

Dual-plasmonic $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ heteronanostructures: Efficient photocatalysts for ammonia borane methanolysis dehydrogenation

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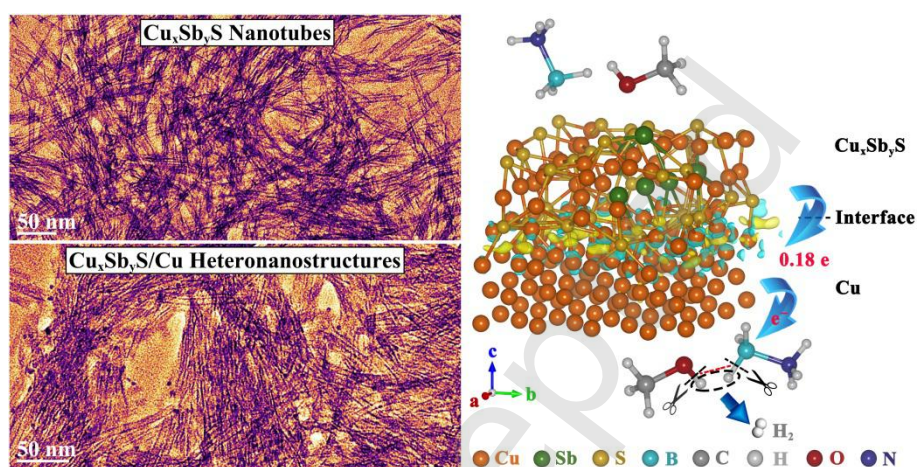
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Uniform $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ dual-plasmonic heteronanostructures synthesized by colloidal hot-injection show enhanced hydrogen production in ammonia borane methanolysis, maintaining stability. Results confirm electron transfer from $\text{Cu}_x\text{Sb}_y\text{S}$ to Cu, enabling efficient charge separation, reduced recombination, and improved stability. DFT identifies $\text{CH}_3\text{OBH}_2\text{NH}_3$ desorption, not O–H cleavage, as the rate-determining step, offering key mechanistic insights.

Dual-plasmonic Cu_xSb_yS/Cu heteronanostructures: Efficient photocatalysts for ammonia borane methanolysis dehydrogenation

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ABSTRACT: Plasmonic nanotubes are promising for photocatalysis due to their hollow structure, strong light-matter coupling, enhanced scattering, short charge paths, and abundant active sites. However, their synthesis is challenging, with few reports. Uniform Cu_xSb_yS nanotubes and Cu_xSb_yS/Cu dual-plasmonic heteronanostructures were synthesized *via* direct colloidal hot-injection by controlling reaction parameters. In ammonia borane methanol dehydrogenation, the heterostructure achieves a hydrogen production rate (690.17 mmol H₂ g⁻¹ cat. h⁻¹) 5.5× higher than Cu_xSb_yS nanotubes (126.21 mmol H₂ g⁻¹ cat. h⁻¹) and 198.9× that of Cu nanoparticles (3.47 mmol H₂ g⁻¹ cat. h⁻¹), demonstrating stability over 10 cycles. Synergistic effects drive activity: hollow structure improves light harvesting and surface exposure; Cu_xSb_yS/Cu interface enables charge separation and transfer, reducing recombination; strong plasmonic absorption enhances photon utilization. Results confirm electron transfer from Cu_xSb_yS to Cu, stabilizing nanoparticles and improving durability. Density functional theory identifies CH₃OBH₂NH₃ desorption (not O–H cleavage) as the rate-determining step, offering new mechanistic insight. This method enables applications in solar hydrogen production, environmental purification, and energy-efficient conversion for sustainable energy and green chemistry.

KEYWORDS: plasmonics, sulfide semiconductors, nanotubes, heteronanostructures, ammonia borane, photocatalytic dehydrogenation

1 Introduction

Nanomaterials exhibit unique physical and chemical properties due to their small size, high surface-to-volume ratio, quantum confinement, and macroscopic quantum tunneling effects. These enable applications in electronics, biomedicine, energy, environment, and materials science^[1]. Hollow nanostructures, such as nanospheres^[2], nanotubes^[3], nanotoroids^[4], and nanocages^[5], offer high surface area and tunable electronic properties, improving performance in catalysis, sensing, photonics, and biotechnology^[6]. Plasmonic nanomaterials support localized surface plasmon resonances (LSPR), leading to strong light-matter interactions and size- and shape-dependent optical responses, with applications in photocatalysis, photothermal therapy, bioimaging, optoelectronics, and sensing^[7–9].

Carbon nanotubes were discovered by Sumio Iijima in 1991 during arc-discharge synthesis of fullerenes^[10]. Their one-dimensional structure gives exceptional electrical,

mechanical, and chemical properties, driving extensive research^[11]. While carbon nanotube synthesis is mature, non-carbon tubular nanostructures (especially plasmonic semiconductor nanotubes) remain rare. McPhillips *et al.* fabricated ordered Au nanotube arrays using a multistep process involving deposition, etching, and electrodeposition, enhancing label-free biosensing, but the method is complex and not scalable^[12]. Sun and colleagues converted Cu nanowires into Ag nanotubes *via* template-assisted galvanic replacement^[13], followed by oxidation to form Ag@AgCl core-shell structures, though Ag degrades easily. For semiconductor nanotubes, Goddeti's group made TiO₂ nanotube arrays by anodization^[14]; Wawrzyniak *et al.* used laser irradiation to transform them into hollow nanocolumns^[15]; Grochowska *et al.* created TiO₂-nanotube/Au hybrid anodes *via* laser-induced dewetting^[16]; Sinha's team synthesized MoS₂ (or WS₂) nanotubes from MoO₃ (or WO₃) nanowhiskers using H₂S, showing strong

inter-tubular coupling^[17]. Despite these advances, direct colloidal synthesis of plasmonic sulfide semiconductor nanotubes has not been reported.

Here, we report a colloidal hot-injection method for synthesizing plasmonic copper-antimony-sulfide ($\text{Cu}_x\text{Sb}_y\text{S}$) nanotubes and dual-plasmonic $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ heteronanostructures, in which the near-infrared (NIR) LSPR arises from the $\text{Cu}_x\text{Sb}_y\text{S}$ component and the visible-range LSPR from Cu nanoparticles. By tuning the $\text{SbCl}_3/\text{CuCl}$ molar ratio, reaction temperature, and time, we obtain uniform, well-defined structures. The heteronanostructure exhibits strong LSPR in the NIR and visible ranges and is highly effective in plasmon-enhanced photocatalysis, specifically for methanolysis of ammonia borane to produce green hydrogen. Combined experimental techniques, including femtosecond transient absorption spectroscopy (fs-TA), ultraviolet photoelectron spectroscopy (UPS), and the Kubelka–Munk plot derived from visible–NIR (Vis–NIR) diffuse reflectance spectroscopy (DRS), along with theoretical simulations (finite-difference time-domain (FDTD) and density functional theory (DFT)), reveal the interfacial dehydrogenation mechanism and identify a new rate-determining step limiting overall reaction efficiency. This work offers a general approach to fabricating plasmonic semiconductor nanotubes and supports their application in advanced energy conversion.

2 Experimental section

See Supplementary Material for details (Figure S1).

3 Results and discussion

3.1 Electron microscopic characterization of plasmonic $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes.

Figure 1 shows transmission electron microscopy (TEM) images of $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes. Low- and high-resolution TEM images (Figures 1A and 1B) reveal uniform size distribution and well-defined tubular morphology. The insets show fast Fourier transform (FFT) patterns with weak diffraction spots and clear rings, confirming crystallinity but low structural order. Figures S2A and S2B display pseudo-contour and pseudo-color maps of the nanotubes in Figure 1A, improving morphological visualization. Statistical analysis (Figure S3) gives average outer and inner diameters (abbreviated as D and d) of 9.65 ± 2.75 nm and 4.88 ± 2.45 nm, respectively; wall thickness (t) is calculated as 2.38 ± 0.15 nm using $t = (D - d)/2$. Figures 1C and 1D show pseudo-color and contour plots of two isolated nanotubes (Figure 1B), highlighting their shape. High-angle annular dark-field scanning TEM (HAADF–STEM) imaging (Figure 1E) and STEM–electron energy loss spectroscopy (STEM–EELS) elemental maps (Figures 1F–1H) show uniform Sb and S distribution, while Cu is localized, confirming ternary $\text{Cu}_x\text{Sb}_y\text{S}$ structure. Energy-dispersive X-ray spectroscopy (EDS) data (Figure S4) verify the presence of Sb, Cu, and S. Atomic force microscopy (AFM) image (Figure S5A) and potential map (Figure S5B) show clear nanotube contours (white arrows). The height profile (Figure S5C) measures approximately 9.35 nm, consistent with the outer diameter from TEM.

3.2 Structural, compositional, and optical characterization of plasmonic $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes.

To investigate the crystallinity and structure of $\text{Cu}_x\text{Sb}_y\text{S}$

nanotubes, powder X-ray diffraction (XRD) was performed. Figure 2A shows distinct peaks at 37.6° , 46.3° , 48.6° , and 54.1° 2θ , matching the (8 0 4), (0 8 0), (12 0 4), and (8 4 6/8 0) facets of monoclinic djurleite-phase $\text{Cu}_{31}\text{S}_{16}$ ($\text{Cu}_{1.94}\text{S}$, JCPDS No: 23–0959), confirming the djurleite structure^[18,19]. The weak peak intensities indicate low crystallinity, consistent with FFT results (Figures 1A and 1B). Figures S6, 2B, and 2C show the X-ray photoelectron spectroscopy (XPS) survey, Sb 3d, and Cu 2p spectra. In Figure 2B, the Sb 3d_{1/2} peak at approximately 531.4 eV corresponds to Sb^{3+} , confirming +3 oxidation state^[20]. Figure 2C shows Cu 2p peaks at ~ 932.6 eV (Cu 2p_{3/2}) and ~ 952.5 eV (Cu 2p_{1/2}), with 19.9 eV spin-orbit splitting. Due to ambiguity from the Cu satellite peak (944.2 eV), the Cu LMM (L and M denote the corresponding electronic shells) Auger spectrum (Figure S7A) was analyzed, confirming dominant Cu^+ ^[20,21]. A satellite at ~ 934.8 eV suggests minor Cu^{2+} from $\text{Cu}(\text{OH})_2$ or CuO ^[22–25]. Elemental contents of Sb, Cu, and S were quantified from peak areas (Table S1). Inductively coupled plasma – atomic emission spectroscopy (ICP–AES) confirmed the composition as $\text{Cu}_{1.74}\text{Sb}_{0.19}\text{S}$, consistent with XPS and EDS. Unless noted, $x = 1.74$ and $y = 0.19$ in $\text{Cu}_x\text{Sb}_y\text{S}$. Figure 2D shows the Vis–NIR DRS with a broad plasmonic absorption peak at ~ 1796 nm (full width at half maximum (FWHM): 0.45 eV)^[20]. The NIR plasmonic absorption peak position of $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes is determined by fitting the experimental spectrum in Figure 2D (red curve), corresponding experimental and fitting parameters are listed in Table S2. Figures 2E and 2F present Brunauer–Emmett–Teller (BET) N_2 adsorption-desorption isotherms and pore size distribution. The BET surface area is $12.90 \text{ m}^2 \text{ g}^{-1}$, average pore diameter 3.05 nm, classifying the material as mesoporous. Pore volume and specific surface area are $1.40 \times 10^{-2} \text{ cm}^3 \text{ g}^{-1}$ and $1.22 \text{ m}^2 \text{ g}^{-1}$ (Table S3).

To assess synthesis reproducibility, controlled experiments varied only the $\text{SbCl}_3:\text{CuCl}$ molar ratio, keeping sulfur dose, temperature, and time constant (Figures S8–S10). Results show this ratio critically controls morphology and crystalline phase. Nanotubes with djurleite structure formed only when $n(\text{SbCl}_3):n(\text{CuCl})$ was between 80:20 and 95:5 (Figure S8). Below 80:20, quasi-circular nanoplatelets of rhombohedral Cu_9S_5 formed^[20]. Between 95:5 and 100:0, orthorhombic Sb_2S_3 nanosheets formed (Figure S9), showing no Vis–NIR plasmonic absorption (Figure S10). Thus, precise precursor ratio control is essential for synthesizing plasmonic $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes.

3.3 Electron microscopic characterization of dual-plasmonic $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ heteronanostructures.

Figure 3 shows TEM images of $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ heteronanostructures. Figures 3A, 3B, and S11 display low- and high-magnification TEM images, pseudo-contour plots, and pseudo-color potential maps at various resolutions. Under xenon lamp irradiation, Cu nanoparticles are primarily located at the tips of the $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes, forming a stable semiconductor/metal heterojunction. Size distributions of end-anchored Cu domains in heteronanostructures are shown in Figure S12. Insets in Figures 3A and 3B, and Figure 3D show the corresponding FFT patterns, featuring faint crystalline spots and strong amorphous rings, indicating weak crystallinity. Figure 3C

presents a high-resolution TEM image of the tubular/quasi-spherical heterostructure, revealing clear tube walls, cavity contours, and end-anchored Cu domains. Figures 3E–3H show HAADF–STEM and STEM–EELS elemental maps. S forms the nanotube framework^[26], Sb is uniformly distributed, and Cu is concentrated at nanoparticle tips and specific lattice sites, confirming successful synthesis of $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ heteronanostructures.

3.4 Structural, compositional, and optical characterization of dual-plasmonic $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ heteronanostructures.

To better understand the $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ heteronanostructures, comprehensive performance evaluations were conducted. Results are summarized in Figure 4. Figure 4A shows the XRD pattern of the heteronanostructures. Peaks at 27.9° , 29.3° , 31.5° , 37.6° , 46.3° , 48.6° , 54.0° , and 61.2° 2θ correspond to the (3 3 3), (4 4 2), (1 3 4), (8 0 4), (0 8 0), (12 0 4), (8 4 6), and (8 8 4) facets of monoclinic djurleite-phase $\text{Cu}_{31}\text{S}_{16}$ (JCPDS No: 23–0959)^[27]. Peaks at 43.3° , 50.4° , and 74.1° match the (1 1 1), (2 0 0), and (2 2 0) facets of cubic Cu (JCPDS No: 89–2838)^[28]. Peaks at 36.4° and 42.3° are assigned to the (1 1 1) and (2 0 0) facets of cubic cuprite-phase Cu_2O (JCPDS No: 78–2076), indicating partial oxidation of Cu^[29]. These results confirm that the $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes retain the djurleite-phase and the tip-anchored Cu nanoparticles exhibit a cubic Cu structure, verifying successful synthesis of crystalline $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ heteronanostructures.

Figures S13, 4B, and 4C show the XPS survey, Sb 3d, and Cu 2p spectra. In Figure 4B, two peaks at 530.2 eV and 539.5 eV with 9.3 eV spin-orbit splitting are assigned to Sb 3d_{1/2} and Sb 3d_{3/2}, confirming Sb³⁺ as the dominant state^[30]. Compared to pure $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes, a 1.2 eV shift to lower binding energy suggests partial reduction of Sb in the heterostructure^[31]. Figure 4C shows Cu 2p peaks at 932.5 eV (Cu 2p_{3/2}) and 952.4 eV (Cu 2p_{1/2}), indicating Cu⁺ in the nanotubes^[23,32]. The “Cu CT” peak at 949.5 eV arises from charge-transfer transitions between Cu⁺ and Cu²⁺ in the $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ heteronanostructure. Peak splitting reflects (i) coexistence of Cu⁺/Cu²⁺ valence states and (ii) their distinct local coordination environments^[9,33]. Cu⁺ occupies tetrahedral sites coordinated by S²⁻, Cu²⁺ resides at interstitial or off-center positions near Cu vacancies, enabling charge compensation and stabilizing the non-stoichiometric phase^[26]. In the plasmonic $\text{Cu}_x\text{Sb}_y\text{S}$ lattice, Cu vacancies generate localized positive charges, prompting oxidation of neighboring Cu⁺ to Cu²⁺ for charge neutrality^[34]. Consistent with XPS (no isolated Cu²⁺ signal) and electron paramagnetic resonance (EPR, no corresponding signal, Figure S14) spectrum, Cu²⁺ is not isolated but strongly coupled to adjacent Cu⁺. Cu⁺ has a closed-shell 3d¹⁰ configuration, whereas Cu²⁺ has an open-shell 3d⁹ configuration with a vacant orbital. This drives delocalization of 3d electrons from Cu⁺ into Cu²⁺'s vacant orbitals, forming antiferromagnetically coupled Cu⁺•Cu²⁺ pairs^[18]. Mobile charge carriers migrate across the heterojunction to the Cu nanoparticle surface, enhancing structural stability and oxidation resistance. The Cu⁺•Cu²⁺ couple is the primary redox-active catalytic center^[35], where synergistic electron transfer facilitates reactant adsorption and activation. The peak at 932.6 eV (red arrow, Figures S13

and S15A) confirms Cu⁰ from metallic nanoparticles^[36,37]. The Auger peak at ~ 918.9 eV (Figure S16) further supports Cu⁰ presence^[38]. The absence of a peak at ~ 934.8 eV indicates no detectable Cu²⁺, suggesting suppressed oxidation and enhanced chemical stability^[22,39]. Elemental compositions from peak integrals agree well with EDS data (Figure S17), though slight differences exist compared to $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes (Table S1).

Figure 4D shows the Vis–NIR DRS spectrum with two absorption peaks: one at ~ 1734 nm (FWHM: 0.44 eV, fitted curve overlaid on experimental spectrum, parameters in Table S4) in the NIR, attributed to plasmonic absorption in Cu-vacancy-rich $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes^[20]; the other at ~ 504 nm in the visible range, due to plasmonic resonance of Cu nanoparticles^[40]. Together, they confirm broadband dual-plasmonic absorption, enabling efficient light harvesting across Vis–NIR for photocatalytic methanolysis of ammonia borane (AB) to produce hydrogen. Figures 4E and 4F show BET N₂ adsorption-desorption isotherms and pore size distribution. The BET surface area is 51.57 m² g^{−1}, average pore diameter 9.57 nm, classifying the material as mesoporous. Pore volume and specific surface area are 0.145 cm³ g^{−1} and 34.50 m² g^{−1} (Table S3). For comparison, BET data for plasmonic Cu nanoparticles are also listed in Table S3, with full characterization provided in the Supplementary Material (Figures S7, S12, S15, S18–S20, Tables S3, S5).

