Supporting Information

3D Yolk@Shell TiO_{2-x}/LDH Architecture: Tailored Structure for Visible Light CO_2 Conversion

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Materials and apparatus:

All the chemical reagents used in our experiments were purchased from Sigma-Aldrich and Merck and were used as received without further purification. Water was purified with a Milli-Q system (≥18 MU.cm).

UV–vis DRS of samples was obtained using AvaSpec-2048 TEC spectrometer. Microscopic morphology of products was visualized by SEM (Tescan, Mira3 and JEOL JSM-6510LV). Powder X-ray diffraction (XRD) was carried out on a Philips diffractometer of X'pert Company with mono chromatized Cu Kα radiation (λ = 1.5406 Å). Raman shift was recorded with a handheld Raman analayzer (Firstguard, Rigaku), that was excited by 1064 nm laser radiation. XPS measurements were performed using a VG scientific photoelectron spectrometer ESCALAB-210 using Al Kα radiation (1486.6 eV) from an X-ray source operating at 15 kV and 20 mA.Transmission electron microscopy (TEM) was obtained on Philips CM30 with an accelerating voltage of 150 kV. High resolution transmission electron microscopy (HRTEM) was obtained on JEOL JEM 2010 - TEM under 220 KV. Photoluminescence of samples were measured by PL (Agilent Cary 5000). Textural properties of the samples were determined by N_2 and CO_2 physisorption using a Micromeritics TriStar II Plus. Gas chromatography (GC) analysis was performed using a Bruker SCION 456-GC instrument with a flame-ionization detector (FID). Photochemical reactions were carried out in a cylindrical glass reactor with a 300 W Xenon lamp (Lelesil innovative system, India), equipped with magnetic stirrer and chiller to control the temperature (15 °C) during the experiments.

Table S1. Comparing the efficiency of different photocatalyst in CO_2 conversion to MeOH

Entry	Photocatalyst	Light source	Reusable (run)	CH_3OH yield ($\mu mol/g_{cat}.h$)	Ref.
1	Bi_2S_3 nanoribbons	Xe lamp (300 W)	3	~ 150	[1]
2	Pd/g-C_3N_4	Xe lamp (300 W)	---	3.17	[2]
3	rGO/CuO	white LED (20 W)	6	~ 160	[3]
4	$CuFe_2O_4/TiO_2$	Xe lamp (300 W)	4	~ 230	[4]
5	CdS(Bi_2S_3)/TiO_2 nanotube	Xe lamp (500 W)	---	~ 95	[5]
6	TiO_2@g-C_3N_4	Xe lamp (300 W)	3	~ 18	[6]
7	carbon@TiO_2 hollow spheres	Xe lamp (300 W)	---	9.11	[7]
8	single-unit-cell Bi_2WO_6	Xe lamp (300 W)	6	75	[8]
9	V_v-rich *o*-$BiVO_4$	Xe lamp (300 W)	---	398.3	[9]
10	Ru(bpy)$_3$/TiO_2	LED (20 W)	4	~ 250	[10]
11	Cu-In_2O_3/TiO_2	Hg lamp (500 W)	---	68	[11]
12	3D Y@S TiO_{2-x}/LDH	Xe lamp (300 W)	7	251	This work

