

SUPPORTING DOCUMENTS

CuO_x Nanotubes via an Unusual Complexation Induced Block Copolymer-like Self-assembly of Poly(acrylic acid)

Absorbance of PAA-Cu²⁺ complex

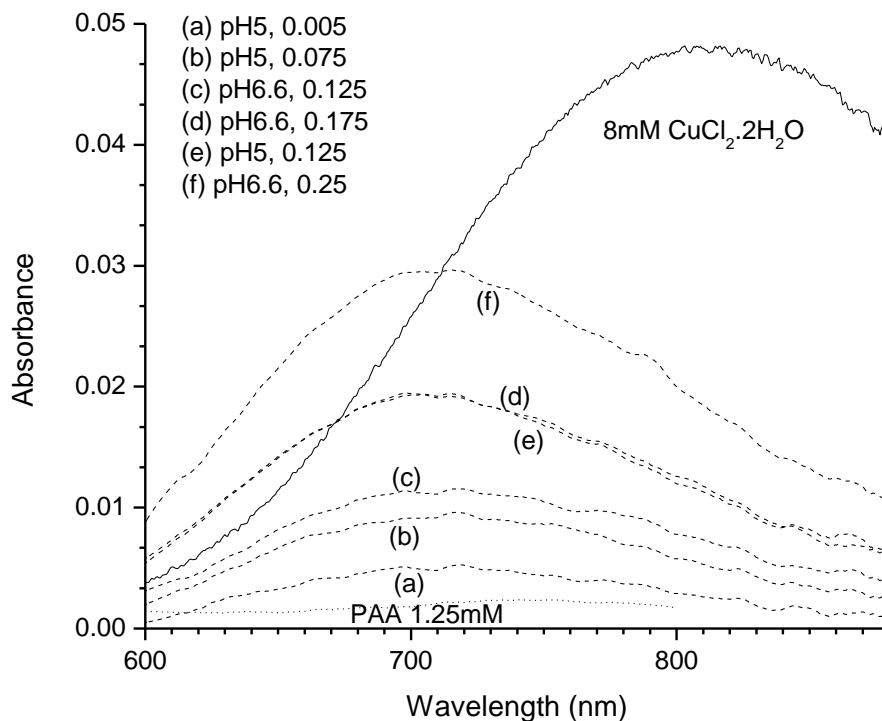


Figure S1. Absorbance spectra of PAA and CuCl₂·2H₂O mixture at different PAA initial pH and [Cu²⁺]:[COOH]₀ ratio; with [COOH]₀ fixed at 1.25mM. After mixing CuCl₂·2H₂O with PAA, absorbance peak of purely CuCl₂·2H₂O at around 810nm disappears and new absorbance peak at around 700nm emerges; indicating complexation of Cu²⁺ and COO⁻. This 700nm peak undergoes slight blue-shift with increased [Cu²⁺].¹

(1) Iatridi, Z.; Bokias, G.; Kallitsis, J. K. *J. Appl. Polym. Sci.* **2008**, 108, 769-776.

