

Electronic Supplementary Information

Hierarchical Branching Cu₂O Nanowires with Enhanced Photocatalytic Activity and Stability for H₂ Generation

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1. Rapid preparation of Cu₂O NS-NWs, NWs and NPs.

All chemicals were of reagent grade quality and were used as received from a commercial source (Sigma-Aldrich). The formation of Cu₂O NS-NWs is based on the success in fabrication of pure Cu NWs. At first, the growth of Cu NWs was performed in a conical flask. In a typical synthesis process, NaOH (85.63 g) is dissolved in an ultrasonic bath of 250 mL of distilled water. Then, CuSO₄·5H₂O (0.44 g) is added to the sodium hydroxide solution and this mixture is transferred into the reaction flask. The reactor cell is connected to the nitrogen-pressure assembly and mechanically stirred (500 rpm) for 20 min under a nitrogen atmosphere at atmospheric pressure to obtain a homogeneous emulsion. Subsequently 2.14 mL of ethanediamine (EDA) and 0.18 mL hydrazine hydrate (HHA) are injected into the flask successively. Afterward, the flask is rotated at 80 °C for 60 min under ambient pressure with stirring and then allowed to cool to room temperature (Figure S1). The mixture is filtered and washed with ethanol and distilled water three times providing the Cu NWs. Finally, the NS-NWs can be achieved by exposing to wet air (humidity: 65% ~ 70%) at 60 °C

for 5 h. The smooth surface of as-grown $\langle 110 \rangle$ Cu NWs indicates that the crystal growth at the radial direction of the NW (in the (110) plane) is effectively turned off (Figure S2A). Because (110) is the most energetically stable plane of Cu materials, the radial growth of Cu materials is actually thermodynamically favorable. Therefore, to realize the epitaxial growth of NSs at the radial direction of NWs requires activation of the NW surface, i.e., overcoming the kinetic hindrance for the NS growth. We found that the NW surface can be activated by exposing the NW to air (Figure S2B).

We produced Cu_2O NWs with uniform diameter (110-130 nm) through the reduction of cupric acetate ($\text{Cu}(\text{Ac})_2$) with pyrrole as the reductant in aqueous solutions under hydrothermal conditions (see ref 1). Typically, 0.44 g of $\text{Cu}(\text{Ac})_2$ was dissolved in 60 mL of deionized water. Afterward, 14.6 mL of an aqueous solution of pyrrole (0.10 M) was added to this solution. The precursor mixture was transferred to a 150 mL autoclave and maintained at 200 °C for 8 h and subsequently cooled to ambient temperature naturally.

Cu_2O NPs were prepared by the capping reagent poly (vinylpyrrolidone) (PVP) originally reported in ref 2. In a typical experiment, solutions were prepared by dissolving 0.44g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 0.368g $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$, 0.288g $\text{C}_6\text{H}_{12}\text{O}_6$ in 60 ml of deionized water within conical flasks. Next, 0.007g PVP (K-30) was added to the homogeneous mixture. Then the pH value of the solution was adjusted to 12 by adding 1.0 mol/L aqueous NaOH solution and heated in a water bath at 60 °C for 1 h and allowed to cool naturally. Finally the precipitates were washed with distilled water and ethanol several times, and dried in vacuum at 25 °C for 5 h.

2. Characterization

The phase, morphology, elemental composition and structure of obtained samples were characterized by PANalytical D/max-III A XRD instrument with Cu K α radiation ($\lambda=1.5406$ Å), Netherlands FEI.Co Sirion 200 scanning electron microscopy with energy dispersive X-ray spectroscopy (EDX) and JEM-2100 transmission electron microscope at an acceleration voltage of 200 kV, respectively. The UV-Vis diffuse spectrogram analysis was carried out by using PerkinElmer LAMBDA 45 spectrophotometer in the range of 200-800 nm. XPS and X-ray induced Cu LMM Auger spectra were used to assess the chemical state and surface composition of the samples. An XPS analysis was carried out in a JPS-9010MC (Japan) with monochromatic X-ray generated from Al K α (200 W). The pressure in the analysis chamber was approximately 5×10^{-10} torr, and the pass energy constant was 20 eV for the high resolution scans.

