Polymorph selection towards photocatalytic gaseous CO₂ hydrogenation

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Titanium dioxide is the only known material that can enable gas-phase CO₂ photocatalysis in its anatase and rutile polymorphic forms. Materials engineering of polymorphism provides a useful strategy for optimizing the performance metrics of a photocatalyst. In this paper, it is shown that the less well known rhombohedral polymorph of indium sesquioxide, like its well-documented cubic polymorph, is a CO₂ hydrogenation photocatalyst for the production of CH₃OH and CO. Significantly, the rhombohedral polymorph exhibits higher activity, superior stability and improved selectivity towards CH₃OH over CO. These gains in catalyst performance originate in the enhanced acidity and basicity of surface frustrated Lewis pairs in the rhombohedral form.
A breakthrough in CO₂ photocatalysis often begins with materials discovery, and then, the challenges of optimizing its performance metrics by materials engineering follows. Through human intelligence and experiential learning, complemented by artificial intelligence and machine learning, one can hone the chemical and physical properties of a material to achieve the desired catalyst optimization for a targeted technology.

In the case of gas-phase heterogeneous hydrogenation of CO₂ to chemicals and fuels, performance optimization usually involves fine tuning the chemical and physical properties of the (photo)catalyst1–3. This can be achieved by doping4,5, isomorphous and aliovalent substitution6,7, size control8,9, morphology changes10,11, heterostructuring12–14, and support and promoter effects15–17.

In this endeavor, a strategy rarely employed in catalyst optimization is polymorph selection, whereby the crystal structure of the catalyst material is changed, whereas its composition is retained. The challenge today is moving beyond titanium dioxide anatase and rutile polymorphs and discovering other compositions that exhibit polymorphism and enable CO₂ (photo)catalysis.

Indium-based semiconductor materials have been reported as promising photocatalysts in terms of their geometric structures and electronic configurations, which can possibly enhance the mobility and separation efficiency of charge carriers and improve photocatalytic activity18,19. Numerous attempts have been made in recent years to develop various indium-based photocatalysts, such as oxides or mixed oxides20,21, binary and ternary sulfides22,23, hydroxides and oxyhydroxides24,25, In-MOF26, and so on. Among them, indium oxide (In₂O₃) is an n-type semiconductor with mainly two polymorphic phases, cubic and metastable rhombohedral phases27. Pan et al.28 and co-workers have demonstrated that cubic In₂O₃ nanobelts coated by carbon layer showed highly enhanced photocatalytic reduction of CO₂ to CO and CH₄ in aqueous solution with Pt as co-catalyst. Our group has reported that the cubic indium oxide nanocrystals with surface defects in the form of oxygen vacancies and hydroxyl groups, denoted as In₂O₃-x(OH)ₓ, can be utilized as an active catalyst towards photocatalytic gaseous CO₂ hydrogenation owing to advantageous surface, optical, and electronic properties29. The CO₂ hydrogenation performance of the cubic In₂O₃-x(OH)ₓ polymorph can be further boosted by assembling nanocrystals into rod-like superstructures, which gives rise to an improved conversion rate for the reverse water gas shift reaction and a champion rate for solar methanol production at atmospheric pressure30,31.

Herein, we have discovered that the rhombohedral form of indium oxide, like its cubic polymorph, is a highly active and selective heterogeneous (photo)catalyst for hydrogenating gaseous CO₂ to CO and CH₃OH. Significantly, the rhombohedral polymorph outperforms the cubic polymorph in terms of its catalytic activity, long-term stability, and selectivity towards CH₃OH. These performance enhancements stem from an increase in the acidity and basicity of surface frustrated Lewis pairs (SFLP) in the rhombohedral compared with the cubic polymorph.

**Results**

**Synthesis and structural characterizations of rhombohedral In₂O₃-x(OH)ₓ.** The rhombohedral In₂O₃-x(OH)ₓ nanocrystals (annealing at 350 °C and denoted as rh-In₂O₃-x(OH)ₓ) were synthesized via a thermal dehydration of an InOOH precursor, which was initially synthesized from a simple solvothermal system31. The obtained InOOH precursor is composed of monodispersed nanoparticles with the size of ~20 nm (Supplementary Fig. 1).

