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A Simple Two-Phase System Involving the Commercial Organophosphorous Extractant Cyanex® 471x for the Preparation of Silver Sulphide Nanoparticles

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ABSTRACT

The facile chemical synthesis of silver sulphide nanocrystals from metal-loaded organic media, containing a silver-selective organophosphorous ligand as extractant, is reported. The method involves the phase-transfer of silver species from aqueous nitrate media to organic solution using the commercial extractant Cyanex® 471x (tri-isobutylphosphine sulphide, Cytec Co.) as extractant, followed by precipitation stripping using ammonium sulphide as strip reagent. The nanoparticles were structurally characterized, and some aspects of the synthetical process, are briefly discussed. Under the conditions studied, the extractant Cyanex® 471x was able to act as stabilizer adsorbing on the particles surface, maintaining the size of the particles nanometrical.

Keywords: Silver Sulphide; Solvent Extraction; Precipitation Stripping; Cyanex® 471x; Tri-Isobutylphosphine Sulphide

1. Introduction

Several approaches are utilised for the colloidochemical preparation of nanoparticles, but, in all cases, the metal precursors need to be highly pure in order to obtain high quality materials. High purity metal-containing solutions can be obtained using separation techniques such as the two-phase system applied in hydrometallurgy, also known as the solvent extraction process. An interesting modification of the conventional extraction is the addition of a crystallization operation (crystallization or precipitation stripping), where low-solubility salts are formed. Yttrium oxalate powders from metal-loaded D2EHPA (di-2-ethylhexylphosphoric acid) were synthesised by Combes *et al.* [1]. By heat-treatment in air the oxalates become the corresponding oxides [2]. Preparation of cobalt ferrite from Versatic Acid solutions was reported [3]. Fu *et al*. reported the preparation of organic fluids containing Ag, Ag_2S, Bi_2S_3, CdS and ZrO_2 from organophosphorous extractants solutions [4-6].

The first report of thiol-stabilized gold nanoparticles prepared by metal extraction, the two-phase approach, appeared in 1993, and a year later a simple but very successful method for preparing larger amounts of nanocrystals appeared, involving the phase transfer of an anionic Au^{3+} complex from aqueous to organic solution using a reagent-grade anion exchanger, followed by reduction with sodium borohydride using a long chain thiol as stabilizer [7]. Similar preparation of silver was also reported [8]. Well-known solvating organophosphorous extractants, such as trioctyl phosphine and trioctyl phosphine oxide, were used for preventing particle growth and aggregation in the one-pot chemical synthesis of quantum dots [9]. CdS nanowires and Bi_2S_3 nanorods were prepared by extraction of Cd^{2+} or Bi^{3+} ions using Cyanex® 301, followed by solvothermal treatment [10]. Therefore we hoped other extractants from the Cyanex® family (Cytec Co.), and particularly Cyanex® 471x (tri-isobutylphosphine sulphide, TIBPS), could behave as phase transfer reagents, and as effective capping ligands during the synthesis of semiconductor nanoparticles by the facile two-phase approach. The effectiveness of different ligands in nanoparticles stabilisation is influenced by the difference in Lewis base character, where a firmly bound moiety stabilises growth. As Ag^+ is a soft acid, the stability of the moiety would increase with increasing ligand softness, and so was expected that the sulphur containing TIBPS could act as good capping agent during the synthesis of Ag_2S nanocrystals. Silver sulphide, an intrinsic n-type semiconductor with a band gap of 1.03 eV and

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relatively high absorption coefficient, 104 $M^{-1}\cdot cm^{-1}$ [15-17], has attracted attention owing to its potential as opto-electronic and thermoelectric material, for uses in devices such as photovoltaic cells, photoconductors, IR detectors, superionic conductors and photosensitizer for photographic purposes [11-14]. Radiation of wavelengths under 1210 nm (e.g. ambient light) may induce photoconductivity in Ag_2S, accelerating the rate of electron transfer process. Ag_2S nanocrystals were synthesized by thermal decomposition, reverse micelles, precipitation from thiolate glutathione, and L-Cysteine complexes, or using the already mentioned two-phase system [5,14,18-21].

