Supplementary Materials for

Disproportionation route to monodispersed copper nanoparticles for catalytic synthesis of propygarylamines

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Materials and Methods

Fig. S1to S5

Scheme 1

References

Chemicals and Methods

Chemicals

Oleylamine (80~90%) and tri-octylphosphine (90%) were purchased from Acros Organics and Sigma-Aldrich, respectively. Toluene, n-hexane, acetone, ethanol, oxalic acid, tetraethyl orthosilicate (TEOS) and Hexamethyldisilazane (HMDS) were purchased from Sinopharm Chemical Reagent Co., Ltd. All of these chemicals were used as received without any further purification.

Synthesis of monodisperse Cu nanoparticles

Typically, 0.6 mmol CuBr was dissolved into 7 ml Oleylamine in a three-necked flask, after strong magnetic stirring at 100 ^{o}C with Ar purge for 20 min, 0.32 ml TOP was injected into the blue solution rapidly. After an additional stirring at 100 ^{o}C for 5 min, the blue solution turned into achromatous. Then, the resulting solution was heated up to 260 ^{o}C and refluxed at this temperature for 3 h before cooling down to room temperature naturally. Excess hexane was added to the bright reddish solution to precipitate the Cu nanoparticles out by centrifugation. The obtained Cu nanoparticles were purified by three rounds of centrifugation/redispersion in the mixed solution of hexane and acetone prior to characterization.

As comparison tasks, one conducted experiment without TOP and, in the other one, replace CuBr with $Cu(NO_3)_2$ were carried out by modifying the typical procedure, respectively.

Preparation of oleophylic SiO_2 aerogel

TEOS was mixed with ethanol and oxalic acid with a molar ratio of 1:0.8:0.0023 followed by magnetic stirring for 15 min, and then standing for 18 h to allow fully hydrolyze. Then ammonia with a molar ratio of 0.09 was injected followed by standing for 30 min to form an ethanol gel. After drying at 50^{o}C for 1h, the gel was soaking in ethanol. Solvent displacement was carried out by soaking the gel in n-hexane for 3 times per 8 h. Next, surface modification was implemented by dipping the gel in the mixed solution of HMDS and n-hexane (with a molar ratio of 1:0.36) for 24 h and then washing with n-hexane for 8h. After drying at 50 ^{o}C for 10 h, a programed calcining at 150 ^{o}C for 10 h and 200 ^{o}C for 1h was applied to obtain the final product.

Support Cu nanoparticles on SiO_2 aerogel

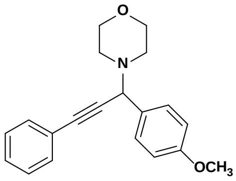
75 mg of Cu nanoparticles was dissolved in 15 ml toluene in a 50 ml vial to form solution A.

425 mg of SiO_2 aerogel was dissolved in 15 ml toluene in a 50 ml vial to form solution B. Then, A was poured into B followed by mechanical shake for 15 h. After standing the solution for 2h, colorless toluene phase was formed indicating the fully absorption of Cu nanoparticles on SiO_2 aerogel. The colorless toluene phase was decanted and the solid materials were drying in a vacuum oven. The resulting catalysts are denoted as SiO_2@Cu.

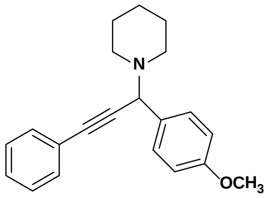
Procedure of one-pot synthesis of Propargylamines catalyzed by SiO_2@Cu nanocatalysts

