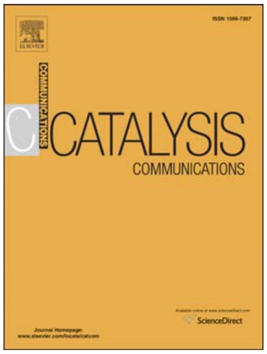

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Sulfur-doped graphene as metal-free carbocatalysts for the solventless aerobic oxidation of styrenes

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Abstract

Pyrolysis of λ–carrageenan at 1000 °C and subsequent exfoliation leads to a S-doped graphene [(S)G]. Increasing pyrolysis temperature to 1200 °C or the use of other carrageenans with lower sulfate content result in the failure of S doping. XPS confirms the presence of S atom (4.5 %) with environments alike to sulfide and sulfoxide. (S)G promotes the aerobic oxidation of styrenes to their corresponding benzaldehydes accompanied by lesser amounts of styrene oxide. In contrast, under the same experimental conditions reduced graphene oxide exhibits a negligible activity. (S)G was reused with almost coincident catalytic performance.

Introduction

For the sake of sustainability, availability and affordability, there is a considerable interest in developing metal-free catalysts.[1-8] Graphene (G) and related materials hold considerable promise as metal-free catalysts,[9-15] due to the combination of the unique features of single-layer sp^2 carbons with the possibility to design active sites on it.[16-19] Doping of G with heteroatoms has been found to be a general way to introduce catalytic activity for a range of reactions,[16] including aerobic oxidation of benzylic hydrocarbons and of electron rich alkenes.[20] Recently, we have reported that N- and B-doped Gs can promote the aerobic oxidation of styrene to a mixture of benzaldehyde and styrene oxide.[20] Continuing in this line of research it would be of interest to determine if doped Gs having other heteroatoms also exhibit activity as catalysts of aerobic oxidation of hydrocarbons.

Specifically in the present work we report a convenient procedure for the preparation of S-doped G [(S)G] and it will be shown that this doped G can promote the aerobic oxidation of styrene. In an earlier precedent we have disclosed that pyrolysis of chitosan in the absence of oxygen and subsequent exfoliation of the resulting graphitic carbon residue renders N-doped G [(N)G].[21] The advantages of this process is that chitosan, a polysaccharide of glucosamine, acts as single source of C and N in the process and N-doping occurs simultaneously with the formation of the G sheet. During the pyrolysis, a fraction of the N atoms of the chitosan amino groups become incorporated into the G layer in three different types of N dopant and in a percentage that decreases as the pyrolysis temperature increases in the range from 900 to 1200 °C.

A logical extension of the preparation of (N)G will be to test if other natural polysaccharides containing heteroatoms can similarly act as precursors of doped G. Carrageenans are linear, high-molecular weight polysaccharide of galactose having sulfate groups. Therefore, they are obvious candidates to become precursors of (S)G that subsequently could be tested as oxidation catalyst. The convenient preparation of (S)G shown below constitutes another example of the methodology that uses pyrolysis of natural biopolymers for the preparation of Gs.

Experimental Section

Preparation of (S)-G

There are three main types of carrageenans commercially available, but it was found that λ-carrageenan with the highest S content is the only one that according to XPS renders after pyrolysis G materials doped with S. λ-Carrageenan (Sigma Aldrich ref. 22049) was pyrolized in argon atmosphere heating at 200 ^{o}C for 2 h and then heating at 10 ^{o}C/min up to 1000 ^{o}C for 6 h. The resulting graphitic powder was sonicated at 700 W for 1 h in water to obtain dispersed (S)G suspensions. This method of preparing doped Gs from pyrolysis of natural polysaccharides was reported previously by our group to obtain N- and B-doped Gs.[21] Two different temperatures were tested (1000 and 1200 ºC) and only the G sample pyrolyzed at 1000 ºC was doped. It is a general observation that the percentage of dopant heteroatoms in doped G prepared by pyrolysis decreases as the pyrolysis temperature increases.[21]

