



*Dedicated to Professor Ionel Haiduc  
on the occasion of his 80th anniversary*

## SYNTHESIS AND CHARACTERIZATION OF COPPER NANOCUBES FROM WASTE COMPLEX CATALYST

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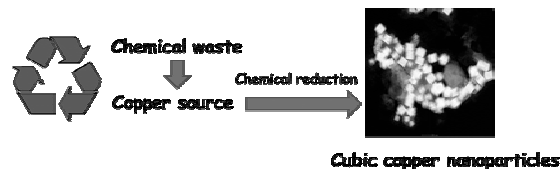
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In the frame of recycling wastes by turning it into a desired resource, herein monodispersed copper nanocubes were obtained from a waste catalyst from Monsanto processes. The nanocubes were synthesized at room temperature in aqueous media, by a chemical reduction method. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), high resolution TEM (HRTEM), energy-dispersive X-ray spectroscopic analysis (EDS) and high-angle annular dark-field scanning TEM (HAADF-STEM) techniques were used to characterize the resulting copper nanocubes. Based on the results, a layered core-shell structure with a porous internal morphology is proposed.



### INTRODUCTION

Responsible management of wastes coming from technological processes is a great priority highlighted by the internal and European legislation.<sup>1</sup> Moreover, the recovery of chemical waste is an obligation of each European Member State.<sup>2</sup> Therefore, obtaining raw materials from wastes and protection of the environment by waste recycling have become one of the greatest priorities for mankind.<sup>3</sup> The

universal strategy is to **minimize** the amount of waste, the natural resources used and to **maximize** recycling of matter and energy.<sup>2,3</sup> The recycling of waste covers two important aspects: resource efficiency and environmental impact.<sup>2,3</sup> The resource efficiency is translated into increased economic value through more productive use of resources over their life cycle; this requires the use of those resources in a sustainable way within the planet's long-term boundaries.<sup>4</sup> This includes

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minimizing impacts of one resource's use on other resources, including the environment. Under EU rules, the recycling method involves replacement of primary resources by turning waste into a desired resource.<sup>2,3,5</sup> One of the economical fields with the greatest potential identified is chemical industry, namely the valorization of wastes from technological processes.

On this background, the used bimetallic complex catalyst CuAlCl<sub>4</sub>\*toluene waste of COSORB processes that consists mainly of aluminum and copper salts dissolved into organic components - mostly toluene, can be considered as an important source of the recovery of aluminum, copper and toluene.<sup>6</sup> During its lifetime, within the chemical industrial process, the complex catalyst suffers several complexation/decomplexion cycles. In time, catalyst poisoning occurs by accumulation of alkylation and polymerization by-products or sulphides. Due to the high metal content the used catalyst has a great pollution effect<sup>7</sup> and cannot be eliminated in waste ponds. Moreover, it is economically and environmentally desirable that the metals and toluene to be recovered in the form of products useful for technical purposes.

On the other hand, copper nanoparticles (CuNPs) have attracted much attention in the last years due to their high electrical conductivities and excellent catalytic properties, being a cheap alternative for gold and silver.<sup>8,9</sup> In general, the control of the shape and size of nanoparticles is one of the most important issues for tailoring their

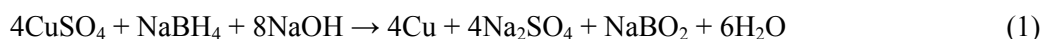
properties enabling them to be used in catalysis, surface-enhanced Raman scattering, or as biosensors, photo-thermal therapy agents, etc.<sup>10</sup>

Regarding the synthesis of CuNPs, several methods have been developed, the most simple, versatile and low cost for industrial production being the chemical reduction in solution.<sup>11</sup> By changing the reaction conditions, reduction or capping agents, spherical shape nanoparticles<sup>12-15</sup> or nanowires<sup>16</sup> in the nanometer or micrometer<sup>17</sup> range were obtained. Moreover, well dispersed cubic CuNPs with an edge length of 100 ± 25 nm were obtained at high temperatures in ethylene glycol in dry conditions, using ascorbic acid as reducing agent and PVP as capping agent.<sup>18</sup>

In the present study, we report the synthesis and characterization of well-defined copper nanocubes in aqueous solution, at room temperature. The synthesis was carried out using a complex copper source isolated during the recovery process of a waste catalyst coming from Monsanto processes.

