



An easy one-pot solvothermal synthesis of poorly crystalline solid ReS₂/C microspheres



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HIGHLIGHTS

- ReS₂/C microspheres were obtained in bulk by a facile one-pot solvothermal synthesis.
- Low-stacking, poorly crystalline ReS₂/C microspheres were produced in mild conditions.
- Aromatic solvents play an important role in the formation of these microspheres.

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ABSTRACT

Dense microspheres consisting of poorly crystalline ReS₂ embedded in carbon were synthesized with a high yield via a facile one-pot solvothermal route, by reacting dirhenium decacarbonyl, elemental sulfur and an aromatic solvent (benzene, toluene or p-xylene) for 24 h at 180 °C. X-ray diffraction (XRD), scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), energy-dispersive X-ray spectroscopy (EDS), Raman spectroscopy, and Fourier transform infrared spectroscopy (FT-IR) techniques were used to characterize the samples. The resulting microspheres were dense, with average diameters between 0.79 and 1.40 μm, had smooth surfaces and were constructed of ReS₂ sheet-like structures with 4.5–9.8 wt % of structural amorphous carbon, which is retained as a textural stabilizer after calcination at 800 °C. The synthesis was repeated using isopropanol and cyclohexane, whose products were agglomerated grains and botryoidal quasi-spherical particles, respectively. A possible formation mechanism of ReS₂/C microspheres was preliminarily presented, in order to clarify the mechanistic differences between the rhenium carbonyl and other transition metal carbonyls used in similar syntheses.

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1. Introduction

Rhenium disulfide (ReS₂) belongs to a class of transition metal dichalcogenides (TMDC) with a layered structure. The robust and rather rigid layers are 2D networks of metal and sulfur atoms bonded by strong ionic–covalent interactions, which in bulk are stacked and held together by van der Waals forces [1]. The peculiar ReS₂ layered structure—in which, contrasting with other TMDC,

there is a Re–Re bond — makes the structure of this sulfide a rhomboidal rhenium cluster framework, comprising Re₄ clusters periodically distributed into a highly anisotropic 2D metal–sulfur matrix [2]. Probable synergy between these structural elements encourages us to extend our research from the chemistry of molybdenum disulfide to that of ReS₂ which, in comparison with other TMDC, has only been scarcely developed until now. ReS₂, like other TMDC is a useful catalyst in hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) reactions, showing higher activity for hydrotreating reactions than that of MoS₂ and WS₂ catalysts [3,4]. Traditionally, rhenium sulfide suspensions incorporating ¹⁸⁸Re have been used in radiotherapy, and it has been demonstrated as an effective radiopharmaceutical for tumor treatment by the

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technique of intralesional therapy, due to its half-life of 16.9 h which minimizes toxicity to the whole body [5]. Rhenium disulfide, alike other TMDC has been synthesized in several morphologies including crystalline layered structures [1,6], inorganic fullerene-like structures [7], colloidal nanoparticles [8,9], as layered compounds supported onto carbon nanotubes [10] and as solid microspheres [11]. The search of spherically-shaped particles of layered metal sulfides has received much attention, among others, because of their anti-wear and friction-reducing properties in lubrication processes [12,13], and efficiency in electrocatalytic reduction of oxygen [14].

There are a number of reports on the synthesis of TMDC with spherical morphology. They have been attained, for instance, by template-assisted solvothermal synthesis [13], or by template-free processes using a transition metal carbonyl and isopropanol as a coordinating solvent. In the latter case, in the synthesis of spherical particles of Mo, Ru, and Rh sulfides, the formation of a colloidal suspension—formed by the interaction of the carbonyl reagent and the solvent—is the key step to obtain homogenous and monodispersed microspheres, whose content of carbon gives them special physicochemical properties [14–16]. Also, it has been established that carbonyl groups, solvents and other carbonaceous species (e.g. glucose or surfactants) may provide carbon during the synthesis process leading in general to TMDC/C composites with special morphologies [17,18]. There, carbon is found intercalated as an amorphous carbon [17], as graphene sheets [19] or replacing sulfur atoms as a carbide on the edges of the TMDC's layers [20].

