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Synthesis and characterization of RuS_2 nanocrystallites

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RuS_2 nanocrystallites were synthesized using a new technique, namely prolonged bubbling of H_2S through a solution of $RuCl_3$ in sulfolane and water at high temperatures. Optically transparent RuS_2 colloidal particles could also be synthesized in hot sulfolane. Optical measurements of the RuS_2 colloidal suspensions and powders showed a broad absorption in the visible spectral region, suggesting the suitability of this material for semiconductor sensitization experiments. The observed X-ray diffraction (XRD) data of the synthesized powder samples were in good agreement with the reported ASTM pattern of RuS_2, confirming that RuS_2 was the prepared compound by this new preparation technique. Scanning electron microscopic (SEM) pictures showed submicrometre sized crystallites. Heat treated powders of water prepared RuS_2 showed < 50 nm particle sizes, and still smaller sizes were observed for the sulfolane prepared sample. Energy dispersive X-ray (EDX) analysis and X-ray fluorescence (XRF) measurements showed an Ru/S ratio of $\sim 1:2$ and also supported the XRD results.

1. Introduction

Research work on synthesis and characterization of semiconductors for the purpose of solar energy conversion have been increasingly reported [1–10] in recent years owing to the importance of this area of research as conventional resources of energy are depleting. The energy conversion efficiencies of the semiconductors highly depend upon the preparation methods which change the physical properties of these materials [3, 4, 8]. A wide variety of methods have been used for the preparation of semiconductors in the form of powders, colloids and thin films [1–10]. These prepared materials are usually characterized by techniques such as X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), etc. Nanocrystallites of high quality cadmium chalcogenides were prepared by pyrolysis of organometallic reagents by injecting into a hot coordinating solvent [3]. XRD and TEM in combination with computer simulations indicated the presence of bulk structural properties in crystallites as small as 2.0 nm in diameter. Spectroscopic analysis in combination with electron microscopic studies gave an insight into the geometrical and energy structure of HgS colloids-coated CdS layers [11]. XRD and SEM were used to analyse the surface modifications due to metal ions loading on WO_3 powders [12] and for the structural characterization of CdS films grown by cathodic electrodeposition [13] and CdS microcrystals deposited on TiO_2 and ZnO [14]. The use of different instrumental techniques to structurally characterize various semiconductor materials has also been dealt in detail in a review article [15]. Ammonia-passivated CdS cluster (in nafion) size was determined by XRD measurements [16]. A three-dimensional network of SnO_2 nanocrystallites of particle diameter ~ 5.0 nm prepared as a thin film on optically transparent electrodes, could also be identified with these techniques [17]. A comparison of bonding structure and crystallization nature between sputtered TiO_2/SiO_2 multilayer films and TiO_2/SiO_2 composite films was investigated using Fourier transform infrared analysis (FTIR) and XRD [5]. Nosaka *et al.* [4] have reported a new method of laser chemical vapour deposition (CVD) process to prepare high quality thin films of ZnS. EDX and XRF are also useful techniques to determine the bulk composition of different materials. Ultrathin polycrystalline FeS_2 films were grown on TiO_2 by CVD, to spectrally sensitize TiO_2, where EDX was used to determine Fe/S ratio [18].

Ruthenium disulfide is a narrow band-gap semiconductor (Eg ~ 1.85 eV) and its high stability against hydrogen and oxygen evolution from aqueous solutions makes it interesting to use this material for the photoelectrolysis of water with visible light [19–21]. The photoelectrochemical properties of ruthenium disulfide have been extensively investigated [22]. Many of these studies were carried out with

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RuS_2 single crystals synthesized by reacting stoichiometric amounts of Ru powder and S lumps followed by chemical vapour transport (CVT). A detailed method of crystal growth is reported [23]. Polycrystalline RuS_2 (prepared from respective elements) photoanodes showed poor photoelectrochemical efficiency [24].

The authors have recently reported the photosensitization behaviour of RuS_2 over TiO_2 electrodes [25]. In spite of extensive investigations on the photoelectrochemical behaviour of RuS_2, characterization studies of this material using different instrumental techniques have not been carried out in detail. In this article, the authors report a new method of synthesizing RuS_2 in colloidal and powder forms, and their characterization by optical, XRD, SEM, EDX and XRF measurements.

2. Experimental procedure

All the chemicals used were of research grade: $RuCl_3$ (99.9%), sodium polyphosphate (PP), sulfolane (tetrahydrothiophene 1,1-dioxide; > 98.0%) and polyvinyl alcohol (PVA; No. 2000).

