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Supporting Information

Experimental Section

Synthesis of MoO_{3-x} single-layer nanobelts: in a typical synthesis, 1.8 g of molybdenum acetylacetonate was added into 200 ml of distilled water. The obtained solution was then loaded into a Teflon-lined autoclave. The autoclave was sealed, heated in an oven of 180 °C for 20 h, and then naturally cooled to room temperature, and a blue flocculent product (MoO_{3-x}) formed, which was then collected, washed with ethanol and distilled water three times to remove ions and possible remnants.

Characterization: XRD patterns of the products were recorded on a Bruker D8 focus X–ray diffractometer by using CuKα radiation (λ = 1.54178 Å). Scanning electron microscopy (SEM) images were obtained on a Hitachi S4800. Transmission electron microscopy (TEM) and high–resolution TEM (HRTEM) characterizations were performed with a Tecnai G F30 operated at 300 kV. UV–Vis–NIR absorption spectra were recorded with a Shimadzu UV3600. X-ray Photoelectron Spectroscopy (XPS) experiments were performed in a Theta probe (Thermo Fisher) using monochromated Al Kα X-rays at hυ = 1486.6 eV. Peak positions were internally referenced to the C1s peak at 284.6 eV. Fourier transform infrared (FTIR) spectra were obtained from THERMO Iz10. Surface area was measured in a Micro Tristar II 3020.

Photocatalyzed propylene evolution: 0.1 g of catalyst was uniformly dispersed on a glass reactor with an area of about 6 cm^2. A 300W Xenon arc lamp equipped with cutoff filter (420 nm) was used as the light source for the photocatalytic reaction (light intensity: 27 mW m^{-2}). The volume of the reaction system was about 200 mL. The

reaction setup was vacuum-treated several times, and then 0.5 mL of liquid IPA was introduced into the reaction by micro-Injector. During the visible light irradiation, about 0.5 mL of reaction gas was taken from the reaction cell at given intervals for subsequent C_3H_6 concentration analysis with a gas chromatograph (GC-14B, Shimadzu Corp., Japan).

Photoelectrochemical properties: photoelectrochemical measurements were carried out by using a conventional three-electrode, single-compartment glass cell fitted with a synthetic-quartz window with a potentiostat. The saturated Ag/AgCl and platinum wire were used as the reference electrode and the counter electrode, respectively. In a typical process, sample of 1 mg was dispersed in 1 mL anhydrous ethanol and then evenly grinded to slurry. The slurry was spread onto ITO glass and the exposed area was kept at 0.4 cm^2. The prepared ITO/samples was dried overnight under ambient conditions and then used as the working electrode with 0.1 M Na_2SO_4 aqueous solution as the electrolyte. The MoO_{3-x} nanobelts served as the working electrode. The potential was swept linearly at a scan rate of 1 mV s^{-1}. The photocurrent measurements was performed by using an electrochemical system (CHI-660B).

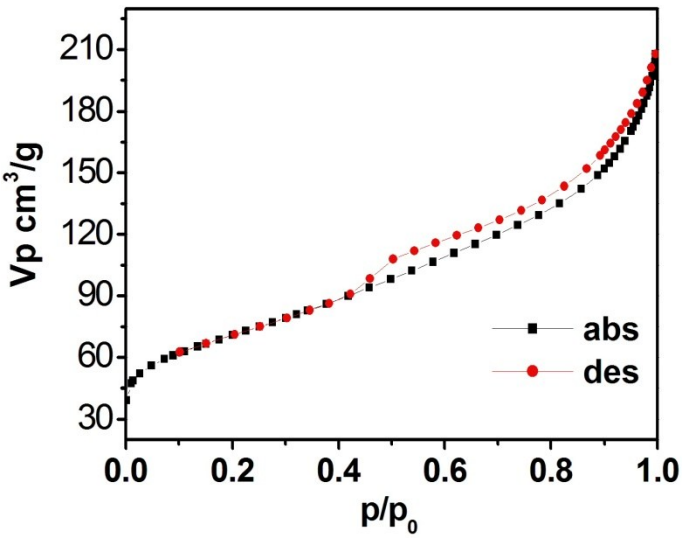

Figure S1. Nitrogen adsorption–desorption isotherm plot of the as-synthesized MoO_{3-x} ultrathin nanobelts.