Absorbance of solutions at different stages of the synthesis

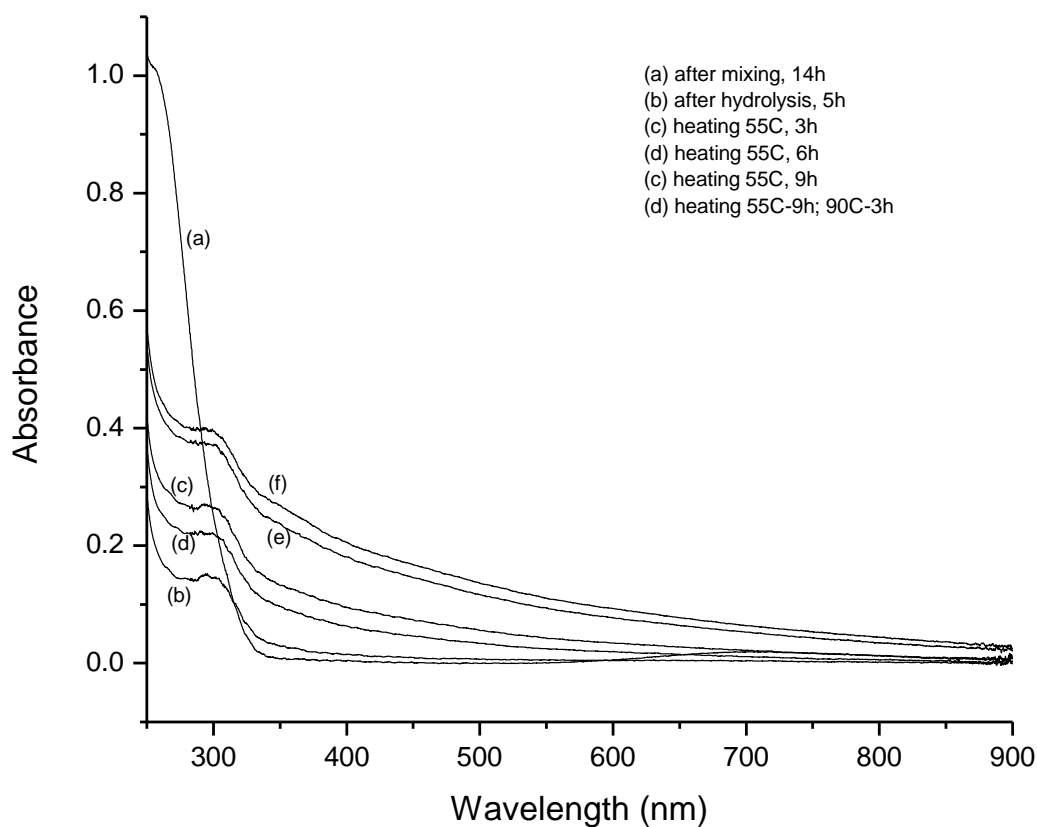


Figure S2. The figure shows the evolution of absorbance characteristics in different steps of templated synthesis.

As observed from Figure S2, there was no characteristic absorbance peak of usual Cu nanocrystals (~580nm) and this was attributed to the low concentration. Oxidation of the Cu with prolonged heating could be observed from small absorbance peak at ~360nm and increased overall absorbance across the entire measured wavelength. Interestingly, clear appearance of NO_3^- absorption peak ($n \rightarrow \pi^*$ transition) at ~300nm after the hydrolysis step was found. This peak was not observed inside (i) PAA solution with NaNO_3 or (iii) mixture of all three components (PAA, CuCl_2 and NaNO_3). This directly evidenced that the vicinity of COO^- (i.e., the PAA chain) undergoes changes of chemical species as repulsion of NO_3^- from COO^- sites happened during hydrolysis. This is important as it suggests, after the hydrolysis step, the

structure of PAA-Cu²⁺ complexes is highly condensed and the Cu²⁺ are strongly bound to the backbone (repelling the inert salt species).

pK_a- α relationship (titration experiment B)

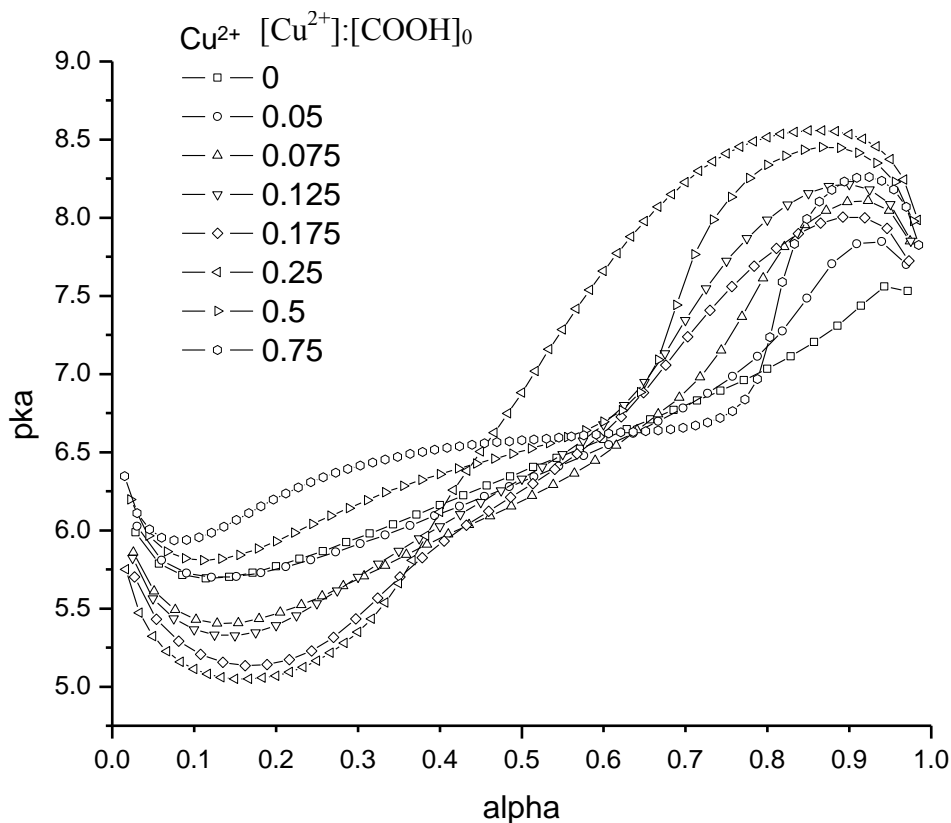


Figure S3. pK_a- α relationship of mixture of 1.25mM PAA and CuCl₂.2H₂O with different [Cu²⁺]:[COOH]₀ ratio.

