Supporting Information

$W_{18}O_{49}$ nanowire networks for catalyzed dehydration of isopropyl alcohol to propylene under visible light

Experimental Section

Synthesis of hierarchical $W_{18}O_{49}$ Nanostructures: in a typical procedure, a W^{6+} precursor (WCl_6, 2.5 g) was dissolved in 80 ml of absolute ethanol, and a transparent yellow solution was formed. The obtained transparent yellow solution was then cooled at -5 °C for 20 h, and then transferred to a Teflon-lined stainless steel autoclave and heated at 180 °C for 24 h. A blue flocculent precipitate was collected, purified with absolute and distilled water, and dried in vacuum at 50 °C.

Photocatalyzed dehydration of IPA into propylene under visible light: 0.1 g of sample was uniformly dispersed on a glass dish with a surface area of 8 cm^2. A 300W Xenon arc lamp equipped with cutoff filter L42 (Hoya Optics) was used as the light source for the photocatalytic reaction (30 mW cm^{-2}). The volume of the reaction system was about 390 mL. The reaction setup was vacuum-treated several times, and then 0.5 mL of IPA was introduced into the reaction. During the irradiation, about 0.5 mL of reaction gas was taken from the reaction cell at given intervals for subsequent propylene concentration analysis with a gas chromatograph (GC-14B, Shimadzu Corp., Japan).

Characterization: XRD patterns of the products were recorded on a Rigaku (Japan) D/max–γA X–ray diffractometer equipped with graphite monochromatized Cu–Kα radiation (λ = 1.54178 Å). Scanning electron microscopy (SEM) images were recorded with a field emission scanning electron microscopy (HITACHI, S–4800). Samples for transmission electron microscopy (TEM) analysis were prepared by drying a drop of nanocrystal dispersion in absolute ethanol on amorphous carbon–coated copper grids. High–resolution TEM (HRTEM) characterization was performed with a JEOL 2010 operated at 200 kV. UV–vis absorption spectra were recorded with a Shimadzu UV-3600. X-ray Photoelectron Spectroscopy (XPS) experiments were performed in a Bruker D8 using monochromated Al Kα X-rays at hυ = 1486.6 eV. Peak positions were internally referenced to the C1s peak at 284.6 eV. UV-Vis-NIR absorption spectra were obtained by recorded with a Shimadzu UV-3600 with integrating sphere. Fourier transform infrared (FTIR) spectra were obtained from THERMO Iz10.

Apparent Quantum Yield calculation: the apparent quantum yield of C_3H_6 evolution over the as–synthesized $W_{18}O_{49}$ networks was measured by inserting 420 ± 15 nm band–pass filters in front of the reaction cell to supply the irradiant light with wavelength of 420 ± 15 nm. The volume of the reaction cell

is about 500 mL, and the light intensity is about 837 μW/cm^2. 0.1 g of catalyst was uniformly dispersed on a glass dish with a surface area of 8 cm^2. The apparent quantum yield of photocatalytic C_3H_6 evolution was calculated according to as–below equations,

$$A.Q.Y. = [N(C_3H_6) \times 1]/N(Photons) \times 100\%$$

in which $N(C_3H_6)$ and N(Photons) signify the molecular number of generated C_3H_6 in unit time and the number of incident photons in unit time, respectively. (Generation of one C_3H_6 molecule will consume 1 photoelectrons, since $CH_3CH(OH)CH_3 + e^- \rightarrow C_3H_6 + H_2O$). By calculating, the A.Q.Y for the photocatalytic evolution of C_3H_6 is about 2.1 %.