3. Optical spectroscopy of Cu₂O NS-NWs, NPs and NWs

The ultraviolet-visible (UV-Vis) spectrum for the Cu₂O NS-NWs architecture is shown in Figure S4. Substantially, there was a blue shift for the absorption of the hierarchical branching nanostructures in comparison with that of the NPs and NWs. This indicates that the band gap energy of Cu₂O NS-NW samples in this study was increased, which was also reflected through the plot of $(\alpha E_{\text{photon}})^2$ versus E_{photon} . The direct band gap obtained from intercepts of the tangents to the plot with the abscissa is $E_g=2.53$ eV. This value is drastically larger than the bulk direct gap of 2.17 eV and absorption edge energies corresponding to the NWs (2.26 eV) and NPs (2.07 eV). Likewise, some Cu₂O NWs of thinness compare to burrs from our NS-NWs (10-25 nm) with large band gap were also reported.^[3] Previous studies

have suggested that quantum confinement arise from the size and the morphology of Cu_2O is the main factor for the effect on the band gap.^[4] A quantum confinement threshold has been deduced to be 14 nm for Cu_2O nanocrystallites.^[5] The lateral size of our on-wire NSs is between 8-12 nm. We therefore propose the quantum confinement caused by novel architecture here may be attributed to our large observed optical gap.

4. Photocatalytic reaction test

The photocatalytic reactions were carried out in a quartz reaction cell connected to a closed gas circulation and evacuation system. In order to compare the catalytic performance of the as-prepared samples, the sacrificial agent (i.e. $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$) was used in current work to react with photoinduced hole for efficiently driving hydrogen production. In our experiment, photocatalyst, 0.1 g, was dispersed in 200 mL of aqueous solution containing 0.5 M Na_2S and 0.5 M Na_2SO_3 as the sacrificial reagents. The loading of Pt was realized by *in-situ* deposition. For instance, 1mL H_2PtCl_6 aqueous solution (1mg/mL) was added dropwise to a suspension of Cu_2O NS-NWs dispersed in $\text{Na}_2\text{S}-\text{Na}_2\text{SO}_3$ aqueous solution. For the reference experiment, bare Cu_2O NWs and Cu_2O NPs were test in the same procedures. Then the mixture was deaerated under vacuum and then irradiated with 300 W Xe lamp (Perkin Elmer Technology; PE300BF) which is equipped with an optical filter (HOYA, $\lambda > 420$ nm) to cut off the light in the ultraviolet region for 30 min. Ultrasonic dispersing technology was also used to make small Pt particles. After co-loading was made, the suspension was then thoroughly irradiated by the same Xe lamp under visible or UV/Vis light. The temperature of the reaction solution was maintained at room temperature (20°C) by a flow of cooling water.

The amount of hydrogen evolved was determined with on-line gas chromatography (Agilent Technology 6820; Porapak-Q column; TCD; Ar Carrier).

References:

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3. D. P. Singh, N. R. Neti, A. S. K. Sinha, O. N. Srivastava, *J. Phys. Chem. C*, 2007, **111**, 1638.
4. C. Lu, L. Qi, J. Yang, X. Wang, D. Zhang, J. Xia, J. Ma, *Adv. Mater.*, 2005, **17**, 2562.
5. Y. Chang, J.J. Teo, H.C. Zeng, *Langmuir*, 2005, **21**, 1074.