Characterization techniques

FT-Raman spectra were recorded at ambient temperature with 514 nm laser excitation at 2 mW power by using a Renishaw In Via Raman spectrophotometer equipped with a CCD detector. TEM images were recorded in a Philips CM300 FEG system with an operating voltage of 100 kV. XP spectra were recorded on a SPECS spectrometer equipped with a Phoibos 150 9MCD detector using a non monochromatic X-ray source (Al and Mg) operating at 200 W. The samples were evacuated in the pre-chamber of the spectrometer at 1×10^{-9} mbar. The samples have been activated *in situ* in nitrogen flow at 450 °C for 3 h followed by evacuation at 10^{-8} mbar. Deconvolution and fitting of the experimental peaks were carried out after nonlinear Shirley-type background subtraction and peak correction by the transmission function of the spectrometer. Combustion elemental analyses were measured using a Perkin-Elmer CHNOS analyzer. The detection limit of the technique was 10 ppm.

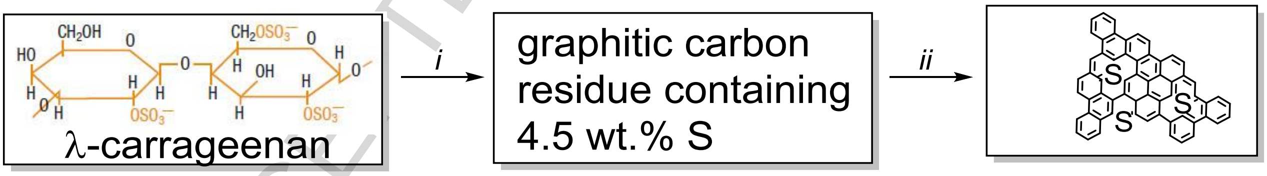
Experimental procedure for aerobic oxidation

A 3 mL microreactor was charged with the catalyst (10 mg), followed by the addition of substrate (1 mL). The resulting slurry was sonicated for 30 min (700 W, horn sonicator). The reaction was carried out under magnetic stirring by heating the suspension at 100 ^{o}C in most of the experiments or the indicated temperature using a preheated thermostated oil bath. This reaction mixture was maintained with oxygen atmosphere. The course of the reaction was periodically monitored by analyzing the sample with GC. An aliquot of 1 µL of the reaction mixture was taken at different time intervals with a syringe, diluted with 0.1 mL of acetonitrile and filtered throughout a 0.2 µm Nylon filter prior to GC injection and analysed immediately without delay to minimise possible on-going room temperature oxidations. The mass balances of the reaction mixture accounted for more than 96 % of the initial substrate, as estimated by GC using nitrobenzene as the external standard. The yields of the product were determined by using nitrobenzene as the external standard considering the response factors unity. The reaction products were further confirmed by GC-MS and co-injecting with authentic samples.

Results and discussion

Scheme 1 summarizes the pyrolytic procedure followed in the preparation of (S)G. Combustion chemical analysis of the three commercial K, I and λ carrageenan samples differing in the number of sulfate groups per disaccharide unit, one two or three, respectively, shows that only the residue from λ-carrageenan having the maximum sulfate content pyrolysed at 1000 ^{o}C contains S. The elemental analysis of (S)G was 80.8 % C and 4.5 % S. The presence of some residual percentage of N (0.2 %) and H (0.3 %) was also detected.

When λ-carrageenan was pyrolysed at 1200 °C, no S was detected. Pyrolysis under inert atmosphere leading to G are strongly reducing conditions.[22] In earlier precedent using the phosphate ester of alginate, it has been observed the formation of elemental phosphorous that partly sublimes as the red allotrope in the pyrolysis process and partly becomes incorporated in the G sheet.[23] Also, alginate borate ester as precursor of (B)G should require a chemical reduction step of B atoms in the process of G doping.[20] Similarly, it is proposed here that the sulfate groups present in natural carrageenan would be reduced to elemental sulfur that partly would become incorporated during the formation of carbon residue on the G sheets and partly will sublime. In earlier precedents it was found that an excess of the precursor containing the heteroatom is necessary to produce G doping. For this reason, under our conditions, other carrageenans have been found to lead to carbon residues in which no sulfur is detected by combustion chemical analysis.



Scheme 1. Preparation procedure of (S)G using λ-carrageenan as precursor that is pyrolysed at 1000 °C (*i*) and exfoliated by sonication (*ii*).

