Electronic Supplementary Material (ESI) for Nanoscale.

Copper (I)-Alkylamine Mediated Synthesis of Copper Nanowires

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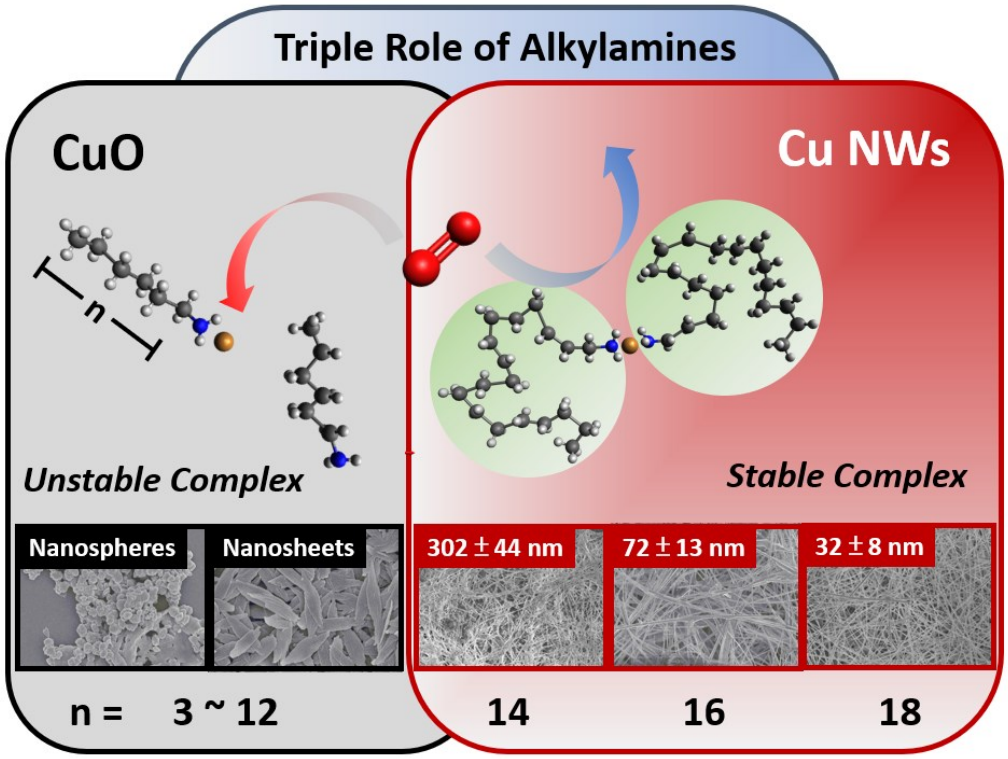
Supporting Information



S1. Cu nanowire synthesis methods

Synthesis of Cu nanowires using wet chemistry consists of three main methods: oil phase, aqueous/alkaline and aqueous/neutral synthesis. Oil phase synthesis involves using Cu(I) salts, alkylamines and/or high boiling point organic solvents at high temperatures (180℃ or above). Aqueous/alkaline synthesis usually uses Cu(II) salts, ethylenediamine, hydrazine and a high concentration of NaOH or KOH in an aqueous solution. Aqueous/neutral synthesis is conducted using Cu(II) salts, alkylamine and glucose in an aqueous precursor. Aqueous/neutral synthesis becomes more popular recently because it is eco-friendly, cost-effective and safe to practice. The synthetic methods documented in *Web of Science* are counted and their percentages are shown in Figure S1.

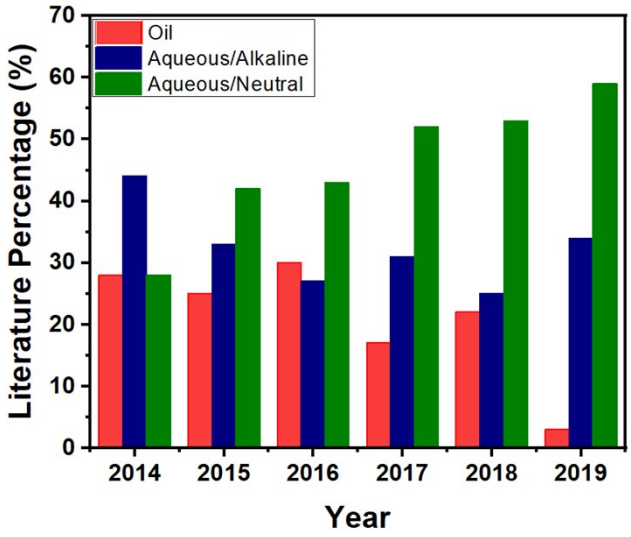


Figure S1. The percentages of the different wet chemistry methods used for Cu nanowire synthesis in the published articles from *Web of Science*.

