Supplementary Information for:

Synthesis, structure anatomy, and catalytic properties of $Ag_{14}Cu_2$ nanoclusters co-protected by alkynyl and phosphine ligands

Quanli Shen,‡[a] Xuzi Cong,‡[b] Leyi Chen,[a] Lei Wang,[a] Yonggang Liu,[a] Likai Wang,*[b] and Zhenghua Tang*[a]

[a] *New Energy Research Institute, School of Environment and Energy, South China University of Technology, Guangzhou Higher Education Mega Centre, Guangzhou, 510006, China.*
**E-mail: zhht@scut.edu.cn*
[b] *School of Chemistry and Chemical Engineering, Shandong University of Technology, Zibo, 255049, China.*
**E-mail: lkwangchem@sdut.edu.cn*
‡These two authors contributed equally.

List of contents

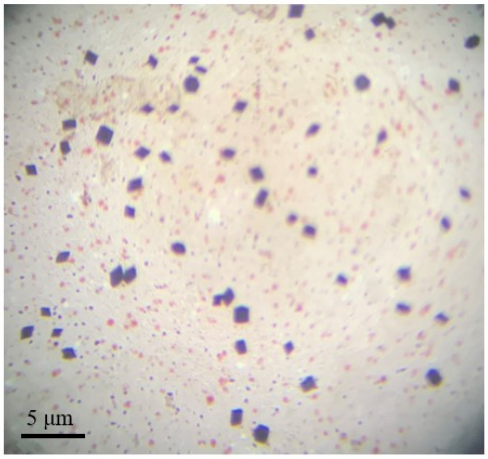

Figure S1. The images of $Ag_{14}Cu_2$ crystals under an optical microscope.

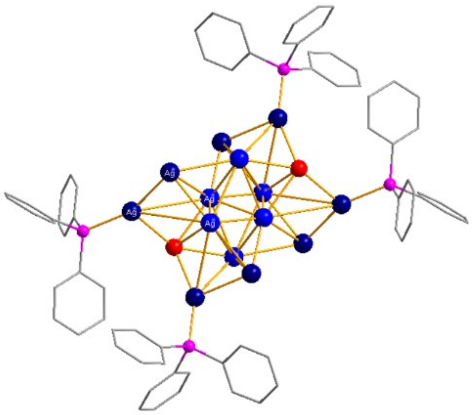

Figure S2. Coordination of the 4 PPh_3 ligands with Ag atoms. Color code: Ag, bule and dark blue; Cu, red; C, green; F, gray; P, pink. All hydrogen atoms are omitted for clarity.

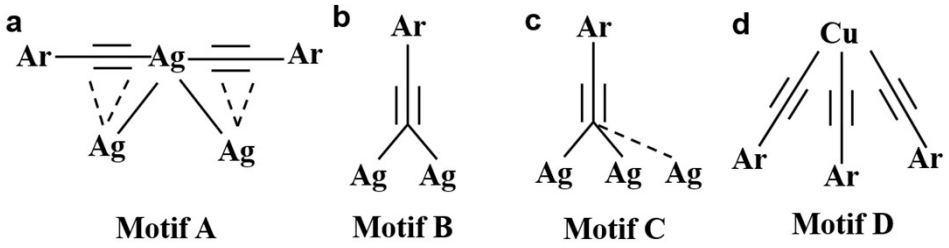

Figure S3. Coordination modes of the alkynyl ligands with Ag or Cu atoms.

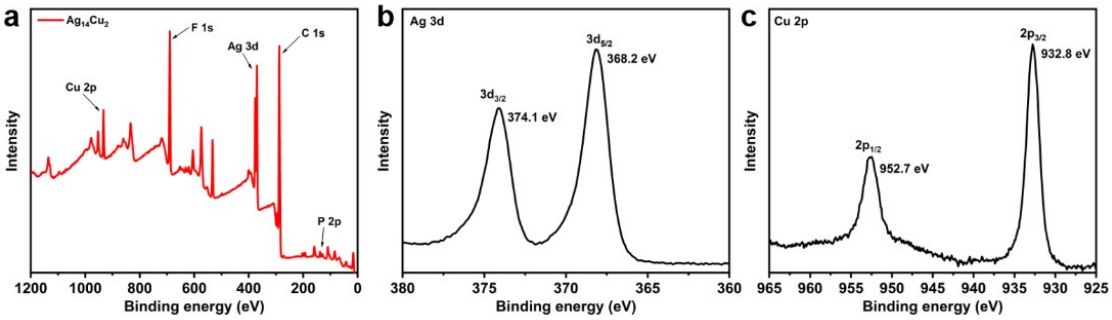

Figure S4. (a) XPS survey-scan spectra of the $Ag_{14}Cu_2$ nanoclusters; High-resolution (b) Ag 3d and (c) Cu 2p XPS spectrum of the $Ag_{14}Cu_2$ nanoclusters.

