

Supporting Information

Synthesis of Highly Crystalline $\text{In}_2\text{Ge}_2\text{O}_7(\text{En})$ Hybrid Sub-Nanowires with Ultraviolet Photoluminescence Emission and Selectively Photocatalytic Reduction of CO_2 into Renewable Fuel †

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Experimental sections and characterizations

Experimental sections

Preparation of the $\text{In}_2\text{Ge}_2\text{O}_7(\text{En})$ nanowires

All the chemicals were of analytical grade and used as received without further purification. The $\text{In}_2\text{Ge}_2\text{O}_7(\text{En})$ NWs were synthesized using a solvothermal synthesis method. In a typical synthesis, 0.312g of GeO_2 (3 mmol) and 0.584g of $\text{In}(\text{CH}_3\text{COO})_3$ (2 mmol) were added to 15 mL of solvents which includes H_2O and ethylenediamine (En). The mixture was stirred for 40 min and then transferred to a stainless Teflon-lined autoclave of 25 mL inner volume. The solvothermal synthesis was performed under an auto-generated pressure at 180 °C for 24 h in an electric

oven, followed by cooling naturally to room temperature. The product was collected by centrifugation, washed thoroughly with deionized water and alcohol several times, and then dried at 60 °C for 12h. A white powder was finally obtained.

Loading the Pt Co-catalyst

The loading of Pt was performed by a photocatalytic reduction method. $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ was used for the source of Pt. Typically, 0.2 g photocatalyst, 40 mL distilled water, 15 mL CH_3OH and a given amount of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ were placed in a glass vessel. The reactant solution was irradiated by a 300W Xe arc lamp for 8 h with stirring. Then, the photocatalyst with Pt was filtered, washed thoroughly with deionized water and alcohol, dried at 60°C for 12h.

Characterization

The crystal structures of the powder samples were investigated by an X-ray diffractometer (XRD) (Rigaku Ultima III, Japan) using Cu $K\alpha$ radiation ($\lambda = 0.154178$ nm) at 40 kV and 40 mA. The XRD patterns were obtained over the scanning range of 10° - 80° at room temperature with a scan rate of $10^\circ \text{ min}^{-1}$. The morphology of the powders was examined by field emission scanning electron microscopy (FESEM, FEI NOVA NANOSEM 230). Transmission electron microscopy (TEM) images, high-resolution transmission electron microscopy (HRTEM) images were obtained on a JEOL JEM-2100 microscope with a LaB_6 filament and an accelerating voltage of 200 kV. The element ratio was confirmed with ICP analysis (J-A1100, Jarrell-Ash, USA). DSC, DTA and TG was operated on TA2100/SDT2960, USA. The Brunauer-Emmett-Teller (BET) surface area was measured by nitrogen sorption at

77K on surface area and porosity analyzer (Micromeritics TriStar USA) and calculated by the BET method. The UV-vis diffuse reflectance spectrum was recorded with a UV-vis spectrophotometer (UV-2550, Shimadzu) at room temperature and transformed to the absorption spectrum according to the Kubelka–Munk relationship. FTIR spectra were measured with a Thermo Nexus 870 FTIR spectrometer (Thermo Nicolet USA).

Photocatalytic conversion of CO₂ into CO

The photocatalytic reduction of CO₂ was carried out with 0.1 g of the powdered photocatalyst, which was uniformly placed at the bottom of a Pyrex glass cell. The reaction was in a gastight system. 0.4mL of didistilled water was injected into the system, which was filled with CO₂ to generate a water vapour. After adsorption of CO₂ had reached equilibrium in the dark, light photoirradiation was performed using a 300 W Xe arc lamp. A gas pump was used to accelerate gas diffusion. The concentration of product in the tube was withdrawn with a gas-tight syringe and detected by gas chromatograph (Shimadzu, GC-14B and GC8A with FID detector, Japan). The quantification of CO yield was based on the external standard and the use of calibration curve.

