Electronic Supplementary Material (ESI) for Nanoscale.

Electronic Supporting Information

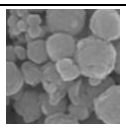
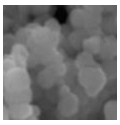
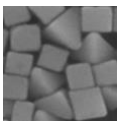
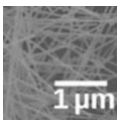
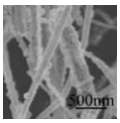
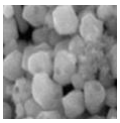
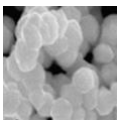
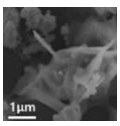
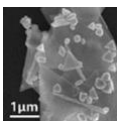
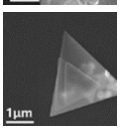
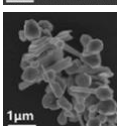
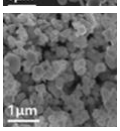
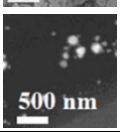
Shape control in aqueous seed-mediated synthesis of non-elongated Cu nanoparticles and their optical properties

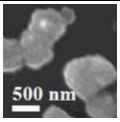
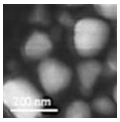
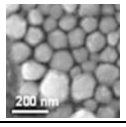
Xenia V. Medvedeva[a], Feng Li[a], Alex Maokhamphiou[a], Jury J. Medvedev[a], Aftab Ahmed[b] and Anna Klinkova[a]*

[a]Department of Chemistry, University of Waterloo, 200 University Avenue West, Waterloo, Ontario N2L 3G1, Canada

[b]Department of Electrical Engineering, California State University Long Beach, 1250 Bellflower Boulevard Long Beach, California 90840, United States

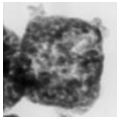
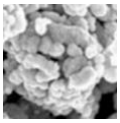
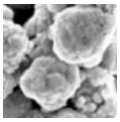
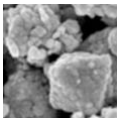
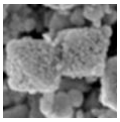
Table S1. Cu NPs synthesised in aqueous solutions of cationic surfactants

Nanoparticle description	SEM/TEM	Surfactant, reducing agent	T, °C	Ref.
[1]Cu NPs, ~120±49 nm		0.1 M CTAB, glucose	85	[6]
[1]Cu NPs, ~33±26 nm		0.1 M CTAB, hydrazine	85	[6]
[2]Cu cubes, 82, 95, and 108 nm		0.015 M CTAC, sodium ascorbate	100	[7]
[2]Cu nanowires		0.015 M CTAC, sodium ascorbate	100	[7]
[3]Rough Cu nanowires		0-0.004 M CTAC, ascorbic acid	120	[8]
[4]Cu NPs ~400 nm		0.06 M CTAB, ascorbic acid	85	[9]
[4]Cu NPs ~400 nm		0.09 M CTAB, ascorbic acid	85	[9]
[5]Cu NPs		0.06 M CTAB, ascorbic acid (pH 4)	85	[10]
[5]Cu NPs		0.06 M CTAB, ascorbic acid (pH 6)	85	[10]
[5]Cu NPs		0.06 M CTAB, ascorbic acid (pH 7)	85	[10]
[5]Cu NPs		0.06 M CTAB, ascorbic acid (pH 10)	85	[10]
[5]Cu NPs		0.06 M CTAB, ascorbic acid (pH 12)	85	[10]
[6]Cu NPs		0.01 M CPC, hydrazine	23	[11]

[6]Cu NPs		0.01 M CTAB, hydrazine	23	[11]
[7]Cu NPs		0.01 M CPC, hydrazine	30	[12]
[7]Cu NPs		0.01 M CPC, hydrazine	30	[12]

[1]Reprinted by permission from Springer Nature Customer Service Centre GmbH: Springer Nature, Journal of Nanoparticle Research ref [6], Copyright 2016. [2]Reprinted in part with permission from ref [7], Copyright 2017 John Wiley and Sons. [3]Reprinted in part with permission from ref [8], Copyright 2013 Royal Society of Chemistry. [4]Reprinted from ref [9], Copyright 2010 with permission from Elsevier. [5]Reprinted from ref [10] Published by The Royal Society of Chemistry. [6]Reprinted from ref [11] published under licence by IOP Publishing Ltd. [7]Reprinted from ref [12].