Supporting Figures:

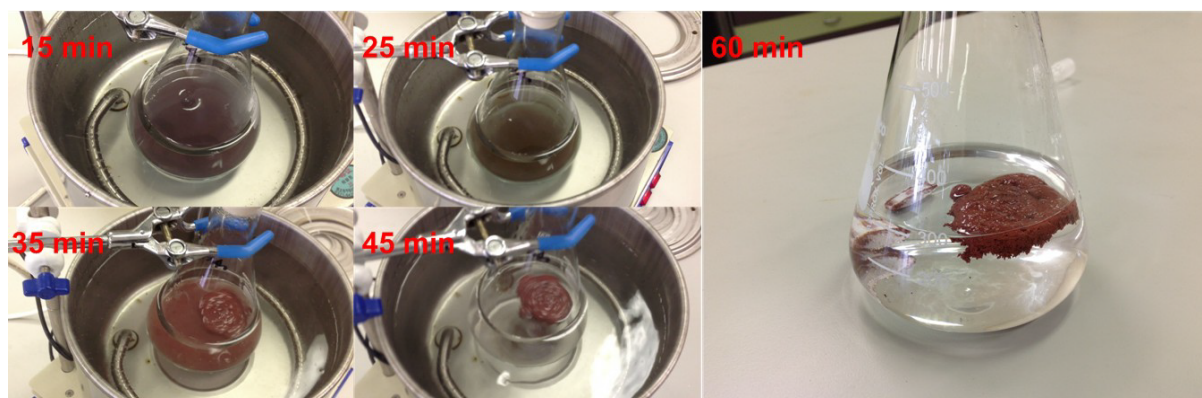


Figure S1. Digital photos of Cu NWs preparation process stages.

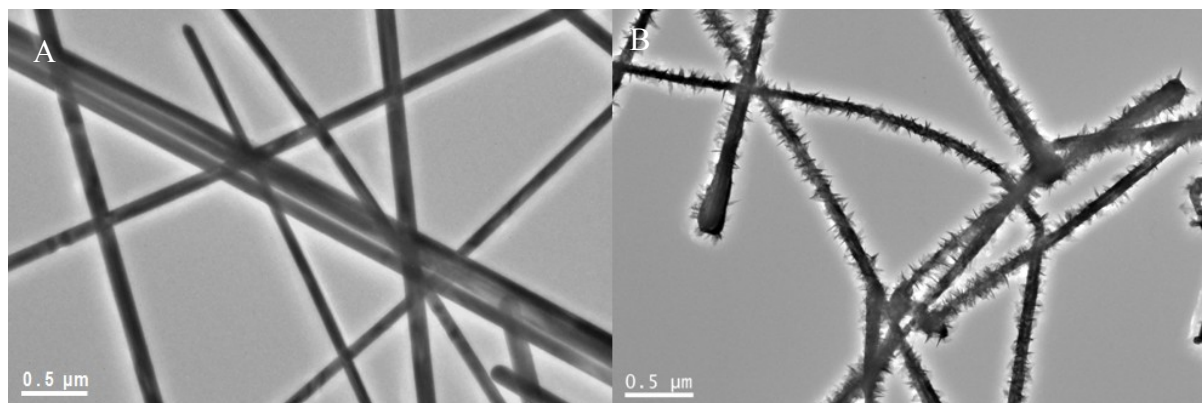


Figure S2. TEM images of NWs synthesized by using HHA at 80 ° C for 1 h A) before and B)

after wet air exposure.

