Supporting Information for

Enhancement of Cu⁺ stability under a reducing atmosphere by remote electromagnetic effects of Au

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Address: Shanxi University, 92 Wucheng Road ,Taiyuan 030006, China. Haitao Li, Email: htli@sxu.edu.cn Yongxiang Zhao, Email:yxzhao@sxu.edu.cn Li Fang, Email:fangli@sxu.edu.cn **Preparation of Au NPs**. Monodispersed spherical Au NPs with diameters of ~16 nm were prepared by the Frens method.¹ 200 ml of 0.01wt% HAuCl₄ solution was placed in a 250 ml three-neck flask, and the solution was stirred under reflux and heated to boiling (400 rpm). 3.6 ml of preheated 1.0 wt% sodium citrate solution was added, the mixture was boiled for 30 min, cooled to room temperature (25°C) to obtain burgundy Au NPs.



Fig. S1. (a) TEM image with inset photo (b) partical size histogram of Au NPs.

Catalysts –	Weight ratio (<i>wt</i> %)		n _{Cu}	Catalytic performance ^[a]	
	Cu	Au	$(\times 10^{-2} \mathrm{mol}^{\bullet}\mathrm{g}^{-1})$	propargyl alcohol yield (%) ^[b]	propargyl alcohol selectivity (%) ^[c]
pure Cu ₂ O	74.53		11.73	0.53	1.38
Au@Cu ₂ O- 27	44.97	5.85	7.08	1.37	2.93
Au@Cu ₂ O- 33	55.54	4.58	8.74	1.36	2.42
Au@Cu2O- 40	62.61	3.84	9.85	1.67	2.72
Au@Cu ₂ O- 47	69.68	3.02	10.96	2.13	3.21
Au@Cu ₂ O- 55	72.16	2.12	11.35	1.68	2.47

Table S1. Cu and Au Content in different catalysts analyzed by ICP-OES and catalytic performance of propargyl alcohol.

[a] Reaction conditions: the catalyst was dispersed in 35wt% formaldehyde solution, and reacted at 90°C for10 h with the C₂H₂ flow rate of 30 ml/min.

[b] propargylalcohol yield (%) = $\frac{m_{\text{propargylalcohol}} \times 30.03}{m_0 \times 56.07} \times 100\%$; where $m_{\text{propargyl alcohol}}$ is the total

mass of propargyl alcohol in the reaction solution, g; m_{θ} is the total mass of formaldehyde added, g.

[c] propargylalcohol selectivity (%) = $\frac{\text{propargylalcohol yield}}{\text{formaldehyde conversion}} \times 100\%$



Fig. S2. High-resolution Au 4f XPS spectra for fresh Au@Cu₂O core-shell NPs with different Cu₂O shell thickness.



Fig. S3. (a) XRD patterns of the activated-catalysts. (b) Diagram of the proportion of Au_x Cu₂O and Cu₂C₂ to carbyne. (c) XRD patterns of the used pure Cu₂O and Au@Cu₂O catalyst after 9th recycle. As shown in Fig. S3, both the used pure Cu₂O and Au@Cu₂O catalysts showed significant characteristic diffraction peaks corresponding to Cu₂C₂ at 32.0° and 42.3°.² Dispersion peaks with low intensity at 27.2°, 29.1°, and 51.2° were attributed to the linear carbon characteristic peaks containing terminal copper in the catalyst after reaction.^{3,4} The amorphous graphite-like structure diffraction peaks (JCPDS no.26-1079)^{4,5} at 26.6°, 46.3°,54.2°, and 63.6° were attributed to the presence of linear carbon with poorly crystallinity in the catalyst after the reaction. After the catalysts treated in formaldehyde and acetylene

atmosphere for 10h, no characteristic diffraction peaks corresponding to Cu_2O were observed in spectra of Au@Cu₂O core-shell catalysts, while the weak characteristic diffraction peak of Cu₂O (111) can still be observed at 36.4° in spectra of pure Cu₂O catalyst. The literature² reported that X-ray diffraction intensity can usually be used as the basis for quantitative analysis of the relative safety of cuprous acetylene due to the explosive nature of cuprous acetylene. The analysis results are shown in the Fig.S3b and listed in Table 1 of the text.



Fig. S4. (a-b) Au 4f XPS spectra of Au@Cu₂O catalysts after formaldehyde acetynylation. (c) Cu LMM XAES of Au@Cu₂O catalysts after 1*st* recycle. (d) Cu LMM XAES of pure Cu₂O and Au@Cu₂O-55 catalyst after different reaction cycles.



Fig. S5. ln C_{FA} VS. reaction time plots of the rate-determining step over pure Cu₂O and Au@Cu₂O-55 catalyst at 70 - 90°C.

References

- 1 G.Frens, Nat. Phy. Sci., 1973, 241, 20–22.
- 2 B. Helmut, Springer Science & Business Media, 1987, 140–142.
- 3 H. Werner, D. Herein, J. Blöcker, B .Henschke, U. Tegtmeyer, Th. Schedel-Niedrig, M. Keil, A.M. Bradshaw, R. Schlögl, *Chem. Phys. Lett.*, 1992, 194, 62–66.
- 4 F. Cataldo, Polym. Int., 1997, 44, 191-200.
- 5 F. Cataldo, *Carbon*, 1999, **37**, 161–163.