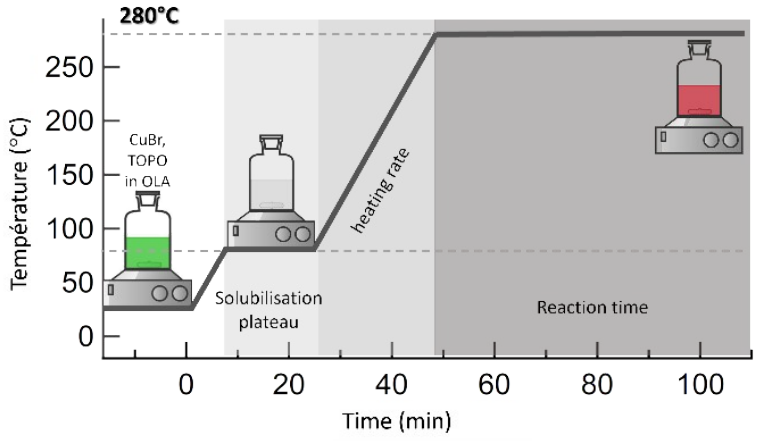
Versatile Role of Oleylamine in the Controlled Synthesis of Copper Nanoparticles with Diverse Morphologies

Supplementary Information



Scheme S1 Schematic illustration of the synthesis protocol of Cu NPs. The heating rate refers to the duration of temperature increase from the solubilization plateau at 90°C to the reaction temperature at 280°C. The reaction time refers to the duration of the reaction starting from the moment the 280°C plateau is reached.

Table S1 : Measured interarticular distances (Å) obtained from electron diffraction of cubic, octahedral, and spherical-shaped NPs, reference distances, and corresponding planes for metallic copper with face-centered cubic (fcc) structure are taken from *The American Mineralogist Crystal Structure Database. American Mineralogist 88, 247-250.*

D_{hkl} cubic NPs	**D_{hkl} octahedral NPs**	**D_{hkl} spherical NPs**	**Reference for fcc**	**Corresponding inter-reticular planes**
	2,50		2,56	110
2,10	2,09	2,11	2,09	111
1,80	1,87	1,85	1,8	200
1,29	1,26	1,29	1,28	220
1,09	1,09	1,10	1,09	311
0,90		0.87	0,9	400
0,82	0,84	0.77	0,83	331

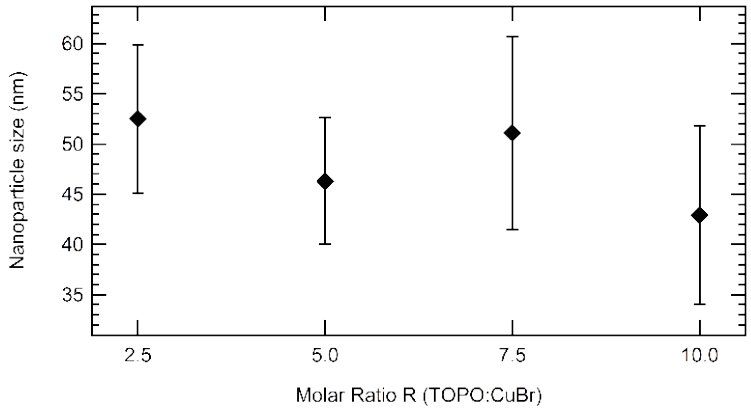


Figure S1 Evolution of the mean size and size distributions of cubic NPs as a function of the TOPO:CuBr molar ratio.