Supporting Figures

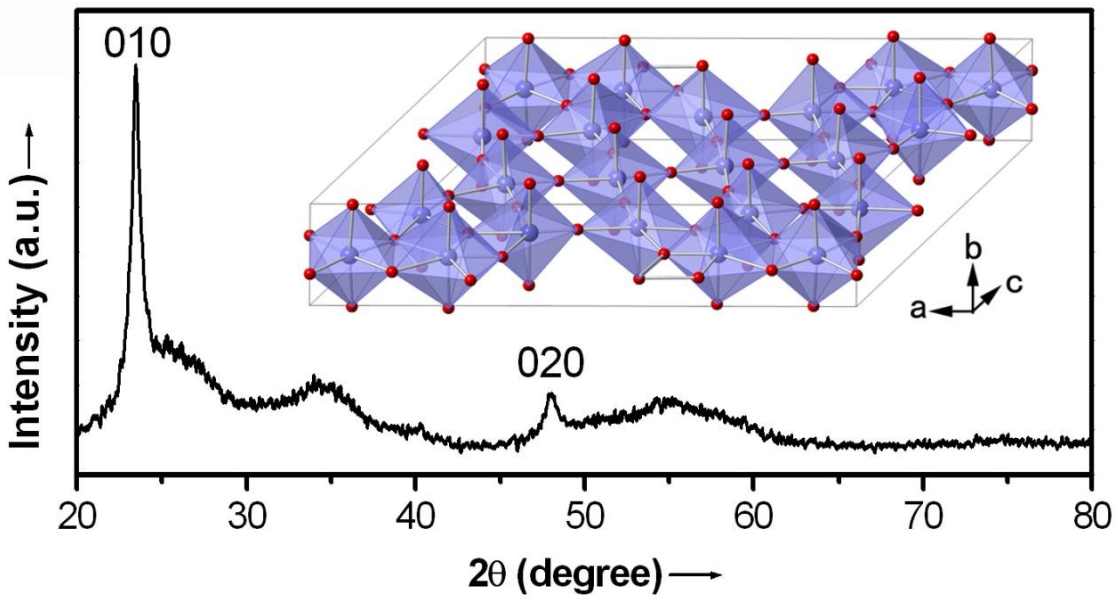

Fig. S1 A typical XRD pattern of the $W_{18}O_{49}$ sample, inset: crystal structure of the monoclinic phase $W_{18}O_{49}$.