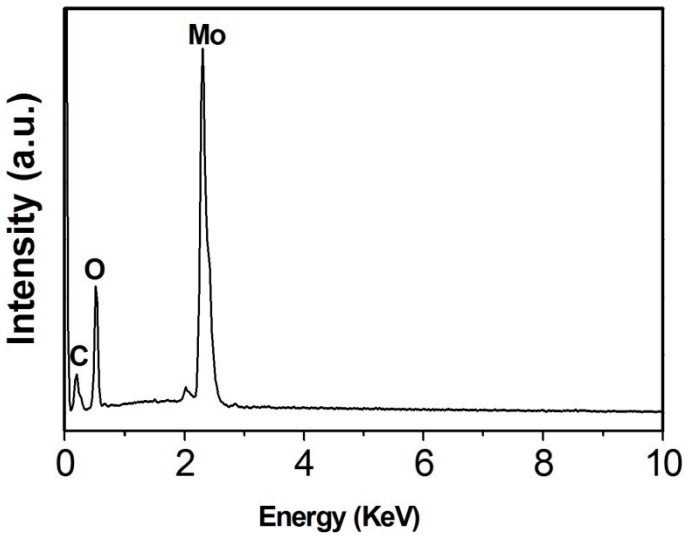

Figure S2. EDS spectrum of the ultrathin MoO_{3-x} ultrathin nanobelts. The C signal come from the carbon-coated grid.

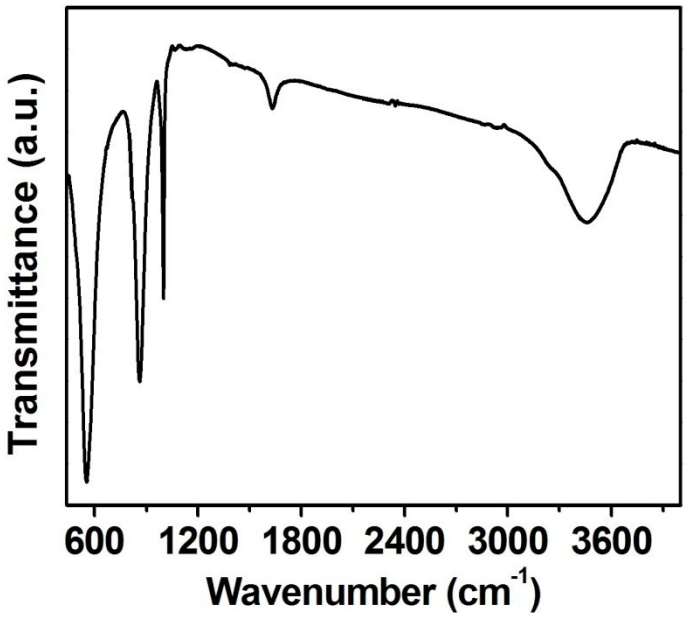

Figure S3. FTIR spectrum of the single-layer MoO_{3-x} ultrathin nanobelts. From this spectrum, we can see that no organics are presented in the sample, which demonstrates that the surface of the ultrathin nanobelts is very clean.

Table 1. Reported plasmonic semiconductors

Compounds	Peak (nm)	Morphology	References
MoO_{3-x}	550	ultrathin nanobelts	Present work
Cu_{2-x} S	1750	quantum dots	Ref. 25
Cu_{2-x} Se	1100	quantum dots	Ref. 26
Cu_{2-x} S	1800	nanodisks	Ref. 27
$Cu_{2-x}S$	1650	quantum dots	Ref. 28
$Cu_{2-x}Se$	1500	quantum dots	Ref. 28
$Cu_{2-x}Te$	900	quantum dots	Ref. 28
Si	740	nanowires	Ref. 29
$W_{24}O_{68}$	900	nanorods	Ref. 30
$W_{18}O_{49}$	1400	ultrathin nanowires	Ref. 31
TiO_{2-x}	3400	tetragonal bipyramidals	Ref. 32
MoO_{3-x}	680-900	nanosheets	Ref. 23
Al doped ZnO	2500	nanoparticles	Ref. 32