S2. Color changes for the $CuCl_2$/HDA solution with or without glucose at 110℃

As seen in Figure S2, the white color solution appears after around 20~30 min in the precursor solution (with glucose) at 110℃. This white solution lasts for a few minutes and then turns into reddish brown color. Compared with the precursor solution, the white solution appears slightly later, after around 40 min; for the $CuCl_2$/HDA solution without glucose at 110℃ would remain white throughout. It should be noted that the time needed for the white and the reddish brown colors to appear may vary (± 10 min) dependent of the concentrations and the purities of the reactants in the solution.

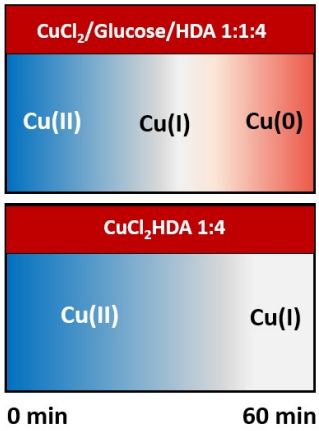


Figure S2. Schematic color changes of the precursor and $CuCl_2$/HDA solution within the first hour of reaction at 110℃.

S3. XRD spectra of Cu(II)/Cu(I)-HDA complex

As seen in Figure S3, the XRD spectra for Cu(II)-HDA (blue) and Cu(I)-HDA (white) sample show that Cu(0) does not form in these samples. The results suggest that HDA alone cannot reduce Cu(II) to Cu(0) at 110℃, and a disproportionation of Cu(I) does not occur in the presence of HDA in an aqueous solution.

XRD spectra reveal the formation of heterogenous Cu(II)/Cu(I)-HDA complexes. Cu(I)-HDA complex shows the characteristic peaks of the alkyl chains from HDA, but their packing is somewhat interrupted. A group of new diffraction peaks is observed between 20~25˚ for Cu(II)-HDA complexes, indicating the presence of liquid-crystalline domains (*J. Mater. Chem.* 2004, **14**: 121-126). These observations agree with the DSC and FTIR results where different HDA aggregates (coordinated, intercalated and bulk-like) are present in the precursors, which generates complex diffraction patterns.

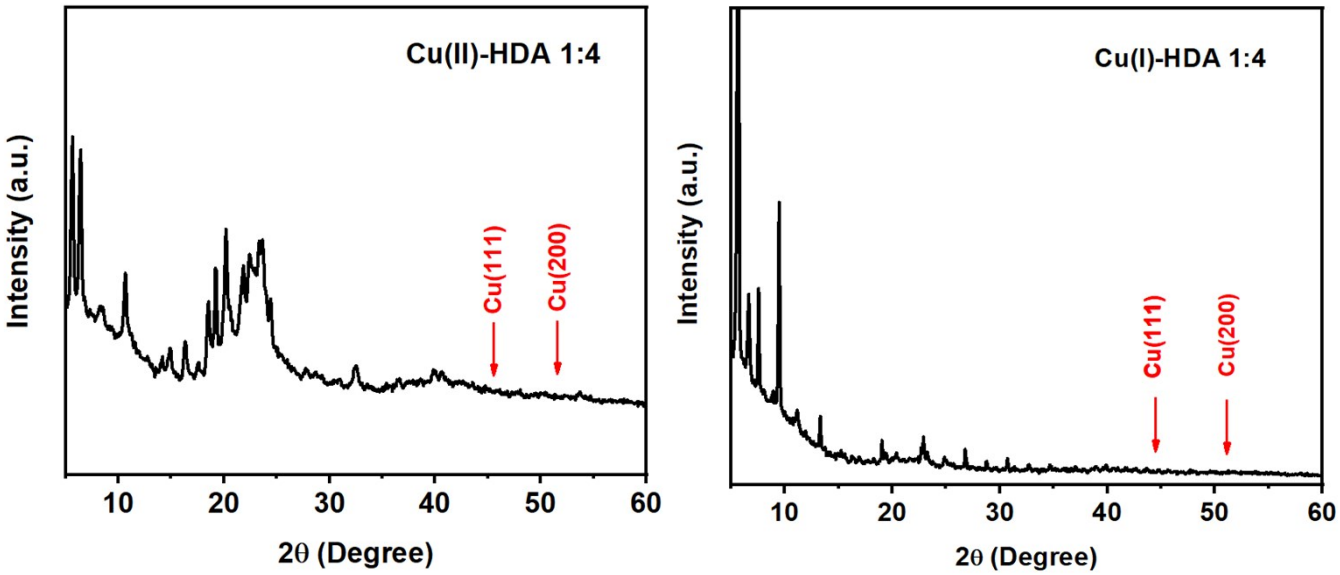


Figure S3. XRD spectra of Cu(II)-HDA and Cu(I)-HDA complex.