Depending on the leaching media, different reagents are suitable for separating silver ions from aqueous solutions. Paiva *et al.* revised examples of application of trialkyl-, triarylthiophosphates and triphenylphosphine to silver extraction [22-24]. TIBPS is a well-known extractant for silver and Pd/Pt separation, extracting Ag^+ from nitrate solutions via a "solvating" mechanism by coordination through a sulphur atom, with simultaneous transfer of a nitrate to form an ion-pair [22-28]:

$$Ag^+ + 2TIBPS(org) + NO_3^- = Ag(TIBPS)_2\,NO_3(org) \quad (1)$$

$$\begin{aligned} &2Ag^+ + 3TIBPS(org) + 2NO_3^- \\ &= Ag_2(TIBPS)_3(NO_3)_2(org) \end{aligned} \quad (2)$$

where (org) represents the organic phase.

We expected the reactions involved during precipitation stripping could involve the reversal of (1) or (2) promoted by the formation of silver ammonium complexes (3), which are not well extracted by TIBPS [25]:

$$Ag^+ + iNH_3 = Ag(NH_3)_i^+ \quad (3)$$

Finally, the low solubility product appears:

$$2Ag^+ + S^{2-} = Ag_2S(s) \quad (4)$$

In this work, the chemical synthesis and the characterisation of the Ag_2S nanocrystals obtained from organic phases containing Cyanex® 471x and silver ions using a very simple method involving solvent extraction and precipitation stripping, are reported.

2. Procedures

The extractant Cyanex® 471x was kindly donated by Cytec Co. and used as received. The silver nitrate solutions used were: 0.005 and 0.01 M Ag^+ in 0.1 M HNO_3. The silver phase-transfer was carried out at room temperature (about 20˚C) in separatory funnels shaken mechanically at a fixed frequency of 90 min^{-1}. Unless otherwise stated, the metal loading was performed by shaking 0.01 L of Ag^+ aqueous solution with 0.01 L of the organic phase (0.005, 0.01 and 0.05 mol/L of Cyanex® 471x in p-xylene). In order to obtain enough material for XRD (powder X-ray diffraction) characterisation, some experiments were performed by mixing 0.5 L of silver aqueous solution with 0.5 L of the selected organic phase. After 30 minutes shaking, the two phases were allowed to separate. The metal concentration of the aqueous phase before and after extraction was determined using an Atomic Absorption Spectrometer Varian model Spectra AA 220 (AAS) with graphite furnace GTA-110 and the organic phase metal content was calculated by mass balance.

At the beginning of this work, the silver-loaded organic phases were transferred into separatory funnels, and the precipitates were obtained by adding a 0.01 L (or 0.5 L in case of materials prepared in order to perform the XDR characterisation) of a freshly prepared stripping solution (0.005, 0.01, 0.05, 0.1 mol/L ammonium sulphide). After 30 minutes shaking, both phases were allowed to separate and filtered. The obtained powders were washed with methanol and acetone and dried. Depending on the experimental conditions, some of the particles prepared do not precipitated and remained dispersed, in the organic or aqueous solutions. They were separated by centrifugation, washed and dried. Residual metal concentration in the organic phases was determined after digestion using AAS. After improving of the preparation method, the precipitation stripping was carried out in a stirred reaction vessel, both phases were stirred for 30 minutes, and after that the two phases were transferred to a separatory funnel for phase separation and particles recovery.

The X-ray diffraction pattern was obtained in a Rigaku 2200 diffractometer equipped with a nickel monochromator using Cu Kα (λ = 1.54 Å) radiation. The Rietveld analysis was performed using the program MAUD (Materials Analysis Using Diffraction), software developed to analyze diffraction spectra and obtain crystal structures, quantity and microstructure of phases along with the texture and residual stresses. It applies the RITA/RISTA method as developed by Wenk *et al.* and Ferrari and Lutterotti [29,30]. As initial model for the refinement, the structure of silver sulfide (monoclinic, space group: P21/n) was used [31]. The SEM images were obtained using a XL-30 scanning electron microscope (Philips, Netherlands). The size and morphology of selected nanocrystals were examined using a JEOL JEM 2000 FXII operating at 100 kV, and a high resolution trans- mission electron microscopy (HRTEM Tecnai, 300 kV), the crystallinity was confirmed by FFT simulation. The samples were prepared by dispersing of the powders in acetone using an ultrasound bath, and putting a drop of the dispersion over the carbon-supported copper grid and letting it dry at room temperature. Dynamic Light Scattering

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analysis (DLS) was performed in a Malvern Zetasizer Nano S. Organic adsorption on the precipitates was checked by thermal analysis (Perkin Elmer TGA), using nitrogen or argon as a purging gas, at a scanning rate of 10˚C/min. FTIR measurements were carried out using a Perkin-Elmer FT-IR coupled to a diffuse reflectance device. Since the sample was diluted, to minimize interfereences from impurities in the KBr matrix, the spectra were rationed to the background spectrum taken for a blank KBr pellet. In order to find out if the extractant was adsorbed on the surface of the materials prepared, the spectrum of one of the samples was obtained using pure Ag_2S synthesized with this purpose.

