Synthesis of highly destacked ReS$_2$ layers embedded in amorphous carbon from a metal-organic precursor

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**Abstract**

In the current study, a new approach to the synthesis of highly destacked ReS$_2$ layers embedded in amorphous carbon via the thermal decomposition of a tetraoctylammonium perrhenate precursor, under sulfidizing atmosphere (15% v/v H$_2$S mixture H$_2$S/H$_2$ gas), is described. X-ray diffraction, scanning electron microscopy, scanning transmission electron microscopy, energy-dispersive X-ray spectroscopy and X-ray photoelectron spectroscopy analysis of the thermolysis product confirm the formation of rhenium disulfide. The synthesized compound is found as single layers with a minor proportion of few-layer arrangements, embedded in amorphous carbon. X-ray diffraction, UV–visible diffuse reflectance, and thermogravimetry analysis were made in order to characterize the metal-organic salt precursor, showing that the perrhenate ions are dispersed widely from each other in the matrix of the organic cations, forming an inorganic–organic salt. The special arrangement of these ReS$_2$ layers has a potential use as a heterogeneous catalyst due to the high proportion of edge sites.

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**1. Introduction**

Rhenium disulfide (ReS$_2$) is a transition metal dichalcogenide (TMDC), composed of S-Re-S 2D layers stacked and held together perpendicularly to the layer plane by van der Waals forces [1]. One of the most remarkable characteristics of the solid ReS$_2$ is the low interaction energy between layers and the direct band gap value near to that of a single layer [2,3]. The typical high anisotropy of this layered compound in particular is further increased by the unique feature of presenting an intralayer Re—Re bond, and improving in-plane anisotropic transport and optical properties to thin 2D layered ReS$_2$ materials [4]. Even when this is one of the least studied TMDCs, ReS$_2$ has recently called the attention because the vibrational and optical properties of their bulk behaves like individual monolayers, which strongly contrast with the properties of other TMDCs like MoS$_2$ and WS$_2$ [2,5]. The chemistry of ReS$_2$ is still incipient, however it has been used as a catalyst in hydrotreating reactions [6], as an electrocatalyst in hydrogen evolution reactions [7], in radiation synovectomy [8], in field effect transistors [9] and in high current density lithium ion batteries [10]. Until now, various ReS$_2$ structures have been attained in a relatively controllable way by methods of solid-state and soft chemistry using an appropriate selection of precursors, solvent, additives and/or reaction conditions [11–13].

Poorly-crystalline TMDC-based nanostructured products with high surface area have been obtained using the strategy proposed by Alonso et al. [14,15] using tetraalkylammonium thiometallates (M = Mo or W) as a source of both metal and carbon. In these compounds the stacking along the c-axis of the sulfide layers is prevented in a certain grade by the carbon component, leading to more amorphous materials. Concerning rhenium sulfide in particular, as far as we know, there is only one report dealing with the synthesis of rhenium disulfide using tetraethylammonium thioperrhenate as a precursor (Et$_4$N)ReO$_4$; however the structural characterization of the product and possible effects of the carbon component involved in the synthesis were not reported at the time [16]. Herein, we present a facile new approach for the synthesis of ReS$_2$/C nanocomposites by direct sulfidization (H$_2$S/H$_2$) of a bulky perrhenate metal-organic salt (Oct$_4$N)ReO$_4$; the isolation of the perrhenate ions in the organic cation matrix modulates the sulfidizing
reaction, leading to rhenium sulfide layers embedded in a carbonaceous medium with small sizes and high exposure of the edges sites.

2. Experimental details

2.1. Preparation of ReS$_2$/C

Ammonium perrenate NH$_4$ReO$_4$ (6.0 mmol) was dissolved in water (30 ml), and this solution was added to 6.0 mmol of tetra-n-octylammonium bromide (Oct$_4$N)Br which was previously dissolved in a solution of 10 ml of water and 5 ml of ethanol at 70 °C. A white precipitate was immediately formed by an ionic exchange reaction; this white powder was washed with distilled water and let dry at room temperature. To obtain the rhenium sulfide monolayers, the precursor was decomposed under a reductive atmosphere; (Oct$_4$N)ReO$_4$ was placed in a tubular reactor, heated up to 400 °C at 2 °C/min under a flow of H$_2$/S$_2$ (15%) in hydrogen gas, and kept under these conditions for 4 h. The sample was then cooled down naturally at room temperature.