3.5 Femtosecond transient absorption dynamics.

Ultrafast carrier relaxation dynamics in dual-plasmonic $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ heteronanostructures is critical for understanding carrier lifetime and interfacial charge transfer. To probe plasmon-driven relaxation, femtosecond transient absorption (fs-TA) spectroscopy was performed on the heteronanostructure and compared with pure $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes. Excitation was set at 800 nm (~ 1.55 eV), an energy below both the $\text{Cu}_x\text{Sb}_y\text{S}$ band-edge onset and the visible plasmonic absorption of the Cu nanoparticles, yet still sufficient to excite $\text{Cu}_x\text{Sb}_y\text{S}$ NIR plasmonic resonance^[41]. At this wavelength, free electrons near the Fermi level are promoted into virtual high-energy plasmonic states, generating hot electrons. In the heteronanostructure, these hot electrons rapidly cross the interface barrier and transfer to the Cu Fermi level, dissipating within nanoseconds instead of relaxing back to the $\text{Cu}_x\text{Sb}_y\text{S}$ ground state.

fs-TA spectra were acquired at multiple time delays (Figures 5A and 5B), and kinetics at the main bleach peak (~ 2.46 eV, 504 nm) and the transient absorption peak (~ 2.73 eV, 455 nm) were extracted and fitted to obtain carrier lifetimes (Figures 5C, 5D, and Table S6). The bleach signal aligns closely with the Vis–NIR absorption (Figures 2D and 4D) and matches the DRS-determined bandgap maximum (Figure 6D). Both samples show a negative bleach at 2.46 eV (ground-state depletion of $\text{Cu}_x\text{Sb}_y\text{S}$) and a positive shoulder at 2.73 eV (hot-electron relaxation, possibly involving interband transitions)^[42].

In aqueous dispersion, the $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ heteronanostructures exhibit a markedly extended excited-state lifetime (8596 ± 1668 ps, Table S6), with clear bleach and TA signals persisting beyond 3000 ps (Figures 5B and 5D). In contrast, pure $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes decay rapidly (956

± 113 ps, Table S6) and return to the ground state approximately an order of magnitude faster (Figures 5A and 5C). This stark contrast confirms that the heterointerface suppresses recombination and enables efficient interfacial charge transfer, which is key to the enhanced dehydrogenation activity in AB methanolysis. The underlying mechanism is detailed in Sections 3.6–3.9.

3.6 $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ interfacial charge transfer mechanism.

To investigate the interfacial charge transfer mechanism in the $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ heteronanostructures, the work functions (ϕ , see Table S7 for term definitions) of $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes and Cu nanoparticles, along with the band structure of $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes, were examined. The experimental results are presented in Figure 6. Based on the ultraviolet photoelectron spectroscopy (UPS, Figures 6A–6C) and the band gap of 1.71 eV derived from the Kubelka–Munk plot (Figure 6D), the valence band maximum (VBM) and conduction band minimum (CBM) of $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes are determined to be -1.28 eV and 0.43 eV, respectively, relative to the Fermi level (E_F). This specific band structure endows $\text{Cu}_x\text{Sb}_y\text{S}$ with sufficient reduction ability, enabling it to activate and dehydrogenate AB and methanol, generating active intermediates such as hydrogen radicals ($\bullet\text{H}$), BH_2NH_3 radicals ($\bullet\text{BH}_2\text{NH}_3$), and methoxy radicals ($\bullet\text{OCH}_3$), which are ultimately converted into H_2 and $\text{CH}_3\text{OBH}_2\text{NH}_3$. These findings are crucial for studying the AB–methanol hydrogen production process and understanding its underlying mechanism.

From the calculated electrostatic potential energy, the work functions of $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes and Cu nanoparticles are 4.46 eV and 4.12 eV, respectively (Figure 6E), indicating that the E_F of $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes is lower than that of Cu nanoparticles. During the composite formation and contact process (Figure 6E, left and middle panels), the E_F difference drives electron transfer from Cu nanoparticles to $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes near the interface, thereby forming a built-in electron (Fermi potential) field (BIEF) directed from Cu to $\text{Cu}_x\text{Sb}_y\text{S}$ and causing band bending of $\text{Cu}_x\text{Sb}_y\text{S}$ at the interface (Figure 6E, middle panel)^[43,44]. Under light irradiation (Figure 6E, right panel), electrons in the valence band (VB) of $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes are photoexcited to the conduction band (CB), leaving holes in the VB. Owing to the synergistic effect of the BIEF and band bending, the photogenerated electrons in the CB migrate across the interfacial potential barrier to the adjacent Cu nanoparticle surface, while the photogenerated holes remain in the VB. This interfacial charge transfer pathway indicates the formation of a Schottky heterojunction between $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes and Cu nanoparticles, which facilitates efficient separation and transfer of photogenerated charge carriers in $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes and enhances their participation in the subsequent AB–methanol dehydrogenation reaction (see Sections 3.7–3.9 below).

3.7 Photocatalytic AB dehydrogenation in methanolysis and recyclability.

It is well established that semiconductor/metal heterostructures with high surface areas reduce interfacial potential barriers and promote charge carrier separation and transport, significantly enhancing catalytic performance^[7,45]. Here, a dual-plasmonic $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$

heteronanostructure was used as a model system to evaluate photocatalytic dehydrogenation of AB in methanolysis. Hydrogen is a promising clean energy carrier, but efficient storage and release remain major challenges. AB has attracted attention due to its high hydrogen content (19.6 wt%), low molecular weight (30.87), solution stability, and potential reversibility^[46–48]. However, activating the AB– CH_3OH system for hydrogen production remains challenging.

To address this, we designed and synthesized a dual-plasmonic $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ heteronanostructure that achieved a hydrogen production rate of $690.17 \text{ mmol H}_2 \text{ g}^{-1} \text{ cat. h}^{-1}$, 5.5 and 198.9 times higher than plasmonic $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes and Cu nanoparticles, respectively (Figure 7A, Table S8). Cu nanoparticles showed negligible activity due to low surface area, oxidation, and aggregation, which degrade plasmonic properties^[49]. Thus, the $\text{Cu}_x\text{Sb}_y\text{S}$ nanotube surface serves as the primary catalytic site^[23,50], supported by surface area data (Figures 4E, 2E, S15C, Table S3). We compared this catalyst with 35 reported systems (Catalysts 1–35) for AB methanolysis (or hydrolysis). The results (Figure 7A, Table S8) show the $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ heteronanostructure greatly enhances hydrogen evolution, owing to rational heterostructure design and synergistic dual plasmonic effects that improve charge separation and photocatalytic efficiency.

Beyond activity, stability under cycling is critical. Figure 7B shows the recyclability over ten cycles. After ten runs, the hydrogen production rate retains 83.1% of the initial value, indicating good cycling stability. The heterostructure also enhances antioxidation stability of Cu nanoparticles. In conventional systems, Cu nanoparticles oxidize or aggregate due to surface electron loss, forming unstable $\text{Cu}_2\text{O}/\text{CuO}$ layers that promote degradation^[40,49,51]. By contrast, maintaining surface electron neutrality or enrichment (enabled by engineered interfaces) suppresses sintering and improves thermal stability^[52]. In this work, interfacial electronic modulation directs electron transfer from $\text{Cu}_x\text{Sb}_y\text{S}$ to Cu, creating an electron-enriched state on Cu nanoparticles. XPS, fs-TA, and DFT results confirm this charge transfer, enhancing structural robustness and practical viability.

3.8 Plasmonic near-field enhancement.

The electronic states at the interface between plasmonic nanostructures and molecules are primarily driven by the plasmonic electric field^[53]. The confined plasmonic field carries sufficient energy to selectively excite and activate specific chemical bonds in target molecules^[54]. Field intensity decays exponentially with distance from the surface, generating a strong gradient force that traps and polarizes molecules, enhancing their accumulation and response in hotspots^[55,56]. Here, the finite-difference time-domain method was used to simulate the plasmonic fields of $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ and map surface electric field distribution. Results are shown in Figures 8A–8C. Figures 8A and 8B show nearly identical near-field enhancement (NFE, factor = 5.3) in the xy and xz planes, where the incident electric field (EF) is aligned and wave vectors (k) are perpendicular, due to geometric symmetry, uniform elemental distribution, and isotropic dielectric response^[30,41]. Figure 8C shows weaker

enhancement (factor = 3.2) in the yz plane, where the EF is orthogonal and k orientation is perpendicular or parallel. The comparison reveals strong anisotropy: axial enhancement exceeds radial enhancement by $\sim 65.6\%$, with peak intensity localized at the heterointerface and nanotube/nanoparticle ends. This reflects synergistic plasmonic localization driven by interfacial charge separation and end-field confinement, accelerating interfacial charge transfer and yielding superior performance to pure-phase $\text{Cu}_x\text{Sb}_y\text{S}$ under identical conditions.

The $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ exhibits strong NFE, enabling efficient charge generation, molecular adsorption, and selective bond activation. Strong interactions with $\text{AB}/\text{CH}_3\text{OH}$ form a stable complex ($\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}-\text{AB}/\text{CH}_3\text{OH}$), promoting B–H bond activation in AB and O–H bond activation in adjacent CH_3OH through plasmon-mediated energy transfer, significantly boosting photocatalytic dehydrogenation efficiency. While similar to the CuAg -catalyzed pathway reported by Tong *et al.*^[57], key differences remain. The mechanism is illustrated in Figures 8D and 8E and detailed in Section 3.9.

3.9 DFT calculations and photocatalytic dehydrogenation mechanism.

To clarify the catalytic enhancement mechanism of $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ in Vis–NIR $\text{AB}/\text{CH}_3\text{OH}$ dehydrogenation, DFT calculations were performed (Section 2.5; Figures 8, S21–S23, and Table S9), focusing on surface interactions, reaction pathways, charge transfer, and Bader charges. Figure S21 shows AB adsorption energy (E_{ads}) on $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ is -0.577 eV, weaker than -0.702 eV on pristine $\text{Cu}_x\text{Sb}_y\text{S}$; CH_3OH E_{ads} is -0.952 eV *versus* -1.026 eV, indicating preferential adsorption on Cu-vacancy-rich $\text{Cu}_x\text{Sb}_y\text{S}$ rather than Cu nanoparticles. AB binds more weakly than CH_3OH on both materials, so CH_3OH occupies active sites more readily. The B–H bond in AB (~ 3.5 eV) is weaker than the O–H bond in CH_3OH (~ 4.8 eV), making it easier to cleave and generate radicals ($^*\text{BH}_2\text{NH}_3 + ^*\text{H}$). Thus, the $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ heterojunction enhances catalysis by tuning adsorption and promoting dehydrogenation.

Figures 8D and 8E depict the plasmon-enhanced mechanism for AB methanolysis. In $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes, rapid recombination of photogenerated carriers under illumination limits catalytic activity and H_2 production rate (Figure 7A, Table S8). Plasmonic Cu nanoparticles show almost negligible activity and poor stability. In contrast, the $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ heteronanostructure uses hot electrons and localized electric fields (Figures 8A–8C) to boost hydrogen evolution. DFT (Figure 8D) confirms AB and CH_3OH stably adsorb, forming $^*\text{BH}_3\text{NH}_3 + ^*\text{CH}_3\text{OH}$ complexes near plasmonic hotspots (* :bare catalyst; * :adsorbate: non-adsorbed; * :adsorbate: adsorbed). Hot electrons inject directly into adsorbed molecules, lowering activation barriers and weakening bonds^[58]. High-energy electrons fill unoccupied orbitals, generating transient species ($^*\text{BH}_3\text{NH}_3 + ^*\text{CH}_3\text{OH}$) and accelerating B–H/O–H bond weakening^[59,60]. Direct “plasmonic structure $\rightarrow$ AB” charge transfer remains dominant. O–H activation is key, its oxidation addition supports the reductive cycle^[61]. While O–H cleavage was once rate-limiting in $\text{Cu}_3\text{Mo}_2\text{O}_9/\text{NiMoO}_4$ ^[62], here, the barrier drops from 0.67 eV to 0.37 eV, while

$\text{CH}_3\text{OBH}_2\text{NH}_3$ desorption decreases only slightly ($1.32 \rightarrow 1.18$ eV), making desorption the new rate-determining step (RDS). This shift explains the enhanced activity. Under $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$, all B–H and O–H transition states have lower free energies than reactants, confirming spontaneous, efficient activation. The hydridic B–H bond enables hydrogen bonding ($\text{CH}_3\text{O}-\text{H}\cdots[\text{HBH}_2\text{NH}_3]$)^[63,64]. $^*\text{BH}_3\text{NH}_3$ then reacts with $^*\text{CH}_3\text{OH}$ to form $^*\text{CH}_3\text{OBH}_2\text{NH}_3$, releasing H_2 *via* $^*\text{BH}_2\text{NH}_3$ and $^*\text{CH}_3\text{O}$. Structures are shown in Figures S22 and S23. Sequential reactions with additional $^*\text{CH}_3\text{OH}$ yield up to three H_2 equivalents per cycle.

Differential charge density analysis shows $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ strongly modulates interfacial electronic structure^[60]. Figure 8E reveals charge buildup on Cu and depletion on $\text{Cu}_x\text{Sb}_y\text{S}$, confirming electron transfer and redistribution. Cu vacancies enhance this effect, with a Bader charge difference (Δq) of 0.18 e (Table S9), consistent with XPS. Excess electrons on Cu stabilize the heterojunction, improving AB methanolysis durability.

4 Conclusions

This study reports the synthesis of uniform plasmonic $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes and dual-plasmonic $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ heteronanostructures *via* a direct colloidal hot-injection method by controlling precursor ratios, temperature, and time. The structures are reproducible and controllable. In photocatalytic dehydrogenation of ammonia borane in CH_3OH , the $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ heterostructure achieves a hydrogen production rate 5.5 times higher than $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes and 198.9 times higher than Cu nanoparticles, with stable performance over ten cycles. Enhanced activity arises from synergistic effects: the hollow structure increases surface area and light harvesting; the $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ interface enables charge separation and directional electron transfer, reducing recombination; strong LSPR absorption in the near-infrared to visible range improves photon utilization. Experimental and theoretical calculations confirm that electron transfer from $\text{Cu}_x\text{Sb}_y\text{S}$ to Cu stabilizes Cu nanoparticles and significantly enhances the system’s stability and durability. DFT identifies desorption of $\text{CH}_3\text{OBH}_2\text{NH}_3$ (not O–H bond cleavage) as the rate-determining step, offering new mechanistic insight. This scalable strategy allows precise control over plasmonic tubular nanostructures, supporting their application in solar hydrogen production, environmental remediation, and energy-efficient chemical conversions for sustainable energy and green chemistry.

Electronic Supplementary Material: Supplementary material (including Experimental section, Figures S1–S23, Tables S1–S9, and Supplementary References) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94908963>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and/or the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

Guoning Liu: Conceptualization, data curation, formal analysis, funding acquisition, investigation, methodology, project administration, supervision, validation, visualization, writing – original draft, writing – review & editing. **Dan Wang:** Data curation, writing – review & editing. **Yihe Zhu:** Data curation, investigation. **Chaonan Zeng:** Investigation. **Yujin Li:** Writing – review & editing. **Shaopeng Qi:** Investigation. **Chongyi Ling:** Software. **Xiuyun Zhang:** Software. All the authors have approved the final manuscript.

^ΔThese authors contributed equally to this work.

Informed consent

Not applicable.

Ethics statement

Not applicable.

Use of AI statement

None.

Abbreviations

Localized surface plasmon resonances (LSPR), copper-antimony-sulfide ($\text{Cu}_x\text{Sb}_y\text{S}$), near-infrared (NIR), finite-difference time-domain (FDTD), density functional theory (DFT), transmission electron microscopy (TEM), fast Fourier transform (FFT), outer diameter (D), inner diameter (d), thickness (t), high-angle annular dark-field scanning TEM (HAADF-STEM), electron energy loss spectroscopy (EELS), energy-dispersive X-ray spectroscopy (EDS), atomic force microscopy (AFM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), inductively coupled plasma – atomic emission spectroscopy (ICP-AES), visible-near infrared diffuse reflectance spectroscopy (Vis-NIR DRS), full width at half maximum (FWHM), Brunauer-Emmett-Teller (BET), electron paramagnetic resonance (EPR), femtosecond transient absorption (fs-TA), ultraviolet photoelectron spectroscopy (UPS), valence band maximum (VBM), conduction band minimum (CBM), ammonia borane (AB), near-field enhancement (NFE), adsorption energy (E_{ads}), rate-determining step (RDS).

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FIGURES.

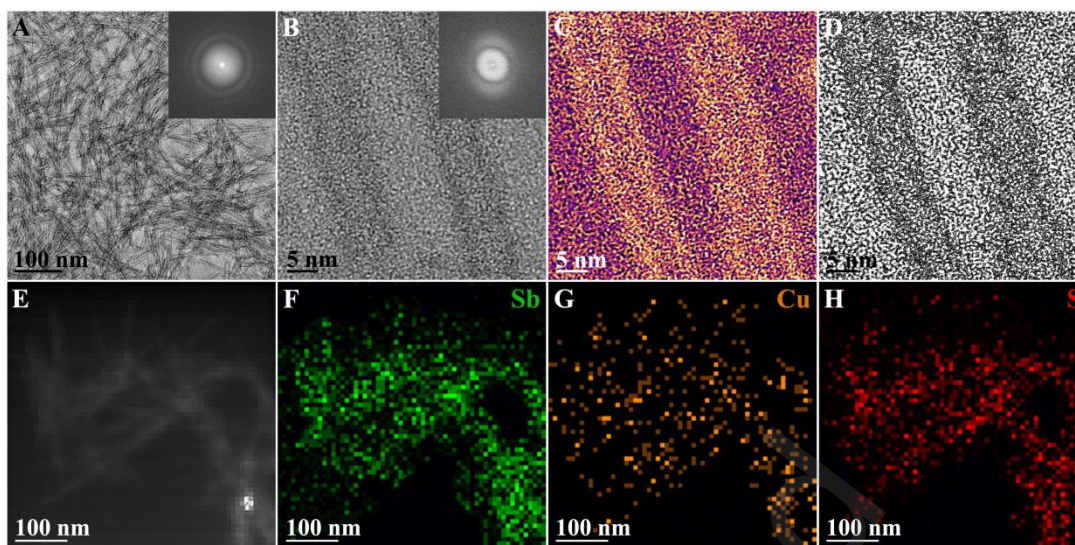


Figure 1 TEM (A, inset: FFT), HRTEM (B, inset: FFT), pseudo-color potential mapping (C), contour plot (D), HAADF-STEM (E), and STEM-EELS elemental maps (F-H) of plasmonic $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes.

