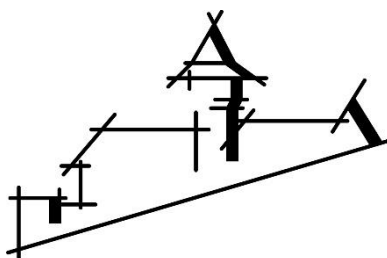


PROGRESSIVE TRENDS IN COORDINATION, BIOINORGANIC, AND APPLIED INORGANIC CHEMISTRY



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Preparation of Cu-Sn bimetallic nanoparticles *via* ball milling – the effect of various additives on the structure

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Bimetallic nanoparticles (BNP) are composed of two metals in elemental state and possess unique electric, optical, catalytic and photocatalytic properties. BNPs display novel properties due to a synergy between the two constituting metals.

Among others, mechanical milling is one of the most popular techniques in the fabrication of such bimetallic powders. In the present work, BNPs were prepared *via* using ball milling method. Upon preparation, various solid (NaCl, PVP) and liquid (oleylamine, ethylene glycol, polyethyleneglycol) modifiers were added to a mixture of copper and tin powder.

The aim of the current study is to establish the effect of the quantity and quality of various additives on the structure and morphology of the products thus obtained. We found that upon addition of liquid additives, the products obtained contained the two metals separately (as physical mixture). However, the presence of solid additives resulted in the formation of alloys. The effect of the quality and amount of the various additives on the primary particle size as well as on the degree of aggregation was also studied.

INTRODUCTION

BNPs consist of two metals in their elemental state. Several examples can be found in the literature on their unique electric, optical, catalytic and photocatalytic properties [1,2]. It is also of importance that synergy may be present between the two constituting metals, and as a result of this, BNPs have the potential of displaying novel physico-chemical properties.

The structure of BNPs is primarily affected by the preparation conditions and the properties of the metals. Depending on the synthetic approach used, the distribution of each metal within a particle and their organization will vary and, for instance a random alloy, an alloy with an intermetallic compound, a cluster in cluster, a core-shell, *etc.* may be formed [3].

Mechanical milling is known to be one of the most efficient techniques in the fabrication of such bimetallic powders [4-6]. In the present work, BNPs were prepared *via* ball milling method. Upon preparation, various solid and liquid modifiers were added to a mixture of copper and tin powder. The milling parameters (milling time, milling frequency, ball to powder weight ratio, temperature) were held constant, and the effect of the quantity and quality of various additives was investigated. To characterize the samples, powder X-ray diffractometry (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and dynamic light scattering (DLS) were employed.

EXPERIMENTAL PART

Reagents and solutions

In the experiments, copper powder (99% purity, Sigma-Aldrich), tin powder (99,5% purity, Alfa Aesar), oleylamine (OAm, C18 content 80-90%, Acros Organics), ethylene glycol (EG, 99,8% VWR), polyethylene glycol 400 (PEG, Merck), sodium chloride (VWR), polyvinylpyrrolidone (PVP, M.W. 40.000, Alfa Aesar) were employed. All chemicals were used without further purification. Absolute alcohol ($\geq 99.8\%$) was received from Panreac Company. In this work, deionized water was used throughout.

Apparatus and equipment

For the grinding of the copper and tin powders (employed in a molar ratio of 1:1) a mixer mill (Retsch MM 400) having two stainless steel with 50 cm³ grinding jars and two stainless steel grinding balls (volume: ~ 8.2 cm³, diameter: 25 mm) was applied. The mill was operated using constant ball/sample weight ratio (100) and 120 min milling time. The grinding frequency was 12 Hz. Grinding was performed without excluding air. During the treatment, the mass of the mixture of copper and tin powder was 0.6 g in the grinding jar.

Two types of additives were applied. The first series of grindings were carried out *via* adding various liquids to the system, namely oleylamine, ethylene glycol or polyethylene glycol. The added amount varied between 50 and 500 μ L. During the second series, solid compounds, namely NaCl or polyvinylpyrrolidone (PVP-40000) were employed. Their amounts were varied between 0.5-5.0 m/m%. Following the milling, the products were washed with water and absolute alcohol, and stored in closed glass tubes under N₂ atmosphere.

Powder X-ray diffractograms were recorded on a Rigaku Miniflex II instrument in the $2\Theta = 5-85^\circ$ range. $4^\circ/\text{min}$ scan speed was used and CuK α ($\lambda = 1.5418 \text{ \AA}$) radiation was employed. The characteristic reflections of the materials thus prepared were identified *via* using the JCPDS (Joint Committee of Powder Diffraction Standards) database.