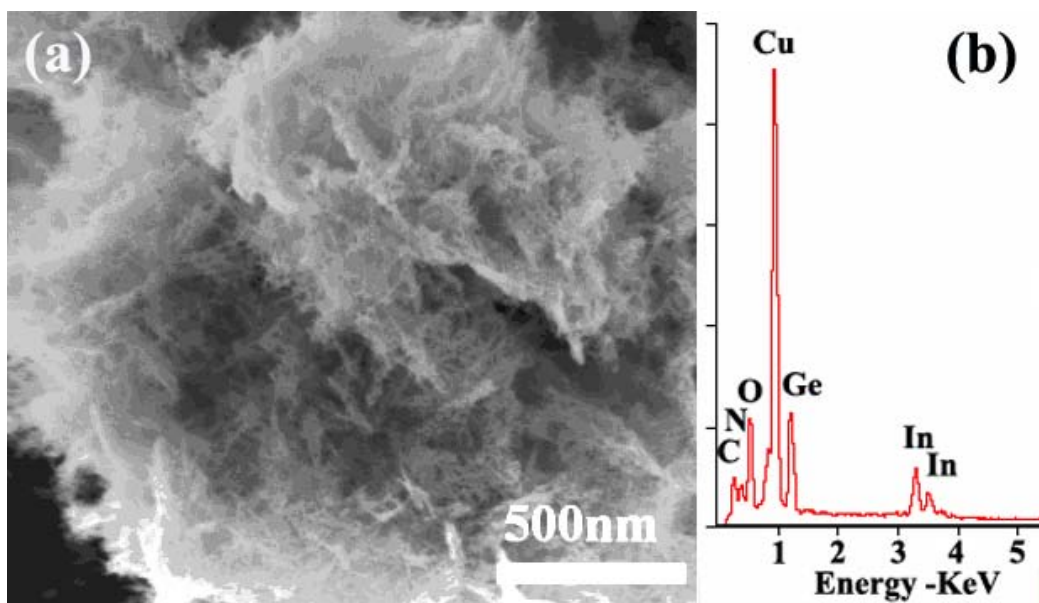


Figure S1. (a) FE-SEM image of the $\text{In}_2\text{Ge}_2\text{O}_7(\text{En})$ ultrathin nanowire and (b) corresponding EDX analysis.

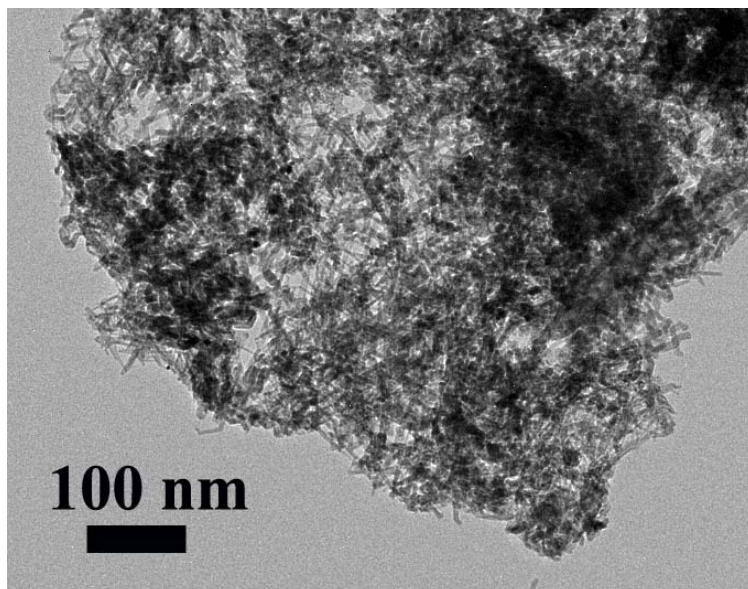


Figure S2. Low-magnification TEM image, demonstrating high-yield production of the ultrathin nanowire.