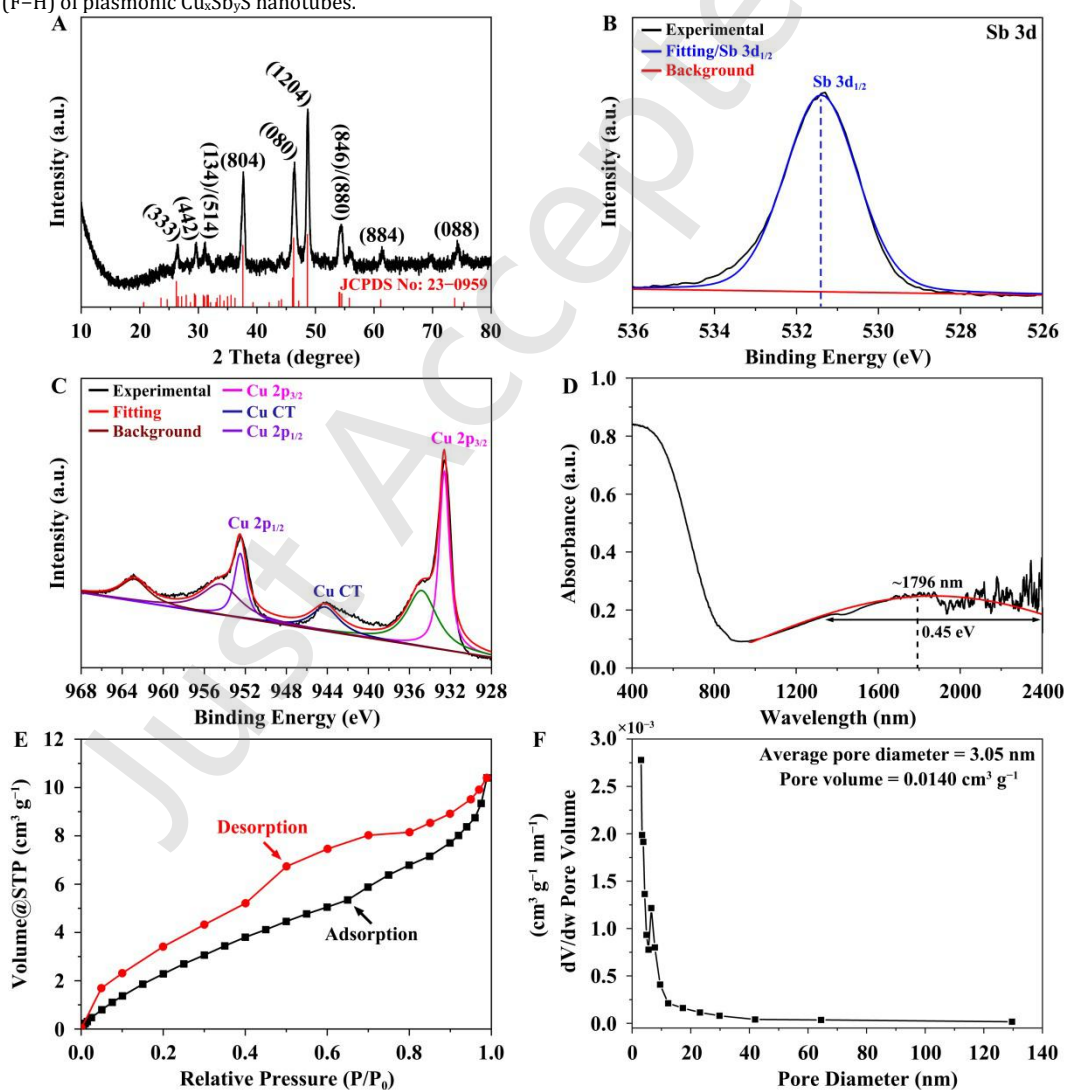


Figure 2 XRD pattern (A), high-resolution XPS spectra of Sb 3d (B) and Cu 2p (C), Vis-NIR DRS (D), BET N_2 isotherm (E), and pore size distribution (F) for plasmonic $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes.

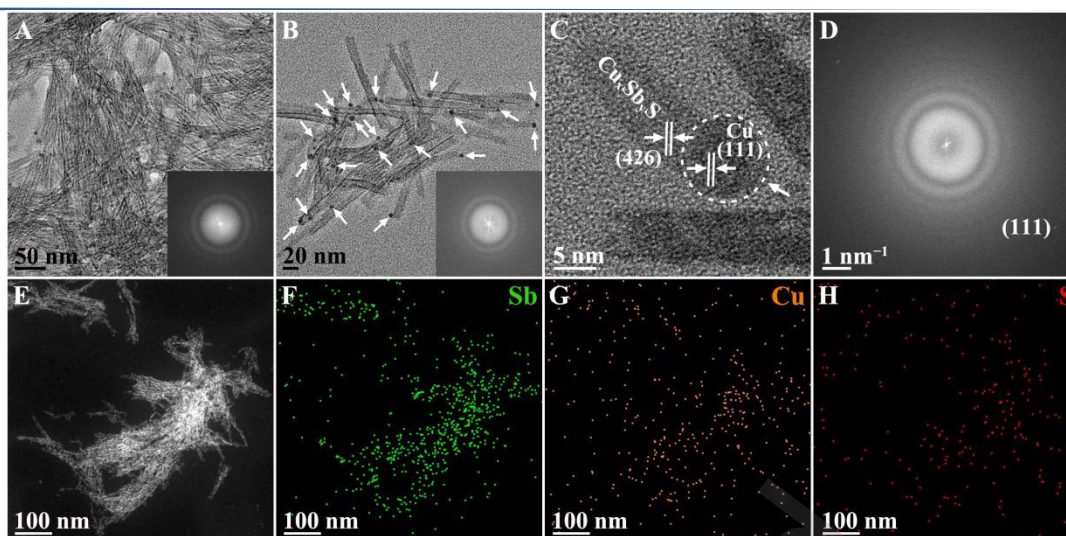


Figure 3 TEM images at various resolutions (A, B, insets: FFT; the arrows mark the end-anchored Cu sites), HRTEM (C), FFT (D), HAADF-STEM (E), and STEM-EELS elemental maps (F-H) of dual-plasmonic $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ heteronanostructures.

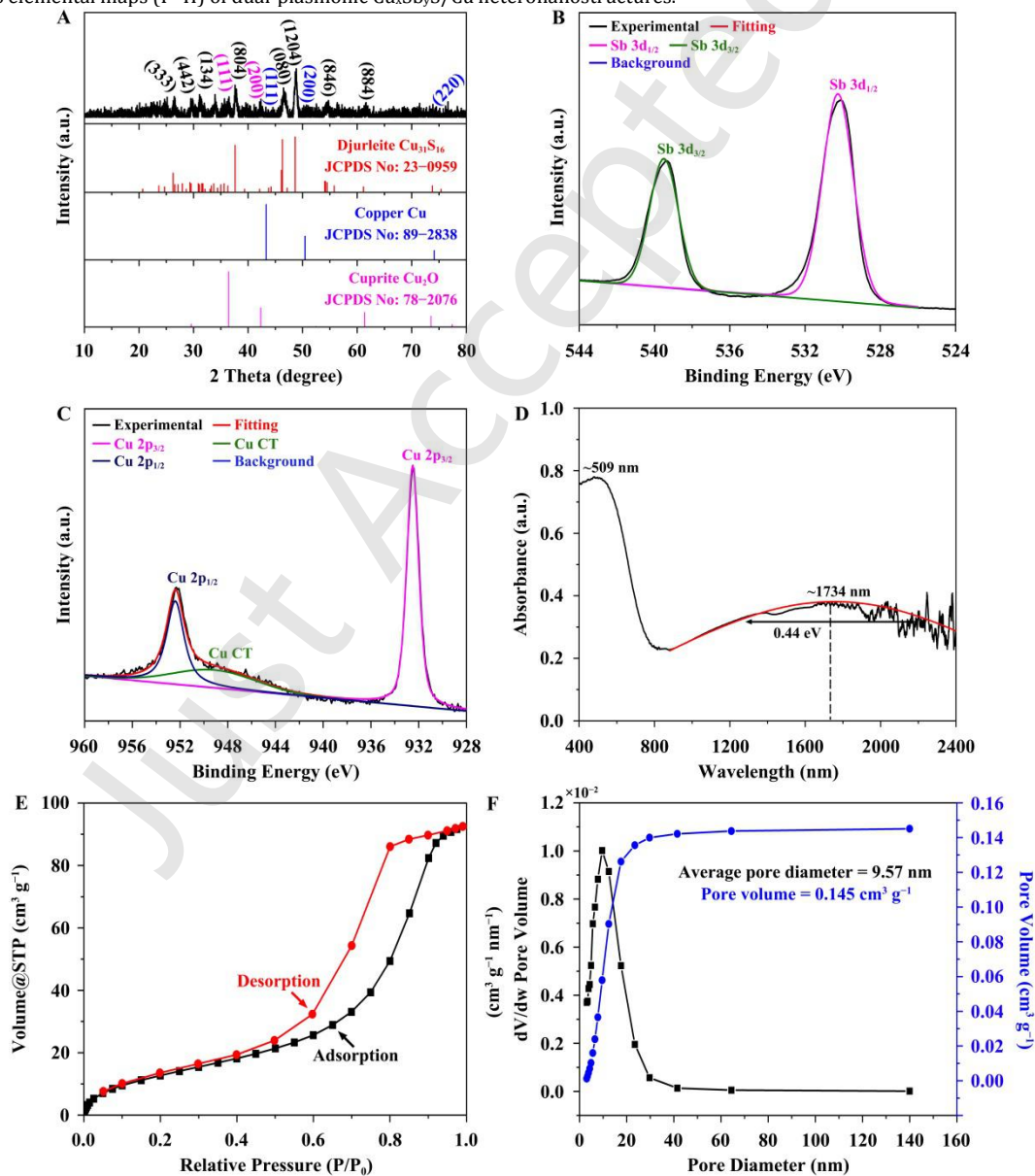


Figure 4 XRD pattern (A), high-resolution XPS spectra of Sb 3d (B) and Cu 2p (C), Vis-NIR DRS (D), BET N_2 isotherm (E), and pore size distribution (F) for dual-plasmonic $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ heteronanostructures.

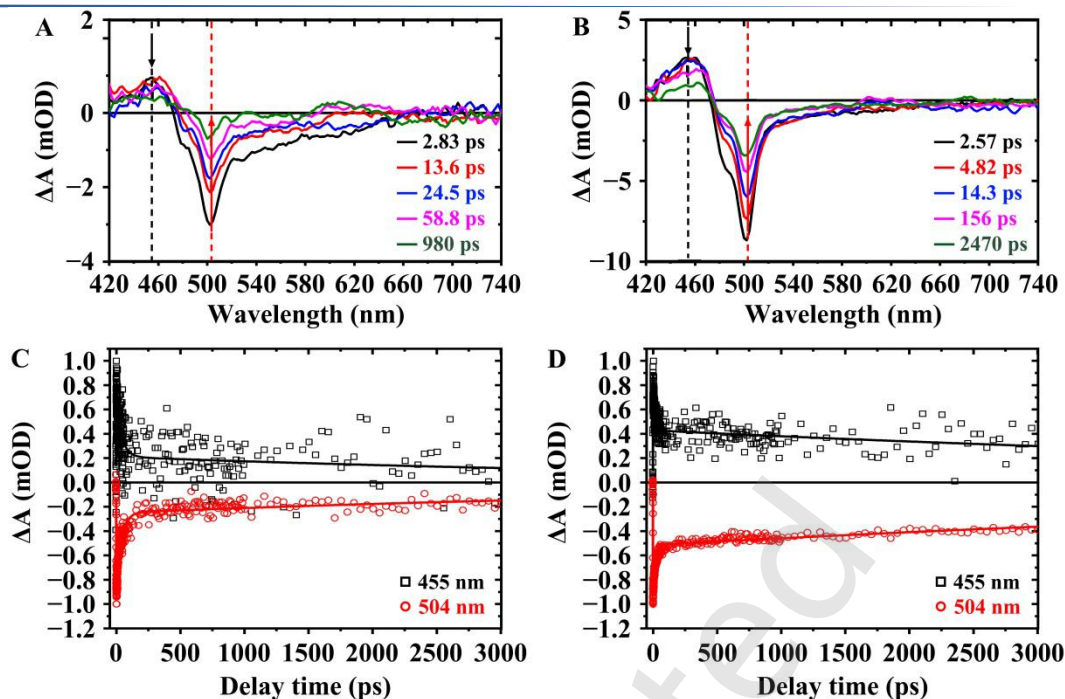


Figure 5 Femtosecond transient absorption spectra at different delay times for plasmonic $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes (A) and dual-plasmonic $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ heteronanostructures (B). Arrows show bleach recovery at low and high energies. Normalized kinetic traces at 455 nm and 504 nm, marked by vertical dashed lines, are shown in panels (C) and (D) with fitting curves. Excitation: 800 nm. Fluence: $5.0 \mu\text{J cm}^{-2}$.

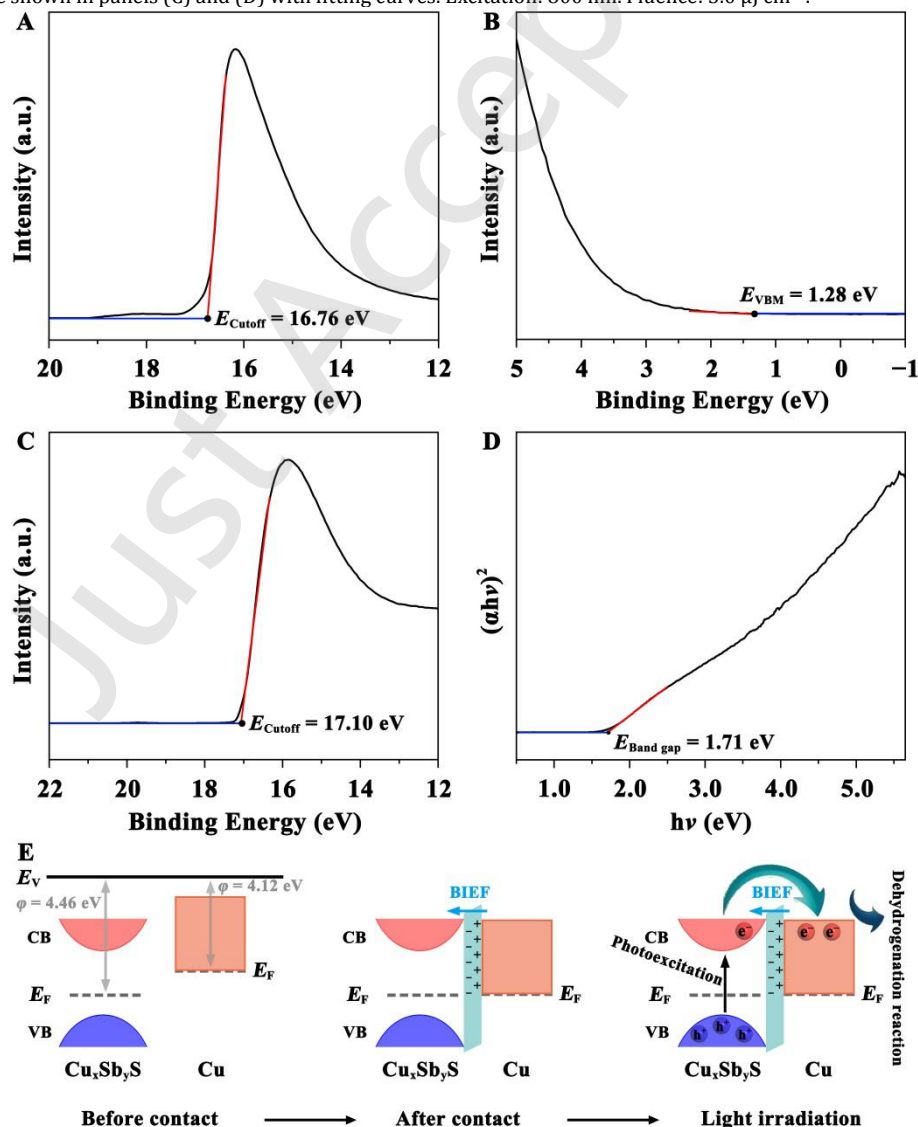


Figure 6 $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ interfacial charge transfer mechanism. UPS spectra of $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes (A, B) and Cu nanoparticles (C). (D) Kubelka-Munk function derived from Vis-NIR DRS of $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes. (E) Schematic of the $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ Schottky heterojunction and proposed interfacial charge transfer mechanism.

transfer and separation mechanism.

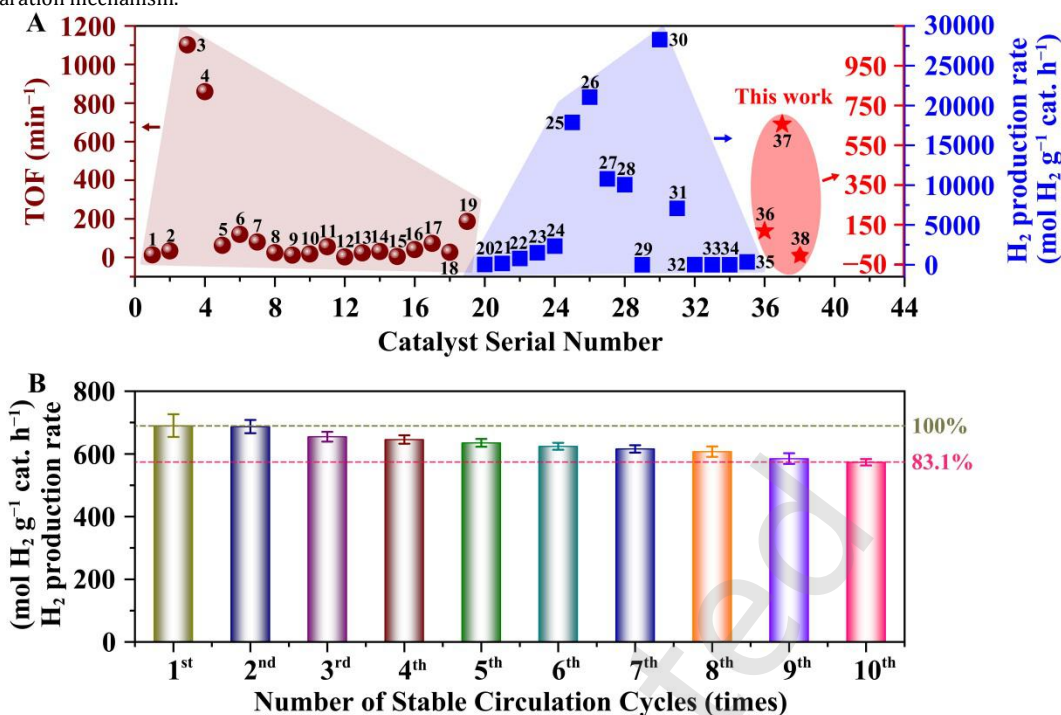


Figure 7 Photocatalytic ammonia borane methanolysis dehydrogenation (A) and recyclability (B).