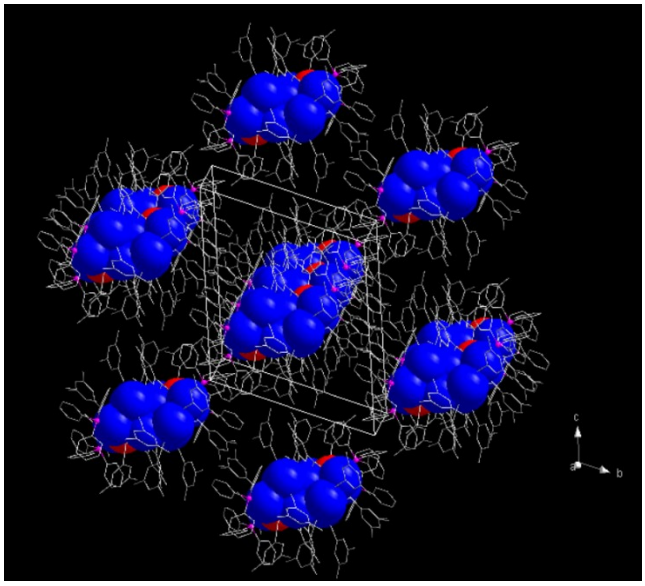

Figure S5. The packing of $Ag_{14}Cu_2$ nanocluster. Color code: Ag, blue; Cu, red; C, gray; P, pink. All hydrogen and fluorine atoms are omitted for clarity.

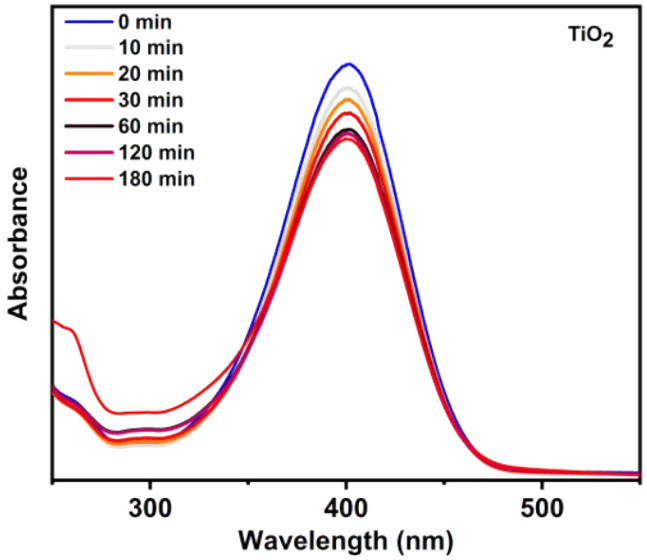

Figure S6. The absorbance spectra during the reduction process of 4-nitrophenol using TiO_2 as catalyst.

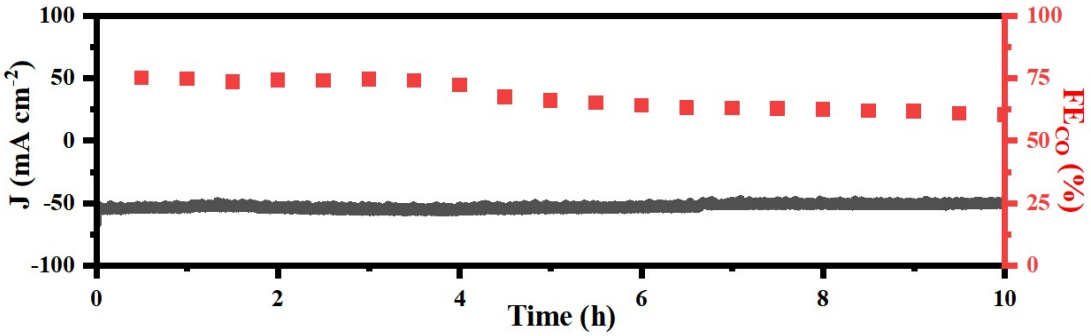

Figure S7. Stability test of the $Ag_{14}Cu_2$/CNTs catalyst in eCO_2RR.

Table S1. Crystal data and structure refinement for $Ag_{14}Cu_2$.

Identification code	$Ag_{14}Cu_2(C{\equiv}CAr)_{14}(PPh_3)_4$
Empirical formula	$C_{212}H_{102}F_{84}Ag_{14}Cu_2P_4$
Formula weight	6006.07
Temperature	100 K
Crystal system	triclinic
Space group	P -1
a	18.68860 (10) Å
b	19.6047 (2) Å
c	19.8873 (2) Å
α	105.4210°
β	105.0070°
γ	116.992°
Volume	5614.56(3)
Z	1
Calculated density	1.776 g/cm^3
Absorption coefficient	1.522 mm^{-1}
F (000)	2906
F (000)’	2896.42
Crystal size	0.3 * 0.3 * 0.2 mm
Radiation	Mo Kα (λ = 0.71073)
Index ranges	-25 ≤ h ≤ 27, -27 ≤ k ≤ 28 -27 ≤ I ≤ 28
Reflections collected	145426
2θ range for date collection	2.2910 to 31.2000
Largest diff. peak/hole	2.82/ -1.13 e Å^{-3}