

Hydrazine free synthesis of Cu nanostructures: Exploring vitamin-C as environmental benign reducing agent to synthesize Cu nanowires

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Among the other syntheses procedures, Cu nanowires synthesized using hydrazine as reducing agent and ethylene diamine (EDA) as shape directing agent are well established for the fabrication of transparent conducting electrodes and for the large scale production. In this article, we explore the synthesis Cu nanowires by above method without using hydrazine, a highly toxic chemical reagent. Our investigation shows that vitamin-C (L-ascorbic acid) can be used as efficient alternative to hydrazine to produce Cu nanowires. Varying the EDA/Cu molar ratio resulted Cu nanowires and micron size flower like dendritic structures of copper.

Keywords: Cu nanowires, EDA, hydrazine, ascorbic acid, vitamin-C, green procedure.

Introduction

Transparent conducting electrodes (TCEs) are important components in the optoelectronic applications¹. Indium doped tin oxide (ITO) is the widely used material for TCE applications. The scarcity of the indium element, brittle nature of the ITO limit the usage of ITO for low cost, flexible optoelectronic applications². In this scenario, coinage metal nanowires are explored as alternatives to ITO by other research groups^{3,4}. However, using the elements like Au and Ag, cost reduction in the fabrication of TCE cannot be achieved. Moreover, their sources are also scarce like indium. Hence Cu nanowires would be the ideal material as low cost alternative to ITO for TCE applications^{5,6}. As compared to Ag, abundance of Cu is 1000 times more, 100 times low cost and only with 6% less conductivity⁷. In addition to the above mentioned electronic applications, Cu and Cu based materials are known to have well established applications in the area of electrochemical biosensors^{8,9}. Although Cu nanowire synthesis involves several protocols, the promising chemical methods to produce Cu nanowire can be summarized as (i) synthesis of Cu nanowires using hydrazine as reducing agent in the presence of ethylene diamine (EDA), (ii) long chain alkyl amine mediated synthesis of Cu nanowires using glucose as reducing agent¹⁰⁻¹². Nevertheless, the aspect ratio

of Cu nanowires produced in EDA method is lower than alkyl amine mediated synthesis, other advantages like low reaction temperature (60–80°C), less reaction time (30–60 min) and the dispensability of Cu nanowires are associate with EDA based method bring this method as first choice to synthesize Cu nanowires in large scale and to fabricate the Cu nanowires based TCEs on various substrates. Here it is important to mention that hydrazine is highly toxic compound and it is also a susceptible carcinogen. Hence it is necessary to develop a green, hydrazine free protocol to synthesize Cu nanowires. At the same time, the above advantages should be retained. In this regard, we explore L-ascorbic acid popularly known as vitamin-C as environmental benign alternative reducing agent to hydrazine for the synthesis of Cu nanowires. Fernández-Merino *et al.* used ascorbic acid as alternative to hydrazine to disperse graphene¹³. Wu and co-workers synthesized monodisperse Cu nanoparticles in which ascorbic acid used as reducing and capping agent¹⁴. In this paper, we synthesized Cu nanowires using ascorbic acid as reducing agent in the presence of EDA. We believe, this method has potentiality to replace hydrazine from the conventional procedure to synthesize Cu nanowires and to extend the synthesis in large scale. Moreover, it can further be explored to fabricate the TCE on various substrates.

Experimental

Materials: $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, ethylene diamine (EDA), L-ascorbic acid (AA), NaOH were obtained from SRL Chemicals, India. Isopropyl alcohol (IPA), hexane were obtained from Loba Chemicals. All the chemical obtained were with AR grade. They were used as received without any further purification. Millipore water was used to carry out the synthesis of nanostructures.

Methods: In a glass reactor of 60 mL capacity, 20 mL of 15 molar NaOH solution was taken. To this solution 1.5 mL of 0.1 molar $\text{Cu}(\text{NO}_3)_2$ solution, different amounts of EDA were added. The contents were gently swirled after the addition of each reagent. Then, known amount of L-ascorbic acid (AA/Cu molar ratio 1:1) was added to the above contents and glass reactor heated to 70°C for one hour without any mechanical agitation. After the desire reaction time, one can observe the floating of reddish brown compound on the air-water interface or the formation of reddish brown solution, depending on the amount of EDA added. This confirms the formation of Cu nanostructures. Cu nanostructures formed at the air water interface were carefully separated purified and subjected to further characterization.