S4. Aqueous/neutral synthesis using short-chain alkylamines (<C12)

Short-chain alkylamines (C10, C8, C6, C4 and C3) were used to form a precursor solution with $CuCl_2$ and glucose. The molar ratios of the precursors are the same as those for the long-chain alkylamines at $CuCl_2$/glucose/short-chain alkylamine = 1:1:4. At room temperature, these precursors formed with short-chain alkylamines are in light green or cyan color. Compared with long-chain alkylamines, the alkylamines with a short alkyl chains (C12 or fewer) are more hydrophilic. They are prone to solubilization in water, and are easily dissociated from Cu ions. The colors on the precursor solution indicate that anions in the solution, such as Cl^- and OH^-, involve in the coordination complexation with Cu(II) ions (*J. Am. Chem. Soc*. 2017, **139**: 277-284; *Phys. Chem. Chem. Phys.* 2014, **16**: 22107-22115; *Acc. Chem. Res*. 2016, **49**: 442-451). With these coordinated water-soluble small anions, Cu(I) cannot be protected in an aqueous environment. As a result, black CuO solids form in the solution after keeping at 110℃ within 30min, as seen in Figure S4.

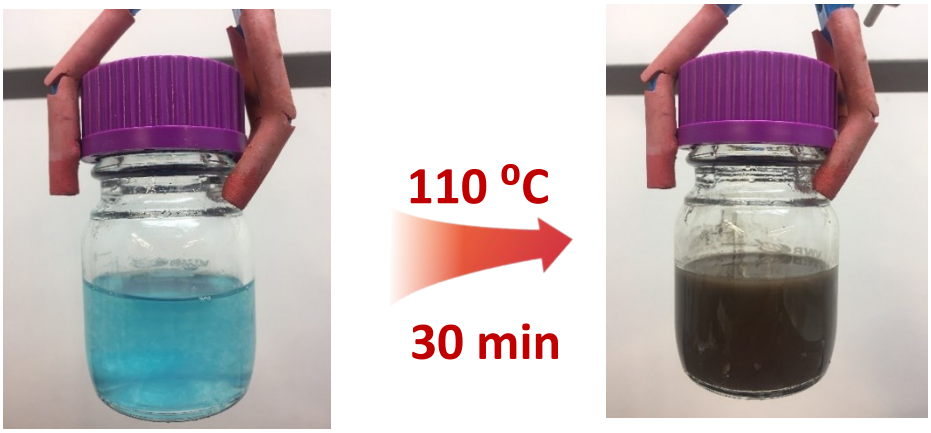


Figure S4. The representative precursor containing octylamine at room temperature and after keeping at 110℃ for 30min.

S5. Stability of Cu(I)-alkylamine complex in the presence of ascorbic acid

The precursor solutions containing $CuCl_2$, ascorbic acid and alkylamine (HDA or DDA) with a molar ratio of 1:1:4 were prepared. After 5 min of mixing at room temperature, the solution with HDA turned white (Figure S5), suggesting the formation of Cu(I)-HDA complexes. With ascorbic acid, the Cu(I)-HDA complex is stable in air. However, the one with DDA is blue green, and its color shifts to light blue upon air exposure. This suggests that the effect of alkylamine chain length on the stability of Cu(I) complexes is independent of the strength of the reducing agent.

It is worthy to mention that the effect of alkyl chain length becomes irrelevant with increased concentration of ascorbic acid. For example, with a 1:3:4 ratio for $CuCl_2$/ascorbic acid/alkylamine, both precursors with HDA and DDA turned white Cu(I) solutions after a few minutes of mixing at room temperature. This is because a high concentration of ascorbic acid will neutralize all the oxidizing species (solubilized oxygen etc.) in the solution to prevent oxidation of Cu(I) ions. In the absence of LMCT (room temperature), the oxidation resistance for Cu(I)-alkylamine complexes is provided by strong reducing agent, ascorbic acid. When the concentration of ascorbic acid is decreased to 1:1, it is possible that some oxidizing species may remain in the solution to allow for oxidation of Cu(I) complexes when a short alkylamine (DDA) is used.