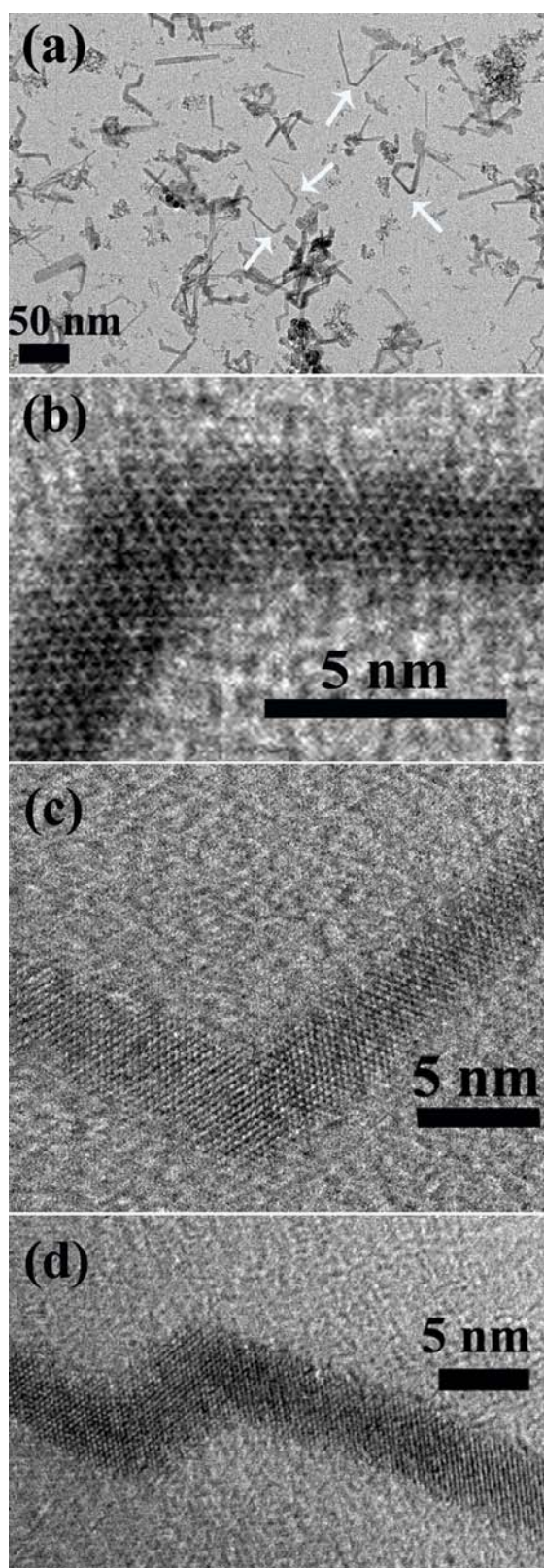


Figure S3. TEM and HRTEM of the ultrathin nanowires with V- and Z-shaped structures. The arrows in (a) mark typical nonlinear nanowires.