Aldehyde (1.0 mmol), amine (1.2 mmol), alkyne (1.5 mmol) and SiO_2@Cu (50 mg) in 1.5 mL of toluene were stirred at 110 ^{o}C in a sealed pressure tube vessel. After the completion of the reaction (monitored by TLC,) the reaction mixture was filtered through celite pad to remove SiO_2@Cu the nanoparticle. The filtrate containing the reaction mixture was concentrated under reduced pressure to remove the toluene. The residue that was obtained was then diluted with water (20 mL), and then extracted with EtOAc (3 X 10 mL). The combined organic layers were washed with brine solution (10 mL), and then dried over anhydrous Na_2SO_4. Then, the solvent was again evaporated under reduced pressure to yield the crude product, which was then purified by column chromatography using silica gel (100–200 mesh) using hexane/ethyl acetate as an eluent to afford the pure product. All compounds are well characterized and reported in the literatures.[1 2, 3]

Spectral Interpretation of synthesized compounds



4-(1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-yl)morpholine: Obtained in 95 % yield**;** ^{1}H NMR ($CDCl_3$) d: 7.57-7.50 (m, 4H), 7.33 (s, 3H), 6.90 (d, *J*=8 Hz, 2H), 4.82(s, 1H, -CH), 3.82(s, 3H, $-OCH_3$), 3.78 (bs, 4H), 2.69 (s, 4H).



1-[1-(4-Methoxyphenyl)-3-phenylprop-2-yn-1-yl]piperidine: Obtained in 93 % yield;^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59 –7.49 (m, 4 H), 7.38–7.27 (m, 3H), 6.92–6.86 (m, 2 H), 4.72 (s, 1 H, -CH), 3.81(s, 3 H, OCH_3), 2.64- 2.45 (m, 4 H), 1.66–1.52 (m, 4 H), 1.48–1.39 (m, 2 H).

Characterization

Transmission electron microscopy (TEM).

A portion of the as-prepared powders was dispersed in toluene via ultrasound concussion for 15 min. The TEM samples were prepared by dropping the particle suspensions in toluene onto a gold grid coated with carbon film before drying at room temperature under ambient conditions. TEM images, selective area electron diffraction (SAED) data were collected on a JEM-2100 transmission electron microscope operating at 200 kV.

Scanning electron microscopy (SEM).

The samples for SEM observation were prepared by dropping the powder suspensions in toluene onto a silicon wafer before drying at room temperature under ambient conditions. The SEM images were collected on a LEO 1530 scanning electron microscope operated at 20 kV.

X-ray diffraction (XRD).

The samples for XRD analyses were prepared by dropping the powder suspensions in toluene onto a glass wafer before drying at room temperature under ambient conditions. XRD measurements were taken on a Panalytical X'pert PRO diffractometer using Cu Kα radiation, operating at 40 kV and 30 mA.

Optical spectra data.

Visible-Near Infrared (NIR) extinction spectra were obtained at room temperature with a Shimadzu UV-2550 ultraviolet-visible spectrophotometer. NMR spectra were recorded on a Bruker 400, 5 mm probe at 400 MHz.

