Supplementary Information

Illuminating CO₂ Reduction: Investigating the Role of Surface Hydroxides and Oxygen Vacancies on Nanocrystalline In₂O_{3-x}(OH)_y

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1.0 Results and Discussion

1.1 Space velocity dependence calculations:

The photochemical and photothermal rate law based on the mass of catalyst depends on the reaction temperatures, the pressures, the concentrations of all active species, the light (spectral distribution and intensity), and the catalyst surface, which is given by:

$$r_{CO}\left(\frac{\mu mol}{g_{cat}hrs}\right) = k(T) * f(C_{H_2}, C_{CO_2}, C_{H_2O}, C_{CO}, I(\lambda), etc)$$
(1)

In this equation r_{co} is the rate of production of CO, k is the rate constant, C_i is the concentration of species i, and I is the light intensity. In order to assess the effect of product inhibition (in this case H₂O) while all other parameters are held constant, assume that the rate law for the photocatalyst can be rewritten as:

$$r_{CO}\left(\frac{\mu mol}{g_{cat}hrs}\right) = K'\left(C_{H_2}, C_{CO_2}\right) * C_{H_2O}^n$$
(2)

In this equation K' is the rate coefficient which is a combined rate expression at a particular reaction conditions for all parameters except H₂O. Since the conversion is so low in our experiments the concentrations of reactants can be treated as constant. The result is the H₂O dependence is cast as a power law expression. For this test case, we use n = -1 (as predicted for simple site hogging in Langmuir-Hinshelwood kinetics). Also, for each "mole" of this reaction (CO₂ + H₂ <=> CO + H₂O) that occurs, one mole of H₂O will be produced along with one moles of CO. Finally, the plug flow (no axial mixing) reactor can be modelled as a continuously moving series of differential batch reactors. Therefore, the differential mass balance for plug flow reactor is given by:

$$dF_x = r_{cat} dm_{cat} \tag{3}$$

Here F_x is the molar flow rate of products (water) and the equation balances the differential change in product flow rate passing over a differential amount of catalyst. The product builds up as the gas contacts the catalyst charge. Substituting our rate expression and rearranging:

$$dF_x = K' * C_{H_2O}^{-1} * dm_{cat}$$
(4)

In the flowing fluid, C_{H2O}^{-1} can be written q/F_X where q is the volumetric flow rate of the gas. With this substitution, we can write:

$$\int F_{x} * dF_{x} = \int K' * q * dm_{cat}$$
⁽⁵⁾

Integrating equation (5) gives us the following:

$$0.5F_x^2 = K' * q * m_{cat}$$
(6)

Rearranging for F_x , which in this case is CO since it is the measured quantity, we get the following expression:

$$F_{CO} = 1.414 \left(m_{cat} * K' * q \right)^{0.5}$$
(7)

Equation (7) tells us that a reaction the follows power law kinetics with a negative first order inhibiting reactant, the molar flow rate of CO (as well as the production rate of CO) will depend on the flow rate (and space velocity which is the total volumetric flow rate divided by the reactor volume) to the half power. Additionally, if we consider the rate coefficient, defined in equation (2) to be proportional to the rate constant and partial pressure of the reactants, we can get the following expression:

$$K' = k p^{\alpha}_{CO_{\gamma}} p^{\beta}_{H_{\gamma}} \tag{8}$$

Substituting (8) into (7) gives us the following:

$$F_{CO} = 1.414 \left(m_{cat} * k * p_{CO_2}^{\alpha} * p_{H_2}^{\beta} * q \right)^{.5}$$
(9)

Equation (9) is an expression that relates the molar flow rate of CO (as well as the production rate of CO) to the partial pressures of CO_2 and H_2 . In this case, an intrinsic first order dependence of either the reactants would result in an observed half order dependence.

1.2 Demonstrating catalyst stability:



Fig. S1 Demonstration of stable CO production over a 10 hour period by $In_2O_{3-x}(OH)_y$ nanoparticles at 190°C under flowing H_2 and CO_2 (1:1) at two total volumetric flow rates.



Fig. S2 CO production rate over $In_2O_{3-x}(OH)_y$ nanoparticles in a batch photoreactor at 150°C under dry and wet atmospheres of H_2 and CO_2 at 1:1 over 16 hours of reaction under light irradiation by a 300 W Xe lamp.



Fig. S3 Background spectra of $In_2O_{3-x}(OH)_y$ used for DRIFTS measurements in flowing He at RT.



Fig. S4: Photograph of an exposed packed bed photoreactor. Under testing operation the reactor is covered with insulation.

2.0 Fundamental mechanism proposed from DFT calculations

The adsorption energy of an adsorbate on the various surfaces considered in this study was calculated as:

 $\Delta H_{ads} = E_{tot} - E_{bare} - E_{ad}, \quad (10)$

where, E_{tot} , (E_{bare}) are the energy of the slab with (without) adsorbate and E_{ad} is the energy of the isolated adsorbate species calculated in the same supercell. Hence, a negative ΔH_{ads} indicates stable adsorption whereas a positive value indicates instability.

Interaction of CO_2 with pristine In_2O_3 (111) surface was first investigated by placing it on top of multiple unique adsorption sites (on either In or O atoms) at various distances from the surface ranging between 1 to 3Å. Table S1 below shows the corresponding adsorption energies.

