Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Vacancy Assisted Growth of Copper Tantalum Sulfide Nanocrystals

Anamul Haque,[1,2] Soheil Ershadrad,[3] Trupthi Devaiah Chonamada,[1,2] Dipankar Saha,[4]

Biplab Sanyal,[3,*] and Pralay K. Santra[1,*]

[1]Centre for Nano and Soft Matter Sciences (CeNS), Bengaluru 562162, India

[2]Manipal Academy of Higher Education (MAHE), Manipal, 576104, India

[3]Department of Physics and Astronomy, Materials Theory, Uppsala University, Box 516, SE-751 20 Uppsala, Sweden

[4]School of Chemical and Process Engineering, University of Leeds & CMAC, Leeds-LS29JT, United Kingdom.

[*]E-mail address: psantra@cens.res.in; biplab.sanyal@physics.uu.se

Table S1. The amount of precursor salts and solvents used during the synthesis of Cu-Ta-S NCs.

Cu:Ta	Precursor			Solvent
	CuCl g (mmol)	$TaCl_5$ g (mmol)	CS_2 mL (mmol)	OLA mL (mmol)
3:1	0.43 (4.38)	0.52 (1.46)	1.35 (22.50)	14.76 (44.80)
1:1	0.288 (2.92)	1.04 (2.92)	1.35 (22.50)	14.76 (44.80)
1:3	0.144 (1.46)	1.56 (4.38)	1.35 (22.50)	14.76 (44.80)

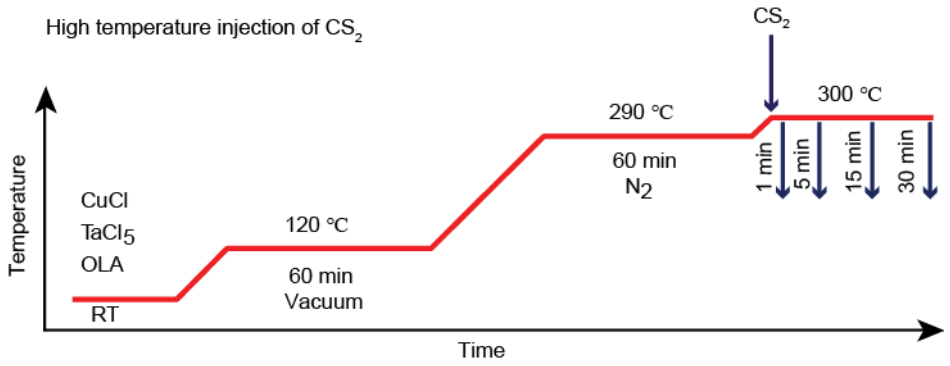

Figure S1. The schematic of the synthesis of copper tantalum sulfide nanocrystals for high temperature injection of CS_2.

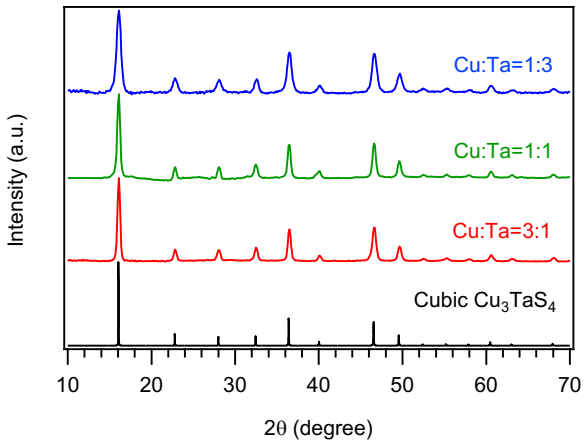

Figure S2. PXRD pattern of the synthesized NCs for Cu:Ta=3:1, 1:1, and 1:3 reactions. In all three cases, the NCs are crystallizes in cubic phase Cu_3TaS_4.

Table S2. The formation energies of Cu-Ta-S and Cu-S systems.

