

Supporting Information

Designer hydrogenated wrinkled Yolk@Shell TiO₂ architectures: towards advanced visible light photocatalysts for selective alcohol oxidations

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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.

UV–vis DRS of samples was obtained using AvaSpec-2048 TEC spectrometer. Microscopic morphology of products was visualized by SEM (Tescan, Mira3). The compositional analysis was done by energy dispersive analysis of X-ray (EDX, Kevex, Delta Class I). Powder X-ray diffraction (XRD) was carried out on a Philips diffractometer of X'pert Company with monochromatized Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). Raman shift was recorded with a handheld Raman analyzer (Firstguard, Rigaku), that was excited by 1064 nm laser radiation. XPS measurements were performed using a VG Scientific photoelectron spectrometer ESCALAB-210 using Al K α 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. Textural properties of the samples were determined by N₂ physisorption using a Micromeritics TriStar II Plus. high performance liquid chromatography (HPLC, Waters Model 590 pump) equipped with a Dual Absorbance Detector (Waters 2487) and the SunFireTM C18 (3.5 μ m, 150 mm length, 4.6 mm inner diameter) column provided by Waters. Gas chromatography (GC) analysis was performed using a Varian CP 3800 instrument with a flame-ionization detector (FID) using silicon DC-200 or carbowax 20 M columns. The conversion and selectivity of the oxidation reactions were defined as follows:

$$\text{Conversion (\%)} = [(C_0 - C_{BA})/C_0] \times 100$$

$$\text{Selectivity (\%)} = [C_{BAD}/(C_0 - C_{BA})] \times 100$$

where C_0 is the initial concentration of benzyl alcohol, C_{BA} and C_{BAD} are the concentrations of the reaction substrate benzyl alcohol and corresponding benzaldehyde at a certain time after the photocatalytic reaction, respectively.

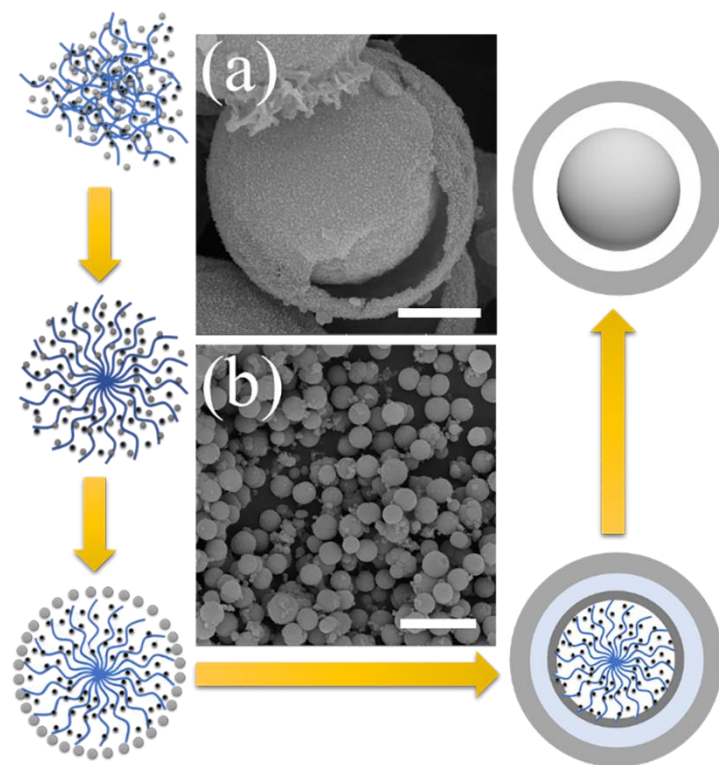


Fig. S1. Schematic diagram of the formation of Y@S-TiO₂ microspheres. The scale bar is 1 μm . The scale bars are 1 μm (a) and 10 μm (b).

