Functionalization of mesostructured silica-carbon
composites

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Abstract

A strategy for synthesizing highly functionalized porous silica-carbon composites made up of a sulphur- or nitrogen-doped carbon layer coating the pores of two mesostructured silica samples (*i.e.* SBA-15 and KIT-6) is presented. The synthesis scheme involves several steps: a) infiltration of the silica pores by sulphur-rich (thiophene) or nitrogen-rich (pyrrole) monomers, b) *in situ* polymerization of these precursors to form polythiophene or polypyrrole, and c) carbonization of the polymers. The resulting silica-carbon composites contain ~25 wt % of carbonaceous matter and a large number of nitrogen and sulphur functional groups attached to the deposited carbon (up to 4.2 wt % of nitrogen and 6.1 wt % of sulphur). The structural characteristics of the parent silica are retained in the composite materials, which exhibit high surface area, large pore volume and a well-ordered porosity made up of uniform mesopores.

Keywords: Silica; Carbon; Composite; Mesoporous; Nitrogen; Sulphur.

1. Introduction

Mesostructured silica materials have become the focus of widespread attention due to their unique properties: a) a well-defined morphology, size and porosity, b) a large porosity made up of uniform mesopores in the 2–10 nm range, c) a well-organized pore arrangement (2D hexagonal, wormhole, 3D cubic, etc) and d) an ability to attach a variety of functional groups [1]. These properties make mesoporous silica materials attractive for a broad range of applications e.g., as catalytic supports [2], selective adsorbents [3], drug delivery carriers [4], supports for the immobilization of biomolecules [5], etc. These materials have also been used as templates for the fabrication of mesoporous carbons that exhibit complementary properties with respect to the silica [6]. For example such carbons have very large porosity in the mesopore range, a good electrical conductivity and an excellent chemical stability. These properties make them especially useful for energy storage (in supercapacitors and Li-ion batteries), [7] gas storage [8], as carriers for enzyme immobilization [9], and as adsorbents [10].

In spite of their practical interest, mesoporous silica materials have several drawbacks that limit their applicability. They have a poor electrical conductivity and the introduction of organic functionalities entails complex and expensive procedures. Thus, the controlled incorporation of a certain amount of carbon into the silica pores could open up new possibilities for the application of these materials. Indeed, a silica-carbon-composite would combine the structural properties of silica (*i.e.* uniform and large mesopores, and a well-defined pore arrangement) with those characteristic of carbon materials, such as a good electrical conductivity. The incorporation of different types of functional groups to the carbon layer would extend the range of potential applications even further. Several synthesis strategies have been reported for coating silica

mesopores with a carbon layer. Thus, Zhang et al. [11] and He et al. [12] reported modifying the size of the pore entrances of SBA-15 by depositing a carbon layer using a chemical vapor deposition technique. The usual procedure for preparing silica-carbon composites consists in attaching organic moieties to the silica surface followed by a carbonization step [13–15]. Yokoi et al. fabricated silica-carbon composites by means of an esterification method, based on the esterification of furfuryl alcohol with silanol groups on the pore walls of SBA-15 followed by a carbonization step [16]. Recently, we reported a new method for fabricating silica-carbon composites whereby the carbon layer coating the silica pores is produced by carbonizing the surfactant employed as structure-directing agent in the synthesis of mesostructured silica [17].

The ability of graphene layers to covalently attach heteroatoms (e. g. O, N, S) has been normally exploited in order to incorporate oxygen, nitrogen or sulphur-based functional groups into carbonaceous materials [18]. In the present work, this approach is adopted in order to incorporate nitrogen and sulphur functionalities into a layer of carbon deposited inside the pores of silica. The incorporation of such functionalities may enhance the range of potential applications of silica-carbon composites. Indeed, it has been reported that N-doped carbons exhibit a much better performance as supercapacitors [19], for the capture of CO₂ [20], and for the removal of contaminants and heavy metals from aqueous media [21] due to their basic character and enhanced electrical conductivity. On the other hand, S-doped carbons show an excellent behaviour as catalytic supports due to the intense interaction of sulphur with metal nanoparticles [22] and would therefore make good sorbents for certain heavy metals [23]. In the present work we fabricated carbon-coated mesostructured silica materials by incorporating nitrogen or sulphur functionalities into the carbon layer. Two types of mesostructured silica materials (*i.e.* SBA-15 and KIT-6) were selected as

substrates for these experiments. The synthesis strategy adopted involves the following steps: i) filling the silica pores with a monomer rich in nitrogen (pyrrole) or sulphur (thiophene), ii) *in situ* polymerization of these precursors to form polypyrrole or polythiophene and iii) carbonization of the polymer. Transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), infrared spectroscopy (IR), thermogravimetric analysis (TGA) and physisorption analysis were used to investigate the morphology, crystalline structure, chemical properties and textural characteristics of the synthesised silica-carbon composites.