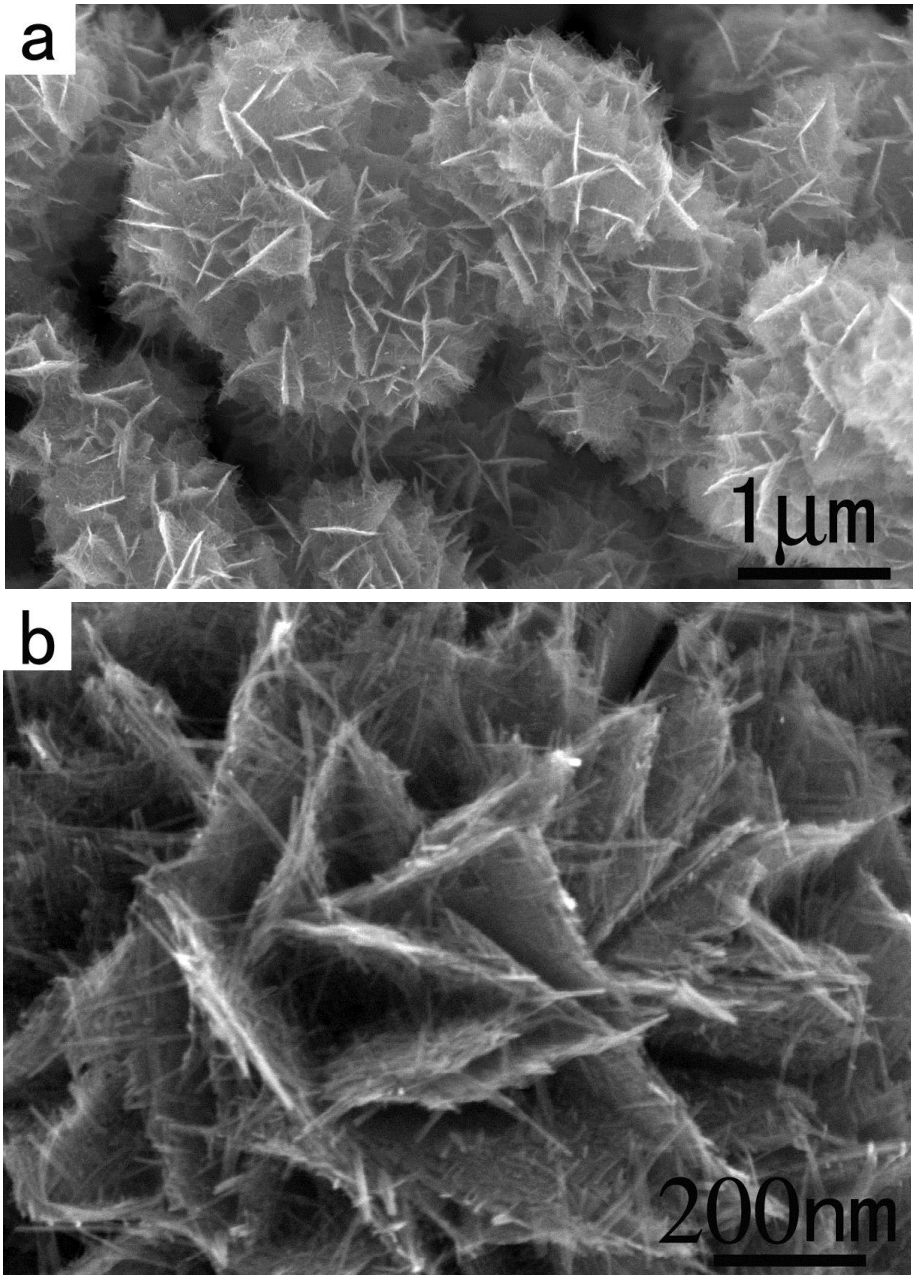

Fig. S2 High-magnification SEM images of the as-prepared $W_{18}O_{49}$ networks.

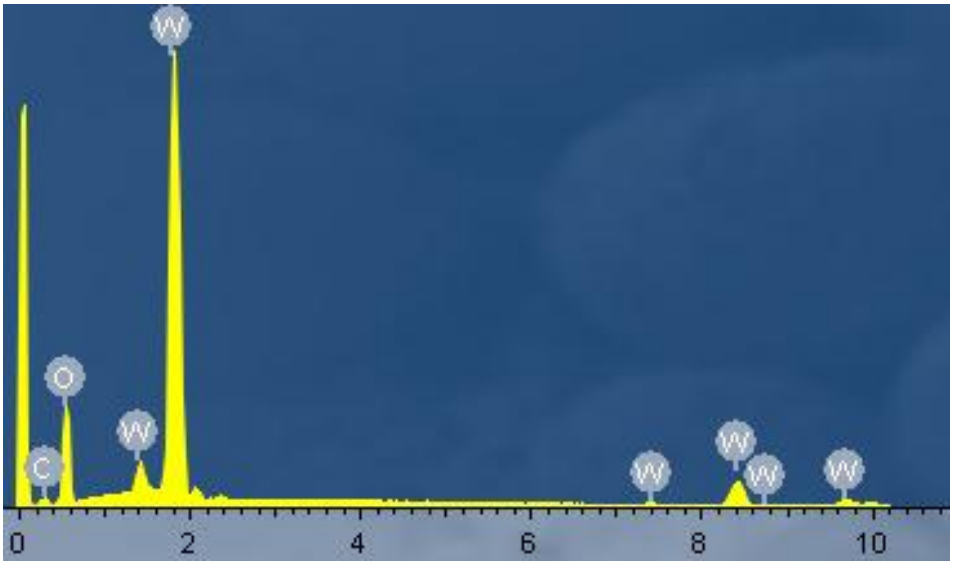

Fig. S3 EDS spectrum of the as-synthesized $W_{18}O_{49}$ nanowire networks.

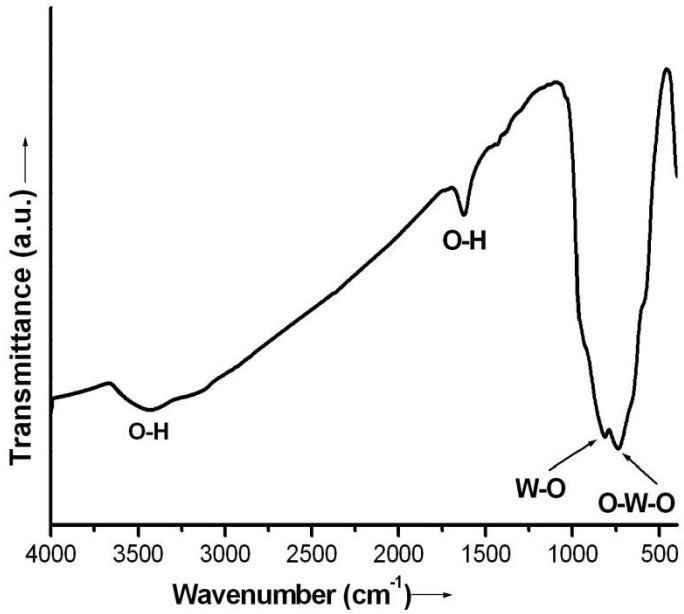

Fig. S4 FTIR spectrum of the as-prepared $W_{18}O_{49}$ nanowire networks.

