

## Electronic Supplementary Information

# Surface plasmon resonances enhanced click chemistry through synergist photothermal and hot electron effect

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## Experimental Methods

**Chemicals.** Benzyl azide (94%) and L-ascorbic acid sodium salt (sodium ascorbate) were purchased from Alfa Aesar. Hexamethylenetetramine (HMTA), copper(II) nitrate, phenylacetylene, and 1, 3, 5-trimethoxybenzene (98%) were purchased from Aladdin Chemistry Co., Ltd. Bathocuproine (BCS, 96%) was purchased from Sigma-Aldrich. Deuterated chloroform (99.8 atom%D), sodium chloride, copper(II) sulfate pentahydrate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ), triethylamine, trisodium citrate dihydrate, polyvinylpyrrolidone (PVP, K30), ethyl acetate (EtOAc), L-ascorbic acid, and tetrachloroauric (III) acid tetrahydrate ( $\geq 47.8\%$ ) were purchased from Shanghai Chemical Reagent Co., Ltd. All the chemicals were used without further purification.

**Characterizations.** Solution absorption spectra were collected on a Shimadzu UV-3600 using 10 mm optical path quartz cuvette.  $^1\text{H}$  NMR spectra of benzyl azide, alkyne, and their cycloaddition product were taken using a Varian NMR System 400 MHz NMR Spectrometer with automated triple broadband (ATB) probe. Transmission electron microscopy (TEM) images were captured on a FEI Technai G2 S-Twin. Photoirradiation was carried out under visible light (420-780nm) using a Xenon lamp (PLS-SXE300, Perfect Light) with a nominal total power of 19.6 W in the visible range. Elemental quantification was obtained using inductively coupled

plasma emission spectrometry (ICP-OES).

**Synthesis of Au nanoparticles.** 2.55 mL of 10 mM  $\text{HAuCl}_4$  was added to 100 mL deionized water in a 250 mL flask, which was heated to boiling in an oil bath for 15 min. Then, 2 mL of 10 mg  $\text{mL}^{-1}$  trisodium citrate was added in, and the boiling was continued for another 15 min. Finally, to the reaction solution, 1 mL of 20 mg  $\text{mL}^{-1}$  PVP was added in. After the reaction mixture was cooled down to room temperature under stirring, it was centrifuged at 11,000 rpm for 15 min, with the precipitate collected and redispersed in deionized water. This protocol produces Au NPs with average diameter of 18 nm. By varying the added amount of trisodium citrate, different sized Au NPs can be similarly synthesized.

**Synthesis of CuO and Au-CuO nanohybrids.** 40 nm Au nanoparticles was synthesized under similar conditions described as above, except 0.7 mL of trisodium citrate was used to grow larger NPs. After cooled down to room temperature, Au NPs were obtained by centrifuging at 8000 rpm for 10 min, and redispersed in 3 mL water. The obtained Au colloidal dispersion was mixed with 45 mL of 110 mM PVP solution, and then 1 mL of 50 mM HMTA and 1 mL of 50 mM  $\text{Cu}(\text{NO}_3)_2$  solutions were added to the mixture. The reaction mixture was transferred heated to 95 °C in an oil bath for 3 h. After the reaction mixture was cooled down to room temperature, it was centrifuged at 11,000 rpm for 15 min, and washed with water, then redispersed in deionized water for further use.

CuO NPs were synthesized at the same conditions, but in the absence of Au NP seeds.