Characterization: Obtained nanostructures were washed with water and IPA by centrifuging the solution at 4000 rpm. Settled precipitate was re-dispersed and the procedure was repeated for 2–3 times. Final product was dispersed in Millipore water. UV-Vis spectrum of the nanostructures was recorded on Jasco V-760 UV-Visible spectrophotometer. Water dispersed nanostructures were drop casted on glass slides and dried at ambient conditions. These glass slides on which Cu nanostructures coated as thin films were characterized with Rigaku X-ray diffractometer using $\text{Cu K}\alpha$ radiation with wavelength 1.54 \AA . FT-IR spectra of the sample was recorded on Thermo SCIENTIFIC-Nicolet iS10. Water dispersed samples were drop casted on Si wafer, dried at ambient conditions. Morphology of the nanostructures coated on these Si wafers was recorded using scanning electron microscope Carl Zeiss EVO18.

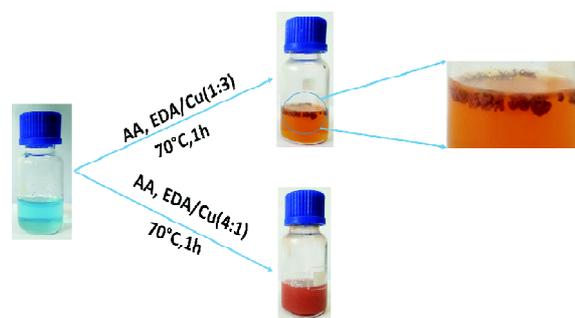
Results and discussion

As we mentioned in the introduction, although synthesis of Cu nanowires using EDA and hydrazine has several advantages, toxicity of hydrazine¹⁵ limit the scope of this process to extend towards large scale synthesis of Cu nanowires. In this regard, our search for alternative reducing agent to

hydrazine gave fruitful results with ascorbic acid. Table 1 compares the toxicity of hydrazine and ascorbic acids from materials safety data^{15,16}. It clearly show the terrible toxicity of hydrazine and environmentally benign nature of ascorbic acid. After one hour of the reaction time, depending on the amount of EDA used, we observed two kinds of solutions. In one sample (EDA/Cu molar ratio 1:3) reddish brown compound was observed at air-water interface (Scheme 1, encircled photograph). Similar observations were noted by Zeng and coworkers in the synthesis of Cu nanowires¹⁷. This hints the sample settled at air-water interface could be nanowires. In another sample (EDA/Cu molar ratio 4:1), the complete solution was reddish brown in colour (Scheme 1), suggesting the formations of Cu nanostructures.

Table 1. Comparison of toxicity of commonly used reducing agent hydrazine for the synthesis of Cu nanowires and ascorbic acid used in this work

Reducing agent used for the Cu nanowire synthesis	Toxicity of the compound from MSDS
Hydrazine	 GHS05, GHS06, GHS08, GHS09
Ascorbic acid	Not a hazardous substance



Scheme 1. Synthesis of Cu nanowires using ascorbic acid. Encircled photograph shows the Cu nanowires formed at air-water interface.

XRD results of these samples show the formation of the peaks at 43, 51 and at 74 corresponds to (111), (200) and (220) of Cu with JCPDS 04-0836. As the amount of EDA increased (EDA/Cu – 4:1), we also observed additional peaks of Cu_2O at 42 (200), 52 (211), 61 (220) and CuO at 38 (111) other than FCC Cu (Fig. 1). This can be attributed to the

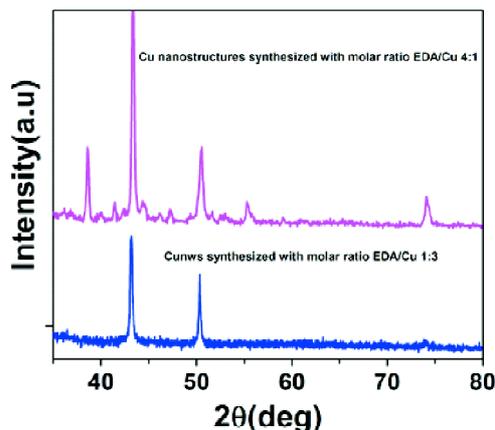


Fig. 1. XRD patterns of Cu nanostructures synthesized at different EDA/Cu molar ratios.