After thermal treatment at 350 °C, the resultant rh-In₂O₃-x(OH)ₓ nanocrystals maintained a similar particle size and exhibited a walnut shell-like morphology, which contained considerable nanopores in each nanocrystal (Fig. 1a). Such unique morphology could be caused by the loss of water from the lattice of the InOOH nanocrystal, which was confirmed by thermogravimetry (TG) and derivative thermogravimetry (DTG) analysis (Supplementary Fig. 2). In this case, the presence of these nanopores did not contribute much to the specific surface area of rh-In₂O₃-x(OH)ₓ. As a result, the as-prepared rh-In₂O₃-x(OH)ₓ has a specific surface area of 56 m² g⁻¹ and a pore size of 11 nm (Supplementary Fig. 3). The high-resolution transmission electron microscopy (HRTEM) images (Fig. 1b and Supplementary Fig. 4) indicate well-defined lattice fringes with inter-planar distances of 0.274 nm and 0.288 nm, which correspond to the (110) and (104) facets of rhombohedral In₂O₃, respectively. The powder X-ray diffraction (PXRD) patterns confirm that the precursor is orthorhombic InOOH, and leads to the formation of the corundum structure type of In₂O₃ (Fig. 1c). An obvious shift in binding energy was observed from the high-resolution X-ray photoelectron spectroscopy (XPS) of In 3d core level spectra for samples before and after annealing, indicating the conversion from InOOH to In₂O₃-x(OH)ₓ (Supplementary Fig. 5). The O 1s core level XPS spectra (Fig. 1d) could be fitted into three peaks at 529.3 eV, 530.7 eV, and 531.8 eV, which can be assigned to oxides, oxygen vacancies, and hydroxyl groups, respectively29. The existence of oxygen vacancies is further evidenced by a strong diagnostic luminescent peak centered at ca. 500 nm in the PL spectrum (Supplementary Fig. 6). These results confirm the formation of oxygen vacancies as well as the coexistence of oxides, vacancies, and hydroxyl groups in rh-In₂O₃-x(OH)ₓ, which play a key role in the formation of SFLP32–34.

**CO₂ hydrogenation performance.** The catalytic properties of the as-prepared rh-In₂O₃-x(OH)ₓ nanocrystals toward CO₂ hydrogenation with and without solar irradiation were evaluated in a flow reactor at different temperatures, under atmospheric pressure with a mixed feed gas of CO₂ and H₂ (H₂:CO₂ = 3:1) (Fig. 2a, b). To investigate the photocatalytic effect of indium oxide on CO₂ hydrogenation performance, the cubic In₂O₃-x(OH)ₓ nanocrystals (annealing at 300 °C and denoted as c-In₂O₃-x(OH)ₓ) with similar porous morphology and crystalline size (Supplementary Fig. 7) were synthesized based on previous studies29 and utilized as a reference material for comparison. The catalytic performance of the selected photocatalysts was tested from 200 °C to 300 °C. Only the as-prepared rh-In₂O₃-x(OH)ₓ was found to be able to catalyze the reverse water gas shift reaction (RWGS) reaction at 200 °C with a CO rate of 51 μmol g⁻¹ h⁻¹ and 60 μmol g⁻¹ h⁻¹ for dark and light conditions, respectively. When the reaction temperature was increased to 230 °C, the rh-In₂O₃-x(OH)ₓ showed an increased CO formation rate of 185 μmol g⁻¹ h⁻¹ (in dark) and 201 μmol g⁻¹ h⁻¹ (in light). Furthermore, at this specific temperature, only the rh-In₂O₃-x(OH)ₓ was found to be capable of synthesizing CH₃OH with a rate of 55 μmol g⁻¹ h⁻¹ (in dark) and 76 μmol g⁻¹ h⁻¹ (in light).

When the temperature was increased to 250 °C, the rh-In₂O₃-x(OH)ₓ exhibited a CH₃OH rate of 105 μmol g⁻¹ h⁻¹ (in dark) and 126 μmol g⁻¹ h⁻¹ (in light). Thereafter, increasing the reaction temperature to 270 °C resulted in a CH₃OH formation rate of 180 μmol g⁻¹ h⁻¹ and 144 μmol g⁻¹ h⁻¹ with and without light irradiation. Such a solar powered CH₃OH rate of 180 μmol g⁻¹ h⁻¹ is a performance record35–38 and about two times higher than the best reported solar CH₃OH maker (c-In₂O₃-x(OH)ₓ nanorods)30 and 3.5 times higher than...
the reference \(\text{c-In}_2\text{O}_3\cdot\text{x(OH)}_\text{y}\) nanocrystals at similar reaction conditions. If catalytic performance is normalized on the basis of the specific surface area, the rh-\(\text{In}_2\text{O}_3\cdot\text{x(OH)}_\text{y}\) would show a solar CH\(_3\text{OH}\) rate of 3.2 μmol h\(^{-1}\) m\(^{-2}\), which is ~5.8 times higher than that of \(\text{c-In}_2\text{O}_3\cdot\text{x(OH)}_\text{y}\) nanorods, or 8.6 times higher than that of \(\text{c-In}_2\text{O}_3\cdot\text{x(OH)}_\text{y}\) nanocrystals. A control experiment shows that the CH\(_3\text{OH}\) selectivity of the commercial thermal catalyst (alumina supported copper zinc oxide) under the same photo-thermal reaction conditions and ambient pressure is ~0.4 %, which is 32 times lower than rh-\(\text{In}_2\text{O}_3\cdot\text{x(OH)}_\text{y}\). Although the
CH₃OH productivity of rh-In₂O₃₋ₓ(OH)ₓ under high pressure needs further research, the rh-In₂O₃₋ₓ(OH)ₓ shows great potential for the future development of a solar fuels economy. Compared with traditional therocatalytic technologies, solar-driven photocatalytic and photothermal catalytic CO₂ hydrogenation are proving to be promising strategies as they enable the utilization of abundant and clean solar energy, and during the catalytic process the photoexcitation of electrons into higher-energy states can lower the energy barrier of reaction 39.

