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Supplementary Information

Structural and electronic insight into the effect of indium doping on the photocatalytic performance of TiO_2 for CO_2 conversion

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Table S1. Results of EXAFS fit. N is the coordination number, R the bond-distance, σ^2 the Debye-Waller factor, ΔE_0 the inner potential correction. The amplitude reduction factor, S_0^2, was fitted for In_2O_3 and its value of 0.91 fixed for all the samples. The * symbol indicates the parameters fixed during the fit.

Sample	Atom	N	R(Å)	σ^2 (10^{-3} Å)	ΔE_0 (eV)	R-factor
In_2O_3	O	6*	2.159±0.005	5.8±0.7	2.8±0.5	0.010
	In	6*	3.363±0.005	5.8±0.4		
	In	6*	3.843±0.007	8.1±0.7		
In-TiO_2-1	O	6*	2.135±0.006	6.0±0.4	2.1±0.5	0.003
Ag/In-TiO_2-1	O	6*	2.14±0.01	6.0±0.6	2.4±0.8	0.004
In-TiO_2-5	O	6*	2.120±0.008	7.0±0.5	2.2±0.6	0.003
In-TiO_2-10	O	6*	2.127±0.009	7.0±0.6	1.2±0.8	0.0033

Table S2. DFT calculated In-O bonds for two possible structures, A) Stoichiometry and B) Vacancy.

Atoms[1]		Stoichiometry $E_{In_xTi_{1-x}O_2}$	Vacancy $E_{In_xTi_{1-x}O_{2-y}}$
Apical			
In1	**O1**	2.204	2.0568
In1	**O2**	2.204	2.1003
In2	**O3**	2.204	2.1514
In2	**O4**	2.204	2.1119
Equatorial			
In1	**O5**	2.0141	1.9833
In1	**O6**	2.0141	1.9833
In1	**O7**	2.0141	2.0316
In1	**O8**	2.0141	-
In2	**O9**	2.0141	2.0046
In2	**O10**	2.0141	2.0149
In2	**O11**	2.0141	2.0866
In2	**O12**	2.0141	2.0866

[1]Distances Oxygen nearest neighbouring (NN) Indium. In the case of $E_{In_xTi_{1-x}O_{2-y}}$: In1: Close to O_V, In2: Opposite to O_V.

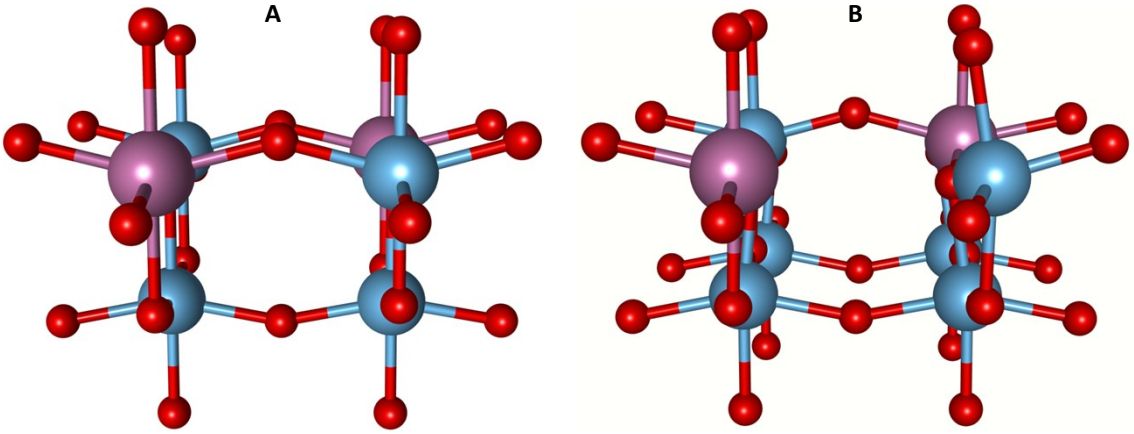

Table S3. Results of XANES peak fitting. The parameters of arctan function were fitted for In_2O_3 and then fixed for the rest of samples.