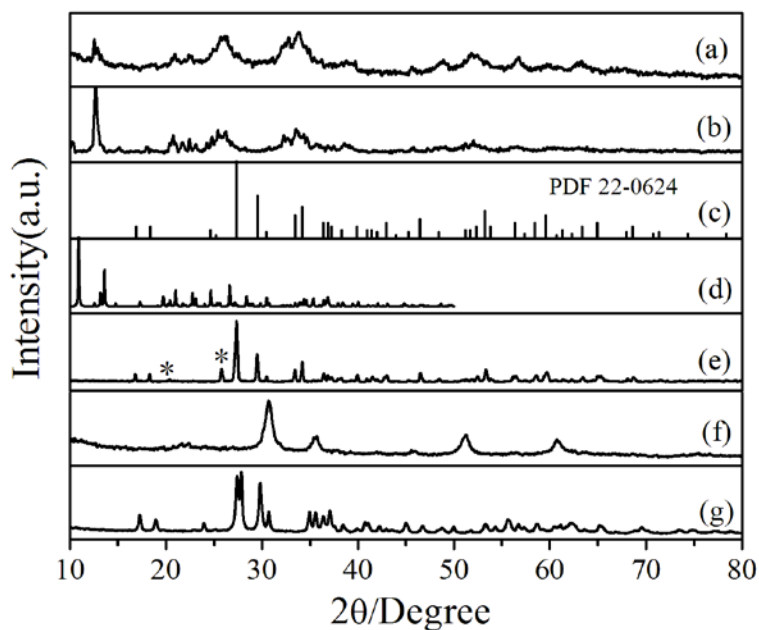


Figure S4. XRD patterns: (a) ultrathin nanowires. (b) the powder obtained with the synthetic time prolonged to 3 days. (c) In₂Ge₂O₇ Powder Diffraction Standards (JCPDS)-International Centre for Diffraction Data (ICDD). (d) In₂Ge₆O₁₅(en)₂ cited from Ref. [12b]. (e) product obtained by calcinations of the ultrathin nanowires at 1000 °C. * marked the diffraction peaks of GeO₂. (f) In₂O₃ obtained with pure En as solvent. (g) In₂Ge₂O₇ obtained with pure water as solvent.

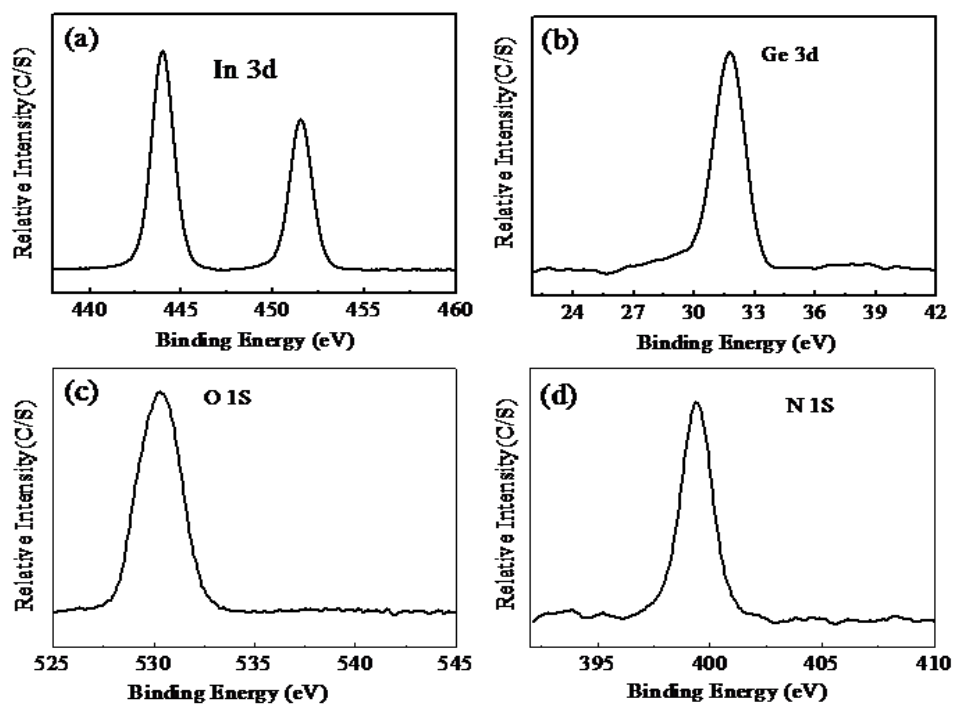


Figure S5. XPS spectra of the ultrathin nanowire.

