

Supplementary Information to “Relating Surface Defect energetics with Reactant Gas Adsorption during the Photo-catalytic Reduction of CO₂ by partially hydrolyzed In₂O₃ Nanorods”.

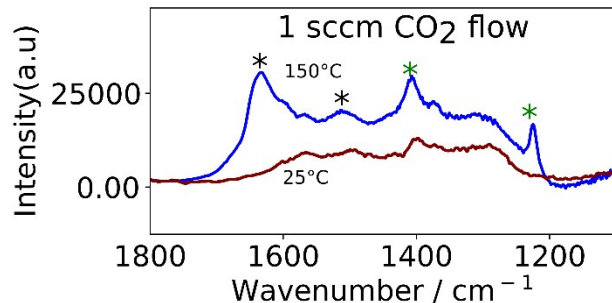
Material Synthesis and other discussion

The In₂O_{3-x}OH_y nanorod structures were fabricated through the following steps: 0.397g of InCl₃ was dissolved in 6ml ethanol with stirring, a separate mixture of 2.5ml NH₃OH and 7.5ml ethanol and 2ml H₂O was mixed in the InCl₃, creating a white suspension. To control for uniform size distributions, the white suspension was immersed in a heated oil bath at 80°C with stirring for 10 minutes. The suspension was then centrifuged; removal of excess solvent and subsequently washed with deionized water. This step was done 3 times, before a vacuum drying procedure of 70°C at 12 hours. The dried powder was then calcined for 12 hours at 250°C to form the In₂O_{3-x}OH_y phase nanorod structures. The nanorods have an averaged 13-15 nm diameter, and BET derived surface area of 129m²/g.

The FTIR phase transition study¹ showed that during the onset of thermal dehydration from 200-225°C, the set of peaks associated with edge sharing In-OH rapidly decay, but also showed the introduction of new types of In-OH centres with bending and stretching modes at 915cm⁻¹ / 975 cm⁻¹ and 3437cm⁻¹ / 3650cm⁻¹, respectively, which disappeared at 400°C. This correlates with our earlier principal findings: that CO₂ reduction products were detected with In(OH)₃ dehydrolyzed at 250°C but not below, and that the CO product rates decrease with increasing temperature from 250°C to 450°C, where no CO was detected with samples annealed above 450°C. Because the IR signals associated with the original OH bridging disappeared completely at 225°C, we associate the new OH peaks as interstructural hydrogen bonding with lattice oxygen sites to form terminal In-OH groups.

The approximately 2:1 peak area ratio of OH type groups to O_{vac} in manuscript **Figure 3a**, indicate that the protonation of lattice oxygen is necessary to minimize net surface charge during de-hydrolyzation at the transitional phase boundary, which can indicate that the oxygen vacancies are intrinsically singly ionized, through an elementary reaction of an hydrogen adatom and lattice oxygen site after water dissociation by ambient moisture adsorption on the surface: $H^+ + O_L^{2-} \rightarrow OH + e^-$, an electron can be injected into any intrinsically doubly positively charged O_{vac}^{**} site and the 1:1 OH:O_{vac} ratio thus indicates that two electrons are injected for every O_{vac}^{**} to form singly ionized O_{vac}^{\bullet} . This is validated by electron paramagnetic resonance results, where the EPR spectra for indium oxide is typically associated with singly ionized oxygen vacancies.

DRIFTS in CO₂

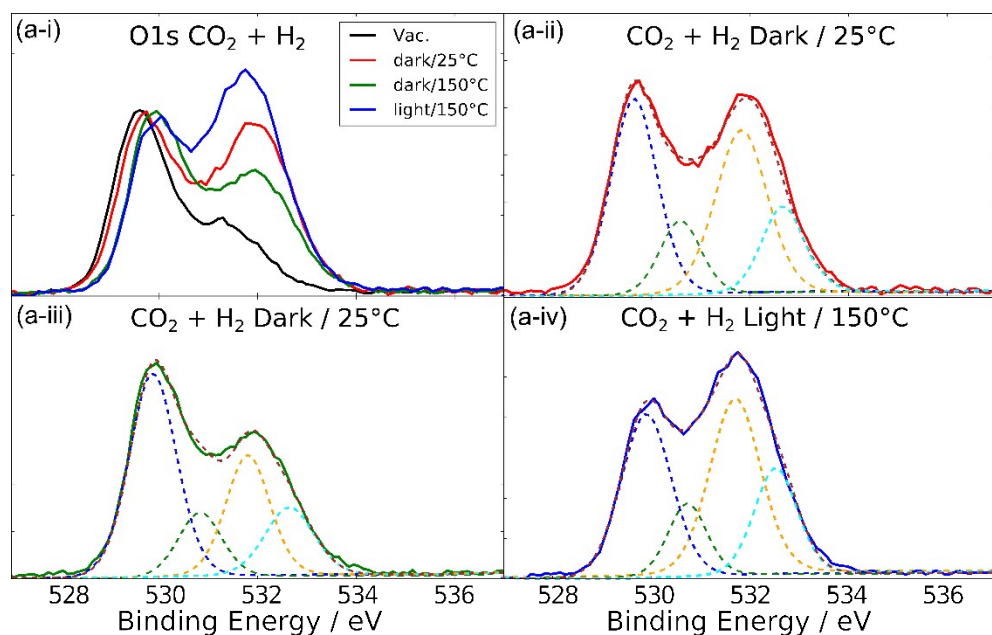


SI Figure 1. Bidentate (1632 cm⁻¹, 1564 cm⁻¹) (black asterisks) and monodentate (1403 cm⁻¹ and 1511 cm⁻¹) (green asterisks) carbonate species observed in 1sccm CO₂ flow.