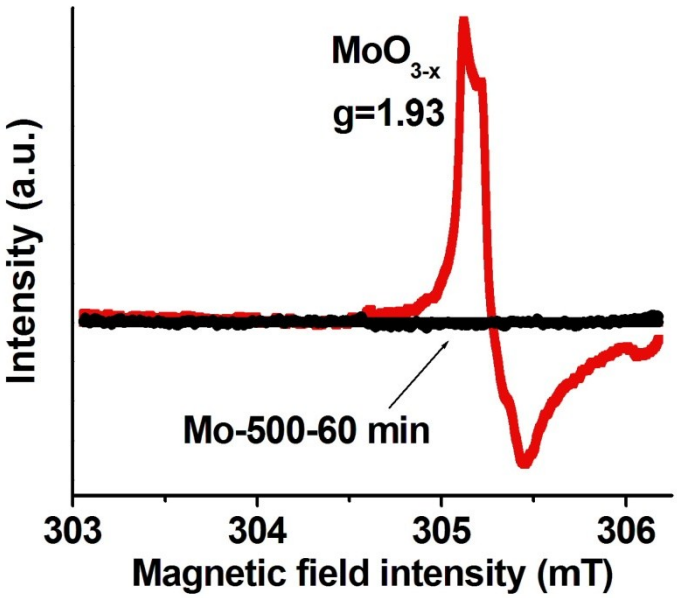

Figure S4. ESR spectrum of the MoO_{3-x} ultrathin nanobelts before and after heating at 500 °C in air. The sample of blue MoO_{3-x} shows a strong ESR signal at g = 1.93, which is a direct evidence for the existence of a single electron. As Mo^{6+} is a d^0 species and Mo^{5+} is a d^1 species, the existence of Mo^{5+} in the blue nanobelts is undoubted.

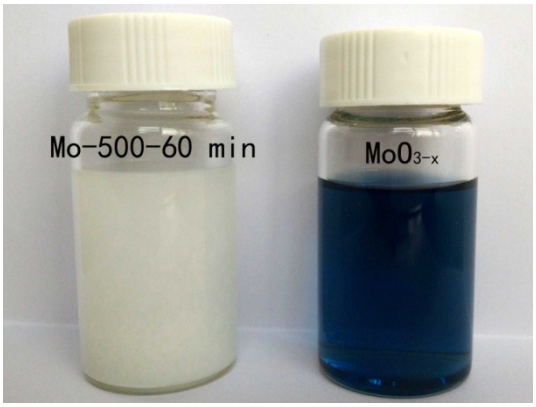

Figure S5. Photograph image of the MoO_3 ultrathin nanobelts before and after heating at 500 °C in air.

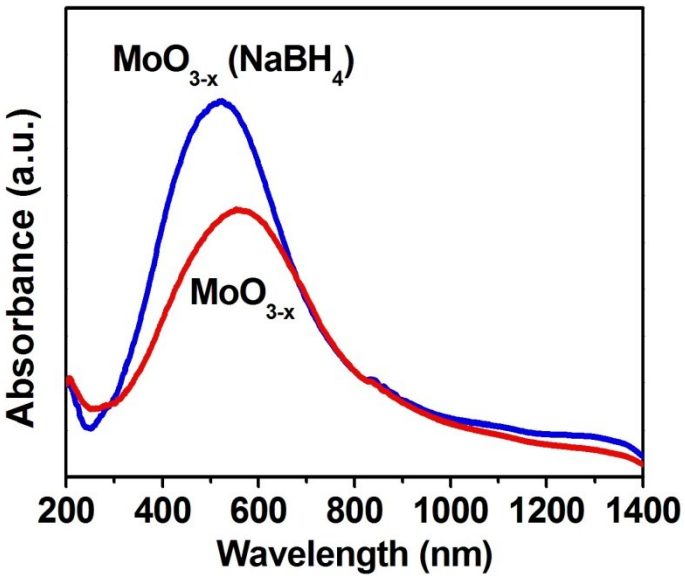

Figure S6. UV-Vis-NIR absorptions of the MoO_{3-x} ultrathin nanobelt before and after treating by $NaBH_4$.

