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Synthesis and Characterization of Copper Nanoparticles by Bis-(Acetylacetonato)-Copper (II) Using Nonionic Surfactants and the Effect of Their Structures on Nanoparticles Size and Yield

Hamidreza Kamrani

Department of Chemistry, Nanotechnology Laboratory, University of Isfahan, Isfahan, Iran
Email: Hr.kamrani@gmail.com

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Abstract

Between all precursors of copper complex, bis-(acetylacetonato)-copper (II) and bis-oxalate copper (II) with very close structures are two of the best representatives for copper nanoparticles synthesis. In this research, only bis-(acetylacetonato)-copper (II) in presence of some effective non-ionic surfactants such as Triton X-100, Dodecylamine, Tween 80 and also triphenylphosphine as a reducing agent via thermal decomposition process was used for copper nanopaticles synthesis. Two shif-base E19 and E22 complexes were also used for the investigation of these kinds of shif-base complexes capabilities by this method as precursors and all results were compared with each other. Between all surfactants, Triton X-100 gave the best yield with the largest grains. The techniques used for characterization of copper nanoparticles were TEM, EDX, FT-IR and XRD. TG-DTA and CV were used for characterization of bis-(acetylacetonato)-copper (II) complex.

Keywords

Bis-Acetylacetonato-Copper (II), Thermal Decomposition, Nonionic Surfactants, Copper Nanoparticles, Shif-Base Complexes

1. Introduction

What caused the appearance of nanotechnology was the impact of high ratio area of materials to their volume that stimulated many researches to open new doors to the science world. In nano scale, some properties especially physical

properties are breached in comparison of their bulk features. Nanotechnology is divided to three main parts in dried, humid and countable that are usable in some sciences, such as electrical, medical, agriculture and food industry. Totally, there are different methods for synthesis of nanoparticles [1]-[30]. Four main ways are gas phase, humid, mechanical, and *in situ*. Between all nanoparticles, copper nanoparticles, because of their various precursors and especially because of very different applications, such as electrical, catalytical and optical, are so important [31] [32]. There are different methods for copper nanoparticles fabrication [33]-[41]. But mechanical methods are the methods that are more common for copper nanoparticles fabrication and thermal decomposition is the most economical and easy way [42] [43] [44]. Bis-(acetylacetonato)-copper (II) was selected as a precursor, because its behavior is very same to bis-oxalate copper (II) which has been applied before and is decomposed at enough low temperature (about 200˚C) to prevent very probable precipitation of the produced metallic particles, and its decomposition gives water and carbon compounds, which does not lead to real human health problems [33] [42]. It was investigated the effect of surfactants structural role in the yield and grain size of nanoparticles too. The role of surfactant here is making of micelle structure that can help for copper nanoparticles dispersion. In other words, they can be considered in dual roles, as a capping agent and also extractants. Different surfactants have the same behavior but with different effects on nanoparticles yield and size [45]. The control of temperature during surfactant and triphenylphosphine addition in dispersion process is very important.

2. Experimental

2.1. Chemicals

All surfactants consist of Triton X-100, Tween 80, Propane Diol and also Ethylene Glychol, Triphenyl Phosphine, Aqueous Amonia, Acethyl acetonato, Nitrate Tri hydrate and choloroform were purchased from Merck company. Bis-acethyl acetonato copper (II) was synthesized in the laboratory.

2.2. APPARATUS

2.2.1 XRD

The crystalline phase of colloids was studied by X-ray diffraction (XRD) technique with a bruker D8 advance X-Ray diffractometer (http://www.bruker-axs.com/). Main obvious peaks are in 36.5 and 61.5 degree for CuO and 43.5, 50.5 and 74 degree for metallic copper nanoparticles. F.c.c lattice copper nanoparticle cell was detected by this technique. The crystallite size D of the sample was estimated using the Scherer's equation, $(0.9\lambda)/(\cos\beta)$, by measuring the line broadening of main intensity peak, where λ is the wavelength of Cu Kα radiation, β is the full width at half-maximum, and θ is the Brag's angle. An estimation of particle size by usage of Scherrer's equation revealed the crystallite size of about 21, 18 and 12 nm using Triton X-100 (t-octyl-(OCH2CH2)xOH, x = 9, 10), Tween-80, and

dodecyl amine as surfactants respectively that is shin own in Figure 1.