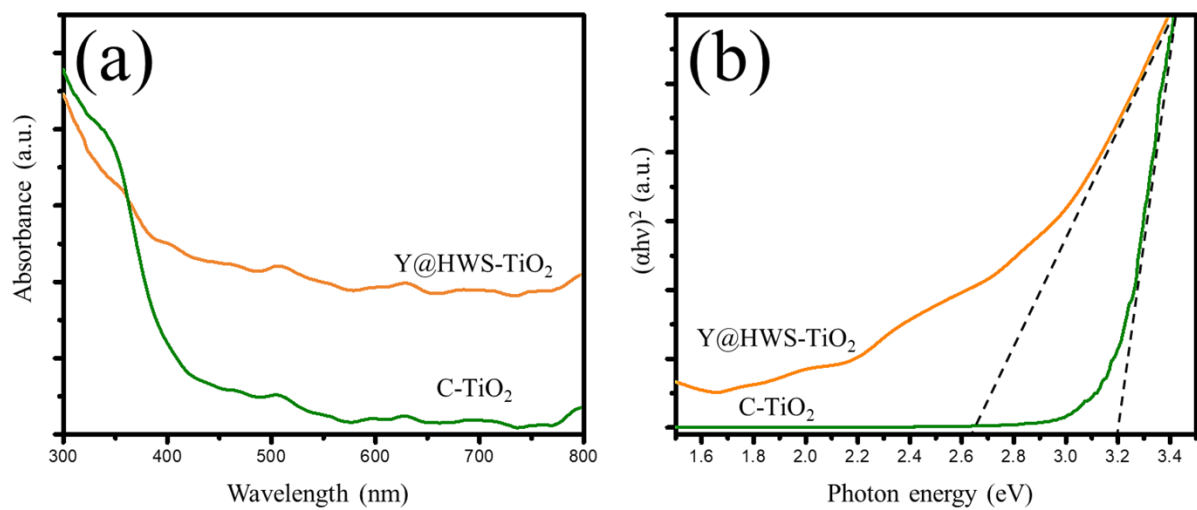


Fig. S2. UV-Vis spectra of C-TiO₂ and Y@HWS-TiO₂ (a); plot of $(\alpha h\nu)^2$ vs. $h\nu$ for C-TiO₂ and Y@HWS-TiO₂ (b)