2. Experimental

2.1. Synthesis of functionalized silica-carbon composites

Preparation of the silica samples. SBA-15 and KIT-6 mesostructured silica materials were used to prepare the composites. SBA-15 silica was synthesised according to the procedure reported by Zhao et al. [24] whereas KIT-6 silica was prepared as described by Kleitz et al. [25].

Synthesis of N-doped composites. Polypyrrole was introduced into the pores of calcined silica according to the procedure reported by our group elsewhere [26]. Briefly, the calcined silica was kept in contact with pyrrole vapour at 40 °C for 20 h. The resulting solid, containing around 30 wt % pyrrole, was then immersed in an aqueous solution of FeCl₃ (0.5 M) at room temperature for 2 h. Afterwards, the silica impregnated with polypyrrole was collected by filtration, washed with abundant distilled water and acetone, and dried at 60 °C under vacuum. Finally, the silica-polymer composite was carbonized under vacuum up to the desired temperature. The carbonized samples were denoted as *XCN-y* where *X* is *S* or *K* for the SBA-15 or KIT-6 silica substrates respectively and *y* is the carbonization temperature in °C.

Synthesis of S-doped composites. First, the pores of the calcined silica samples were impregnated with *p*-toluenesulfonic acid to increase surface acidity. In a typical experiment, the silica samples were impregnated with *p*-toluenesulfonic acid (>98 %, Aldrich) (0.5 M in ethanol) for 1 h, filtered, washed with a small volume of ethanol and dried at 80 °C. Afterwards, a solution of 2-thiophenemethanol (Aldrich) in acetone was infiltrated into the porosity of the silica (~ 0.9 g of 2-thiophenemethanol per gram of silica). Subsequently, the impregnated sample was heated to 100 °C for 16 h to polymerize the monomer and the resulting brown powder was carbonized up to 500 °C or 800 °C under vacuum for 1 h (heating rate: 5 °C/min). The carbonized samples were denoted as $XCS-y$ where X is S or K for the SBA-15 or KIT-6 silica substrates respectively and y is the carbonization temperature in °C.

Templated carbons obtained from the functionalized composites. Nitrogen- and sulphur-rich templated carbons were obtained by dissolving the silica framework (HF, 40 wt %) in the silica-carbon composites. The resulting carbon samples were denoted as $CN(X)-y$ or $CS(X)-y$ for the nitrogen or sulphur doped carbons respectively (X and y as indicated above).

2.2. Characterisation of the materials

Small and wide angle X-ray diffraction (XRD) patterns were obtained on a Siemens D5000 instrument operating at 40 kV and 20 mA and using $CuK\alpha$ radiation ($\lambda=0.15406$ nm). Nitrogen sorption isotherms were performed at -196 °C on a Micromeritics ASAP 2020 volumetric adsorption system. The Brunauer-Emmet-Teller (BET) surface area was deduced from an analysis of the isotherms in the relative pressure range of 0.04–0.20. The pore volume was calculated from the amount adsorbed at a relative pressure of 0.99. The pore size distributions (PSDs) were determined by applying the Kruk-Jaroniec-Sayari (KJS) method to the adsorption branch [27].

Transmission electron micrographs (TEM) were taken on a JEOL (JEM-2000 EX II) microscope operating at 160 kV. Diffuse reflectance Fourier–Transform Infrared (FT–IR) spectra of the materials were recorded on a Nicolet Magna–IR 560 spectrometer fitted with a diffuse reflection attachment. The percentage of carbonaceous material in the composites was deduced by thermogravimetric analysis which was performed on a CI Electronics system. X-ray photoelectron spectroscopy (XPS) was carried out on a Specs spectrometer, using MgK α (1253.6 eV) radiation from a double anode at 50 w. Binding energies for the high-resolution spectra were calibrated by setting C 1s to 284.6 eV. The chemical composition of the samples was determined by elemental analysis using a LECO CHNS–932 analyzer and the total sulphur content was corroborated by means of a LECO S–144DR device.

3. Results and Discussion

3.1. Structural properties

Silica–carbon composites

Nitrogen and sulphur functionalized silica–carbon composites were prepared using two types of mesoporous silica as starting materials, *i.e.* SBA–15 and KIT–6. The physical and chemical properties of the mesostructured silica substrates and the corresponding functionalized silica–carbon composites are summarized in Table 1. The silica–carbon composites contain around 20–25 wt % of carbonaceous matter, which decreases slightly as the carbonization temperature increases from 500 °C to 800 °C. Figure 1 shows the SEM images for the SBA–15 silica (Figure 1a) and the SBA–15/carbon composites with N or S (Figures 1 b, 1 c and 1 d). Both the silica and composite particles have a similar particle size ($\sim 1\ \mu\text{m}$). It can be seen that for the silica–carbon particles doped with S the external appearance of the particles is similar to

that of the silica indicating that the carbon layer has been deposited exclusively inside the pore network (Figures 1 c and 1 d). In contrast, in the case of the silica-carbon samples doped with N (Figure 1 b), the external surface of the particles shows a certain roughness, which suggests that a fraction of the deposited carbon is coating the silica particles.