2.2. Materials characterization

X-ray diffraction patterns (XRD) were obtained by a Philips X’pert MPD powder diffractometer operating at 30 mA and 40 kV, using CuKα radiation (k = 1.54060 Å). Scanning electron microscopy (SEM) images were taken in a JEOL JIB 4500 electron microscope operated at 15 kV. Scanning transmission electron microscopy (STEM) and energy-dispersive X-ray spectroscopy (EDS) were conducted using a JEOL 2000FS operating at 200 kV. Differential thermal gravimetry (TG) and thermal gravimetry (TG) measurements were carried out on Q600 TA instrument; the sample was heated under a helium atmosphere at a rate of 10 °C/min to 800 °C. UV–vis diffuse reflectance spectrometry (DR) were recorded by a CARY 300 SCAN VARIAN spectrophotometer. X-ray photoelectron spectra (XPS) of sulfide catalysts were carried out in a SPECS GmbH custom made system using a PHOBIOS 150 WAL hemispherical analyzer and a μ-FOCUS 500 X-ray source. All data was acquired using monochromated AlKα X-rays (1486.6 eV, 110 W), pass energy of 50 eV and high-intensity lens mode. The diameter of the area analyzed was 0.88 mm. The pressure in the analysis chamber was maintained lower than 2 × 10$^{-9}$ mbar.

3. Results

3.1. XRD analysis

The XRD pattern of the product as-prepared by the thermal decomposition of (Oct$_4$N)ReO$_4$ under H$_2$/H$_2$S atmosphere is shown in Fig. 1. The diffractogram shows two broad low-intensity diffraction peaks centered on 2θ = 33° and 44°, which can be indexed as the Bragg reflections (200) and (006) of layered ReS$_2$ (JCPDS 89-0341). The shape of the diffractogram is the typical one of a poorly-crystalline ReS$_2$ phase [18]. The conspicuous absence of the (002) peak at 2θ = 14.5° points out an extremely low stacking degree along the crystallographic c-axis of the ReS$_2$, characteristic of monolayered structures [19].

3.2. Morphology and composition

The morphology of the product was examined by scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM). The sample is composed by microscopic irregular grains (Fig. 2a), with diameters between 0.1 and 2.0 μm. However, a closer analysis shows that the grains appear to be formed by agglomeration of sub-micrometric platelets. The STEM images of the product reveal a higher proportion of poorly stacked nanosheets with random orientation (Fig. 2b). In Figs. 2b–c we can detect a few thin arrangements of some stacked layers along the c-axis with an average interplanar distance of 0.62 nm. The latter is corroborated by the diffuse diffraction rings observed in the corresponding selected area electron diffraction (SAED) patterns (inset Fig. 2b). A quantitative layer length was obtained through statistical analysis based on 400 layers taken from different parts of the STEM images; the longitudinal slab length of the layers account in average approximately 4.81 nm ± 1.52 nm in length (Fig. 2d). An estimation of the composition of the product was attempted by energy-dispersive X-ray spectroscopy (EDS). As observed in Fig. 5, the sample contains rhenium, sulfur, and carbon; however a significant amount of oxygen is also detected. The analysis reveals a S:Re ratio of about 1:1.55, and carbon and oxygen contents of about 35.2% and 31.4% at. respectively.

The composition of the product was also investigated by X-ray photoelectron spectroscopy. The spectra in Figs. 3a and 3b corroborate the presence of ReS$_2$ in the sample. Fig. 3c and Fig. S2 shows the XPS spectra in the regions of rhenium, sulfur and carbon. Indeed, peaks at 41.9 ± 0.1 eV (Fig. 3a) and 162.7 ± 0.1 eV (Fig. 2Sb) that are respectively characteristic for Re 4f$_{5/2}$ and S 2p$_{3/2}$ electrons in the ReS$_2$ are clearly observed [20,21]. However, the rhenium spectrum (Fig. 3a) also reveals the presence of other photogenerated Re electrons with higher relative binding energies. The deconvolution of three additional doublets on the rhenium curve (Fig. 3a) indicate the presence of oxides on the surface of...
the sample; traces of ReO$_2$ (43.5 ± 0.1 eV), ReO$_3$ (45.7 ± 0.1 eV) and Re$_2$O$_7$ (46.6 ± 0.1 eV) respectively for Re 4f$_{4/7}$ [22,23]. Moreover in the sulfur spectrum (Fig. S2a) an emission attributable to sulfate is also apparent (169.2 ± 0.1 eV). The spectrum of carbon (Fig. S2b) shows in turn the typical shape of carbonaceous materials where emissions assignable to several organic groups, aromatic C=C (284 ± 0.1 eV), aliphatic C=C (285 ± 0.1 eV) and hydroxyl carbon C=O (286.1 ± 0.1 eV) can be identified [24].

3.3. Spectroscopic and thermal study of the precursor

The peculiar arrangement of ReS$_2$ nanosheets communicated in this paper is clearly determined by the nature of the rhenium precursor used in the synthesis. In order to rationalize our results, a more detailed study of the (Oct$_4$N)ReO$_4$ was undertaken. The Fig. 4(a) shows the diffuse reflectance spectra of NH$_4$ReO$_4$ and (Oct$_4$N)ReO$_4$; ammonium perrhenate is used as reference, showing a single absorption band at ~275 nm, product of the ReO$_4$$^-$ units, while that of the octylammonium derivative is centered at 251 nm. This high energy shift is indicative of isolated and distorted ReO$_4$ units [25].