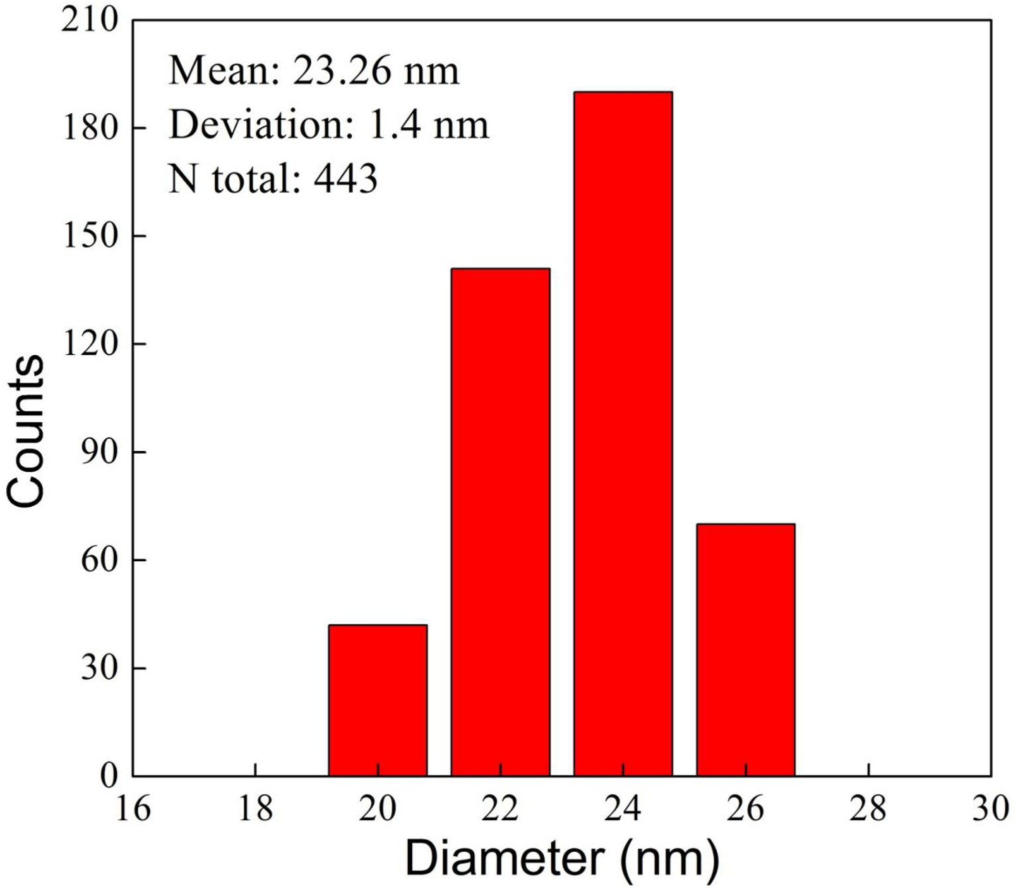


Fig. S1.

Statistic result of particle size distribution determined from 443 Cu nanoparticles synthesized in the typical procedure.

