

# Sonochemical synthesis of nanocrystallites of ruthenium sulfide, RuS<sub>1.7</sub>

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Nanocrystalline ruthenium sulfide has been synthesised sonochemically using ruthenium chloride and thiourea as precursors. Sonication of an aqueous solution of ruthenium chloride and thiourea yields an X-ray amorphous product which on heating at 650 °C yields nanocrystalline ruthenium sulfide of stoichiometry RuS<sub>1.7</sub> with a characteristic XRD pattern. The products have been characterized by powder XRD, TEM, DSC, TGA, CHN analysis, XPS and DRS.

## 1. Introduction

Ruthenium sulfide is an interesting material from both fundamental and technological points of view. It belongs to the family of transition metal dichalcogenides crystallizing in the pyrite structure.<sup>1</sup> Ruthenium sulfide has potential applications in energy related technologies and it is a promising material for thermal catalytic processing as an effective catalyst in petroleum refining and also for photoelectrochemical energy conversion.<sup>2</sup> Ruthenium sulfide is highly stable against photocorrosion and absorbs visible light and these properties have been exploited in photoelectrochemical energy conversion.<sup>3</sup> It is also used in the photocatalytic decomposition of water.<sup>4</sup>

Traditionally, ruthenium sulfide has been synthesized as a polycrystalline powder by a solid state reaction between elemental ruthenium and sulfur at 1070 °C for ten days. In a recent report,<sup>5</sup> nanocrystallites of ruthenium sulfide were synthesized as powders or colloids depending upon the conditions by mixing an acetonitrile solution of RuCl<sub>3</sub> with an aqueous solution of Na<sub>2</sub>S. Ruthenium sulfide has been synthesised as films using electrochemical deposition.<sup>6</sup> Single crystals of ruthenium sulfide have also been synthesised using a tellurium flux method.<sup>7</sup> In the present study, nanocrystallites of ruthenium sulfide with a size of *ca.* 25 nm have been synthesized using a sonochemical method.

Ultrasound irradiation has been routinely used in the field of materials science. Its chemical effects have recently come under investigation for the acceleration of chemical reactions and for the synthesis of new materials<sup>8</sup> as well as for generating novel materials with unusual properties.<sup>9</sup> The chemical effects of ultrasound irradiation arise from acoustic cavitation: the formation, growth and collapse of bubbles in a liquid. The extremely high temperatures ( $\approx 5000$  K), pressures (> 20 MPa) and cooling rates ( $> 10^{10}$  K s<sup>-1</sup>) attained during cavitation lead to many unique properties in the irradiated solution and these extreme conditions have been exploited to prepare nanoscale metals, metal oxides, metal sulfides and nanocomposites.<sup>10,11</sup>

## 2. Experimental

### Preparation

Typically, to an aqueous solution of 0.69 g of RuCl<sub>3</sub>, 0.51 g of thiourea was added in a sonication flask (total capacity 80 ml, 26 mm o.d.). The solution was purged with argon for 30 min and irradiated with high intensity ultrasound radiation for 2 h

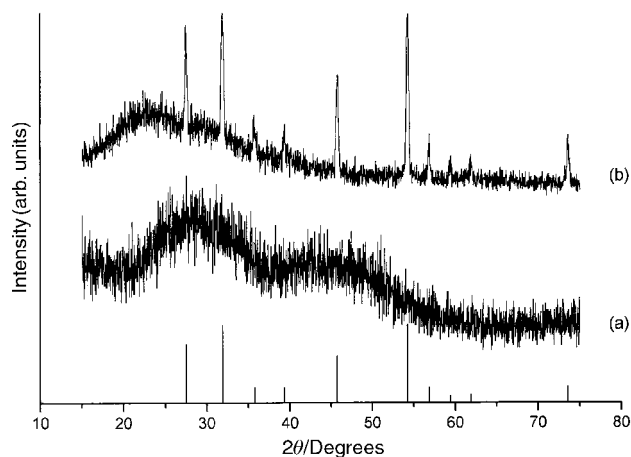
by employing a direct immersion titanium horn (Sonics and Materials, 20 kHz, 100 W cm<sup>-2</sup>). The titanium horn was inserted to a depth of  $\sim 1$  cm in the solution. The temperature during the sonication experiment increased to 80 °C as measured by an iron–constantan thermocouple.