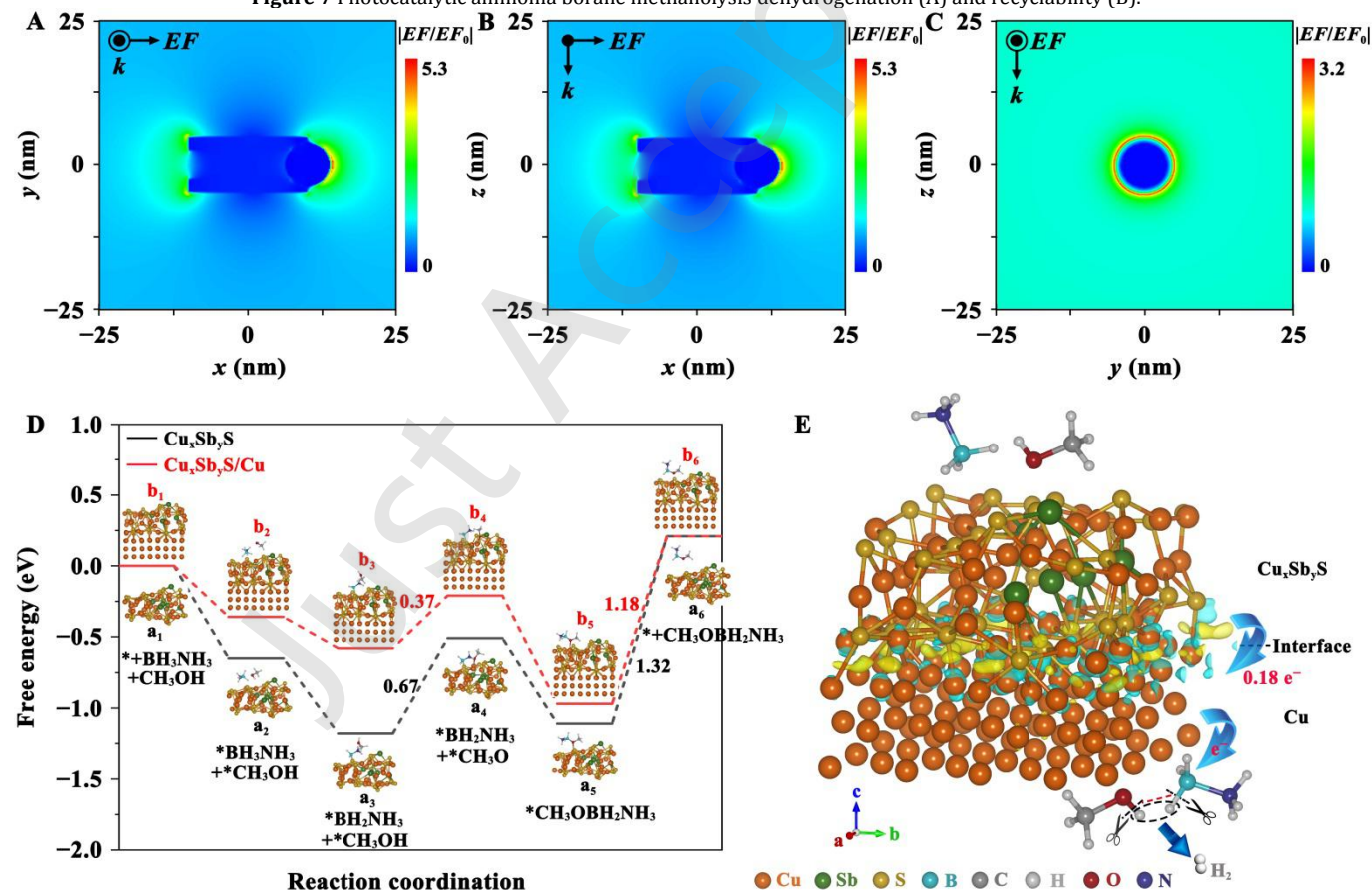


Figure 8 (A–C) Near-field enhancement of dual-plasmonic Cu₃Sb₇S/Cu heteronanostructures under light polarized along the electric field (EF) and wave vector (k). (D) Reaction pathways of AB and CH₃OH on catalyst surfaces (a: Cu₃Sb₇S; b: Cu₃Sb₇S/Cu). *: bare catalyst; * + BH₃NH₃ (or * + CH₃OH): initial state before adsorption; *BH₃NH₃ (or *CH₃OH): adsorbed state. (E) Differential charge density, Bader charge transfer, and proposed plasmonic-catalyzed, CH₃OH-assisted AB dehydrogenation.

Electronic Supplementary Material

Dual-plasmonic $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ heteronanostructures: Efficient photocatalysts for ammonia borane methanolysis dehydrogenation

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2 Experimental section

2.1 Materials.

Copper(II) acetate monohydrate ($\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, AR, 99.0%, Aladdin), tetradecylphosphonic acid (TDPA, 98.0+%, Aladdin), trioctylamine (TOA, AR, 96%, Shanghai yuanye), cuprous chloride (CuCl , trace metals basis, 99.995+%, Sigma-Aldrich), antimony(III) chloride (SbCl_3 , 99.0+%, Sigma-Aldrich), oleylamine (OAm, 80–90%, Sigma-Aldrich), 1-octadecene (ODE, 90%, Sigma-Aldrich), and sulfur powder (S, 99.5+%, Sinopharm) were purchased and stored in an argon-filled glovebox. Ammonia borane (AB, H_3NBH_3 , 97%, Shanghai Yansu) was used as received. n-Hexane (AR, 97%), ethanol (AR, 99.5%), and methanol (AR, 98.0+%) were obtained from Aladdin for washing or redispersion. Deionized water was provided by the School of Chemistry and Chemical Engineering at Huaibei Normal University. All chemicals were used without further purification.

2.2 Methods.

All nanoproductions were synthesized under an argon (Ar) atmosphere with magnetic stirring using standard Schlenk techniques and three-neck round-bottom flasks (100 or 250 mL), with minor modifications to reported procedures.

2.2.1 Synthesis of Cu nanoparticles (NPs) or nanoseeds (NSs). In a three-neck round-bottom flask, a mixture of 1.4 mmol (0.2796 g) $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, 0.8 mmol (0.2226 g) TDPA, and 20 mL TOA was stirred under ambient conditions. The mixture was degassed at room temperature under vacuum for 5 min and purged with Ar gas, this cycle was repeated several times. A continuous Ar flow was maintained to preserve an inert atmosphere. The solution was heated to 130 °C for 25 min, then to 180 °C for another 25 min, and finally to 240 °C for 8 min to yield Cu NPs (for NSs, reaction time: 4–5 min). After cooling to room temperature, 10 mL n-hexane and 30 mL anhydrous ethanol were added. The mixture was sonicated for 2 min and centrifuged at 8,000 rpm for 10 min to collect the precipitate. The precipitate was redispersed in 1 mL n-hexane and 20 mL anhydrous ethanol, sonicated for 5 min, and centrifuged at 8,000 rpm for 10 min to obtain purified Cu NPs or NSs.

2.2.2 Synthesis of OAm/ODE-CuCl precursor. 0.1 mmol (0.0099 g) CuCl was mixed with 12 mL OAm/ODE (1:3 $V_{\text{OAm}}/V_{\text{ODE}}$) under stirring at room temperature for 30 min. The deep blue dispersion was rapidly heated to 110 °C and degassed for 30 min until color changed to faint yellow. The flask was purged with Ar, heated to 200 °C, and held at this temperature for 20 min until the solution became transparent yellow. The precursor was then cooled to room temperature and stored in a glovebox for further use.

2.2.3 Synthesis of OAm/ODE-SbCl₃ precursor. 0.9 mmol (0.2052 g) SbCl_3 and 12 mL OAm/ODE (1:3 $V_{\text{OAm}}/V_{\text{ODE}}$) were mixed at room temperature with stirring for 30 min and deaerated at 110 °C for another 30 min, turning opalescent. The flask was purged with Ar, heated to 160 °C, held for 20 min until gray, then cooled to room temperature and stored in a glovebox for further use.

2.2.4 Synthesis of OAm/ODE-S precursor. A mixture of 5.0 mmol (0.1603 g) S powder in 12 mL OAm/ODE (1:3 $V_{\text{OAm}}/V_{\text{ODE}}$) was stirred and degassed at room temperature for 30 min. The yellow dispersion was rapidly heated to 110 °C and degassed for 30 min. After purging with Ar, the solution was heated to 150 °C, held for 20 min until transparent yellow, then cooled and stored in a glovebox.

2.2.5 Synthesis of plasmonic Cu_xSb_yS nanotubes. In a typical synthesis, OAm/ODE-Cu and OAm/ODE-Sb precursors were combined in a Schlenk-fitted three-neck round-bottom flask. Another flask containing OAm/ODE-S precursor was connected to the same system. Both solutions were degassed at room temperature for 30 min, then heated to 80 °C under vacuum for 30 min. Ar was introduced while gradually raising the temperature. At 110 °C, the OAm/ODE-S precursor was slowly injected into the metal precursor mixture. After returning to 110 °C, the reaction was maintained for 30 min. The mixture was rapidly cooled to room temperature, centrifuged at 8,000 rpm for 10 min, and the supernatant removed. The precipitate was washed with n-hexane/anhydrous ethanol by repeated centrifugation until clear (typically 2–3 times), then redispersed in n-hexane or vacuum-dried at 80 °C for at least 48 h before use.

2.2.6 Synthesis of dual-plasmonic Cu_xSb_yS/Cu heteronanostructures. Cu_xSb_yS nanotube dispersion was held at 110 °C under Ar for 30 min (Solution I). Separately, Cu NPs were synthesized by heating to 240 °C under Ar for ~ 5 min, then cooling naturally to 110 °C (Solution II). Solution II was added dropwise to Solution I under xenon lamp irradiation for approximately 5 min to promote directional anchoring of Cu NPs onto nanotube ends. The product was purified by repeated centrifugation until optically clear, dried under vacuum at 80 °C for ≥ 48 h, or redispersed in n-hexane and stored in a glovebox for stability.

Digital photographs showing solution color evolution during synthesis are provided in Figure S1.

2.2.7 Photocatalytic methanolysis dehydrogenation of ammonia borane. Equal masses of catalysts (dual-plasmonic Cu_xSb_yS/Cu heteronanostructures, plasmonic Cu_xSb_yS nanotubes, or Cu NPs) were added to a 25 mL single-neck round-bottom flask, followed by 10 mL anhydrous methanol. The mixture was sonicated for 30 min at room temperature to ensure uniform dispersion. The flask was placed in a thermostatic oil bath at 25 °C and stirred for 10 min to reach thermal equilibrium. Then, under xenon lamp irradiation (or dark conditions), 0.0617 g (2 mmol) of ammonia borane (AB) was rapidly injected into the gently stirred system to initiate H₂ evolution. Evolved gas was collected *via* water displacement using a silicone tube connected to an inverted graduated cylinder in a water bath. The volume of displaced water was recorded and converted to molar H₂ using the ideal gas law. The reaction was considered complete when H₂ evolution plateaued with no further increase. To confirm the gas identity and quantify yield, control experiments were conducted using a photocatalytic system coupled with gas chromatography (GC, GB-9890), with 20% of the original AB mass and all other parameters unchanged.

2.2.8 Recyclability assessment. The first cycle followed the standard procedure. After each cycle, H₂ was fully removed, and fresh AB (same amount) was added under identical conditions. This was repeated for ten consecutive cycles to evaluate catalyst stability and reusability.

2.3 Characterization.

2.3.1 Low-magnification transmission electron microscopy (TEM), high-resolution TEM (HRTEM), selected area electron diffraction (SAED), and fast Fourier transform (FFT). Samples were prepared by drop-casting diluted, sonicated dispersions of plasmonic Cu_xSb_yS nanotubes, dual-plasmonic Cu_xSb_yS/Cu heteronanostructures, and plasmonic Cu NPs onto carbon-coated 400-mesh Mo TEM grids and air-drying. Measurements were performed on a JEOL JEM-F200 microscope at 200 kV.

2.3.2 High-angle annular dark-field – scanning TEM (HAADF-STEM) and STEM – electron energy loss spectrometer

(STEM–EELS) elemental mapping. HAADF–STEM and STEM–EELS elemental mapping of plasmonic $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes, dual-plasmonic $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ heteronanostructures, and plasmonic Cu NPs were performed on a JEOL JEM-ARM200F (200 kV) and a JEOL Grand ARM CF300 (300 kV).

2.3.3 Energy dispersive X-ray spectroscopy (EDS). Compositional analysis of plasmonic $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes, dual-plasmonic $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ heteronanostructures, and plasmonic Cu NPs was performed using an Oxford Instruments X-Max 20 mm² EDS detector on a FEI Tecnai™ G2 20 TEM.

2.3.4 Elemental analysis. The atomic contents of Sb, Cu, and S in plasmonic $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes, dual-plasmonic $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ heteronanostructures, and plasmonic Cu NPs were determined by inductively coupled plasma – atomic emission spectrometer (ICP–AES) using a SPECTROBLUE ICP–OES spectrometer. Samples were washed, vacuum-dried, and digested in aqua regia (concentrated HCl/HNO_3 , 3:1, V/V).

2.3.5 Powder X-ray diffraction (XRD). The crystal phase and structure of plasmonic $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes, dual-plasmonic $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ heteronanostructures, and Cu NPs were analyzed by powder XRD using a Rigaku Ultima IV diffractometer with Cu $\text{K}\alpha$ radiation ($\lambda = 0.1547$ nm) at 40 kV and 150 mA. Diffraction patterns were collected from 10° to 80° 2 θ with a step size of 0.08° under ambient conditions.

2.3.6 X-ray photoelectron spectroscopy (XPS). XPS measurements of plasmonic $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes, dual-plasmonic $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ heteronanostructures, and Cu NPs were performed on a Thermo ESCALAB 250 XI spectrometer (Thermo Fisher Scientific, USA) with a 300 W Al $\text{K}\alpha$ X-ray source (15 kV, 20 mA). Samples were vacuum-dried, stored in an Ar-filled glovebox or vacuum-sealed, and transferred to the XPS system without air exposure. All spectra were referenced to the C1s peak at 284.8 eV for calibration.

2.3.7 Visible-near infrared spectroscopy (Vis–NIR). Vis–NIR diffuse reflectance spectra (DRS) of plasmonic $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes, dual-plasmonic $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ heteronanostructures, and Cu NPs were recorded on a Shimadzu UV–3600 spectrophotometer with an integrating sphere (400–2400 nm), using BaSO_4 as reference. Colloidal Cu NP dispersions in n-hexane were measured over 480–800 nm on the same instrument after varying exposure times.

2.3.8 Brunauer–Emmett–Teller (BET) surface area and pore size measurements. Plasmonic $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes, dual-plasmonic $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ heteronanostructures, and Cu NPs were degassed under vacuum at 100 °C for 12 h before measurement. BET surface area and pore size distribution were then analyzed by N_2 adsorption/desorption at 77.35 K using a Quantachrome Autosorb-iQ instrument.

2.3.9 Atomic force microscopy (AFM). AFM analysis of plasmonic $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes was performed on a Bruker Multimode 8 in tapping mode.

2.3.10 Electron paramagnetic resonance (EPR) spectroscopy. EPR spectra were recorded on a Bruker EMXplus-6/1 spectrometer. Load the sample into a quartz tube, align its bottom with the resonant cavity center, then perform EPR tuning and scanning.

2.3.11 Femtosecond transient absorption (fs-TA) spectroscopy. Carrier dynamics of $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes and $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ heteronanostructures in aqueous suspension were probed by fs-TA spectroscopy over 1 ps–3 ns. Ultrafast fs-TA measurements were performed on the Ultrafast Systems Helios pump-probe system, equipped with an electric optical delay line (max delay: 8 ns), at room temperature. Pump excitation: 800 nm; fluence: 5.0 $\mu\text{J cm}^{-2}$.

2.3.12 Ultraviolet photoelectron spectroscopy (UPS). UPS spectra were acquired on a Thermo Fisher Scientific ESCALAB Xi spectrometer using He I radiation ($h\nu = 21.2$ eV) at –5 V and 0 V sample bias.

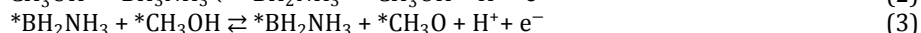
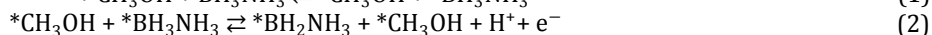
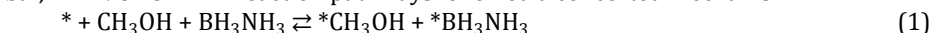
2.4 Finite-difference time-domain (FDTD) simulations.

FDTD simulations were performed to calculate the electric field distributions of $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes and $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ heteronanostructures using Lumerical FDTD Solutions (Lumerical Solutions Inc., Sweden). Perfectly matched layer (PML) boundary conditions were applied in the x, y, and z directions to suppress unphysical reflections. A uniform mesh with a cell size of $0.25 \times 0.25 \times 0.25$ nm³ was used throughout the simulation domain to ensure high accuracy. Dielectric constants for Cu NPs and $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes were taken from literature, the effective complex dielectric constant of $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ heteronanostructures was derived by combining the optical properties of the constituent materials. A total-field scattered-field (TFSF) plane wave source was used, covering the Vis-to-NIR range, with normal incidence along the z-direction. Simulations ran until convergence at 1×10^{-5} fs. An electric field monitor recorded the field distribution. Structural dimensions were extracted from TEM images.

