Electronic supplementary information

Au-Catalyzed Ultrathin Copper Nanowires

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Experimental

Chemicals

HAuCl₄·3H₂O (99%), NaBH₄ (98%), citrate acid (99%), ascorbic acid (99%), Poly(vinylpyrrolidone) (Mw = 1300 000) and AgNO₃ (99%) were purchased from Sigma-Aldrich. Hexadecylamine (HDA, 95%) were obtained from TCI. Copric chloride dihydrate (CuCl₂·2H₂O, 98%), glucose (98%), cetyltrimethylammonium chloride (CTAC, 97%), cetyltrimethylammonium bromide (CTAB, 99%), sodium hydroxide (NaOH, 98%) and sodium iodide (NaI, 99%) were purchased from Aladdin Reagent. Palladium chloride (PdCl₂, 99%), hexane (99%) and toluene (99%) were purchased from Sinopharm Chemical Reagent. Deionized water with a resistivity of 18.2 M Ω cm produced by a Direct-Q 5 ultraviolet water purification system was used in all experiments.

Synthesis of 4-nm Au nanoparticles

Au nanoparticle solution was prepared by mixing HAuCl₄ (0.2 mL, 0.01 M), ascorbic acid (4 mL, 0.01 M), NaOH (1.2 mL, 0.1 M) with CTAC (4 mL, 0.1 M) at 30 °C. Then a freshly prepared,

ice-cold NaBH₄ solution (0.5 mL, 0.01 M) was quickly injected into the solution under vigorous stirring. After 2 min, the obtained solutions were then ripened at 90 °C for 90 min under gentle stirring.

Synthesis of 8-nm and 13-nm Au nanoparticles

Briefly, a freshly prepared, ice-cold NaBH₄ solution (0.5 mL, 0.1 M) was injected quickly into an aqueous solution that was pre-made by mixing together HAuCl₄ (0.2 mL, 0.01 M), ascorbic acid (4 mL, 0.01 M) and CTAC (4 mL, 0.1 M). After 2 min, the obtained solutions were then ripened at 90 °C for 60 and 90 min under gentle stirring for 8-nm and 13-nm Au nanoparticles, respectively.

Synthesis of 20-nm Au nanoparticles

1 mL of the as-prepared 4-nm Au nanoparticle was added into a pre-mixed aqueous solution containing HAuCl₄ (0.12 mL, 0.01 M), CTAB (5 mL, 0.04 M) and ascorbic acid (0.024 mL, 0.1 M). The resultant seed solution was kept at room temperature for 3 h before use. Subsequently, 2 mL of the overgrowthed Au nanoparticle was added into a pre-mixed aqueous solution containing HAuCl₄ (0.25 mL, 0.01 M), CTAB (20 mL, 8 mM) and AA (0.063 mL, 0.1 M). The 20-nm Au nanoparticle solution was obtained after keeping at room temperature for 3 h.

Synthesis of ultrathin Cu nanowires

A total of 42 mg of $CuCl_2 \cdot 2H_2O$, 50 mg of glucose, and 0.27 g HDA were dispersed in 20 mL deionized water in room temperature. The mixture was stirred for 12 h to form a sky-blue homogeneous emulsion. 0.5 mL of as-prepared Au nanoparticles were injected into the solution and stirred for 15 min. The mixture was kept at 110 °C for 6 h under gentle stirring, and the color of the solution changed gradually to reddish brown. The diameter and length of the Cu nanowires could be adjusted through changing the type or volume of Au nanoparticles with reaction condition remained.

Purification of ultrathin Cu nanowires

The produced Cu nanowires were obtained by centrifugation for 10 min and washed with DI water for 4 times. The supernatant containing excess HDA was carefully piptted away and the

precipitate was redispersed into DI water. Subsequently, adding hexane to the Cu nanowire solution and then shaking for about 60 s. It was obviously observed that the hexane and water separated with a distinct interface. The purified Cu nanowires were completely dispersed in up hexane.

Synthesis of ultrathin Pd nanowires

First of all, PdCl₂ (40 mg), PVP (2 g), NaI (600 mg) were dissolved in water (30 mL) to form a dark red solution. 2 mL of 4-nm Au nanoparticle was added into the as-prepared solution and stirred for 30 min. The obtained solution was subsequently transferred into a 50 mL Teflon-lined stainless-steel autoclave and heated at 190 °C for 3 h. The resulting Pd nanowires were separated using centrifugation after cooling to room temperature.

Fabrication of Cu nanowire flexible transparent conductive films

The Cu nanowires were collected by centrifugation and sufficiently redispersed in toluene. The thin film was constructed by filtering down the nanowires from the dispersion onto a cellulose porous membrane (pore size 220 nm) via vacuum filtration. After the filtration, the Cu nanowires on the filter membrane were kept in air for about 10 s at room temperature for drying. Then, a PET substrate was placed on the side of the filter membrane with captured Cu nanowires and then pressed against the back side of the filter membrane using a tablet press with 10 Mpa pressure for 1 min. The Cu nanowire flexible transparent conductive films were treated with 0.1 M NaBH₄ for 30 s to improve the contact at junction and remove any formed Cu oxide phases. After washed with DI water and dried with nitrogen gas, the high-performance Cu nanowire flexible transparent conductive films were treated.

