Supplementary Information

ZnO/CuO Core-Branch Nanocatalysts for Ultrasound-Assisted Azide-Alkyne Cycloaddition Reactions

Ji Chan Park, A Young Kim, Jae Young Kim, Sungkyun Park, Kang Hyun Park, and Hyunjoon Song*

Experimental Details

Chemicals: Copper(II) acetylacetonate (Cu(acac)₂, 99.99%), 1,5-pentanediol (PD, 96%), poly(vinyl pyrrolidione (PVP, $M_w = 55,000$), zinc(II) acetylacetonate hydrate (99.995%), and sodium hydroxide (NaOH, 99.99%) were purchased from Aldrich, and used as received without further purification.

Synthesis of polycrystalline ZnO nanospheres: The mixture of zinc(II) acetylacetonate hydrate (0.10 g, 0.40 mmol) and PVP (1.0 g, 9.0 mmol) was dissolved in 40 mL of PD, and then slowly heated to 230 °C for 12 min under an inert condition. The mixture solution was allowed to stir at the same temperature for 3 min. After that, the colloidal dispersion was cooled to room temperature, and the product was separated by adding 120 mL of ethanol with centrifugation. The precipitates were washed with ethanol several times and re-dispersed in 10 mL of ethanol.

Synthesis of ZnO/Cu₂O hybrid nanoparticles: The mixture of zinc acetylacetonate hydrate (0.10 g, 0.40 mmol) and PVP (1.0 g, 9.0 mmol) was dissolved in 40 mL of PD, and then slowly heated to 230 °C for 12 min under an inert condition. The mixture solution was allowed to stir at the same temperature for 3 min. Then, Cu(acac)₂ (0.1 g, 0.40 mmol) dissolved in 5.0 mL of PD was injected into the hot zinc-PVP mixture solution at 230 °C and the mixture was stirred for 10 min at the same temperature. The colloidal dispersion was cooled to room temperature, and the product was separated by adding 120 mL of ethanol with centrifugation. The precipitates were washed with ethanol several times and re-dispersed in 10 mL of ethanol.

Synthesis of ZnO/CuO core-branch nanoparticles: An aqueous sodium hydroxide solution (1.0 M, 1.0 mL) was added into 25 mL of the ZnO/Cu₂O hybrid nanoparticle dispersion in ethanol (8.0 mM with

respect to the precursor concentration). The mixture was subjected to stirring at room temperature for 1 h. After the reaction, the product was collected by centrifugation. Finally, the particles were dispersed in ethanol.

Synthesis of CuO hollow nanoparticles: CuO hollow spheres were prepared by the controlled oxidation of Cu₂O nanocubes according to the previous report.¹ For the preparation Cu₂O nanocubes, PVP dissolved in 45 mL of PD was heated to 240 °C under inert conditions. Then, 4.0 mmol of Cu(acac)₂ dissolved in 15 mL of PD was injected into the hot PVP solution at 240 °C and the mixture was stirred for 15 min at the same temperature. The colloidal dispersion was cooled to room temperature, and the product was separated by adding 150mL of acetone with centrifugation. The precipitates were washed with ethanol several times, and re-dispersed in 50 mL of ethanol. For the synthesis of CuO hollow particles, an aqueous ammonia solution (2.0 mL, 3.7 M)) was added into 25 mL of the Cu₂O cube dispersion in ethanol (16 mM with respect to the precursor concentration). The mixture was subjected to stirring at room temperature for 2 h. After the reaction, the products were collected by centrifugation.

General procedure for the azide-alkyne cycloaddition with ultrasound: In a 10 mL pressure tube schlenk, ZnO/CuO hybrid nanoparticles (4.2 mg, 0.018 mmol), benzyl azide (0.075 mL, 0.60 mmol), phenylacetylene (0.10 mL, 0.90 mmol) and 2.4 mL H₂O/t-BuOH (1.6 mL:0.8 mL) were added. The reaction mixture was sonicated for 10 min at room temperature by using a Fisher Scientific Sonic Dismembrator 500 (Pittsburgh, PA, USA). After 10 min, the reaction mixture was poured into 20 mL of the saturated NH₄Cl aqueous solution. The product was extracted three times with 20 mL dichloromethane and dried using MgSO₄. The ZnO/CuO nanocatalysts were recovered by centrifugation and the supernatant was analyzed by 300 MHz NMR.