Sample	PVF			Arctan			R-factor
	Center (eV)	Area (arb. units)	FWHM (eV)	Center (eV)	Height (arb. units)	Width (eV)	
In_2O_3	27952	6.3±0.1	10.8±0.2	27944	0.98	4.1	0.00020
In-TiO_2-1	27952	7.1±0.1	11.5±0.2	27944	0.98	4.1	0.00025
Ag/In-TiO_2-1	27952	7.2±0.2	11.6±0.2	27944	0.98	4.1	0.00022
In-TiO_2-5	27952	7.4±0.2	11.7±0.3	27944	0.98	4.1	0.00018
In-TiO_2-10	27952	6.7±0.1	11.5±0.2	27944	0.98	4.1	0.00017

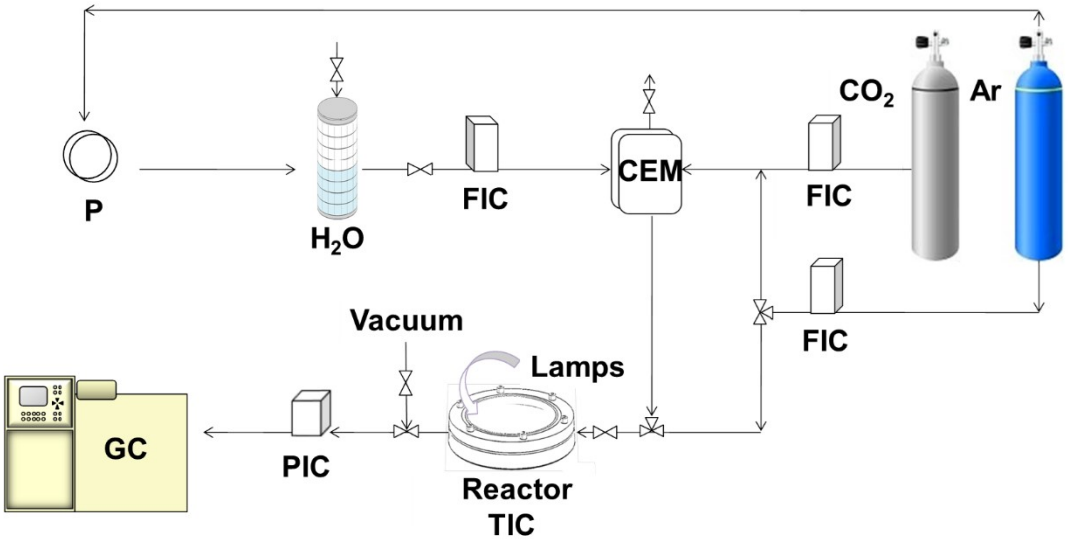

Figure S1. Reaction system employed for photocatalytic CO_2 reduction tests [P: pressurized valve; FIC: flow indicator and controller; CEM: controlled evaporation and mixing unit; TIC: temperature indicator and controller; PIC: pressure indication and controller; GC: gas chromatograph].