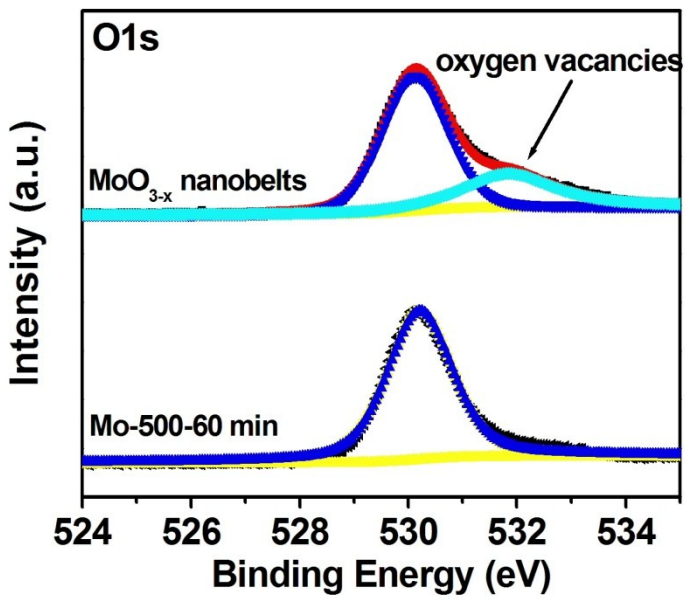

Figure S7. The O 1s XPS spectra of the MoO_{3-x} ultrathin nanobelts before and after heating at 500 °C in air.

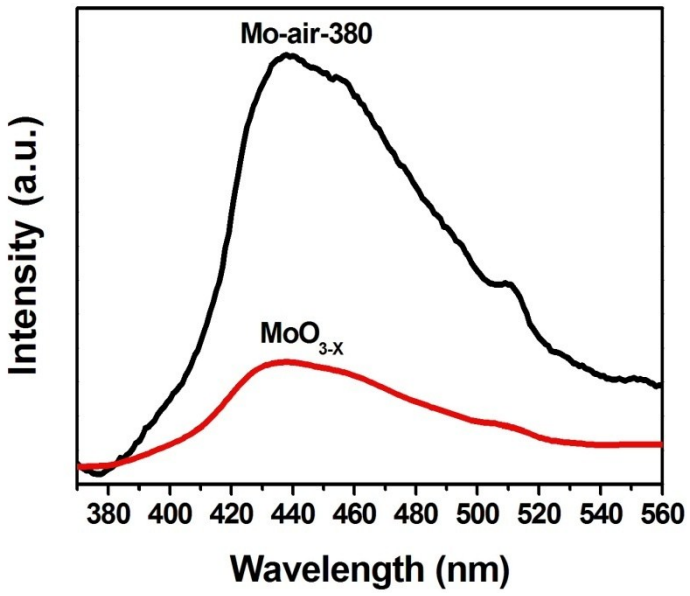

Figure S8. Photoluminescence spectra of the MoO_{3-x} ultrathin nanobelts before and after heating at 500 °C in air.measured at –10 °C.

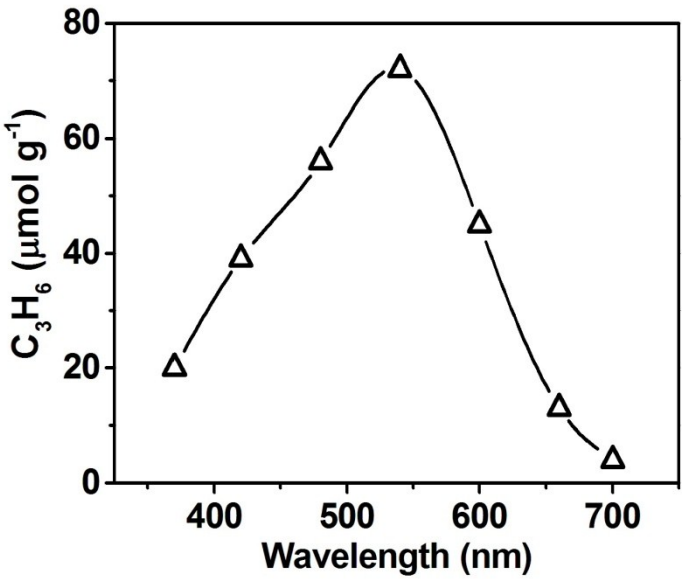

Figure S9. Wavelength-dependent C_3H_6 evolution with the MoO_{3-x} ultrathin nanobelts as photocatalysts.

