Benzoin Free Radical as an Effective Reducing Agent for Copper Nanowire Synthesis

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Supporting Information Placeholder

ABSTRACT: In this work, we report a new, general synthesis approach that uses heat driven benzoin radicals to grow ultrathin copper nanowires with tunable diameters. This is the first time to use organic radicals as a reducing agent in metal nanowire synthesis. *In-situ* temperature dependent electron paramagnetic resonance (EPR) spectroscopic studies prevail that the active reducing agent is the free radicals produced by benzoins under elevated temperature. Furthermore, the reducing power of benzoin can be readily tuned by symmetrically decorating functional groups on the two benzene rings. When the aromatic rings are modified with electron donating (withdrawing) groups, the reducing power is promoted (suppressed). The controllable reactivity gives it great potential as a versatile reducing agent that can be easily generalized in other metallic nanowire synthesis.

One-dimensional metal nanowires have many unique properties different from their bulk form. They have been demonstrated by a number of works and used as crucial building blocks in various applications such as electronics,[1] optics,[2] catalysts,[3] and sensors.[4] In particular, metal nanowires have been extensively studied in their application of making high performance transparent conductors.[5] Copper's high earth abundance and intrinsic conductivity makes it among the most popular materials in the field of nanowire mesh electrode. Copper nanowires (Cu NWs) have been successfully synthesized, mainly via colloidal chemistry, by a number of groups. The general colloidal method is to reduce copper ion/ion complex in presence of capping ligands with efficient reducing agents including primary amine,[6] glucose,[7] ascorbic acid,[8] hydrazine,[9] or via catalyst assisted methods.[10] The quality of the Cu NWs synthesis is usually the key factor achieving high performance nanowire based devices. Monodispersing, high aspect-ratio-wire, diameter controllable and low-cost approaches are always desired.

Recently, we developed a successful synthesis to grow ultra-thin Cu NWs using silane based free radicals.[11] Stable reducing radicals show great potential in metal nanostructure synthesis, especially in one-dimensional nanowire growth where the nucleation rate needs to be well controlled. However, the difficulty in tuning of its reducing power, the sensitivity to air/oxygen and the high unit price hinder silane from being a general reducing agent in nanomaterial synthesis. Here, we report a new synthetic approach: using benzoin based organic free radicals as a reducing agent to synthesize Cu NWs. This method can easily produce monodispersed, size-controllable Cu NWs with diameter ranging from ~50 to ~18 nm. The reaction mechanism was investigated using *in-situ* EPR. Moreover, we demonstrate the reactivity tunability by introducing electron-donating/electron-withdrawing functional groups on benzoin.
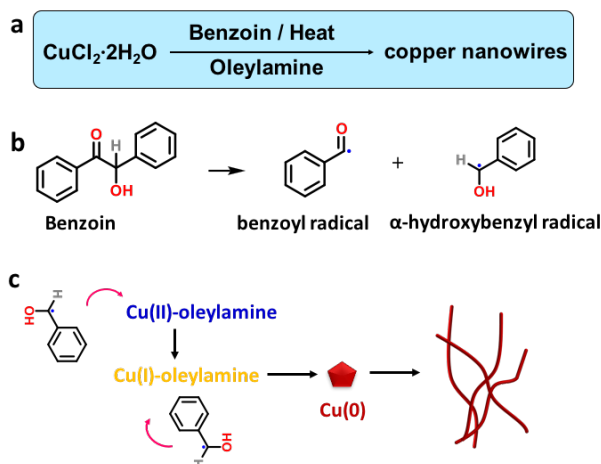
Figure 1. (a) Overall reaction formula of copper nanowire synthesis using benzoin as reducing agents. (b) Heat induced radical generation from benzoin. (c) Proposed mechanism of copper complex reduction via benzoin radicals and one-dimensional nanowire growth.
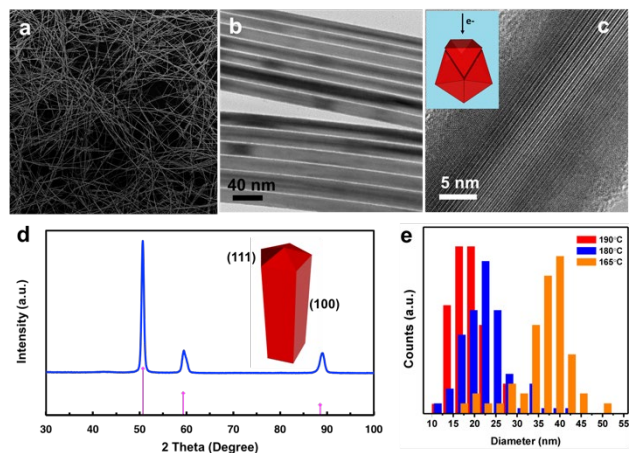

Figure 2. (a) SEM and (b) TEM and (c) high resolution TEM images of as synthesized Cu NW at 190 °C. (d) XRD pattern of as made Cu NWs, inset is a schematic representation of the nanowire's micro structure. Pink lines are the standard XRD pattern of FCC copper. (e) Diameter distribution of Cu NWs synthesized at 190 °C (red), 180 °C (blue), and 160 °C (orange).

