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Supporting Information

Microwave-Activated CuO Nanotip/ZnO Nanorod Nanoarchitectures for Efficient Hydrogen Production

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Experimental Details

Synthesis of CuO nanostructures

The starting solution of copper (10 mM) was prepared by mixing $Cu(NO_3)_2 \cdot 3H_2O$ (99.5 %, Aldrich) in deionized water (18.2 MΩ). $Cu(NH_3)_4^{2+}$ complex cations were prepared by adding a concentrated ammonia solution (28-30 wt %) dropwise into the above aqueous solution until the pH value reached 11 under vigorous stirring. The resulting homogeneous solutions were then gently heated in an oven at 90 ^oC for over 2 h. Finally, freestanding CuO nanostructures were formed in the solution.

Synthesis of CuO nanotip/ZnO nanorod catalyst precursors

For synthesis of ZnO nanorods inside the microchannels, chemical bath deposition growth was performed using the equimolecular mixtures of zinc nitrate hexahydrate (99.5 %, Aldrich) and hexamethylenetetramine (99 %, Aldrich) as source precursors, at a reaction temperature of 90 ^{o}C for 7 h. Other details for the NR array growth process were similar to the procedure proposed by Vayssieres.[1] Typically, the one-step direct impregnation method involved impregnation of ZnO nanorods/microchannel with $Cu(NH_3)_4^{2+}$ complex cations aqueous solution. The reaction conditions were same as those in synthesis of CuO nanostructures. Finally, CuO nanotip/ZnO nanorod nanoarchitectures on the inner surface of microchannels were formed.

The as-derived CuO nanotip/ZnO nanorod catalyst precursors were processed in a microwave oven (2.45 GHz; TMO-17MA; TATUNG CO., Ltd.; Taiwan) for 10 min to obtain the final microwave-irradiated CuO nanotip/ZnO nanorod catalyst precursors. The microwave chamber was 452 mm in length, 262 mm in width, and 325 mm in height. During the microwave irradiation, the substrate temperature, environmental atmosphere and microwave power were maintained at room temperature, air and 600 W, respectively. For comparison, the as-derived CuO nanotip/ZnO nanorod catalyst precursors were also treated in a conventional annealing furnace at 450 ^{o}C for 1 h to obtain the conventional thermal-treated CuO nanotip/ZnO nanorod catalyst precursors.

Characterization

For microstructural investigations, XRD analyses were performed on a Bruker D8 Advance diffractometer with Cu (40 kV, 40 mA) radiation. SEM images were obtained on a JEOL 6700 filed-emission SEM. XPS analyses were carried out using a Microlab 350 system. For TEM (JEOL JEM-2100) observation, the products formed on the CuO-ZnO/microchannel substrate were scratched and dispersed on a carbon-coated Cu grid. XAS analyses were performed on a beamline BL17C1 at the National Synchrotron Radiation Research Center (NSRRC), Taiwan. Micro-Raman analyses were performed on a Jobin Yivon Labram HR800 spectrometer. TPR and N_2O titration were carried out with a Micromeritics AutoChem II 2920 instrument. The catalytic performance

tests were conducted using an integrated microchannel-reactor under atmospheric pressure. Ten microchannels per Al-alloy chip were separated by 800 μm fins; with width, depth and length of 500μm, 200μm and 4.3 cm, respectively. After H_2 pre-reduction of CuO nanotip/ZnO nanorod catalyst precursors in a H_2/N_2 (5/95), flown at the rate of 50 mL min^{-1} at 200 ^oC for 1 hr, premixed water, oxygen and methanol with a H_2O/O_2/MeOH molar ratio of 1/0.125/1 were fed into the preheater maintained at 200 ^oC by means of microfeeder. The feed and product gas streams were analyzed with a thermal-conductivity-detector gas chromatograph (TCD-GC) and CO detector.

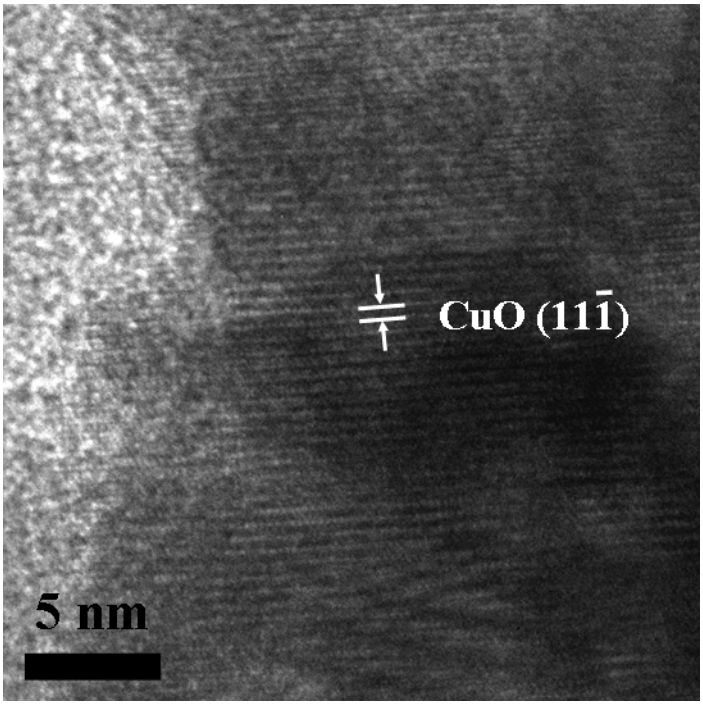

Fig. S1 HRTEM image of CuO nanodandelions, showing specific structural information about an individual nanosheet grown along the [11$\bar{1}$] direction.