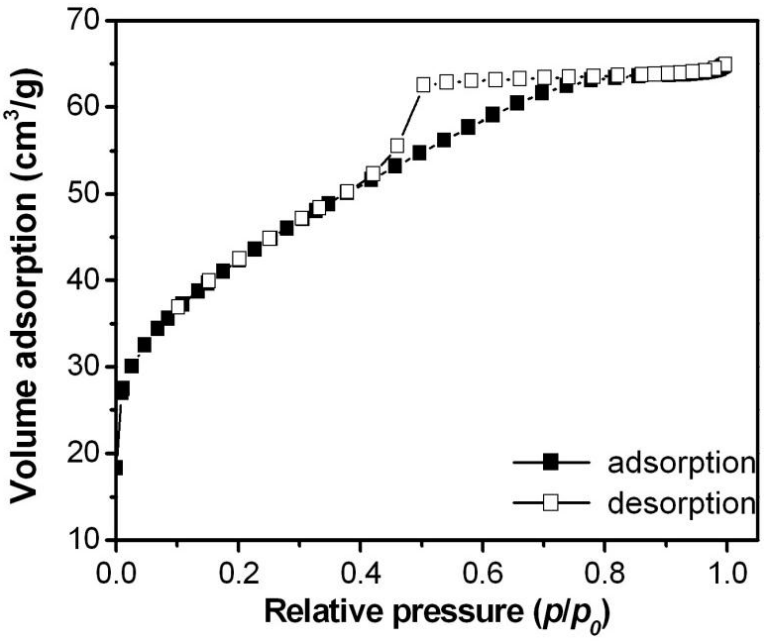

Fig. S5 N_2 adsorption/desorption isotherms of the as-synthesized $W_{18}O_{49}$ nanowire networks.

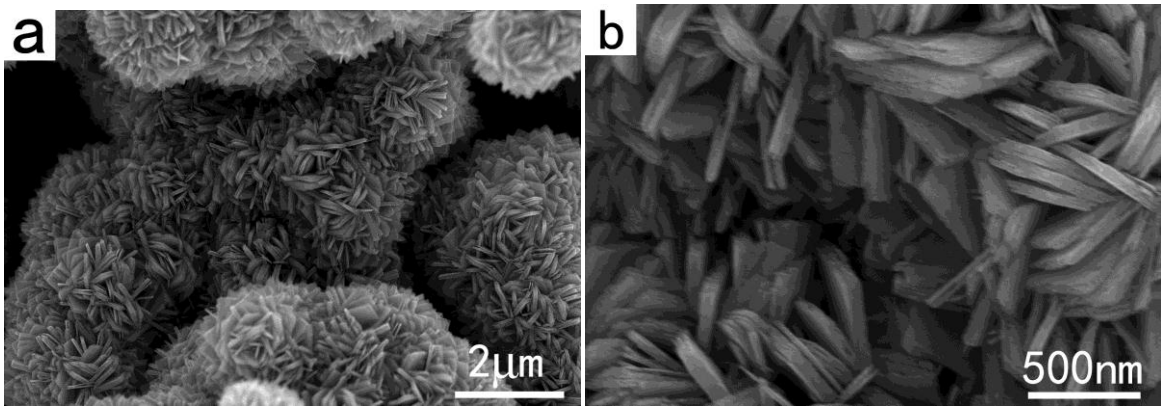

Fig. S6 Typical SEM images of the plate-like $W_{18}O_{49}$ nanostructures.