Fig. 4(b) shows the TGA–DTG curves of the precursor (Oct$_4$N)ReO$_4$; the 2% weight loss in the range of 190°–260° corresponds to the evaporation of water and other volatile impurities trapped in the material. The second and most important weight loss of 64.9% (theoretical 65.1 wt%) observed in the range of 270°–370° is assigned to the thermal decomposition of tetraoctylammonium. The single-step decomposition of the tetraoctylammonium cation agrees with results reported by Alonso et al. [14], while the weight loss in the range 350–450 °C may correspond to the volatilization of a small amount of Re$_2$O$_7$, arising from the thermal dehydration of perrhenic acid generated by the presence of water and
by the concomitant formation of ReO$_2$ species. The remaining solid corresponds to residual ReO$_2$ [26].

3.4. XRD analysis of the precursor

Fig. 5 shows the XRD pattern of ammonium perrhenate (Fig. 5a) and of synthesized tetaoctylammonium perrhenate (Fig. 5b). Diffractograms indicate that (Oct$_4$N)ReO$_4$ crystallizes in a scheelite-like structure similar to that of the NH$_4$ReO$_4$ reported by Swaison et al. [27], but much more expanded, due to the large size of the tetraoctylammonium cation. All diffraction peaks (Fig. 5b) can be indexed as a pure tetragonal structure with a space group of $I_4$/$a$, with unit cell parameters $a = b = 17.971$ Å and $c = 37.337$ Å ($\alpha = \beta = \gamma = 90$). The lattice sample parameters were obtained with the general lattice analysis system program CHECKCELL. Although both perrhenate salts, the ammonium and the tetaoctylammonium ones have similar crystallographic structures; in the latter, the connectivity among perrhenate species results rather peculiar. In the scheme of Fig. 6 the structure of the metal organic salt is represented showing the preferential (011) plane in the proposed reaction.

4. Discussion

Strategies leading to the synthesis of TMDC-based catalysts, avoiding crystallization extensive processes are in general important in order to enhance the concentration of active sites [28]. The catalyst dispersion in carbon matrices has proved to be a valuable approach for preparing numerous products based on sulfides of molybdenum [14] or rhenium sulfides [29]. The aim of this work was to produce ReS$_2$/carbon composites with high proportion of edges sites using the carbon-rich rhenium-precursor tetaoctylammonium perrhenate, (Oct$_4$N)ReO$_4$.

The direct reductive sulfidization of solid tetaoctylammonium perrhenate with the gaseous mixture 15% H$_2$S in H$_2$ at 400 °C leads to the formation of ReS$_2$ and carbonaceous matter. The XRD pattern of the product indicates that the ReS$_2$ is formed in a highly amorphous state; as expected for these materials, the two Bragg reflections at $2\theta = 33^\circ$ and $44^\circ$, characteristic for layered ReS$_2$, are observed as broad, low-intensity peaks [18]. However, it results rather remarkable that none of the typical low-angle (00l) reflections, typical of layered TMDC, are observed. Thus, this points to a product where the layer stacking is highly inhibited. This feature was corroborated by the electron microscopy analysis of the sample; indeed, STEM images show that the sample contains highly disordered and bent ReS$_2$ nanosheets. Most of the rhenium disulfide is represented by single layers, with a minor proportion of a few-layer arrangements, where the layers are stacked with a d-spacing (d002) of 0.62 nm, in agreement with the d-spacing for crystalline ReS$_2$ (JCPDS 89–0341). This also agrees with SAED measurements leading to a diffuse (002) ring.

The XPS analysis of the sample corroborated the formation of ReS$_2$. Additionally, these spectra revealed that the sample also contains rhenium oxides, namely ReO$_2$, ReO$_3$ and Re$_2$O$_7$ (by the deconvolution of three additional doublets), as well as carbonaceous matter. This agrees with the composition of the sample estimated by EDS. Since XRD data does not show any reflection assignable to these oxides, they may be found as amorphous phases, either dispersed in the bulk or adsorbed within the ReS$_2$-carbonaceous composite.