Composition	Formation energy (/unit cell)	Crystal structure
Cu_3TaS_4	-4.990 eV	Cubic
$CuTaS_3$	-2.490 eV	Orthorhombic
Cu_2S	-0.161 eV	Cubic
$Cu_{1.8}S$	-0.299 eV	Cubic
$Cu_{1.6}S$	-0.241 eV	Cubic

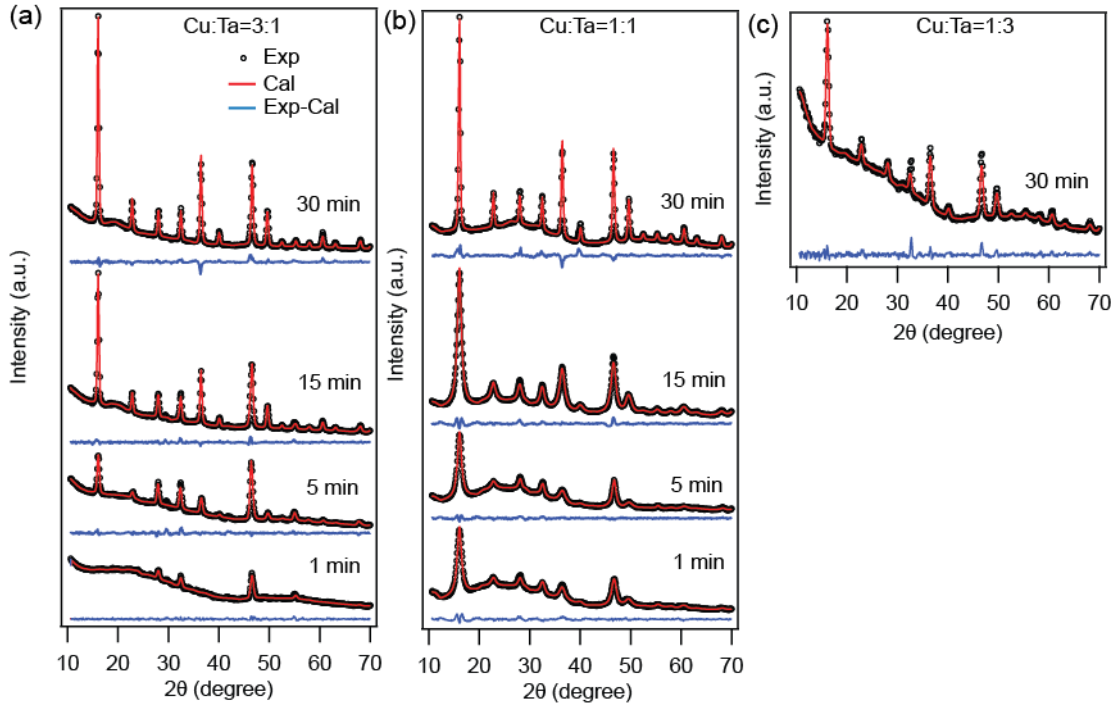

Figure S3. Rietveld refinement profile for (a) Cu:Ta=3:1, (b) Cu:Ta=1:1, and (c) Cu:Ta=1:3 reactions. XRD patterns are vertically shifted for representing data at different reaction times. The black open circles represent the experimental XRD pattern, red solid line is calculated pattern, and the blue line is the difference between the observed and calculated XRD pattern.

Table S3. Lattice parameters calculated from Rietveld refinement for Cu:Ta=3:1 and 1:1 reactions.

Cu:Ta=3:1	Lattice parameter (Å)				
	$Cu_{2-X}S$ (calculated)	$Cu_{1.8}S$ Space group: Fm-3m	$Cu_{1.6}S$ Space group: F-43m	Cu_3TaS_4 (calculated)	Cu_3TaS_4 Space group: P-43m
1 min	5.5130 ± 0.0006	5.5640	5.4100	-	5.5140
5 min	5.5338 ± 0.0003			5.4977 ± 0.0006	
15 min	5.5410 ± 0.0008			5.5078 ± 0.0012	
30 min	-			5.5100 ± 0.0002	

Cu:Ta=1:1	Lattice parameter (Å)				
	$Cu_{2-X}S$ (calculated)	$Cu_{1.8}S$ Space group: Fm-3m	$Cu_{1.6}S$ Space group: F-43m	Cu_3TaS_4 (calculated)	Cu_3TaS_4 Space group: P-43m
1 min	5.4927 ± 0.0004	5.5640	5.4100	5.5124 ± 0.0004	5.5140
5 min	5.4936 ± 0.0006			5.5065 ± 0.0005	
15 min	5.4937 ± 0.0007			5.5097 ± 0.0004	
30 min	-			5.5098 ± 0.0002	

Table S4. Rietveld refinement factors for Cu:Ta=3:1 and 1:1 reactions.