As far as we know there are only two reports on the synthesis of spherically shaped ReS_2 particles: Chianelli et al. [11] attained to obtain ReS_2 microspheres starting from ReCl_5 in a chemical solution, but in a low yield and more recently, the hydrothermal synthesis of rhenium sulfide microspheres has been mentioned in a patent reporting several TMDC particles, synthesized by solvothermal methods from carbonyl reagents, as catalysts for fuel cells and electrolysis [21]. Here, we report a facile synthesis of ReS_2/C microspheres based on the direct sulfurization of rhenium carbonyl in a standard single-step solvothermal process. An approach to understand the mechanism involved in the formation of this kind of composites is attempted by discussing the effect of the nature of the solvent used in the synthesis on the morphology of the products. The method described in this report could be an easy and effective procedure to obtain encapsulated rhenium in a carbon matrix to be used in medical applications [22], in hydro-treating [11] and lubrication processes [23].

2. Experimental

0.3 mmol of analytically pure $\text{Re}_2(\text{CO})_{10}$, 6.0 mmol of sulfur powder (excess) and about 8 mL of diverse solvents (benzene, cyclohexane, isopropanol, p-xylene and toluene) were put into a Teflon-lined 10 ml stainless steel autoclave and heated in an electrical oven for 24 h at 180 °C and then cooled down naturally giving a black powder. The product was washed twice with both, the reaction solvent and diethyl ether, filtered and dried in vacuum for 10 h. Annealing of the sample prepared in p-xylene was carried out by heating it at a rate of 3 °C per min in a conventional tube furnace under Ar flow at about 20 sccm (standard cubic centimeter per minute) up to 800 °C, and then maintained at this temperature for 1 h.

X-ray powder diffraction (XRD) patterns were obtained by a SIEMENS D5000 powder diffractometer operating at 30 mA and 40 kV, using a $\text{CuK}\alpha$ radiation ($k = 1.54060 \text{ \AA}$). Scanning electron microscopy (SEM) photographs were taken in a SEM LEO 1420VP, Oxford Instruments equipped with EDS. High resolution transmission electron microscopy (HRTEM) were performed using a

JEOL JEM-2100F. Raman spectra were recorded with a Renishaw Raman RM1000 instrument equipped with a 514-nm laser line. Fourier transformed infrared (FT-IR) spectra ($4000\text{--}500 \text{ cm}^{-1}$) were recorded on a Bruker IFS 25 model infrared spectrophotometer. Samples for FT-IR were prepared using the pressed KBr disc technique.

3. Results and discussion

Crystallinity and phase purity of all samples were analyzed by XRD. Diffraction patterns of both, as-synthesized and annealed products are, in general similar to those depicted in Fig. 1a and b respectively, which correspond to samples obtained using p-xylene as solvent. Two weak, broad diffraction peaks, centered at around $2\theta = 13^\circ$ and 39° respectively, are consistent with those expected for an amorphous ReS_2 phase [9]. As shown in Fig. 1b, the crystallinity of the products results clearly improved after annealing and, although still broad, the peaks are sharper and with higher intensities than those observed for the as-prepared samples. The protruding and broad (002) diffraction peak at near $2\theta = 14^\circ$ is indicative of low stacking and highly disordered packing of ReS_2 layers, characteristic for poorly crystalline phases [11]. The shift to a lower angle of the (002) reflection, respect to that in triclinic ReS_2 (JPCD 89-0341), indicates a lattice expansion in the *c*-axis of about 10%. The latter may be attributed to the insertion of a perceptible amount of carbonaceous matter and/or to strain arising from the curvature of sulfide layers [24]. The absence of graphite diffraction peaks indicates that carbon would only be present in an amorphous phase.