After the sonication was completed, the product was separated from the solution by centrifugation. The recovered product was washed several times with distilled water and ethanol, then dried under vacuum. The as-prepared sonication product was heated at 650 °C for 2 h under an argon atmosphere to yield nanocrystallites of ruthenium sulfide.

### Product characterization

The powder X-ray diffraction patterns were recorded by employing a Rigaku X-ray diffractometer (Model-2028, CuK $\alpha$ ,  $\lambda = 1.5418$  Å). The morphology of the products was determined by transmission electron microscopy (TEM) (JEOL-JEM 100SX microscope). Samples for TEM were prepared by placing a drop of the sample suspension in ethanol on a copper grid coated with carbon film (400 mesh, Electron Microscopy Sciences) and were allowed to dry in air. The thermogravimetric analysis was carried out using a Mettler Toledo TGA/SDTA851 instrument in the temperature range of 30 to 900 °C, at the rate of 10 °C per minute, in an argon atmosphere. The DSC pattern was recorded using a Mettler DSC-30 instrument in an atmosphere of nitrogen with a heating rate of 10 °C min<sup>-1</sup>. Elemental analysis of C, H, N and S was carried out using an Eager 200 CE Instruments EA 1110 elemental analyzer. Diffuse reflectance spectroscopy (DRS) measurement was carried out on a Cary (Varian 1E) spectrophotometer.

X-Ray photoelectron spectroscopy measurements were made using an AXIS HS Kratos Analytical instrument. The XPS spectra were acquired with monochromatic Al K $\alpha$  radiation, excitation at 13 kV and 5 mA, at a pass energy of 40 eV and step size of 25 meV, without electron flood. The energy resolution was about 0.7 eV. The base pressure in the analysis chamber of the spectrometer was better than 10<sup>-9</sup> Torr. The Ru 3d doublet peak falls in the region of the C 1s peak and hence the utilization of the C 1s peak as an internal standard was not possible. The spectrometer was calibrated with reference to Ag 4d<sub>5/2</sub> = 368.2 eV and Au 4f<sub>7/2</sub> = 84.0 eV. The accuracy of the reported binding energy is better than 0.1 eV. Although ruthenium disulfide is a semiconductor, no charging effect could be discerned in the XPS spectra.



**Fig. 1** Powder XRD patterns of (a) the as-prepared sonication product and (b) the product after heating at 650 °C for 2 h in an argon atmosphere. The diffraction pattern of RuS<sub>2</sub> (JCPDS file no. 19-1107) is shown by vertical lines for comparison.

### 3. Results and discussion

From the elemental analysis in combination with the results obtained from thermal gravimetric measurements, the stoichiometry of the as-prepared sonochemical product was found to be RuS<sub>2</sub>(NH<sub>2</sub>CSNH<sub>2</sub>)<sub>1.5</sub>(H<sub>2</sub>O)<sub>1.2</sub>. The powder XRD patterns of the as-prepared sonochemical product and the heated material are shown in Fig. 1. As can be seen, the as-prepared product is X-ray amorphous (Fig. 1a). If this material was heated at temperatures below 650 °C, the XRD pattern still showed only broad humps. However, the product heated at 650 °C for 2 h showed an X-ray pattern (Fig. 1b) characteristic of polycrystalline ruthenium sulfide (JCPDS file no. 19-1107). The crystallite size as calculated from the powder XRD pattern using the Debye–Scherrer formula is *ca.* 33 nm. From the energy dispersive X-ray analysis (EDX) of the nanocrystallites, the stoichiometry was found to be RuS<sub>1.7</sub>.