Table S2. Cu cages

Nanoparticle description	SEM/TEM	Solvent	Capping agent, reducing agent	T, °C	Ref.
[1]Cu porous cube ~200nm		H_2O	Sodium oleate (SOA), hydrazine	80	[13]
[2]Octahedral Cu nanocages ~500nm		H_2O	Poly(vinyl pyrrolidone) (PVP), hydrazine	27	[14]
[2]Octahedral Cu nanocages ~350 nm		H_2O	SOA, hydrazine	27	[14]
[2]Octahedral Cu nanocages ~500 nm		H_2O	CTAB, hydrazine	27	[14]
[2]Octahedral Cu nanocages ~300 nm		H_2O	No surfactant, hydrazine	27	[14]

[1]Reprinted with permission ref [13], Copyright 2007 American Chemical Society. [2]Reprinted from ref [14], Copyright 2013 with permission from Elsevier.

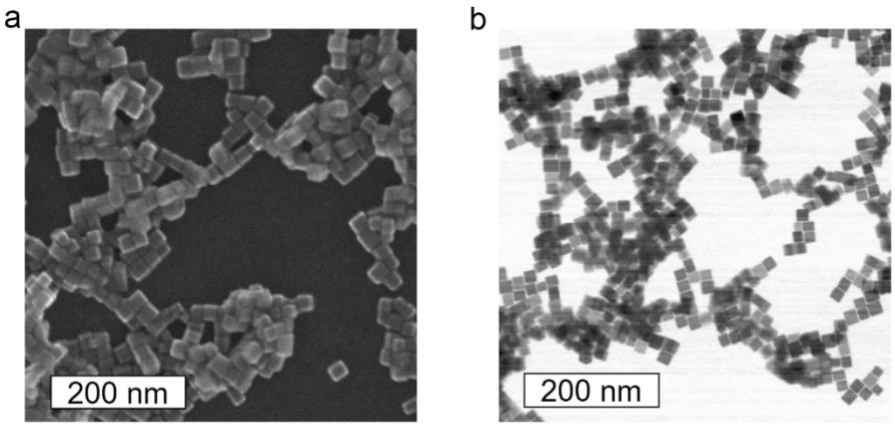


Figure S1. SEM (a) and TEM (b) images of Pd cubes used as seeds for Cu NP synthesis.

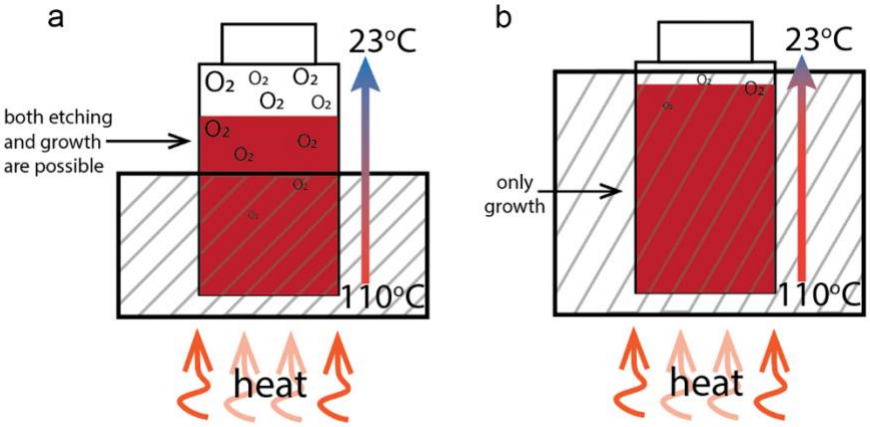


Figure S2. Set ups for Cu NPs formation. Set up for Cu cages formation (a) and other shapes of Cu NPs formation (b).