## RESULTS AND DISCUSSION

The copper fine particles synthesized in this study have been prepared from a copper source recovered from a waste catalyst from Monsanto processes. PVP was chosen as stabilizing agent who may also act as shape controller,<sup>19</sup> whereas NaBH<sub>4</sub> was used as reducing agent according to eq. (1):



Moreover, ascorbic acid was added to prevent the oxidation of copper during the synthesis process and in storage.<sup>20</sup> In reality, we cannot exclude also a contribution of the ascorbic acid in the reduction process of the Cu<sup>2+</sup> ions.<sup>14</sup> The synthesis was undertaken in aqueous media, taking into account also the influence of the temperature on the formation of regular structures with high monodispersity. In this aim, the syntheses were performed at r.t. (Cu\_1) and at 55°C (Cu\_2).

The morphology of the copper particles was determined using a scanning electron microscope (SEM). As showed in Figure 1a for Cu\_1, at r.t. nanoparticles of cubic shapes were obtained. The increase of temperature seems to be unfavorable for the formation of regular structures, as showed in Figure 1b for Cu\_2, for which smaller structures with an irregular shape are also observed. It is important to underline that to the best of our

knowledge, cubic copper nanoparticles were obtained only in ethylene glycol solution.<sup>18</sup>

Since a better uniformity in terms of size and shape of the nanoparticles was obtained at r.t., furthermore a new synthesis was carried out (Cu\_3), with the optimization of the purification procedure (4 times repeated sonication and centrifugation in ethanol). The nanoparticles structure and morphology were analyzed by X-ray diffraction and electron microscopy techniques.

The X-Ray diffraction pattern of the copper nanoparticles (Figure 2), reveals that metallic copper nanoparticles crystallized in cubic system was obtained. Moreover, additional peaks observed in the diffractogram are associated with Na<sub>2</sub>SO<sub>4</sub> large crystallites (the associated peaks are narrow). The crystallites may be formed in the preparatory process of the sample from some salt existent on the surface of the nanoparticles.

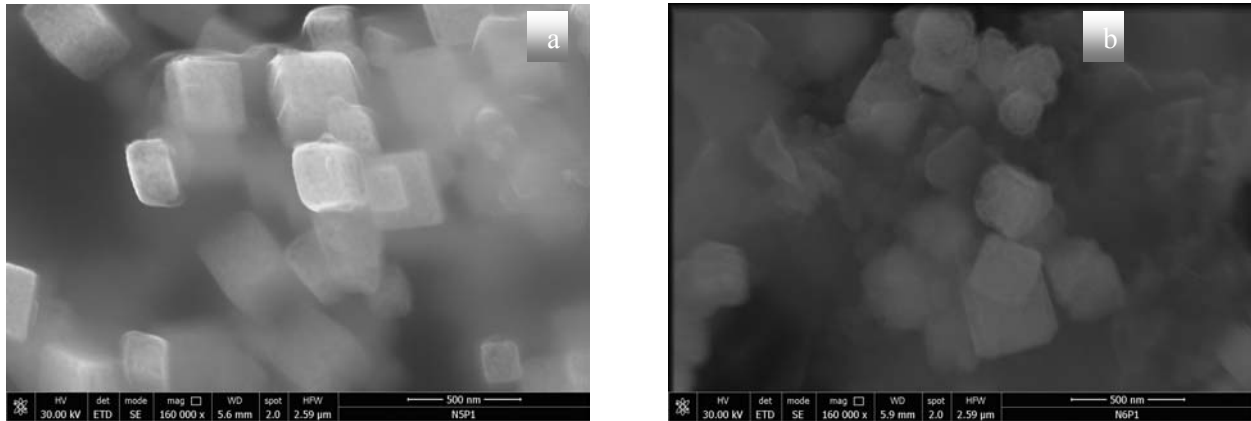


Fig. 1 – SEM images (scale bare = 500 nm) of a) Cu\_1 and b) Cu\_2.

