Controllable modification of the $In^{\delta+}$-O_v interface on In_2O_3 for efficient carbon dioxide hydrogenation to methanol

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The specific surface area of the catalyst was calculated by N_2 adsorption and desorption characterization (Fig. S1) and BET equation. The specific surface area of CP-In_2O_3-N_2 is calculated to be 95.5 m^2g^{-1}, which is slightly larger than that of H-In_2O_3-O_2 and H-In_2O_3-N_2 prepared by the hydrothermal method. The C-In_2O_3-N_2 sample has a specific surface area of only 24.7 m^2g^{-1}. The data are presented in Table S1.

Table S1 shows that all catalysts show a small increase in grain size after high temperature and pressure reaction due to the occurrence of different degrees of agglomeration of In_2O_3. Meanwhile, the catalyst grain sizes after all four reactions are in the range of 16-23 nm. In particular, the grain sizes of CP-In_2O_3-N_2, H-In_2O_3-O_2 and H-In_2O_3-N_2 are smaller. It is shown that In_2O_3 is very stable at high temperatures and has good sintering resistance.

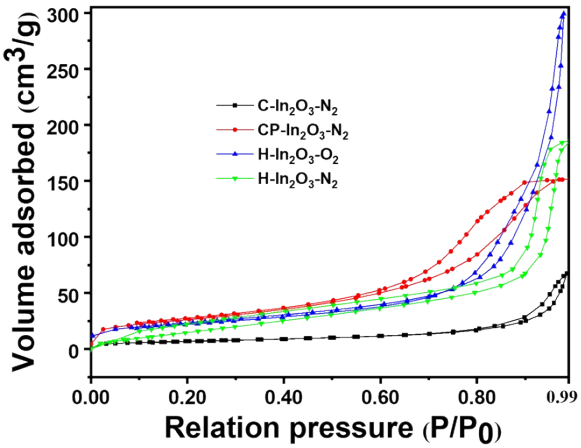

Fig. S1 Nitrogen adsorption–desorption isotherm of different In_2O_3 catalysts.

Table S1 Basic structure property of catalysts.

Sample	BET surface area (m^2/g) [a]	In_2O_3 crystal size (nm) [b]	
		fresh	used
C-In_2O_3-N_2	24.7	17.0	22.3
CP-In_2O_3-N_2	95.5	9.0	17.2
H-In_2O_3-O_2	83.6	10.3	16.7
H-In_2O_3-N_2	76.1	9.5	18.4

[a] BET specific surface area was obtained by N_2 adsorption-desorption tests.

[b] Calculated from XRD data using the Scherrer equation.

The morphology and structure of the sample after reaction are analyzed using field emission scanning electron microscopy (FE-SEM) and high-resolution projection electron microscopy (HRTEM). The experimental results are shown in Fig. S2. From the SEM images (Fig. S2(a-b)), it can be seen that the morphology of CP-In_2O_3-N_2 and H-In_2O_3-N_2 are similar, with fluffy and stacked nanoparticle structures. The HRTEM images (Fig. S2(c-d)) show an average particle size of about 20.0 nm for both samples, which is consistent with the grain size calculated by the Scherrer's formula above. Moreover, the stripe spacing d=0.253 and 0.293 nm correspond to the (400) and (222) crystal faces of cubic phase In_2O_3, respectively. It should be noted that some amorphous In_2O_{3-X} components can be clearly found in the middle and edges of the sample in the HRTEM image. This is due to the continuous between the crystalline and amorphous states as the reaction time increases. The formation of molten In^0 species gradually occupy the surface. In addition, TSoukalou et a.[1] reported that the molten In^0 species are highly correlated with the formation of oxygen vacancies on the catalyst surface.

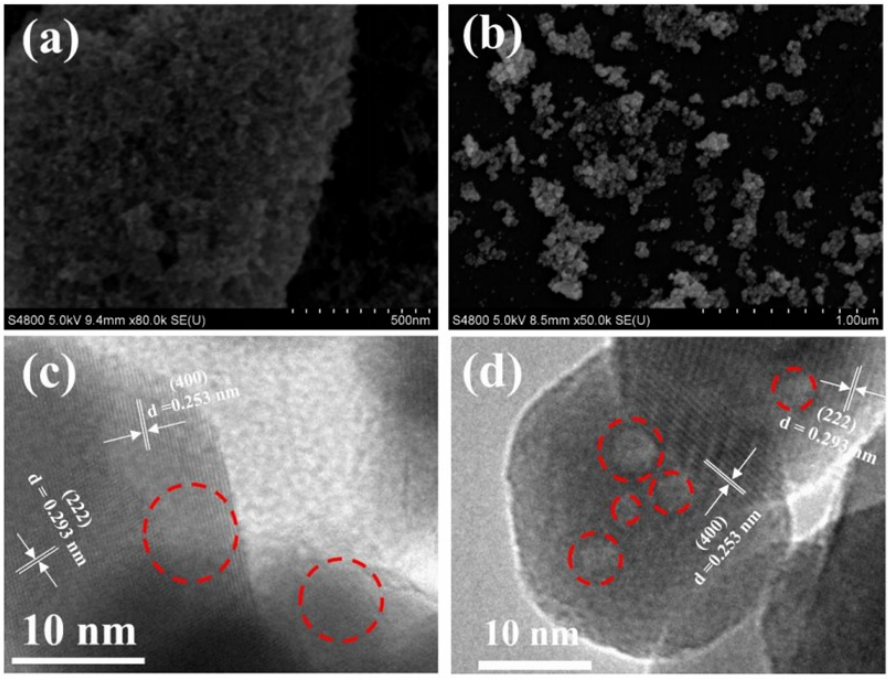

Fig. S2 (a) SEM image of CP-In_2O_3-N_2, (b) SEM image of H-In_2O_3-N_2, (c) HRTEM image of CP-In_2O_3-N_2, (d) HRTEM image of H-In_2O_3-N_2.

1. A. Tsoukalou, P. M. Abdala, D. Stoian, X. Huang, M.-G. Willinger, A. Fedorov and C. R. Mueller, *Journal of the American Chemical Society*, 2019, **141**, 13497-13505.