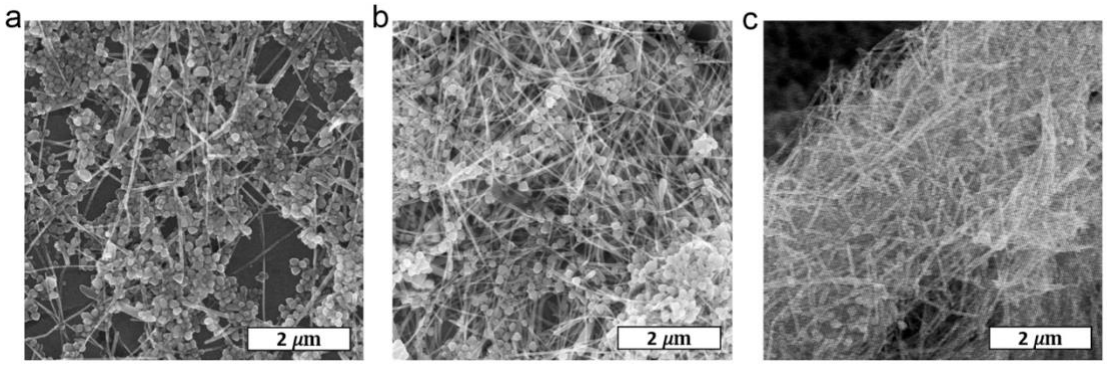


Figure S3. SEM images of Cu NPs formed without Pd seeds. Experiments at 90 °C, 100 °C, 110 °C (1.5h each).