possibility of oxidation of the synthesized Cu sample, as the purified samples are dispersed in water and XRD samples are prepared by coating and drying of the water dispersed samples on glass slides. Formation of surface plasmon resonance (SPR) peak at 640 nm observed in UV-Visible spectrum of the EDA/Cu–1:3 sample (Fig. 2) also indicates the formation of Cu nanostructures¹⁸. Hence, these observations show that ascorbic acid can successfully reduce the Cu^{2+} to Cu^0 . This reduction process could happen through the formation of semidehydro ascorbic acid and followed by dehydroascorbic acid. Redox couple of these products is sufficient to reduce Cu^{2+} to Cu^0 as reported by Wu and co-workers¹⁴.

Morphology of the nanostructures is revealed by scanning electron micrographs shows the formation of Cu nanowires when the molar ratio of EDA/Cu is 1:3 (Fig. 3). These nanowires are observed with particle aggregation at the one end of the nanowire, similar to the nanowires syn-

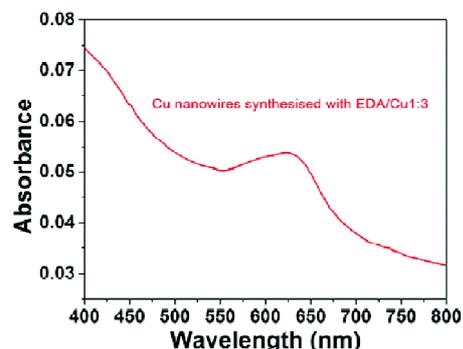


Fig 2. UV-Vis spectrum of Cu nanowires.

thesized using EDA and hydrazine^{5,19}. Role of EDA as shape directing agent is inevitable, it also plays an important role in the formation of particle aggregates at the one end of the wire.

Interestingly, alkylamine mediated synthesis of Cu nanowires does not yield such kind of wires that are described above²⁰. Earlier studies on the growth mechanism of the Cu nanowire formation by EDA based synthesis show that the nanowires grow from spherical seeds that are formed in the initial stages of the reaction⁵. As the concentration of EDA increased further (EDA/Cu – molar ratio 4:1) we observed Cu nanostructures and micron size flower like dendritic structures (Fig. 4). In this process, EDA not only acts as shape directing agent, its role as complexing agent with Cu^{2+} ions cannot be unidentified. Moreover, it is a stronger ligand than OH^- , which forms a necessary precursor complex $[\text{Cu}(\text{OH})_4]^{2-}$ with Cu^{2+} to produce Cu nanowires. In the presence of higher concentrations of EDA, there could be formation of the complexes such as

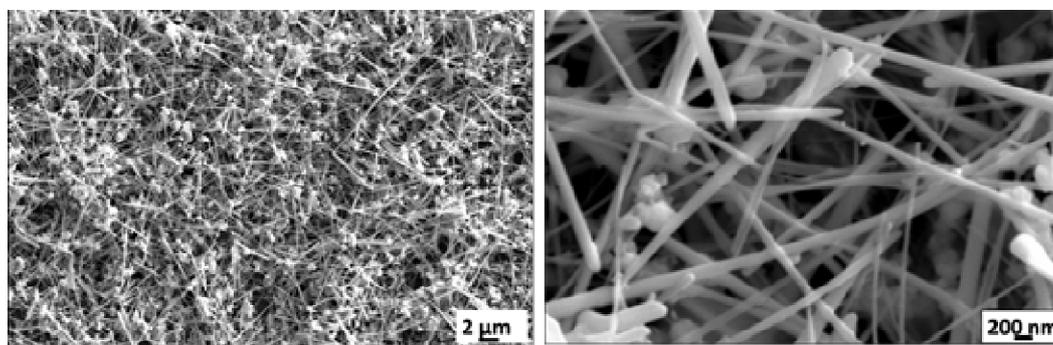
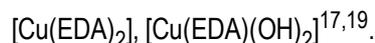


Fig. 3. SEM images of Cu nanowires.