**Experimental condition for CuAAC reactions.** Benzyl azide (0.5 mmol) and phenylacetylene (0.6 mmol) were added to 1 mL of deionized water in a 20 mL glass vial. Then,  $\text{CuSO}_4$  (0.2 mL, 25 mM) and freshly prepared sodium ascorbate solution (0.2 mL, 125 mM) were added in, and the mixture was allowed to react for different duration at room temperature (17-19 °C) in air. Reaction products after 15, 30, 45, 60, and 90 min were extracted by adding 5 mL of ethyl acetate (EtOAc) to the reaction vial, and the solvent EtOAc was removed by rotary evaporation. Finally, the obtained substance was dissolved in deuterated chloroform, and the yield of cycloaddition product was determined by  $^1\text{H}$  NMR, using 1,3,5-trimethoxybenzene as an internal standard.  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ) data:  $\delta$ =7.55-7.60 (s, 1H), 5.50-5.60 (s, 2H), 4.25-4.38 (s, 2H), 3.07-3.10 (s, 1H), 6.08-6.11 (s, 3H). All experiments were repeated for three times.

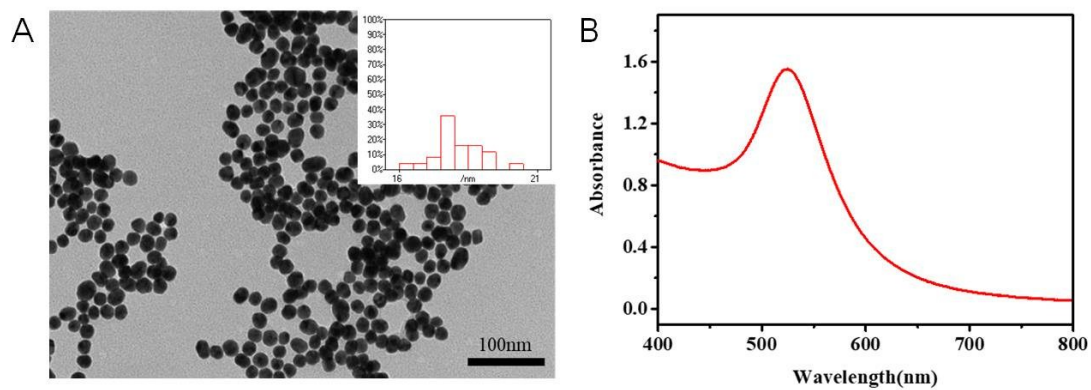
For surface plasmon enhanced CuAAC reactions, instead of 1 mL of deionized water, 0.5 mL of deionized water and 0.5 mL of 18 nm Au NPs (19.9 mM Au) were added in. The reaction vessel was placed under constant Xenon lamp illumination with UV and NIR cutoff filters. The solution reaction temperature was monitored by a thermal infrared camera as well as thermocouple.

For the reaction using a sacrificial agent, 0.125 mmol TEA was added after the addition of benzyl azide (0.5 mmol) and phenylacetylene (0.6 mmol).

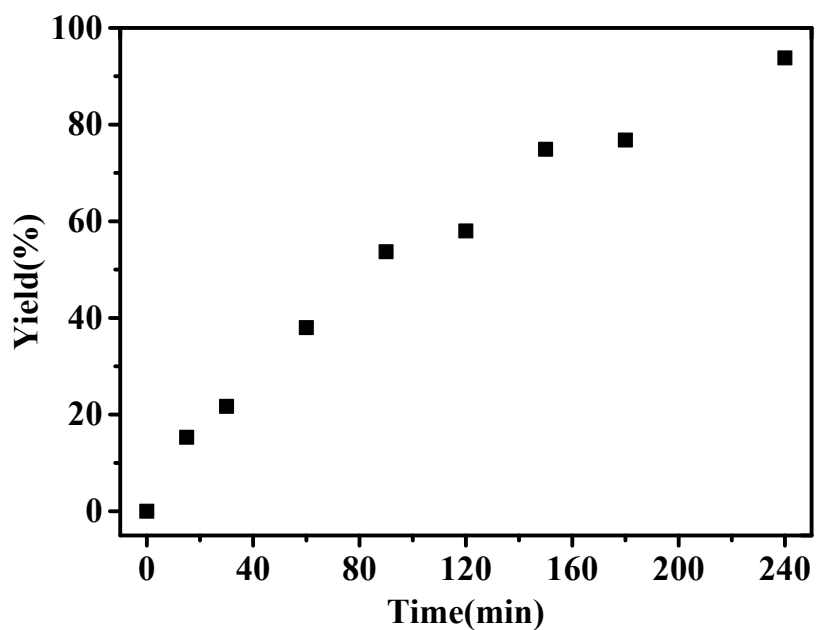
For CuAAC reactions using Au-CuO and CuO NPs, to a 20 mL glass vial, benzyl azide (0.5 mmol), phenylacetylene (0.6 mmol), 0.6 mL of deionized water and 0.4 mL of Au-CuO or CuO NPs (Cu: 1 mol%) were added in. The rest procedures are the same as above.