3. Results

During the experiments the extraction conditions were chosen such as they ensure the extent of silver extraction by the commercial organophosphorus reagent was in all cases quantitative. Under the stripping conditions chosen, the quantitative and efficient precipitation of Ag_2S from organic solutions could be observed. MEB images (not shown) showed the products to be nanometrical in size, but the agglomeration degree was in general high, as confirmed in experiments varying the sulphide concentration (0.1, 0.05, 0.01 to 0.005 M [S^{2-}], metal and extractant concentrations were kept constant at 0.005 mol/L), where the particles average size obtained from dynamic light scattering measurements varied from 160 nm to 301 nm (**Figure 1**).

In order to obtain information about the crystal structure of the powders, for the following experiment the extraction conditions were 0.5 L aqueous phase (0.01 M Ag^+ in HNO_3 0.1 mol/L), and 0.5 L organic phase (0.05 mol/L of Cyanex® 471x). Ammonium sulphide concentration during stripping was 0.1 mol/L and the volume

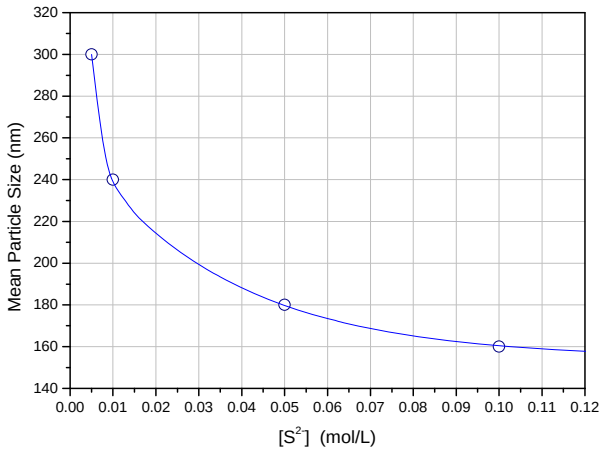

Figure 1. Average size of the Ag_2S powders as a function of sulphide ions concentration obtained from dynamic light scattering measurements.

was also 0.5 L. The reflections on the XRD patterns of the product could be indexed to the monoclinic acanthite (α-Ag_2S) crystal structure (**Figure 2**, JCPDS Card File 14-0072), which is the stable form of silver sulphide at room temperature in the bulk phase, also called the β-Ag_2S phase [14].

Figure 2(a) represents the experimental (original data) and calculated diffractograms (computed data from Rietveld analysis), with good agreement between them indicating that the used initial structural model was correct. **Figures 2(b) and (c)** show that the materials are ellipsoidal in shape with some other irregular particles. The FFT simulated pattern (**Figure 2(c)**) contains spots, confirming the high crystalline quality. **Table 1** shows the refined atomic positions from the computed data and **Table 2** the unit cell parameters along with the X-ray

