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# SYNTHESIS AND CHARACTERIZATION OF COPPER NANOPARTICLE - CHITOSAN

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SUMMARY

*Copper nanoparticles were synthesized in the presence of chitosan via reduction of $Cu(NO_3)_2$ with sodium borohydride with the ratio of 4 ml 2.0 mg/ml chitosan : 2ml $Cu(NO_3)_2$10 mM : 1 ml $NaBH_4$ 0.1 M in aqueous solution. Chitosan molecules absorbing on the surface of prepared copper nanoparticles formed the corresponding copper nanoparticle-chitosan. The resulting copper nanoparticles were characterized by transmission electron microscopy (TEM) and UV-visible (UV-VIS) spectroscopy. It was found that an absorbance band at 805 nm was observed in UV-VIS spectra and the copper nanoparticles were found to be spherical with a narrow size distribution, the average diameter was about 3 nm.*

## I - INTRODUCTION

Many people already consider nanotechnology as the key technology of the 21$^{st}$ century. In some consumer products, nano-sized particles are used because of their physical and chemical properties. Recently, much work has been done on metal nanoparticles as potentially useful materials showing novel electronic, optical, magnetic properties, especially as improving the quality of catalyst [1, 2]. To stabilize the dispersion of nanoparticles, it is necessary to use protective agents, such as polymers, surfactants and chelating agents [1]. Some functional groups such as cyano (-CN), mercapto (-SH), and amino ($-NH_2$) groups are known to have high affinity for copper. Protective polymers having such functional groups are expected to produce small copper nanoparticles with a quite narrow size distribution [1, 3, 4].

Chitosan is a transformed polysaccharide obtained by deacetylation of natural polymer, which is one of the most important natural polymers constituting of the sells of crustaceans and the cell war of many fungi. Due to the interaction between the amino groups ($-NH_2$) in chitosan and metal nanoparticles, chitosan was chosen as a protecting agent in synthesis of metal nanoparticles [1, 3 - 5].

In this study we report on the synthesis and characterization of copper nanoparticle-chitosan materials by chemical reduction of $Cu^{2+}$ ions into zero valent nanoparticles in the presence of chitosan.

## II - EXPERIMENTAL

### 1. Materials and methods

β-chitin was extracted from squid pen and β-chitosan was prepared by deacetylation of chitin in alkali solution as reported previously. The degree of acetylating (DA) found by IR was about 10%, molecular weight was 3500.000 Da [5];

Sodium borohydride was purchased form Riedel- de Haen, Germany. Acetic acid (China) was diluted to a 1% aqueous solution before use;

The metal salts chosen $Cu(NO_3)_2$ were analytical reagent grade, China. All aqueous solutions were made with bi-distilled water.

## 2. Preparation

A solution of 2 mg/ml chitosan in 1% acetic acid solution was prepared first. The mixture was kept overnight then filtrated through 0.22 μm mili-pore syringe filters to remove any impurity.

In general, metal nanoparticles were obtained by chemical reduction of metal salt to yield the corresponding zero valent metal nanoparticles. To ensure the entire reduction, the concentration of $NaBH_4$ was about 10 times that of metal salt.

In our report, an aqueous solution of 2 ml $Cu(NO_3)_2$ 10 mM was added to 4 ml chitosan 2 mg/ml under magnetic stirring at room temperature in haft an hour, then a freshly prepared aqueous solution of 1 ml $NaBH_4$ 0.1 M was added drop wise, stirring for another 120 minutes until entire reduction of copper salts. The resulted products were kept at room temperature for characterization.

## 3. Characterization

*a) UV-VIS spectroscopy*

The optical properties of copper nanoparticle-chitosan were characterized by UV-VIS spectroscopy, CINTRA 40 GBC, Shimadzu Co., Japan.

*b) Transmission electron microscopy (TEM)*

The morphology of copper nanoparticles in the prepared product was carried out with a JEOL-JEM 1010 transmission electron microscopy (TEM), operating at 100 kV. Samples for inspection of TEM were prepared by slow evaporation of one drop of a dilute aqueous solution of the copper nanoparticles-chitosan product on a carbon coated copper mesh grid.

# III - RESULTS AND DISCUSSION

## 1. UV-visible analysis

Many researchers pointed out that, amine groups in chitosan chain are strongly reactive with metal ions, though hydroxyl groups (especially in the C-3 position) may contribute to adsorption. In deed, nitrogen atoms hold free electron doublets that can react with metal cations. Amine groups are thus responsible for the uptake of metal cations by a chelation mechanism [4]. Domard pointed out that, chitosan form a unique complex with copper, whose structure is close to $[CuNH_2(OH)_2]$. Considering the co-ordination sphere of copper, the forth site can be occupied by either a water molecule or the –OH group in C3 position. Monteiro and Airoldi confirmed this hypothesis by calorimetric measurements. Copper bonds to three oxygen atoms and one nitrogen atom with square-planar of tetrahedral geometry [4].

Figure 1 show the UV spectra of $Cu(NO)_2$ aqueous solutions in the presence of chitosan after addition of sodium borohydride. The spectra exhibit an adsorption band at 805.6 nm, suggesting the formation of copper nanoparticles [1, 6, 7]. When the concentration of chitosan is increased, the intensity of the adsorption band decreases. This is indicated that the size of copper nanoparticles formed is altered with the concentration of chitosan, which operates as a controller of nucleation as well as stabilizer. This result is consistent with that reported by Kunio Esumi et al, who investigated the antioxidant-potentially of gold-chitosan nanocomposite and Haizhen Huang et al who investigated the preparation and characterization of metal-chitosan nanocomposite. And they have given a detail explanation for the change of particle size of gold particle with various concentration of chitosan. Similarly, the number of nucleation, the interaction between chitosan and $Cu^{++}$ and the protective action of chitosan may be responsible for the particle size change of copper particles prepared in the presence of different of concentration of chitosan [1, 6 - 8].