The synthesis of Cu NWs is summarized in Fig. 1a. Copper chloride, which is dissolved in oleylamine can be slowly reduced by benzoin under heating condition and eventually grow into one-dimensional nanowires. Benzoin here acts as the key reducing agent, which readily reduces copper (II) species to copper (I) and then to copper metal. Commonly used as a photoinitiator in polymerization,[12] benzoin's application in colloidal nanomaterial synthesis is rarely documented,[13] even more rare so under heating conditions. It is well known that, under UV illumination, benzoin produces two radicals via α-cleavage, in which the carbon-carbon sigma bond undergoes homolytic bond cleavage upon absorption of light.[14] We hypothesize here that under heating condition, benzoin behaves in a similar manner. At elevated temperature, it yields radicals in an inert environment and the resulting radicals can act as efficient electron donors. The detailed proposed reaction mechanism is shown Fig. 1 b, c. When benzoin is heated, it decomposes into two radical segments, benzoyl radical and α-hydroxybenzyl radical. In an air-free atmosphere, the radicals are relatively stable due to the conjugation of benzene ring, thus have a long enough lifetime to reduce metal ions in solution. The reduction of copper complex takes place in two steps: at lower temperature Cu (II) species are first reduced to Cu (I) which is indicated by the disappearing the fingerprint blue color; then at higher temperature, Cu (I) ions are further reduced to Cu metal. With oleylamine as coordinating surfactants, the copper nucleation is known to favor five-fold-twinned structure. With (100) facets selective protected by amine groups, newly formed copper metal preferentially deposits on to (111) surfaces, promoting one-dimensional growth.[11]

The morphologies of the product are examined by SEM and TEM as shown in Fig. 2 a, b. The majority of the products are uniform nanowires with minimum portion of nanoparticles. Such nanowires have length of up to 20 μm, and diameter of 18.5 ±3.5 nm. The detailed structure of the Cu NW is studied using high resolution TEM and XRD. We believe that the nanowire has the five-fold twinned structure, which is consist of five face centered cubic (FCC) single crystalline units. Fig. 2c shows the HRTEM image taken when the incident electron beam is perpendicular to one of the side facets. Clear Moiré pattern is observed in the center of the nanowire, which correspond to the overlap between the upper single unit and the underline two units as drawn in the inset cartoon.[11] Fig. 2d shows the XRD pattern of the as-made Cu NWs. The wires adopt the common FCC pattern. The clean pattern indicates the products are pure from other crystalline species. The inset cartoon demonstrates the overall microstructure of the five-fold twining Cu NW, with {100} facets as side surfaces and [110] being the growth direction. This structure has been well documented within oleylamine modulated Cu NW synthesis. [6(b), 10, 11]

The diameter of the as-grown Cu NWs can be readily tuned by changing reaction temperatures. We observed that when the reaction temperature is higher, the nanowires synthesized are of a smaller diameter (Fig. S1). Fig. 2e summarizes the diameter distribution of Cu NWs grown under different temperatures. The averaged nanowire diameter is increased from 18.5 nm with the reaction temperature of 190 °C, to 23.0 nm with 180 °C and to 36.2 nm with 165 °C. The logic behind the diameter control can be explained by close examination of the nucleation stage. At a higher

temperature, the reduction of copper ion complex is faster which leads to a faster nucleation. A faster nucleation means more nucleation sites at the same time frame. Considering that the precursor concentration is kept the same for all experiments, more nucleation sites imply smaller volume for each nucleates, which later will grow into thinner nanowires.

To investigate the reaction mechanism, we carried out a series of control experiments and the results are summarized in Table S1. Benzaldehyde shows no activity towards reduction of copper salt at the condition of interest, excluding the possibility that benzoin's decomposition byproduct serves as the effective reducing agent.[13] Benzoin ester derivatives are also tested in the similar reaction condition. Despite the fact that benzoin esters exhibit similar behavior and activity when used as photoinitiator,[12] no reactivity towards copper reduction is observed. This suggests that the actual reductants are the α-hydroxybenzyl radicals, rather than its benzoyl counterpart. Another interesting observation is that, when we attach a single chloride atom to the anomeric ring (4-chlorobenzoin), again no reduction of copper complex happens. This is probably because that the asymmetrical structure makes homolytic bond cleavage no longer favorable, and thus radicals are not among the major product anymore. This further implies the radical-involving nature of this reaction.