In both cases the formation of oxide phases may be explained by considering some particularities of the synthesis method used for producing this composite. We can distinguish two processes involving the formation of oxides. On one side, a surface process associated with the sulfidization of the rhenium precursor by using hydrogen in the sulfidizing mixture (H$_2$S/H$_2$) implies the formation of low-valence rhenium species, as well as of sulfur-deficient ReS$_2-x$ [23]. These metastable, highly reactive intermediates are very susceptible to oxidation, so that they could react with air to produce stable rhenium oxides at sample surface while manipulation. On the other side, the presence of oxides in the bulk could arise from an incomplete sulfidization process due to a shielding phenomenon [30]. Independently of complexities inherent to the solid-gas reaction used here — among them the formation of rhenium oxidized species already discussed — the morphology of the as-synthesized ReS$_2$ deserves further attention. The known trend of ReS$_2$ to produce disordered phases with low stacking degree is expected to further increase the disorder when inserted in a carbonaceous matrix. However, to the best of our knowledge, the preparation of ReS$_2$ solid phases with a distacking degree like the one described here has not been reported until now, even in other preparations of ReS$_2$/C nano-composites [16,31]. Therefore, we propose that the high dispersion of...
the sulfide layers is a consequence of the nature of the precursor (Oct4N)ReO4; particularly due to its alkylc component, which leads to the concomitantly formation of carbonaceous matter during the thermal decomposition. In that direction we undertake a somewhat more detailed study of the precursor (Oct4N)ReO4. Hypothesizing that the peculiar effect of this salt on ReS2 morphology (destacked small layers) is mainly due to the voluminous tetraalkylammonium cation, we centered our attention in the structure, stability, and interactions of (Oct4N)ReO4 in the solid state in comparison with those of the (NH4)ReO4.

The diffraction pattern of the (Oct4N)ReO4 can be indexed as a Scheelite-like structure, similar to that reported for the NH4ReO4 in the literature [32]. In spite of the similitude of both structures, the expansion caused by the volume of the tetraalkylammonium cation changes significantly the connectivity among the perrenenate anions. Contrasting with the NH4ReO4 where the distance between two perrenenate ions is 5.36 Å, in the metal organic salt these ions are much more distant from each other 16.38 Å along the (011) plane (Fig. S3). In both compounds the high energy shift is in agreement with the XRD patterns and they indicate isolated anions due to the spacing effect of the tetraalkylammonium cation. ReO4\(^{-}\) anions are enough apart restricting the diffusion during the reaction. The role of (Oct4N)ReO4 in modulating the morphology of obtained ReS2/C composite may be rationalized at the light of the properties of the precursor already commented. We assume that the mechanism of sulfidization of this precursor is similar to that of the NH4ReO4 [28]; i.e. an initial condensation of ReO4\(^{-}\) units to produce Re2O7 clusters followed by their reaction with H2S for generating the ReS2 layers. Consequently, the growth of products, intermediary and final, is expected to be mainly modulated by the mobility of the ReO4\(^{-}\) ions in the precursor.

This synthesis strategy resembles the use of liquid ions to synthesize inorganic nanomaterials with special morphological properties; for example in the preparation of ZnSe hollow nanospheres using a quaternary ammonium liquid ionic [32]. However, it differs in that the reaction described here occurs in a solid state. Moreover, though tetraalkylammonium salts have been used for designing ionic liquid analogues, these salts are not themselves liquid ionic. Therefore, we suggest that the mobility of the ReO4\(^{-}\) ions, required for their condensation into Re2O7 crystals, arises from the behavior of the Oct4N as ionic plastic crystal. The short-range structural disorder in these materials typically associated with rotational and/or configuration changes of the ions, enhances ion mobility beyond the steric hindrances and electrostatic interactions common in normal ionic compounds. These effects should gradually increase with increasing temperature until the precursor decomposes to produce carbonaceous materials.

Thus, the high confinement degree of the perrenenate anions in the (Oct4N)ReO4 demonstrated above, together with the ionic plastic nature of this salt, explains satisfactorily the small size of the ReS2/C particles observed. Additionally, the concomitant formation of carbonaceous material by thermal decomposition of the metal-organic precursor, would further limit the agglomeration Re2O7-crystallite as well as the stacking of ReS2 sheets.

5. Conclusions

Highly destacked ReS2 layers dispersed in amorphous carbon were successfully obtained from the decomposition of (Oct4N)ReO4 at 400 °C, sulfidized under a reductive atmosphere. (Oct4N)ReO4 was previously synthesized via an anionic exchange reaction of (Oct4N)Br and NH4ReO4. The ReS2/C product consists in randomly oriented and poorly stacked layers of rhenium disulfide — with a large proportion of edge sites — embedded in amorphous carbon. The sample contained about 35 at.% of amorphous carbon, derived from the decomposition of the tetraoctylammonium cation; this carbonaceous matter hinders the further stacking between the rhenium sulfide layers and its growth. The special arrangement of these ReS2 layers has a potential use in hydrodesulfurization catalysts and opens the path to the preparation of new rhenium complexes by changing the size of the alkylammonium group, in comparatively mild-energy solvothermal synthesis processes.

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Appendix A. Supplementary data

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References