2.2.2. TEM

The microstructure, particle size and morphologies were investigated by a Leo 912 AB transmission electron microscopy (TEM). Micrograph shows the uniform dispersion of synthesized nanoparticles. The result of copper nanoparticles production by Triton X100 and bis-(acetylacetonato)-copper (II) with TEM micrograph shows about 20 nm grain size (Figure 2).

2.2.3. FT-IR

Fourier transform infrared spectroscopy (FT-IR), JASCO.JAPAN 6300 (400 - 4000 cm^{-1}) was used for determination of copper nanoparticles and their purity. Two obvious peaks are 3427 cm^{-1} for stretching frequency of O-H bond of Triton X-100 and 697 cm^{-1} for Cu-O vibration frequency. All both peaks show that there are some non reacted Triton X-100 on the surface of copper nanoparticles and some CuO as impurity. All impurities are less than 1 percent. Other obvious remaining peaks are related to metallic copper nanoparticles (Figure 3).

2.2.4. EDX

EDX spectrum by Seron-AIS 2300 Korea was run just for qualitative analysis and copper nanoarticles production confirmation. In EDAX spectrum with three surfactants Triton X-100, Tween 80 and dodecyl amine just metallic copper in all spectrums was specified. The spectrum of bis-acetyl acetonato copper (II) and Triton X-100 as an example is shown in Figure 4. This spectrum can be used just for qualitative determination.

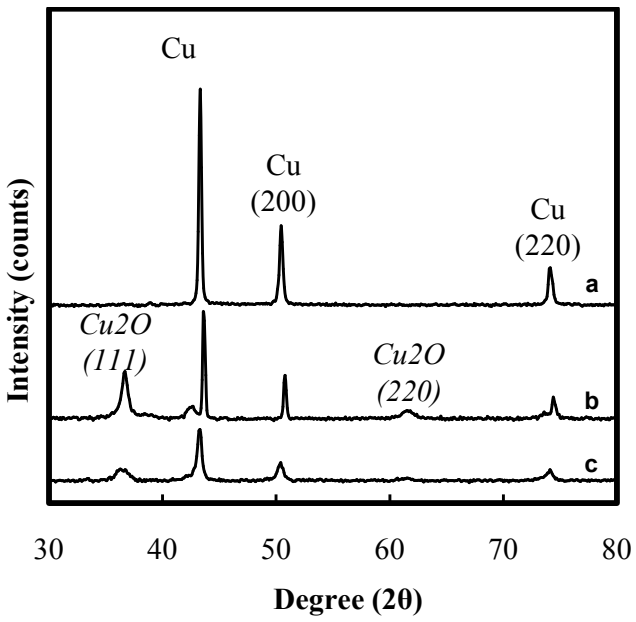

Figure 1. XRD pattern of the copper nanoparticles synthesized using bis-acetylacetonato copper (II) as precursor and (a) Tween 80, (b) Triton X100 and (c) dodecylamine as capping agenta (a) Triton X-100 (b) Tween 80 (c) Dodecyl Amine.

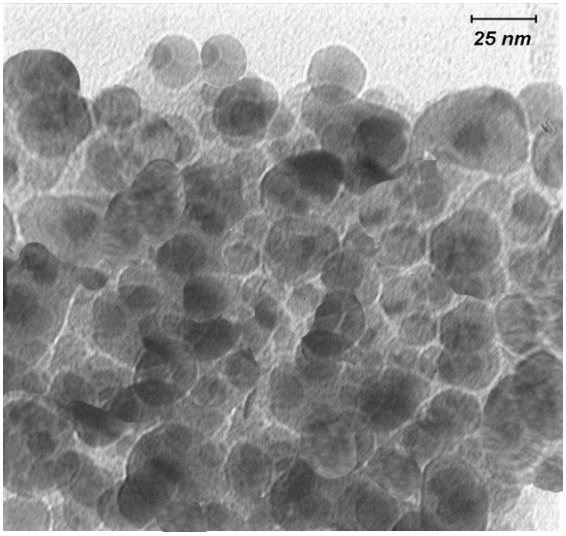

Figure 2. TEM image of the copper nanoparticles synthesized using bis-acetylacetonato-copper (II) as precursor and Triton X-100 as capping agent.