A Hitachi S-4700 scanning electron microscope (SEM) was used to characterize the morphology of the samples. Images were obtained at various magnifications and at 10 kV acceleration voltage. To get better contrast, the surface of the samples was coated with thin gold layer. The elemental analysis was performed by energy dispersive X-ray analysis (EDX). The Röntec QX2 spectrometer (equipped with Be window) was coupled to the microscope.

To describe the size distribution of the samples, a Malvern NanoZS dynamic light scattering (DLS) instrument was applied with 4 mW helium-neon laser light source ($\lambda = 633 \text{ nm}$) at room temperature. Detection was made in back scattering mode at 173° . The samples were ultrasonically dispersed in ethylene glycol over 1 h. The concentration of the samples was uniformly 0.2 g/L.

RESULTS AND DISCUSSION

In Fig. 1, the X-ray diffractogram of the physical mixture (1:1 molar ratio, obtained without milling) of Cu and Sn is shown and compared with that of the pure phases. It can be seen that when a physical mixture is formed, the reflections of the constituting metals appear separately.

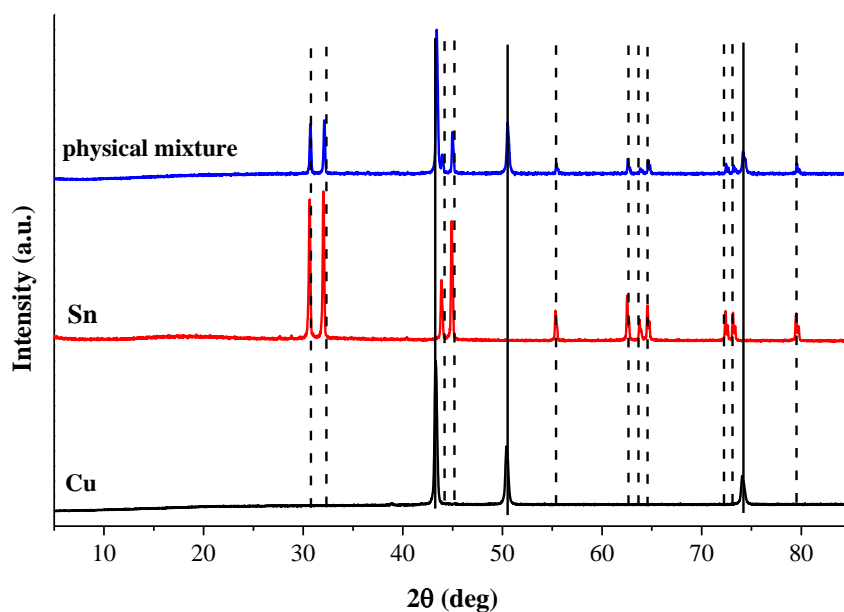
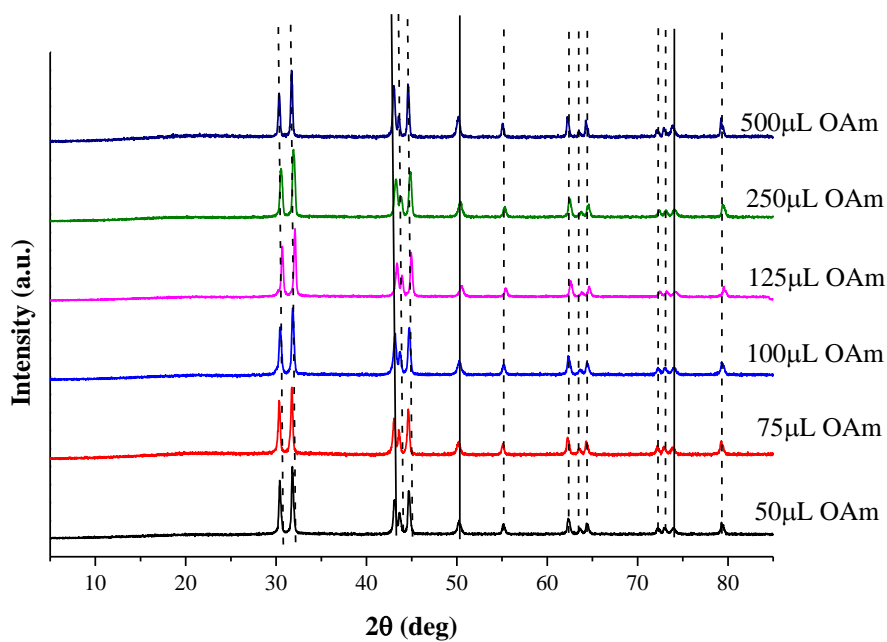
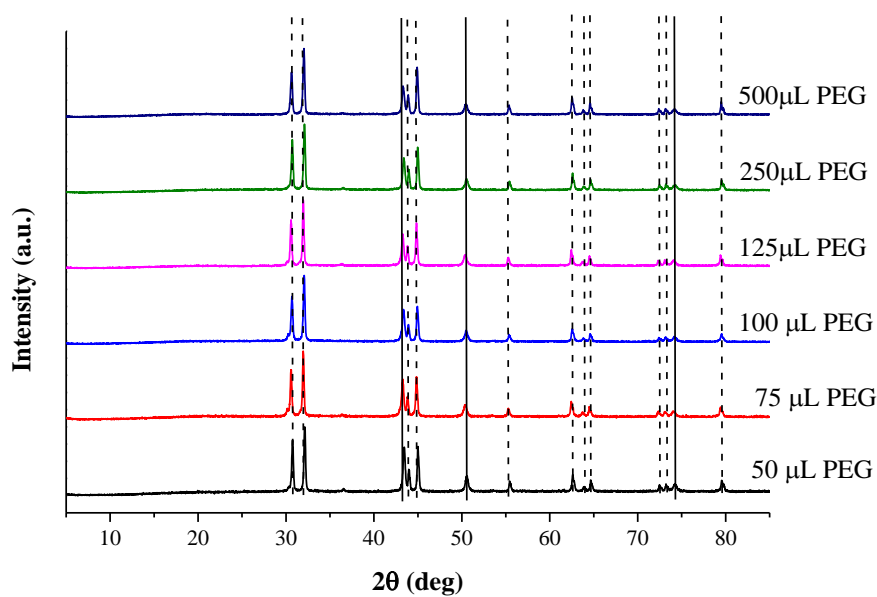