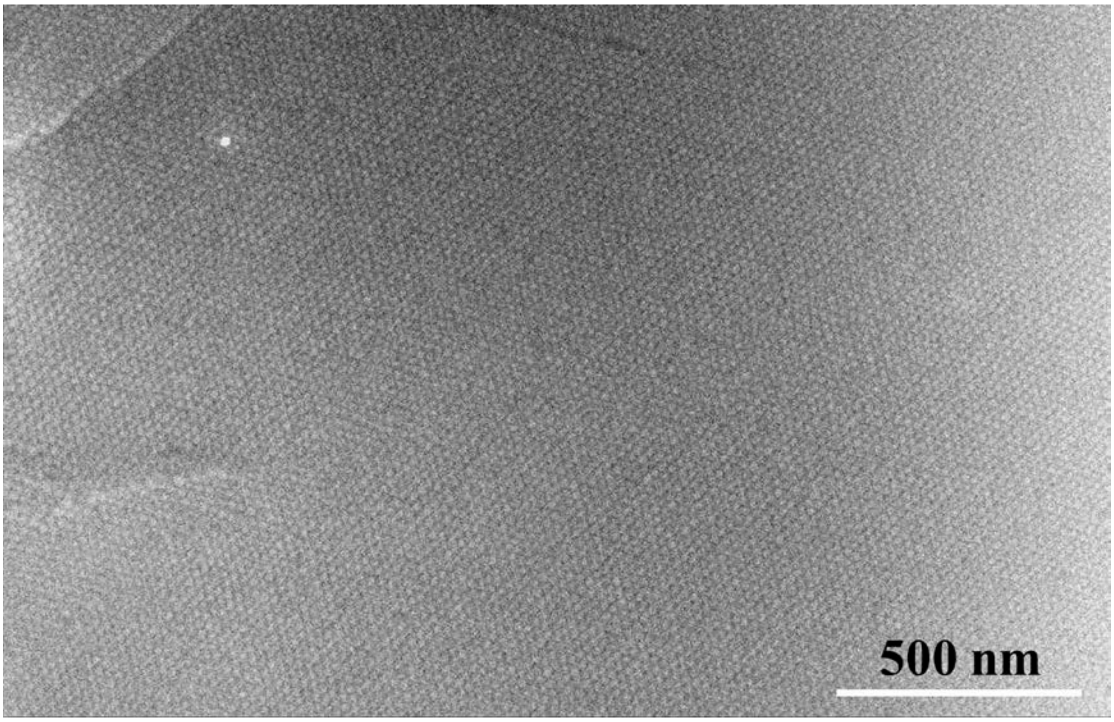


Fig. S2.

SEM image of the two-dimensional supper lattices assembled on Si wafer by slow evaporation of the toluene solution of Cu nanoparticles in a thermostat.

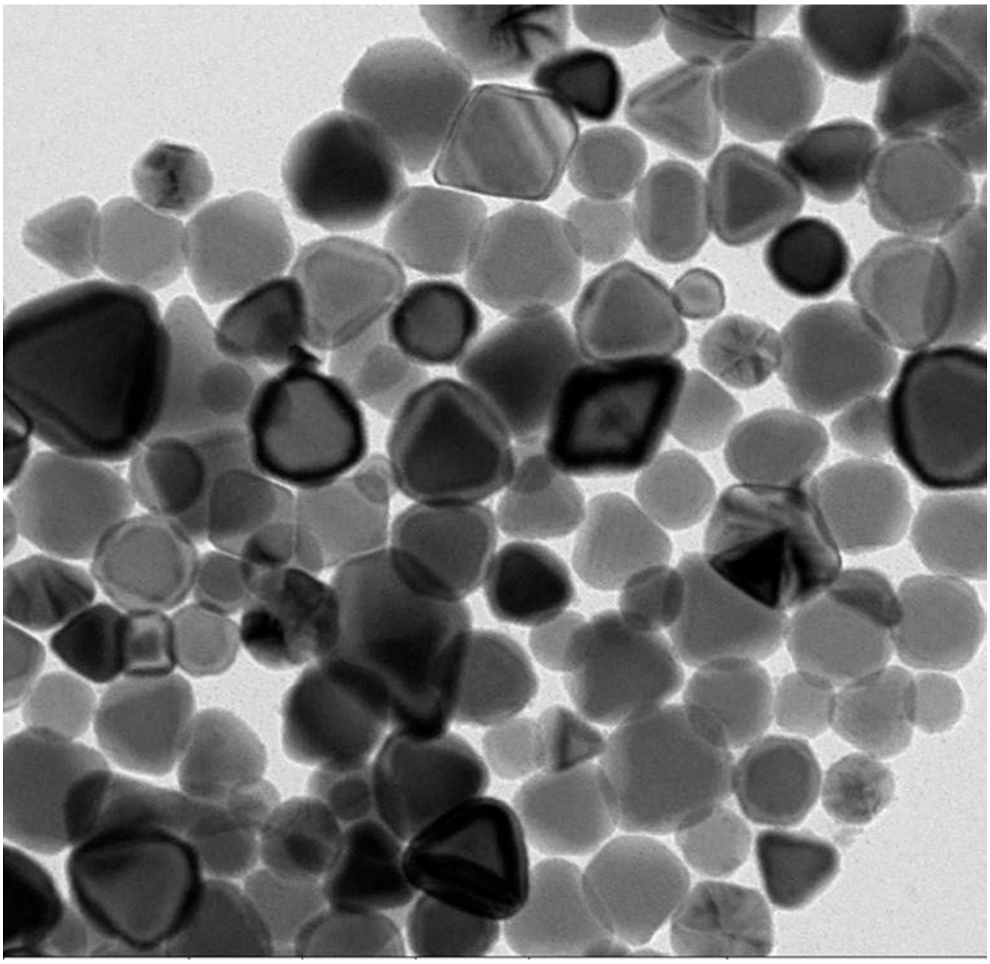


Fig. S3.