## 2. TEM measurement

Fig. 2 shows the TEM image of copper nanoparticles. The image revealed mono-disperse copper nanoparticles, which were homogeneously distributed in the prepared product. The particle were found to be spherical with a narrow size distribution, the average particle diameter was about 3 nm.

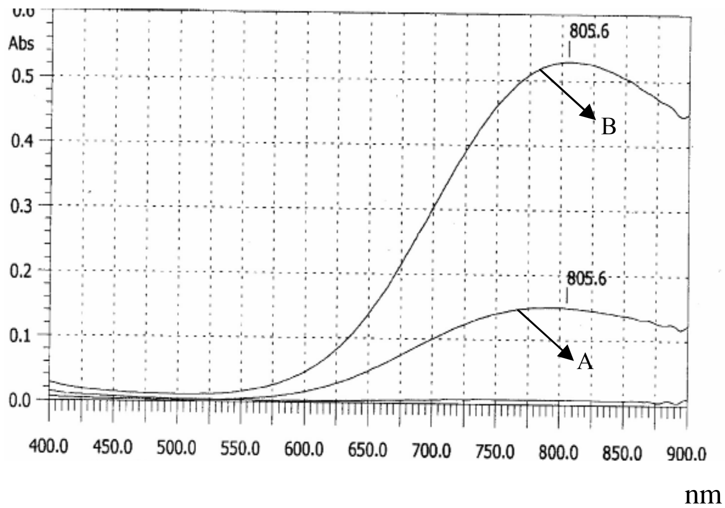


*Figure 1*: UV-VIS spectra of $Cu(NO_3)_2$ aqueous solutions in the presence of 4 ml chitosan 2 mg/ml (A) and 2 ml chitosan 2 mg/ml (B) after addition of sodium borohydride

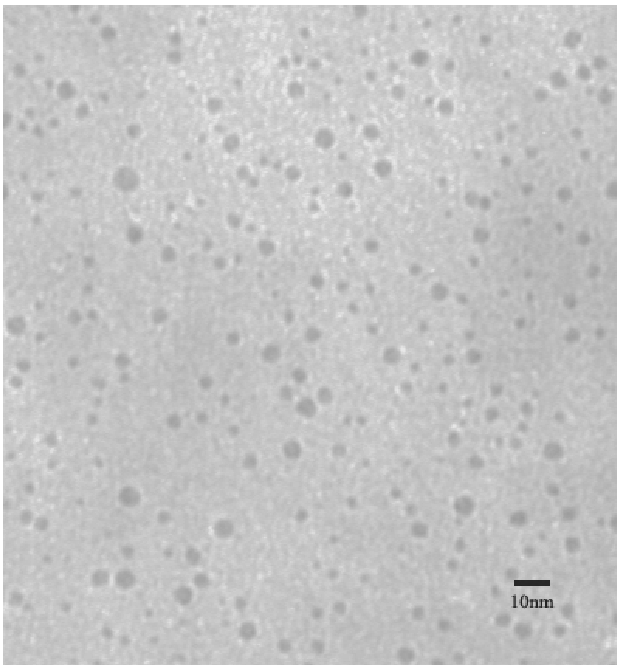


*Figure 2*: TEM image of particle size of copper nanoparticles in copper nanoparticle-chitosan product

The figure 3 showed the histogram of copper nanoparticle size distribution based on the diameter measurement of 100 copper particles at five sizes selected at random. We can see that about 30% copper nanoparticles with diameter of 3 nm, 30% of 3.5 nm. The smallest particle size is only about 1nm and the biggest particle size is about 6 nm.

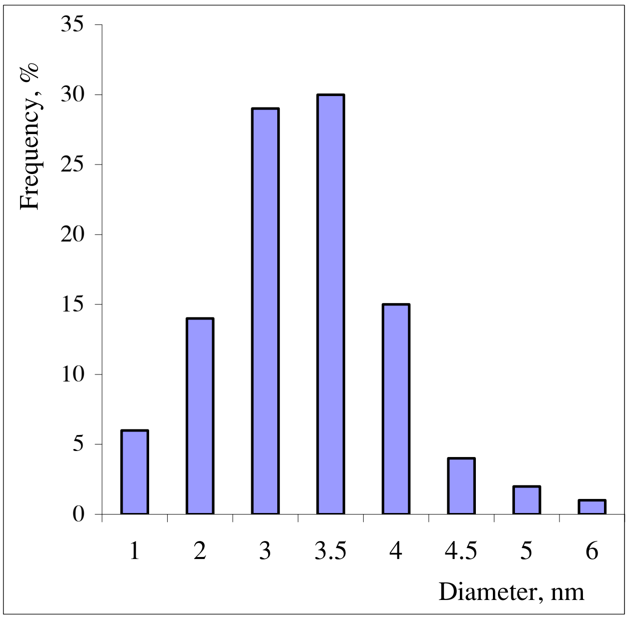


*Figure 3*: Size distribution of copper nanoparticles

## IV - CONCLUSION

Copper nanoparticle-chitosan was successfully synthesized and chitosan was found to be a very effective protective agent for the synthesis of copper nanoparticles. The UV-VIS of copper nanoparticle-chitosan showed the adsorption band at 805 nm and the average diameter of copper nanoparticles observed by TEM imagine is about 3 nm with a narrow size distribution.

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