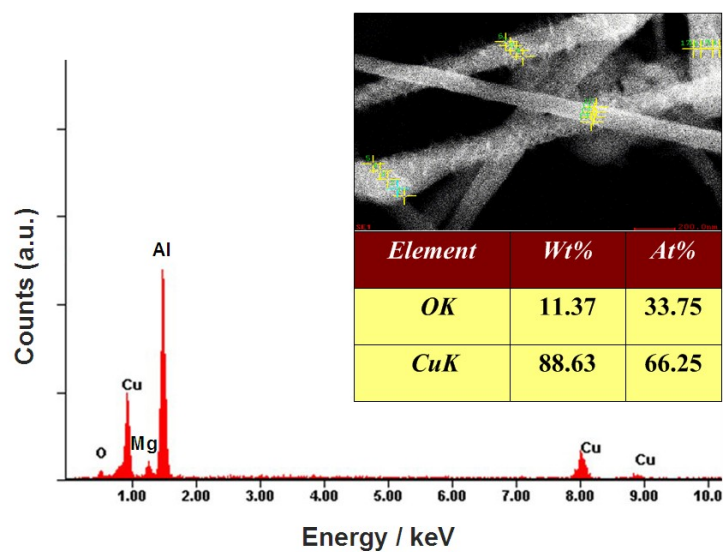


Figure S3. EDX spectrum and typical element content acquired from selected NS-NWs.

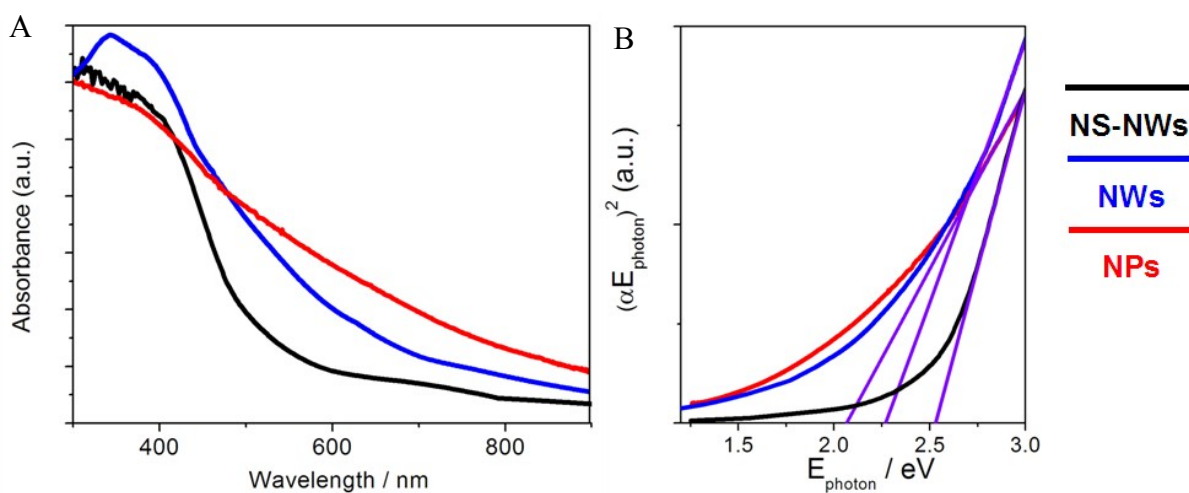


Figure S4. A) UV-Vis diffuse reflection absorptive spectra of as-obtained Cu_2O architecture (i.e. NS-NWs, NWs and NPs) and B) their corresponding band gap evaluation from the plots of $(\alpha E_{\text{photon}})^2$ versus E_{photon} .

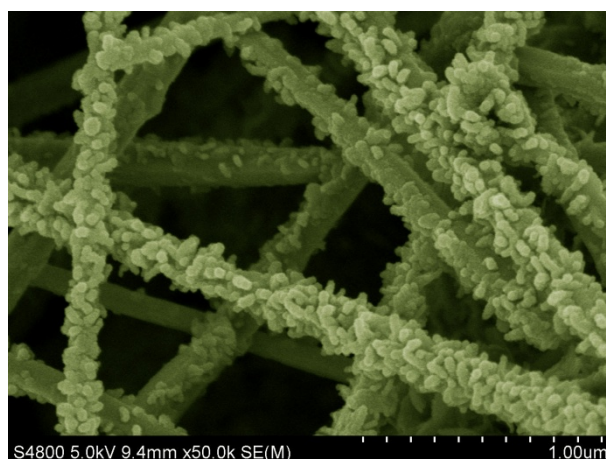


Figure S5. SEM image of as-obtained 1 wt% Pt loading Cu₂O NS-NWs after 30 min irradiation by using 300 W Xe lamp.