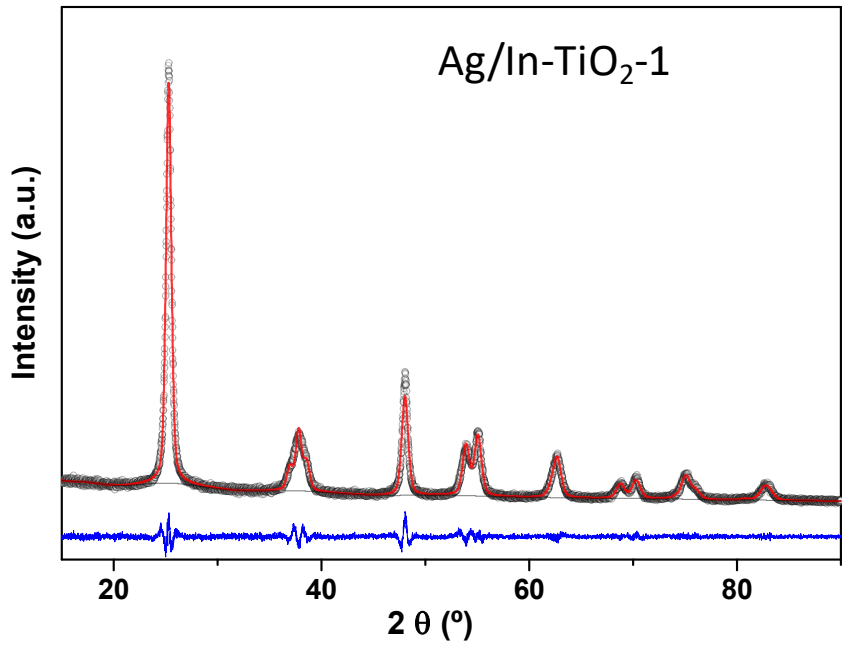

Figure S2. Pawley refinement of X-ray diffractograms of Ag/In-TiO_2-1. Circles: experimental data; red line: fitting; grey line: background; blue line: experiential-simulation difference.

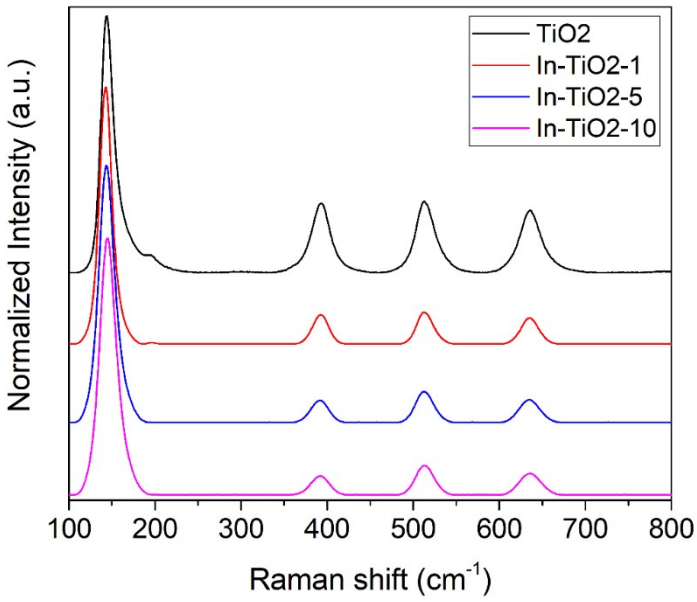

Figure S3. Raman spectra of the different In-doped TiO_2 catalysts.

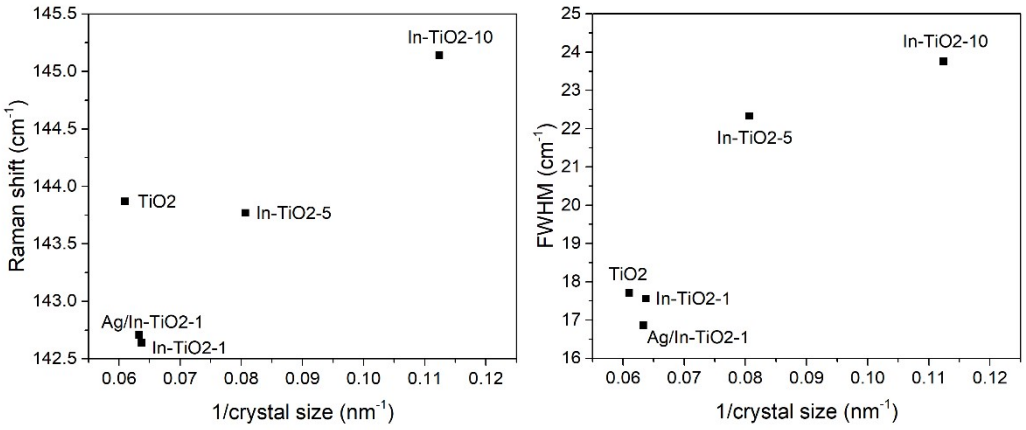

Figure S4. Raman shift and bandwith of the first E_g vibrational mode of anatase in the different catalysts, against the reciprocal of crystal size.