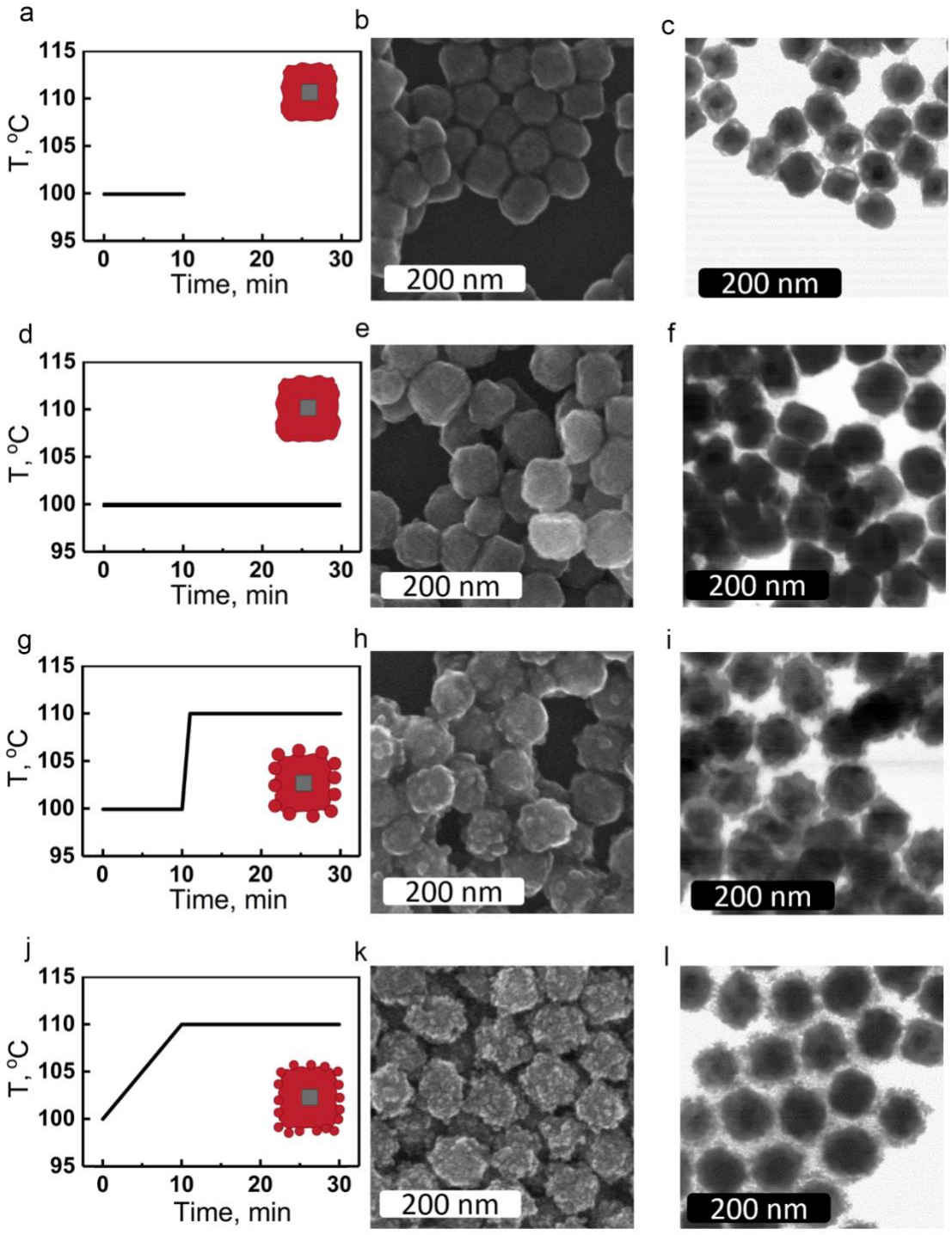


Figure S4. The effect of the oil bath temperature on the Cu NP formation. Temperature regimes and formed particle cartoons (a,d,g,j), SEM images (b,e,h,k) and TEM images (c, f, I, l) of formed nanostructures.

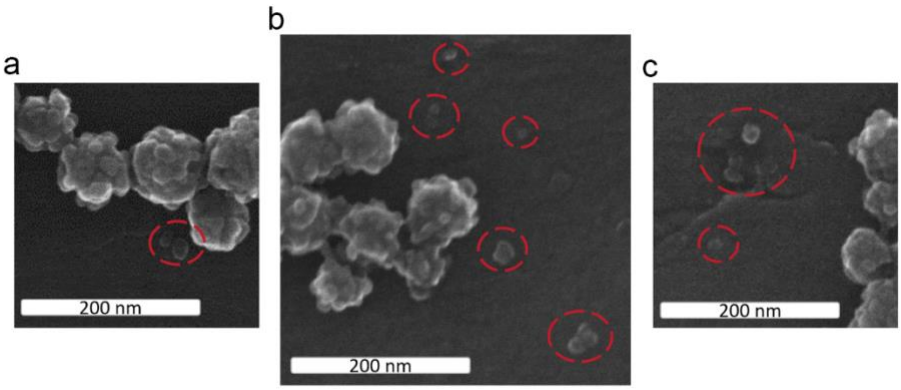


Figure S5. SEM images of not assembled small Cu NPs formed during raspberry-like Cu NPs formation.