Owing to the exothermic nature of the CH₃OH synthesis from H₂–CO₂, the CH₃OH rate at 300 °C decreases slightly to 139 μmol g⁻¹ h⁻¹ (in light) and 130 μmol g⁻¹ h⁻¹ (in dark). The enhancement of the CH₃OH rate with light irradiation can be attributed to the lower activation energy of the photocatalytic process as compared with the thermochemical process 40. The Arrhenius plots over rh-In₂O₃₋ₓ(OH)ₓ (Supplementary Fig. 8a) yield the apparent activation energy for CH₃OH production reaction, photocatalytically, at 38.4 kJ mol⁻¹, much smaller than 59.8 kJ mol⁻¹ for the thermochemical reaction. Moreover, the activation energy for CH₃OH production over rh-In₂O₃₋ₓ(OH)ₓ is much lower than that of c-In₂O₃₋ₓ(OH)ₓ under the same conditions (Supplementary Fig. 8b) and also lower than the reported value (103 kJ mol⁻¹) for cubic indium oxide under dark condition 41.

To further support that CH₃OH production mainly proceeds through a photochemistry process, we also examined the dependence of CH₃OH rate on the wavelength of incident light. The results showed that the CH₃OH rate decreased with decreasing wavelength of the light (Supplementary Fig. 9), which matches well with the optical absorption spectra of rh-In₂O₃₋ₓ(OH)ₓ. The photocatalytic CH₃OH production almost disappeared when a 500 nm cutoff filter near the absorption edge was applied for the same light intensity.

Conversely, owing to the endothermic nature of the RWGS reaction, the CO formation rate is dramatically enhanced with increasing temperature and reaches about 2.4 mmol g⁻¹ h⁻¹ at 300 °C. Such a CO formation rate is comparable to some of the most active noble metal decorated catalysts 13,42 and ~3.2 times higher than that of the reference c-In₂O₃₋ₓ(OH)ₓ. Unlike CH₃OH performance, which can be enhanced by the light irradiation, CO performance was only enhanced by ~0.5 % under light irradiation (activation energy of ~84.8 kJ mol⁻¹ for both light and dark), which results in an enhanced solar CH₂OH selectivity (Supplementary Fig. 10). The distinct light-dependent trend reveals that the rate determining step for the production of CO appears to occur mainly by a thermochemical pathway in the electronic excited state, whereas the production of methanol has a contributing photochemical pathway involving electrons and holes in the electronic excited state thereby enhancing the activity of the SFLP. Moreover, to confirm the veracity of the CO and CH₂OH products from CO₂, isotope tracing experiments were conducted, where the ¹³CO₂ feedstock was utilized and the product gases were analyzed by gas chromatography–mass spectrometry (GC-MS), which confirmed the presence of ¹³CO and ¹³CH₂OH and the verity of the CO₂ derived products (Supplementary Fig. 11).

Tuning of SFLP toward CO₂ hydrogenation on rhombohedral In₂O₃₋ₓ(OH)ₓ. The structural parameters including concentration of oxygen vacancies and hydroxides are of great importance in forming the SFLP, and subsequently influence the photocatalytic performance. Accordingly, a series of rh-In₂O₃₋ₓ(OH)ₓ nanocrystals were synthesized from the InOOH precursor with different annealing temperatures of 250, 300, 350, and 400 °C, and denoted as rh-250, rh-300, rh-350, and rh-400, respectively. PXRD patterns are found to be similar for samples annealed above 300 °C and could be assigned to the corundum structure type of In₂O₃ (Supplementary Fig. 12). Interestingly, the sample annealed at 250 °C exhibited a similar PXRD pattern to the InOOH precursor, which indicated a similar structure to InOOH, but with more oxygen vacancies and less hydroxide groups. The grain sizes for the prepared rh-In₂O₃₋ₓ(OH)ₓ nanocrystals showed a gradual decrease with elevated annealing temperatures, along with more nanopores generated during the dehydroxylation reaction (Supplementary Figs. 13 and 14). The specific surface areas of the rh-In₂O₃₋ₓ(OH)ₓ nanocrystals are slightly larger than the precursor InOOH, but are lower than the c-In₂O₃₋ₓ(OH)ₓ. All rh-In₂O₃₋ₓ(OH)ₓ samples show the same In(III) oxidation state, and the concentration of oxygen vacancies increases with increasing annealing temperatures, whereas the concentration of hydroxides decreases simultaneously (Supplementary Fig. 15). The band-edge absorption for all rh-In₂O₃₋ₓ(OH)ₓ nanocrystals and c-In₂O₃₋ₓ(OH)ₓ is located at ~450 nm, indicating similar electronic band structures (Supplementary Fig. 16).