To further understand the proposed radical-involving mechanism of reaction, *in-situ* temperature dependent electron paramagnetic resonance (EPR) spectroscopy is used to track the reduction progress. EPR measurement is a spectroscopic technique which detects species with unpaired electrons, and is informative towards reactions involving free radicals and/or active metal complexes. In this study, we aim to relate the Cu nanowire growth to the evolution of unpaired electron species within the system.
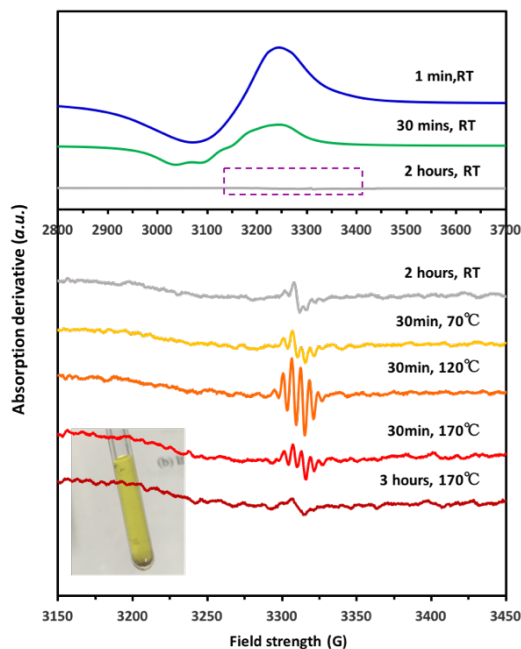

Figure 3. In-situ EPR spectra of copper complex reduction by benzoin radicals

The results of the EPR measurements are shown in Fig. 3. The first spectrum Fig. 3a of is taken soon after the reactants are mixed up at room temperature. Broad EPR signal centering at 3165 G (g=2.09559) is observed. This strong and broad feature can be assigned to Cu(II) species which originated from Cu losing two electrons, and taking $3d^9$ electron configuration, rendering one unpaired electron.[15] The absence of subtle features is due to line broadening caused by strong dipolar interaction.[16] This broadening is commonly observed in concentrated solution.[17] After 30 minutes in room temperature, the broad feature preserves its general centering position but with intensity visibly reduced. In addition, subtle patterns are resolved due to lowered concentration. 2 hours later, the Cu(II) pattern is undetectable. Coupled with the disappearance of signature blue color, we believe that Cu(II) complex is completely reduced to Cu(I) species at this stage.

Fig. 3b keeps track of the EPR response during the heating of the reaction solution. Sharp features with g factor calculated as 2.00331 are observed. EPR lines with g-value close to 2, correspond to a free radical signal,[17] which we believe is produced by the decomposition of benzoin. In the first spectrum, which is taken at room temperature, a sharp radical-like feature is already resolved. This echoes with the observation of room-temperature reduction of Cu (II) complex. It indicates that, without heating, benzoin is already slowly decomposing and producing radicals. This decomposition, even though slow, could already build up a steady-state concentration which can be detected by EPR spectroscopy. And the radicals produced have efficient reducing power to reduce Cu (II) ion to Cu (I) but no further, probably due to low

concentration. In consideration that oleylamine might also act as reductant towards Cu(II), we also conducted a control experiment to compare the reducing power between benzoin radicals and oleylamine towards copper ions. As shown in Fig. S2, oleylamine does have enough reducing power to reduce Cu (II) into Cu (I) at elevated temperature in inert environment. However, this reducing ability is not activated at room temperature.

As the temperature reaches 70 °C, the radical signal becomes stronger. Evidently as temperature is increased, the decomposition of benzoin goes up in rate, and the concentration of radicals also increases.

As the reaction temperature goes up to 120 °C, reddish copper product starts to precipitate out in the EPR tubes. At this period, we also see the strongest signal in the radical region. The asymmetric shape of the EPR spectrum infers that there are multiple radical species present in the sample, causing superposition of lines with different g-value.[17] The spectrum of the primary radicals in the system has six well resolved hyperfine lines. The missing of one intense central line suggests that there exist an odd number of equivalent hydrogens contributing in hyperfine coupling.[17] Assuming from the evidence before that the α-hydroxylbenzyl radicals are more active, the EPR signal should mainly account for benzoyl species. Interestingly, the spectrum obtained here does not match with previously reported data for low temperature benzoyl (three lines with one strong center)[18], nor α-hydroxylbenzyl radical (evenly distributed 21 lines[19]). Considering the high-temperature caused increased line shift/broadening effect,[16(b)] a comprehensive understanding of this spectrum is not straightforward. One possible explanation is that at high temperature, benzoyl radicals (σ-radical) , resonance into its π-isomer (Fig. S3).[20] The energy barrier of this transformation is easily overcome by thermal input and there exist comparable amount of both species under the reaction condition.[21]