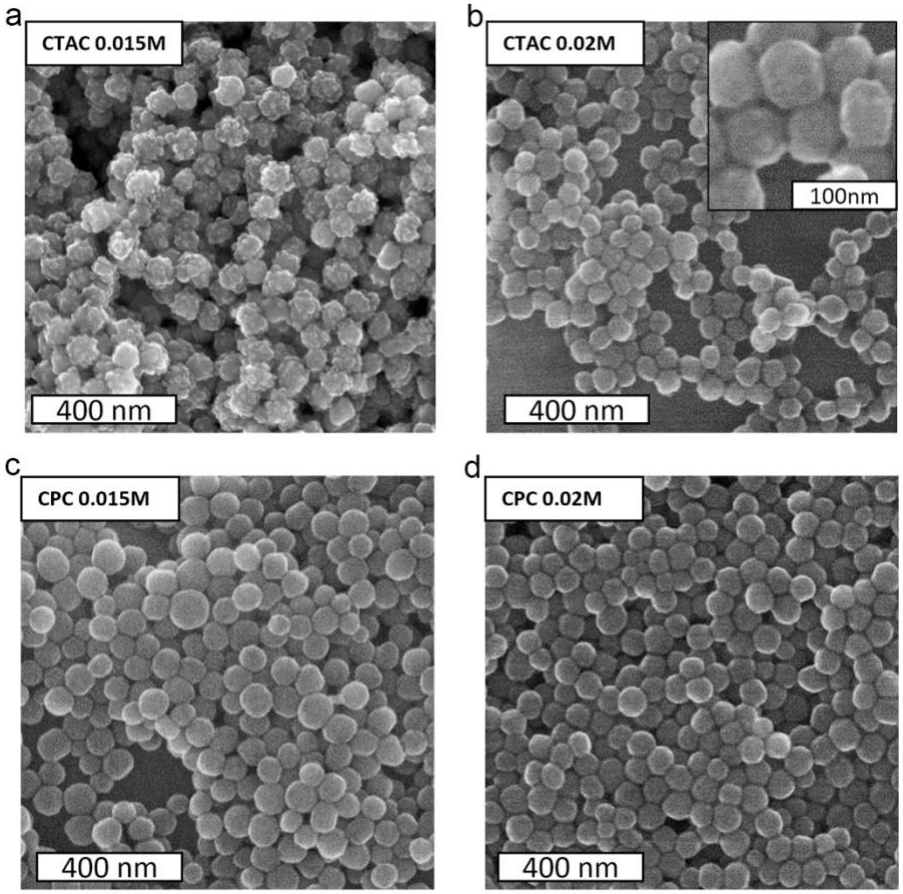


Figure S6. The effect of surfactant nature and concentration on the standard raspberry-like NP synthesis. Cu NPs formed under standard reaction conditions (a), under higher CTAC concentration (0.02 M) with other conditions kept same (b), under standard reaction conditions with CTAC changed to equimolar CPC (c), under higher CPC concentration (0.02M) with other conditions kept same (d).

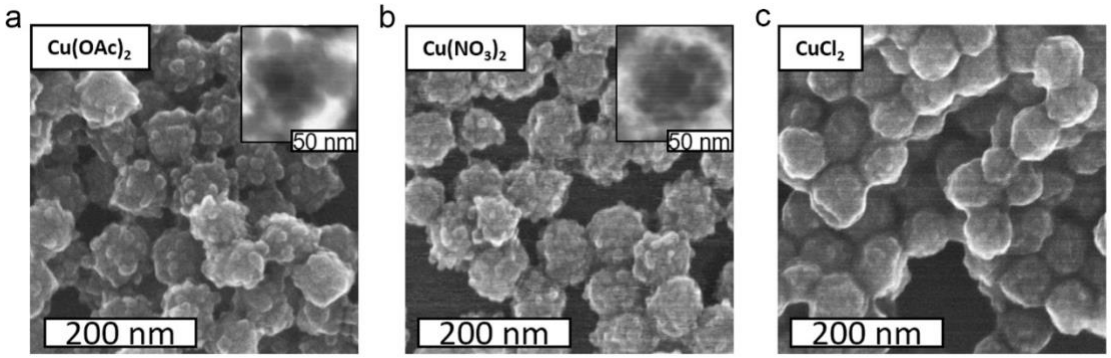


Figure S7. The effect of Cu precursor anion on the Cu NP shape in standard synthesis of raspberry-like NPs. SEM images of Cu NPs synthesised using $Cu(OAc)_2$ (a), $Cu(NO_3)_2$ (b), and $CuCl_2$ (c).