TEM image of the Cu nanocrystals synthesized in the absence of TOP with no other change from the typical procedure.

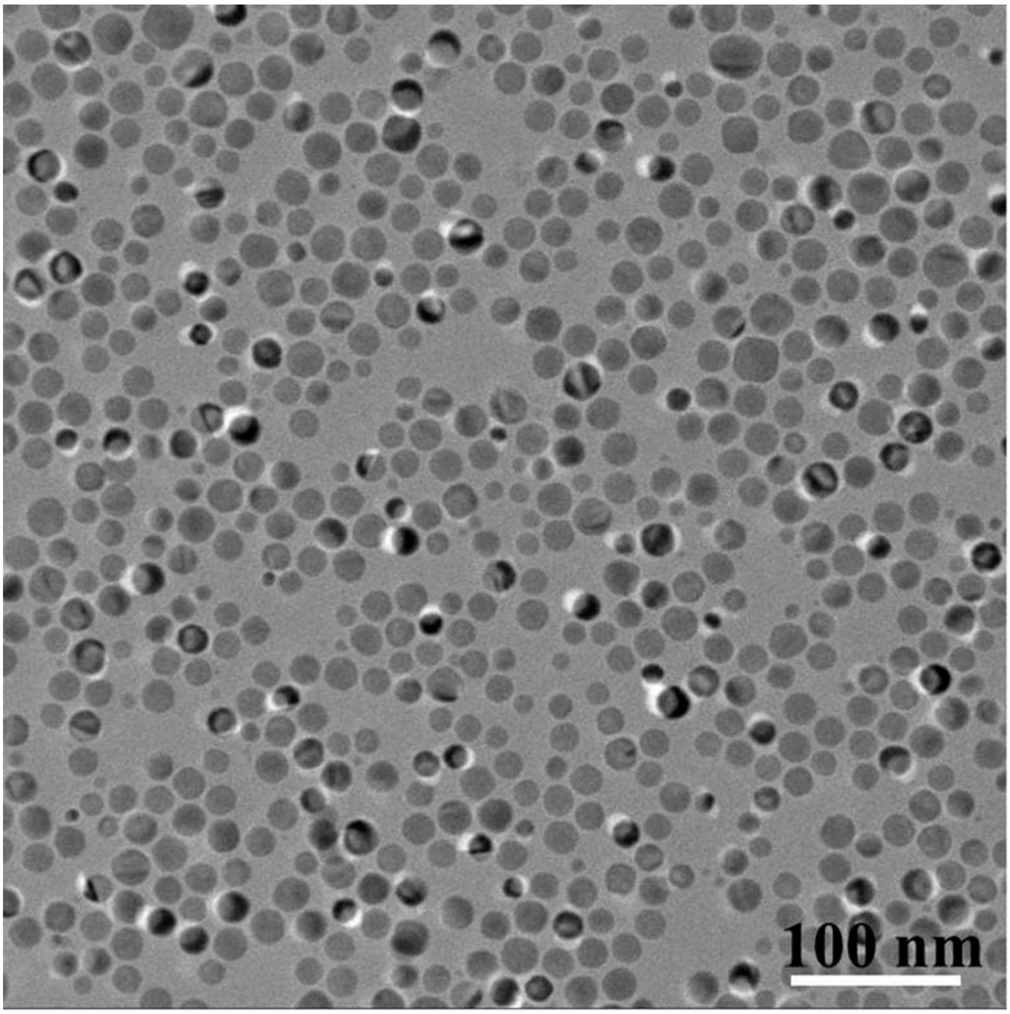


Fig. S4.

TEM image of Cu nanoparticles using $Cu(NO_3)_2$ instead of CuBr as precursor in the typical procedure with no other change.