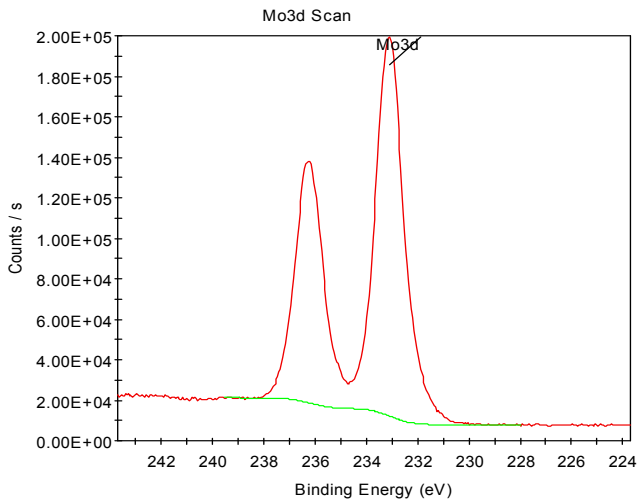

Figure S10. XPS spectrum of the sample of Mo-H_2O_2-2 h, from which can be see that the Mo^{5+} ions have bee completely oxidized into Mo^{6+} ions.

DFT and Adsorption Energies Calculations: All the periodic DFT calculations were carried out by using the Vienna ab initio simulation package (VASP).[1] Exchange and correlation potentials were described by using the generalized gradient approximation (GGA) with Perdew–Burke–Ernzerh of (PBE).[2] A plane-wave basis set with an energy cutoff of 400 eV was used to expand the one-electron wave function, and the atomic relaxation was stopped when forces on each atom were smaller than 0.02eV/Å. Spin polarization was considered in all calculations. DFT + U[3] method introduces an on-site Coulomb interaction to overcome partially the self-interaction error.[4] So in order to treat highly localized 4d orbital of molybdenum, the DFT+U method was applied in all our calculation with a the U–J parameter of 6.3eV according to previous reports.[5] The Brillouin zones are sampled with Monkhorst-Pack mesh k-points of 28 × 8 × 28 and 5 × 1 × 5 for bulk and surface calculations, respectively. For the calculation of density of states (DOS), a larger 15 × 1 × 15 k-point set was used. And spin polarization were included in all calculation.

In the layered MoO_3 crystal, the neighboring layers are connected by weak van der Walls forces along b direction. As is well known, DFT methods is unable to describe Van der Waals forces correctly since the dispersion is poorly represented. Thus, in this work, we adopted the method proposed by Coquet and Willock,[5] which keeps the b lattice parameter at the experimental value of 13.855 Å and optimizes the a and c lattice parameters. The optimized results are given in Table S2.

We choose a 2 × 1 × 2 periodic supercell with a four-atom-thick MoO_3 slab in our calculations (Figure S9). A vacuum thickness of 1.4 nm was used to remove any

interaction between the neighboring slabs. The top two layers were allowed to fully relax while the bottom two layers were fixed. The geometry optimization was stopped when the forces on all unconstrained atoms were less than 0.02 eV/Å. The nanobelt length along [001] direction is assumed to be infinity and the lattice fringes perpendicular to the growth direction has a spacing of 1.42 nm, as shown in Figure S10a-b, consistent with the experimental results. A vacuum gap of 1.4 nm along *b*-direction was adopted to remove any interactions between the belt and its periodic images.There are three types of oxygen atom: asymmetric (O_a), symmetric (O_s) and terminal (O_t), and the defect at the O_t site are most likely to be formed because of the lowest vacancy formation energy based on the previous study.[6] Thus, in the present work, the defective MoO_{3-x} nanobelt was constructed with one terminal oxygen removed from perfect MoO_3 nanobelt (Figure S10c-d).