2.5 Density functional theory (DFT) calculations.

All first-principles calculations were performed within the framework of DFT using the Vienna *Ab initio* Simulation Package (VASP). Ion–electron interactions were described using the projector augmented wave (PAW) method, and the exchange–correlation functional was treated with the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA)^[1,2]. A plane-wave energy cutoff of 500 eV was used, with convergence thresholds for electronic energy and atomic forces set to 10^{-5} eV/atom and 0.01 eV/Å, respectively. The Brillouin zone was sampled with a $1 \times 1 \times 1$ Monkhorst–Pack k-point grid. Van der Waals (vdW) interactions were included *via* the DFT–D3 empirical dispersion correction^[3]. Zero-point energies and entropic contributions were computed using VASPKIT^[4].

Gibbs free energies were obtained by combining DFT with the computational standard hydrogen electrode (SHE) model at standard conditions: $U = 0$ V, pH = 0, $p = 1$ bar, $T = 298.15$ K^[5,6]. Reaction pathways followed a concerted mechanism:

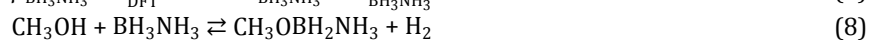


where * denotes the bare catalyst; * + CH_3OH (or * + BH_3NH_3) represents the initial state with no adsorption or interaction between the molecule and catalyst; * CH_3OH (or * BH_3NH_3) denotes the adsorbed state where CH_3OH (or BH_3NH_3) is bound to the catalyst surface. The chemical potential of the H^+/e^- pair was referenced using half a gaseous H_2 molecule, CH_3OH , or BH_3NH_3 as thermodynamically equivalent species. All calculations were performed under standard conditions (1 bar, 298.15 K).

$$\mu_{\text{H}^+} + \mu_{\text{e}^-} = \frac{1}{2} \mu_{\text{H}_2(\text{g})} \quad (5)$$

$$\mu_{\text{CH}_3\text{OH}} = E_{\text{DFT}}^{\text{CH}_3\text{OH}} + ZPE_{\text{CH}_3\text{OH}} - TS_{\text{CH}_3\text{OH(g)}}^0 \quad (6)$$

$$\mu_{\text{BH}_3\text{NH}_3} = E_{\text{DFT}}^{\text{BH}_3\text{NH}_3} + ZPE_{\text{BH}_3\text{NH}_3} - TS_{\text{BH}_3\text{NH}_3}^0 \quad (7)$$



where ZPE and S represent the zero-point energy correction term and entropy, respectively, with their values derived from vibrational frequency analysis of the corresponding molecules^[5,6].

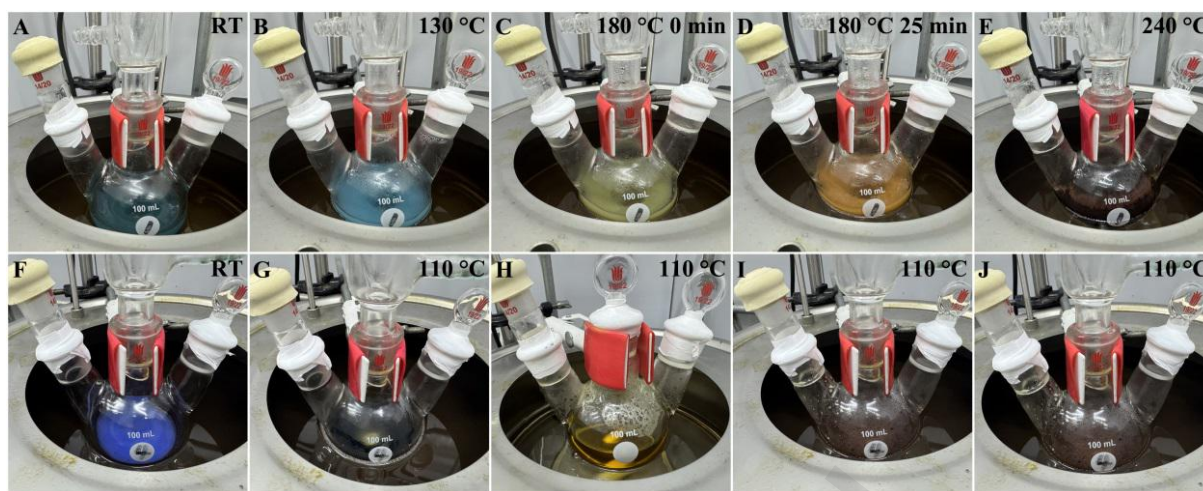


Figure S1 Digital photographs showing solution color changes during the synthesis of plasmonic Cu nanoparticles (or nanoseeds, A–E), Cu_xSb_yS nanotubes (F–I), and dual-plasmonic Cu_xSb_yS/Cu heteronanostructures (J).

All nanoproducts were synthesized under Ar with magnetic stirring using standard Schlenk line techniques and 100 or 250 mL three-neck round-bottom flasks, with minor modifications to literature procedures^[7,8]. Figures S1A–S1E show digital photographs of the synthesis of plasmonic Cu NPs or NSs. As seen in Figure S1A, the solution was pale blue at room temperature (RT). Upon heating to 130 °C (Figure S1B), it turned lighter milky blue or cyan. At 180 °C (Figure S1C), the color shifted to faintly milky yellow. After holding at 180 °C for 25 min (Figure S1D), the solution became milky orange. When heated to 240 °C (Figure S1E), it developed a purplish red color, characteristic of the resulting plasmonic Cu NPs or NSs. Figures S1F–S1J show the preparation of plasmonic Cu_xSb_yS nanotubes and dual-plasmonic Cu_xSb_yS/Cu heteronanostructures. The precursor solution of oleylamine-cuprous chloride (OAm–CuCl) and oleylamine-antimony chloride (OAm–SbCl₃) appeared deep blue at RT (Figure S1F) and lightened to light blue at 110 °C (Figure S1G). The oleic acid-sulfur (OA–S) precursor solution was transparent yellow (Figure S1H). The Cu_xSb_yS nanotube solution was brownish (Figure S1I), while the dual-plasmonic Cu_xSb_yS/Cu heteronanostructure solution was brownish red (Figure S1J).

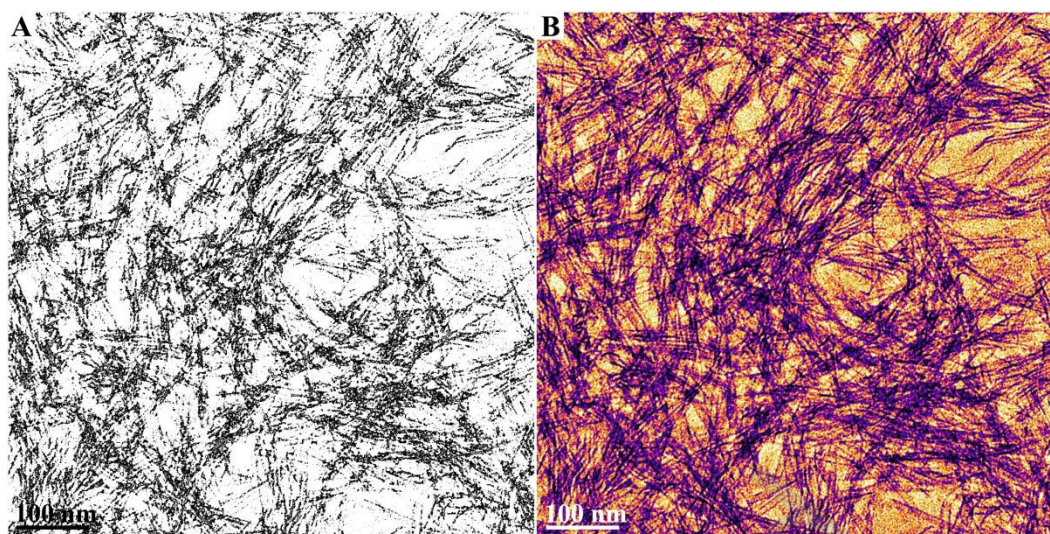


Figure S2 Pseudo contour plot (A) and corresponding pseudo-color equilibrium potential map (B), derived from the inverse FFT of plasmonic Cu_xSb_yS nanotubes, provide a vivid visualization of their morphological features.

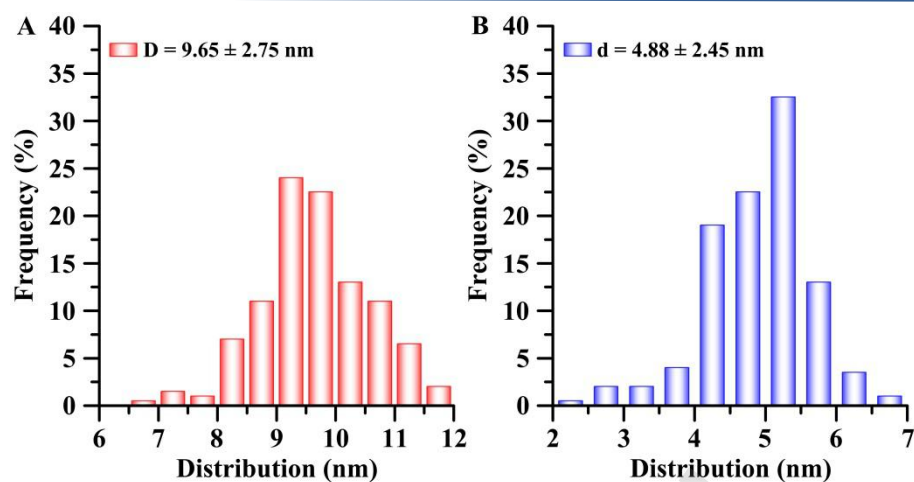


Figure S3 Size distribution histograms of plasmonic $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes.

The nanotubes have an outer diameter (D) of 9.65 ± 2.75 nm and an inner diameter (d) of 4.88 ± 2.45 nm (Figure S3). Wall thickness (t), calculated as $t = (D - d)/2$, is approximately 2.38 ± 0.15 nm. Statistics are based on 1,000 nanotubes.

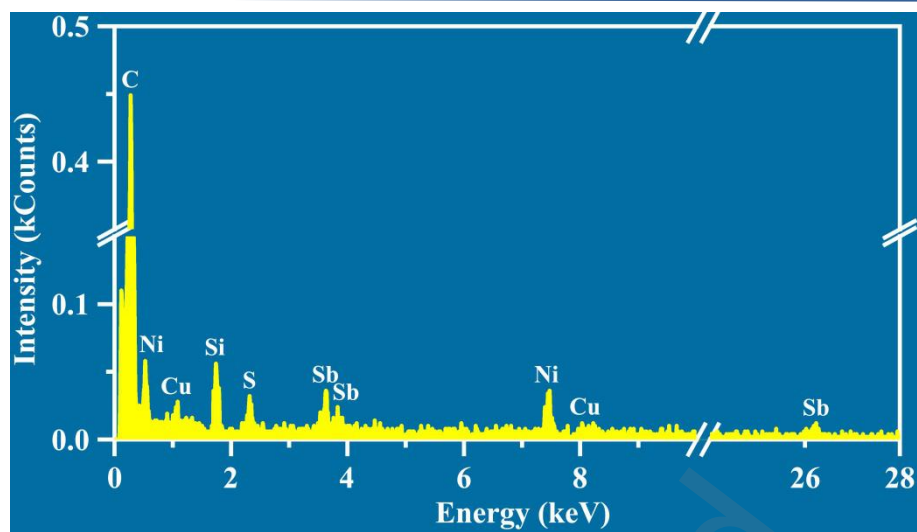


Figure S4 EDS spectrum of plasmonic Cu_xSb_yS nanotubes.

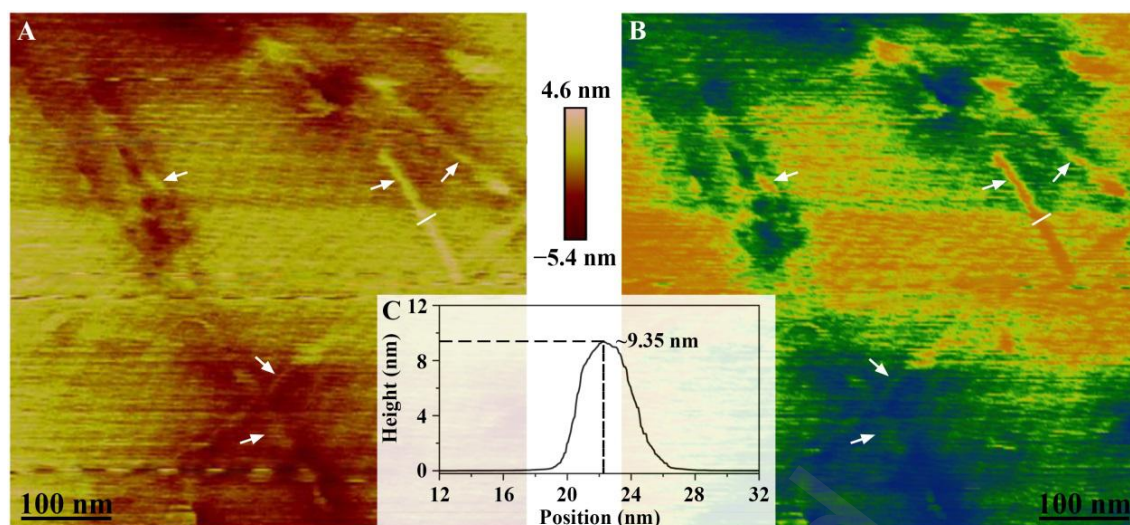


Figure S5 AFM image (A), pseudo-color potential map (B), and height profile (C) of plasmonic $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes.

Figures S5A and S5B show the AFM image and pseudo-color potential map of plasmonic $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes. White arrows highlight distinct nanotube contour morphologies. The tapping height profile along the short solid lines is shown in Figure S5C, where the nanotube height is approximately 9.35 nm, consistent with the outer diameter ($D = 9.65 \pm 2.75$ nm) from Figures 1A, S2, and S3A.

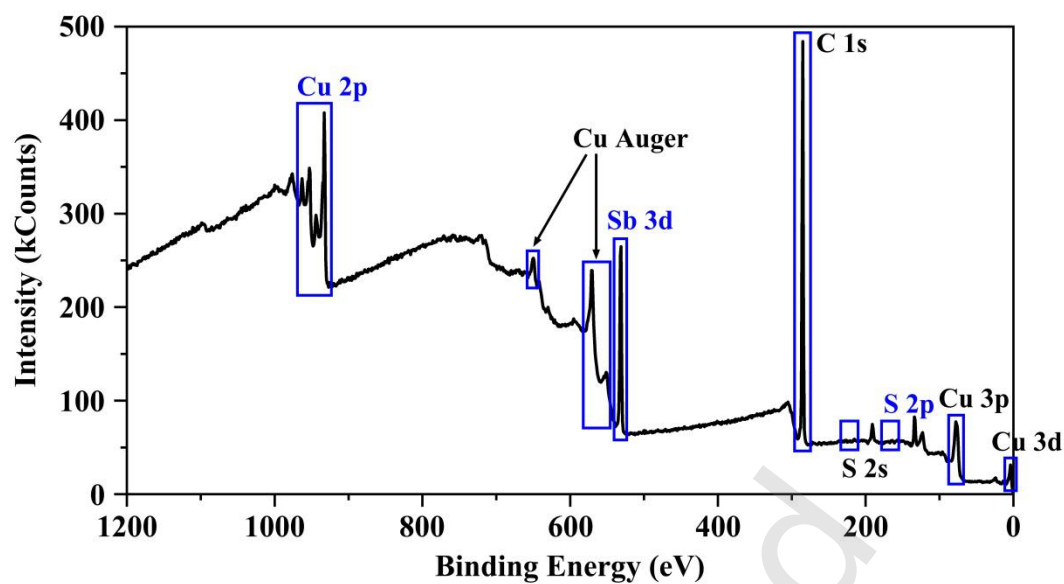


Figure S6 XPS survey scan of plasmonic $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes.

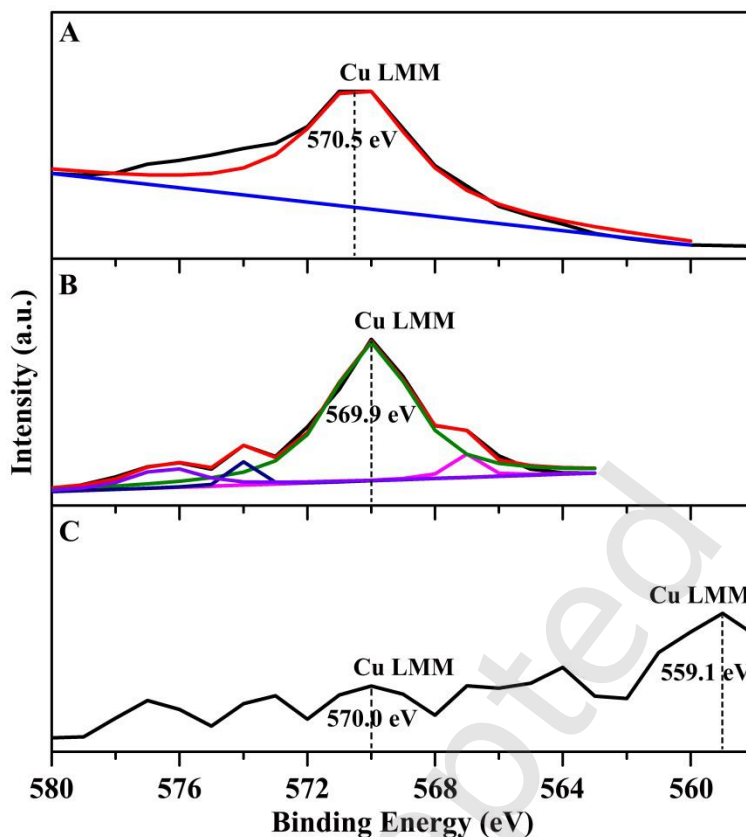


Figure S7 High-resolution Cu LMM Auger XPS spectra of plasmonic $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes (A), dual-plasmonic $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ heteronanostructures (B), and Cu nanoparticles (C).

Due to ambiguity from a single Cu 2p satellite peak (at 944.2, 949.1, and 947.5 eV) in $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes, $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ heteronanostructures, and Cu nanoparticles (NPs), the Cu LMM Auger spectra were analyzed to clarify copper's chemical state. Results are shown in Figure S7. The peak at ~ 570.5 eV corresponds to Cu^+ in $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes (Figure S7A), while that at ~ 569.9 eV indicates Cu^+ in $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ heteronanostructures (Figure S7B), confirming copper predominantly exists as Cu^+ in both materials^[9], consistent with prior studies^[7,8,10]. Additionally, the peak at ~ 918.9 eV is attributed to Cu^0 from Cu NPs at the ends of heteronanostructures (Figure S16)^[11]. The high-resolution spectrum of Cu NPs (Figure S7C) shows doublet peaks at 570.0 eV (surface Cu^+) and 559.1 eV (Cu^0)^[12], with a Cu^0/Cu^+ ratio of 89.47% and 10.53%. This partial oxidation during washing aligns with TEM, XRD, and Vis-NIR data (Figures S18–S20).