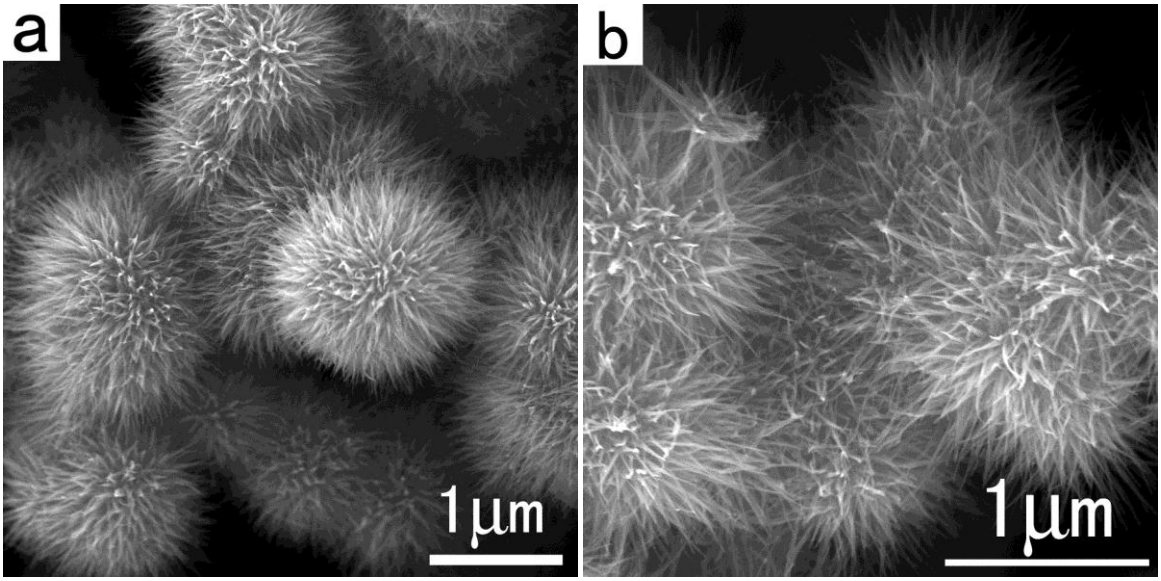

Fig. S7 Typical SEM images of the sea urchin-like $W_{18}O_{49}$ nanostructures composed of numbers of radial nanowires.

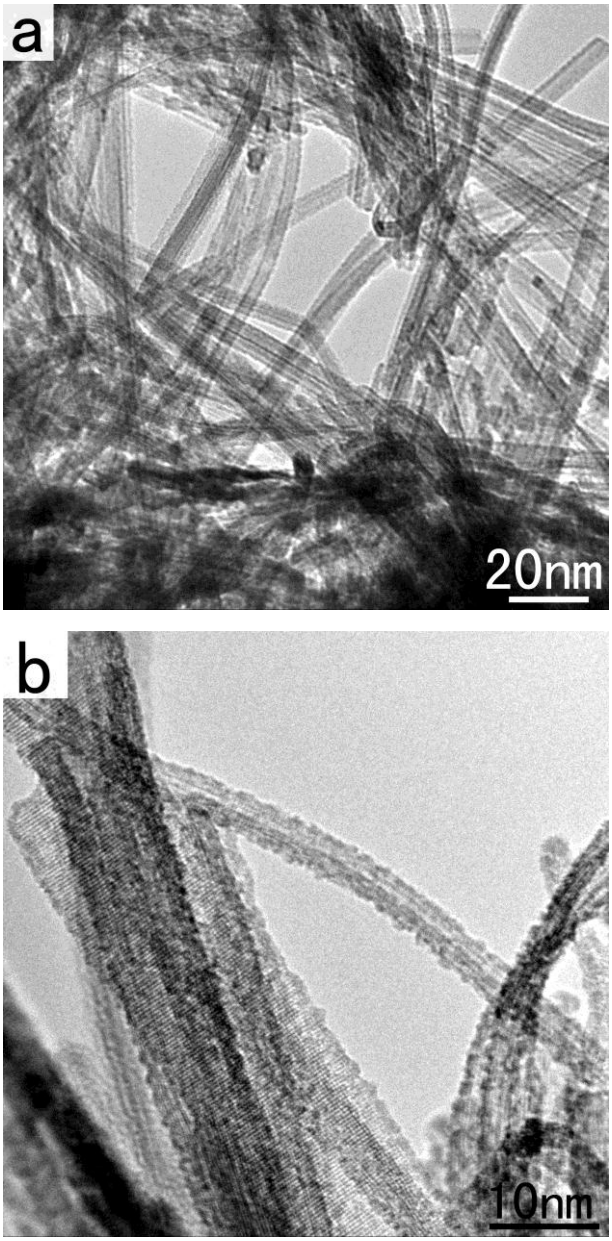

Fig. S8. TEM (a) and HRTEM (b) images of the tungsten oxide samples obtained by air oxidizing with 7 days.