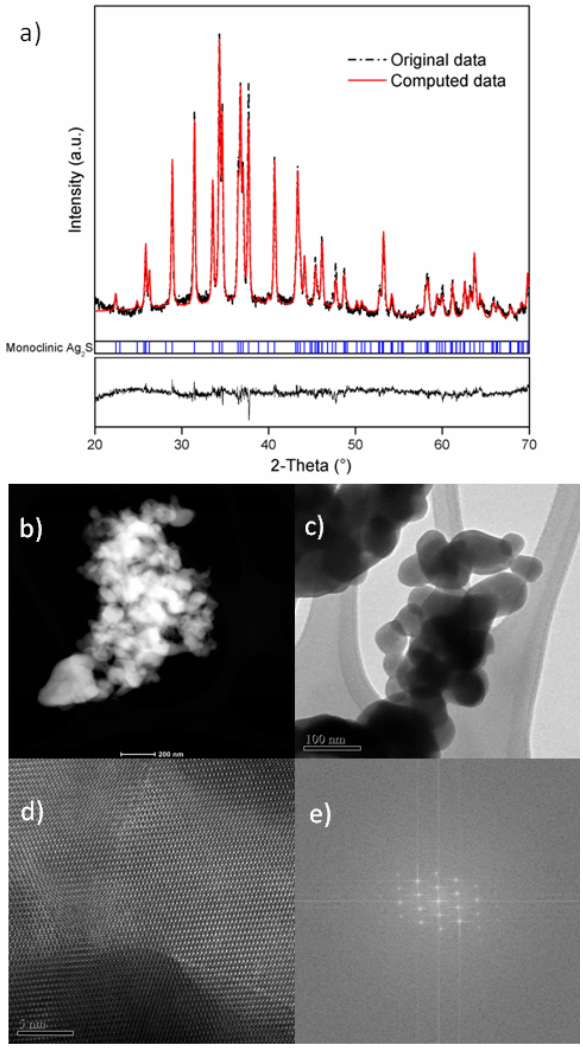

Figure 2. (a) Plot of the measured and calculated diffractogram along with the Bragg positions of silver sulphide; (b) STEM; (c) and (d) TEM images and (e) FFT pattern of Ag_2S from Cyanex® 471x solution.

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Table 1. Atomic positions in the unit cell of Ag_2S.

Compound	Atom	*X/a*	*Y/b*	*Z/c*
Monoclinic Ag_2S	Ag1	0.2903 (7)	0.3241 (4)	0.4378 (4)
	Ag2	0.7592 (7)	0.0138 (4)	0.3075 (3)
	S1	0.3507 (15)	0.2371 (9)	0.1292 (9)

Table 2. Unit cell parameters, X-ray density and crystallite size of Ag_2S obtained from the refinement of the structure.

Simmetry	Space group	X-ray density (kg/m^3)	Crystallite size (nm)
Monoclinic	P21/c	7.244	94 (0)
a (Å)	b (Å)	c (Å)	β (°)
4.2276 (1)	6.9291 (2)	7.8662 (2)	99.628 (3)

density and crystallite size. According to the Rietveld analysis, the extractant was able to maintain the size of the particles nanometrical, but was less capable to prevent some agglomeration degree. The size of particles measured by DLS is much larger than that from XRD; because DLS measures aggregates size, where Rietveld analysis gives the crystallite size.

The following precipitation experiments were carried out in a reaction vessel by varying the extractant concentrations (0.01 and 0.05 mol/L, **Figure 3**) and using a metal concentration of 0.005 mol/L. The particle size remains at the first sight almost constant. The size distributions of both products were also studied using TEM images and image analysis. The sample prepared from Cyanex® 471x 0.05 mol/L solution has an average size of 85.7 nm^2 (area), with a standard deviation of 47.7 nm^2 (**Figure 4**). The value is large due to the presence of clusters of about 223 nm^2. The sample prepared from Cyanex® 471x 0.01 mol/L solution has an average size of 83.8 nm^2, with a standard deviation of ~59.5 nm^2. This value is so large due to the presence of clusters of about 293 nm^2.

For the same percentage of particles, an adjustment to an elliptical shape of the area was made. The image processing and analysis with ImageJ for the sample Ag^+ 0.005 mol/L-Cyanex® 471x 0.01 mol/L yielded a value of 83.7 nm^2 for the average size (area) with a standard deviation equal to 71.1 nm^2, and –0.2 and 0.6 for the skewness and kurtosis, respectively (**Figure 5**). The average circularity of particles was equal to 0.2 with a standard deviation of 0.1 nm^2. The distribution in the shape of the particles is better suited to an ellipsoidal shape for the sample. In both samples dominate particles having ellipsoidal shape, being the particles prepared at higher ligand concentration slightly larger and more spherical, as shown in **Table 3**. Although it was hoped that the particle size could be controlled by tuning the reaction parameters, particularly the extractant concentration, the results show that under the experimental conditions used the size and size distribution of the as-obtained Ag_2S QDs did not change distinctly with the concentration, taking into account the fact that a commercial reagent was used