The S : Re ratio and the relative amount of carbon in the product obtained by using p-xylene were determined by EDS analysis. Figure S1 shows a S : Re ratio of 2.91 for the as-prepared sample and of 1.59 for its calcined product. Carbon concentration in these microspheres diminishes during the calcination process, from 9.79 to 4.51 wt % of carbon. The low S : Re ratio in the annealed product may be explained by the replacement of deficient sulfur with carbon, as evidenced for similar transition metal sulfides [20].

The amorphous character of carbon and the formation of ReS_2 in

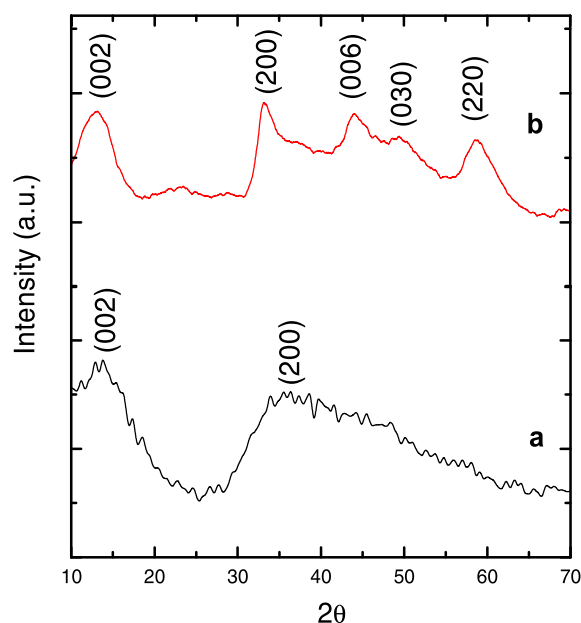


Fig. 1. XRD patterns of a typical sample (a) as-synthesized at 180 °C and (b) annealed product at 800 °C.

the samples is corroborated by Raman spectra (Fig. 2), where no obvious graphitic D and G carbon bands were observed, suggesting that carbon in the microspheres should be amorphous, alike to MoS₂/C microspheres previously reported in similar synthesis conditions [15]. The formation of ReS₂ in the annealed sample was confirmed also by the presence of two characteristic peaks at 157 and 212 cm⁻¹, which correspond to the in-plane (*E_g*) and out-of-plane (*A_g*-like) vibration modes of the ReS₂ layers, respectively. These results agree with the recently reported Raman spectra by Tongay et al. [25]. The slight shift of the peak at 157 cm⁻¹ — in comparison with the 163 cm⁻¹ of the crystalline ReS₂—may arise from the random arrangement of these poorly stacked, and partially bent, layers in these samples.

The chemical nature of the carbonaceous matter in the composites was characterized by infrared spectroscopy. The FT-IR spectra of the microspheres prepared in p-xylene and of its annealed product are shown in Fig. 3. Characteristic bands of the polymerization product of p-xylene (poly-p-xylylene) are found in the as-prepared sample at 1496 cm⁻¹ for aryl carbon stretching, at 1020 cm⁻¹ for aryl hydrogen rocking, two low intensity bands at 2923 cm⁻¹ and 2860 cm⁻¹ for C–H stretching, and in 1445 cm⁻¹ for a C–H₂ bending mode [26]. The conspicuous broad signal in the region between 1000 and 1200 cm⁻¹, found in both the as-prepared and annealed samples, may correspond to an overlapping of a number of bands attributed to carbonaceous species, including some bands associated to poly-p-xylylene [27]. Also, two broad and weak bands around 1936 and 2021 cm⁻¹ are observed, in the as-prepared sample, which are characteristic for rhenium tricarbonyl complexes occurring during the oxidative decarbonylation of the precursor [28]. In the annealed sample, these bands are absent, indicating the complete decarbonylation of the rhenium precursor due to the formation of rhenium disulfide. The barely visible signals between 1500 and 1600 cm⁻¹ can be assigned to the asymmetrical stretching of the C=O and C–O–C of ester groups associated to oxidation products of the polymer, these bands disappear during the annealing process. Clearly, the nature of the carbonaceous matter in the as-prepared sample is mostly polymeric, derived from the polymerization and cross-linking of the aromatic solvents. This