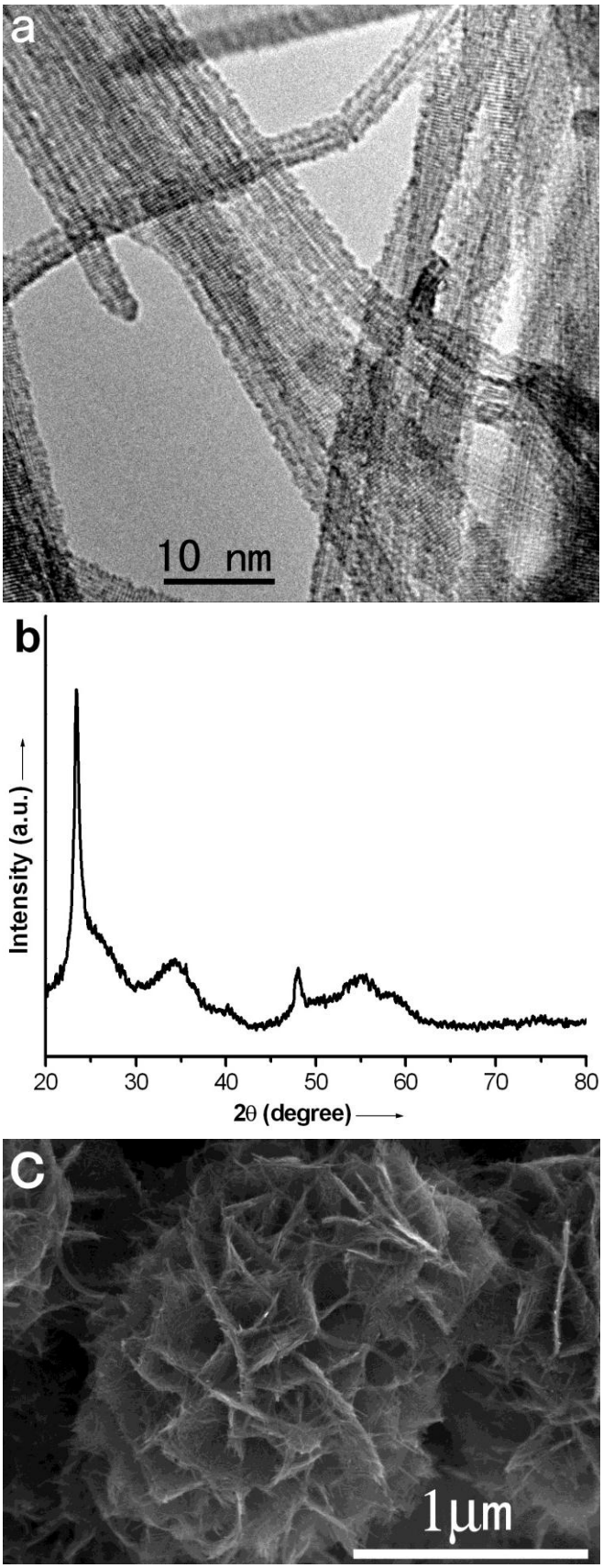

Fig. S9. HRTEM image (a), XRD pattern (b), and SEM image (c) of the sample after 80 min photocatalytic reaction.