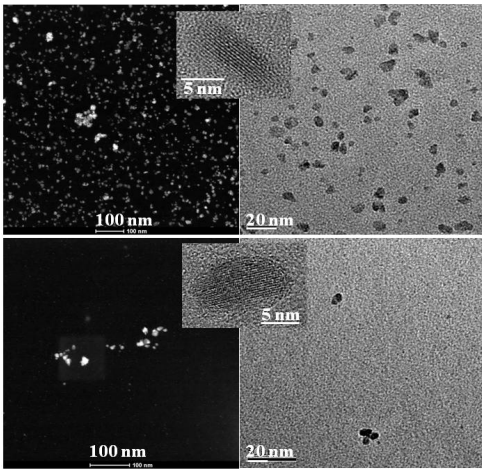


Figure 3. SEM, HRTEM and TEM images of Ag_2S nanoparticles prepared from Ag(I)-Cyanex® 471 solutions at two different ligand concentrations (Ag^+ 0.005 mol/L, upper figure: Cyanex® 471x 0.01 mol/L, down: Cyanex® 471x 0.05 mol/L).

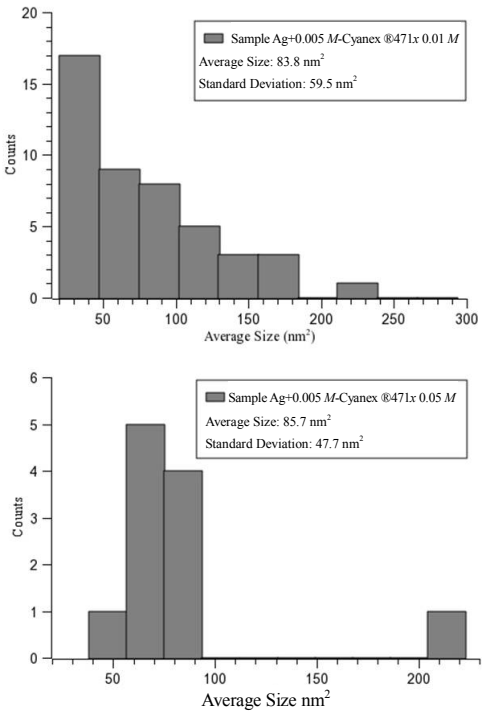
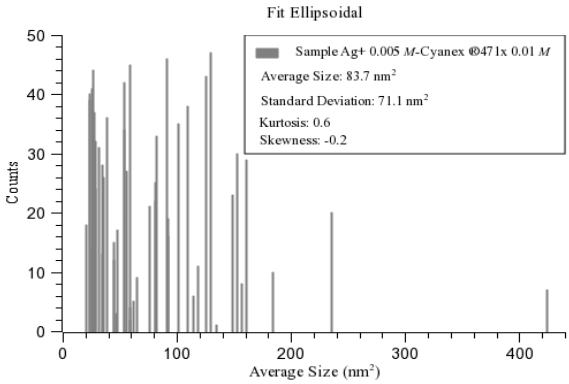
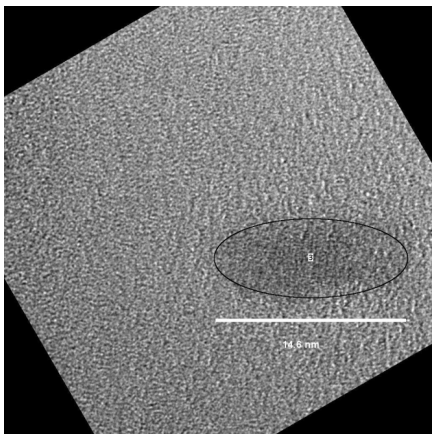


Figure 4. Histograms of the particle size distribution as determined from TEM images for the two Ag_2S nanocrystals samples. A1: Ag^+ 0.005 mol/L-Cyanex® 471x 0.01 mol/L, A2: Ag^+ 0.005 mol/L-Cyanex® 471x 0.05 mol/L.



(a)



(b)

Figure 5. (a) Adjustment to an elliptical shape of the area, and (b) TEM image of Ag_2S nanoparticle fitting the elliptical shape.

Table 3. Summary of the results for the size analysis for a selection of particles (ellipsoidal shape). A1: Cyanex® 471x 0.01 mol/L, A2: Cyanex® 471x 0.05 mol/L.

Sample	Area, nm²	Major, nm	Minor, nm	Circularity
A1	83.7	12.1	7.8	0.2
A2	85.7	12.0	8.7	0.9

and the reproducibility of the experiments might not be good. Nevertheless, it is evident that the extractant is not only a good stabilizer but also works as a morphology control agent.