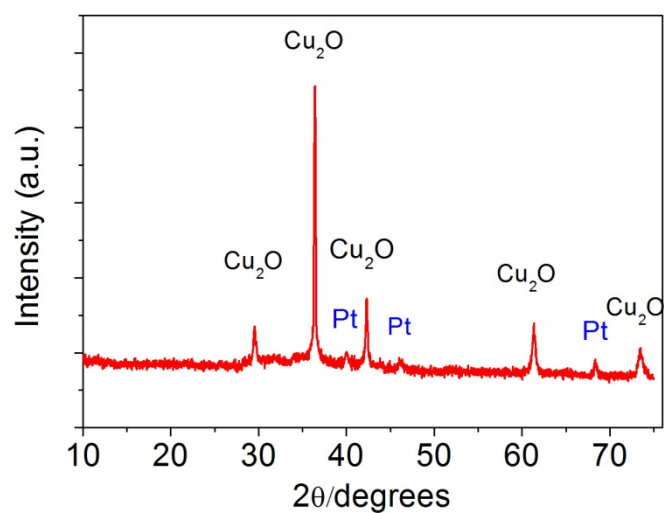


Figure S6. XRD patterns of Pt/Cu₂O NS-NWs, blue represents the peaks for Pt and black represents the peaks for the Cu₂O.

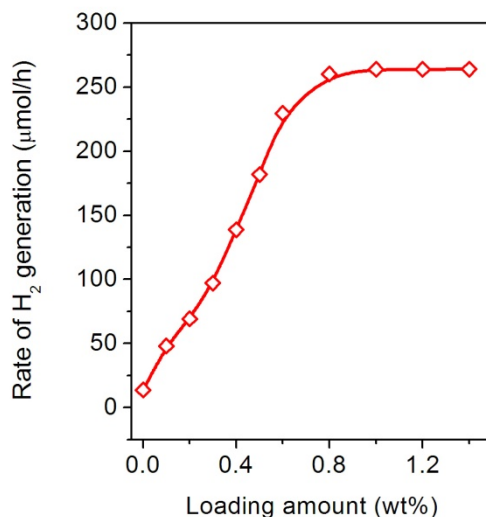


Figure S7. The dependence of the photocatalytic activity on the loading amount of Pt. Catalyst: 0.1 g; 0.5 M Na₂S-0.5 M Na₂SO₃ aqueous solution (200 mL); Light source: Xe lamp (300 W), UV-Vis region.

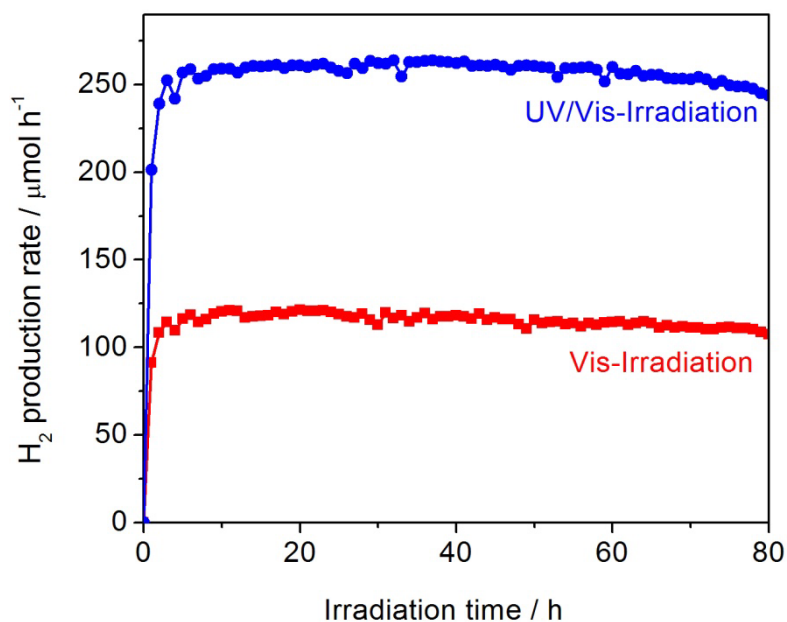


Figure S8. H₂ production rates as a function of time on photodeposited Pt/Cu₂O NS-NWs composites from Na₂S-Na₂SO₃ aqueous solutions by irradiation in the UV/Vis region (blue) or by visible light region (red).