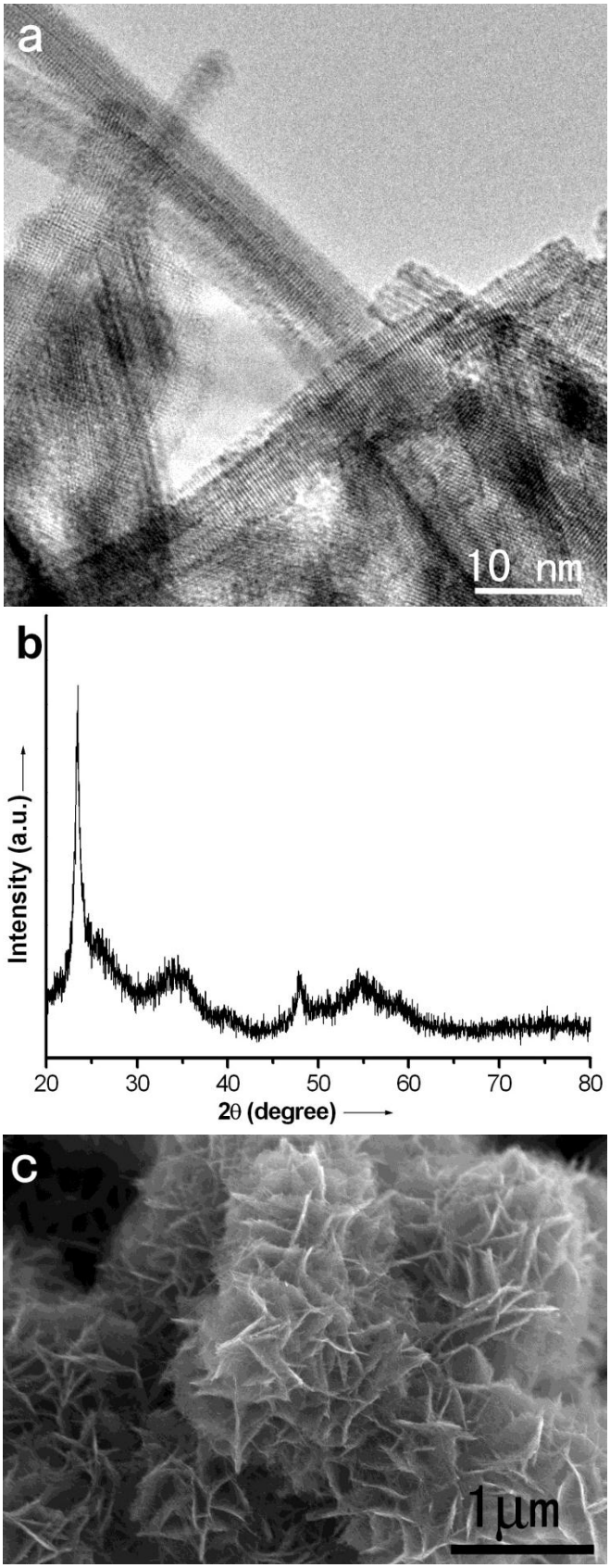

Fig. S10 HRTEM image (a), XRD pattern (b), and SEM image (c) of the sample after 160 min photocatalytic reaction.

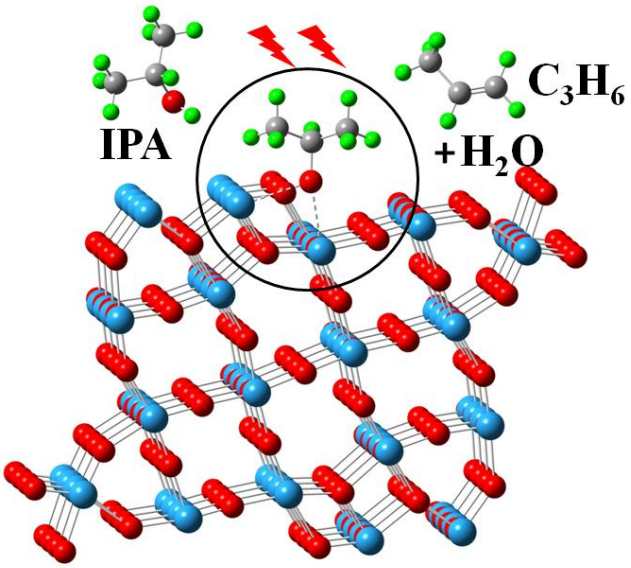

Fig. S11 Schematic illumination of the "trap" effect in the catalytic reaction. Due to its natural defect structure and 1-D nanostructure, large quantity of oxygen vacancy contain in the nanowires. Every oxygen vacancy could be considered as a trap, and the traps can attract IPA molecules by chemical and physical interactions.