The normalized catalytic activity for the various surface tuned rh-In₂O₃₋ₓ(OH)ₓ nanocrystals toward CO₂ hydrogenation, at 270 °C and 300 °C, with and without illumination, are shown in Fig. 3a, b, Supplementary Fig. 17 and summarized in Table 1. Although the rh-250 still showed similar PXRD patterns to InOOH, the thermal treatment was able to remove some lattice oxygen as well as hydroxide groups, which may result in the formation of SFLP and exhibit catalytic performance toward CO₂ hydrogenation. Other than the rh-250, the as-prepared rh-300, rh-350 and rh-400 exhibited diagnostic PXRD patterns, which can be assigned to the rhombohedral In₂O₃ structure with major exposed facets of (110) and (104) (Supplementary Fig. 18). The calculated grain size of rh-In₂O₃₋ₓ(OH)ₓ were ~11.5 ± 1.5 nm for all selected samples. All samples exhibited similar structural and morphological properties as well as photocatalytic performance, whereas the rh-350 showed the best catalytic performance.

The CO₂ adsorption properties were further investigated by CO₂-TPD experiments. As shown in Supplementary Fig. 19 and Table 1, the desorption temperature of CO₂ molecules on c-In₂O₃₋ₓ(OH)ₓ (~157 °C) is higher than that of all rhombohedral samples (~140 °C), indicating that the CO₂ molecules are more tightly adsorbed on the surface of c-In₂O₃₋ₓ(OH)ₓ. Moreover, the c-In₂O₃₋ₓ(OH)ₓ shows a larger peak area, reflecting an enhanced CO₂ adsorption. The reason for the higher CO₂ adsorption capacity of c-In₂O₃₋ₓ(OH)ₓ may simply be due to its larger surface area as compared with rhombohedral samples, so that the c-In₂O₃₋ₓ(OH)ₓ could provide a larger population of capture sites for CO₂. Even so, the enhanced CO₂ adsorption capacity of c-In₂O₃₋ₓ(OH)ₓ cannot contribute much to its photocatalytic CO₂ hydrogenation performance as the activity of rhombohedral samples greatly exceeded that of c-In₂O₃₋ₓ(OH)ₓ, and indicates the SFLP site served as the catalytically active site for CO₂ hydrogenation.

As SFLP can be considered as the active sites for the catalytic performance, the thermal treatment at 350 °C can efficiently remove lattice oxygen as well as hydroxide group to tune the surface into a ratio of 1:0.67 between oxygen vacancy and hydroxide group, which results in the optimal composition among all the samples tested. This can be further confirmed by the decreased activity of a H₂ treated rh-350 sample, which possessed relatively more oxygen vacancies and hydroxide groups (Supplementary Fig. 20). Furthermore, as compared with CO₂, the production of methanol was significantly improved when irradiating with light, and exhibited an enhanced methanol selectivity as well.

Owing to its resulting best photocatalytic performance, the rh-350 was selected for further long-term stability testing at 270 °C.
under atmospheric pressure with light irradiation. As shown in Fig. 3c, excellent stability resulted, with no significant change in production rate as well as selectivity in rh-350 over more than 100 h of continuous testing. As a result, methanol selectivity was maintained at 13% throughout the test, with the methanol rate of 170 μmol g\textsubscript{cat} \textsuperscript{−1} h \textsuperscript{−1} and CO rate of 1150 μmol g\textsubscript{cat} \textsuperscript{−1} h \textsuperscript{−1}. Moreover, the used catalyst was also evaluated by XPS, PXRD, TEM, and no obvious oxidation state and structural changes were observed (Supplementary Figs. 21–23).

The SFLP on rhombohedral In\textsubscript{2}O\textsubscript{3-x}(OH)\textsubscript{y}. The surface vacancy breaks the stable Lewis acid–base adjuncts (bridging In–O or In–OH), which can then create novel surface Lewis acidic sites, and the nearby surface hydroxide groups can function as the Lewis basic sites. As such, the strong charge difference between the resulting unsaturated In atom and the hydroxide group can form the SFLP on the single component metal oxide, which could further activate the small H\textsubscript{2} molecules. The determination of the presence of this SFLP on defect laden rh-In\textsubscript{2}O\textsubscript{3-x}(OH)\textsubscript{y} was performed as follows.

Density functional theory (DFT) simulations were carried out to investigate the properties of the rhombohedral In\textsubscript{2}O\textsubscript{3} nanocrystal. Based on PXRD patterns and HRTEM images, both of the major facets, (110) and (104), were used for the determination of the removal of lattice oxygen and addition of OH (as hydroxide). The (110) facet has been chosen for further calculation and explanation owing to the much stronger Bader charge of the present SFLP. To investigate this further, the bulk rhombohedral In\textsubscript{2}O\textsubscript{3} structure was cut along the direction of (110) and generated the corresponding surface. As shown in Supplementary Fig. 24, possible vacancy sites were determined on the (110) rhombohedral In\textsubscript{2}O\textsubscript{3} surface, and the formation energies of vacancies were calculated by using a known approach from the literature\textsuperscript{40,43}. All atomic removal steps were found to be endothermic in which the adsorption energy would range from 4.15 (for site 1) to 4.94 eV (for site 3) (Supplementary Table 2). To simulate the rh-In\textsubscript{2}O\textsubscript{3-x}(OH)\textsubscript{y} surfaces, which contain the OH