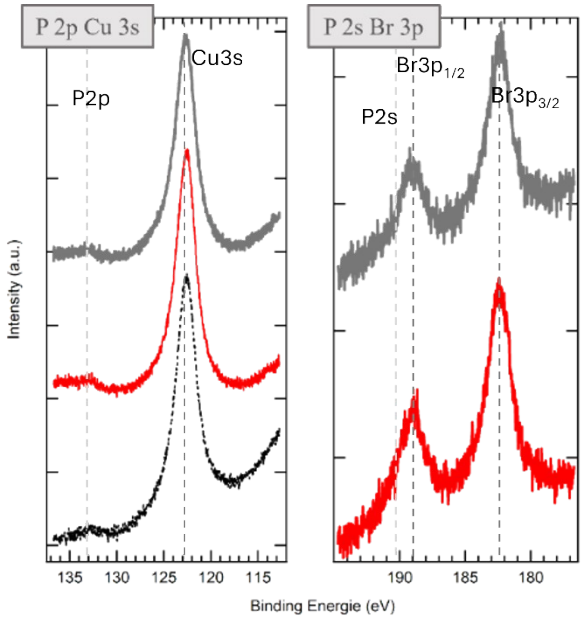


Figure S2 : XPS spectra of the core levels of P 2p and Cu 3s, then of P 2s and Br 3p for Cu NP samples prepared in the presence of TOPO (grey) and TOP (red). The dotted black curve corresponds to the spectrum of NPs grown in the absence of phosphine ligands. The syntheses are conducted at 280°C and with R=2.5.

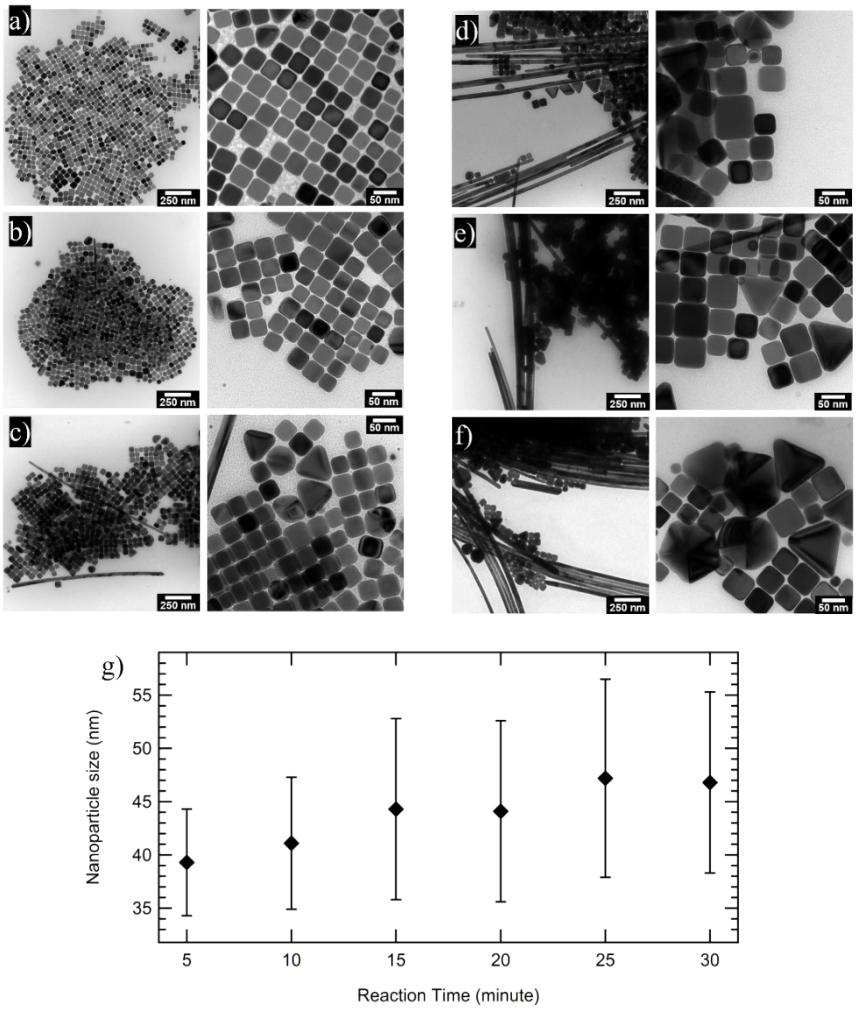


Figure S3 : TEM images at various magnifications of copper nanoparticles obtained after different reaction times: (a) 5 min, (b) 10 min, (c) 15 min, (d) 20 min, (e) 25 min, (f) 30 min. The NPs mean size and size dispersity for each reaction time are reported in graph (g). All syntheses are conducted at 280°C and with R = 2.5.