Figure 6 is a HRTEM bright field image carried out in Ag_2S nanoparticles on an amorphous carbon support film. Even if lattice fringes are not direct images of the structure, it can give lattice spacing information. In this case, the measured distance between $\{\bar{1}01\}$ planes was 3.919 Å, a value slightly different from the value of 3.960 Å generally reported for the Ag_2S monoclinic structure. Besides, the Fast Fourier Transform (FFT) simulated from the particle (**Figure 7**) showed spots that strongly suggest the $\{\bar{1}01\}$ and $\{\bar{1}21\}$ planes characteristic of monoclinic Ag_2S structure. A particle growth direction along the normal of $\{\bar{1}01\}$ was suggested by Wen for Ag_2S nanowires synthesised by a mild gas-solid reaction approach, with fringe spacing measures of 0.40 nm [16]. Deeper studies are needed in order to clarify the particles crystal growth kinetics.

It was speculated that the extractant molecules could be adsorbed onto the particles surface to form organic layers and were apparently not washed off by methanol or acetone. In order to clarify this subject, thermal analysis and FTIR analysis were conducted in order to examine the organic adsorption on the particles, which is also important because the presence of even small amounts of organic impurities on the nanoparticles surface might alter the material properties.

The thermogravimmetrical analysis (**Figure 8(a)**) showed two weight losses, the first between 150˚C and 400˚C (5% mass loss), and second, a small mass loss of 0.5% between 400˚C and 525˚C, both probably due to desorption of extractant molecules. The temperature range in the first weight loss temperature (250˚C) was broad, possibly corresponding to a "desorption" process.

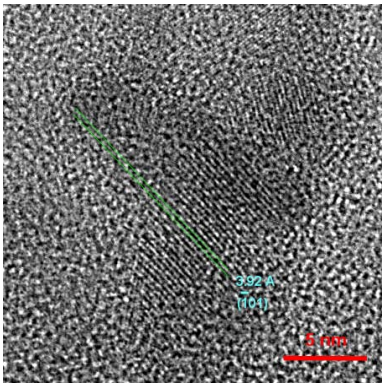


Figure 6. Illustration of lattice image from Ag_2S nanometric particles.

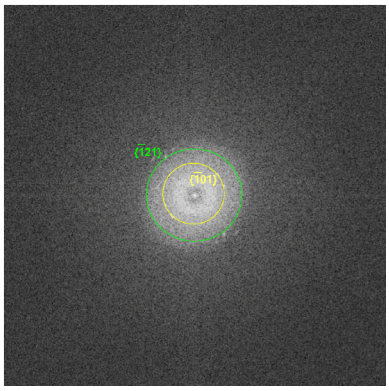


Figure 7. Indexed FFT pattern showing the $\{\bar{1}01\}$ and $\{\bar{1}21\}$ reflections.

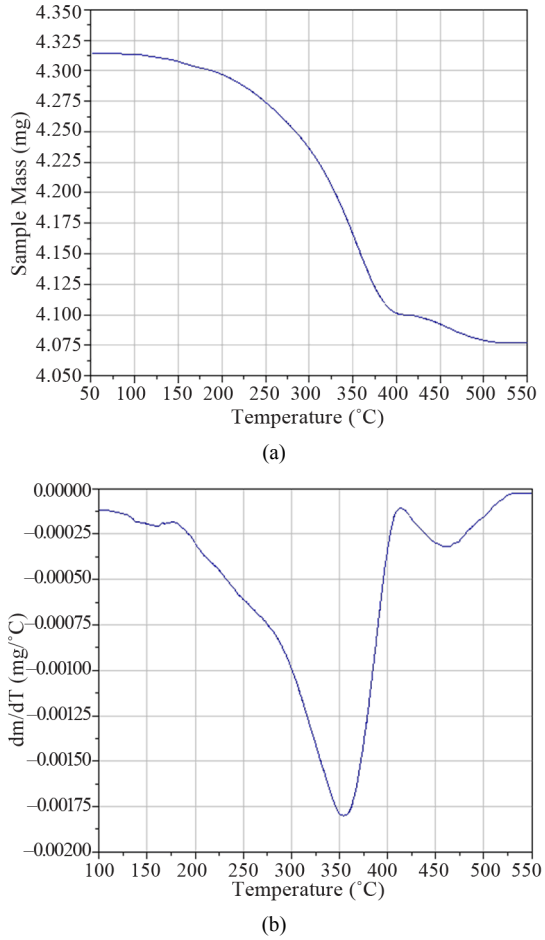
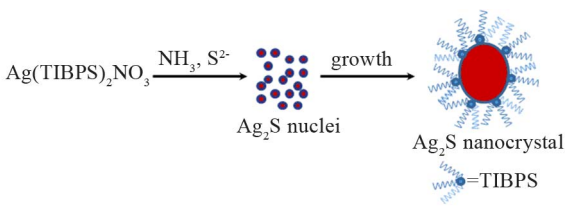