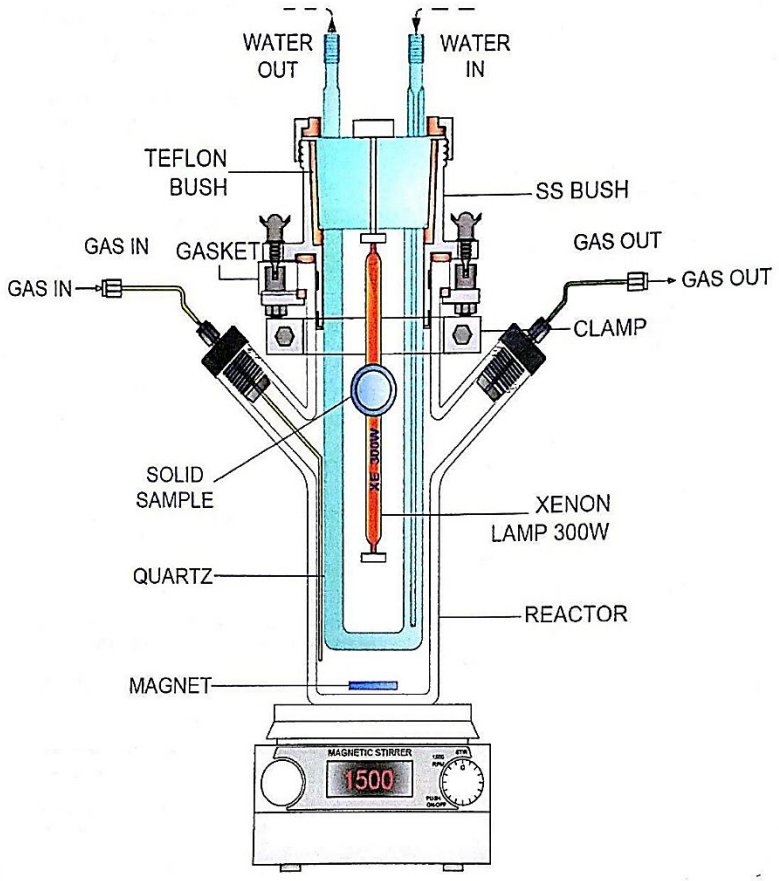

Figure S1. Schematic of used photo-reactor for photoreduction of CO_2.

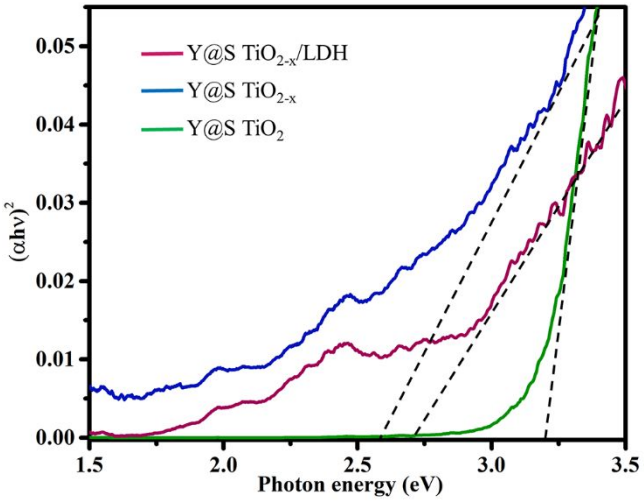

Figure S2. plot of$(\alpha h\nu)^2$ vs. *hv* of Y@S TiO_2, Y@S TiO_{2-x} and 3D Y@S TiO_{2-x}/LDH.

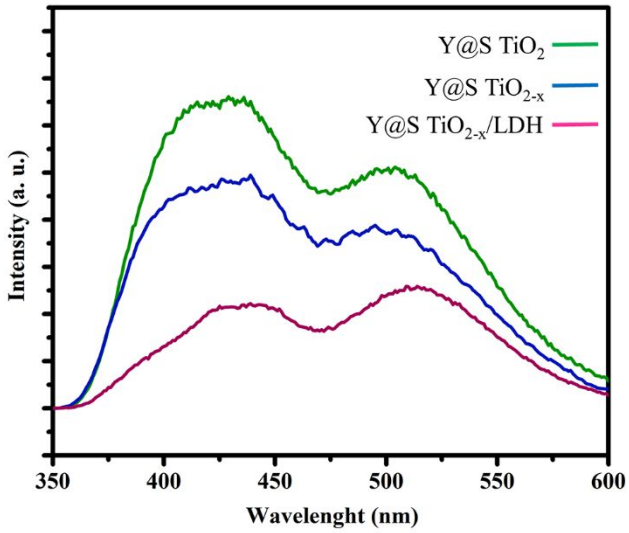

Figure S3. PL spectra of Y@S TiO_2, Y@S TiO_{2-x} and 3D Y@S TiO_{2-x}/LDH.

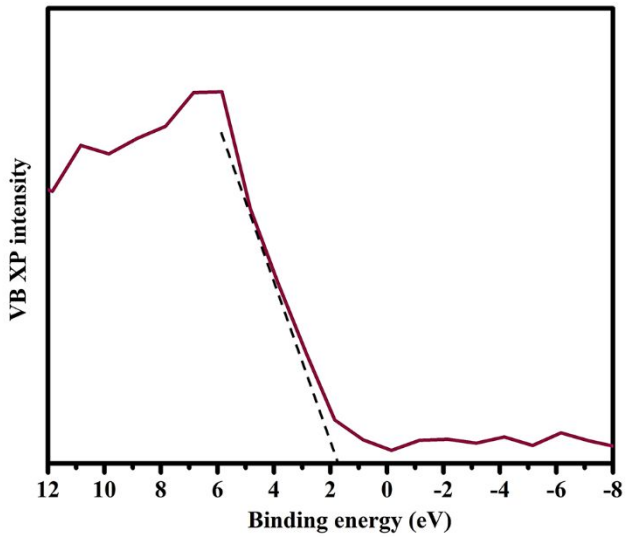

Figure S4. Valence-band XPS spectra for 3D Y@S TiO_{2-x}/LDH.