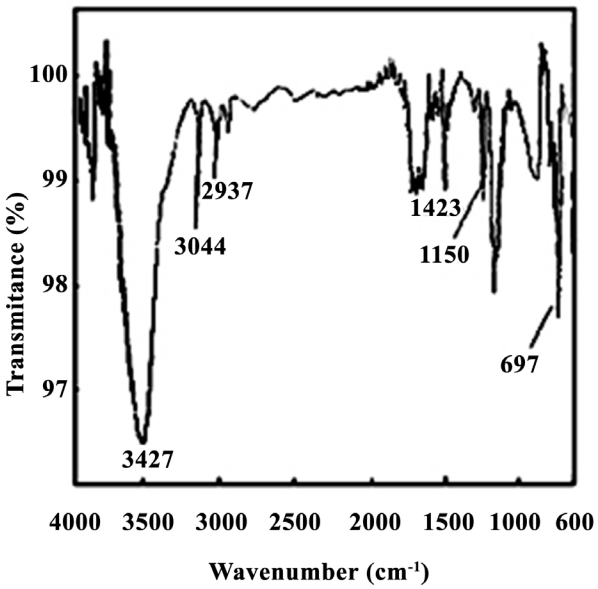

Figure 3. FT-IR spectroscope for copper nanoparticles synthesized by Triton X-100 and bis-acetylacetonato copper (II).

2.3. The Techniques used for Characterization of Bis-Acetylacetonato-Copper (II)

2.3.1. CV

Cyclic voltammograms (CV) were recorded by using a SAMA Research Analyzer M-500 for copper complex Precursor. The cyclic voltammograms of $Cu(acac)_2$ exhibits an electrochemically irreversible reduction process at ca −0.445 V and 0.072 with unequal ratio of anodic to cathodic peak currents (ipa/ipc) and peak potential difference of 0.517 V·s which is due to the process $[Cu(II)(acac)_2]$ to $[Cu(I)(acac)_2]^-$ that is shown in Figure 5.

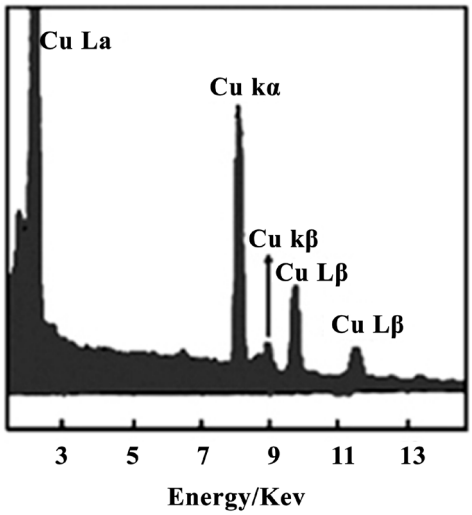

Figure 4. EDAX of copper nanoparticles prepared by Triton X-100 and bis-acacetonato-copper (II).

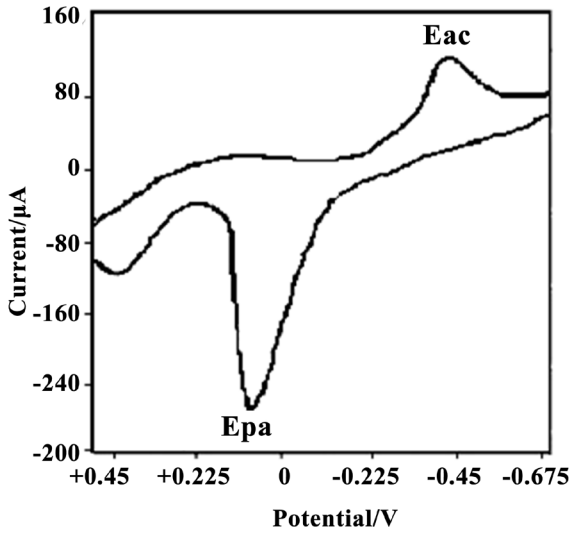

Figure 5. Cyclic voltammogram of bis-(acetylacetonato)-copper (II) as precursor, c = 3 × 10^{-3} mol·L^{-1}, in DMF (25 mL) containing 0.1 mol·L^{-1} TBAP as supporting electrolyte at 298 K. Scan rate, 0.1 V·s^{-1}.