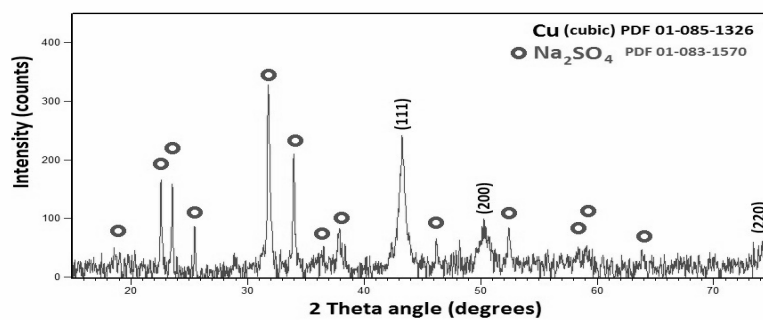


Fig. 2 – XRD spectrum of copper nanocubes (Cu\_3).

The grain size of the crystallites was determined using the Scherrer equation (2):

$$D = k \cdot \lambda / (\beta \cdot \cos \theta) \quad (2)$$

where:  $k$  is the shape factor which was considered 0.94 for cubic morphology nanoparticles;  $\lambda$  is the X-ray wavelength;  $\beta$  is broadening at half the maximum intensity and  $\theta$  is Bragg angle.

The size of the copper crystallites obtained using equation (2) is 14.5 nm, more than one order of magnitude lower than observed in TEM images (Figure 3a). This suggests that the cubic

nanoparticles are polycrystalline structures, as observed in Figure 3b for the same sample at higher magnification.

Large cubes with edge lengths of several hundred nm may be observed from the micrographs shown in Figure 3a, b. The interplanar distance measured for 10 crystalline planes is 2.05 nm (Figure 4), which corresponds to an interatomic distance of 2.050 Å, close to the 2.087 Å value determined from the XRD spectrum for the crystallographic plane (111) as PDF 01-085-1326 (Figure 2).

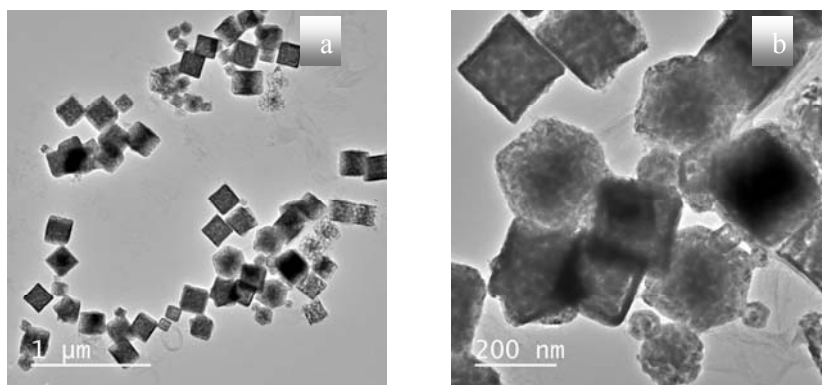


Fig. 3 – TEM micrographs of Cu\_3 with different magnifications.