First-principles calculations

The simulation of adsorption energy was performed from first-principles calculations based on density functional theory. All the calculations were performed within VASP simulation package. The exchange and correlation functional in Kohn-Sham equation was described by Perdew-Burke-Ernzerhof (PBE) of generalized gradient approximation (GGA). The core electronics and nucleus were equivalently addressed by ultra-soft pseudopotentials. Considering the tiny effects on the atomization energy and the orbital energy of small metal clusters, we have neglected the spin-orbit coupling (SOC) effects. All the systems were fully relaxed with the energy convergence less than 10^{-5} eV. To get optimized structures, total Hellmann-Feynman forces was reduced to 0.01 eV/Å. The energy alteration of each step was reduced to 10^{-5} eV and the maximum displacement of atoms was less than 0.001 Å between each iteration step. A cut-off energy of 500 eV was set for the plane wave expansion. The k-mesh was set by $8 \times 8 \times 8$ centered at Γ point of Brilouin zone (BZ). The Au seed in the calculation was composed of 105 Au atoms with a regular decahedral structure. The adsorption was calculated by: $E_{ads} = E_{deposited} - E_{initial} - \mu_{Cu}$, where $E_{deposited}$ and $E_{initial}$ are the ground-state energy of the optimized models of Cu deposited surface and the initial surface, respectively. μ_{Cu} is the chemical potential of a single Cu atom.

Instrumentation

The extinction spectra were measured on a Shimadzu UV-3600 Plus ultraviolet/visible/nearinfrared spectrophotometer. TEM imaging was carried out on a FEI Tecnai 12 microscope operated at 120 kV. SEM imaging was performed on an FEI Quanta 400 FEG microscope operated at 10 kV. HRTEM imaging, HAADF-STEM characterization and elemental mapping were performed on a FEI Tecnai F20 microscope operated at 200 kV and equipped with an Oxford energy-dispersive X-ray analysis system. The sheet resistance values were measured using the four-probe method (RTS-8). X-ray diffraction (XRD) was performed using a Panalytical Empytean diffractometer. X-ray photoelectron spectroscopy (XPS) was performed using a SHIMADZU AXIS Ultra DLD.



Fig. S1 Characteristic of the Au nanoparticles. (a) Extinction spectrum and (b) TEM image of the Au nanoparticle sample. (c) Diameter histogram showing the distribution of the Au nanoparticles.



Fig. S2 TEM images of the ultrathin Cu nanowires (a) before and (b) after purification. (c) TEM image of the impurity among purification process.



Fig. S3 TEM image of the purified Cu nanowires. The wire highlighted in red background has a length of about 9.6 μm.



Fig. S4 TEM image of the Cu nanowires synthesized without Au nanoparticles.



Fig. S5 Shape evolution of Cu nanowires obtained with varied volume of Au nanoparticles. (a–d) TEM images of Cu nanowires obtained with 0.5 mL, 2 mL, 4 mL, and 6 mL of Au nanoparticles, respectively. (e) Variations of the diameter and length as a function of the varied volume of Au nanoparticles.



Fig. S6 HAADF-STEM images of the Cu nanoparticles.



Fig. S7 HRTEM image of a penta-twinned Au nanoparticle.



Fig. S8 Single-crystal Au nanoparticles-directed growth of Cu nanostructures. (a) HRTEM images of a single-crystal Au nanoparticle. (b) TEM image of Cu nanostructures grown from single-crystal Au nanoparticles.



Fig. S9 Head structure of the Cu nanowires. (a) HAADF-STEM image of the head structure of a single Cu nanowire. (b) The line-scan elemental profiles of the head structure of a single Cu nanowire recorded along the orange line in (a).



Fig. S10 Shape evolution of Cu nanowires among synthesis process. (a–f) TEM images of Cu nanowires obtained at 1 h, 2 h, 3 h, 4 h, 5 h, and 6 h, respectively.



Fig. S11 SEM images of Cu nanowires with different diameters: (a) 7 nm, (b) 10 nm, (c) 15 nm, and (d) 21 nm.



Fig. S12 Large-scale synthesis of Cu nanowires. (a) Photograph of the synthesis in a 500-mL glass reaction vessel. (b) TEM image of obtained Cu nanowires.



Fig. S13 TEM image of the Pd nanowires.



Fig. S14 Sheet resistance and transmittance of the Cu nanowire flexible transparent conductive films after 10000 bending-release cycles.



Fig. S15 XPS spectra of the Cu nanowires. (a) Cu $2p_{3/2}$, Cu $2p_{1/2}$ and (b) Cu LMM.