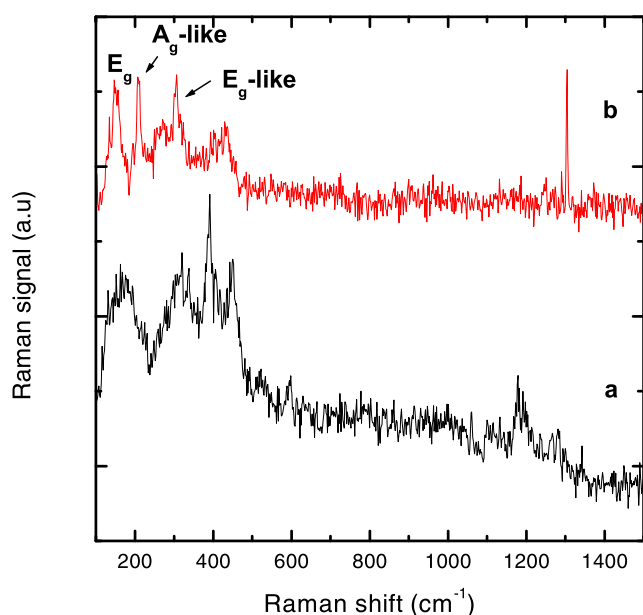


Fig. 2. Raman spectra of ReS₂/C microspheres obtained with p-xylene: (a) as-prepared at 180 °C, (b) annealed at 800 °C.

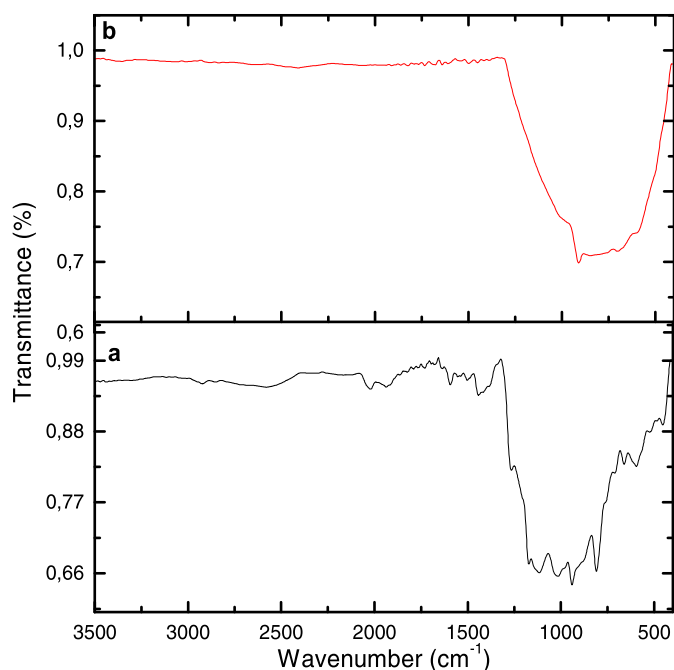


Fig. 3. FTIR spectra of ReS₂/C microspheres obtained with p-xylene: (a) as-prepared at 180 °C, (b) annealed at 800 °C.

polymeric matter may then act as a surfactant, wrapping ReS₂ layers during the microsphere synthesis. Further carbonization of these polymers —to amorphous carbon— occurs during the annealing process.