RuS_2 precipitates and colloidal suspensions were prepared by bubbling H_2S through a solution of $RuCl_3$ (0.1–0.5 M) in water, aqueous PVA, aqueous PP and sulfolane. Thin films of the dark brown colloidal particles (PVA and sulfolane prepared) were made on a glass substrate by spreading the colloidal suspension, followed by drying at 150 °C under vacuum. The RuS_2 precipitates (in water and sulfolane) were filtered, dried under vacuum at 150 °C and heat treated at 400–500 °C for about 3 h.

Optical, XRD, SEM, EDX and XRF measurements were carried out using an ultraviolet visible spectrophotometer (Shimadzu, UV–2100PC), scanning electron microscopy (Jeol JSM-T220) coupled with EDX analysis (Philips, EDAX-9900), XRF spectrometer (Horiba, MESA-1130) and XRD (CuK_α) spectrometer (Jeol, JDX-8S), respectively.

3. Results and discussion

For simplicity, different conditions used during preparation and the observations are summarized in Table I. Prolonged H_2S bubbling in an aqueous solution of 0.1–0.5 M $RuCl_3$ at room temperature resulted in a brown precipitate. A similar procedure at higher temperature (80 °C) gave a black precipitate. However, use of stabilizing agents such as PVA (0.1–0.5 M) and PP (0.1–0.5 M) in water gave a dark brown, optically transparent colloidal suspension. The stability of RuS_2 colloids prepared in aqueous medium depends upon the nature of the stabilizing agent, lasting for only a few hours in PP, whereas they were stable for several weeks in PVA.

Both colloidal suspension and powders of RuS_2 could be obtained by changing $RuCl_3$ concentrations, when sulfolane was used as a solvent. H_2S bubbling for ~ 3 h through a solution of $RuCl_3$ (upto 0.1 M concentration) in sulfolane, at ~ 200 °C, produced dark brown RuS_2 colloidal particles that were optically transparent. These colloids were also remarkably stable in sulfolane. The special advantages of sulfolane are its high boiling point (285 °C), which allowed one to maintain a fairly high temperature during preparation and its stabilizing nature that keeps the colloidal particles stable for three to four weeks. Such a method of synthesis of nanocrystalline semiconductor particles in hot co-ordinating solvents is also reported [3]. However, prolonged standing of the colloidal suspension resulted in coagulation of these colloids, leading to precipitation of black RuS_2 particles. When a higher concentration (0.3–0.5 M) of $RuCl_3$ was used, direct precipitation of these black particles could be achieved. When H_2S was bubbled through the concentrated solution, a dark brown colloidal suspension formed at the beginning immediately coagulated to give a black precipitate. The black powder thus obtained by preparing at higher temperatures (in water and sulfolane) showed a metallic shine.

3.1. Optical measurements

Absorption spectra of RuS_2 colloidal suspension in aqueous PVA solution and sulfolane and those of thin films on glass substrate are given in Fig. 1. The absorption of PVA prepared RuS_2 colloidal suspension and thin film (Fig. 1a, b) is weaker at longer wavelength region than that of sulfolane prepared samples (Fig. 1c, d). From this observation, one could confirm the good stabilizing property of PVA and predict that the colloidal particle sizes are smaller in PVA showing size quantization effect. The absorption spectra (derived from the diffuse reflection measurements) of as-dried and heat treated RuS_2 powders are similar to that of Fig. 1d. Normally, an increase in

TABLE I RuS_2 preparation conditons[a] in different solvents and observations

Solvent	$RuCl_3$ (Mol^{-1})	$T_{preparation}$ (°C)	Observation
Water	0.1–0.5	20–25	Brown precipitate
Water	0.1–0.5	80	Black precipitate
Aqueous PVA (0.1–0.5 M)	< 0.1	80	Dark brown, optically transparent colloids (stable)
Aqueous PP (0.1–0.5 M)	< 0.1	80	Dark brown, optically transparent colloids (not stable)
Sulfolane	< 0.1	200	Dark brown, optically transparent colloids (stable)
Sulfolane	0.3–0.5	200	Black precipitate

[a] In all cases H_2S was bubbled for 3 h.