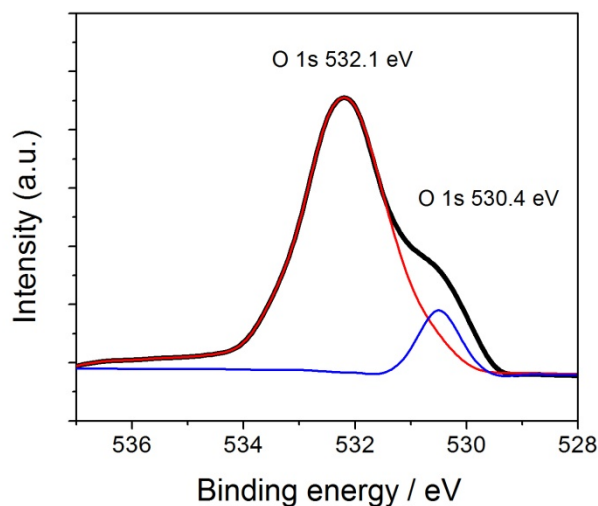


Figure S9. XPS survey (black) and curve fitting (red and blue) of O1s peak in the XPS spectra of fresh prepared Cu₂O NS-NWs. The peak at 530.4 eV is related to the oxygen in cuprous oxide, and the other peak at 532.1 eV is characteristic of oxygen contamination.

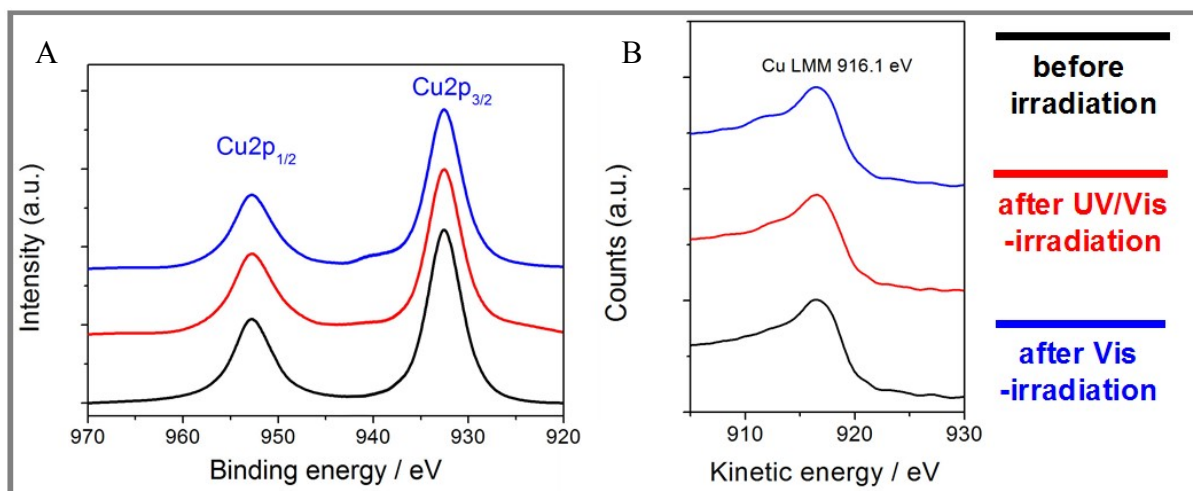


Figure S10. A) XPS spectra of Cu2p and B) Cu LMM Auger spectra before and after reaction for 80 h.