Electronic Supplementary Information

Nano-size effects on CuO/TiO_2 catalysts for highly efficient H_2 production under solar light irradiation

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1. Experimental

1.1 Preparation of photocatalysts

High purity chemicals were used without further purification. Titanium dioxide nanotubes were synthesized by hydrothermal method. In a typical synthesis process, TiO_2 (Merck) µm-sized particles (2.5 g) were dispersed into 10 M NaOH aqueous solution (200 mL) in Teflon-lined autoclave (capacity 250 mL) and heated at 130°C for 20 h. The white precipitate was washed twice with distilled H_2O, dil.HCl and ethanol solution, dried at 80°C for 12 h, calcined at 350°C for 5 h @ 2°C /min. CuTNT photocatalysts were prepared by wet impregnation method. One gram of calcined TiO_2 nanotube was dispersed into appropriate concentration of $Cu(NO_3)_2.3H_2O$ aqueous solution, dried and calcined at 350°C for 5 h @ 2°C /min.

1.2. Characterization of photocatalysts

The photocatalysts were thoroughly examined using different characterization techniques. The XRD patterns were recorded on Siemens D-5000 X-ray diffracto meter. The Diffuse Reflectance UV-Visible spectra was recorded on a GBC UV-visible Cintra 10_e spectrometer, in the wavelength range 200-800 nm. BET surface area and pore size distribution were determined at liquid nitrogen temperature (77 K) using a Micromeritics ASAP 2010 system. A Philips Technai G2 FEI F12 transmission electron microscope operating at 80-100 kV was used to record the transmission electron microscopy (TEM) patterns. X-ray photoelectron spectra (XPS) were recorded on a KRATOS AXIC 165 equipped with Mg Kα radiation. All binding energies were referenced to C 1s at 284.8 eV.

1.3. Solar Photocatalytic H_2 Production

The photocatalytic experiments were carried out in Quartz reactor (volume: 150 ml). Glycerol produced in bio-diesel production was used as hole scavenger at ambient temperature and pressure. Experiments were conducted under natural solar irradiation on the terrace of Nano Catalysis Research Lab. Photocatalyst powder was dispersed in pure water or 5 vol.% glycerol-water mixture (50 mL). The solution conditioned for 30 min under dark condition followed by evacuation and purged with N_2 gas. Photocatalytic experiments are performed under magnetic stirring to maintain uniform dispersion and gas generated was collected periodically for analysis using an off-line Gas Chromatograph with TCD detector (Shimadzu GC-2014 with Molecular Sieve/5A) using N_2 as a carrier gas. The results of blank experiments revealed that the presence of photocatalyst, solar light and scavenger are essential for H_2 generation.