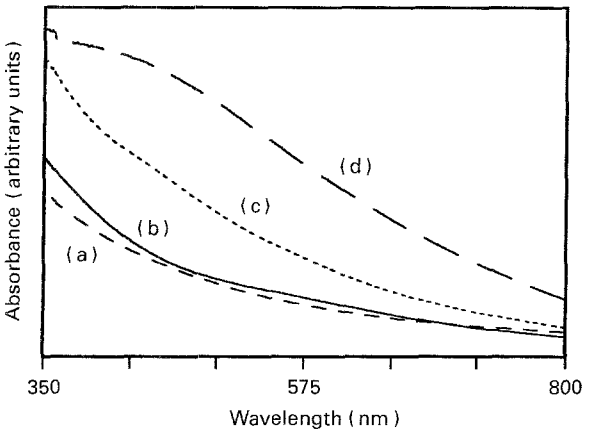

Figure 1 Absorption spectra of RuS_2: (a) colloidal suspension in aqueous PVA, (b) thin film of PVA prepared colloids, (c) colloidal suspension in sulfolane, and (d) thin film of sulfolane prepared colloids.

crystal size of RuS_2 is expected due to heat treatment, which would cause a red shift in the absorption spectrum for the heat treated samples. Absence of such a red shift for the heat treated RuS_2 powders shows that the crystal sizes were not considerably increased during heat treatment. It is worth mentioning that RuS_2 has a wide spectral absorption in the visible region, which supports the suitability of this material for solar energy conversion experiments and for the photosensitization of wide band-gap semiconductors. Further details on the photoelectrochemical experimental results of the sensitization behaviour of RuS_2 will also be published elsewhere [26] in addition to a recent communication [25].

3.2. XRD

RuS_2 has a non-stoichiometric form, with a gross composition of $RuS_{1.90}$ [27] and a pyrite structure with each cation surrounded by six anion pairs in a distorted octahedral symmetry and each anion counterpart has a distorted tetrahedral symmetry. A schematic representation of the RuS_2 crystal lattice is also given in an earlier report [28]. It has disulfide units and ruthenium is in 2^+ state. X-ray diffraction measurements were carried out for the RuS_2 powder samples before and after heat treatment, and are shown in Fig. 2. The XRD patterns of these samples match very well with the ASTM data of RuS_2 [29]. The point to be noted is the difference between as-dried and heat treated samples. The as-dried, water- and sulfolane-prepared RuS_2 powders show very broad XRD spectra, indicating that they are almost amorphous to XRD (Fig. 2a, c). However, by heat treatment comparatively sharper peaks appear in the spectra, even though they are still broad (Fig. 2b, d). The broad peaks of the heat treated samples are due to submicrometre sized colloidal particles. Generally, the photoactivity of any semiconductor is enhanced (due to effective electron–hole separation) by increased crystallinity of the material. Thus, XRD results show that the photoelectrochemical efficiency of RuS_2 might have been enhanced by the small increase in the crystallinity of the amorphous powders during heat