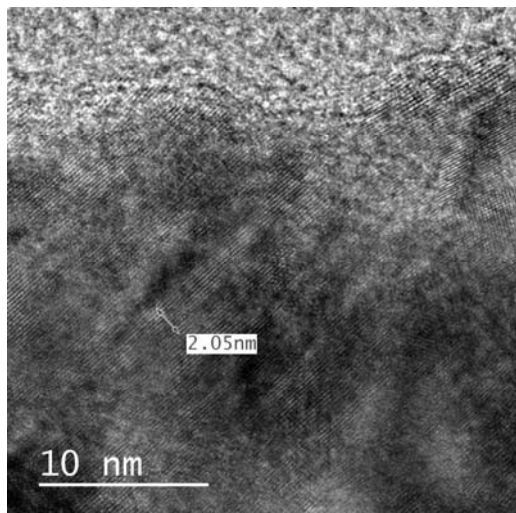
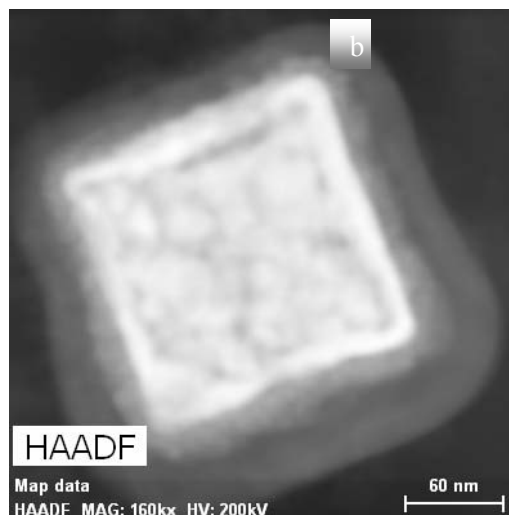
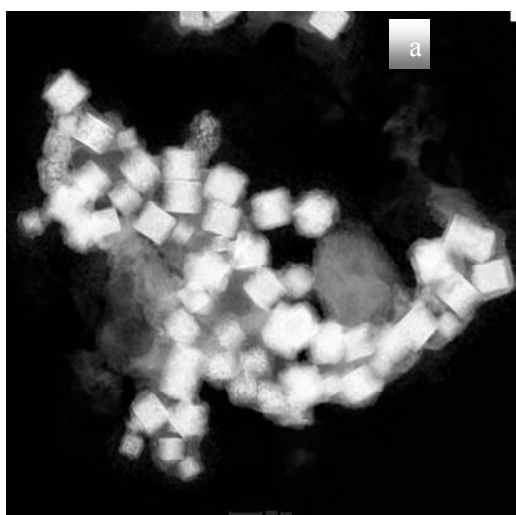
Fig. 4 – HR-TEM image of Cu<sub>3</sub>.

Fig. 5 – STEM images of copper nanocubes at a) low (scale bare = 200 nm) and b) high magnification (scale bare = 60 nm).

A closer view of the cubic structures, from STEM at higher magnification (Figure 5b), show a very interesting core-shell structure formed by several layers. Looking from the outside to the inside of the nananocube (Figure 5b) two layers can be detected, the first one less uniform with a thickness of about 20 nm and the second one of about 10 nm; then a compact mass of metallic copper with a thickness of about 10 nm is clearly distinguished, whereas the central part of the cube seems to have a spongy structure.

The EDS mapping analysis (Figure 6) revealed that the core of each square nanostructure contains mainly copper, whereas sulphur and nitrogen are concentrated at the edges of the square, indicating that the surfactant is located most likely on the surface of the nanostructure. Probably the first layer rich in oxygen and poor in copper and nitrogen is formed from citrate ions adsorbed on

the second layer formed by PVP and traces of Na<sub>2</sub>SO<sub>4</sub>. As mentioned before, the PVP is chemisorbed on the {111} surfaces of the copper nanocubes. The presence of the adsorbed PVP hinders the crystallization of the basic copper sulphate which, together with PVP forms the second layer. This is supported by the fact that the second layer has a high concentration of nitrogen and sulfur and medium of copper and oxygen (Figure 6-b,c,d and e). The third layer is formed by a copper sheet representing the sides of the cube. In this layer the concentration of the oxygen is extremely low (Figure 6e), indicating that this copper layer is not oxidized. The HR-TEM images (Figure 4) showing an interplanar distance of 2.05 Å in the third layer support this supposition. The interior of the cube is formed by highly oxidized copper nanoparticles (Figure 6-b and e).