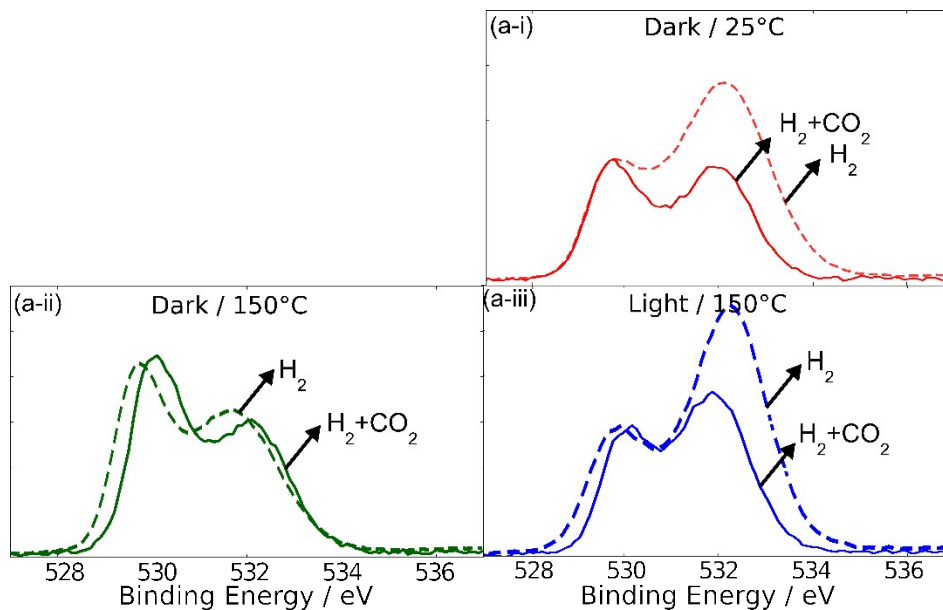
XPS results

	O _L	O _{vac}	OH	H ⁺ OH
Vacuum	0.53	0.19	0.18	0.11
H ₂ , dark/25C	0.19	0.19	0.35	0.27
H ₂ , dark/150C	0.36	0.17	0.25	0.22
H ₂ , light/150°C	0.17	0.16	0.41	0.26
	O _L	O _{vac}	OH / CO	H ⁺ OH
CO ₂ +H ₂ , dark/25°C	0.34	0.14	0.34	0.18
CO ₂ +H ₂ , dark/150°C	0.38	0.18	0.25	0.19
CO ₂ +H ₂ , light/150°C	0.36	0.13	0.33	0.18

SI Table 1. Fractional amount (of the entire O1s spectrum) of O1s species for In₂O_{3-x}(OH)_y nanorods under vacuum and CO₂+ H₂ conditions.

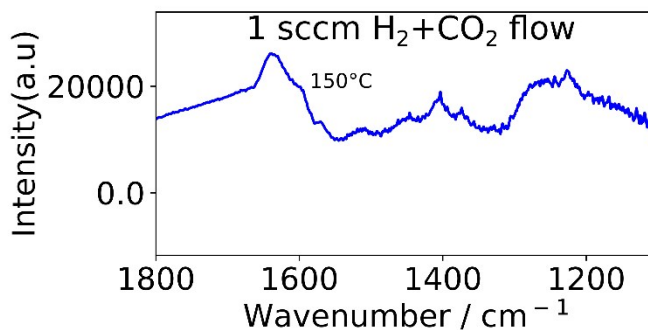


SI Figure 2. (a-i) O1s spectra for H₂+CO₂ and deconvolution for dark ambient temperature (a-ii), dark thermal condition (a-iii), and photo-thermal condition (a-iv).



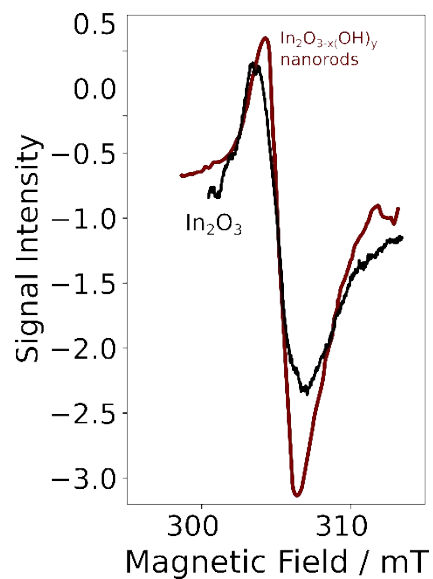
SI Figure 3. Comparison of the O1s spectra between H₂ and H₂+CO₂ under dark ambient temperature, dark 150°C and photo-illuminated 150°C.

DRIFTS in H₂+CO₂



SI Figure 4. Bidentate and monodentate (green asterisks) carbonate species observed in 1sccm CO₂ and 1sccm H₂ flow. However, the amount of monodentate species is less prevalent than in the CO₂ only case, which agrees with the XPS C1s spectrum showing the removal of O=C-O species under thermal condition.

EPR results



SI Figure 5. EPR measurements of ~0.5mg each of commercially purchased In₂O₃ powder (SpecPure™) and synthesized In₂O_{3-x}(OH)_y nanorods. The EPR signals in In₂O₃ materials are typically associated with singly ionized oxygen vacancies. The signal detected for the In₂O₃ is smaller, which indicates a higher population of defects for the In₂O_{3-x}(OH)_y photo-catalyst material.