Figure 1. Powder XRD of pure Sn and Cu powders and their physical mixture at 1:1 molar ratio, obtained without milling.

In Fig. 2, the X-ray diffractograms of the bimetallic nanoparticles obtained in the presence of various additives are seen (the amount of the additive used is also shown in the figure). It can be established that the solid and the liquid additives exert different effect on the structure of the nanoparticles formed. Liquid additives always result in the formation of physical mixtures, the reflections characteristic to the two metals are clearly distinguishable. (Results obtained using EG are identical to those for PEG and OAm, therefore they are not shown.) The primary particle sizes were found to be between 30-40 nm for Sn and 20-30 nm for Cu, and are independent on the additive, both in terms of quantity and quality. On the contrary, addition of any of the two solid materials to the metal powder *prior to* milling resulted in the formation of alloys, with the composition of Cu_6Sn_5 (based on the reflections obtained from the JCPDS database, No. 45-1488). Additionally, the primary particle sizes were found to decrease significantly relative to those found for liquid additives, and were determined to be in the range of 15-25 nm. At the highest amount of PVP added, the segregation of some pure metals could also be observed (marked by asterisk in Fig. 2(d).)

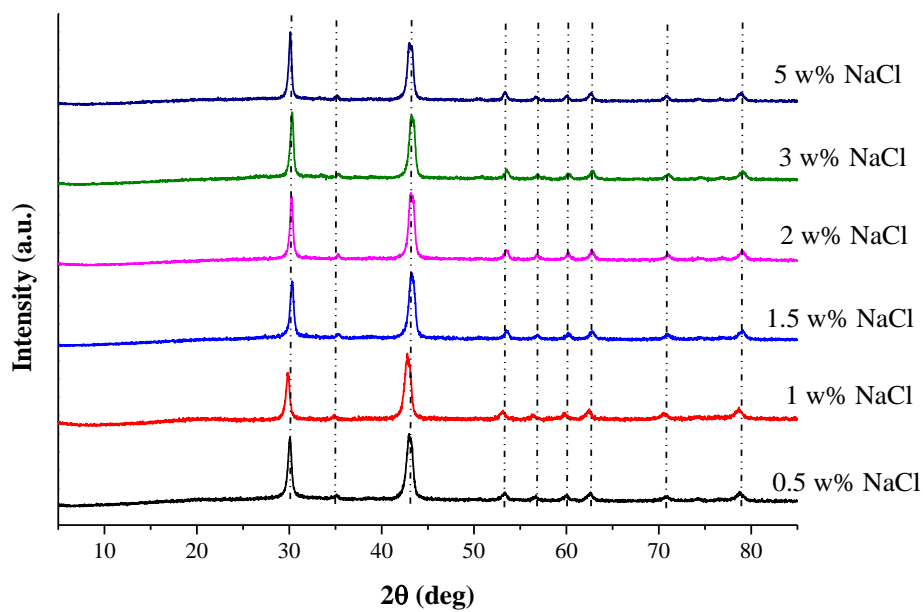


(a)