2. Results & Discussion

2.1. XRD Pattern

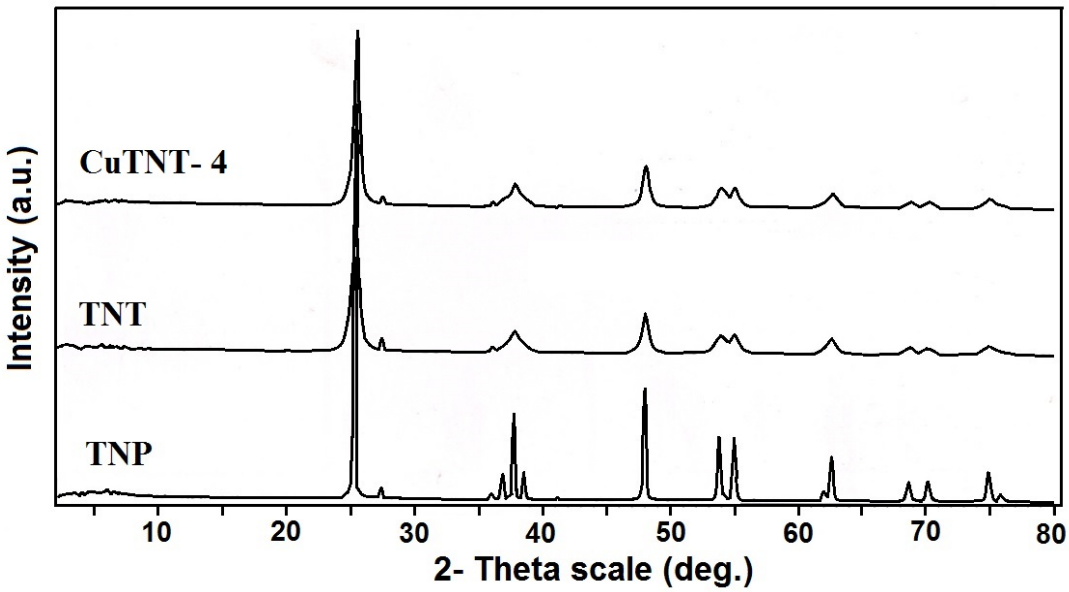
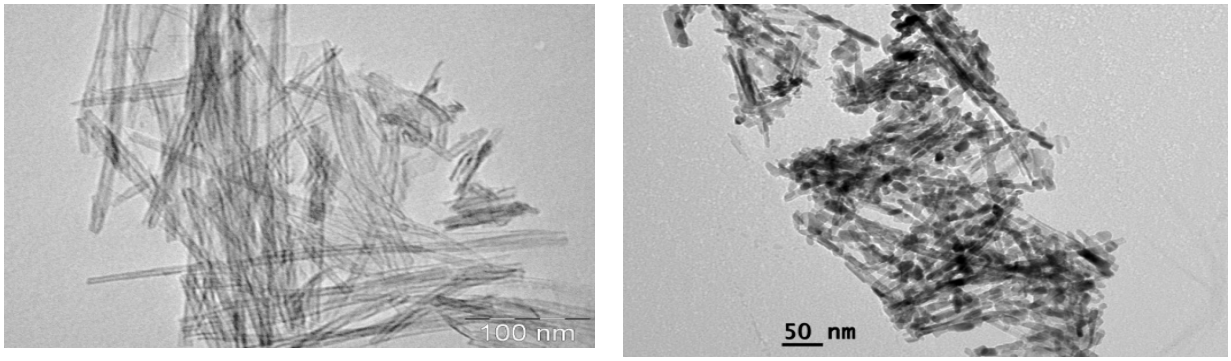


Fig. S1 XRD patterns of TNP, TNT and CuTNT-4 photocatalysts

2.2. TEM image



(a) (b)

Fig. S2 TEM images of (a) TNT (b) CuTNT-4 photocatalysts

2.3 DRS UV-Vis spectrum

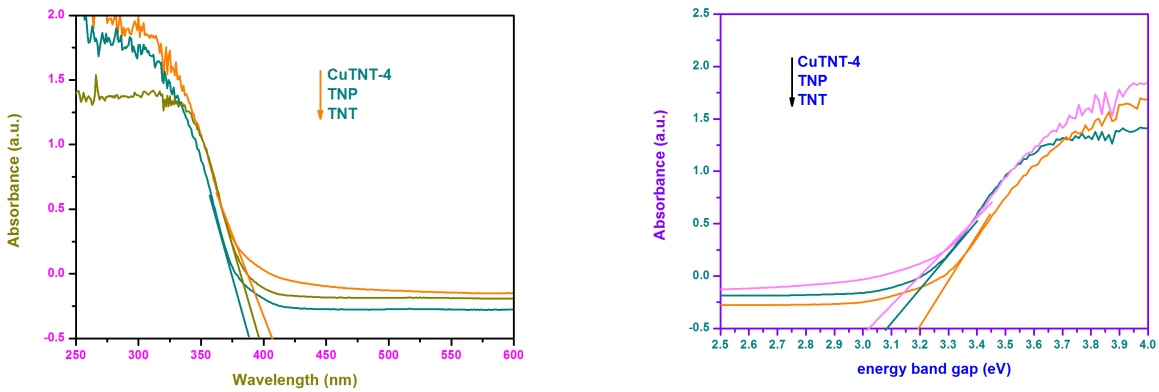


Fig. S3 DRS UV-Vis spectrum of TNP, TNT and CuTNT-4 photocatalysts

2.4 XPS Spectra:

XPS studies are conducted to understand the chemical environment of copper in optimized CuTNT-4 catalysts. XPS spectra of Ti2p, Cu2p, O1s and C1s core level are shown in Fig. S4. The characteristic peaks of C1s appear at binding energy values of 284.6, 285.7 and 287.3. The carbon peak is attributed to the residual carbon from the sample and trace hydrocarbon from XPS instrument itself. It is noticed that O1s spectra the binding energy values for O1s drift slightly toward higher binding energy values and appear at 530.69 eV. Further, it is also observed that Ti $2p_{3/2}$ and $2p_{1/2}$ binding energy values are slightly moved to higher binding energy regions and

appear at 459.476 and 465.434 eV. The measured binding energy values of Cu $2p_{3/2}$ and Cu $2p_{1/2}$ are 933.7 and 952.5 eV, confirmed the presence of CuO in CuTNT-4 catalysts.