Table S1 The chemical composition and non-stoichiometric ratio of plasmonic Cu_xSb_yS nanotubes were analyzed by ICP–AES, XPS, and EDS.

ICP–AES analysis (mean atom percent/%)			XPS analysis (mean atom percent/%)			EDS analysis (mean atom percent/%)			Non-stoichiometry Cu _x Sb _y S nanotubes
Sb	Cu	S	Sb	Cu	S	Sb	Cu	S	
59.29	6.60	34.11	58.37	7.63	34.00	56.75	7.42	35.83	Cu _{1.74} Sb _{0.19} S

Table S2 Cu_xSb_yS nanotube NIR DRS: Experimental vs. fitted spectral data.

Experimental and fitted data are provided in Supplementary Tables S1 and S2 (.txt).

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Table S3 BET surface area and pore size of plasmonic Cu nanoparticles (nanoseeds), Cu_xSb_yS nanotubes, and dual-plasmonic Cu_xSb_yS/Cu heteronanostructures.

Thermophysical properties	Cu NPs ^a (NSs ^b)	Cu _x Sb _y S nanotubes	Cu _x Sb _y S/Cu heteronanostructures
BET surface area (m ² g ⁻¹)	8.02/4.13	12.90	51.57
Pore volume (cm ³ g ⁻¹)	5.00 × 10 ⁻³	1.40 × 10 ⁻²	1.45 × 10 ⁻¹
Pore area (m ² g ⁻¹)	6.02 × 10 ⁻¹	1.22	34.50
Average pore diameter (nm)	3.06	3.05	9.57

Note: ^aNPs: nanoparticles. ^bNSs: nanoseeds.

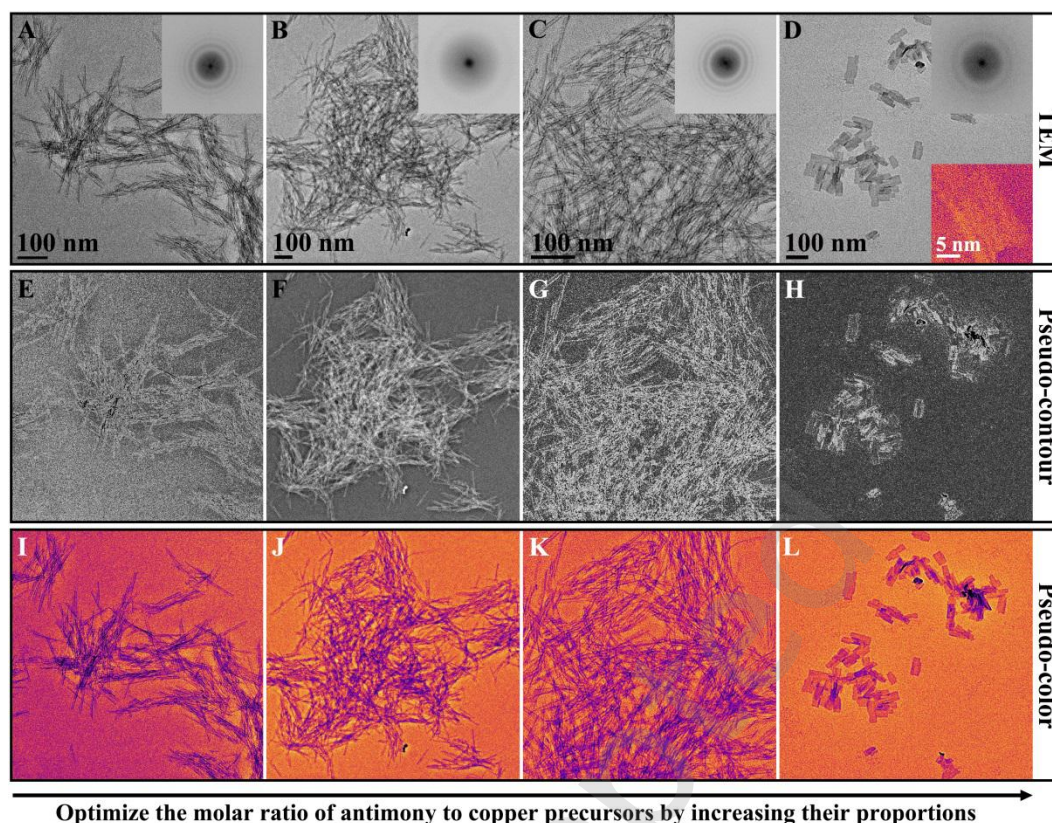


Figure S8 TEM images (A–D), pseudo-contour images (E–H), and pseudo-color potential maps (I–L) of plasmonic $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes synthesized with varying SbCl_3 to CuCl molar ratios.

To evaluate the reproducibility and robustness of the synthesis, experiments were conducted under standardized conditions with consistent sulfur precursor dosage, temperature, and time. By varying the SbCl_3 to CuCl molar ratio ($n(\text{SbCl}_3):n(\text{CuCl})$), the morphological evolution of $\text{Cu}_x\text{Sb}_y\text{S}$ nanomaterials was investigated (Figure S8). At 85:15 (Figure S8A), the product retained a nanotubular structure, which persisted at 92:8 (Figure S8B) and 95:5 (Figure S8C). In contrast, without CuCl (100:0, Figure S8D), quasi-rectangular nanosheets formed. Previous studies show that below 80:20, morphology shifts to quasi-circular nanosheets^[7]. XRD analysis (Figure S9) confirms orthorhombic stibnite-phase Sb_2S_3 formation under these conditions. Pseudo-contour and pseudo-color images corresponding to Figures S8A–S8D are shown in Figures S8E–S8H and S8I–S8L, respectively. Together, these results indicate that the nanotubular morphology is stable only within a narrow range (85:15 to 95:5), highlighting the critical role of stoichiometric control. This study provides key insights for the rational design of semiconductor nanomaterials with defined morphologies, relevant to functional applications.

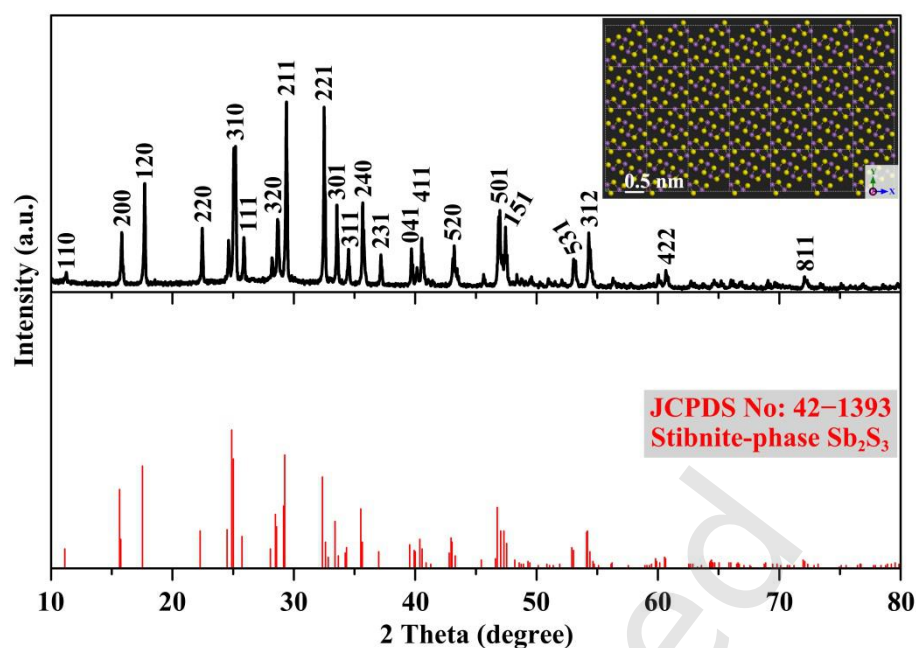


Figure S9 XRD pattern of quasi-rectangular Sb_2S_3 nanosheets.

Without CuCl precursor, the XRD pattern of quasi-rectangular Sb_2S_3 thin nanosheets (Figures S9 and S8D) matches well with orthorhombic stibnite-phase Sb_2S_3 in peak positions and intensities, confirming pure Sb_2S_3 formation instead of $\text{Cu}_x\text{Sb}_y\text{S}^{[13]}$. In contrast, adding trace CuCl leads to monoclinic djurleite-phase $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes, as shown in Figures 2 and S8. These results demonstrate that CuCl critically controls the product's composition, crystal structure, and morphology.

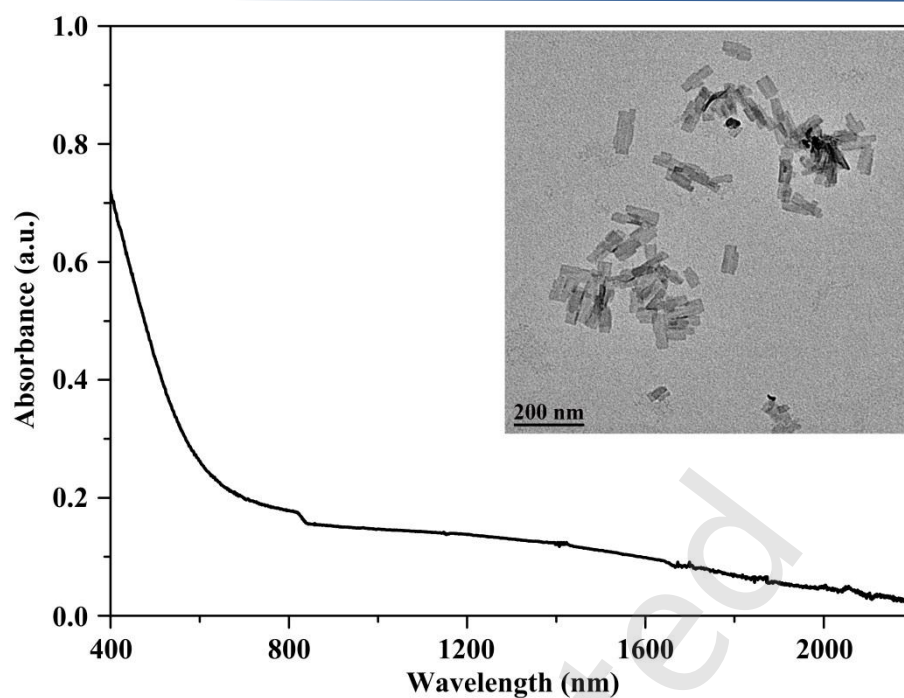


Figure S10 Vis-NIR absorbance spectrum of quasi-rectangular Sb_2S_3 nanosheets.

Without CuCl precursor, the Vis-NIR absorption spectrum of quasi-rectangular Sb_2S_3 nanosheets (Figure S10) shows no significant plasmonic resonance peak in the NIR region, due to the insufficient Cu vacancy density to generate free charge carriers in these sheet-like nanomaterials.

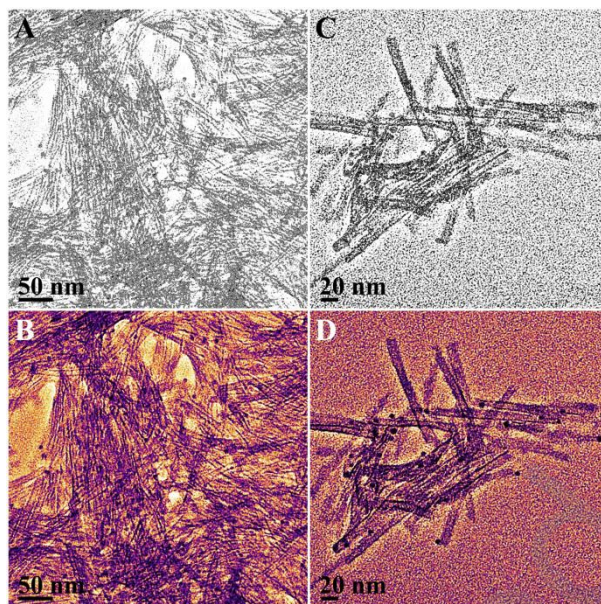


Figure S11 Pseudo contour plots (A, C) and corresponding pseudo-color equilibrium potential maps (B, D), derived from inverse FFT patterns of dual-plasmonic $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ heteronanostructures (Figures 3A and 3B), provide a clearer visualization of their morphological features.

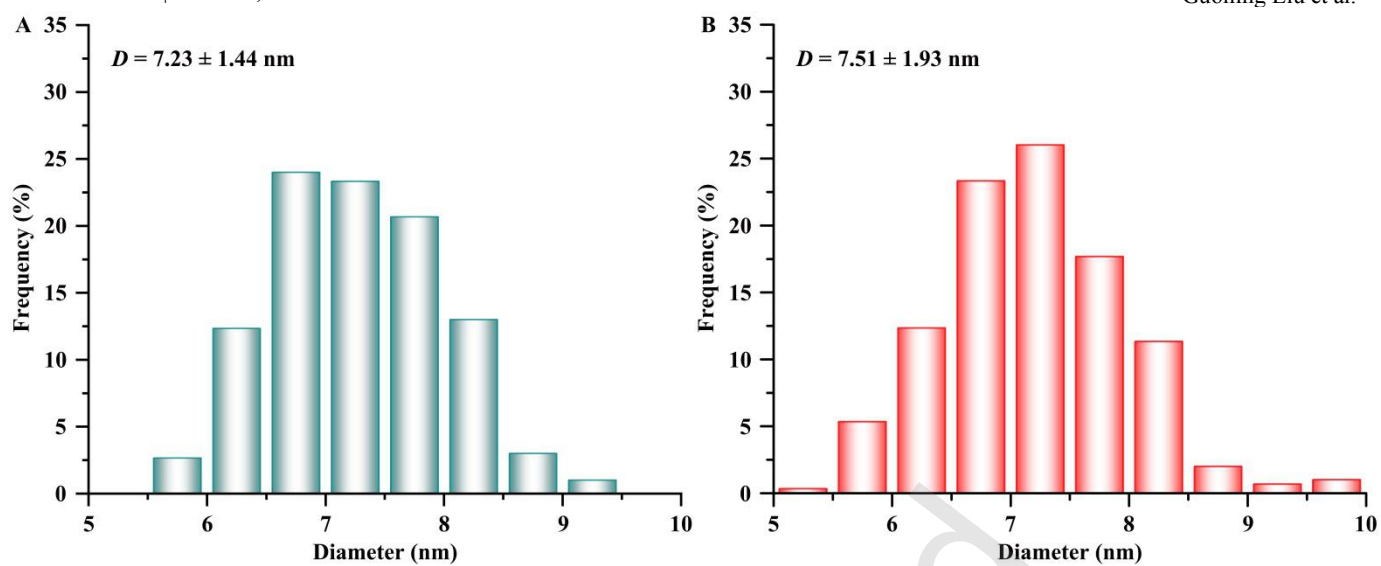


Figure S12 Size distribution histograms of end-anchored Cu domains in the Cu_xSb_yS/Cu heteronanostructures (A) and pure Cu nanoparticles (B).

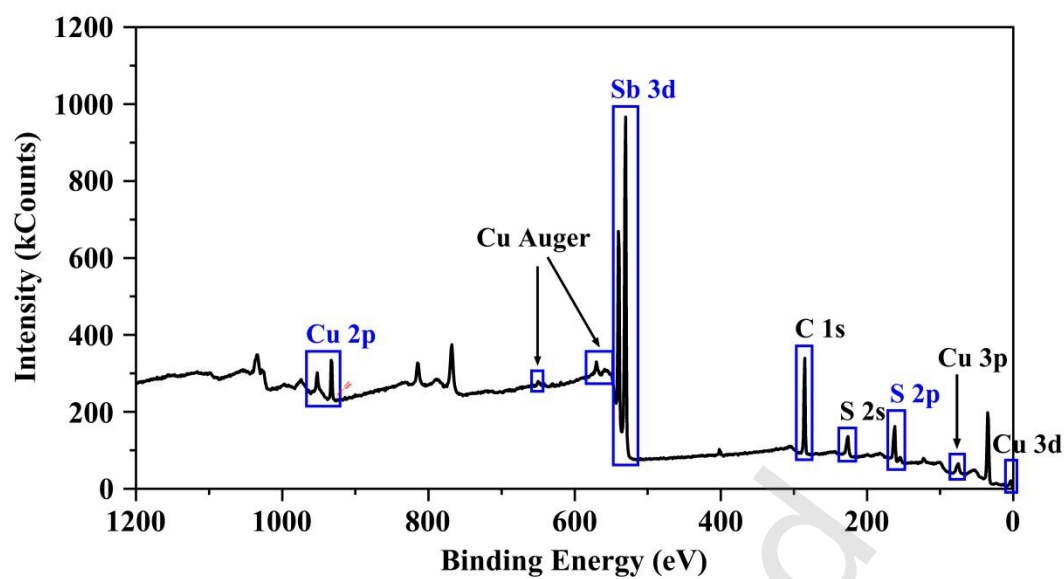


Figure S13 XPS survey scan of dual-plasmonic Cu_xSb_yS/Cu heteronanostructures.

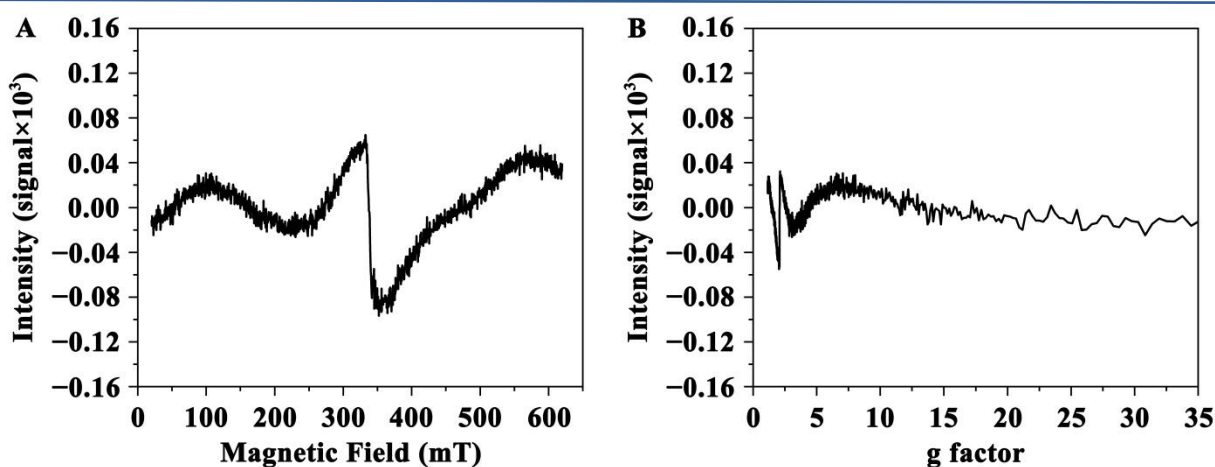


Figure S14 EPR spectrum (A) and corresponding g factor fit (B) of dual-plasmonic $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ heteronanostructures.