Characterization: The nanoparticles were characterized by HRTEM (Philips F20 Tecnai operated at 200 kV, KAIST), HRTEM (Tecnai G2 F30 operated at 300 kV, KAIST), and EDX (attached to F30 Tecnai). For EDX and scanning TEM analysis, the samples were prepared by putting a few drops of the corresponding colloidal solutions on nickel grids (Ted Pellar, Inc). FE-SEM (Nova 230) and XRD (Rigaku D/Max-IIIC) were also used for the analyses. The copper and zinc loading amounts were measured by ICP-AES (POLY SCAN 60 E). Nitrogen sorption isotherms were measured at 77 K with a BELSORP mini-II (BEL Japan Inc.). Before measurements, the samples were degassed in a vacuum at 150 °C for 6 h. Ultrasonic radiation was supplied with Dismembrator 500 (Fisher Scientific Inc.). The XPS core-level spectra of nanoparticles before and after reaction were obtained using the monochromatized Al K α (hv = 1486.6 eV) radiation (ESCALAB 250, Thermo). The base pressure inside the X-ray photoelectron spectrometer was kept at 4.2 x 10⁻⁹ Torr. The 50 eV pass energy, 0.1 eV/step,

and the dwell time of 100 ms were chosen to obtain an optimum count-rate of XPS. The obtained spectra were calibrated using the C (1s) line (284.5 eV).

1 J. C. Park, J. Kim, H. Kwon and H. Song, Adv. Mater. 2009, 21, 803.



Fig. S1 (a,b) FESEM and (c) HRTEM images, and (d) XRD spectrum of ZnO nanospheres. The bars represent (a) 500 nm, (b) 100 nm, and (c) 50 nm.



Fig. S2 (a) TEM image of ZnO/Cu_2O hybrid nanoparticles and EDX spectra of (b) the entire range, and the ranges marked with (c) the blue cross and (d) the green cross in (a). The Ni peaks are originated from the TEM grids. The bar represents 50 nm.



Fig. S3 High-resolution TEM images of (a) ZnO nanospheres, (b) a Cu₂O nanocube in ZnO/Cu₂O heteroaggregates, and (c) CuO branches in ZnO/CuO hybrid nanoparticles. All bars represent 5 nm.



Fig. S4 Low-resolution TEM images of (a) ZnO nanospheres, (b) ZnO/Cu₂O hetero-aggregates, and (c) ZnO/CuO hybrid nanoparticles. All bars represent 500 nm.



Fig. S5 (a) TEM image of ZnO/CuO core-branch nanoparticles and EDX spectra of (b) the entire range, and the ranges marked with (c) the blue cross and (d) the green cross in (a). The Ni peaks are originated from the TEM grids. The bar represents 100 nm.



Fig. S6 Two representative HRTEM images of the CuO branches on ZnO/CuO core-branch nanoparticles. All bars represent 5 nm.



Fig. S7 (a) SEM and (b) TEM images of CuO hollow spheres. The bars represent a) 200 nm and b) 50 nm.



Fig. S8 TEM images of ZnO/CuO core-branch nanoparticles after 5th recycling of the reaction. The bars represent (a) 200 nm and (b) 50 nm.



Fig. S9 The core-level XPS spectra of Cu $2p_{3/2}$ before and after the cycloaddition reaction (entry 2). The solid curves represent the best-fitted results by deconvolution. XPSPEAK4.1 (written by Raymond Kwok) was used to analyze the XPS data (http://www.uksaf.org/software.html).

Table S1 The fitted binding energies (BEs) of the Cu $2p_{3/2}$ XPS spectra of ZnO/CuO core-branch nanoparticles before and after the cycloaddition reaction (entry 2).

Cycloaddition reaction	Cu 2p _{3/2}		
	Peak 1(eV) Cu ₂ O	Peak 2 (eV) CuO	I1/I2 (intensity ratio)
Before	932.07	933.31	0.47
After	932.81	934.8	1.11