Figure 8. (a) Thermal analysis, and (b) maximum rate of mass losses (dm/dt) of silver sulphide synthesized from Cyanex® 471x solution (0.005 mol/L). 0.01 M Ag^+ in HNO_3 0.1 mol/L.



Scheme 1. Synthesis of Ag_2S nanocrystals from silver(I)-loaded Cyanex® 471x solutions.

Moreover, the small mass loss starting around 400˚C, could indicate a second desorption process giving a hint of the existence of two kinds of modifier molecules. The peak found at around 350˚C (DTG curve, **Figure 8(b)**) could represent the characteristic desorption temperature of TIBPS.

The FTIR characterization of the crystals shows the absorption characteristic of the P = S group belonging to Cyanex® 471x at 597 cm^{-1} [34-36]. Lou *et al*. Reported a sharp peak at 619 cm^{-1} in the IR spectrum of Ag_2S nanocrystals, synthesized by the thermal treatment of silver dialkyldithiophosphates, indexed to ν(P = S) [37]. The band at 818 (for the sample) and 823 cm^{-1} (for Cyanex® 471x) can be ascribed to the P-C stretching vibration, and the C-H stretching frequencies appear at 2960 and 2872 cm^{-1}.

The C-H deformation vibrations show a frequency of 1468 cm^{-1}, and bands in the 1367 - 1399 cm^{-1} region confirm the presence of more than one $-CH_3$ group on a carbon atom [34], giving a hint of the adsorption of the extractant on the nanoparticles.

Interestingly, the strong absorption band at 923 cm^{-1} could corresponds to the P-O stretching vibration from the phosphine oxide analogue, present in the extractant as impurity, and apparently also adsorbed on the particles. No significant shift in the P-S and P-O bands toward lower or higher frequencies was noted.

The donor atoms of common bases have electronegativities increasing in the order: S < Br < N < Cl < O < F. Therefore, reagents containing sulphur atoms are expected to be strong stabilizers for Ag_2S nanoparticles. Cyanex® 471x has been previously used as an effective ligand for silver extraction based on the relatively strong interaction between silver ions and the sulphur atom of the extractant moiety. In this work, it was confirmed that through a two-step synthetic method, nanometrical Ag_2S particles can be controllably formed.

As expected, the sulphur sustitution in Cyanex® 471x favors the adsorption of the extractant onto the particles, as predicted by the Hard-Soft Acid-Base (HSAB) principle. After the formation of the nucleii, the preferential growth direction along the normal of $\{\bar{1}01\}$, may develop as an entry to the formation of the ellipsoids. The strong coordination ability of Cyanex® 471x for Ag^+ can decrease the formation rate of Ag_2S nanocrystals. The reaction between the ligand and Ag^+ competes with Ag_2S crystal growth and leads to the controlled growth of Ag_2S particles, keeping them as nanocrystals and hindering aggregation. Furthermore, the growth rate in all directions is not the same, leading to the final morphology of ellipsoids.

4. Conclusion

Silver sulphide particles were prepared by a simple method involving solvent extraction and precipitation from a commercial organophosphorous extractant, and their structural properties were discussed. Investigation revealed that Cyanex® 471x is an effective capping agent, depending on the extraction and stripping experimental conditions chosen. The metal-extractant complex in the organic solution serves as an excellent nanoparticle precursor due to the capability of Cyanex® 471x to compete for the metal binding sites and thus avoiding the incur-

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poration of the sulphide ions during the nucleation process. The Ag_2S nanocrystals are possibly coated by two kinds of organic molecules present in the commercial extractant, the tri-isobutylphosphine sulphide and its corresponding oxide. Although further studies are required for a better understanding of the correlation between the mechanism of nanoparticles stabilization and the stripping process, solvent extraction combined with precipitation stripping is a viable alternative for nanomaterials synthesis, because this purification technique is widely used in hydrometallurgy for the recovery and purification of a variety of metals.

5. Acknowledgements

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