at ca. 100 °C, which corresponds to the physical desorption of CO<sub>2</sub>. In region II, both M1 and M4 have a significant desorption peak at ca. 250 °C, which can be attributed to the chemisorption of negatively charged CO<sub>2</sub> [38,39]. There is also a clear CO desorption peak in region II, which is consistent with the CO signal detected in the products of the photocatalytic reduction of CO<sub>2</sub>. It also matches well with previous reports that oxygen vacancies on In<sub>2</sub>O<sub>3</sub> not only enhance the adsorption and activation of CO<sub>2</sub> but also promote the dissociation of CO<sub>2</sub> to CO [40]. Region III is located in the high-temperature region (350-600 °C). In this region, two weak desorption peaks can be observed for M1 and M4 clearly, which can be attributed to the decomposition of surface HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> species [37]. In general, M4 has stronger CO<sub>2</sub> desorption peaks, which indicates that M4 has more CO<sub>2</sub> adsorption sites (i.e., oxygen vacancies), and thereby has a higher ability in adsorbing and activating  $CO_2$ . The results of XPS analyses also confirm that more oxygen vacancies are present on N-In<sub>2</sub>O<sub>3</sub> photocatalysts. In addition, the CO<sub>2</sub> desorption peak of M4 shifts to higher temperatures as compared with that of M1, suggesting that the binding strength of CO<sub>2</sub> with M4 is stronger than that of CO<sub>2</sub> with M1. The improved CO<sub>2</sub> adsorption on M4 is another reason for the enhanced photocatalytic activity of M4.



**Fig. 4.** Surface chemistry of photocatalysts. (a) CO<sub>2</sub>-TPD profiles of M1 and M4. (b) CO<sub>2</sub> adsorption energy as a function of nitrogen doping content. (c) Bader charge difference between the active In and O species. (d) CO<sub>2</sub>-DRIFT spectra for M1-M7. (e) Electronic localization function (ELF) contour mappings of pristine In<sub>2</sub>O<sub>3</sub> and N-In<sub>2</sub>O<sub>3</sub>.

DFT calculations were carried out to further investigate the influence of nitrogen doping on  $CO_2$  adsorption on the photocatalysts. Previous studies have shown that the  $In_2O_3(111)$  facet is active toward  $CO_2$  adsorption and activation with high stability [41]. Figs. 1a and 1b confirm the exposure of  $In_2O_3(111)$  facet on pristine  $In_2O_3$  (M1) and N-In<sub>2</sub>O<sub>3</sub> (M4). The stability of the surface oxygen atoms is evaluated on the  $In_2O_3(111)$  facet on which there are four kinds of oxygen atoms (Fig. S9 and Table S2). According to the stability of surface oxygen atoms, the oxygen vacancy and nitrogen doping sites are determined. Fig. 4b plots the DFT-calculated  $CO_2$  adsorption energy as a function of nitrogen doping content. It shows that increasing nitrogen doping content significantly enhances the adsorption energy of  $CO_2$  at oxygen vacancies. This finding is consistent with the results of  $CO_2$ -TPD. When the nitrogen doping content increases to 3.36%, the  $CO_2$  adsorption energy reaches the maximum, and remains unchanged even further rising the nitrogen doping content.

To explain the promotion effect of nitrogen doping on  $CO_2$  adsorption, the Bader charge distributions of pristine  $In_2O_3$  and  $N-In_2O_3$  are analysed. It has been reported that the unsaturated In and adjacent O species caused by oxygen defects may form SFLPs sites, which are more active to adsorb and activate  $CO_2$  [42-45]. The active In specie that is most likely to form SFLPs is selected as the center to examine the effect of nitrogen doping. As shown in Fig. 4c, the Bader charge difference between the related Lewis acid ( $In^{3+}$ ) and Lewis base ( $O^{2-}$  or  $N^{3-}$ ) substantially increases after nitrogen doping, forming more active SFLPs, which is easier to adsorb and activate  $CO_2$ . It can also be visually observed that the difference in charge density between the active In and O species increases after nitrogen doping (Fig. 4e).

The adsorption of CO<sub>2</sub> on M1-M7 is also studied by DRIFT spectra (Fig. 4d). At room temperature and CO<sub>2</sub> atmosphere, gaseous CO<sub>2</sub> fingerprint patterns are observed at 3,500-3,800 cm<sup>-1</sup> and 2,300-2,400 cm<sup>-1</sup> [20]. The fingerprint peaks of gaseous CO<sub>2</sub> (3,500-3,800 cm<sup>-1</sup>) decrease gradually from M1 to M4, indicating that the CO<sub>2</sub> adsorption capacity of the photocatalysts increases. These suggest that the CO<sub>2</sub> adsorption capacity of the photocatalyst is closely related to the content of nitrogen doping. For N-In<sub>2</sub>O<sub>3</sub> photocatalysts, a higher nitrogen doping content results in a stronger CO<sub>2</sub> adsorption, which is in good agreement with the results of CO<sub>2</sub>-TPD and DFT calculations. The *in situ* DRIFT spectra of M1-M7 are shown in Fig. S10.