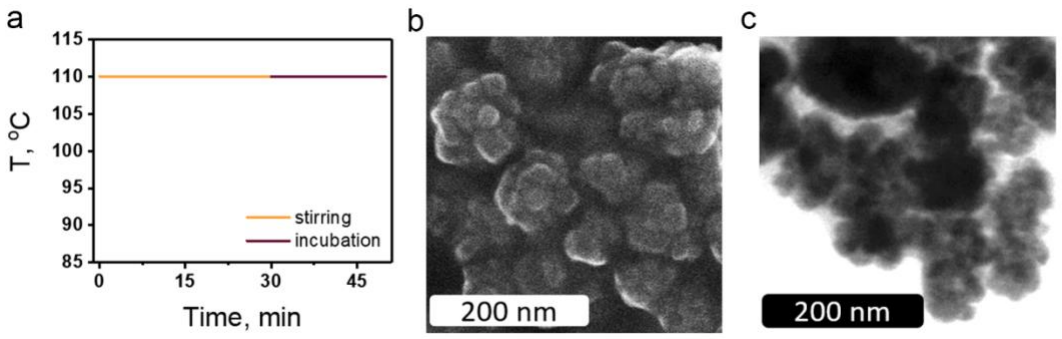


Figure S8. Reaction timeline (a), SEM (b) image and TEM (c) image of Cu NPs formed with initial vigorous stirring of reaction mixture for 30 minutes with air present in the headspace.

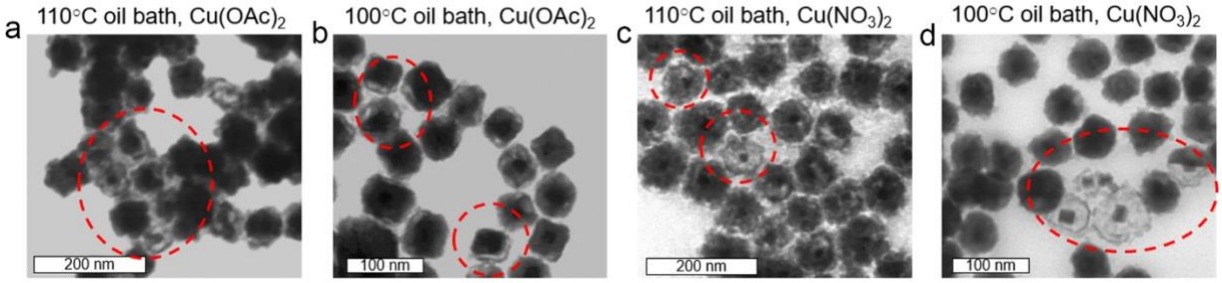


Figure S9. TEM images of etched Cu particles found in different experiments (reaction conditions are shown above each image).

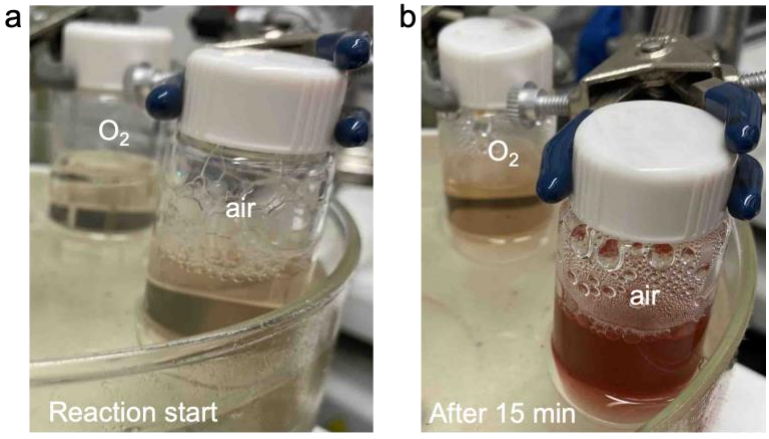


Figure S10. Photographs comparing the visual appearance of the reaction mixtures after 15 min of reaction with air and oxygen in the headspace.