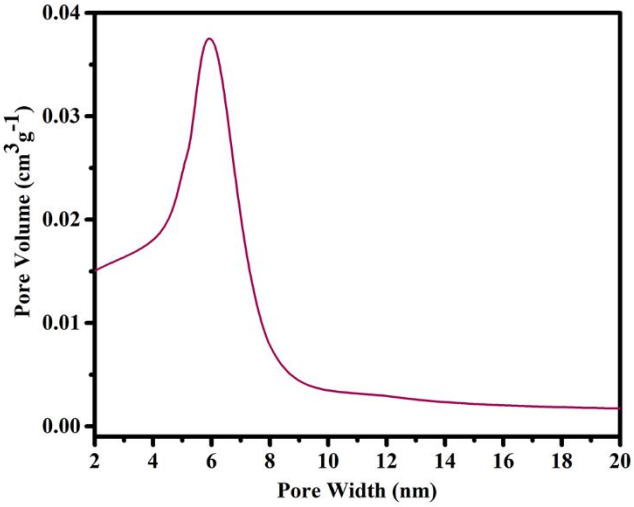

Figure S5. Pore volume distribution of C-TiO_2, Y@S-TiO_2 and 3D Y@S TiO_{2-x}/LDH.

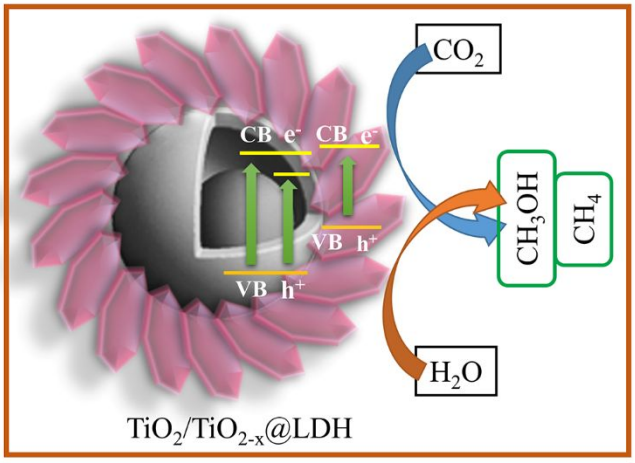

Figure S6. Schematic of the proposed mechanism for CO_2 photoreduction by 3D Y@S TiO_{2-x}/LDH architecture.

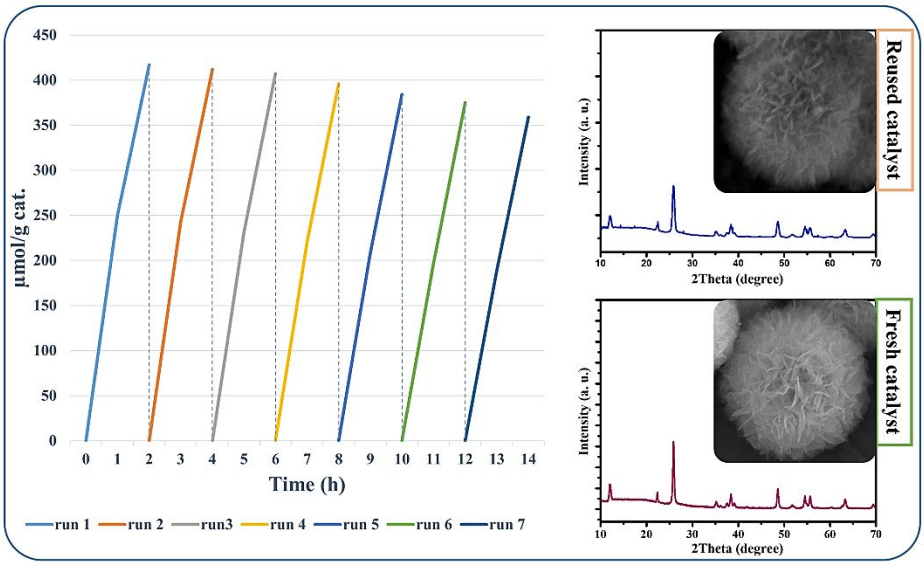

Figure S7. Reusability study of 3D Y@S TiO_{2-x}/LDH architecture in the photocatalytic CO_2 conversion to methanol.

References

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