**Colorimetric quantification of Cu(I).** 4 mM BCS and 1 mM CuSO<sub>4</sub> aqueous solution were prepared separately in advance. Then, 2 mL of each solution was mixed well by vortexing, together with 2 mL sodium ascorbate stock solution with concentration ranging from 0.02 to 0.4 mM. The final concentrations of each substance in the mixtures were 1 mM BCS, 0.25 mM CuSO<sub>4</sub>, and 0.01-0.2 mM sodium ascorbate. Quantification of Cu(I) by sodium ascorbate reduction of Cu(II) was made by measuring the characteristic solution absorbance of Cu(I)-BCS complex at 483 nm, and then plotting out a working calibration curve.

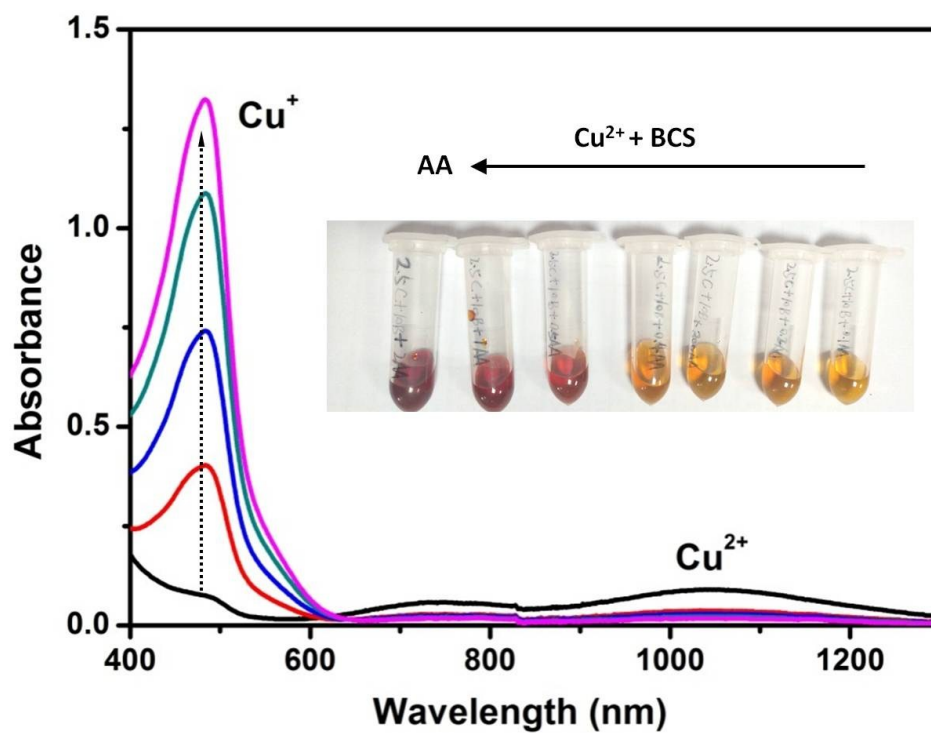
**Photoreduction of Cu(II) by hot electrons.** CuSO<sub>4</sub> (0.25 mM), BCS (1 mM), and 18 nm Au NPs (1.73 mM Au) were added into a glass vial, with the total volume at 17.5 mL. This mixture solution was then placed under xenon lamp illumination with output wavelength limited in 420-780 nm region by UV and IR blocking filters. Aliquots of 2.5 mL were taken from the mixture every 10 min, which were placed into a high speed centrifuge at 12,000 rpm for 10 min to separate out Au NPs. The absorption spectrum of the supernatant was taken, and the 483 nm absorbance was used to quantify the reduced Cu(I) amount based on the previously obtained Cu(I)-BCS calibration curve.