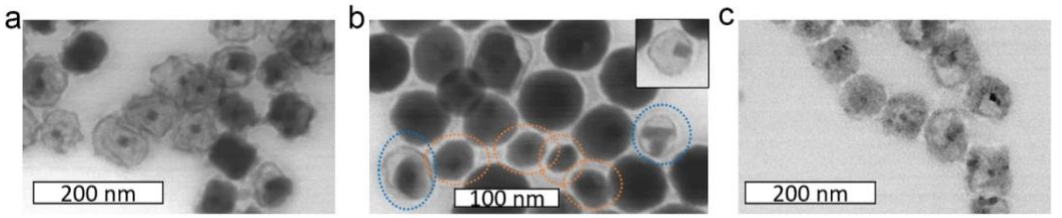


Figure S11. The structural stability of Cu cages. TEM images of freshly prepared Cu cages (a), Cu cages left in ice-cold solution for 8 hours (b, orange dotted circles shows collapsed cages, blue dotted circles highlights almost collapsed cages), Cu cages that were left for >1 year on a TEM grid on air (c).

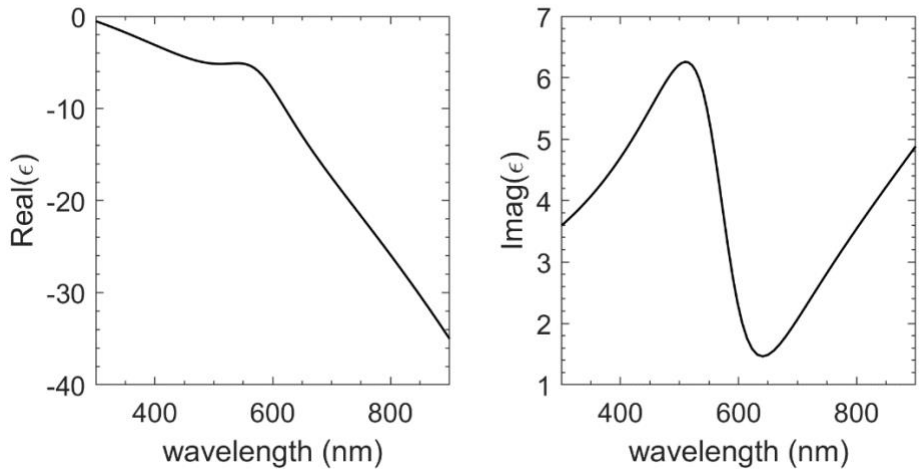


Figure S12. Permittivity of copper.

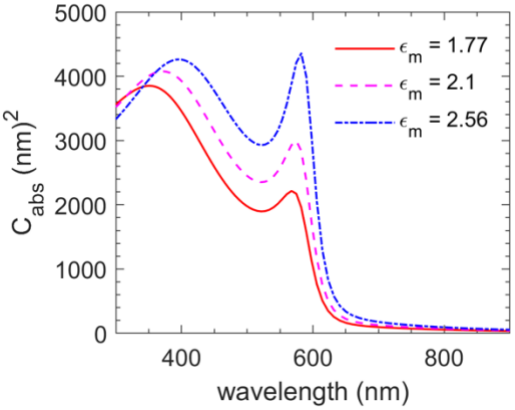


Figure S13. Theoretical results using quasistatic approximation - absorption cross-section of a 50 nm copper sphere for varying surrounding medium permittivities.

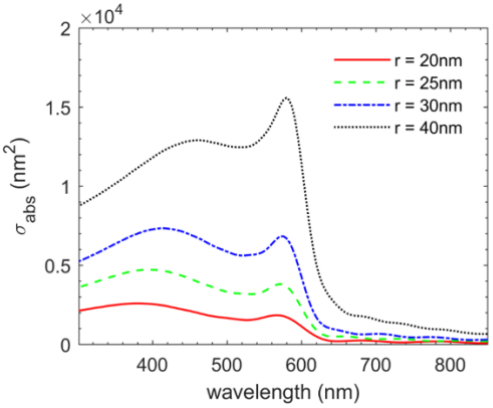


Figure S14. FDTD simulations results - absorption cross-section of solid copper sphere with radii shown in the legend.