As the temperature continue to increase, more copper product emerges from the tube, meanwhile, the radical signal decreases in strength due to the consumption of the material. Then, the solution was left to react at 170 °C for 3 hours before removed from heat. In the final spectrum, the radical signal is barely resolved. The inset picture shows the reddish copper product after the reaction.
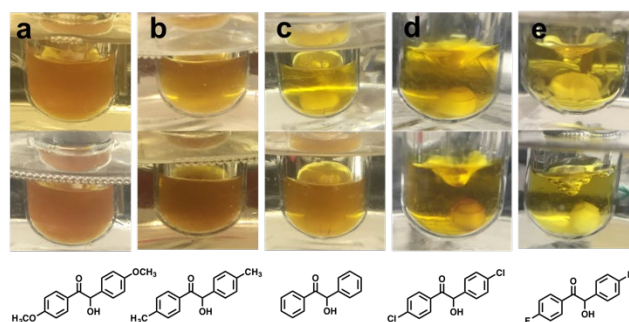

Figure 4. Pictures of different reaction stages of Cu NWs synthesis using (a), 4,4-dimethoxybenzoin, (b), 4,4-dimethylbenzoin, (c), benzoin, (d), 4,4-dichlorobenzoin[22] and (e), 4,4-difluorobenzoin[22] as reducing agents. The upper and middle panel show the pictures of reactions run for 1 hour and 2 hours respectively; the lower panel shows the chemical structures used in corresponding reactions. The reactions were all carried out at 180 °C.

The reactivity of benzoin can be tuned by introducing electron-donating/electron-withdrawing groups on the benzoin molecule. We find that, with electron-donating group as substitution, the reducing power is largely promoted; while electron-withdrawing substitution diminishes benzoin's reduction reactivity. Fig. 4 shows the series of control experiments carried out to test the reactivity of benzoin derivatives. One hour into the reaction, considerate amount of copper is already reduced out using dimethyloxylbenzoin as reducing agent, comparing to the smaller amount of copper nucleation in the case of dimethylbenzoin, and minimum to zero visible nucleation in the case of benzoin, dichlorobenzoin and difluorobenzoin. Two hours into the reaction, the production of copper follows the same trend, with electron donating modification promotes the reaction while the electron withdrawing case suppress the reducing. It is obvious that benzoin with CH_3O- functional group, the strongest electron donating group, is the most active one. As the functional groups get more into the electron withdrawing region, the reaction rate gets slower. Meanwhile, if F- is used as the decorating group, the reaction does not happen at all. The yield of copper product after three hours' reaction time are measured to be 94.0%, 65.3%, 31.3%, 2.5% and 0% for reactions with 4,4'-dimethoxybenzoin, 4,4'-dimethylbenzoin, benzoin, 4,4'-dichlorobenzoin and 4,4'-diflorobenzoin, respectively. The TEM images of the products are shown in Fig S4.

Benzoin can be readily used in other metal nanowire structures too. High-quality, silver and gold nanowire can be synthesized using benzoin as reducing agent, in the presence of organic surfactants (Fig. S5). Additionally, benzoin's compatibility with both hydrophilic/hydrophobic solvent systems would potentially free up more space for other inorganic nanomaterials synthesis.

In conclusion, we demonstrate a new synthetic approach that used benzoin and its derivatives as reducing agent to grow high quality Cu NWs. The active species during the reduction are attributed to the free radicals produced via heat decomposition of benzoins. The reaction mechanism is then studied in detail using temperature-dependent EPR spectroscopy. Reduction of copper is observed in line with evolution of free radicals. Furthermore, benzoin is shown to have a wide tunability of reducing powers through its substitution derivatives. These unique features make benzoin and its derivatives useful in metal nanostructure synthesis.

ASSOCIATED CONTENT

Supporting information

Experimental details, additional TEM images, EPR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.
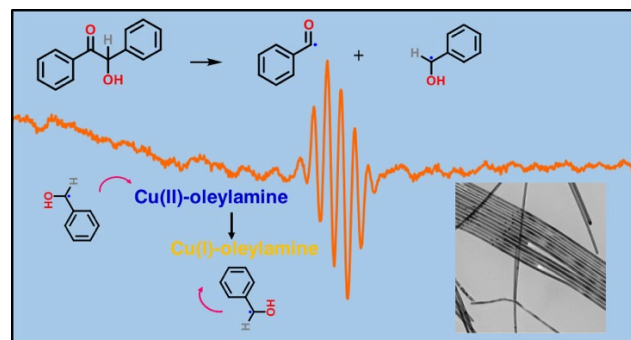
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