Addition of NaOH into PAA would result in neutralization of COO⁻ (not bound with Cu²⁺). At high pH (i.e. high α), pure PAA adopts an expanded chain conformation of increased stiffness due to like-charge repulsion. The obtained pK_a- α relationships show that complexed Cu²⁺ initially promotes deprotonation of neighbouring COOH due to lowering of the energy barrier (the pK_a decreases with increased [Cu²⁺]:[COOH]₀). However, this promoted deprotonation competes with increased chain stiffness and decreased accessibility of COOH (due to PAA chain shrinkage) in terms of both neutralization and further Cu²⁺ binding. Therefore, above certain [Cu²⁺]:[COOH]₀, the pK_a increases with increased [Cu²⁺]:[COOH]₀. At much higher

$[\text{Cu}^{2+}]:[\text{COOH}]_0$ (exceeding maximum theoretical binding limit of 0.5), the hydrolyzed $\text{Cu}(\text{OH})_2$ will be wrapped around by the PAA and further stiffens the PAA- Cu^{2+} complex; an abrupt increase of pK_a was found at high α .

Construction of 3D diagram showing the relationship among pH, α , and $[\text{Cu}^{2+}]:[\text{COOH}]_0$

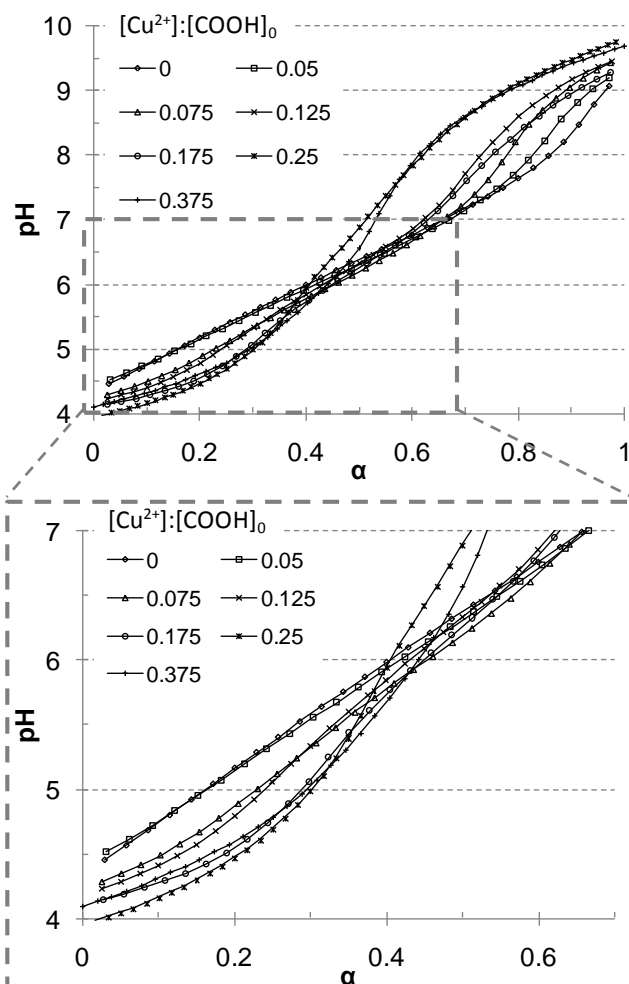


Figure S4. pH- α relationship of mixture of 1.25mM PAA and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ with different $[\text{Cu}^{2+}]:[\text{COOH}]_0$ ratio, obtained in titration experiment B. Only the data within range of pH 4 to 7 was used in the 3D diagram construction.

Curve-fitting of the pH- α curves within region from pH 4 to pH 7 was done. After that, a regular array of data ('estimated α ' based on known pH and $[\text{Cu}^{2+}]:[\text{COOH}]_0$) can be generated using Matlab software (griddata function, linear estimation); as shown in Table S1. The construction of 3D diagram based on the data array can then be done, as shown in Figure S5.

Table S1: The degree of deprotonation (α) estimated using Matlab software.