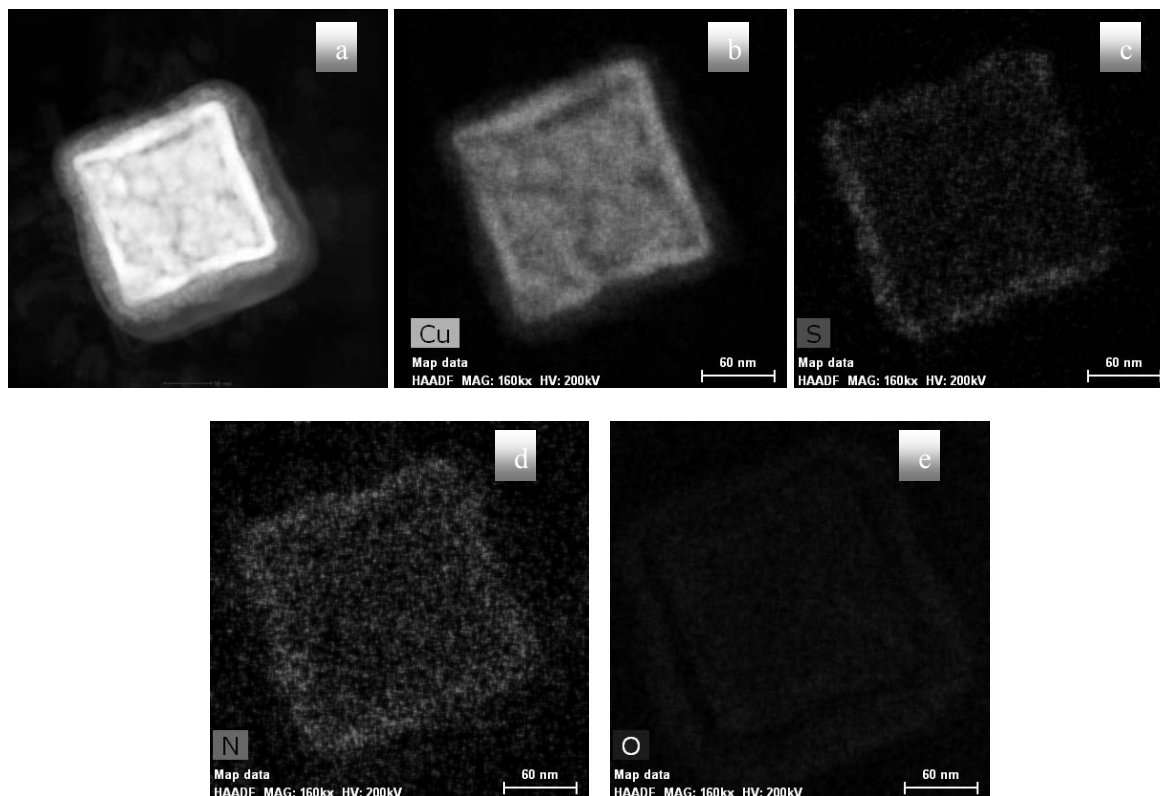


Fig. 6 – EDS mapping of Cu<sub>3</sub> porous copper nanocubes.

The aspect of the interior of copper nanostructures may also suggest a porous structure similar to those observed by Ham et al.<sup>21</sup> in the synthesis of gold nanocubes using as templates less noble metal nanocubes. This is supported also by the shape of nanocubes, respectively by the curved edges. Indeed, during the preparation process of the samples for TEM analysis, where high vacuum is required, the solvent from the holes evaporated, and the nanocube edges curves go inside due to the solvent surface tension that causes extremely high forces at nanometer scale.