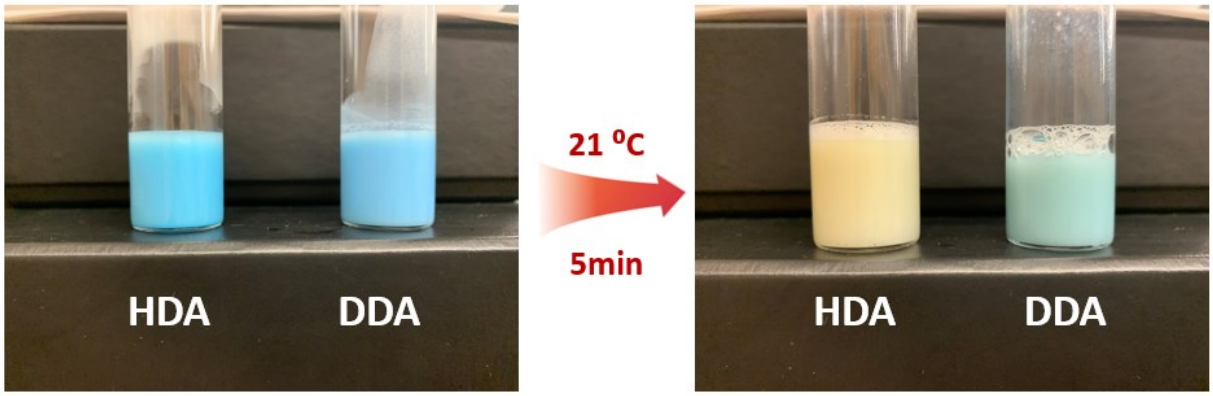


Figure S5. The precursor solutions containing HDA or DDA and after mixing for 5 min at room temperature in the presence of ascorbic acid.

S6. Effect of anions on the stability of Cu ion-alkylamine complex

Considering that the complexation of Cu ions and alkylamine is a dynamic equilibrium, the exchange between the alkylamines and anions (chloride, hydroxide, bromide etc.) should take a place on Cu ions concurrently. The complexation is likely dependent of the concentration of these anions and the chain length of alkylamines (Figure 2a and S4).

To further validate this hypothesis, NaCl was added to the precursor solution ($CuCl_2$:glucose:HDA:NaCl 1:1:4:1). As seen in Figure S6a, a phase separation is observed. This is because the additional chloride ions destabilize the Cu(II)-alkylamine complexes, resulting in Cu(II)-chloride complexes.

Additionally, in order to see how different types of counterion play a role in the synthesis, we used $CuSO_4$ to replace $CuCl_2$ in the precursor solution. The $CuSO_4$/HDA solution is dark blue, and turns into translucent upon heating at 110℃. After adding glucose, the solution remains translucent without formation of Cu.

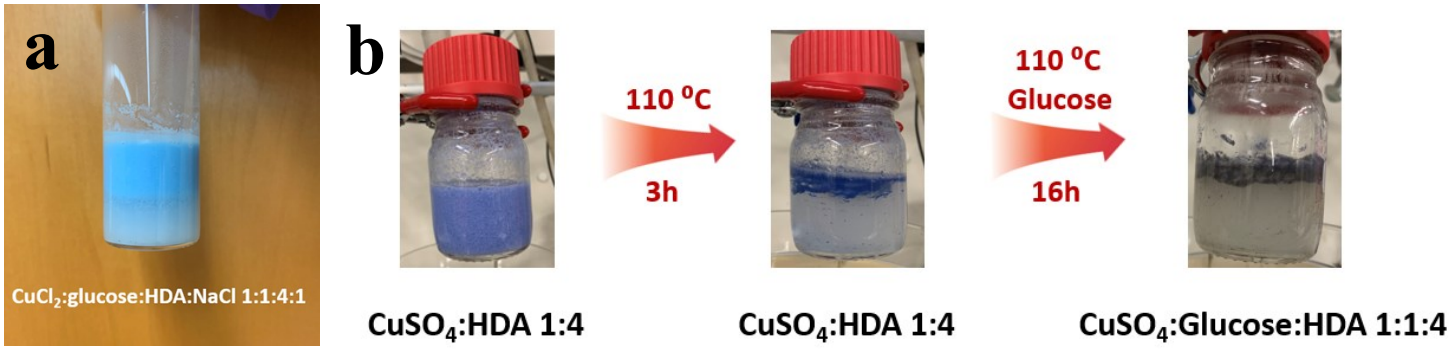


Figure S6. (a) The precursor solution with additional NaCl and (b) The precursor using $CuSO_4$ and after reacting at 110℃ with or without glucose.