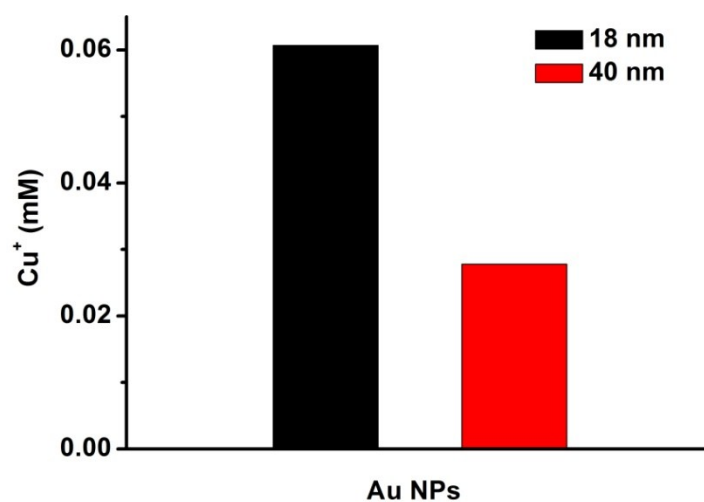
**Fig. S1** (A) TEM image of the synthesized 18 nm gold nanoparticles (inset: the particle size distribution); (B) UV-vis absorption spectrum of the Au NP aqueous dispersion.



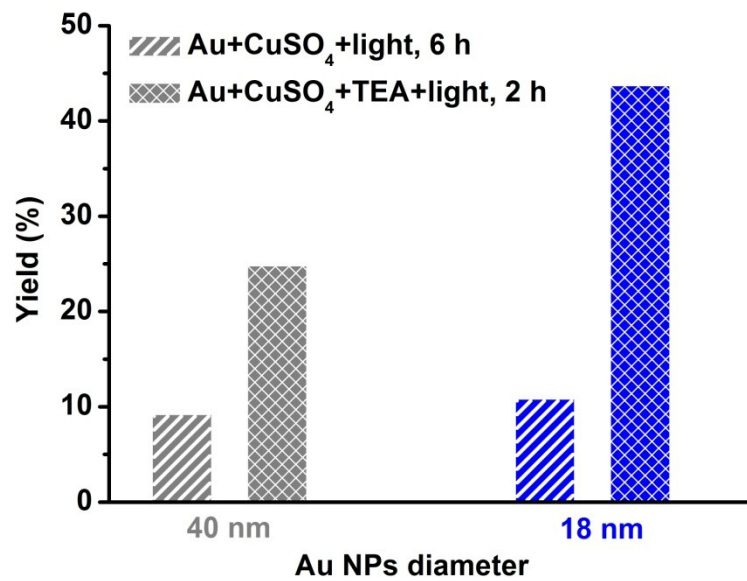
**Fig. S2** Kinetics of CuAAC reaction catalyzed by  $\text{CuSO}_4$ -sodium ascorbate at room temperature.