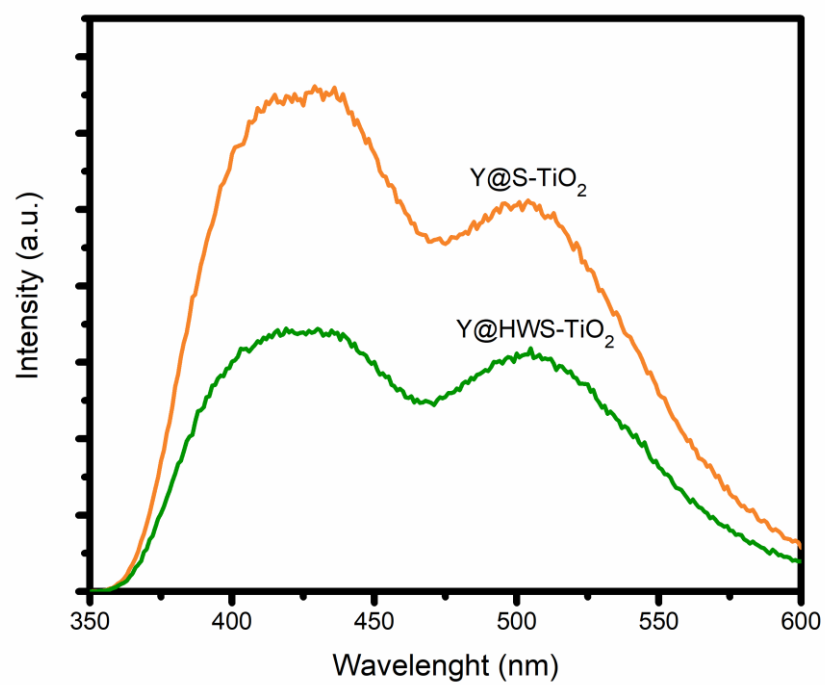


Fig. S3. Photoluminescence spectra of C-TiO₂ and Y@HWS-TiO₂

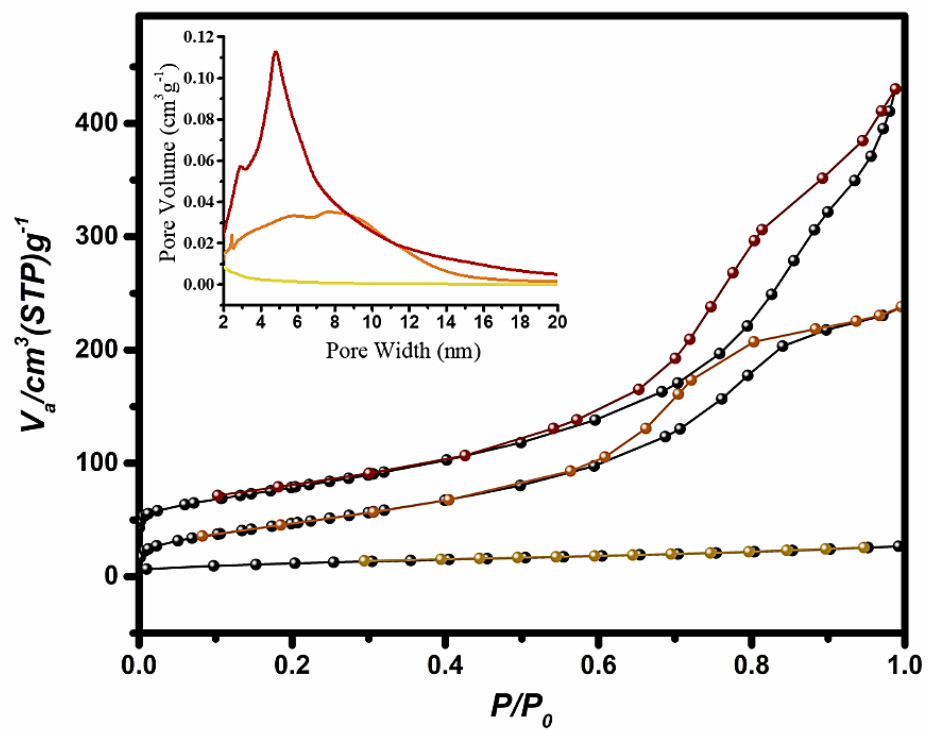


Fig. S4. Nitrogen adsorption-desorption isotherms of C-TiO₂, Y@S-TiO₂ and Y@HWS-TiO₂.

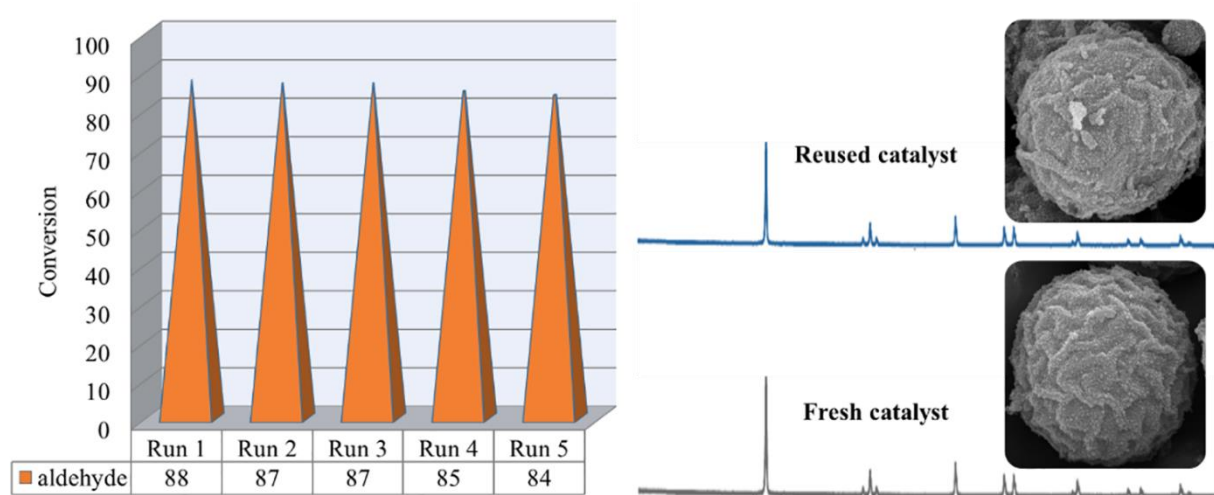


Fig. S5. Reusability study of Y@HWS-TiO₂ in the selective oxidation of benzyl alcohol.

Table S1. Comparing the efficiency of different reported photocatalysts in the selective oxidation of benzyl alcohol

Entry	Catalyst	Time (h)	Noble metal	Reusable (run)	Conversion (%)	Selectivity (%)	Ref
1	UiO-66-NH ₂ -F	24	---	---	53.9	99	[1]
2	AgBr@Ag@TiO ₂	8	✓	3	73	98	[2]
3	Bi ₂ MoO ₆ /Pt	6	✓	---	87	95	[3]
4	Ru/TiO ₂ nanobelts	5	✓	---	72	81	[4]
5	Ni/NH ₂ -MIL-125	10	---	3	21.5	99	[5]
6	hollow Ti ³⁺ /TiO ₂	7	---	---	22.7	99	[6]
7	CdS@SnO ₂ Nanorods	8	---	----	80	90	[7]
8	Meso-porous WO ₃	4	---	---	57	99	[8]
9	Y@HWS-TiO ₂	3	---	5	88	97	This work

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