On In site	Adsorption energy, Δ Hads (eV)
In1	0.093
In2	0.088
In3	0.018
In4	0.186
In5	0.095
In6	0.218
In7	0.130
On O site	Adsorption energy, Δ Hads (eV)
01	0.272
02	0.159
03	0.178
04	0.090
05	-0.073
06	0.176
07	-0.008
08	-0.009
09	0.197

Table S1. CO₂ adsorption energies on pristine (111) In₂O₃ surface

Further, in order to investigate the role of surface hydroxyls and oxygen vacancies on the CO_2 reduction reaction, an analysis was conducted for CO_2 absorption on the In_2O_3 surface with O vacancy defects (In_2O_{3-x}) and the In_2O_3 surface with O vacancy and OH defects $(In_2O_{3-x}(OH)_y)$. For creating O vacancy in pristine In_2O_3 surface various O atoms were removed and corresponding formation energies were calculated using equation,

 $E_{vac} = E(cell_{vac}) + 1/2E(O_2) - E(cell), (11)$

where, E_{vac} is O-vacancy formation energy, $E(cell_{vac})$ is total energies of the optimized supercell with an O-vacancy defect, E(cell) is the total energies of the optimized supercell without an O-vacancy defect and $E(O_2)$ is the total energy for the ground state of an optimized oxygen molecule in the gas phase calculated with the same supercell size and method. The E_{vac} for various oxygen vacancy defects given in Table S2 below, shows that the O1 site is most favored to form a vacancy with the lowest formation energy while the O4 site possess the highest formation energy and hence is the least favored vacancy.

O atom removed to	Vacancy formation
create vacancy defects	energy, ΔE_{vac} (eV)
O1 (lowest E _{vac})	1.194
02	1.197
03	1.773
O4 (highest E _{vac})	1.956
05	1.615
06	1.758
07	1.558
08	1.436
09	1.655

Table S2. Oxygen vacancy formation energies

These results agree with the results reported by A.Walsh [1]. As explained therein, the factors influencing the favorability of vacancy formation are the coordination number (a decrease in coordination from the bulk value results in a lower cost for removal) and the coordination number of surrounding In atoms (the cost of breaking a bond with a highly coordinated In atom is lower). The O4 site has In atoms with much lower coordination (4-fold) than the In atoms surrounding O1 site (6-fold). Hence, the In atoms around O4 are less willing to lose the O atom, an another degree of coordination, and its corresponding charge stability which makes this site less favorable to vacancy formation.

It is found that placing CO₂ molecules both horizontally (O-C-O bonds parallel to the surface) as well as vertically (O-C-O bonds perpendicular to the surface) on top of the least (O1-vac) and most (O4-vac) favorable vacancy sites of In_2O_{3-x} (Table S3) and $In_2O_{3-x}(OH)_y$ (Table S4) surfaces, showed marginal interaction with the surface.

O vacancy position	Adsorption Energy, ∆Hads (eV)	
On most favourable O vacancy (O1) site		
O1 (horizontal)	0.167	
O1 (vertical)	0.045	
On least favorable O vacancy (O4) site		
O4 (horizontal)	0.092	
O4 (vertical)	0.903	
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Table S3. CO_2 adsorption energies on In_2O_{3-x}

CO ₂ adsorption position	Adsorption Energy, ΔHads (eV)		
On most stable OH adsorption site			
O1 horizontal	0.265		
O1 vertical	0.175		
On least stable OH adsorption site			
O4 horizontal	0.172		
O4 vertical	-0.072		

Table S4. CO₂ adsorption energies on In₂O_{3-x}OH_y

Furthermore, molecular adsorption of H_2 on the $In_2O_{3-x}(OH)_y$ surface having highest and the lowest formation energy is investigated by I_1 on the $In_2O_{3-x}(OH)_y$ surface having highest and the lowest formation energy is investigated by placing H₂ very near to the surface horizontally (i.e. H-H bond parallel to the surface) as well as vertically (i.e. H-H bond perpendicular to the surface). The adsorption energies of various configurations of H₂ are tabulated in Table S5.

H ₂ adsorption position	Adsorption Energy, Δ Hads (eV)	
On least stable OH adsorption site		
O-I horizontal	-0.18	
O-I vertical	-0.15	
On most stable OH adsorption site		
O-IV horizontal	0.24	
O-IV vertical	-0.23	
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Table S5. H₂ adsorption energies on $In_2O_{3-x}OH_{y}$.



Fig. S4 Adsorption of H₂ over In₂O_{3-x}(OH)_y surface having O4substituted by OH molecule. The H₂ molecule rotates, forming bonds with an In atom adjacent to the O4-vac and the O atom of OH. Eventually the H₂ molecule undergoes heterolytic dissociation and OH is converted to H₂O.

The difference in stability for different orientations suggests that the angle of adsorbate approach is crucial in allowing it to overcome surface geometrical constraints so that it can access the atoms and charge that it needs for stable adsorption. Further, the description of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) for pristine (111) In_2O_3 surface, O4-vac (In_2O_{3-x}) surface, and a surface having O4-vac substituted by OH ($In_2O_{3-x}(OH)_y$), is represented in Fig. S5 A, B and C respectively. For pristine (111) In_2O_3 surface, HOMO is associated with surface O atoms, while LUMO is delocalized around the In sites (Fig. S5A). However, for O4 deficient In_2O_3 surface, the HOMO (Fig. S5B) is not only associated with surface O atoms but it is also highly delocalized over neighboring In atoms, which make OH substitution at O vacant site favorable leading to stable In_2O_3 . $_x(OH)_y$ surface shown in Fig. S5C.



(c) HOMO (left) and LUMO (right) of the (111) terminated surface of In₂O_{3-x}OH_y

Fig. S5 Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of ground state, (111) terminated (a) In_2O_3 , (b) In_2O_{3-x} and (c) $In_2O_{3-x}(OH)_y$ surfaces. Red, light blue and dark blue balls represent O, In and H atoms, respectively.

References

1. A. Walsh, Appl. Phys. Lett., 2011, 98, 261910.