	$[\text{Cu}^{2+}]:[\text{COOH}]_0$						
	0	0.05	0.075	0.125	0.175	0.25	0.375
pH	α						
4.1	-	-	-	-	0.011	0.077	0.004
4.2	-	-	-	0.013	0.065	0.119	0.054
4.3	-	0.020	0.038	0.061	0.117	0.154	0.098
4.4	0.018	0.019	0.078	0.101	0.159	0.185	0.137
4.5	0.044	0.033	0.112	0.134	0.191	0.212	0.174
4.6	0.070	0.063	0.107	0.162	0.218	0.236	0.206
4.7	0.095	0.092	0.134	0.198	0.241	0.257	0.235
4.8	0.120	0.128	0.153	0.215	0.246	0.275	0.260
4.9	0.145	0.166	0.183	0.227	0.258	0.292	0.282
5.0	0.169	0.202	0.218	0.246	0.288	0.308	0.301
5.1	0.193	0.236	0.250	0.276	0.293	0.321	0.319
5.2	0.217	0.252	0.281	0.302	0.319	0.334	0.336
5.3	0.242	0.268	0.294	0.305	0.321	0.345	0.352
5.4	0.267	0.283	0.292	0.326	0.350	0.355	0.368
5.6	0.292	0.304	0.315	0.341	0.357	0.365	0.383
5.7	0.318	0.336	0.345	0.361	0.386	0.374	0.397
5.8	0.344	0.367	0.370	0.391	0.404	0.383	0.411
5.9	0.369	0.396	0.401	0.406	0.423	0.393	0.425
6.0	0.395	0.424	0.447	0.426	0.418	0.402	0.438
6.1	0.421	0.445	0.472	0.454	0.451	0.413	0.450
6.2	0.447	0.469	0.497	0.484	0.477	0.423	0.462
6.3	0.474	0.494	0.492	0.488	0.504	0.435	0.473
6.4	0.501	0.519	0.527	0.510	0.525	0.446	0.484
6.5	0.529	0.546	0.561	0.531	0.536	0.457	0.493
6.6	0.556	0.574	0.581	0.561	0.538	0.469	0.502
6.7	0.582	0.595	0.587	0.576	0.545	0.480	0.510
6.8	0.608	0.620	0.619	0.603	0.585	0.491	0.518
6.9	0.634	0.639	0.642	0.621	0.585	-	-

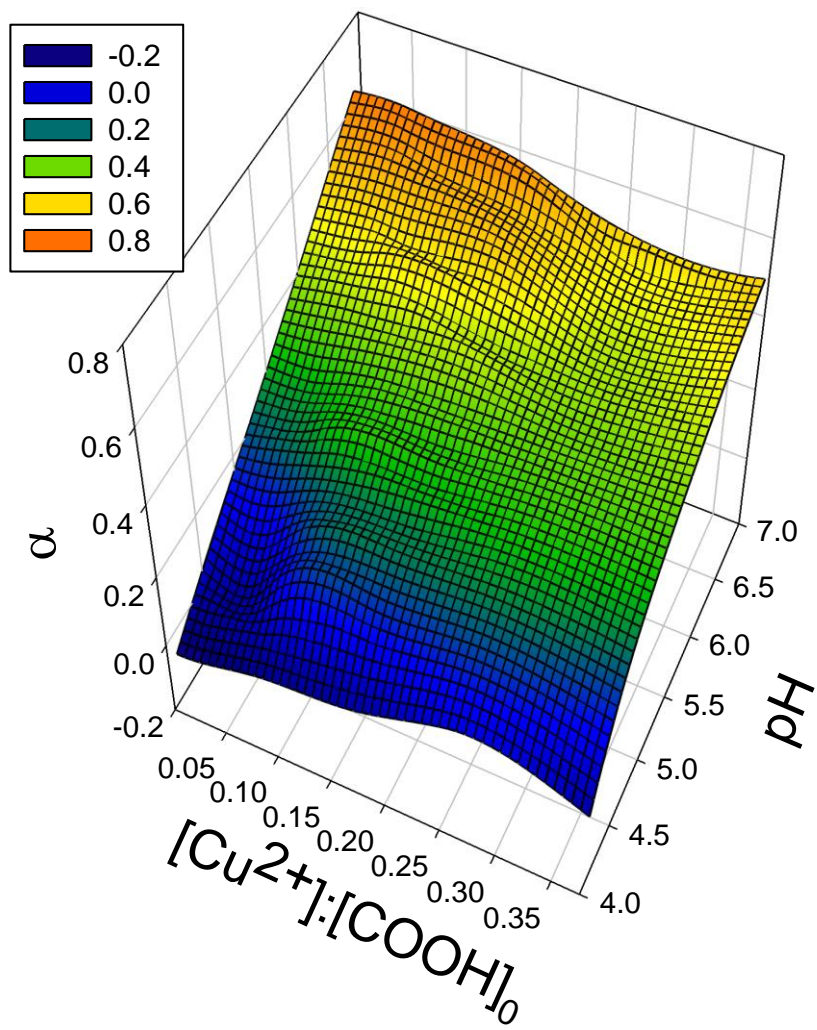


Figure S5. 3D diagram showing the relationship among pH, α , and $[Cu^{2+}]:[COOH]_0$.