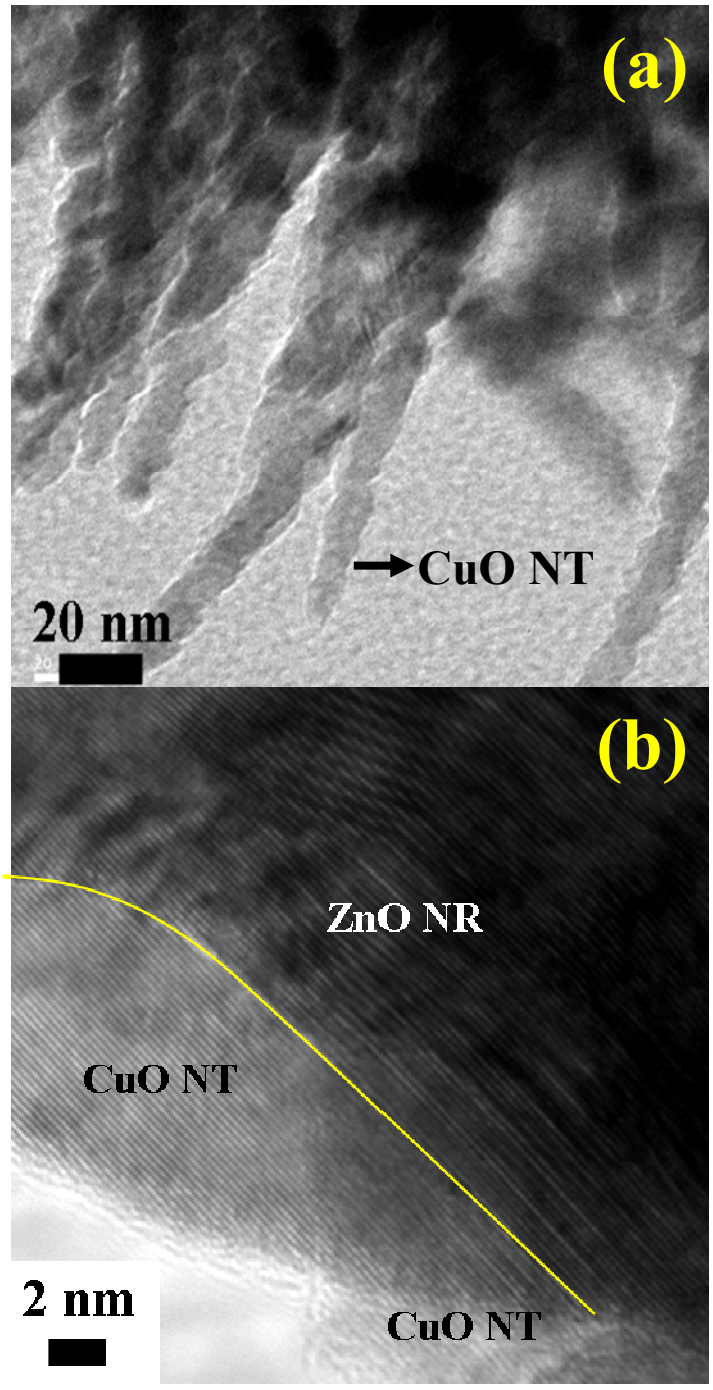

Fig. S2 (a) TEM and (b) HRTEM images of CuO NT/ZnO NR catalyst precursors, showing that NTs not only adhere to NR but also directly conjoin with the NR.

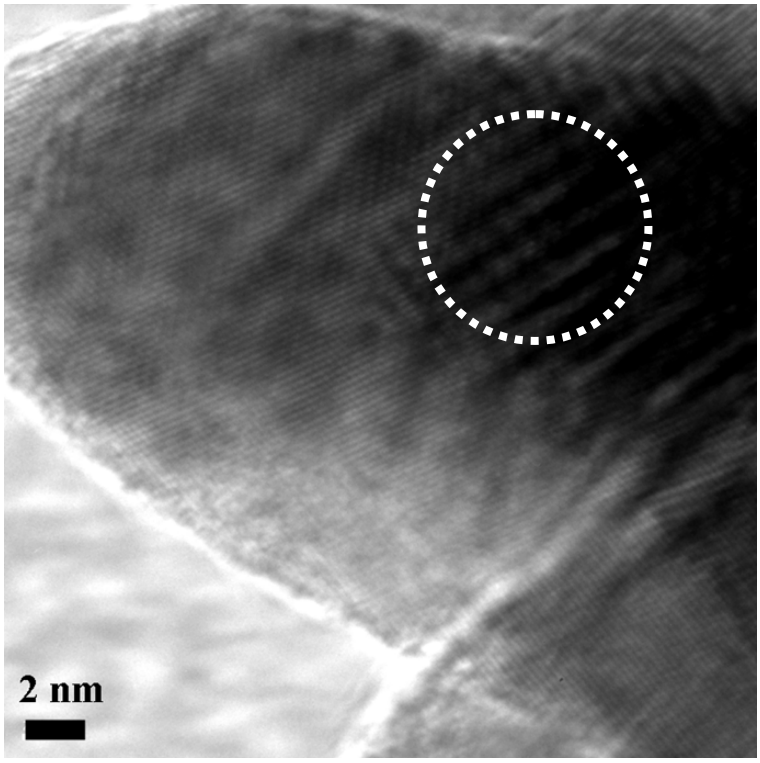

Fig. S3 HRTEM image of one single CuO NT, clearly showing a highly distorted lattice (indicated by the circle) as a result of MW irradiation.

Reference

(1) L. Vayssieres, *Adv. Mater.*, 2003, **15**, 464.