| Sample | D\textsuperscript{a} | A\textsuperscript{b} | E\textsubscript{g}\textsuperscript{c} | O\textsubscript{v}\textsuperscript{d} | O\textsubscript{He} | R\textsubscript{CO}\textsuperscript{f} | R\textsubscript{Methanol}\textsuperscript{g} |
|--------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| rh-250 | 13               | 44               | 3.15             | 20.01            | 31.87            | 55.57            | 2.47             |
| rh-300 | 13               | 54               | 3.01             | 21.35            | 20.64            | 44.87            | 3.10             |
| rh-350 | 11               | 56               | 2.89             | 26.88            | 17.96            | 42.14            | 3.21             |
| rh-400 | 10               | 51               | 2.88             | 30.00            | 16.40            | 38.31            | 2.86             |
| c-In\textsubscript{2}O\textsubscript{3} | 9.5              | 138              | 2.89             | 23.37            | 19.09            | 5.31             | 0.37             |

\textsuperscript{a}Grain size calculated from PXRD patterns (nm)  
\textsuperscript{b}Specific surface area obtained from BET measurement (m\textsuperscript{2} g\textsuperscript{−1})  
\textsuperscript{c}Band gap energy (eV) calculated by fitting the reflectance spectra using K-M theory  
\textsuperscript{d}Concentration of oxygen vacancies calculated from XPS (at. %)  
\textsuperscript{e}Concentration of hydroxide groups calculated from XPS (at. %)  
\textsuperscript{f}Normalized CO rate with solar irradiation obtained at 300 °C (μmol h\textsuperscript{−1} m\textsuperscript{−2})  
\textsuperscript{g}Normalized CH\textsubscript{3}OH rate with solar irradiation obtained at 270 °C (μmol h\textsuperscript{−1} m\textsuperscript{−2})

Table 1 Summary of properties of various In\textsubscript{2}O\textsubscript{3-x}(OH)\textsubscript{y} samples

**Fig. 3** Catalytic performance of various rh-In\textsubscript{2}O\textsubscript{3-x}(OH)\textsubscript{y} nanocrystals. **a** Normalized CH\textsubscript{3}OH production rate at 270 °C with and without light irradiation. **b** Normalized CO production rate at 270 °C with and without light irradiation. **c** Long-term (100 h) catalytic stability of rh-In\textsubscript{2}O\textsubscript{3-x}(OH)\textsubscript{y} nanocrystals (rh-350) in catalyzing hydrogenation of CO\textsubscript{2} with light irradiation; reaction condition: 270 °C, 6 ml min\textsuperscript{−1} H\textsubscript{2} and 2 ml min\textsuperscript{−1} CO\textsubscript{2}.
group, the defected (110) rhombohedral In$_2$O$_3$-$x$ surface was used, which has the vacancies at site 1 and site 3 as the most and least favorable adsorption sites. Then the OH group was added to the defected surface at vacancy sites to form In$_2$O$_3$-$x$(OH)$_y$, and the adsorption energy and charge transfer of binding were calculated (Supplementary Fig. 25). The amounts of total free energy change due to the binding of OH at site 1 and 3 of the defected surface are $-3.97$ eV and $-4.30$ eV, respectively, which indicate that the formation of hydroxylated nanostructures can be highly exothermic. Previous studies for the (111) surface of the c-In$_2$O$_3$-(OH)$_y$ nanostructure suggest that the O atom from the OH group and the In atom (including $+1.66$ e and $-1.50$ e, respectively) can form an SFLP owing to the large charge difference. Thus, Bader charge calculations were performed to probe the localized charges on surface constituents, showing that the related O and In pair involve atomic local charges of $+2.90$ e and $-2.09$ e, and $+2.90$ e and $-2.03$ e, for site 1 and site 3 of the rh-In$_2$O$_3$-(OH)$_y$ nanostructure (Fig. 4a), respectively. The larger Bader charge between the Lewis acid and Lewis base on rh-In$_2$O$_3$-(OH)$_y$ could be caused by the following contributing effects: (i) a larger geometrical distance between the active O atom and In atom (3.65 Å) than that of the c-In$_2$O$_3$-(OH)$_y$ (3.20 Å), and (ii) a higher coordination number of the active In atom (6 in (110) facets) in rh-In$_2$O$_3$-(OH)$_y$ than that in c-In$_2$O$_3$-(OH)$_y$ (4 in (111) facets). Similar to the (110) facets, the SFLP can also be constructed by removing surface oxygen atom and introducing a hydroxide group on (104) facets of rhombohedral In$_2$O$_3$ (Supplementary Figs. 26 and 27). It reveals that the Lewis acidic In and Lewis basic O of the OH sites at the (110) surface possess Bader charges of $+1.61$ e and $-1.12$ e, respectively. In this scenario, the distance between Lewis acid and base is 3.75 Å.