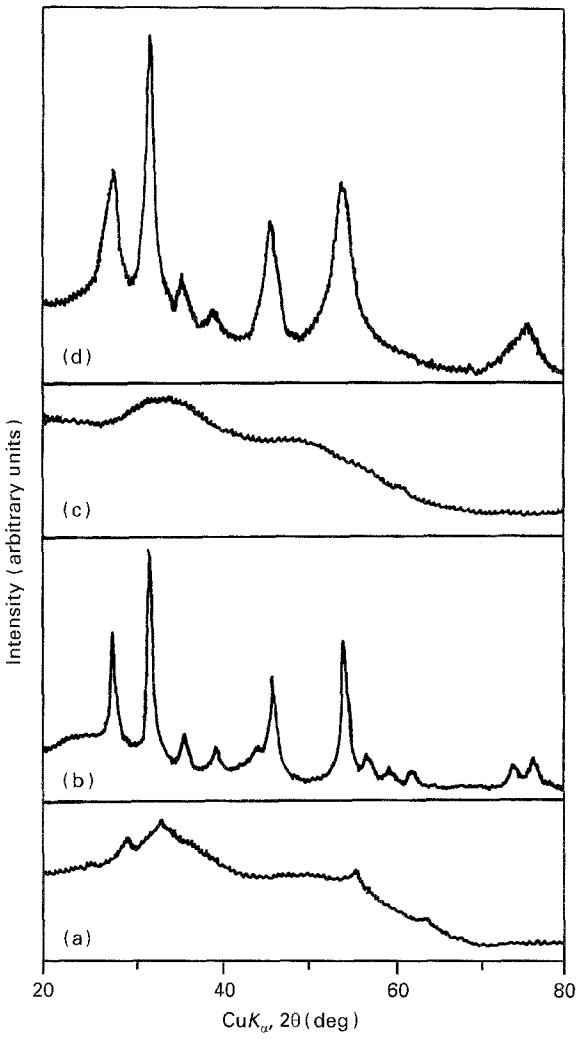

Figure 2 XRD spectra of RuS_2 powder samples: (a) as-dried, water prepared; (b) heat treated, water prepared; (c) as-dried, sulfolane prepared; and (d) heat treated, sulfolane prepared.

treatment. The crystal size is calculated from the half-widths of the XRD peaks using Debye–Scherrer formula [16]. A crystal size of ~ 50 nm is determined for the water prepared RuS_2, which is also supported by the SEM measurements. Comparatively broader peaks observed for sulfolane prepared RuS_2 are quite reasonable if one considers the point that these particles will be of more colloidal nature due to the solvent's stabilizing property, whereas water does not possess this property. Average crystal sizes of ~ 10 nm are determined for the heat treated, sulfolane prepared sample using the above mentioned formula. For the as-dried samples, still smaller crystal sizes could be predicted by comparing the half-widths of the XRD peaks of these samples with those of heat treated powders. Comparatively smaller crystal sizes for the sulfolane prepared RuS_2 colloidal particles compared to those of the water prepared sample could also be confirmed from the XRD spectra of the as-dried powders. Fig. 2c shows that as-dried, sulfolane prepared RuS_2 is more amorphous to XRD than that prepared in water (Fig. 2a). The above results are also supported by the SEM analysis showing that crystal size remains at the submicrometre level even after heat treatment.

3.3. SEM

Scanning electron microscopic analysis showed (Fig. 3) the nature of surface and particle sizes of RuS_2 nanocrystallites, prepared under different conditions. Fig. 3a, b suggests that the crystal sizes are not noticeably changed by heat treatment. Fig. 3c, d shows the real sizes of the nanocrystallites. Crystal sizes of < 50 nm are clearly visible from these micrographs. The large, white particles observed in Fig. 3a–d were identified as sulfur by EDX analysis. In Fig. 3d, the heat treated sulfolane prepared sample shows smaller crystal sizes than the heat treated, water prepared sample (Fig. 3c). This could be understood by the stabilizing property of sulfolane that would lead to the formation of smaller crystallites. This is also confirmed by XRD observations. The most interesting observation is that with the samples after heat treatment. Micrographs of the heat treated samples (Fig. 3c, d) show that the average crystal size is not increased noticeably and remains at the submicrometre range even after heat treatment. This is one of the most important properties that is needed for semiconductor sensitization. Thin films of narrow band-gap semiconductor colloidal particles after coating over wide band-gap semiconductors need heat treatment to increase the stability of these films under different photoelectrochemical conditions [17, 30]. If the heat treatment resulted in growth of these nanocrystallites to larger crystals, that would decrease the contact area between the surfaces of the two semiconductors. This will decrease the electron transfer efficiency from the sensitizer, which in turn will affect the photosensitization efficiency on wide band-gap semiconductors.

3.4. EDX and XRF

Energy dispersive X-ray analysis has been carried out on different areas and with different probe sizes for all the samples prepared. For each sample, an average of at least three different data either by changing the analysing area and/or the probe size was taken. The results are summarized in Table II and a representative EDX spectrum of heat treated, sulfolane prepared RuS_2 powder sample is shown in Fig. 4. As-dried, sulfolane prepared RuS_2 powders showed an Ru/S ratio of 1:2.53. The higher sulfur content in this sample is presumably due to included-solvent molecules. This conclusion is reasonable by looking at the Ru/S ratio of water prepared RuS_2 powder. EDX data for the water prepared sample shows a ratio of $\sim 1:2$ even without heat treatment. After heat treatment, samples prepared in both solvents show a similar ratio confirming the prepared compound as RuS_2. Thin films prepared on glass substrate also show similar results. A higher sulfur content for the sulfolane prepared, as-dried film could be understood with included-solvent molecules, and could also be confirmed by the Ru/S ratio observed for PVA prepared, as-dried film. However, the sulfolane prepared film was unstable during heat treatment on the glass substrate due to physical aggregation of the nanocrystallites. Whereas,