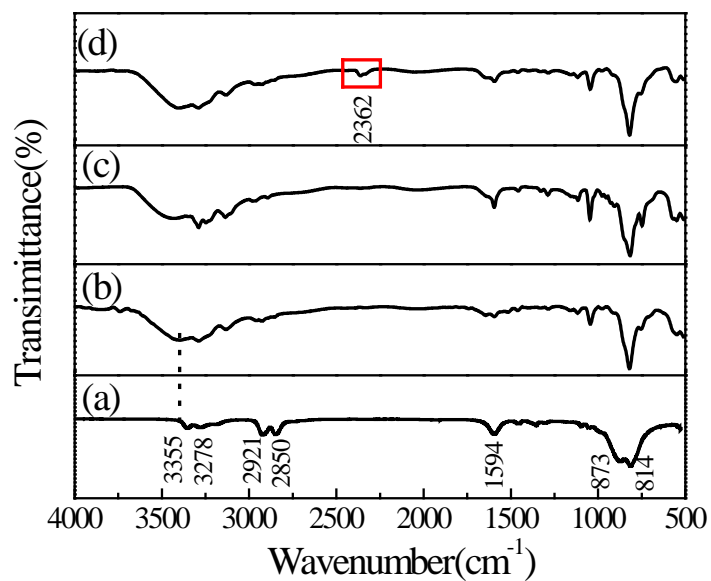


Figure S6. FT-IR spectra of (a) pure En, (b) In₂Ge₂O₇ (En) ultrathin nanowires, (c) In₂Ge₂O₇(En) ultrathin nanowire after photocatalysis reaction.(d) In₂Ge₂O₇(En) ultrathin nanowire after adsorption of CO₂. The band at 2362 cm⁻¹ in (d) is assigned to asymmetric stretch of CO₂.

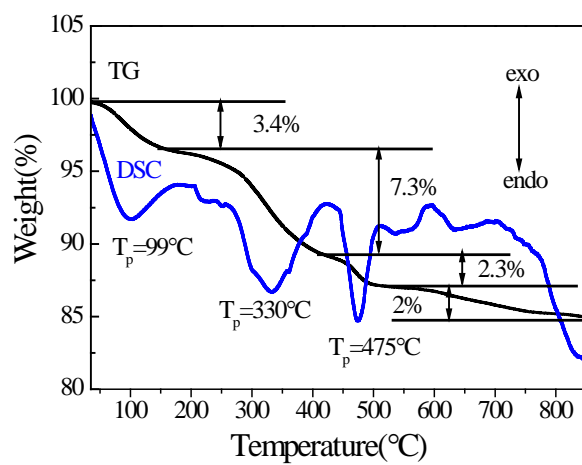


Figure S7. DTA (blue curve) and TG (black curve) analysis of the nanowire.

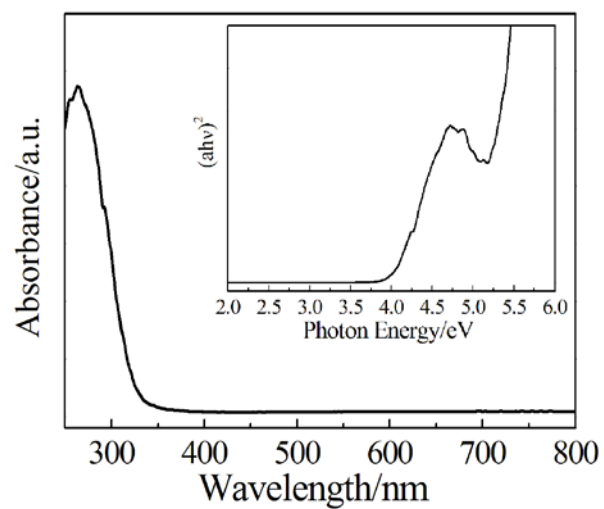


Figure S8. UV-vis adsorption spectrum of the ultrathin nanowires.