The larger charge difference between the Lewis acid and Lewis base pairs in the (110) rh-In$_2$O$_3$-(OH)$_y$ structure compared with that of the (111) c-In$_2$O$_3$-(OH)$_y$ surface, envisages the rh-In$_2$O$_3$-(OH)$_y$ nanostructure would form more active Lewis acid–base pairs than the c-In$_2$O$_3$-(OH)$_y$ pair can muster, and therefore could strongly polarize H–H bonds and dissociate H$_2$ molecules. This prediction can be evidenced by the optimized configuration of hydrogenated rh-In$_2$O$_3$-(OH)$_y$, in which the H–H distance of H$_2$ is enlarged from 0.75 Å to 1.24 Å and the bond length of barrier of 0.45 eV (Fig. 4b), which is much smaller than that in the previous study (0.66 eV) on the (111) c-In$_2$O$_3$-(OH)$_y$ surface. More recently, the experimental data of a faster CO production rate.

Investigation of the CO$_2$ hydrogenation pathway. In order to understand the catalytic pathway for CO$_2$ hydrogenation on rh-In$_2$O$_3$-(OH)$_y$, nanocrystals, in situ DRIFTS measurements were performed in a flow cell under reaction operational conditions. In the initial reaction stage, two primary surface species were observed, as shown in Fig. 5a. The first kind of species with fingerprint modes at 1505, 1465, and 1375 cm$^{-1}$ can be assigned to chemisorbed CO$_2$ species including bicarbonate (HCO$_3^-$) and carbonate (CO$_3^{2-}$). The second kind of species signaled by fingerprint modes at 1580 and 1360 cm$^{-1}$ can be attributed to the asymmetric and symmetric COO stretching vibrations of adsorbed bidentate formate (HCOO$^-$) species. This assignment is supported by two additional modes at 2870 cm$^{-1}$ and 1390 cm$^{-1}$ that are attributed to the stretching vibration v(CH) and bending vibration δ(CH) of the same species. Along with the CO$_2$ hydrogenation the bicarbonate and carbonate species could readily be transformed to formate species, as evidenced by the decrease and disappearance of these bands. Apart from the formation of formate species, another important intermediate appears with diagnostic peaks at 2856, 1448, 1109, and 1090 cm$^{-1}$ in the spectra that are assigned to methoxy (H$_2$CO$^+$) and *HCO or *H$_2$CO intermediates. Simultaneously, we also observe the diagnostic vibrational modes of CO at bands 2227 and 2163 cm$^{-1}$, and water at 1649 cm$^{-1}$, indicative of another reaction pathway featuring CO intermed-iate (Supplementary Fig. 29, RWGS pathway), which is produced from the RWGS reaction via the carboxyl (*HOCO) intermediates. However, such *HOCO intermediates are unstable and cannot be detected even at a low temperature (90 K). To corroborate these experimental observations, free energy profiles for CO$_2$ hydrogenation via the proposed RWGS and formate pathways over rh-In$_2$O$_3$-(OH)$_y$ were calculated. The results suggest that via the RWGS pathway (Fig. 5b), except for product (CO, H$_2$, H$_2$O) desorption, the preceding hydrogenation reactions steps 1–3 are all exothermic. Similarly, steps 1–4 also behave in an exogenic nature via the formate pathway (Fig. 5c). These are different from the previously reported c-In$_2$O$_3$-(OH)$_y$ surface, resulting in the possibility of enhanced catalytic activity for hydrogenation of CO$_2$. Notably, the smaller free energy barrier for the RWGS pathway is consistent with our experimental data of a faster CO production rate.

Discussion

As the first report that an SFLP in cubic In$_2$O$_3$-(OH)$_y$ denoted InOH$^+$••In, can facilitate heterolysis of H$_2$ to form In-OH$^+$••In$^-$, a number of chemical strategies have been devised to modify its Lewis acidity and Lewis basicity in order to tune its activity and selectivity in CO$_2$ (photo)catalysis.

To amplify, following heterolysis of H$_2$ on the SFLP, In-OH$^+$••In$^-$ → InOH$^+$••In$^-$, the proton bound to the hydroxide Lewis base and hydroxide bound to the coordinately unsaturated indium can subsequently react with CO$_2$ to form CO in an endothermic reverse water gas shift reaction (Eq. 1):

$$\text{CO}_2 + \text{H}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O}$$

and CH$_3$OH in an exothermic methanol forming reaction (Eq. 2):

$$\text{CO}_2 + 3\text{H}_2 \leftrightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$$

in both cases with the desorption of co-product H$_2$O.

The rate and selectivity of these two reactions, which proceed simultaneously and by different pathways, facilitated by the SFLP, can be tailored advantageously by engineering the properties of the SFLP. In practice, this requires chemical means of adjusting the geometry of the SFLP and the negative and positive charge on the Lewis base and Lewis acid sites, respectively (Fig. 4a).