FT-Raman spectroscopy is a suitable characterization technique for graphitic materials. The Raman spectrum recorded for (S)G (Figure 1) showed three expected peaks that correspond to the 2D band (2890 cm^{-1}), the G and D bands at 1592 and 1355 cm^{-1}, respectively.

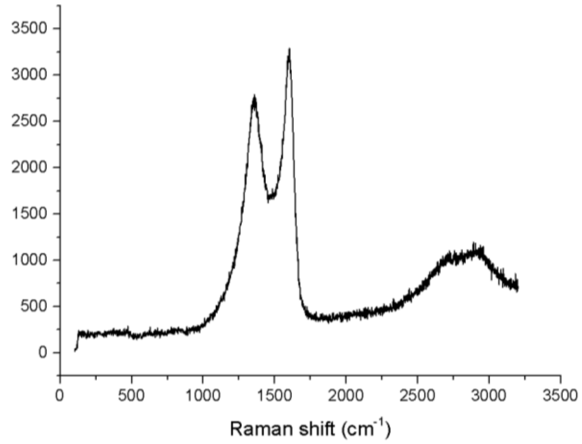


Figure 1. The Raman spectrum of (S)G.

The presence of S atoms and the fact that they are incorporated into G sheets was ascertained by XPS measurements. Deconvolution of the C1s peak (Figure 2) leads to two components at binding energies of 284.5 eV and 285.7 eV that correspond to graphitic carbon atoms and C atoms bonded to S. The S2p peak was deconvoluted into two components at binding energies of 164.1 eV and 168.2 eV (Figure 2), that according to the literature [24] can be attributed to S atoms bonded to C and S atoms bonded to C and O, respectively.

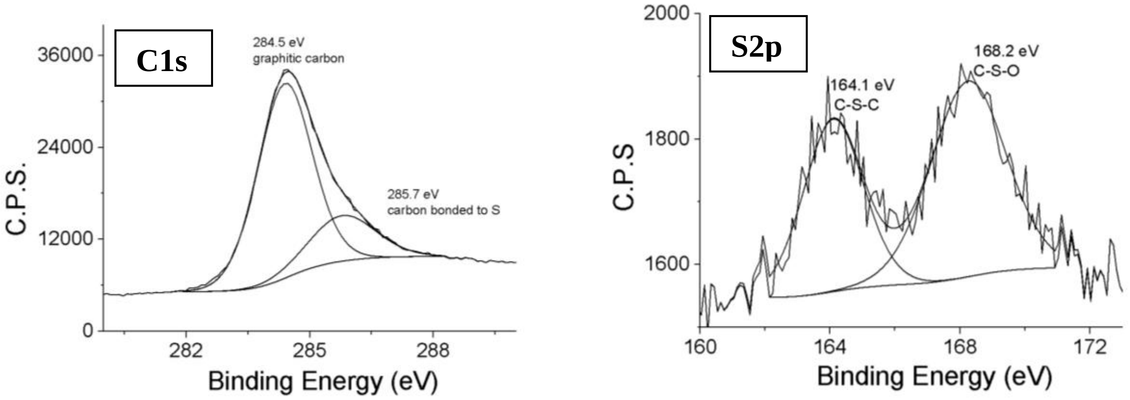


Figure 2. XPS C1s and S2p peaks recorded for (S)G and the best deconvolution peaks.

The typical layered G morphology of (S)G was observed by transmission electron microscopy (TEM). The images showed layers of around 600 nm in size with (S)G.