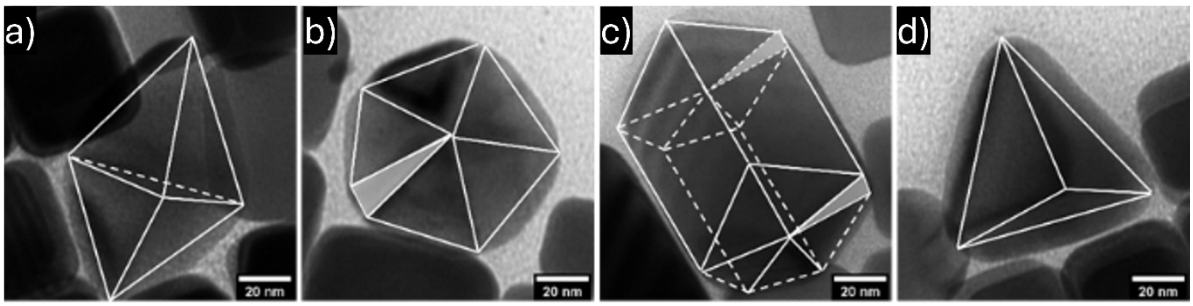


Figure S4 : TEM images of anisotropically shaped copper nanoparticles observed after 15 minutes of reaction, showcasing various morphologies (from left to right): tetrahedral bipyramid, decahedron, early-stage nanowire growth, and tetrahedron. The white lines show the different edges of these shapes. The shaded area visible at the decahedron and nanowire NPs represents the crystalline stacking defect zone between the 5 crystallites (with angles of 70.5° each, thus leading to a 7.5° gap filled by these crystalline defects).

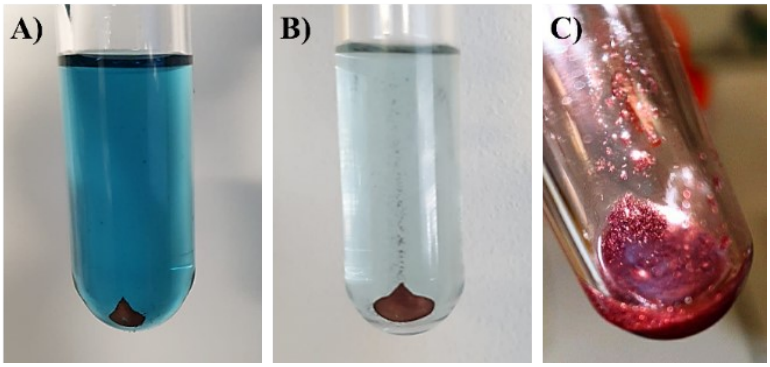


Figure S5 : Photographs of the synthesis solutions after the addition of washing solvents and after centrifugation corresponding to the aliquots at 5 minutes A) and 30 minutes (B), and the corresponding precipitate (C), whose coloration, similar to that of bulk copper, is mainly due to the population of micrometric nanowires.