Note that these approaches to engineering the Lewis acidity and basicity of the SFLP refer to the electronic ground state of In$_2$O$_3$-(OH)$_y$. In the photo-excited state of In$_2$O$_3$-(OH)$_y$, the In$_2$ and InOH sites of the InOH$^+$••In SFLP serve as traps for electrons and holes, respectively, making the proton and hydride of
the SFLP $\text{H}_2$ heterolysis intermediate $\text{InOH}_2^+\cdots\text{InHN}^-$ more acidic and basic towards subsequent reactions with $\text{CO}_2$. These traps also serve to lengthen the electron and hole excited state lifetimes, thereby enhancing the probability of reactions of InO-$\text{H}_2$ with $\text{CO}_2$ to $\text{H}_2\text{O}$ and $\text{CH}_3\text{OH}$, which appear to proceed by different reaction pathways. Based on the results and insight gained from this work, it should prove possible to optimize the Lewis acidity and Lewis basicity of the SFLP towards the binding of reactants, intermediates and products.

Approaches to SFLP engineering that have proven successful so far include control of oxygen vacancies and isomorphous substitution of the indium sites. In the case of [O]$_n$ vacancies, the higher the substituting population is, the lower the oxygen coordination number around the In(III) sites. This makes the In1OH more Lewis basic and the coordinately unsaturated In2 more Lewis acidic. For isomorphous substitution of In(III) by a similar-sized yet more electronegative element like Bi(III), exchange of the In2 site renders it more Lewis acidic, whereas replacement of In1 makes the hydroxide less Lewis basic.

Another strategy for tailoring the SFLP would be to change the distance between the Lewis acid and Lewis base sites (Fig. 4a), which would alter their charges and modify how they interact with $\text{H}_2$. The geometry of the SFLP will vary between different crystal facets, which to implement will require strict control of the crystal morphology. Geometry changes of the SFLP are also achievable by polymorph engineering, a more straightforward method in practice, and the subject of the experimental and computational studies described herein.

In summary, we have demonstrated a polymorph selection strategy to modify the Lewis acidity and Lewis basicity of rhombohedral $\text{In}_2\text{O}_3\cdot3\text{OH}$$_2$ with a view to tuning activity and selectivity in gas-phase $\text{CO}_2$ (photo)catalysis. Significantly, rh-$\text{In}_2\text{O}_3\cdot3\text{OH}$$_2$ turns out to be a high performance photocatalyst, achieving champion $\text{CO}_2$ hydrogenation rates to $\text{CH}_3\text{OH}$ and CO at atmospheric pressure. The superior catalytic performance appears to originate in the enhanced activity of surface Lewis acid–base pairs and strong propensity towards $\text{H}_2$ dissociation.

An operando DRIFT study and DFT calculation provide information on the surface chemistry responsible for the formation of $\text{CH}_3\text{OH}$ and CO, which appear to proceed by different reaction pathways. Based on the results and insight gained from this work, it should prove possible to optimize the Lewis acidity and Lewis basicity and enhance the photocatalytic performance of heterogeneous SFLP photocatalysts through polymorph selection. Furthermore, by understanding the distinct light-dependence of CO and $\text{CH}_3\text{OH}$ formation and the impact of the electronic structure on $\text{CO}_2$ activation and $\text{H}_2$ dissociation by cubic and rhombohedral $\text{In}_2\text{O}_3\cdot3\text{OH}$$_2$, these heterogeneous SFLP systems can be incorporated into multi-component catalytic systems exemplified by polymorphic heterostructures, with distinct structures yet continuously adjustable fractions, enabling efficient $\text{CO}_2$ hydrogenation with front-line status.

**Methods**

**Chemicals.** All reagents used in the present study, including N,N-dimethylformamide (DMF), Indium(III) nitrate hydrate (In(NO$_3$)$_3$·4.5H$_2$O, In 29%), and ethanol (C$_2$H$_5$OH) were analytical reagent grade and obtained from Sigma-
Aldrich. All chemicals were used as received. Deionized water was used throughout the synthesis.

**Synthesis of InOOH precursor and rhombohedral In$_2$O$_{3-x}$(OH)$_y$ nanocrystals.**

In a typical synthesis of InOOH precursor, 0.3 g of In(NO$_3$)$_3$·4.5H$_2$O and 0.8 mL of distilled water were added to a 25 mL autoclave. DMF was then added to bring the total volume up to 17 mL. The aqueous solution was then heated at 150 °C for 24 h. After being cooled to room temperature, the white products were collected through centrifugation and washed with water and ethanol. The sample was finally dried at 60 °C. The dried InOOH precursors were then placed into an oven and treated at various temperatures (250–400 °C) in air for 4 h to obtain the final In$_2$O$_{3-x}$(OH)$_y$ samples.