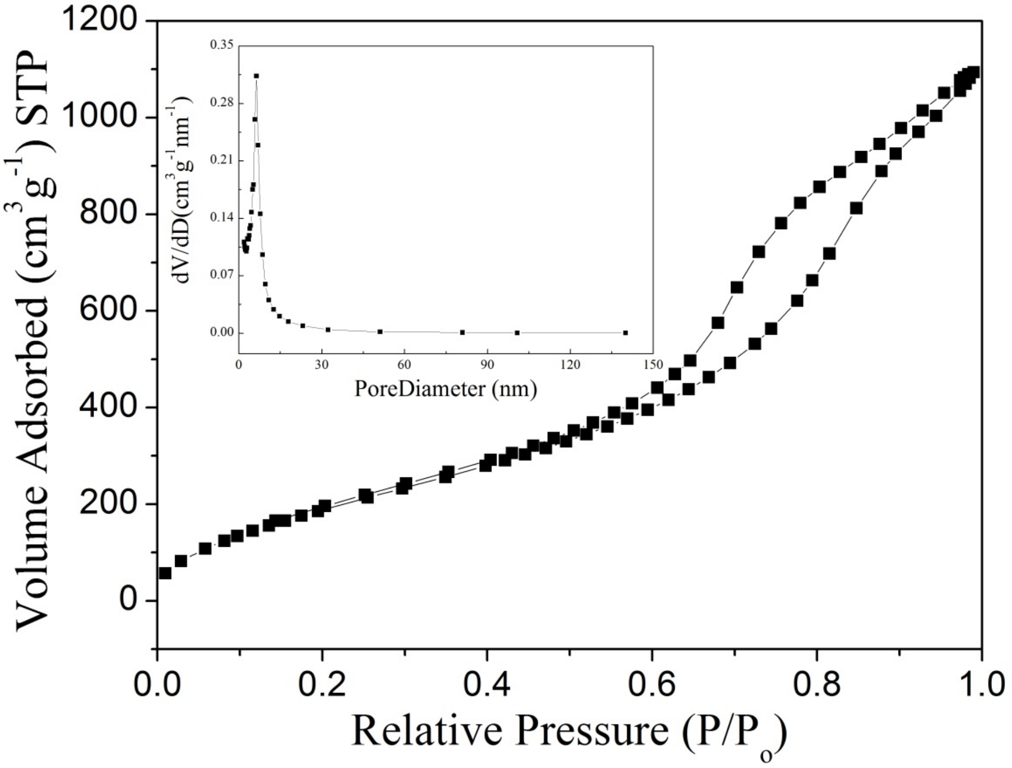
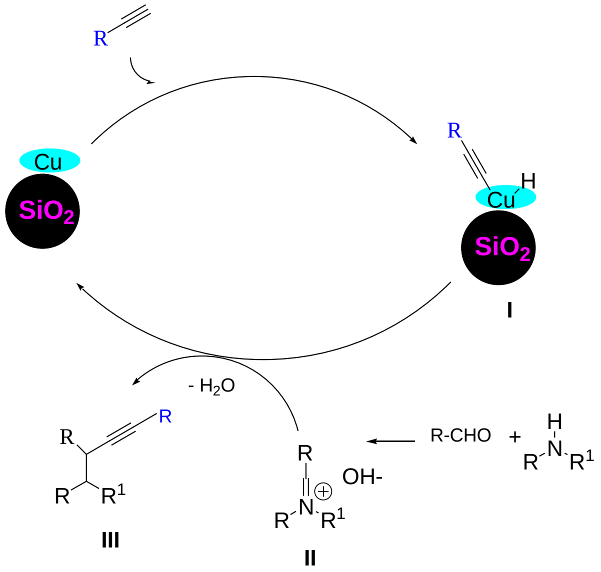


Fig. S5

N_2 adsorption-desorption isotherm and pore size distribution of SiO_2@Cu nanocatalysts.



Scheme 1. Possible mechanism for A3 coupling reaction.

References

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