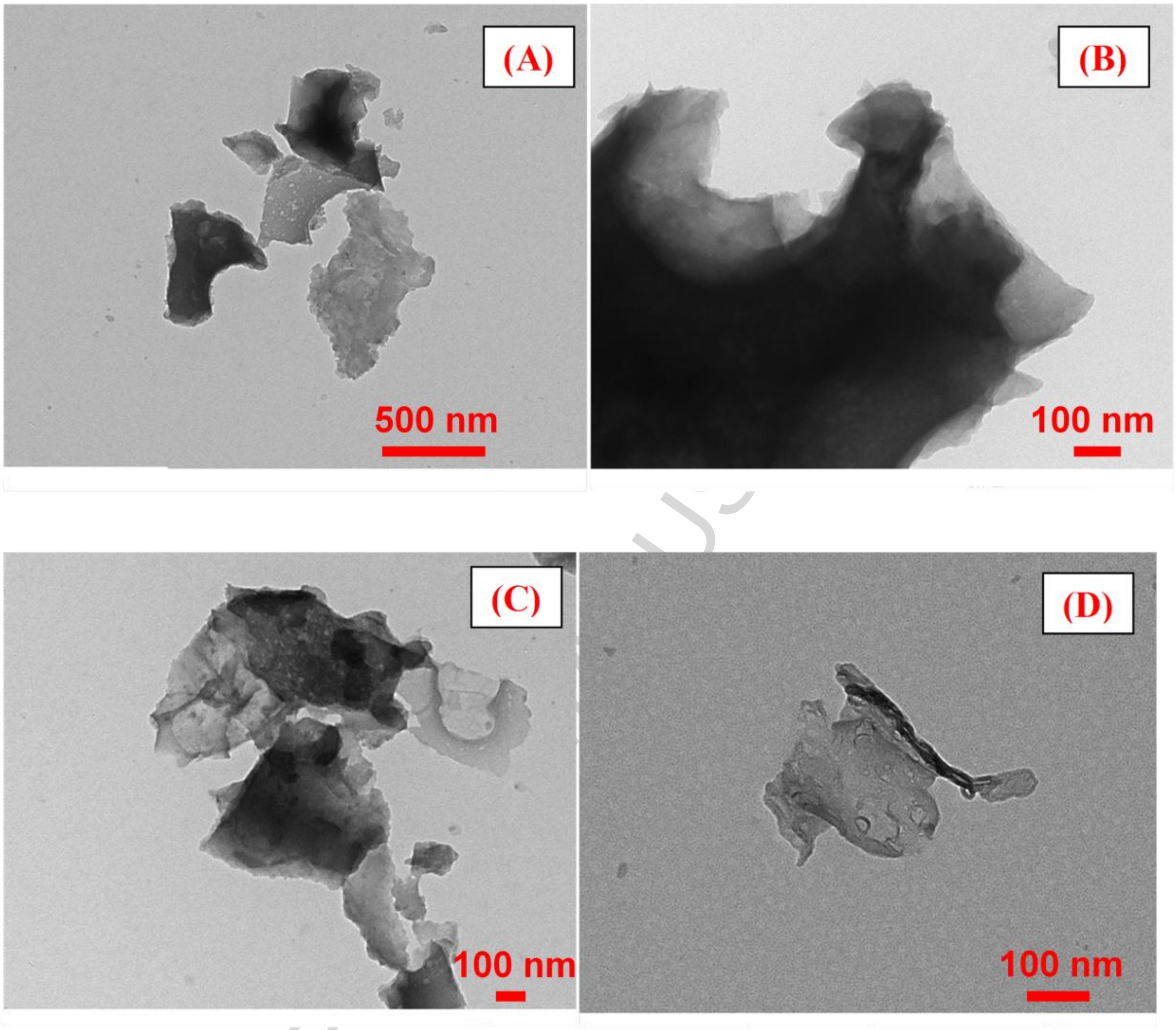


Figure 3. TEM images of (S)-G with different magnifications.

Catalytic studies on aerobic oxidation of styrenes

Aerobic oxidation of olefins to epoxides with high selectivity is a key reaction in industry due to the commercial importance of epoxides. However, this transformation is often accompanied by the formation of many secondary products. In the present work, the catalytic activity of (S)G is evaluated in the aerobic oxidation of styrene under solvent-free conditions. Styrene can undergo oxidative C=C double-bond cleavage to form benzaldehyde (BA) and benzoic acid, but can also can undergo epoxidation to give styrene oxide (SO). The direct conversion of styrene to SO by molecular oxygen as the oxidant is particularly challenging because this reagent typically produces undesirable side reactions and degradation. The importance of this reaction comes from the fact that the aerobic oxidation of alkenes is a reaction of considerable economic importance that is performed using noble or transition metals as catalysts, and, therefore, it would be especially advantageous to develop metal-free catalysts for this process.