On the basis of the above discussions, the mechanism of the photocatalytic reduction of  $CO_2$ on N-In<sub>2</sub>O<sub>3</sub> photocatalysts is proposed as follows. The doped nitrogen creates some additional states in the band structure of In<sub>2</sub>O<sub>3</sub>, thus making the bandgap of M4 smaller than that of pristine In<sub>2</sub>O<sub>3</sub> (M1). This leads the light absorption range of M4 to be evidently extended as compared to that of M1 without nitrogen. Nitrogen doping also promotes the separation of the photogenerated electron-hole pairs, releasing more electrons for the photocatalytic reduction of CO<sub>2</sub> on M4. Furthermore, nitrogen doping not only creates more oxygen vacancies on M4, forming more reaction sites, but also alters the charge distribution on the surface, resulting in more active SFLPs. Thus, nitrogen doping effectively promotes the adsorption and activation of CO<sub>2</sub> on M4. The presence of the nitrogen dopants efficiently suppresses the evolution of H<sub>2</sub>, producing more active hydrogen atoms for the photocatalytic reduction of CO<sub>2</sub> on M4. It is the multiple roles of nitrogen doping that lead to the boosted photocatalytic reduction of CO<sub>2</sub> on N-In<sub>2</sub>O<sub>3</sub> photocatalysts.

### 5. Conclusions

In summary, the present study confirms that  $N-In_2O_3$  is a highly active photocatalyst for selective photocatalytic reduction of  $CO_2$  to methanol. The doped nitrogen generates mid-gap

energy states, reducing the bandgap of the photocatalyst but increasing the collection efficiency of solar photons and facilitating the generation and separation of the photogenerated charge carriers. Moreover, the presence of nitrogen dopants alters the charge distribution on the surface of N-In<sub>2</sub>O<sub>3</sub> photocatalysts, resulting in increased activity of SFLPs. This significantly enhances  $CO_2$  adsorption and activation. Nitrogen doping onto In<sub>2</sub>O<sub>3</sub> also helps to suppress the combination of H atoms to form H<sub>2</sub>, thus generating more active H atoms for the photocatalytic reduction of  $CO_2$ . The efficiency of N-In<sub>2</sub>O<sub>3</sub> in producing methanol from the photocatalytic reduction of  $CO_2$  can be efficiently tuned by changing the nitrogen doping content on N-In<sub>2</sub>O<sub>3</sub>. Nitrogen doping also provides a convenient and low-temperature approach for the preparation of highly efficient and stable N-In<sub>2</sub>O<sub>3</sub> photocatalysts not only for photocatalytic reduction of  $CO_2$  but also for other photocatalytic reactions like photocatalytic H<sub>2</sub>O splitting.

### Credit authorship contribution statement

C.-J. Liu conceived and directed the project. C.-J. Liu and X. Tu designed the nitrogen doping. Y. X. Yang and Y.-X. Pan conducted the experiments. Y. X. Yang, Y.-X. Pan and X. Tu wrote the manuscript. Y. X. Yang performed theoretical calculations. All authors analysed the data, discussed the results and commented on the manuscript.

#### **Conflict of Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

# Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 22138009), the Fundamental Research Funds for the Central Universities and the funding from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement No. 823745.