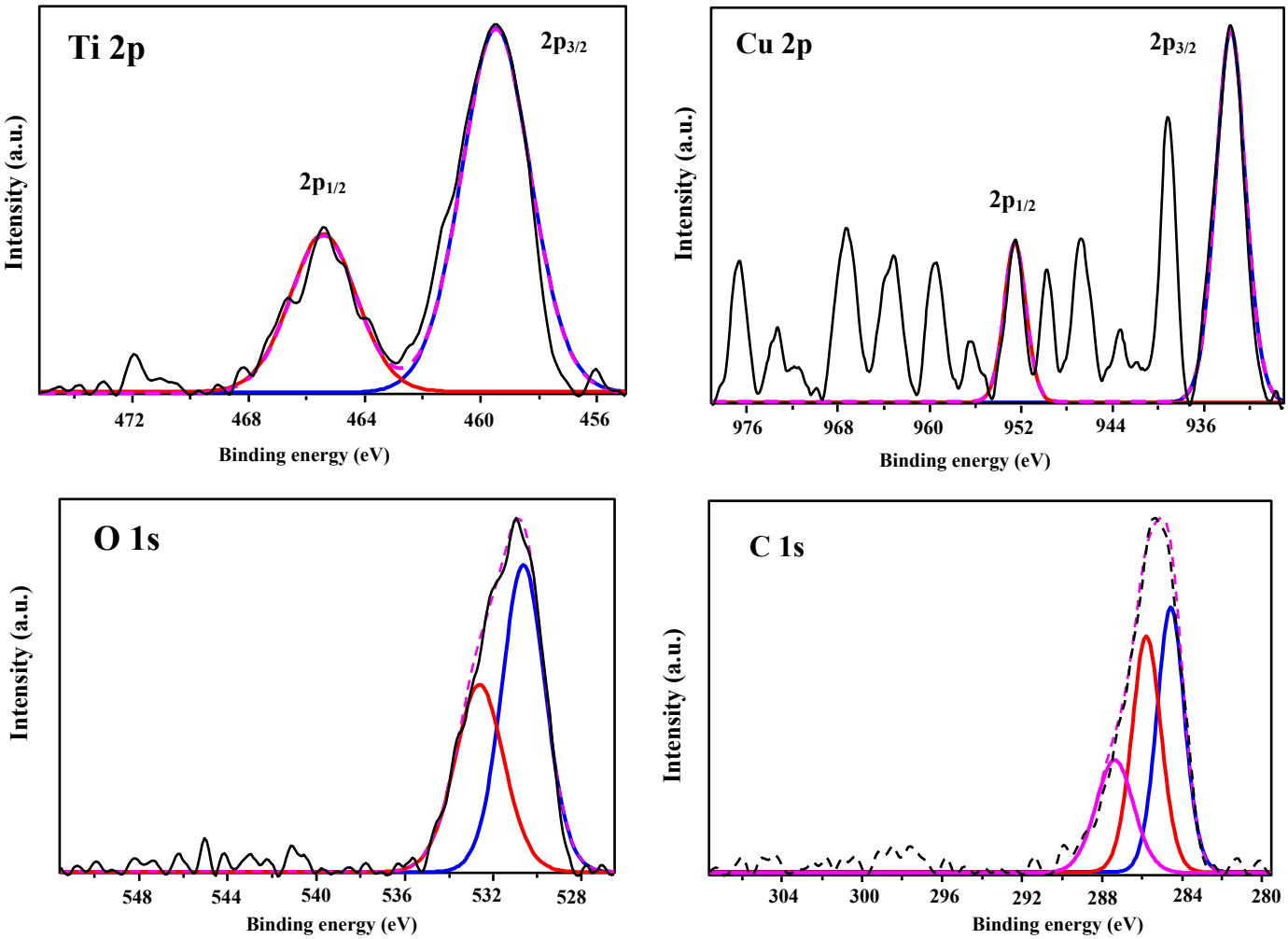


Fig. S4 XPS spectra of CuTNT-4 photocatalyst.