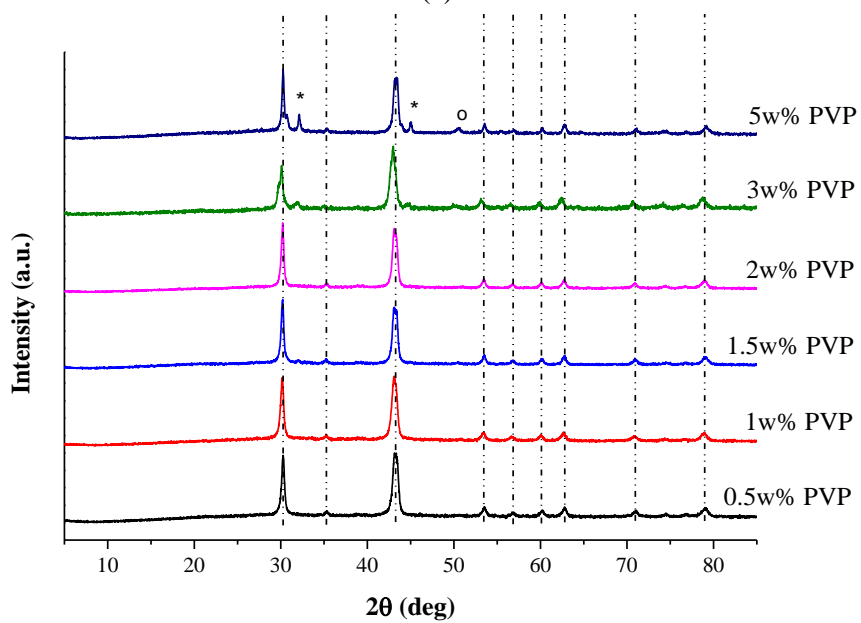


(b)

Figure 2. X-ray powder diffraction patterns of the bimetallic Cu-Sn nanoparticles obtained in the presence of various additives (the amount and type of the additive used are shown in the figure; in Figure 2(d), the reflections of pure Cu and Sn are marked with * and o, respectively).



(c)



(d)

Figure 2. (continued) X-ray powder diffraction patterns of the bimetallic Cu-Sn nanoparticles obtained in the presence of various additives (the amount and type of the additive used are shown in the figure; in Figure 2(d), the reflections of pure Cu and Sn are marked with * and o, respectively).

Table 1. DLS data for Cu-Sn samples comprising of aggregated BNP-s obtained in the presence of various amounts of liquid additives. Z-average is the average particle size, and PDI stands for polydispersity index.

Amount of additive (μL)	OAm		EG		PEG	
	Z-average (nm)	PDI	Z-average (nm)	PDI	Z-average (nm)	PDI
500	1510	0.704	611	0.305	1645	0.758
250	936	0.480	488	0.214	1411	0.610
125	576	0.313	239	0.299	551	0.515
100	767	0.354	332	0.212	492	0.504
75	549	0.368	282	0.237	365	0.247
50	438	0.344	279	0.212	260	0.237

In Tables 1 and 2, the results obtained from dynamic light scattering measurements are displayed. From the shape of the DLS curves (not shown) all the system distributions are bimodal, except for those obtained in the presence of PEG (which was found to be unimodal). When liquid additives are used (Table 1), with the decreasing amount of additive the average particle size systematically decreases, while the PDI decreases for OAm and PEG, while it was found to be practically constant for EG. For solid additives, these parameters change just in the opposite way: the particle size decreases with the increasing amount of additive, and the polydispersity index shows some fluctuations but is practically constant.

Table 2. DLS data for Cu-Sn BNP-s obtained in presence of various amounts of solid additives. Z-average is the average particle size, and PDI stands for polydispersity index.

Amount of additive (w%)	NaCl		PVP	
	Z-average (nm)	PDI	Z-average (nm)	PDI
0.5	518	0.411	468	0.488
1	478	0.458	539	0.541
1.5	246	0.336	472	0.598
2	253	0.351	363	0.440
3	244	0.347	382	0.363
5	227	0.332	271	0.334

In Fig. 3, some characteristic SEM-EDX images are displayed. Regarding the morphology of the BNPs, the specimens are severely deformed (this is supposedly the result of the mechanical treatment) and have no clear contours (the edges are rounded off). However, the distribution of the elements is different depending on the type of additive. When liquid additives are used, the elements appear in segregated way, which is in accord with the XRD findings. However, adding solid additives to the system, the constituents are dispersed at the atomic level indicating the formation of alloys.