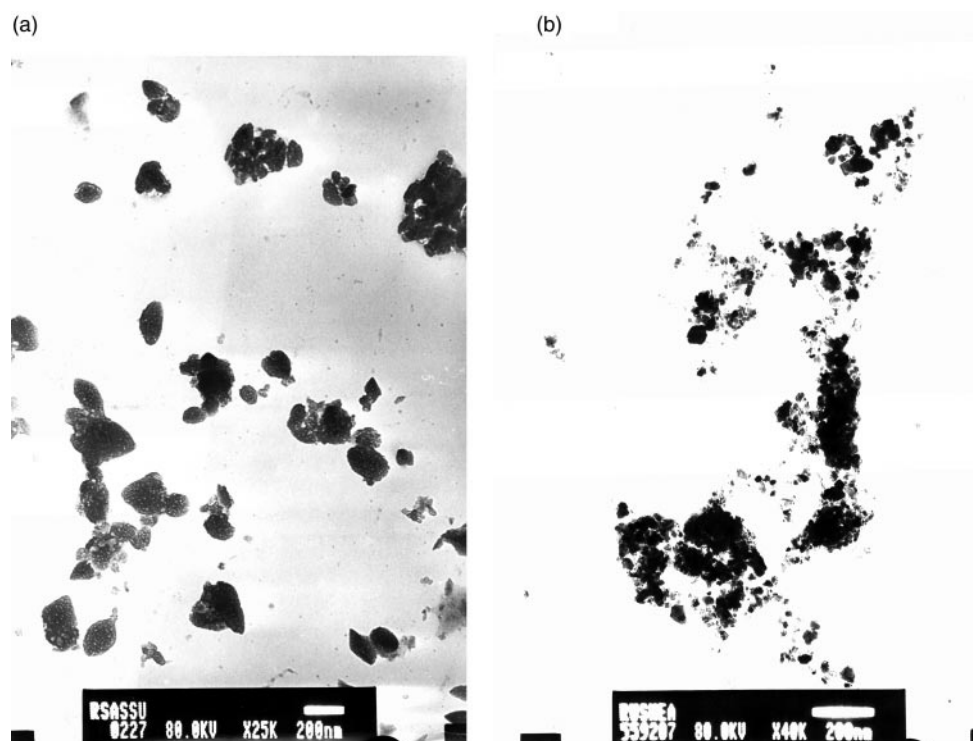
In Fig. 2, the results of transmission electron microscopic

investigations are shown. The as-prepared X-ray amorphous sonication product (Fig. 2a) shows considerable agglomeration. However, the TEM picture (Fig. 2b) of the nanocrystalline ruthenium sulfide prepared by heating the as-prepared sonication product shows particle sizes of *ca.* 25 nm with less aggregation.

Fig. 3 shows the thermogravimetric pattern of the as-prepared sonication product sample in the temperature range 30 to 900 °C. It exhibits multiple steps with an overall weight loss of 48.8%. The first step around 90 °C can be attributed to the loss of water (expected weight loss = 7.2%; observed weight loss = 7.4%). The multiple steps after the loss of water are attributed to the decomposition of the ruthenium sulfide–thiourea complex and residual organics. The overall observed weight loss agrees well with what is expected from the formulae obtained from chemical analysis (expected weight loss = 48.3%; observed weight loss = 48.8%). The final product of the thermal analysis was found to be nanocrystallites of ruthenium sulfide by powder XRD measurements.

The DSC pattern of the as-prepared sonication product in the temperature range 30–500 °C showed two exothermic peaks which are not reversible; one around 157 °C and another one around 227 °C. Both the peaks can be attributed to the exothermic decomposition of the ruthenium sulfide–thiourea complex. The DSC pattern does not show the amorphous to crystalline transition in the present temperature range. This is supported by the fact that the as-prepared sonication product does not crystallize even after heating at 500 °C, the end temperature of the DSC run, for 12 h. From the XRD and DSC results we can conclude that the as-prepared sonication product is amorphous to X-rays, possibly due to crystallite size effects. Smaller crystallite sizes lead to line broadening in the powder XRD pattern<sup>12</sup> and when the crystallite size grows after heating, one observes the characteristic XRD pattern.