Morphology of spherical Cu nano-crystals

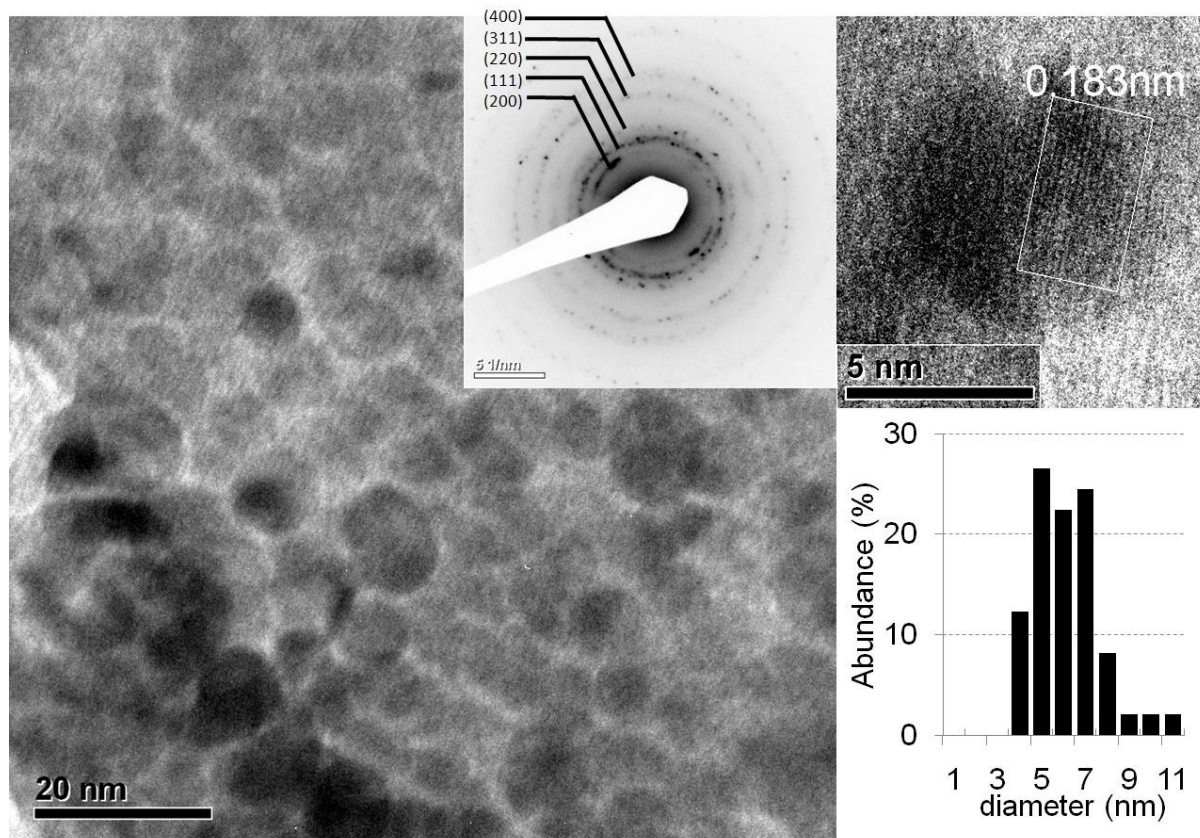


Figure S6. Spherical Cu nano-crystals obtained in the PAA-templated synthesis.

In our work, we observed certain amount of spherical Cu nano-particles with diameter of 8(+/- 3) nm; as shown in Figure S6. Steric hindrance of the PAA chains restricted the spatial amount of Cu^{2+} atoms. During hydrolysis step, further deprotonation of COOH into took place upon addition of NaOH. High charge density resulted in expansion of the PAA chain and more efficient repulsion among charged PAA- Cu^{2+} complexes. This effect further resulted in overall uniform diameters of spherical Cu nano-crystals. The SAED and lattice spacing showed that the nano-crystals were of Cu phase.