Figure S14 shows the EPR spectrum and corresponding g-factor fit of the dual-plasmonic $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ heteronanostructures. The weak signal in Figure S14A is amplified 1000-fold for detection. A broad, low-intensity resonance appears at ~ 337.2 mT ($g_{\parallel} = 2.12$, Figure S14B); no axial Cu^{2+} signal ($g_{\parallel} = 2.2\text{--}2.4$) is observed, confirming that Cu^{2+} is present only in trace amounts and exclusively as antiferromagnetically coupled $\text{Cu}^{2+}\bullet\text{Cu}^+$ pairs (not isolated Cu^{2+}) based on linewidth, intensity, and g-anisotropy^[14,15]. This agrees with XPS evidence of mixed-valence $\text{Cu}^+/\text{Cu}^{2+}$.

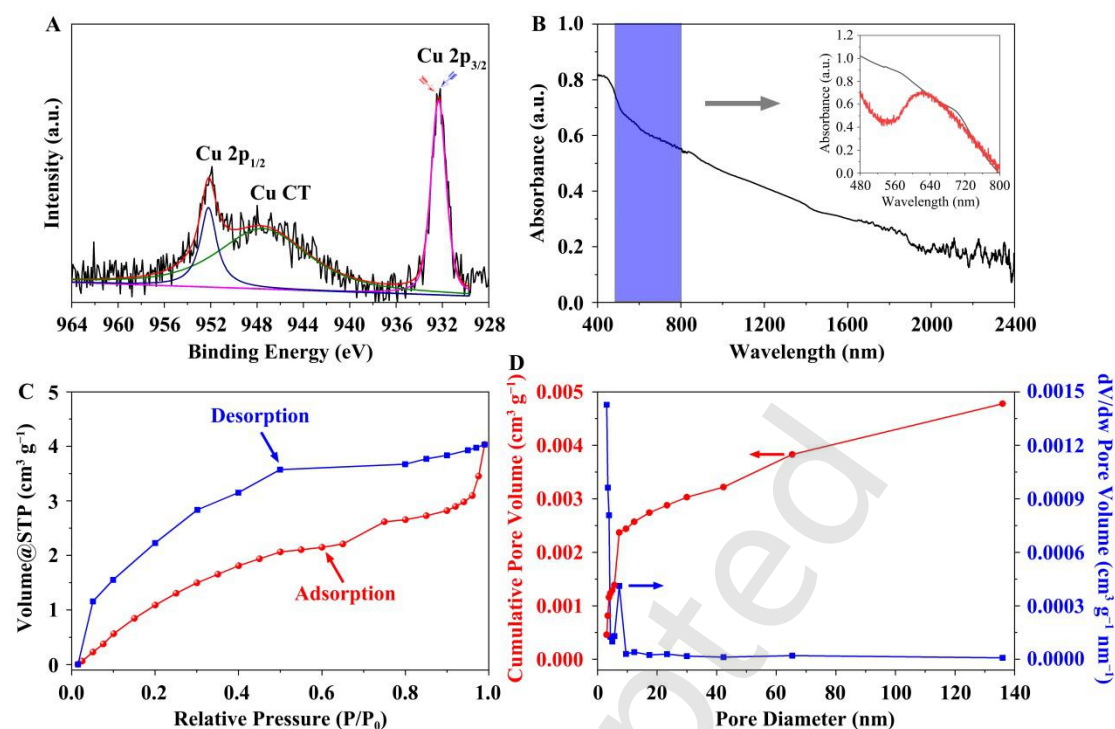


Figure S15 High-resolution XPS spectrum of Cu 2p binding energies (A), Vis-NIR DRS spectrum (B; inset: enlarged region in purple rectangle), BET N_2 adsorption-desorption isotherm (C), and pore size distribution (D) for plasmonic Cu nanoparticles (nanoseeds).

The high-resolution XPS spectrum of Cu 2p binding energies for Cu nanoparticles (Figure S15A) shows peaks at 932.5 eV and 952.2 eV, assigned to $Cu\ 2p_{3/2}$ and $Cu\ 2p_{1/2}$ of Cu^+ , consistent with surface Cu_2O ^[16,17]. A peak at ~ 932.6 eV corresponds to metallic Cu^0 , confirming zero-valent copper^[18]. Due to the nearly identical binding energies of Cu^0 and Cu^+ in the Cu 2p region, distinction is difficult. Therefore, the Cu LMM Auger spectrum (Figure S7C) was used: the peak at 559.1 eV indicates Cu^0 , while 570.0 eV confirms Cu^+ ^[12]. The presence of surface Cu^+ species is thus attributed to ambient oxidation of nanoscale copper, which is inherently unstable. Further details are provided in Figure S7. Figure S15B shows the Vis-NIR DRS spectrum of Cu nanoparticles, the inset enlarges the purple-marked region. The red curve exhibits a plasmonic peak at ~ 623 nm (initial state)^[8], while the black curve after 48 h in air shows a red-shift to ~ 691 nm, indicating partial oxidation to Cu_2O ^[10,19]. Figures S15C and S15D present the BET N_2 adsorption-desorption isotherm and pore size distribution, respectively. The specific surface area is $8.02\ m^2\ g^{-1}$, average pore diameter $3.06\ nm$, and cumulative pore volume and area are $5.00 \times 10^{-3}\ cm^3\ g^{-1}$ and $6.02 \times 10^{-1}\ m^2\ g^{-1}$, confirming mesoporous structure. All values are summarized in Table S3.

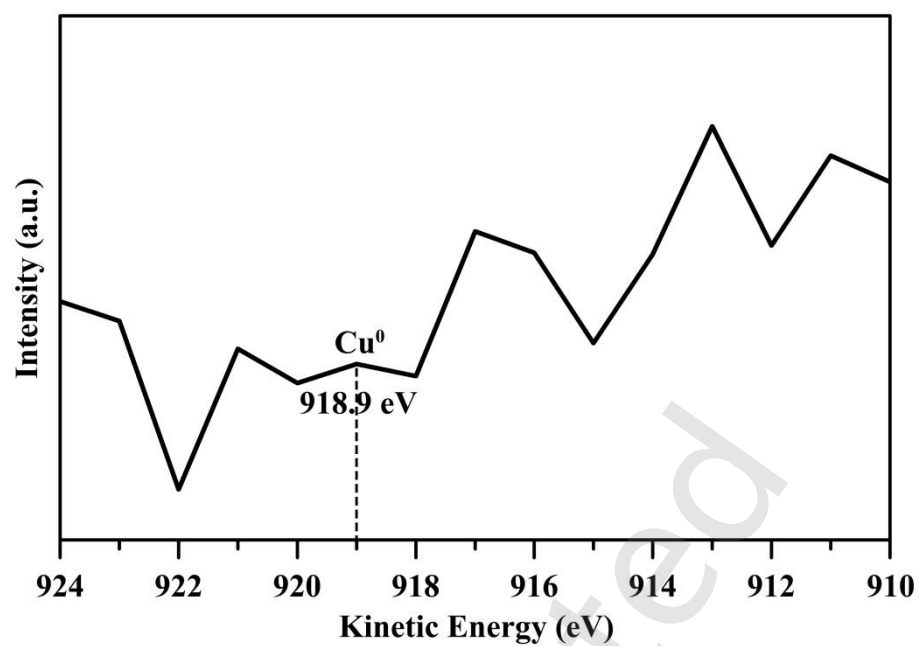


Figure S16 High-resolution Auger XPS spectrum of Cu nanoparticles anchored at the terminal ends of dual-plasmonic Cu_xSb_yS/Cu heteronanostructures.

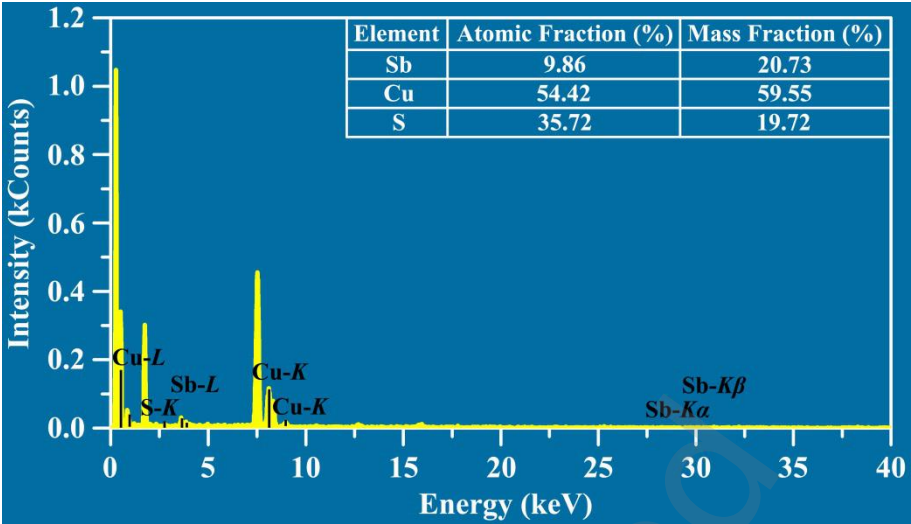


Figure S17 EDS spectrum of dual-plasmonic Cu_xSb_yS/Cu heteronanostructures.

Table S4 NIR DRS plasmonic absorption spectrum of $\text{Cu}_x\text{Sb}_y\text{S}$ domains in $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ heteronanostructures: Experimental and fitted parameters.

Experimental and fitted data are provided in Supplementary Tables S3 and S4 (.txt).

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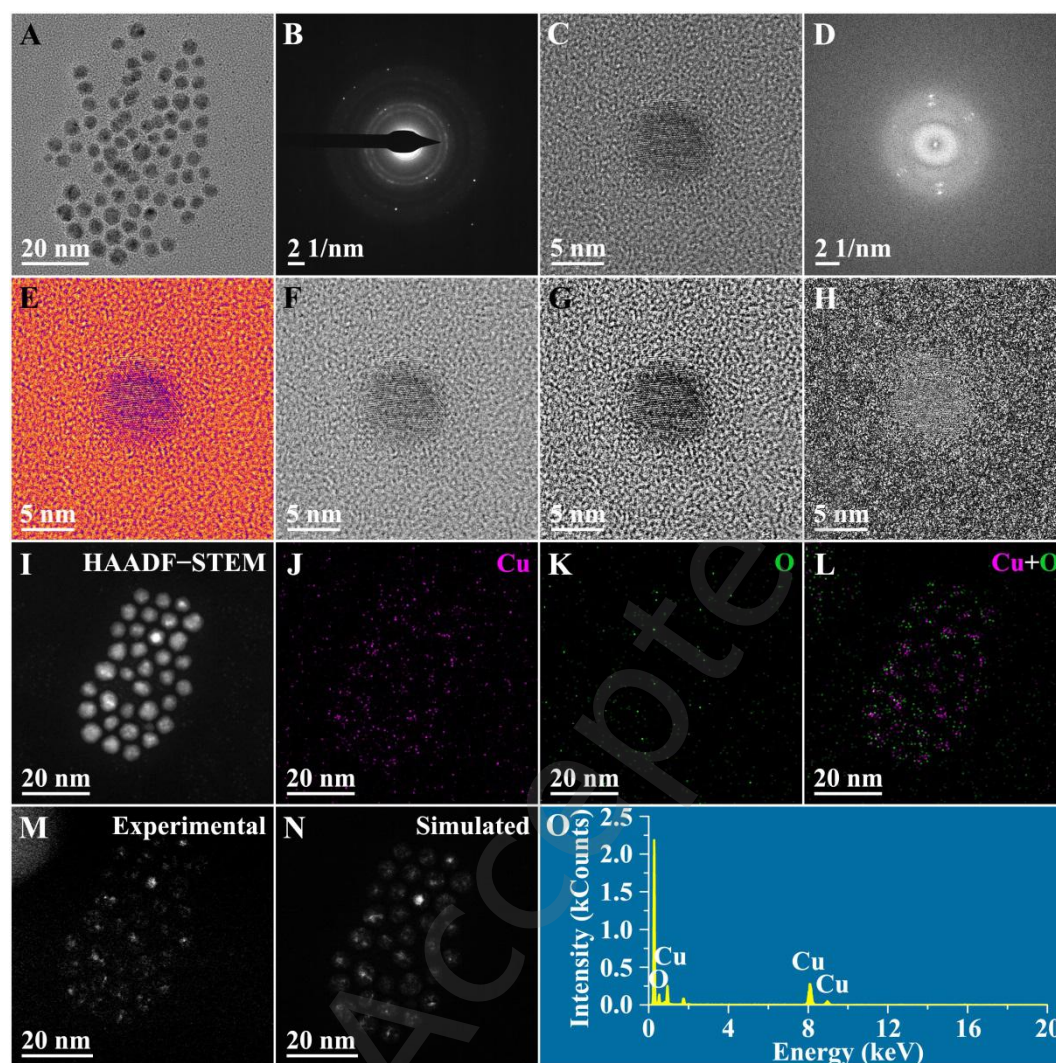


Figure S18 TEM image (A), SAED pattern (B), HRTEM image (C), FFT pattern (D), pseudo-color image (E), linearly enhanced image (F), equalized image (G), pseudo-contour representation (H) of inverse FFT patterns, HAADF-STEM image (I), corresponding STEM-EELS elemental maps (J-L), experimental (M) and simulated (N) oxygen distribution contours, and EDS spectrum (O) of plasmonic Cu nanoparticles.

As a control, the electron microscopy characterization of pure Cu nanoparticles (nanoseeds) is shown in Figure S18. Figure S18A displays a low-resolution TEM image, revealing quasi-spherical nanoparticles with an average diameter of 7.51 ± 1.93 nm (Figure S12B). The SAED pattern (Figure S18B) shows distinct diffraction rings corresponding to metallic Cu facets, confirming nanoparticle crystallinity. HRTEM and FFT images of a single nanoparticle are presented in Figures S18C and S18D: clear lattice fringes are visible in Figure S18C, while Figure S18D shows well-resolved diffraction spots consistent with crystalline facets.

For enhanced morphological visualization, pseudo-color, linearly enhanced, equalized, and pseudo-contour images are provided in Figures S18E–S18H. HAADF-STEM and elemental maps (Figures S18I–S18L) clearly show nanoparticle morphology. Mapping reveals Cu concentrated in the core and O primarily in the outer shell. Figures S18M and S18N compare experimental and simulated O distributions in the surface oxide layer (Cu_2O) under dark-field conditions, matching the O mapping results. This distribution arises from partial oxidation of Cu during sample preparation (*e.g.*, washing), due to ambient O_2 exposure^[10,18]. The EDS spectrum (Figure S18O, corresponding to Figure S18I) confirms the main composition as Cu, with a minor O signal from the Cu_2O shell. These results confirm the successful synthesis of crystalline Cu nanoparticles.

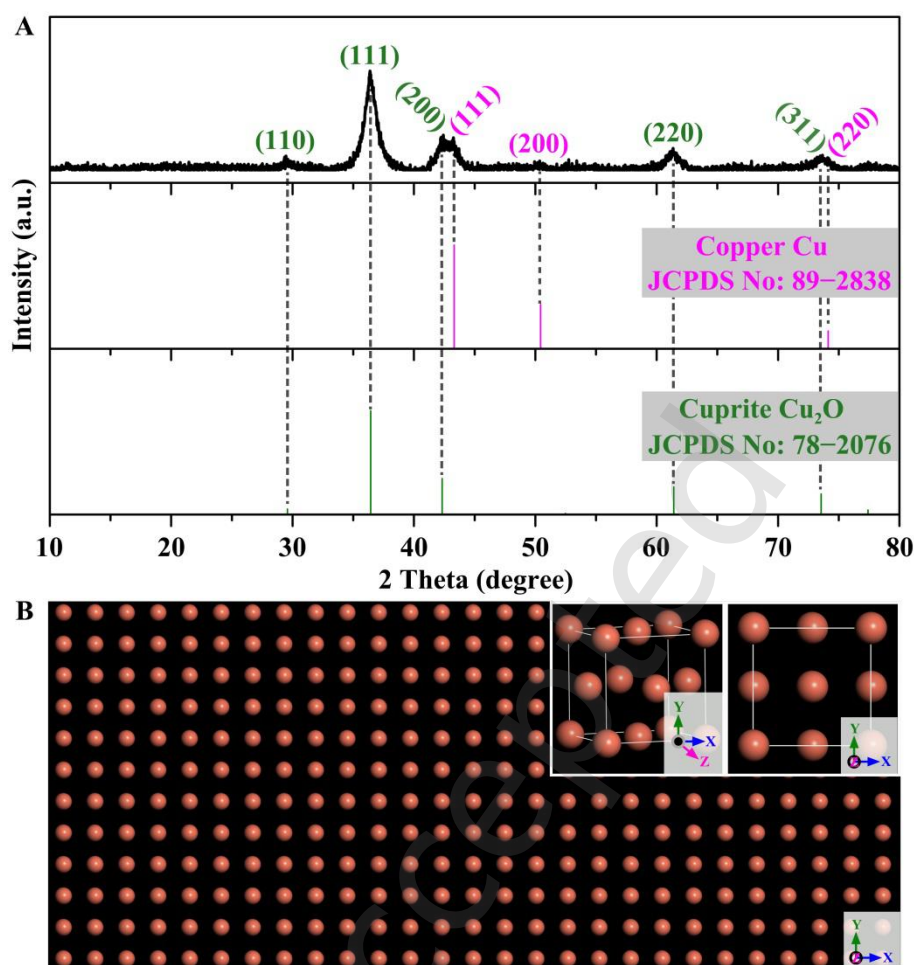


Figure S19 XRD pattern (A) of plasmonic Cu nanoparticles (nanoseeds) and schematic illustrations of their crystalline structures (B, cif: 5000216).