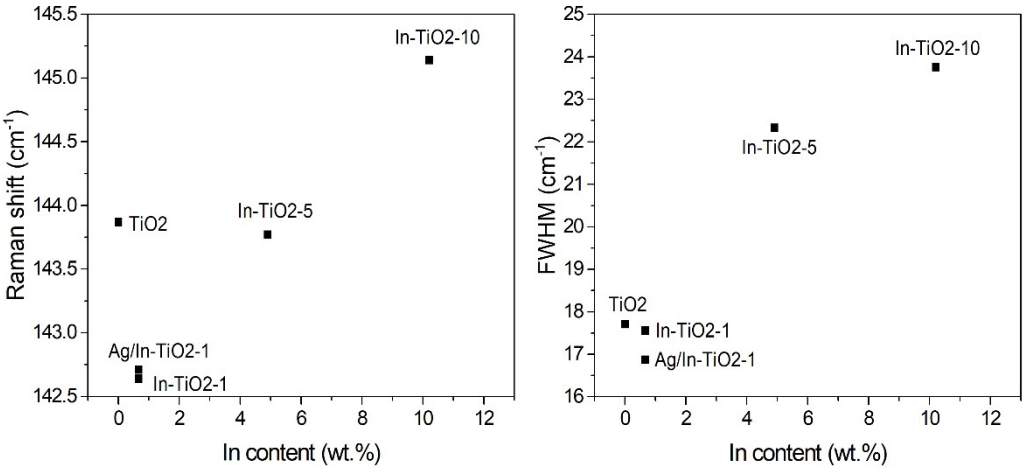

Figure S5. Raman shift and bandwith of the first E_g vibrational mode of anatase in the different catalysts, against the indium content.