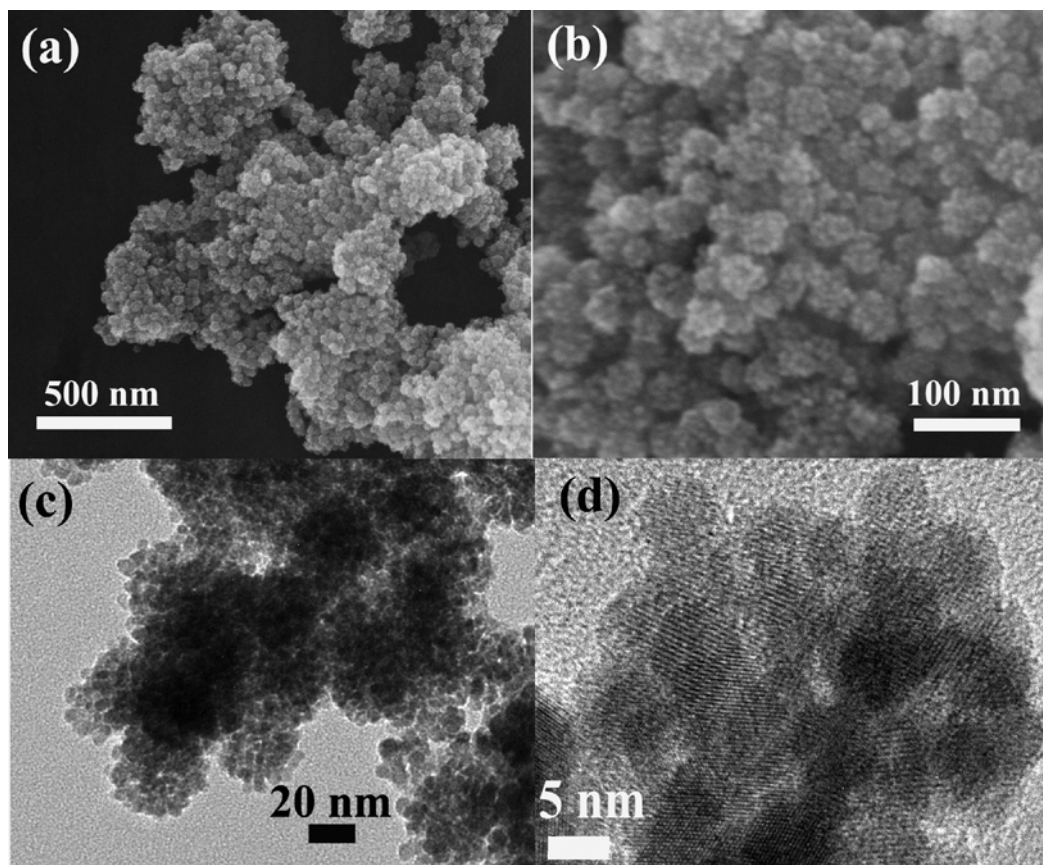


Figure S9. (a) and (b) FE-SEM images, (c) TEM and (d) HRTEM images of the In_2O_3 beads consisting of tiny nanocrystals formed with pure En as solvent.

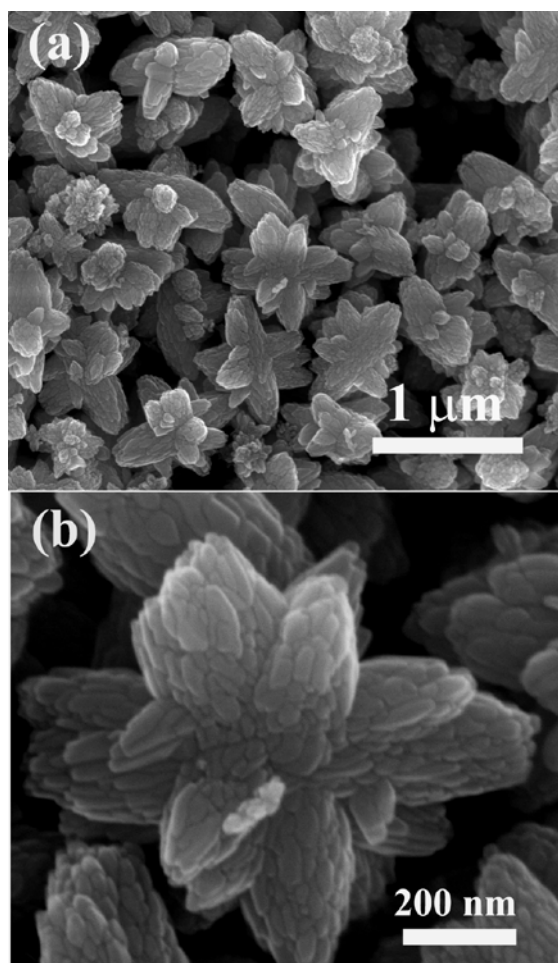


Figure S10. FE-SEM image of $\text{In}_2\text{Ge}_2\text{O}_7$ nanorod aggregates formed with pure H_2O as solvent.