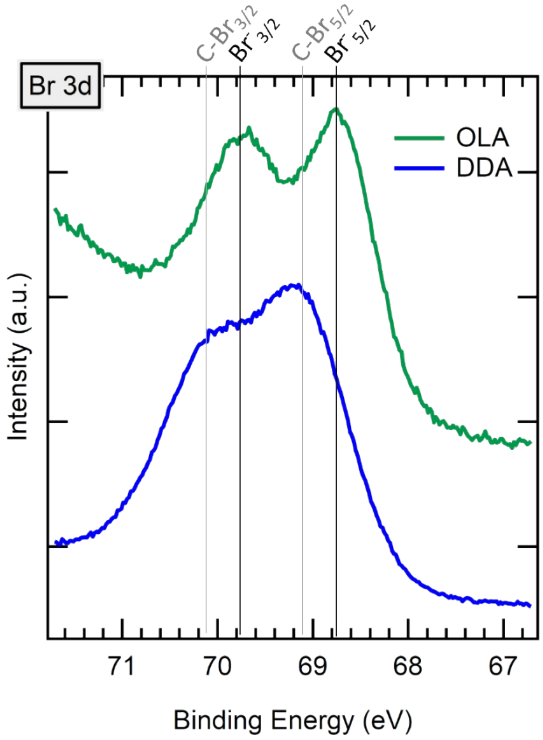


Figure S6 : XPS spectra of Br 3d core hole level of CuNPs obtained from CuBr in OLA (green curve) and DDA (blue curve). Bothsyntheses were carried out at reaction temperatures of 280°C for 1 hour without additional phosphine ligands.

Table S2 : Fit parameters used for XPS N1s spectra recorded for cubic (cb) NPs synthesized in OLA, spherical (sph) NPs DDA, octahedral (Ooh) NPs in OLA and spherical (sph) NPs obtained in OLA. Fits are performed with gaussian functions considering a linear background.

	BE (eV)	*RN-M*	*C-NH2*	*C-NH3+*	*C-NH2+-R*	*C=NR*
Binding Energy (eV)	***cb in OLA***	398,7	399,9	-	-	-
	sph in DDA	398,7	399,9	401,1	402,1	-
	oh in OLA	398,8	400,2	400,9	402,2	-
	sph in OLA	398,8	399,9	401,1	402,2	398,4
FWHM (eV)	***fwhm (eV)***	***RN-M***	***C-NH$_2$***	***C-NH$_3^+$***	***C-NH$_2^+$-R***	***C=NR***
	cb in OLA	1,4	1,4	-	-	-
	sph in DDA	1,5	1,4	1,4	1,4	-
	oh in OLA	1,3	1,3	1,3	1,3	-
	sph in OLA	1,3	1,3	1,4	1,3	1,3

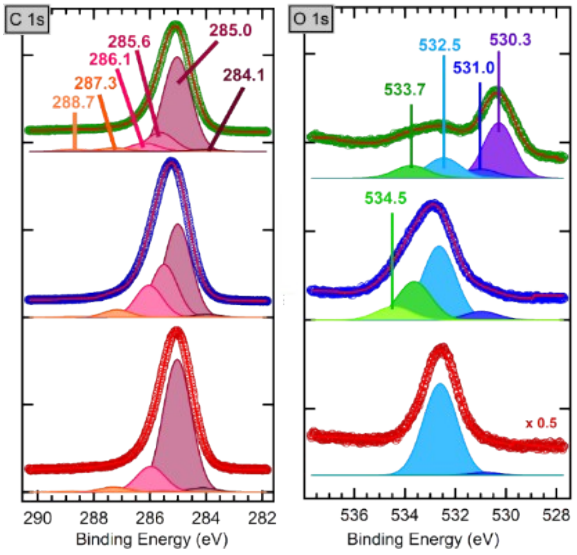


Figure S7 : XPS spectra of C 1s and O 1s core levels of NPs obtained in OLA (green curve), NPs obtained in DDA (blue curve) and NPs obtained in ODE (red curve).

Table S3 : Binding energies and proportions of the different contributions present in the C 1s spectra of samples prepared in OLA, ODE, DDA, and the Au substrate on mica used as an internal reference. The Au/mica substrate, prepared in open air, shows contributions related to the adsorption of atmospheric compounds.