In Fig. 4 the IR spectrum of the as-formed sonication product is shown. It shows bands at about 3140, 3275 and a shoulder at about 3523 cm<sup>-1</sup>. Moreover, two stronger bands were also observed at 1404 cm<sup>-1</sup> and 1615 cm<sup>-1</sup> in addition to a weaker band at 1086 cm<sup>-1</sup> and a shoulder at about 675 cm<sup>-1</sup>.



**Fig. 2** Transmission electron micrographs of (a) the as-prepared sonication product and (b) the product after heating at 650 °C for 2 h in an argon atmosphere.

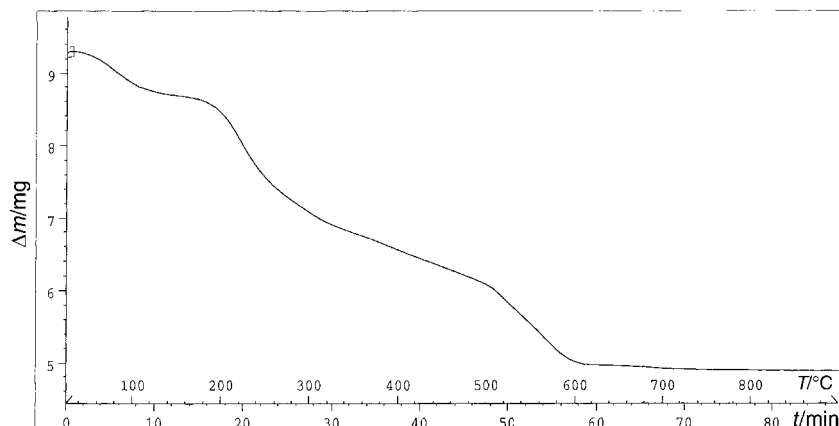


Fig. 3 TG pattern of the as-prepared sonication product.

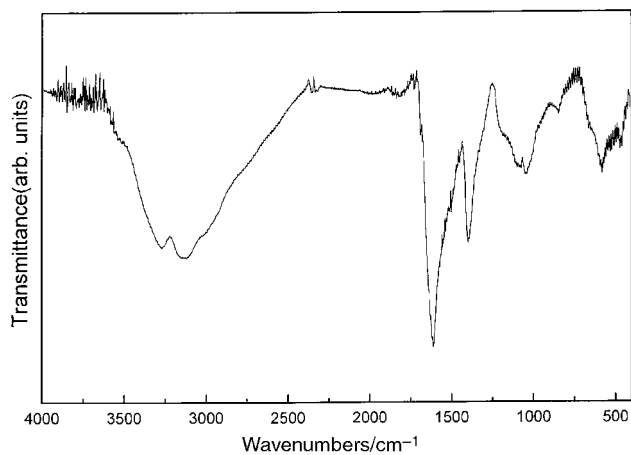


Fig. 4 IR spectrum of the as-prepared sonication product.

Thiourea is an ambidentate ligand capable of bonding to metals *via* the sulfur or nitrogen atom. If it is coordinated *via* the sulfur, a decrease in the frequency for the  $\nu_{C=S}$  mode with a concomitant increase in the  $\nu_{C-N}$  and  $\nu_{NH_2}$  modes is observed. It has also been reported that the strong thiourea band in the  $1080\text{--}1090\text{ cm}^{-1}$  region assigned to the symmetric  $\nu_{NCN}$  stretch is extremely weakened or disappears upon complex formation.<sup>13</sup> The band at  $1086\text{ cm}^{-1}$  in Fig. 4 shows a marginal reduction in intensity when compared to pure thiourea. The strong IR band at  $1404\text{ cm}^{-1}$  is assigned to a combination mode involving  $\nu_{NCN}$ ,  $\delta_{NH_2}$  and  $\nu_{C=S}$ . The other strong IR band at  $1615\text{ cm}^{-1}$  is assigned to the  $\delta_{NH_2}$  mode and this band overlaps with the band that corresponds to the bending vibrational frequency of the water molecules. The above two vibrational modes appear at  $1413$  and  $1610\text{ cm}^{-1}$  for pure thiourea respectively. The vibrational bands observed at  $3140$  and  $3275\text{ cm}^{-1}$  have been attributed to the symmetric and asymmetric  $NH_2$  stretches and these bands appear at  $3097$  and