Control experiments in the absence of catalyst resulted in 4 % conversion of styrene after 7 h probably due to the auto-oxidation process. On the other hand, when the aerobic oxidation was performed at 100 ^{o}C with (S)G as catalyst, the conversion of styrene increased gradually as a function of time. After 7 h, 13 % conversion was observed with the selectivity of BA and SO being 70 and 20 %, respectively. In addition, the reaction mixture also showed some dimeric and oligomeric derivatives of styrene. The formation of styrene oligomers is in agreement with the recent literature report by Bielawski and co-workers that have shown the remarkable catalytic activity of graphene oxide (GO) to promote styrene oligo- and polymerization.[25] In contrast to these results, an analogous sample of GO obtained by the same procedure had been found previously to act as a carbocatalyst for the aerobic oxidation of benzyl alcohol, although about half the weight of GO with respect to the organic substrate was employed than in this reaction.[17] This catalyst to substrate weight ratio is considerably much higher than the one employed here (1 wt.%).

For the sake of comparison, the catalytic activity of reduced graphene (rGO) was tested under the same experimental conditions in the aerobic oxidation of styrene, observing a negligible conversion compared to (S)G as catalyst. Furthermore, no conversion of styrene was also observed in the absence of oxygen or at lower reaction temperature (80 ^{o}C). These control experiments clearly suggest the active role played by molecular oxygen as oxidizing reagent and the importance of the temperature on the reaction rate. Furthermore, these data explain the role of S doping in the promotion of aerobic oxidation by tuning the properties of native G. Figure 4 shows the time-conversion plot for the oxidation of styrene using (S)G and rGO as catalysts.

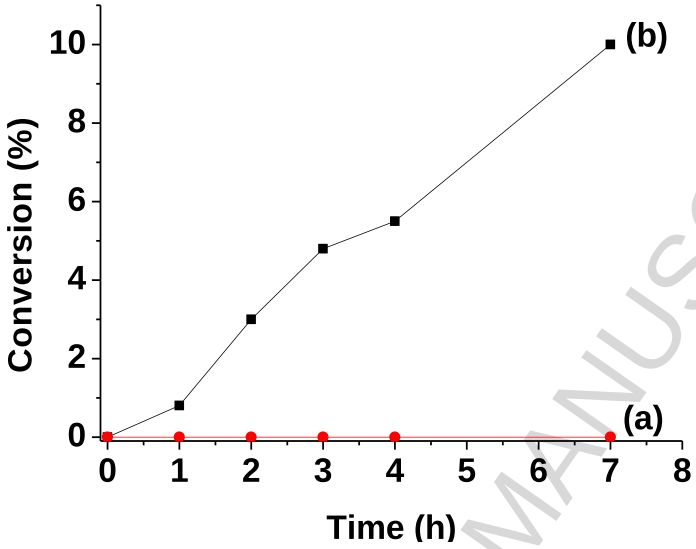


Figure 4. Aerobic oxidation of styrene using rGO (a) and (S)G (b) as catalysts.

Table 1. Aerobic oxidation of styrene and its derivatives using (S)G catalyst.[a]

Run No	Catalyst	T (^{o}C)	Substrate	Time (h)	Conv. (%)[b]	Sel. (%)[b]	
						BA	SO
1	-	100	styrene	7	4	44	18
2	(S)G	100	styrene	1	0.8	100	
3				2	3	82	18
4				3	4.8	74	20
5				4	5.5	72	19
6				7	13	70	20
7[c]	(S)G	100	styrene	7	12	71	18
8[d]	(S)G	100	styrene	7	12	67	19
9	rGO	100	styrene	7	-	-	-

10	(S)G	80	styrene	7	-	-	-
11	(S)G[e]	100	styrene	7	< 1	98	-
12	(S)G	100	α-methylstyrene	1	3	87[f]	10
13				5	9	85	13
14				7	13	76	20
15	(S)G	100	4-chlorostyrene	7	6	12	81[g]
16	(S)G	100	4-methoxystyrene	7	23	-	-

[a] Reaction conditions: substrate (1 mL), catalyst (10 mg), oxygen atmosphere, 100 °C; [b] Determined by GC; [c]First reuse; [d]Second reuse; [e]Reaction performed under inert atmosphere; [f]The product is acetophenone; [g]The selectivity corresponds to the mixture of the epoxide and carbonyl compounds.