## EXPERIMENTAL

### Material and methods

Sodium hydroxide pellets, sulphuric acid 98% used for the isolation of the complex copper source and sodium borohydride 98% were acquired from Merck and used as received. Polyvinylpyrrolidone (PVP) average mol wt. 40000 and ascorbic acid reagent grade were acquired from SigmaAldrich.

SEM images were obtained on a FEI Quanta FEG 250 microscope equipped with an EDX spectrometer EDAX Apollo X at 30 kV accelerating voltage, in high vacuum regime, using ETD secondary electron detector.

The concentration of the metallic ions from the inorganic phase was determined by Atomic absorption spectroscopy (AAS) for simultaneous or sequential analysis of the elements, High-Resolution Continuum Source Atomic Absorption Spectrometer

ContrAA 700, on mineralized samples with HNO<sub>3</sub>/HCl (1/3 volume ratio) according to the international standards.

Transmission electron microscopy (TEM), high resolution TEM (HRTEM), energy-dispersive X-ray spectroscopic analysis (EDS) and high-angle annular dark-field scanning TEM (HAADF-STEM) techniques were obtained with a Titan G2 80-200 transmission electron microscope operating at 200 kV for samples prepared on a carbon-coated copper grid with 200 mesh from toluene/ethanol = 80/20 (v/v) as solvent. Powder X-ray diffraction patterns were collected with an X'Pert Pro MPD – PAN Analytical Instrument, using copper X-ray source with a nickel filter.

### Isolation of copper source

The copper source was isolated from the inorganic phase obtained by a separation procedure of the waste catalyst.<sup>6</sup> The chemical composition of this waste catalyst and the detailed description of the isolation method of the copper source are patented.<sup>22</sup> In particular, the inorganic phase (50 mL) was neutralized with a saturated solution of NaOH and was stirred at 80°C for 30 min to ensure that all the copper source is transformed into CuO.<sup>23</sup> The brown-black precipitate was filtered off, washed with water and characterized by EDAX and AAS. Mass percentage determined by EDAX: Na 23.51%, Al 1.28%, Cl 1.31%, Cu 21.77% and by AAS: Cu 25.2%, Na 21.62%, Al 1.58%.

The CuO was solubilized as sulphate salt with the minimum quantity of concentrated sulphuric acid.

### Synthesis of copper nanocubes

In a three neck flask were added 25 mL of CuSO<sub>4</sub> 0.01 M water solution and 25 mL PVP solution 0.01 M water solution

(1:1 CuSO<sub>4</sub>:PVP molar ratio) at r.t (Cu\_1) and at 55°C (Cu\_2). The mixture is kept under vigorous stirring for 10 minutes and then NaOH solution (3M) is added until pH = 12 when the color of the reaction mixture turned blue. After another 10 minutes of stirring, 10 mL of ascorbic acid solution (0.02 M) was added under argon atmosphere, at r.t. (respectively at 55°C) and the orange-yellow reaction mixture is kept under stirring for 1 hour. The reduction was accomplished by adding 10 mL of aqueous NaBH<sub>4</sub> solution (0.04 g in 10 mL water) under argon atmosphere. The black reaction mixture is left under stirring for another hour and then the copper fine particles are purified by centrifugation and sonication in ethanol (3x).

## CONCLUSIONS

The synthesis of copper nanocubes was performed using a copper source isolated during the recovery process of a waste catalyst from Monsanto processes. The copper nanocubes were obtained by chemical reduction procedure, at room temperature and in aqueous media, using PVP as stabilizing agent, sodium borohydride as reduction agent and citric acid as antioxidant. The presence of high concentration of sulfate ions in the raw material (waste catalyst) does not hinder the synthesis of the copper nanocubes but likely plays an important role in their formation.

The copper nanocubes has a layered core-shell structure, with the PVP adsorbed on the {111} nanocubes surfaces preventing the access of the oxygen by forming a compact and amorphous layer of basic copper sulphate impregnated in the polymer. The inside of the nanocubes seems to be porous because of the concave shape of the edges.

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