2.3.2. (TG-DTA)

Thermal gravimetric differential thermal analysis (TG-DTA) measurement was carried using a Mettler TA4000 system (http://ir.mt.com). By this technique the points of thermal decomposition of bis-(acetylacetonato)-copper (II) can be determined. Thermal lost weight was 67%. Corresponding to the TG result, one weight loss step in the DTA curve at 320˚C is assigned to the decomposition of acetylacetonate (**Figure 6**).

2.4. Synthesis of Bis-(Acetylacetonato)-Copper (II)

10 gr of Copper Nitrate Tri hydrate was dissolved in 100 ml distillated water. To

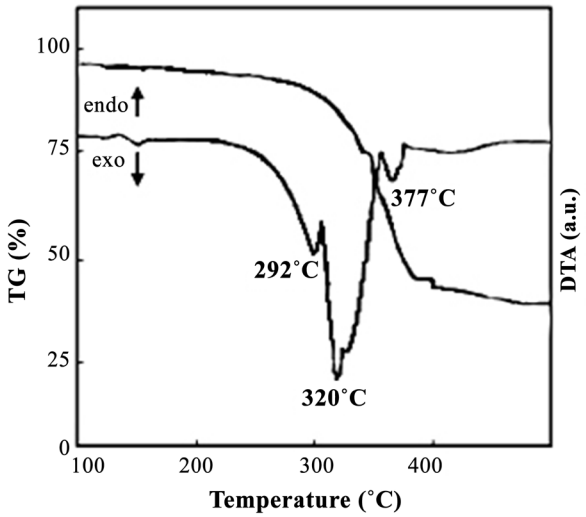

Figure 6. TG-DTA curve for bis-(acetylacetoneto)-copper (II) as precursor.

result $Cu(NH_4)^{2+}$, 15 ml aqueous ammonia was added to form blue precipitate. Then 11 ml acetyl acetonate was mixed with blue precipitate in drop wise stirring manner. The product is non pure Cu(acac)2 that is washed with choloroform to be purred.

2.5. Synthesis of Copper Nanoparticles by Bis-Acetylacetonate Copper (II) and Different Surfactants

Bis-(acetylacetonato)-copper (II) was added to dodecyl amine as surfactant to create a homogenous solution, then refluxed for 1 h at 140˚C. Then triphenyl phosphine (a reducing agent) was heated and stirred. The supernatant was removed, and the nanoparticle sediment was washed, dried (73% yield). The same procedure was used by Tween-80 (72% yield) and Triton X-100 (99% yield) as non-ionic surfactants. Also this was done with propandiol (92% yield) and ethylene glycol (89% yield) as two alcohols.

3. Result and Discussion

From four used surfactants propandiol, Ethylene Glychol, Triton X-100 and Tween 80, the best yield is for Triton X-100. In Triton X-100 structure there is an active polar part and a long non polar tail that helps it to react with acetyl acetonato copper (II) strongly. Tween 80 also has same behavior that produces a good micelle with the $Cu(acac)_2$ too. Another good surfactant is Dodecyle amin that can produces a micelle structure and helps dispersion of colloidal structure of acetonato copper (II). For Propane diol and Ethylene glychol also this issue can be repeatable. The yields of these two alcholols are considerable. So they can be the best alcohols for the thermal decomposition method (Table 1).

But two E19 and E22 shif-base complexes did not give good results with non of mentioned surfactants (Figure 7 & Figure 8).

As it was implied before, the behavior of Bis-oxalato copper (II) and Bis-acetyle

Table 1. The effect of nonionic surfactants on size and yields on copper nanoparticle using bis-(acetylacetonato)-copper (II) as precursor.