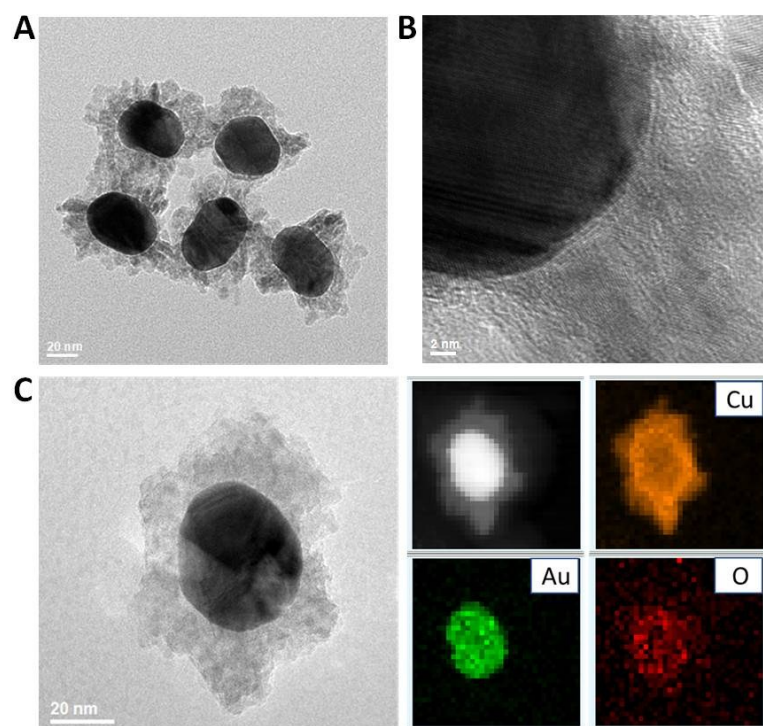
**Fig. S3** Characteristic UV-vis-NIR absorption spectra of Cu(I)-BCS and Cu(II) after different amount of AA was added (inset: visual color changes of the solution upon increasing amount of AA).



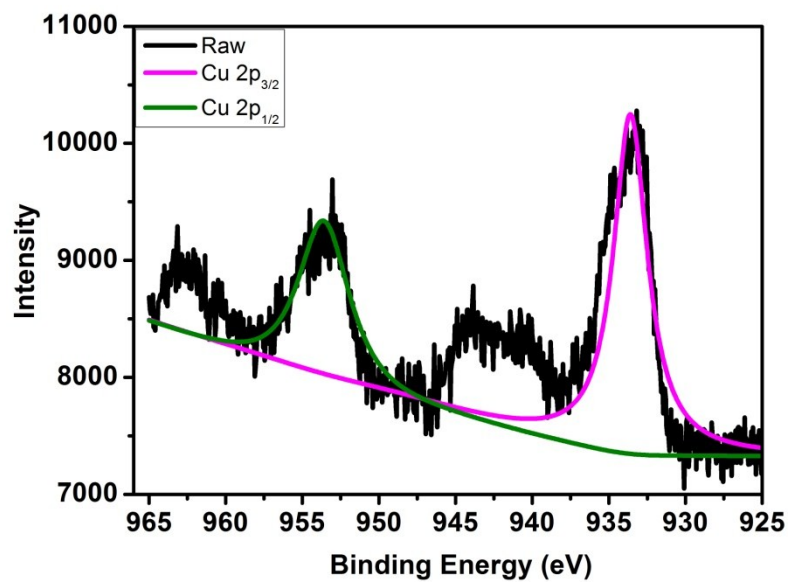
**Fig. S4** Photoreduced Cu(I) by Au hot electrons as a function of NP size at the same Au molar concentration (visible light, 10 min).



**Fig. S5** Hot electron assisted click reaction yield as a function of Au NP sizes.



**Fig. S6** (a) TEM, (b) HRTEM, and (c) elemental mapping of single NP of the as synthesized Au-CuO core-shell nanostructures.



**Fig. S7** XPS analysis of Cu binding energy in Au-CuO nanohybrids, the satellite peaks located near 942 and 962 eV are characteristics for CuO.<sup>1</sup>

**Reference:**

- 1 R. P. Vasquez, *Surface Science Spectra* 1998, **5**, 262