Fig. 4 shows SEM images of bulk samples prepared in p-xylene; they consist entirely of discrete and smooth microspheres with diameters in the range 0.4–2.8 μm. During the annealing process at 400 °C the microspheres conserve their shape and size, notwithstanding at 800 °C of treatment, the spheres tend to lose structural integrity, slightly shrinking in the process; this is mainly due to the loss of carbonaceous material and to the growth of the basal planes of the rhenium sulfide crystallites (Fig. 4a–c). SEM analysis of a broken sphere (Fig. 4d) clearly exhibit structural homogeneity, lacking internal stratification, and ruling out radial or concentric atomic internal arrangement within the spheres. As evidenced by HRTEM (Fig. 4e, f), samples of as-prepared in p-xylene ReS₂/C microspheres have a dense microstructure with well-defined and unclosed borders. HRTEM of the corresponding annealed sample (Fig. 4f) shows clearly a growth of the ReS₂ layers, showing some curved layers in a random arrangement. The distance between the layers (0.657 nm) measured in HRTEM images (Fig. 4f) concurs with the (002) interlayer expansion distance measured by XRD analysis.

SEM images of the microspheres prepared in different solvents are shown in Fig. 5. It is clearly evident that the chemical nature of the solvent influences the spherical morphology, where perfectly-spherical, uniform and discrete particles are only obtained with aromatic solvents. By counting a minimum of 300 particles, the average SEM diameter of microspheres is 0.79 μm, 1.31 μm and 1.40 μm, for the products prepared with toluene, benzene and p-xylene, respectively. In samples prepared with isopropanol the morphology shows almost only botryoidal arrangements of spherical ReS₂/C particles, with just a few discrete microspheres, whose formation can be explained by alcoholic condensation with further agglomeration of carbonaceous matter, in agreement with the mechanism proposed by Tao et al. [15]. Contrasting with the preparation with aromatic solvents, the synthesis using

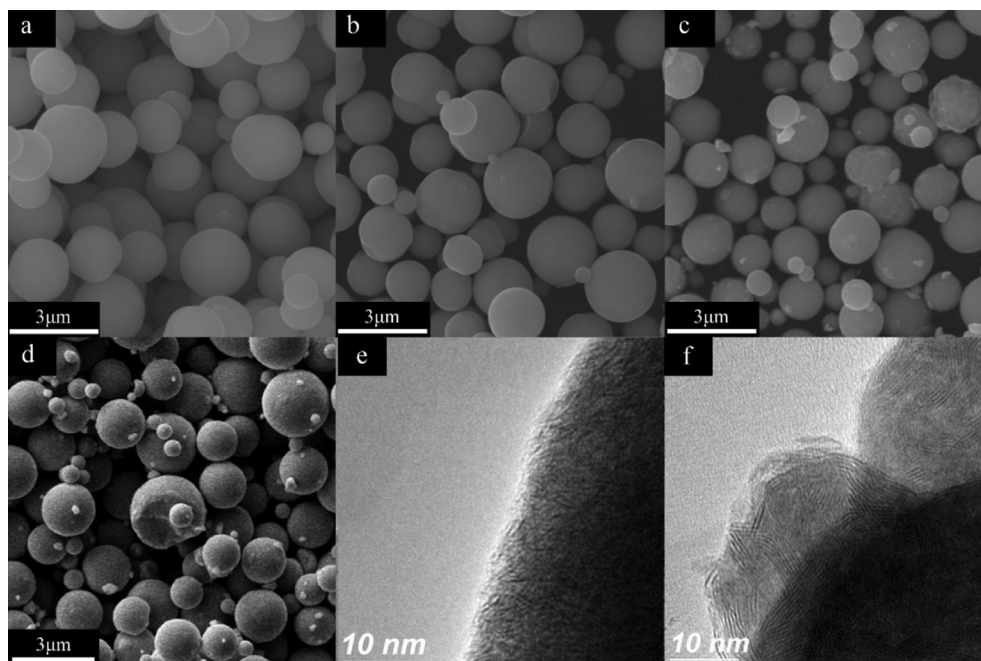


Fig. 4. SEM images of ReS_2/C microspheres synthesized in p-xylene: (a) as-prepared, (b) after annealing at $400\text{ }^\circ\text{C}$ for 0.5 h, (c) after annealing at $800\text{ }^\circ\text{C}$ for 1 h, (d) a broken sphere, (e) HRTEM of as-prepared microsphere, (f) HRTEM image of annealed product at $800\text{ }^\circ\text{C}$ (e).