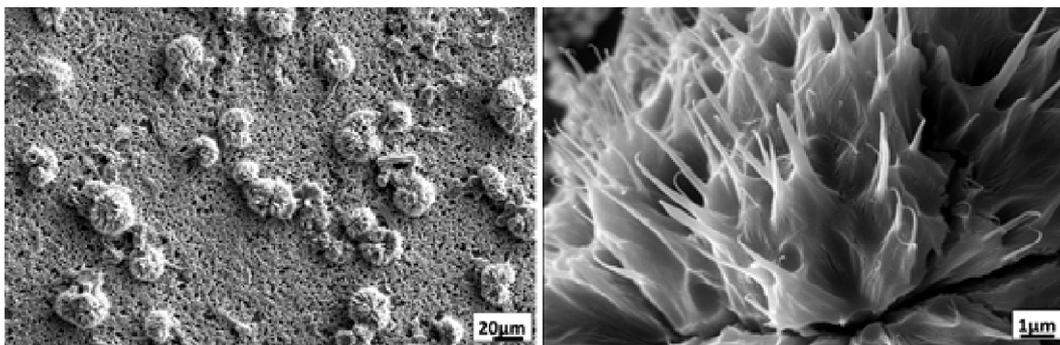


Fig. 4. SEM images of Cu nanostructures (shows dendritic morphology at higher concentration of EDA).

Hence, decreases the concentration of available Cu^{2+} ions to form the necessary precursor complex $[\text{Cu}(\text{OH})_4]^{2-}$. It also important to note the concentration of free EDA that required to promote the growth of Cu^{2+} , also decreases due to complex formation with Cu^{2+} ions. Insufficient amounts of EDA and $[\text{Cu}(\text{OH})_4]^{2-}$ cannot produce long nanowires and hence micron size dendritic structures with petals resembling needle/wire like morphology are evolved from a core particle. In addition to this, in EDA based method, the possibility of evolution of more than one nanowire from single seed particle¹⁹ also supports our observation (Fig. 4).

Wiley and coworker extensively worked on the growth mechanism of Cu nanowires and recently proposed that EDA promotes the reduction of $[\text{Cu}(\text{OH})_2]^-$ on Cu (111) rather than (100) is the reason for the nanowire evolution from the seed particle²¹. However, EDA role as capping agent to the facets of Cu cannot be completely ignored²².

To probe this further, we characterized the synthesized

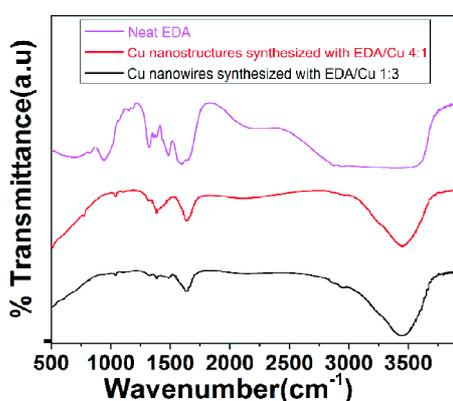


Fig. 5. FT-IR spectra of neat EDA, Cu nanostructures synthesized at different EDA/Cu molar ratios.

nanostructures using FT-IR. Peaks at 3362.44 cm^{-1} and 1597.85 cm^{-1} in pure EDA corresponds to N-H stretching, N-H bending and at 1484.61 cm^{-1} and 1361.99 cm^{-1} corresponds to CH_2 group characteristic absorption and C-N stretching modes respectively²³. The synthesized Cu nanostructures also contain the peaks at the 3442.13 cm^{-1} and 1633.15 cm^{-1} confirms that EDA is capped on the surface of Cu nanostructures.

Conclusions

In conclusion, we developed hydrazine free methodology to synthesize Cu nanowires using EDA. Ascorbic acid acts as efficient reducing agent to replace the hydrazine in the Cu nanowire synthesis. Increase in EDA concentration diminishes the formation of the nanowires structure as it likely to acts as complexing agent with Cu^{2+} . In addition to this, the role of EDA as capping agent was also confirmed.

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