B ..	**Sample**	**C-M**	**C-H, C-C,**	**C-N**	**C-OH,**	**C=O**	**O-C=O**

			C=C		**C-O-C**		
	Au/mica	284.12	284.98	-	286.13	287.31	288.76
	OLA	283.99	285.03	285.63	286.2	287.27	288.73
	ODE	284.12	285.03	-	285.97	287.3	288.76
n d	*DDA*	284.06	285.11	285.6	286.13	287.27	288.73
Proportions (%)	Sample	C-M	C-H, C-C, C=C	C-N	C-OH, C-O-C	C=O	O-C=O
	Au/mica	41.8	32.5	-	14.4	7.6	3.7
	OLA	1.3	73.0	14.8	6.5	2.8	1.6
	ODE	2.5	78.1	-	15.3	3.0	0.6
	DDA	1.6	49.3	27.5	17.0	4.1	0.6

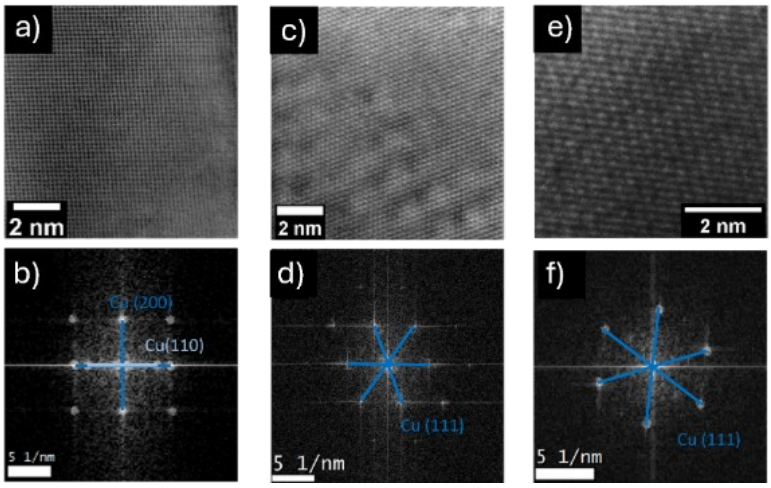


Figure S8 : HRTEM images and associated FT patterns of cubic NPs (a, b), octahedral NPs (c, d) and quasi-spherical NPs (e, f).

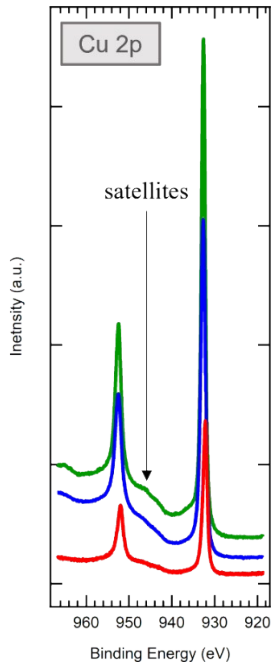


Figure S9 : XPS spectra of the Cu 2p core level of samples prepared in OLA (green curve), DDA (blue), and ODE (red).

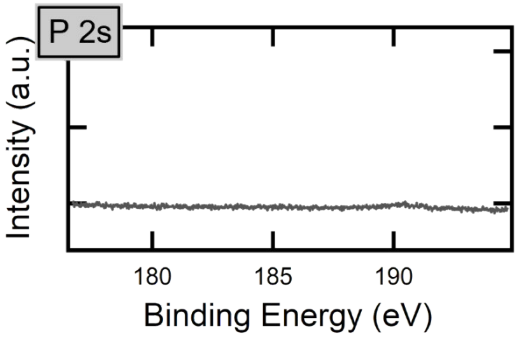


Figure S10 : XPS spectra of P 2s core level of quasi-spherical Cu NPs obtained by the reduction of Cu(OAc) in OLA in presence of TOP.