The initial results achieved with (S)G on the aerobic oxidation of styrene prompted us to extend this catalytic system to other styrene derivatives. Under identical conditions, α-methylstyrene exhibited 13 % conversion with 76 % of acetophenone and 20 % of the corresponding epoxide at 7 h. On the other hand, 4-chlorostyrene gave 6 % conversion after 7 h with 12 % selectivity to benzaldehyde which comes from the dechlorination of 4-chlorobenzaldehyde. This reaction also afforded 4-chlrobenzaldehyde and the corresponding epoxide in 81 % selectivity. In contrast, 4-methoxystyrene resulted in higher conversion of 23 % but mainly undefined oligo- and polymeric product were formed and neither aldehyde nor the corresponding epoxide was detected. These experiments clearly indicate that the rate of the reactions mainly depend on the nature of the substituent present on the aromatic ring. Also, achieving high selectivity to epoxide is challenging due to the fact that the initially formed epoxide may undergo further secondary reactions like ring opening or epoxide rearrangement, thus, leading to other secondary products with lower selectivity of epoxide. These side reactions are generally catalysed by adventitious acid or basic sites.[13] Therefore, it may be that as-synthesised (S)G contains some defects and very low acidic sites that promote these secondary reactions. The key point is to develop a highly efficient and selective catalyst for the aerobic oxidation of olefin to increase the density of the active sites which can promote epoxidation, avoiding the presence of those sites which can act as acid or basic sites activating secondary reactions.

Reusability of (S)G was tested for the aerobic oxidation of styrene, performing two consecutive runs after separation of the (S)G catalyst under identical conditions. No significant changes in styrene conversion compared with the fresh catalyst were observed. On the other hand, the selectivity of the products also remains the same with slight changes. These results indicate that (S)G is a stable catalyst to promote the aerobic oxidation of styrene under the present experimental conditions.

Conclusions

(S)G has been synthesized from naturally occurring λ-carrageenan having high sulfate content upon optimization of the pyrolysis temperature. The G structure of the resulting (S)G was determined by combination of Raman, XPS and TEM measurements. XPS clearly indicated the presence of two types of sulphur atoms on (S)G, alike to sulfide and sulfoxide, respectively. The typical layered structure expected for G based materials was clearly observed by TEM. The catalytic activity of as-synthesized (S)G was tested in the aerobic oxidation of styrenes to their corresponding benzaldehydes accompanied by styrene oxide. In contrast to the catalytic activity of (S)G, rGO exhibited no activity under identical conditions. The (S)G catalyst can be reused two times with no significant changes in conversion and selectivity.

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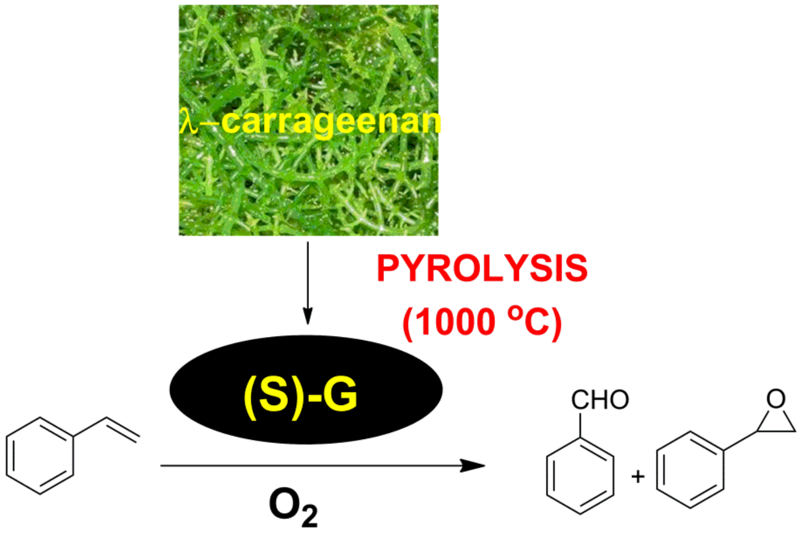

Graphical abstract

Highlights

- Pyrolysis of λ-carrageeenan and exfoliation leads to S-doped graphene.
- XP spectroscopy shows the presence of two types of sulfur atoms.
- S-doped graphene is able to promote the aerobic oxidation of styrenes.