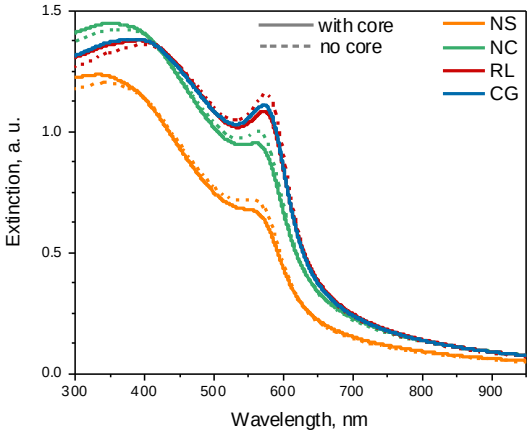


Figure S15. FDTD simulations results - extinction cross-section of copper nanoparticles of different shape with and without palladium core (see the legend within the plot).

References:

1. C. Durante, A. A. Isse, F. Todesco, A. Gennaro, *J. Electrochem. Soc.,* 2013*,* **160**, G3073.
2. Q. Feng, K. Huang, S. Liu, X. Wang, *Electrochimica Acta,* 2010*,* **55**, 5741–5745.
3. H. Taterno, K. Nakabayashi, T. Kashiwagi, H. Senboku, M. Atobe, *Electrochimica Acta,* 2015, **161**, 212–218.
4. L.-X. Wu, Q.-L. Sun, M.-P. Yang, Y.-G. Zhao, Y.-B. Guan, H. Wang, J.-X. Lu, *Catalysts,* 2018, **8**, 273.
5. D. Yimin, N. Lanli, L. Hui, Z. Jiaqi, Y. Linping, F. Qiuju, *Int. J. Electrochem. Sci.,* 2018, **13**, 1084 – 1095.
6. G. Granata, T. Yamaoka, F. Pagnanelli, A. Fuwa, *J. Nanopart. Res.,* 2016*,* **18**, 133.
7. S. Thoka, M. Madasu, C.-F. Hsia, S.-Y. Liu, M. H. Huang, *Chem. Asian J.,* 2017, **12**, 2318-2322.

8. Y. Sun, F. Zhang, L. Xu, Z. Yin, X. Song, *J. Mater. Chem. A,* 2014, **2**, 18583-18592.
9. M. Biçer, I. Şişman, *Powder Technol.,* 2010, **198**, 279-284.
10. J. Wang, X. Guo, Y. He, M. Jiang, R. Sun, *RSC Adv.,* 2017, **7**, 40249-40254.
11. N. N. Begletsova, O. A. Shinkarenko, A. S. Chumakov, A. J. K. Al-Alwani, A. A. Selifonov, E. I. Selifonova, M. V. Pozharov, A. M. Zakharevich, R. K. Chernova, A. S. Kolesnikova, E. G. Glukhovskoy, *Journal of Physics: Conf. Series,* 2017, **917**, 092014. DOI:10.1088/1742-6596/917/9/092014
12. N. N. Begletsova, O. A. Shinkarenko, E. I. Selifonova, O. Y. Tsvetkova, A. M. Zakharevich, R. K. Chernova, A. A. Kletsov, E. G. Glukhovskoy, *Adv. Mater. Lett.,* 2017, **8**, 404-409.
13. X. Su, J. Zhao, H. Bala, Y. Zhu, Y. Gao, S. Ma, Z. Wang, *J. Phys. Chem. C,* 2007, ***111,*** 14689-14693.
14. Y. Zhao, J. Zhao, Z. Su, X. Hao, D. Ma, Y. Lu, J. Guo, *Colloids and Surfaces A: Physicochem Eng Aspects,* 2013, **436**, 34-40.
15. D. Bao, B. Millare, W. Xia, B. G. Steyer, A. A. Gerasimenko, A. Ferreira, A. Conteras, V. I. Vullev, *J. Phys. Chem.,* 2009, **113**, 1259-1267.