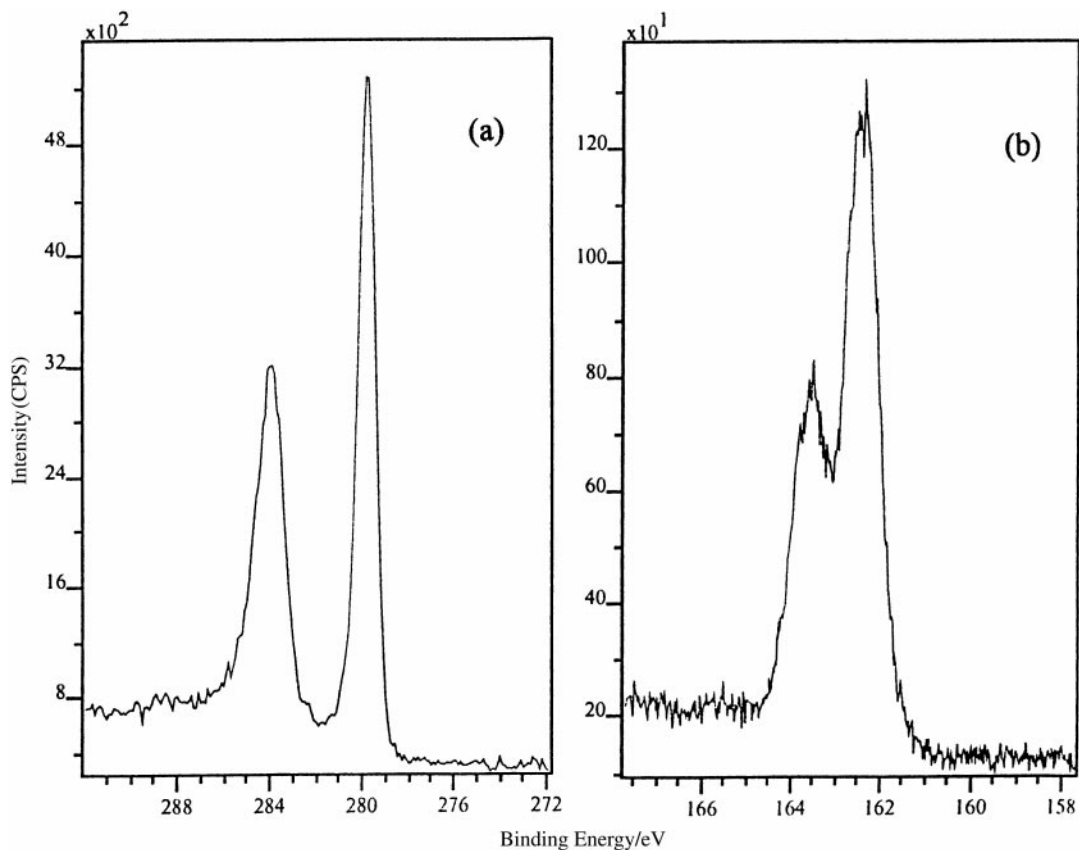


Fig. 5 (a) Ru 3d XPS spectrum and (b) S 2p XPS spectrum of the ruthenium sulfide nanocrystallites.