Cu:Ta=3:1	**1 min**	**5 min**	**15 min**	**30 min**
R_p(%)	1.95	2.39	2.51	3.34
R_{wp}(%)	6.21	3.29	3.53	5.00
$R_{exp(\%)}$	4.29	4.72	5.18	5.09
χ^2	2.09	0.49	0.466	0.967

Cu:Ta=1:1	**1 min**	**5 min**	**15 min**	**30 min**
R_p(%)	2.41	2.09	3.51	3.39
R_{wp}(%)	3.09	2.60	4.62	4.79
$R_{exp(\%)}$	4.08	4.30	4.28	4.06
χ^2	1.12	1.04	1.17	1.31

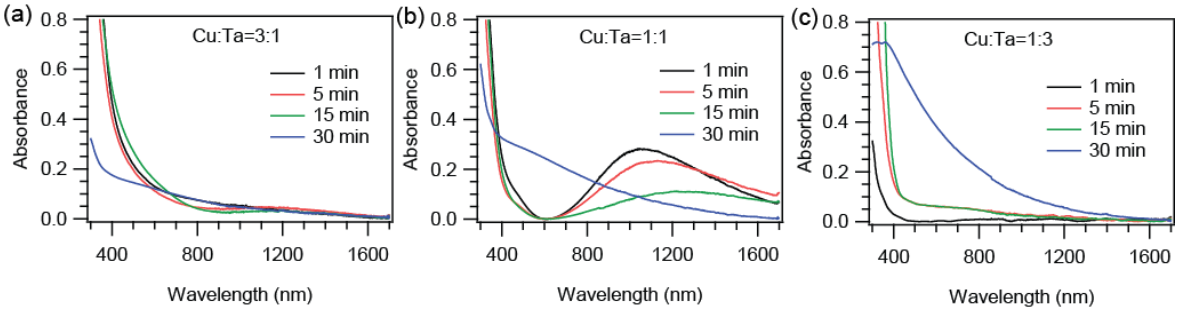

Figure S4. Absorption spectra of the synthesized NCs for (a) Cu:Ta=3:1, (b) Cu:Ta=1:1, (c) Cu:Ta=1:3 reactions after 1 min, 5 min, 15 min, and 30 min.

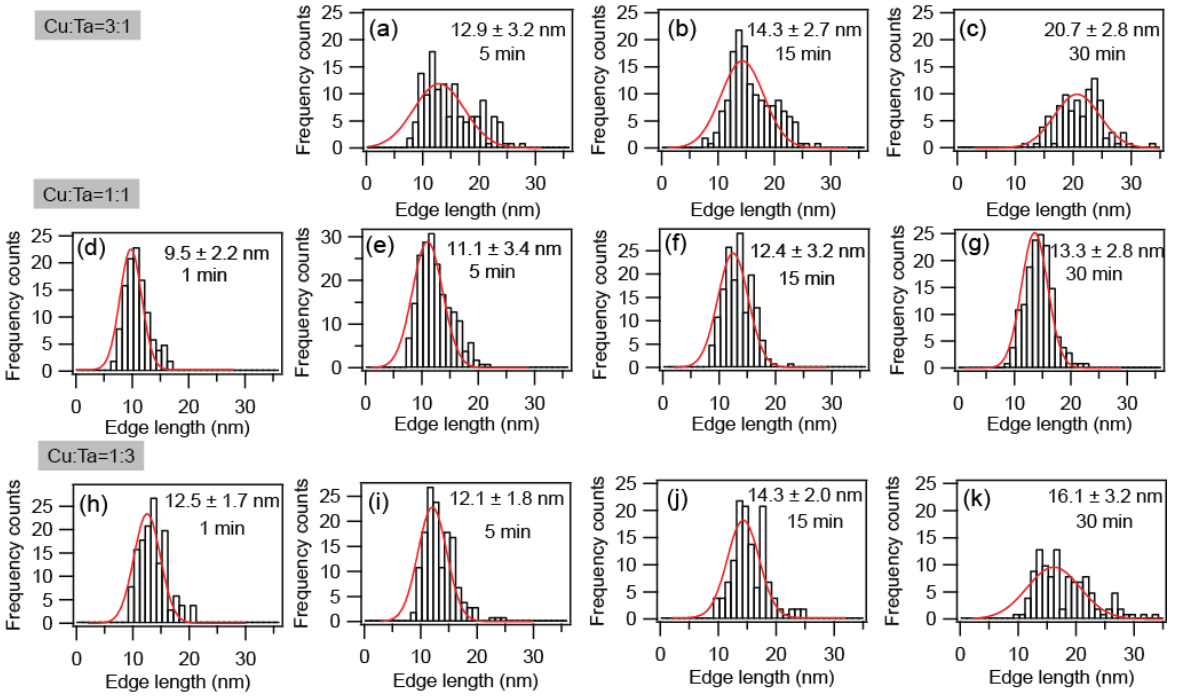

Figure S5. Particle size distribution histogram of (a-c) Cu:Ta=3:1 for 5 min, 15 min, and 30 min reactions and (d-g) Cu:Ta=1:3 for 1 min, 5 min, 15 min, and 30 min reactions. The average edge length and the half width half maximum is mentioned in the figure.