The adsorption energies were defined by the following standard equation:

$$E_{ads} = E_{gas\text{-}surface} - (E_{surface} + E_{gas})$$

where $E_{gas\text{-}surface}$, $E_{surface}$, and E_{gas} are the total energies of the adsorbed system, the clean surface and the corresponding gas phase species, respectively.

Table S2 Lattice parameters for bulk MoO_3

	Lattice constant/A˚			
Lattice parameter	This work	GGA[5]	HF[7]	Experiment[8]
a	4.042	4.022	3.910	3.962
b	13.855	13.855	14.271	13.855
c	3.770	3.752	3.680	3.699

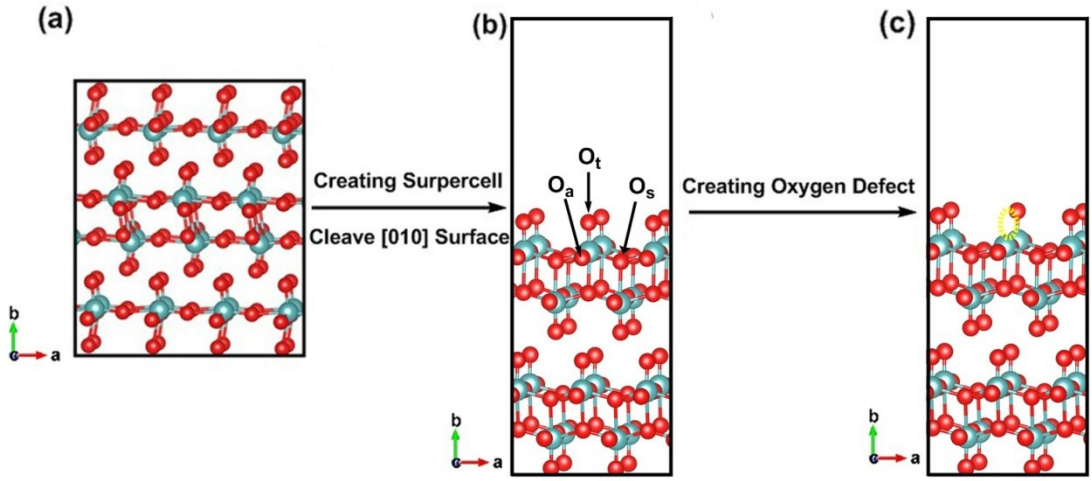

Figure S11. Creating the calculation model of MoO_3(**b**) and MoO_{3-x}(**c**).

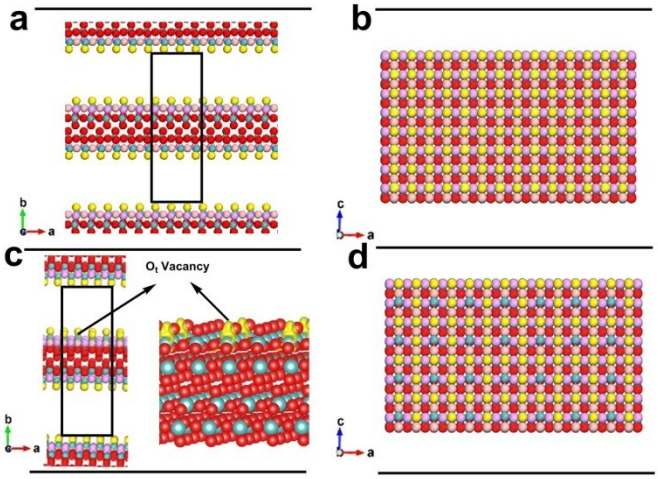

Figure S12. (a) side and (b) top views of the MoO_3 (010) nanobelt; (c) side and (d) top views of the MoO_{3-x} (010) nanobelt. Yellow: oxygen in O_t; pink: oxygen in O_a; purple: oxygen in O_s; bule: molybdenum; red: normal oxygen atom.