The powder XRD pattern of colloidal Cu nanoparticles (nanoseeds) is shown in Figure S19A. Distinct peaks at $2\theta = 43.3^\circ$, 50.4° , and 74.1° correspond to the (111), (200), and (220) facets of cubic Cu (JCPDS No: 89-2838)^[20], confirming the formation of crystalline Cu nanoparticles. Additional peaks at 29.6° , 36.4° , 42.3° , 61.4° , and 73.6° are attributed to the (110), (111), (200), (220), and (311) facets of Cu₂O (JCPDS No: 78-2076)^[20], resulting from surface oxidation during sample handling (*e.g.*, washing and measurement). Figure S19B shows schematic illustrations of crystallographic orientations for cubic Cu. For consistency in describing semiconductor/metal heteronanostructures, the Cu@Cu₂O nanostructure is referred to as Cu nanoparticles throughout this study.

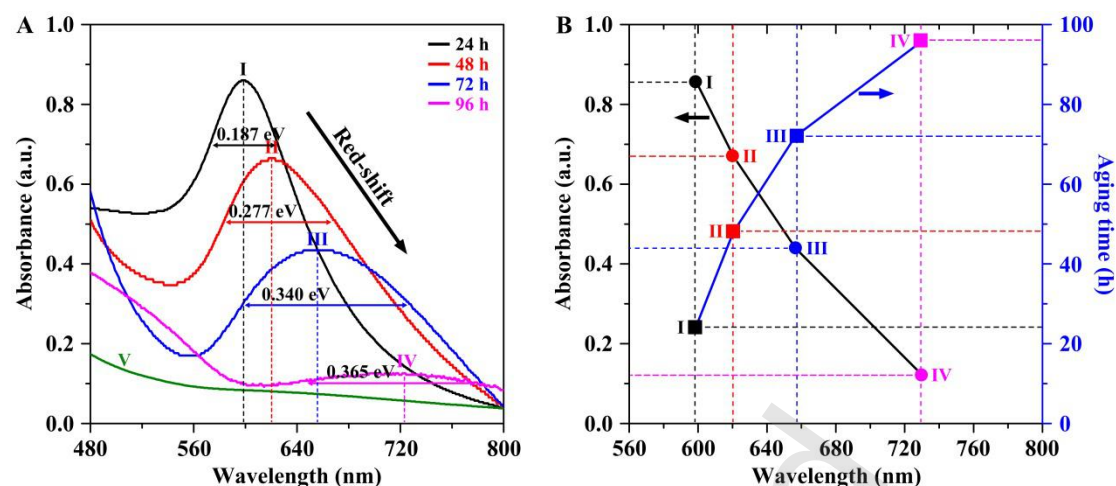


Figure S20 (A) Evolution of optical spectra for plasmonic Cu nanoparticles (nanoseeds) in n-hexane over aging time. The arrow indicates the direction of spectral shift. (B) Peak position *versus* intensity plot for clear analysis of spectral changes.

Cu nanoparticles are chemically unstable under ambient conditions, especially during washing and testing, where rapid oxidation occurs upon exposure to O_2 ^[10]. This leads to the formation of a Cu_2O surface shell. Figure S20A shows the temporal evolution of the localized surface plasmon resonance (LSPR) absorption peak. Upon prolonged air exposure, the peak red-shifts continuously from 598.5 nm (black spectrum I) to 620.5 nm (red II), 656.5 nm (blue III), and finally to 730.5 nm (magenta IV). This shift is attributed to progressive thickening of the Cu_2O shell and shrinking of the metallic Cu core^[21]. Concurrently, the full width at half maximum (FWHM) of the plasmonic (LSPR) peak increases from 0.187 eV to 0.277 eV, 0.340 eV, and 0.365 eV, indicating degradation of the plasmonic response due to decreasing metallic Cu. After ~100 h, the plasmonic signal is nearly undetectable (green spectrum V), confirming complete transformation into Cu_2O . This behavior agrees with previous reports by Hung *et al.* and Qi *et al.*, and the mechanism is detailed in the cited literature^[10,17].

Figure S20B reveals a linear correlation between LSPR peak position, exposure time, and intensity. Extended exposure causes both red shift and reduced intensity (Table S5). These results provide insight into the dynamic optical behavior of plasmonic Cu nanoparticles and their stability in practical applications.

Table S5 Peak positions, relative intensities, and FWHMs of visible absorption bands for plasmonic Cu nanoparticles at various aging times.

Sample	Aging time (h)	Peak position (nm)	FWHM (eV)	Peak intensity (a.u.)
Plasmonic Cu nanoparticles (nanoseeds)	24	598.5	0.187	0.86
	48	620.5	0.277	0.67
	72	656.5	0.340	0.44
	96	730.5	0.365	0.12

Table S6 Kinetic time constants from exponential fitting. Bleach kinetics are shown in gray.

Sample	λ_{mon} (nm)	τ_{rise} (ps)	τ_{decay}^1 (ps)	τ_{decay}^2 (ps)
Cu _x Sb _y S	455	0.41 ± 0.20	4.52 ± 0.23	915 ± 135
	504	0.43 ± 0.15	3.99 ± 0.19	956 ± 113
Cu _x Sb _y S/C u	455	0.37 ± 0.15	14.4 ± 2.1	8323 ± 1500
	504	0.34 ± 0.15	23.7 ± 1.1	8596 ± 1668

Table S7 Supplementary nouns.

Noun	Definition
Work function (ϕ)	The minimum energy required to remove an electron from the interior of a solid to the vacuum level (E_V). A higher ϕ indicates stronger electron binding and lower electron emission tendency.
Fermi level (E_F)	The highest single-particle energy level occupied by electrons at absolute zero in a non-interacting electron gas.
The lowest unoccupied molecular orbital (LUMO)	The lowest-energy unoccupied molecular orbital by electrons, equivalent to the conduction band minimum (CBM).
The highest occupied molecular orbital (HOMO)	The highest-energy molecular orbital occupied by electrons corresponds to the valence band maximum (VBM).
Vacuum level (E_V)	The reference zero point of the energy required for electrons to escape from a material and enter the vacuum.
Ionization energy (IE)	The minimum energy required to remove an electron from the HOMO to the E_V .
Note: UPS data directly yield key electronic structure parameters: VBM/HOMO, IE, and ϕ .	

Table S8 Comparison of TOF and H₂ production rates for representative catalysts in AB methanolysis or hydrolysis dehydrogenation.

Catalyst	TOF (mol H ₂ mol ⁻¹ cat. min ⁻¹)	Ref.	Catalyst	TOF (mol H ₂ mol ⁻¹ cat. min ⁻¹)	Ref.
¹ b-CuO NA/CF	13.30	[22]	¹¹ Co _{0.8} Cu _{0.2} MoO ₄	55.00	[31]
² CuO-Co ₃ O ₄ NPLs	33.40	[23]	¹² Flower-like Cu	2.41	[32]
³ RuCu/Cr ₃ C ₂	1102.00	[24]	¹³ Cu ₆ Fe _{0.8} Co _{3.2} @MIL-101	23.20	[33]
⁴ Cu ₆₈ Pt ₃₂ /KB	859.00	[25]	¹⁴ CuPd _{0.01} @ZIF-67@ZIF-8	30.15	[34]
⁵ Cu ₃ Mo ₂ O ₉ /NiMoO ₄	62.10	[26]	¹⁵ CuO/NiCo ₂ O ₄	4.94	[35]
⁶ Cu _{0.72} Co _{0.18} Mo _{0.1}	119.00	[27]	¹⁶ CuNi-MOFs	40.85	[36]
⁷ CuO-NiO/Co ₃ O ₄	79.10	[28]	¹⁷ CoCu clusters/GO	72.40	[37]
⁸ Cu-Cu ₂ O-CuO/C	24.00	[29]	¹⁸ Co-Cu-P/AC	26.50	[38]
⁹ Co ₁ Cu ₁ /g-C ₃ N ₄	11.56	[30]	¹⁹ Rh/Al ₂ O ₃ -CTAB _{0.4} -500	186.00	[39]
¹⁰ G-Cu/Ni-NiO _x	17.72	[8]			
Catalyst	H ₂ production rate (mmol H ₂ g ⁻¹ cat. h ⁻¹)	Ref.	Catalyst	H ₂ production rate (mmol H ₂ g ⁻¹ cat. h ⁻¹)	Ref.
²⁰ Cu ₇ S ₄ NWs	25.54	[40]	³⁰ Co _{0.50} Cu _{0.50} /NPs	28285.71	[47]
²¹ Cu ₇ S ₄ /Pd	157.04	[40]	³¹ Cu _{0.33} @Co _{0.22} Ni _{0.45}	7087.50	[48]
²² CuO HMSs	787.50	[41]	³² MoO _{3-x} NSs	7.38	[49]
²³ CuO	1500.00	[42]	³³ W ₁₈ O ₄₉ /C	0.0084	[50]
²⁴ CuCo ₂ O ₄ -NiO	2330.36	[43]	³⁴ W ₁₈ O ₄₉ /TiO ₂	0.0132	[51]
²⁵ Cu _{0.3} @Fe _{0.1} Co _{0.6}	17877.32	[44]	³⁵ MoO _{3-x} NSs	344.4	[52]
²⁶ Cu _{0.3} @Fe _{0.1} Co _{0.6} /rGO	21061.61	[44]	³⁶ Cu _x Sb _y S NTs	126.21	Here
²⁷ Cu ₃ P-Co ₂ P NPLs	10794.64	[45]	³⁷ Cu _x Sb _y S/Cu HNSs	690.17	Here
²⁸ G-Cu/Ni-NiO _x	10044.64	[8]	³⁸ Cu NPs	3.47	Here
²⁹ Cu _{0.4} Ag _{0.6} alloy NPs	1.03	[46]			

Notes: TOF: turnover frequencies. AB: ammonia borane. cat.: catalyst. Ref. reference. b-CuO NA/CF: bunch-like copper oxide nanowire array on copper foam. NPLs: nanoplatelets. KB: ketjen black. MOFs: metal-organic frameworks. GO: graphene oxide. AC: (waste-biomass-derived) activated carbon. NWs: nanowires. HMSs: hollow microspheres. rGO: reduced graphene oxide. NPs: nanoparticles. NSs: nanosheets. NTs: nanotubes. HNSs: heteronanostructures. The blue superscript number indicates the serial number of each catalyst.

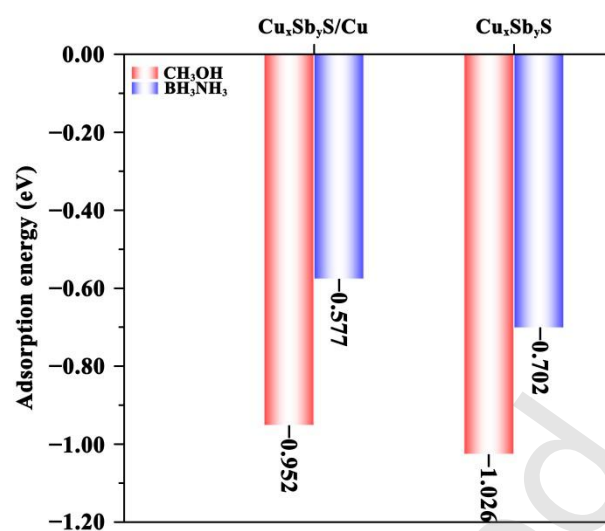


Figure S21 Adsorption energies (E_{ads}) of AB and CH_3OH on active sites of $\text{Cu}_x\text{Sb}_y\text{S}$ nanotubes and $\text{Cu}_x\text{Sb}_y\text{S}/\text{Cu}$ heteronanostructures.

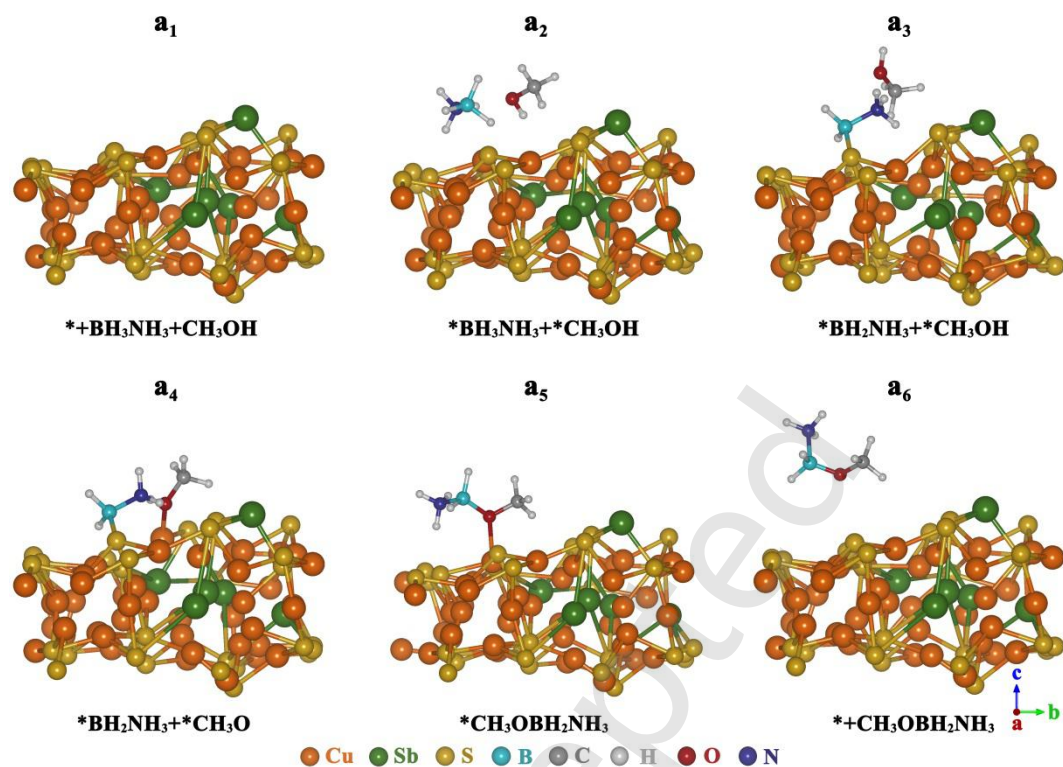


Figure S22 Crystalline structures of AB and CH₃OH during catalytic dehydrogenation over plasmonic Cu_xSb_yS nanotube-like photocatalysts. *: bare catalyst; * + CH₃OH (or * + BH₃NH₃): initial state before adsorption, no interaction; *CH₃OH (or *BH₃NH₃): adsorbed state with CH₃OH (or BH₃NH₃) bound to the catalyst surface.

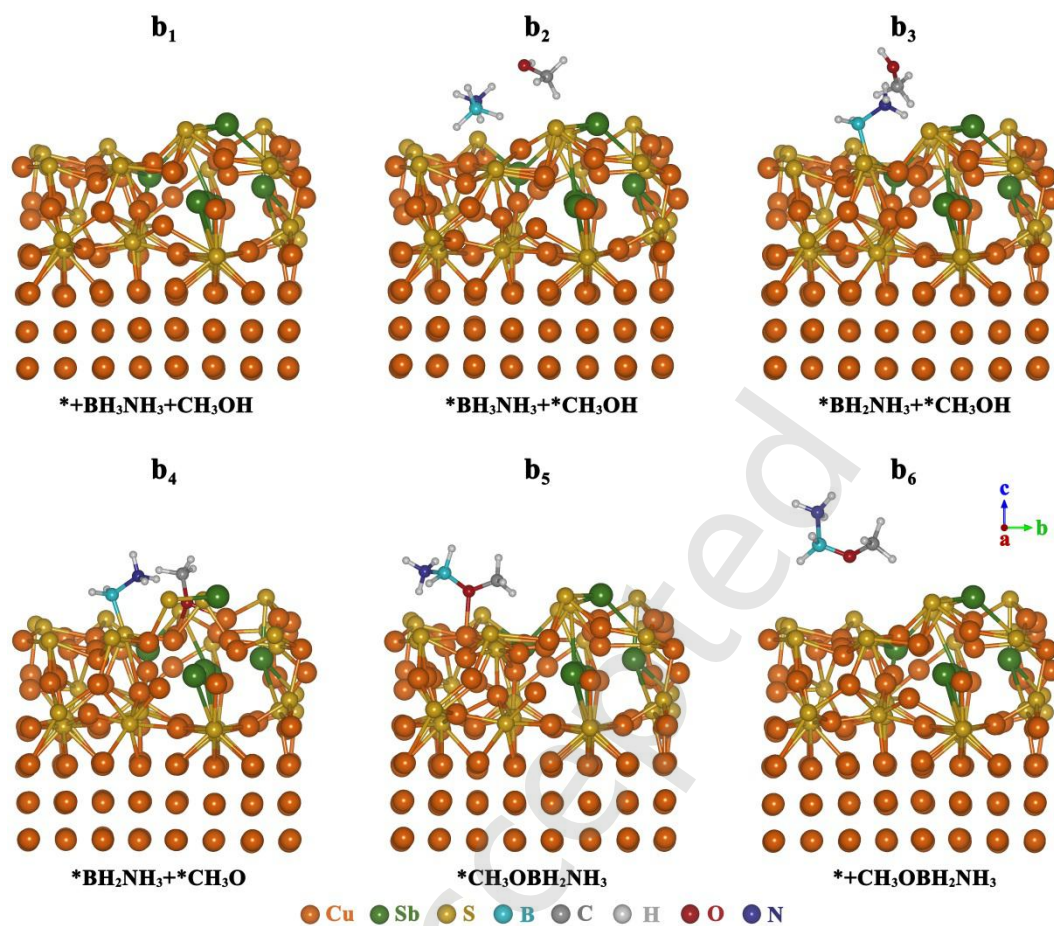


Figure S23 Crystalline structures of AB and CH₃OH during catalytic dehydrogenation over dual-plasmonic Cu_xSb_yS/Cu heteronanostructured photocatalysts. *: bare catalyst; * + CH₃OH (or * + BH₃NH₃): initial state before adsorption, no catalyst-adsorbate interaction; *CH₃OH (or *BH₃NH₃): adsorbed state with CH₃OH (or BH₃NH₃) bound to the surface.

Table S9 Bader charge transfer analysis before and after heterojunction formation.

Structure	Cu_xSb_yS/Cu heteronanostructures			
Component	Cu_xSb_yS nanotubes			Cu nanoparticles
Composition	Cu	Sb	S	Cu
Before contact/e	616.00	30.00	192.00	1056.00
After contact/e	618.96	25.15	193.71	1056.18
Charge variation/e	2.96	−4.85	1.71	0.18
Bader charge transfer/e	−0.18			0.18

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