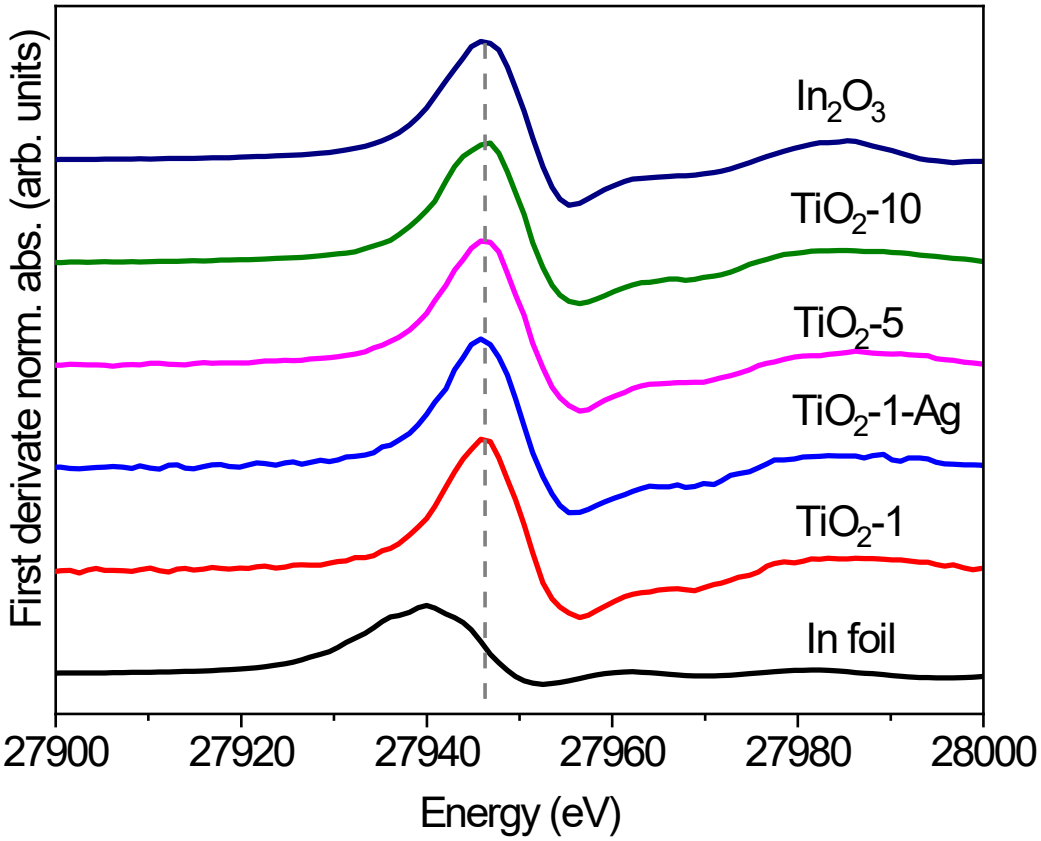

Figure S6. In K-edge first derivative spectra of synthesized-samples and references.

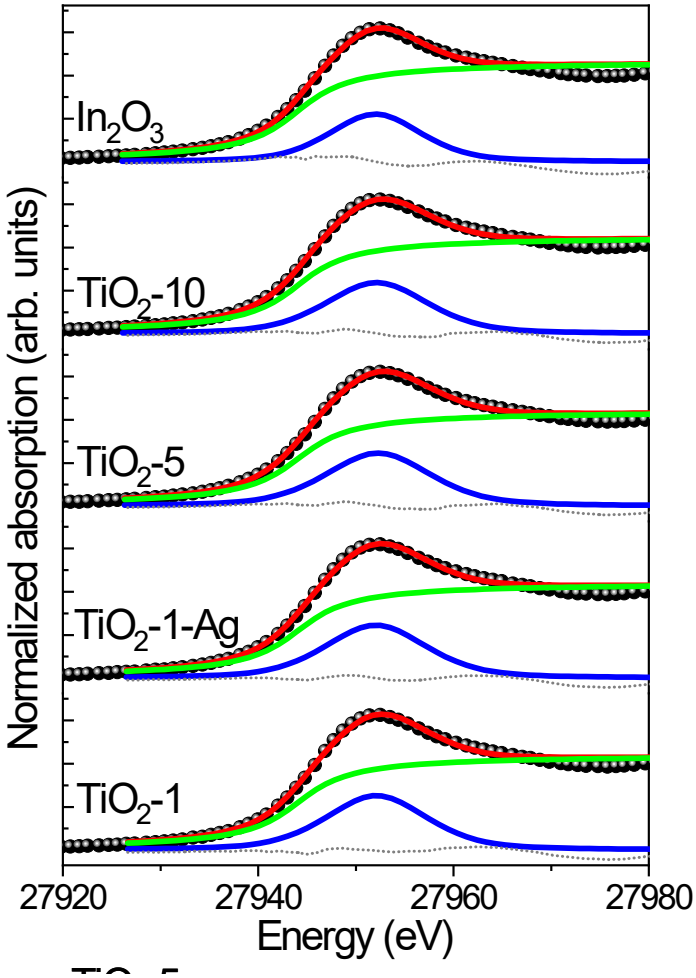

Figure S7. XANES data (black) and peak fitting (red) of synthesized samples with arctan (green) and pseudo Voigt function (blue). The dot grey line indicates the residual of peak fitting and data.