Grain Size in 43.3˚ (nm)	Yeild (%)	Surfactant	Precursor
12.030	73.3	Dodecyl Amine (pure)	Copper acetyl acetonate
18.68	72	Tween 80 (pure)	Copper acetyl acetonate
21.320	99	Triton X-100	Copper Acethyl acetonate
24.019	92.5	Propan Diol	Copper Acethyl acetonate
24.019	89	Etylene glychole	Copper Acethyl acetonate

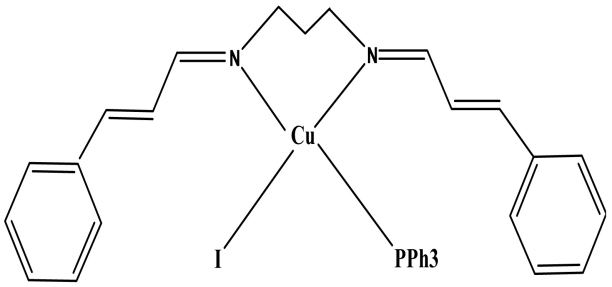

Figure 7. E22 complex.

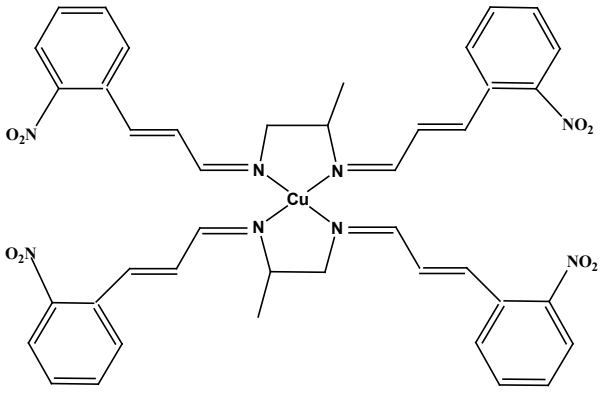

Figure 8. E19 complex.

acetonato copper (II) are very close to each other because of their close structure (Figure 9 & Figure 10).

Figure 11 shows a plot of the average particle size versus the surfactants. This finding is significant, demonstrating the important role of surfactant in control of particle size. These observations may hint at this implication that the mechanistic origin of the particles size depends on capping agent structure and activity of surfactants. These results are achieved by XRD pattern and Scherrer's equation.

4. Conclusion

In copper nanoparticle production, triphenylphosphine is the only agent for

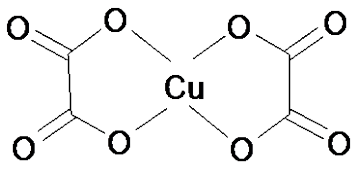

Figure 9. Bis-acetyleacetonato-copper (II).

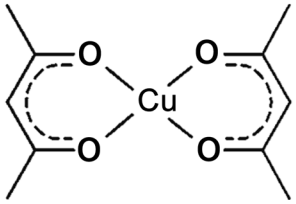

Figure 10. Bis-oxalato-copper (II).

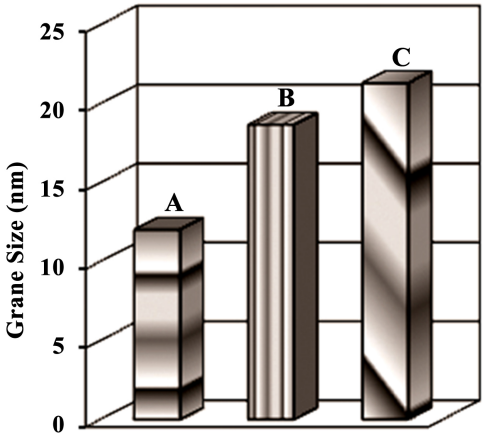

Figure 11. The plot of copper nanoparticle grain sizes synthesized using bis-acetylacetonato-copper (II) as precursor, A = Dodecyl Amine, B = Tween 80 and C = Triton X-100 as capping agents.

reduction of copper (II) cation to metallic copper nano particles. Two main factors in morphology, yield and grain size of produced copper nanoparticles are accurate suitable non ionic surfactants and copper precursors selection via thermal decomposition method. The basis of mechanism in this process is micelle structure formation and nonionic surfactants have a good ability for this purpose. The smallest copper nanoparticles are synthesized by Dodecylamine and the largest by Triton-X100.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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