**Characterization.** PXRD was performed on a Bruker D2-Phaser X-ray diffractometer, using Cu Kα radiation at 30 kV. The HRTEM measurement was conducted using a JEM–2100 microscope working at 200 kV. Nitrogen Brunauer–Emmet–Teller (BET) adsorption isotherms were obtained using an ASAP2020 M apparatus (Micromeritics Instrument Corp., USA). For BET surface area analyses, the samples were degassed in vacuum at 110 °C for 10 h and then measured at 77 K. The weight loss of InOOH precursor was carried out in a TA Instruments SDT Q600 thermogravimetric analyzer in an alumina pan under 100 mL min$^{-1}$ flow of compressed air. The temperature was steadily increased from room temperature (25 °C) to 580 °C at a rate of 5 °C min$^{-1}$. UV-visible diffuse reflectance spectra of the powders were obtained for the dry-pressed disk samples using a Cary 500 Scan Spectrophotometer (Varian, USA) over a range of 200–800 nm. BaSO$_4$ was used as a reflectance standard in the UV-visible diffuse reflectance experiment. XPS was performed using a PerkinElmer Phi 5900 ESCA spectrometer in an ultrahigh vacuum chamber with base pressure of 1 × 10$^{-9}$ Torr. The spectrometer uses an Al Kα X-ray source operating at 15 kV and 27 A. The samples were coated onto carbon tape, and all results were calibrated to C1s 284.5 eV. The room temperature photoluminescence (PL) spectrum was measured on a FL/FS 920 (Edinburgh Instruments) equipped with a 450 W Xe arc lamp as the excitation source and a red sensitive Peltier element cooled Hamamatsu R2658 PMT as the detector. Time-resolved fluorescence decay spectra were recorded on the Delta Pro (HORIBA instruments) using a 357 nm laser as the excitation source.
dioxide temperature-programmed desorption (CO2-TPD) measurements were performed on a Micromeritics AutoChem II 2920 chemisorption analyzer.

Gas-phase photocatalytic measurements. The gas-phase CO2 hydrogenation experiments were conducted in an inner diameter of 2 mm tubular quartz reactor, in which ~ 20 mg of catalyst sample was packed into and fully irradiated with an unfiltered 130 W Xe lamp. The diameter of the light spot was ~ 2 cm, with an area of about 3.14 cm², which could fully cover the sample. An OMEGA temperature controller was attached to a heating cartridge inserted into the copper block along with a thermocouple inserted into the quartz tube in contact with the catalyst bed for control of the catalyst temperature. In a typical run, CO2 or 13C isotope-labeled CO2 was used, and the convergence criteria are set to be 10⁻¹² in resolution.

DFT calculations. Theoretical calculations are carried out with the context of DFT, as implemented in the Vienna ab initio simulation package. The exchange–correlation interactions were treated within the generalized gradient approximation in the form of the Perdew–Burke–Ernzerhof functional. The projector augmented wave approach with plane wave cutoff energy of 400 eV is used, and the convergence criteria are set to be 10⁻⁴ in energy and 0.02 eV Å⁻¹ in force. To model the rhombohedral In2O3 surfaces, four-layer slabs within vacuum spacing larger than 20 Å with the bottom two layers keep fixed are adopted. Brillouin zone integrations are performed over the Gamma point owing to the large supercell. Nudged elastic band method is used to determine the H₂ dissociation path and barrier.

Data availability
The data that support the plots within this paper and other findings of this study are available from the corresponding author upon reasonable request.

Received: 2 January 2019 Accepted: 16 May 2019
Published online: 07 June 2019

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**Acknowledgements**

T.Y. is thankful for financial support from the National Natural Science Foundation of China (21872081), Natural Science Foundation of Shandong Province (ZR2016BM04), China Postdoctoral Science Foundation (2015M572011, 2017T100494). B.H. and Y.Dai acknowledge support from the Taishan Scholars Program of Shandong Province. G.A.O. acknowledges the financial support of the Ontario Ministry of Research and Innovation (MRI), the Ministry of Economic Development, Employment and Infrastructure (MED), the Ministry of the Environment and Climate Change’s (MOECC) Best in Science (BIS) Award, Ontario Center of Excellence Solutions 2030 Challenge Fund, Ministry of Research Innovation and Science (MIRS) Low Carbon Innovation Fund (LCIF), Imperial Oil, the University of Toronto’s Connaught Innovation Fund (CIF), Connaught Global Challenge (CGC) Fund, and the Natural Sciences and Engineering Research Council of Canada (NSERC). Special thanks to Athan Tountas of the Chemical Engineering and Applied Chemistry and Keshav Raina of the Faculty of Forestry from University of Toronto for proofreading the manuscript.

**Author contributions**

T.Y. conducted the catalysts preparation and the catalysts testing flow experiments for CO\textsubscript{2} hydrogenation. L.W. performed the XPS characterization. Y.L., Y.Dai., B.H., and M. M. conducted and analyzed the DFT calculations. T.Y., L.W., and Y.Dong performed the in situ DRIFTS study. T.W. and F.M.A. performed the GC-MS test using \(^{13}\text{CO}_2\) as well as the TEM characterization. T.Y., L.W., and G.A.O. conceived the project and co-wrote the manuscript. T.Y. and L.W. contributed equally to this work, and G.A.O spearheaded the project. The manuscript was written through collective contributions from all authors. All authors approved the final version of the manuscript.

**Additional information**

Supplementary Information accompanies this paper at https://doi.org/10.1038/s41467-019-10524-2.

**Competing interests:** The authors declare no competing interests.

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**Journal Peer Review Information:** Nature Communications thanks the anonymous reviewer(s) for their contribution to the peer review of this work.

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