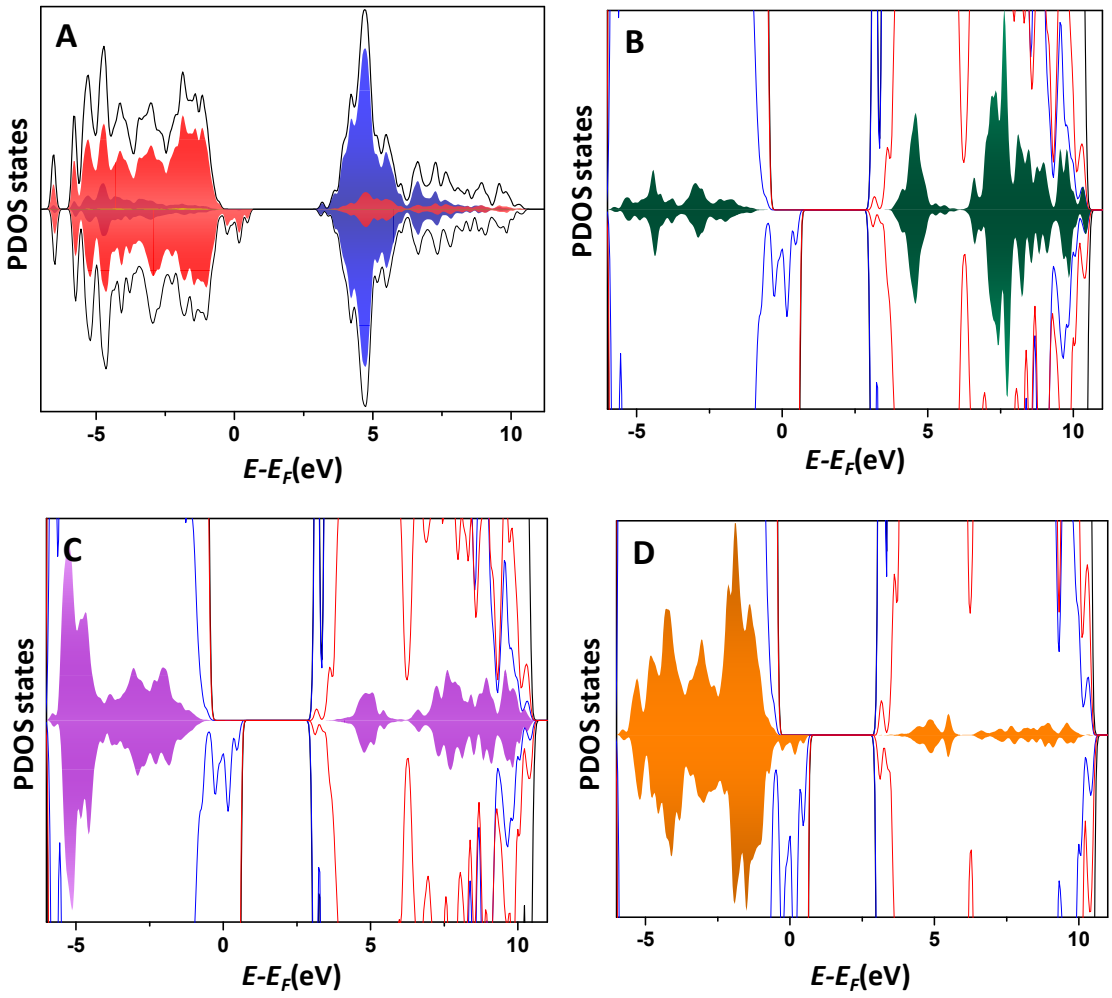

Figure S8. Projected density of states (PDOS) for In-doped anatase with stoichiometry structure: A) total, B) In-s; C) In-p; D) In-d, for all atoms.