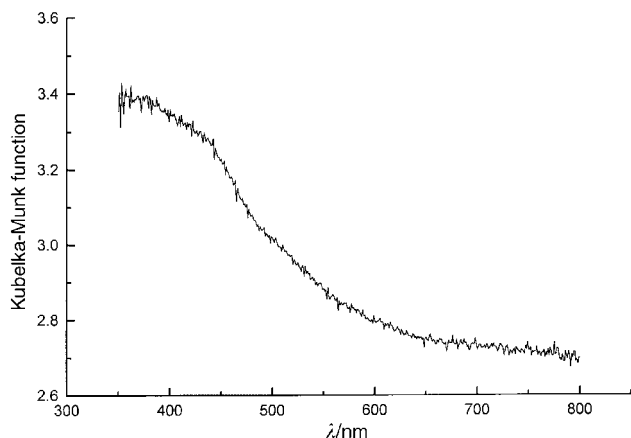


Fig. 6 DRS spectrum of ruthenium sulfide nanocrystallites.

3258  $\text{cm}^{-1}$  respectively for pure thiourea. The shoulder at about 3523  $\text{cm}^{-1}$  has been ascribed to  $\nu_{\text{OH}}$  of the  $\text{H}_2\text{O}$  molecules in the as-formed sonication product and this band too overlaps with  $\text{NH}_2$  stretching vibrations. The shoulder at about 675  $\text{cm}^{-1}$  corresponds to the  $\nu_{\text{C}=\text{S}}$  band of thiourea for which it is observed at 730  $\text{cm}^{-1}$ . This lowering of the frequency can be attributed to the reduced double bond character of the  $\text{C}=\text{S}$  bond on coordination to the metal, ruthenium. On the basis of the IR results, it can be concluded that there is an appreciable interaction between the ligand molecules and the metal ion in the as-formed sonochemical product.

Fig. 5 presents the X-ray photoelectron spectroscopy (XPS) results for the nanocrystalline ruthenium sulfide. XPS allows for the determination of oxidation state and chemical structure of materials.<sup>14</sup> The Ru 3d spectrum of nanocrystalline  $\text{RuS}_{1.7}$ , prepared by heating the as-prepared sonication product, is shown in Fig. 5a. It depicts a broad doublet corresponding to the  $3d_{5/2}$  and  $3d_{3/2}$  states (spin-orbit coupling of a 3d state). The signal centered at 279.9 eV is characteristic of the divalent Ru  $3d_{5/2}$  binding energy. Ru<sup>II</sup> binding energies fall in the range 279.5–281.8 eV.<sup>15</sup> The separation between the two peaks (spin-orbit components) is 4.1 eV. The appearance of a single Ru 3d doublet is representative of a single oxidation state. The sulfur  $2p_{3/2}$  doublet is also depicted in Fig. 5b. The binding energy value observed, 162.4 eV, is consistent with that observed for the  $\text{S}_2^{2-} 2p_{3/2}$  band.<sup>15</sup> A small but detectable O 1s peak was also observed at 530.8 eV (not shown).

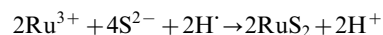
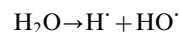
The non-stoichiometry in ruthenium sulfide nanocrystallites may be accounted for by two possibilities: (i) the presence of  $\text{S}^{2-}$  species near a S–S vacancy in the  $\text{RuS}_2$  structure as reported by other workers:<sup>16</sup> it has been reported in the literature that ruthenium sulfide exhibits non-stoichiometry and most of the authors report a stoichiometry of  $\text{RuS}_{1.9}$  and attribute the observed non-stoichiometry to sulfur vacancies;<sup>3a,16</sup> (ii) surface oxidation of the nanocrystallites has occurred with the formation of  $\text{RuO}_2$  on the surface. However,  $\text{RuO}_2$  was not detected in the powder XRD pattern of the nanocrystallites. This may be due to the fact that  $\text{RuO}_2$  may be formed in smaller quantities and XRD is insensitive to such quantities. Recently, Ashokkumar *et al.*<sup>5</sup> reported lower Ru/S ratios of 1:1.8 and 1:1.2 and they have ascribed the lower sulfur content in their samples to partial oxidation of the sample. Since in the XPS measurements an O 1s peak at 530.8 eV could be detected it can be concluded that surface oxidation has occurred on the surface of the nanocrystallites but the concentration of oxidised species is too small to be observed in the powder XRD measurements. Unfortunately, the binding energies of Ru<sup>IV</sup> also fall in the same region as Ru<sup>II</sup> (280.7 to 281 eV).