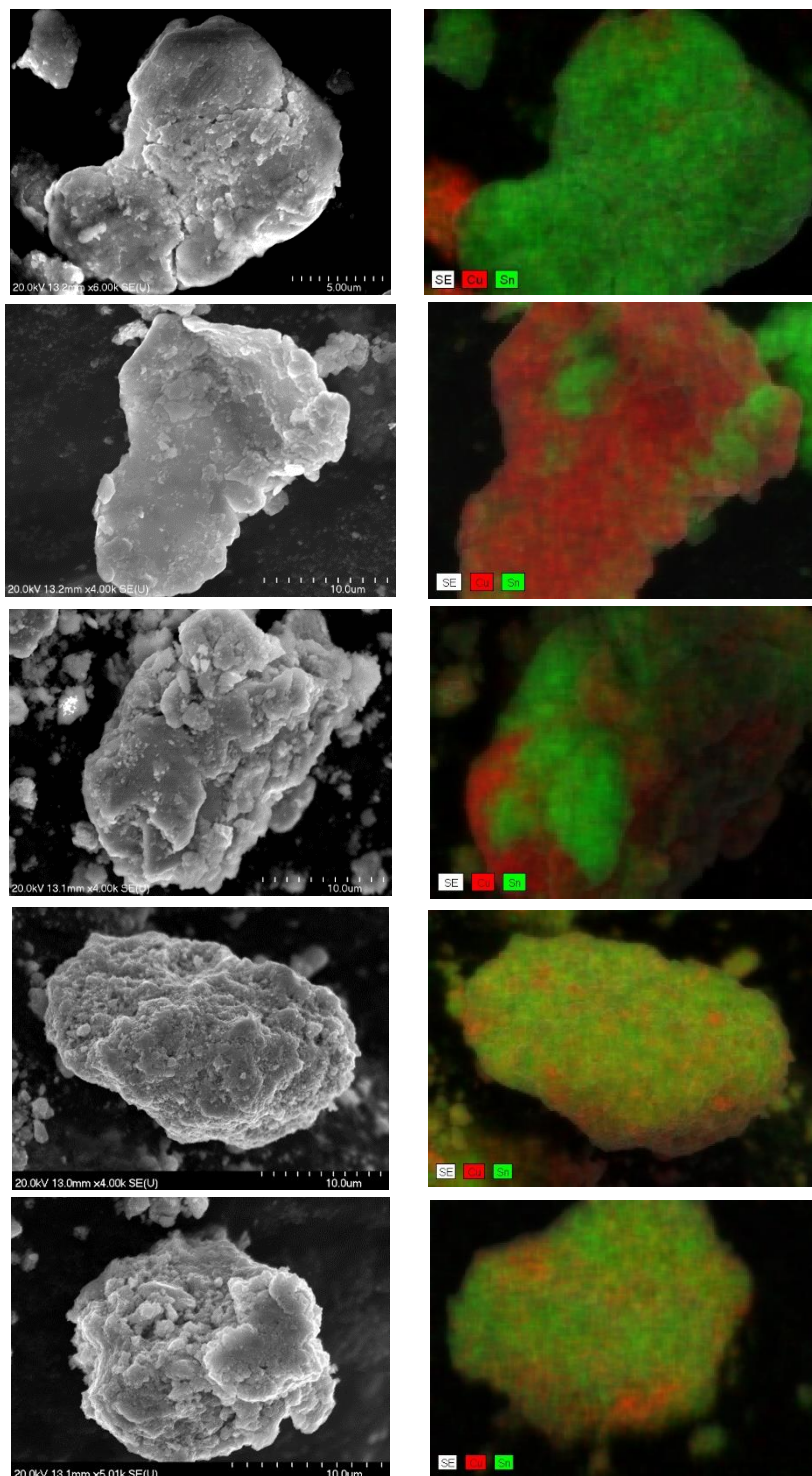


Figure 3. SEM (left) and EDX (right) images of the Cu-Sn BNPs obtained in the presence of various additives, from the top to the bottom: PEG, OAm, EG, NaCl and PVP.

CONCLUSION

In the present study, Cu-Sn BNPs were prepared *via* ball milling. The effect of various additives on the nanostructures formed was investigated. From XRD and SEM-EDX observations, we found that alloys were formed, when NaCl or PVP was added to the powder mixture *prior to* milling; however, the addition of EG, PEG and OAm yielded the formation of physical mixtures. The aggregation of the BNPs is affected by the type of the additive in different ways. Our results demonstrate that ball milling is an efficient way to develop preparation strategies for obtaining BNPs with known nanostructure.

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