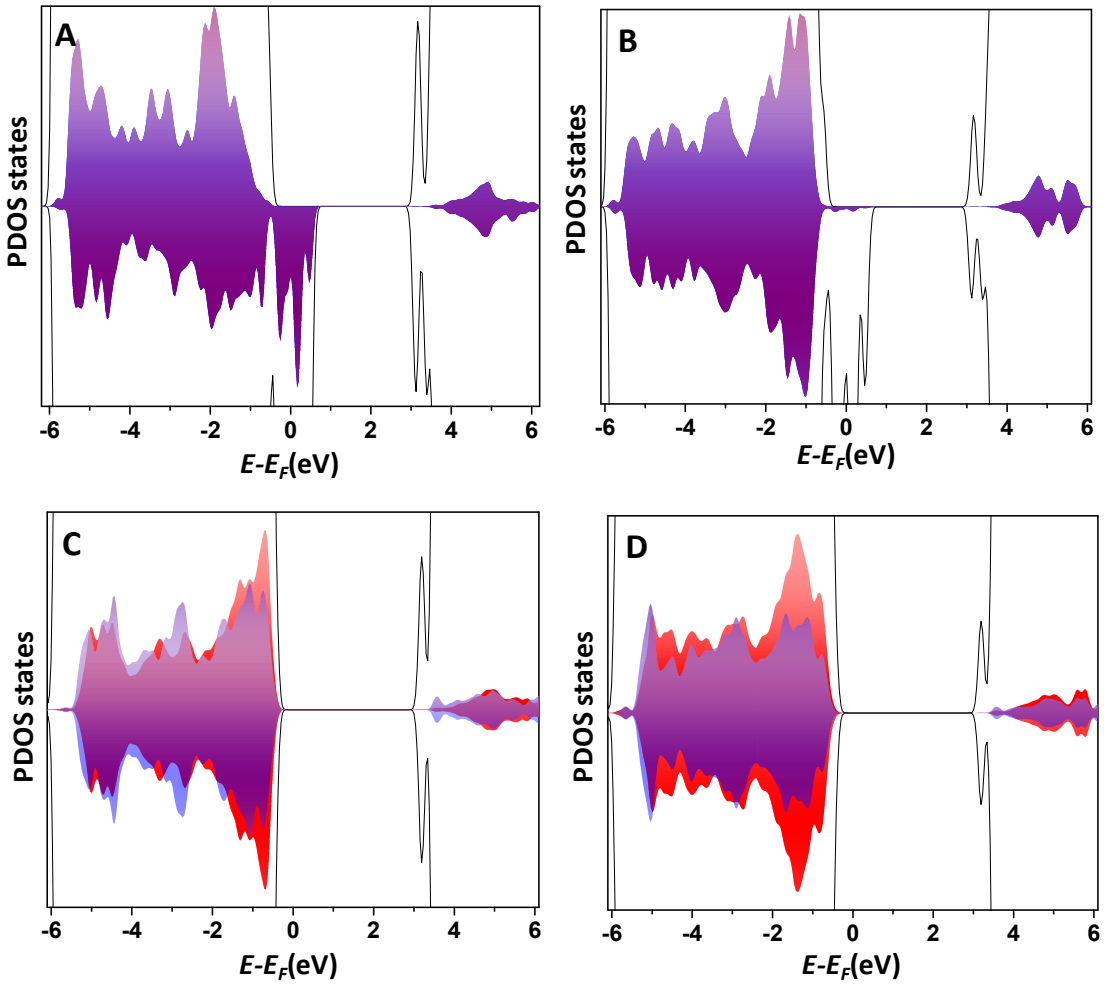

Figure S9. Projected density of states (PDOS) of O 2p band for nearest neighbouring (NN) indium for In-doped anatase with stoichiometry structure: A) apical; B) equatorial and with vacancy; C) apical; D) equatorial. In1: blue; In2: red.

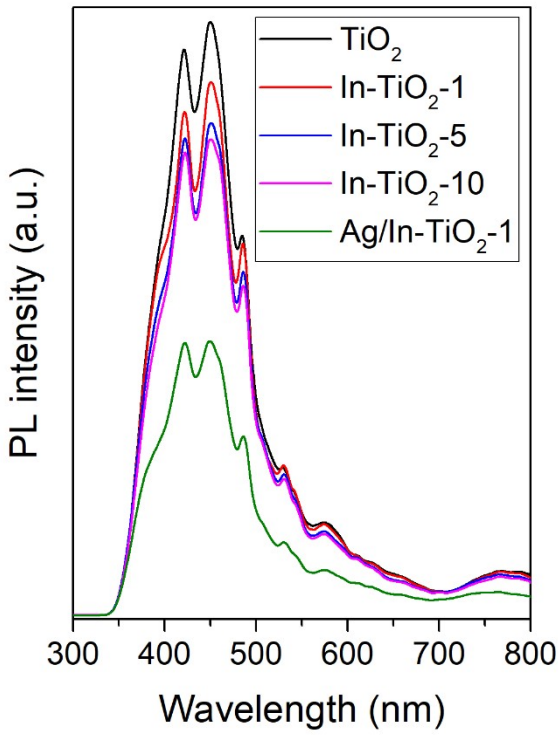

Figure S10. Fluorescence spectra of the synthesized catalysts.