The diffuse reflectance spectrum of ruthenium sulfide

nanocrystallites was measured in order to resolve the excitonic or interband (valence–conduction band) transitions which allows one to calculate the band gap ( $E_g$ ). Fig. 6 shows the DRS spectrum of the nanocrystallites. The band gap was calculated from a plot of  $(F(R) \times hv)^2$  versus  $hv$  ( $F(R)$  is the Kubelka–Munk function and  $R$  is the reflectance). The observed value of the band gap, 2.2 eV, is larger than that reported for bulk ruthenium sulfide (1.8 eV)<sup>1b,17</sup> and this has been attributed to quantum size effects. The value of  $E_g$  is similar to results reported for ruthenium sulfide nanoparticles.<sup>3c</sup> However, the possibility of this increase in band gap owing to the larger degree of non-stoichiometry in the synthesised nanocrystallites can not be ruled out.

The effects of ultrasound radiation on chemical reactions are due to the very high temperatures and pressures which develop during the sonochemical cavity collapse by acoustic cavitation. There are two regions of sonochemical activity, as postulated by Suslick *et al.*:<sup>18,19</sup> the inside of the collapsing bubble, and the interface between the bubble and the liquid which extends to about 200 nm from the bubble surface. If the reaction takes place inside the collapsing bubble as is the case for transition metal carbonyls in organic solvents, the temperature inside the cavitation bubble can be from 5100–2300 K depending on the vapour pressure of the solvent.<sup>18</sup> If water is used as the solvent, the maximum bubble core temperature that can be attained is close to 4000 K.<sup>20</sup> The product obtained is amorphous as a result of the high cooling rates ( $> 10^{10} \text{ K s}^{-1}$ ) obtained during the collapse. On the other hand, if the reaction takes place at the interface, the temperature of which has been measured to be 1900 K,<sup>19</sup> one expects to get nanocrystalline products. However, in some cases the formation of amorphous products is reported owing to the very high quenching rate experienced by the products. If the solute is ionic, which has a low vapour pressure, then during sonication the amount of the ionic species will be very low inside the bubble and little product is expected to occur inside the bubbles. We propose that the formation of ruthenium sulfide occurs at the interface between the bubble and the liquid, yielding nanosized amorphous materials. The amorphous nature of the products is due to the very high quenching rate experienced by the products. The quenching rate is sufficiently high that the material can be frozen before crystallisation occurs.

On the basis of a comparison with radiation chemistry studies,<sup>21</sup> the following mechanism is suggested for the formation of ruthenium sulfide.



The hydrogen radicals generated from water molecules by absorption of ultrasound trigger the reduction of Ru(III) to Ru(II). The  $\text{RuS}_2$  so formed forms an adduct with thiourea and water,  $\text{RuS}_2(\text{NH}_2\text{CSNH}_2)_{1.5}(\text{H}_2\text{O})_{1.2}$ , which on heating produces nanocrystallites of ruthenium sulfide with non-stoichiometry,  $\text{RuS}_{1.7}$ .

#### 4. Conclusions

Synthesis of nanocrystallites of ruthenium sulfide with a size of ca. 25 nm was carried out sonochemically. The as-prepared product from sonication is amorphous to X-rays and if heated to 650 °C, it shows a characteristic powder XRD pattern of ruthenium sulfide. The nanocrystallites were characterised by a variety of techniques including XRD, TEM, TGA, DSC, XPS and DRS.

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