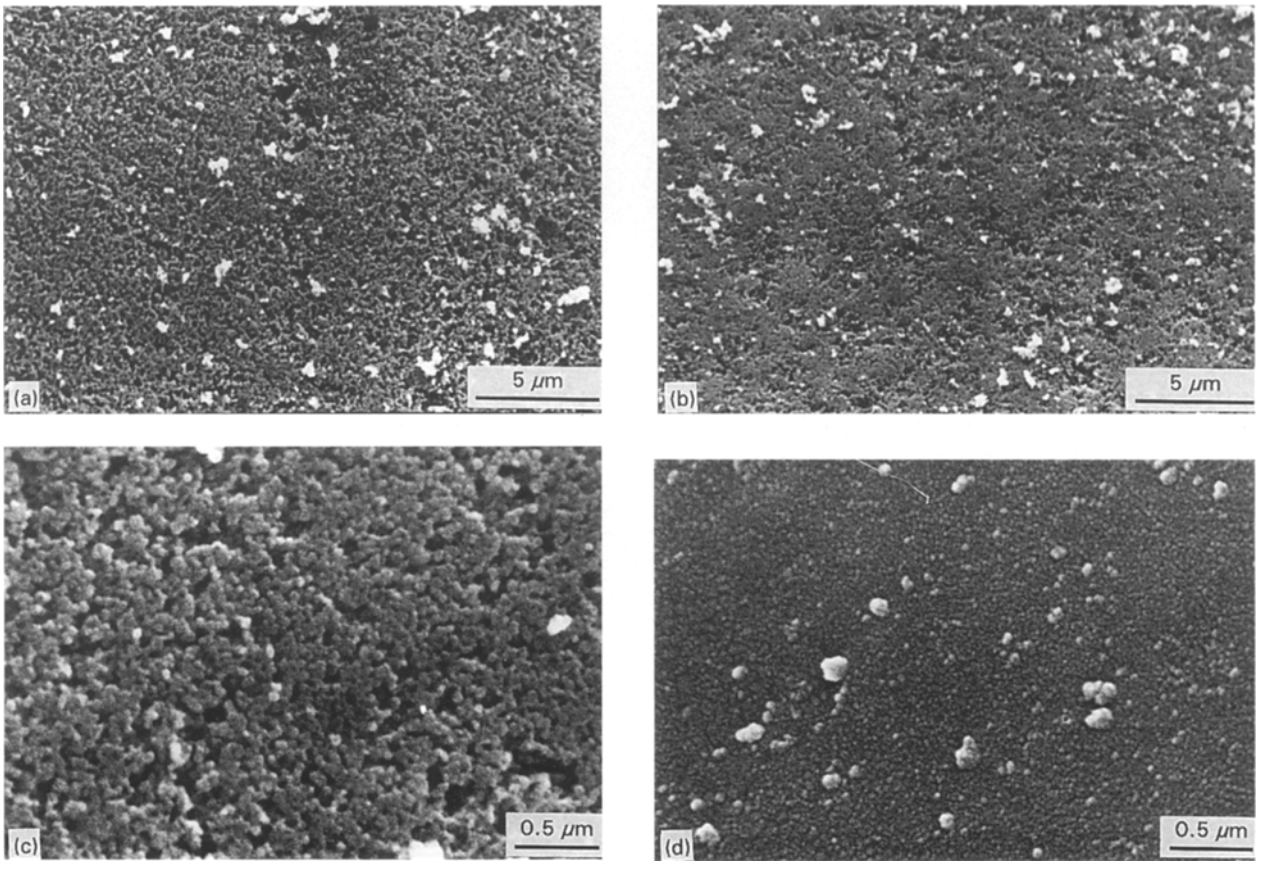

Figure 3 Scanning electron micrographs of RuS_2 powders: (a) as-dried, water prepared; (b) and (c) heat treated, water prepared; (d) heat treated sulfolane prepared.