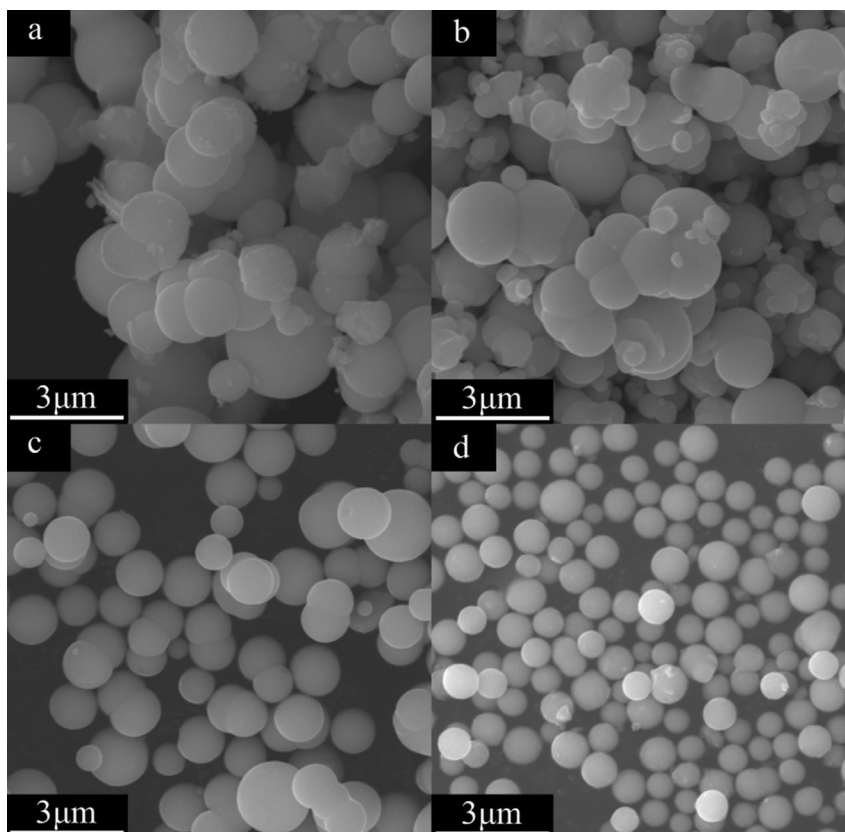


Fig. 5. SEM images of ReS_2/C microspheres prepared with; (a) isopropanol; (b) cyclohexane (c) benzene; (d) toluene.

cyclohexane produced mostly quasi-spherical grains and agglomerates with botryoidal arrangements (Fig. 5b). We can infer in this last example that the amount of carbonaceous matter provided by

the solvent is not enough to reach the saturation concentration, leading to a non-uniform collection of particles.

Taking into account our experimental results, the possible

formation process of the ReS_2/C under one-pot solvothermal conditions could be explained as follows (Fig. 6). On one hand, ReS_2 crystallites are produced by oxidative decarbonylation of $\text{Re}_2(\text{CO})_{10}$ with elemental sulfur in a solvothermal process [7]. On the other hand, and simultaneously, the chemical reactions of the aromatic solvents, under solvothermal conditions, involved polymerization and condensation, leading to the formation of heavy hydrocarbon droplets, which serve as the basis of microspherical structure [29]. These agglomerations of organic matter, whose size is related to the chemical nature of the aromatic hydrocarbons (provided by the solvent), encapsulate the polar rhenium sulfide clusters, scaffolding the spherical morphology of the as-prepared sample. It has been previously reported that carbonaceous matter wrap transition metal sulfides crystallites directing the formation of diverse exotic morphologies [15,18,30]. Particularly, in this reaction, the aromatic solvents are essential to assemble the spherical structure, playing as a fundamental source of carbonaceous matter, derived from its polymerization. In this mild conditions, the $\text{Re}_2(\text{CO})_{10}$ acts as a catalyst, promoting the polymeric reaction, which generally occurs over 600°C (polymerization by pyrolysis of p-xylene) [29, 31]. This can be explained as rhenium carbonyl complexes have been used to promote catalytic polymerization of aromatic rings by formation of new C–C bonds [32]. In these microspheres, the ReS_2 crystallites are randomly dispersed in the carbonaceous matrix which, in turn, prevents the growing and stacking of ReS_2 layers, and keeps the spherical organization after annealing.