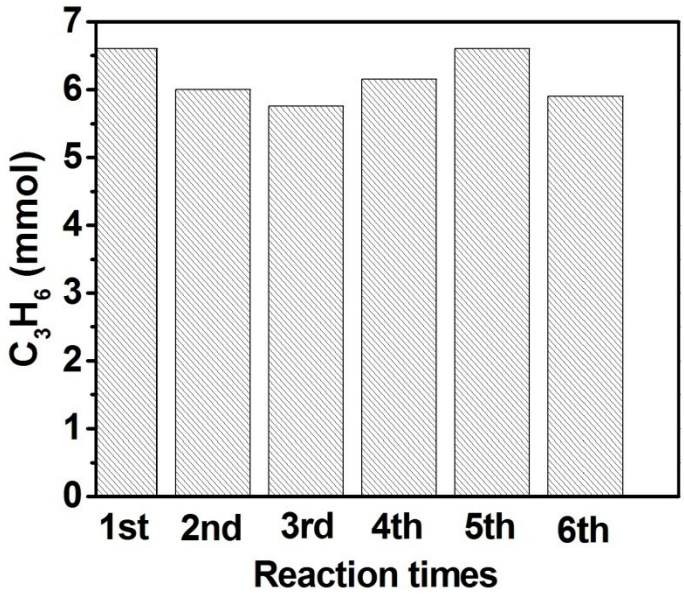

Figure S13. Stability test of C_3H_6 production from IPA under visible light.

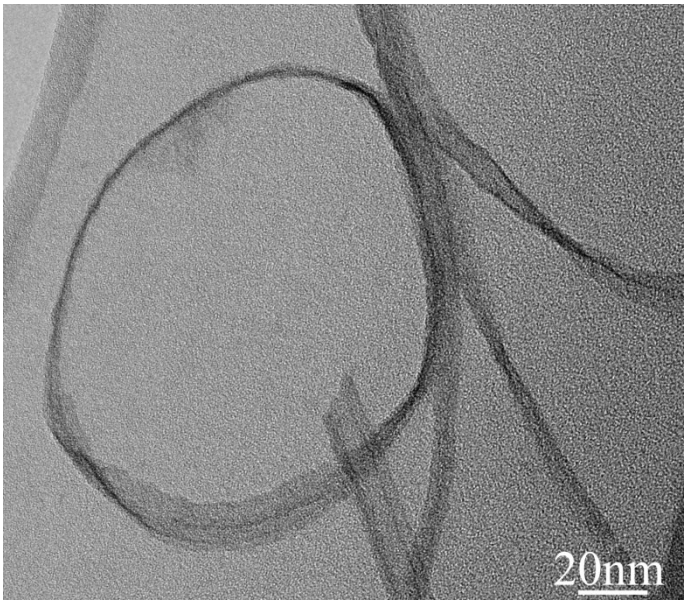

Figure S14. TEM image of the sample after 30 h photocatalytic reaction.

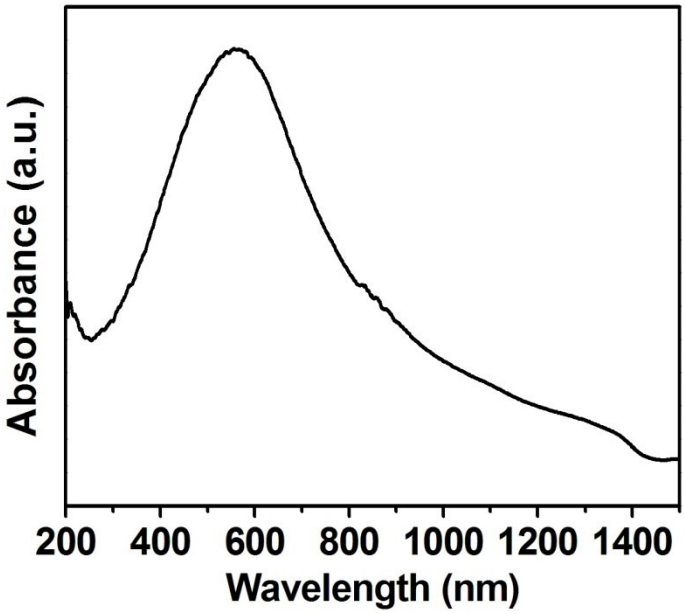

Figure S15. UV-Vis-NIR absorption spectrum of the sample after 30 h photocatalytic reaction.