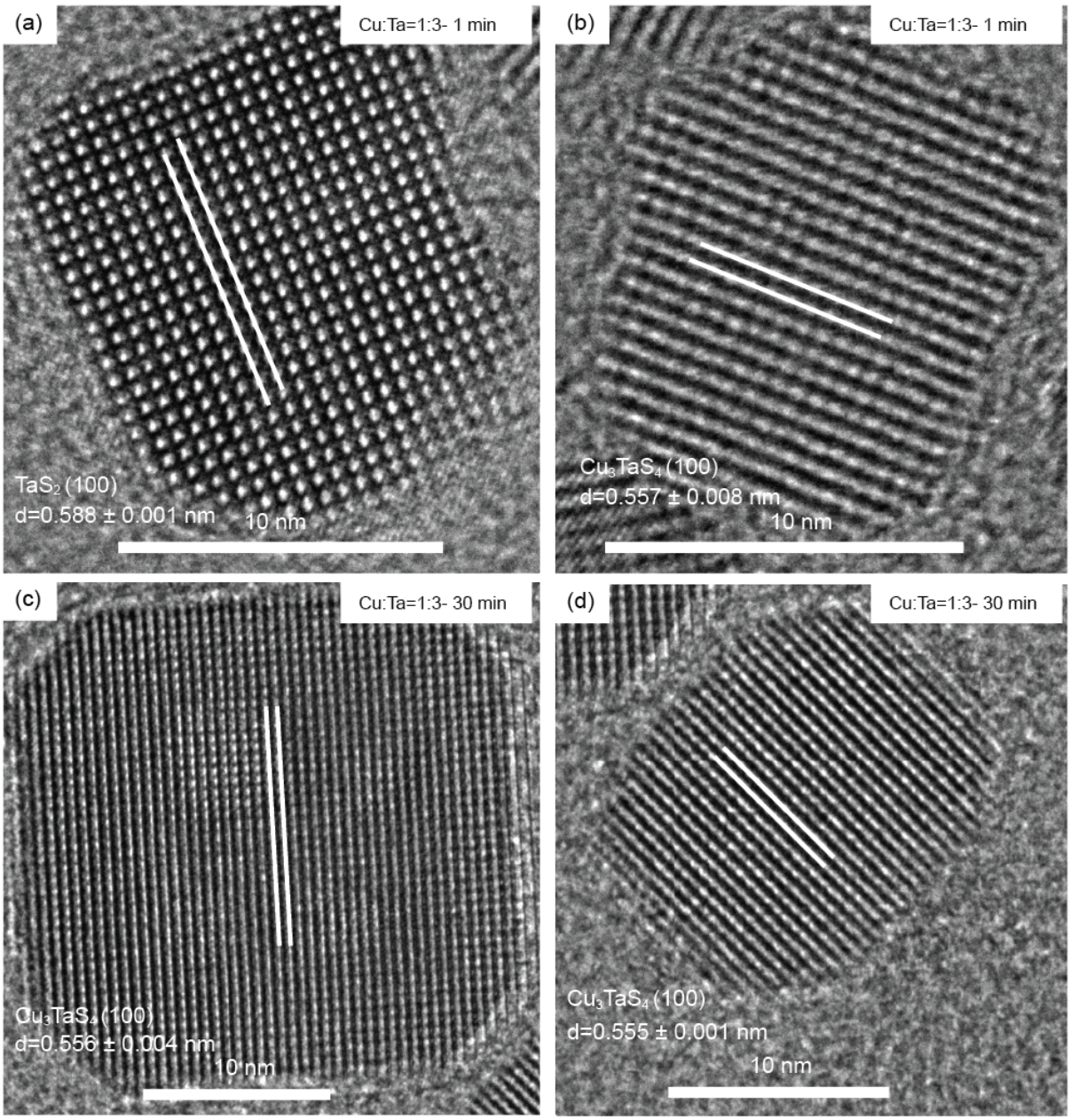

Figure S6. HRTEM images of the synthesized NCs for Cu:Ta=1:3 ratio. (a-b) Two individual particles after 1 min reaction. (c-d) 30 min reaction.