# Appendix A. Supplementary data

Supplementary data to this article can be found online at

#### References

- [1] L. Pan, S. Sun, Y. Chen, P. Wang, J. Wang, X. Zhang, J.-J. Zou, Z.L. Wang, Adv. Energy Mater. 10 (2020) 2000214.
- B. Dai, G.M. Biesold, M. Zhang, H. Zou, Y. Ding, Z.L. Wang, Z. Lin, Chem. Soc. Rev. 50 (2021) 13646-13691.
- [3] Y. Zheng, W. Zhang, Y. Li, J. Chen, B. Yu, J. Wang, L. Zhang, J. Zhang, Nano Energy 40 (2017) 512-539.
- [4] S. Navarro-Jaén, M. Virginie, J. Bonin, M. Robert, R. Wojcieszak, A.Y. Khodakov, Nat. Rev. Chem. 5 (2021) 564-579.
- [5] A.A. Tountas, G.A. Ozin, M.M. Sain, Nat. Catal. 4 (2021) 934-942.
- Y. Dong, P. Duchesne, A. Mohan, K.K. Ghuman, P. Kant, L. Hurtado, U. Ulmer, J.Y.Y.
  Loh, A.A. Tountas, L. Wang, A. Jelle, M. Xia, R. Dittmeyer, G.A. Ozin, Chem. Soc. Rev.
  49 (2020) 5648-5663.
- J. Hou, S. Cao, Y. Wu, F. Liang, Y. Sun, Z. Lin, L. Sun, Nano Energy 32 (2017) 359-366.
- [8] F. Li, L. Zhang, J. Tong, Y. Liu, S. Xu, Y. Cao, S. Cao, Nano Energy 27 (2016) 320-329.
- Y.A. Wu, I. McNulty, C. Liu, K.C. Lau, Q. Liu, A.P. Paulikas, C.-J. Sun, Z. Cai, J.R.
   Guest, Y. Ren, V. Stamenkovic, L.A. Curtiss, Y. Liu, T. Rajh, Nat. Energy 4 (2019) 957-968.
- [10] H.-X. Zhang, Q.-L. Hong, J. Li, F. Wang, X. Huang, S. Chen, W. Tu, D. Yu, R. Xu, T. Zhou, J. Zhang, Angew. Chem. Int. Ed. 58 (2019) 11752-11756.
- [11] J.-H. Zhang, W. Yang, M. Zhang, H.-J. Wang, R. Si, D.-C. Zhong, T.-B. Lu, Nano Energy 80 (2021) 105542.
- [12] L. Liang, X. Li, J. Zhang, P. Ling, Y. Sun, C. Wang, Q. Zhang, Y. Pan, Q. Xu, J. Zhu, Y.
   Luo, Y. Xie, Nano Energy 69 (2020) 104421.
- [13] F. Wang, T. Hou, X. Zhao, W. Yao, R. Fang, K. Shen, Y. Li, Adv. Mater. 33 (2021)

2102690.

- [14] J. Li, H. Huang, W. Xue, K. Sun, X. Song, C. Wu, L. Nie, Y. Li, C. Liu, Y. Pan, H.-L. Jiang, D. Mei, C. Zhong, Nat. Catal. 4 (2021) 719-729.
- T. Billo, I. Shown, A.k. Anbalagan, T.A. Effendi, A. Sabbah, F.-Y. Fu, C.-M. Chu, W.-Y. Woon, R.-S. Chen, C.-H. Lee, K.-H. Chen, L.-C. Chen, Nano Energy 72 (2020) 104717.
- [16] X. Wang, K. Li, J. He, J. Yang, F. Dong, W. Mai, M. Zhu, Nano Energy 78 (2020) 105388.
- [17] K. Feng, S. Wang, D. Zhang, L. Wang, Y. Yu, K. Feng, Z. Li, Z. Zhu, C. Li, M. Cai, Z.
   Wu, N. Kong, B. Yan, J. Zhong, X. Zhang, G.A. Ozin, L. He, Adv. Mater. 32 (2020)
   2000014.
- [18] J. He, P. Lyu, B. Jiang, S. Chang, H. Du, J. Zhu, H. Li, Appl. Catal. B 298 (2021) 120603.
- [19] X.-Y. Meng, C. Peng, J. Jia, P. Liu, Y.-L. Men, Y.-X. Pan, J. CO<sub>2</sub> Util. 55 (2022) 101844.
- [20] L. Wang, Y. Dong, T. Yan, Z. Hu, A.A. Jelle, D.M. Meira, P.N. Duchesne, J.Y.Y. Loh, C. Qiu, E.E. Storey, Y. Xu, W. Sun, M. Ghoussoub, N.P. Kherani, A.S. Helmy, G.A. Ozin, Nat. Commun. 11 (2020) 2432.
- [21] Z. Zhang, C. Mao, D.M. Meira, P.N. Duchesne, A.A. Tountas, Z. Li, C. Qiu, S. Tang, R. Song, X. Ding, J. Sun, J. Yu, J.Y. Howe, W. Tu, L. Wang, G.A. Ozin, Nat. Commun. 13 (2022) 1512.
- [22] Y. Qi, L. Song, S. Ouyang, X. Liang, S. Ning, Q. Zhang, J. Ye, Adv. Mater. 32 (2020) 1903915.
- [23] Y.-X. Pan, Y. You, S. Xin, Y. Li, G. Fu, Z. Cui, Y.-L. Men, F.-F. Cao, S.-H. Yu, J.B. Goodenough, J. Am. Chem. Soc. 139 (2017) 4123-4129.
- [24] Q. Wang, Y. Chen, X. Liu, L. Li, L. Du, G. Tian, Chem. Eng. J. 421 (2021) 129968.
- [25] L.B. Hoch, P.G. O'Brien, A. Jelle, A. Sandhel, D.D. Perovic, C.A. Mims, G.A. Ozin, ACS Nano 10 (2016) 9017-9025.