TABLE II EDX data of RuS_2 samples prepared at different conditions

Solvent	Heat treatment	Ru (at %)	S (at %)	Ru/S ratio
Powder RuS_2				
Sulfolane	No	28.3	71.7	1:2.53
Sulfolane	Yes	33.7	67.3	1:1.96
Water	No	34.9	65.1	1:1.87
Water	Yes	34.7	65.3	1:1.88
Film RuS_2				
Sulfolane	No	26.7	73.3	1:2.75
Sulfolane	Yes	Not stable		
Aqueous PVA	No	32.0	68.0	1:2.13
Aqueous PVA	Yes	43.7	56.3	1:1.29

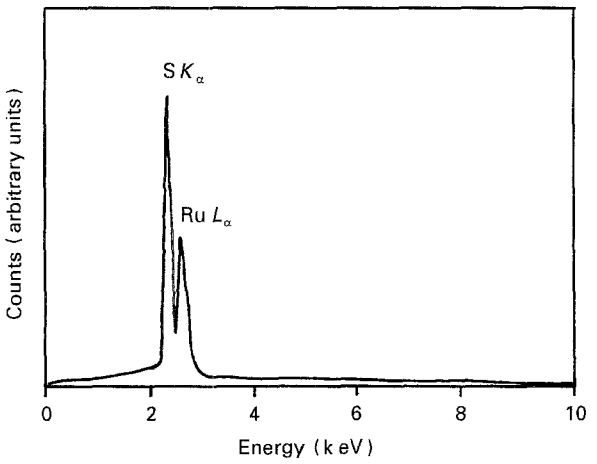

Figure 4 EDX spectrum of heat treated, sulfolane prepared RuS_2 powders.

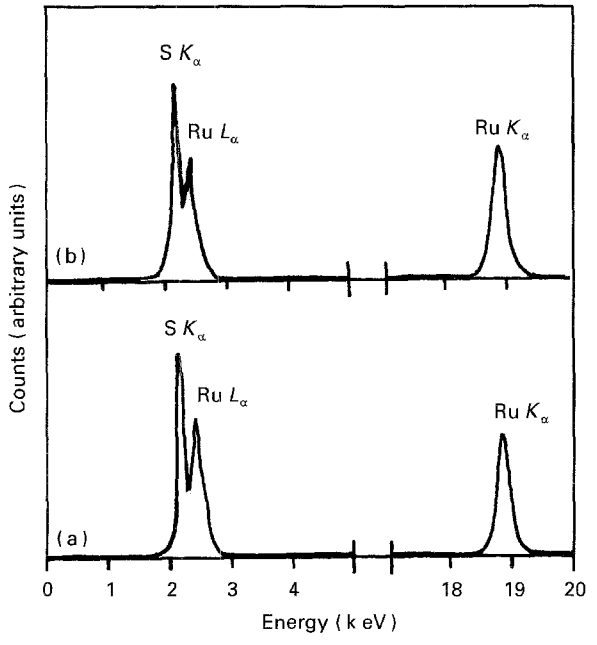

Figure 5 XRF spectra of (a) Ru/S = 1:2 sample prepared by mixing stoichiometric quantities of Ru and S (see text); and (b) heat treated, sulfolane prepared RuS_2 powders.

owing to the good stabilizing property of PVA, films prepared in this medium were stable, even during heat treatment. The low sulfur content for this sample suggests that a part of RuS_2 is oxidized, PVA being an oxygen source at high temperatures. RuS_2 films prepared on TiO_2 and optically transparent electrode (indium–tin oxide–coated glass–ITO) were found to be remarkably stable even after heat treatment. Further analytical details about the physical and photoelectrochemical properties of these electrodes will be published elsewhere [26].

X-ray fluorescence measurement was carried out as an additional analysis to confirm the data of EDX measurements. Elemental ruthenium and sulfur powders were mixed homogeneously in an atomic ratio of 1:2 and used as a reference. XRF spectra of this reference sample and heat treated, sulfolane prepared RuS_2 powders are shown in Fig. 5. The K_α peaks of Ru and S and L_α peaks of Ru are identical for both samples. This measurement supports the EDX measured Ru/S ratio of 1:2 for the black powder samples.

4. Conclusions

Ruthenium disulfide colloidal suspensions and nanocrystallites were successfully synthesized using a new technique at high temperatures. Optical measurement showed their broad absorption in the visible spectral region and the suitability of this material for semiconductor sensitization experiments. XRD measurements showed that the compound prepared using this technique is RuS_2. Scanning electron micrographs showed submicrometre sized RuS_2 crystallites even after heat treatment. Additionally, the observations made from SEM analysis regarding the particle sizes have also been supported by XRD data, confirming the presence of RuS_2 nanocrystallites. EDX and XRF measurements showed Ru/S ratios for different samples prepared and supported the XRD results. Stable films of RuS_2 colloids over wide band-gap semiconductors could also be prepared for semiconductor sensitization experiments [25, 26].

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