2.5 Effect of Copper loading

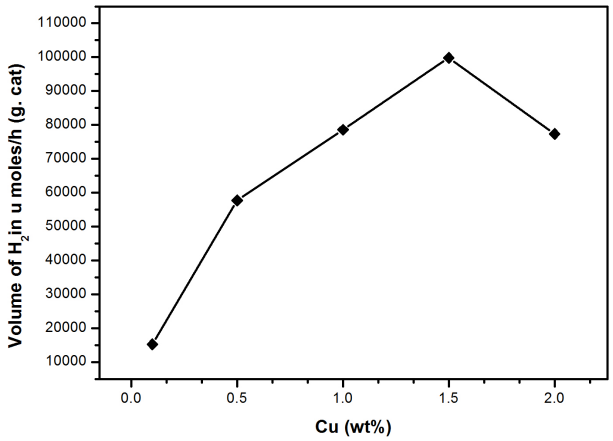


Fig.S5 Effect of copper loading in TNT photocatalyst on rate of H_2 production

2.6 Schematic diagram

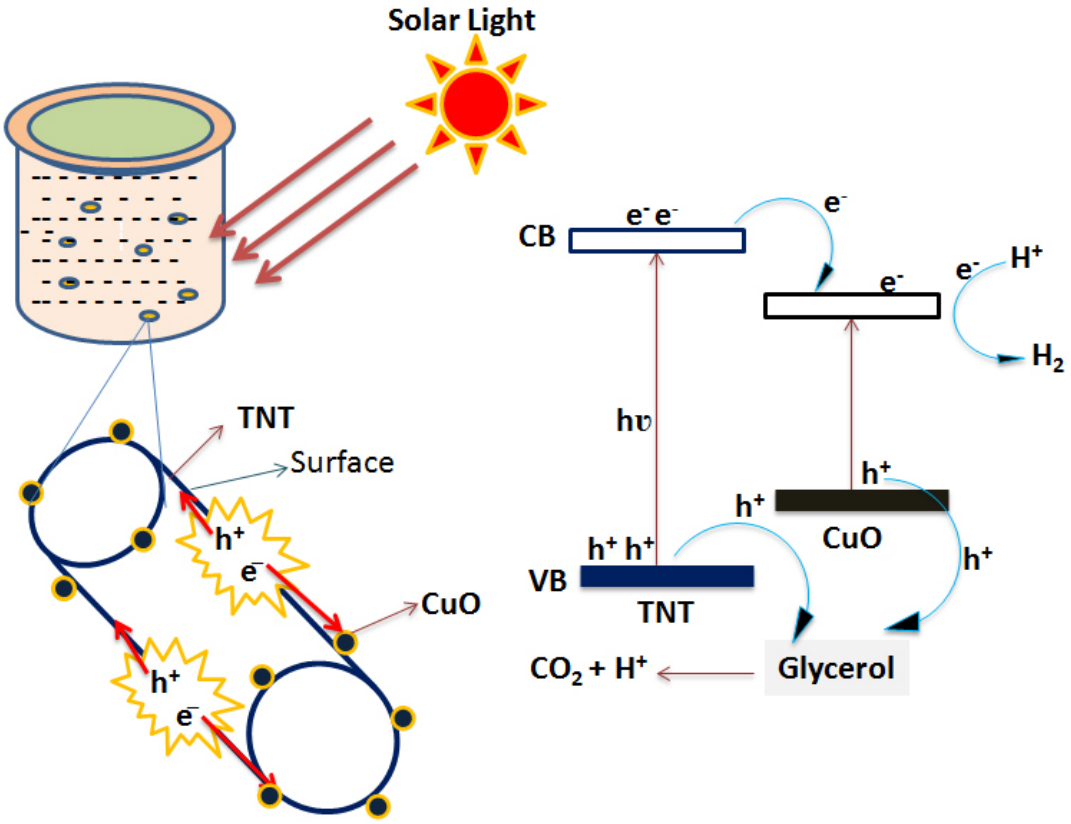


Fig. S6 Schematic diagram of band gap excitation and charge transfer processes in solar photocatalytic H_2 generation.