- [26] Y. Wang, J. Zhao, Y. Li, C. Wang, Appl. Catal. B 226 (2018) 544-553.
- [27] Z. Zhang, C. Shen, K. Sun, X. Jia, J. Ye, C.-j. Liu, J. Mater. Chem. A 10 (2022) 5792-5812.
- [28] Z. Wang, Y. Zhang, E.C. Neyts, X. Cao, X. Zhang, B.W.L. Jang, C.-j. Liu, ACS Catal. 8 (2018) 2093-2110.
- [29] Y. Wang, F. Yu, M. Zhu, C. Ma, D. Zhao, C. Wang, A. Zhou, B. Dai, J. Ji, X. Guo, J. Mater. Chem. A 6 (2018) 2011-2017.
- [30] Q. Chen, A. Ozkan, B. Chattopadhyay, K. Baert, C. Poleunis, A. Tromont, R. Snyders,
   A. Delcorte, H. Terryn, M.-P. Delplancke-Ogletree, Y.H. Geerts, F. Reniers, Langmuir
   35 (2019) 7161-7168.
- [31] N. Rui, X. Zhang, F. Zhang, Z. Liu, X. Cao, Z. Xie, R. Zou, S.D. Senanayake, Y. Yang,J.A. Rodriguez, C.-J. Liu, Appl. Catal. B 282 (2021) 119581.
- [32] Y.-x. Pan, P. Kuai, Y. Liu, Q. Ge, C.-j. Liu, Energy Environ. Sci. 3 (2010) 1322-1325.
- [33] G. Kresse, J. Furthmüller, Phys. Rev. B 54 (1996) 11169-11186.
- [34] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865-3868.
- [35] P.E. Blöchl, Phys. Rev. B 50 (1994) 17953-17979.
- [36] P. Pyykkö, M. Atsumi, Chem.-Eur. J. 15 (2009) 186-197.
- [37] T. Yan, N. Li, L. Wang, W. Ran, P.N. Duchesne, L. Wan, N.T. Nguyen, L. Wang, M. Xia,G.A. Ozin, Nat. Commun. 11 (2020) 6095.
- [38] S. Li, Y. Xu, Y. Chen, W. Li, L. Lin, M. Li, Y. Deng, X. Wang, B. Ge, C. Yang, S. Yao,
   J. Xie, Y. Li, X. Liu, D. Ma, Angew. Chem. Int. Ed. 56 (2017) 10761-10765.
- [39] O. Martin, A.J. Martín, C. Mondelli, S. Mitchell, T.F. Segawa, R. Hauert, C. Drouilly,D. Curulla-Ferré, J. Pérez-Ramírez, Angew. Chem. Int. Ed. 55 (2016) 6261-6265.
- [40] J. Wang, G. Zhang, J. Zhu, X. Zhang, F. Ding, A. Zhang, X. Guo, C. Song, ACS Catal.11 (2021) 1406-1423.
- [41] S. Dang, B. Qin, Y. Yang, H. Wang, J. Cai, Y. Han, S. Li, P. Gao, Y. Sun, Sci. Adv. 6

(2020) eaaz2060.

- [42] L.B. Hoch, P. Szymanski, K.K. Ghuman, L. He, K. Liao, Q. Qiao, L.M. Reyes, Y. Zhu,M.A. El-Sayed, C.V. Singh, G.A. Ozin, Proc. Natl. Acad. Sci. 113 (2016) E8011.
- [43] K.K. Ghuman, L.B. Hoch, P. Szymanski, J.Y.Y. Loh, N.P. Kherani, M.A. El-Sayed, G.A.Ozin, C.V. Singh, J. Am. Chem. Soc. 138 (2016) 1206-1214.
- [44] M. Ghoussoub, S. Yadav, K.K. Ghuman, G.A. Ozin, C.V. Singh, ACS Catal. 6 (2016) 7109-7117.
- [45] T. Yan, L. Wang, Y. Liang, M. Makaremi, T.E. Wood, Y. Dai, B. Huang, A.A. Jelle, Y. Dong, G.A. Ozin, Nat. Commun. 10 (2019) 2521.