4. Conclusions

Dense and poorly crystalline ReS_2/C microspheres were successfully produced from $\text{Re}_2(\text{CO})_{10}$ and sulfur powder in a solvothermal process at 180°C , using benzene, p-xylene and toluene. They were also further calcinated at 800°C , retaining their morphology and improved crystallinity after annealing. The ReS_2/C microspheres, with average diameters between $0.79 - 1.40\ \mu\text{m}$, had smooth surfaces and were constructed by randomly orientated nanosheet-like ReS_2 structures. The microspheres contained between $4.5 - 9.8\ \text{wt}\%$ of amorphous carbon, acting as a structural stabilizer. Results indicate that the microspheres are preferentially obtained with aromatic solvents, while preparations in isopropanol and cyclohexane did not produce discrete particles.

In this work, we show a possible mechanism for the formation

of ReS_2/C microspheres, where $\text{Re}_2(\text{CO})_{10}$ promotes the polymerization of the aromatic solvents for further condensation to a carbonaceous matter, which is essential for the assemblage of the spherical particles. Thus, the catalytic nature of $\text{Re}_2(\text{CO})_{10}$ allows the incorporation of carbonaceous matter to the synthesis of the microspheres in a mechanism of solvent polymerization.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.matchemphys.2014.12.012>.

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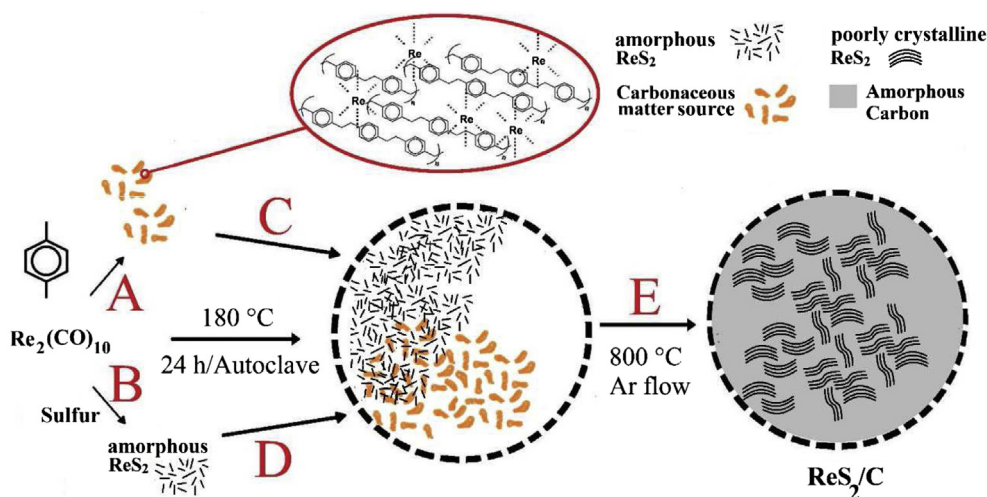


Fig. 6. Scheme of possible formation mechanism of ReS_2/C microspheres prepared by solvothermal synthesis. (A) Polymerization of solvent/Condensation of carbonaceous matter, (B) Oxidative decarbonylation, (C) Decomposition/Amorphous carbon source, (D) Loss of CO/Carbonaceous matter source, (E) Carbonization/Annealing.

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