Because most of the deposited carbonaceous matter is inside the pores of the silica, it is to be expected that the silica-carbon composites will show a reduction in their textural properties with respect to the parent silica. This is confirmed by the results presented in Table 1, which reveal that the silica-carbon composites show, in relation to the silica samples (SBA-15 and KIT-6), a moderate reduction in their BET surface area, pore volume and pore size. This result suggests that there is no blockage of the pores by the deposited carbon. It can also be seen that the reduction in textural properties is more pronounced in the case of the composites treated at 800 °C than in those prepared at 500 °C. This may be due to thermal shrinkage of the silica framework, which becomes more pronounced as the carbonization temperature increases [28]. Figure 2 shows the nitrogen sorption isotherms and the pore size distributions (inset) corresponding to the two silica samples and the silica-carbon composites obtained by carbonization at 500 °C and 800 °C. All the isotherms exhibit a type IV pattern with a well-defined capillary condensation step at $p/p_0 \sim 0.6-0.8$, which is indicative of a well-developed mesoporosity. This is confirmed by the pore size distributions, depicted in the insets of Figure 2, which show that the porosity of both the silica and the composites is made up of uniform mesopores ranging from 8 to 11 nm. It can be seen that as a consequence of the deposition of the carbon layer, there is a reduction in the mean pore size. For example, whereas the pore size of the SBA-15 silica is ~ 9.8 nm, the SCN-500 composite has a pore size of ~ 8.3 nm. This means that the carbon layer has a thickness

of around 0.7 nm (approximately equivalent to the thickness of two graphene sheets), which is similar to the size deduced by Nishihara et al. for SBA-15/carbon composites prepared by using 2,3-dihydroxynaphthalene as carbon source [13]. The composites prepared at 800 °C also exhibit a reduction in pore size, but in this case it is due to shrinkage of the silica framework, as the temperature increases rather than to any modification in the thickness of the carbon layer.

The low-angle range XRD patterns depicted in Figure 3 corresponding to the composites derived from SBA-15 evidence that the incorporation of carbon does not affect the structural order of the silica-carbon composites with respect to the silica. Like the calcined silica samples, the silica-carbon composites display well-resolved XRD peaks, which are assigned to reflections characteristic of a 2D $p6mm$ hexagonal silica mesostructure (SBA-15). These results are in agreement with TEM images, displayed in Figure 4, for the SBA-15 and derived composites (taken along the channel direction and perpendicular to it). It can be seen that the structural order characteristic of the parent silica is still retained in the composites. The KIT-6/carbon composites also retain the structural order of the parent silica as can be deduced from the well-resolved low-angle XRD patterns in Figure S1a.

Templated carbons

Mesoporous carbons doped with N or S were obtained by dissolving the silica skeleton in the silica-carbon composites. The textural properties of the templated carbons (N-doped and S-doped) obtained from the SBA-15 silica were analyzed. Their nitrogen sorption isotherms and pore size distributions are presented in Figure 5 and Table 1 respectively. The results show that these carbons have a large specific surface area and a porosity that is predominantly made up of mesopores with a mean pore size of ~ 4 nm. What is more, they retain the mesostructural order of the parent silica, as can

be deduced from the low-angle range XRD patterns (see Figure S1b) and TEM images shown in Figure 6. The fact that the templated carbons exhibit a well-defined mesostructure suggests that the carbon in the silica-carbon composites is interconnected and uniformly distributed within the pore network. It is also worth mentioning that these templated carbons combine a high surface area and mesoporous structure with a large amount of nitrogen in the case of the CN(S)-800 sample (6.7 wt % N) and sulphur in the case of CS(S)-800 (3.9 wt % S) (see Table 1). Clearly, the combination of these two properties would make these materials useful in several areas such as supercapacitors, CO₂ capture, catalytic supports or sorbents [18].

3.2 Chemical properties of the silica-carbon composites

N-doped composites

Elemental analysis of the N-doped silica-carbon composites shows that these materials have nitrogen contents in the 1.5–4.2 wt % range (see Table 1). It can be seen that this percentage decreases with the carbonization temperature. This is because nitrogen functionalities are preferentially removed during carbonization, as has previously been reported [29]. The nature of the nitrogen functionalities was investigated by means of FT-IR and XPS spectroscopic techniques. Figure 7a shows the infrared spectra of polypyrrole and the carbon coating the silica pores (*i.e.* CN(S)-500 and CN(S)-800). The FT-IR spectrum of polypyrrole contains peaks typical of this polymer [30]. Peaks characteristic of polypyrrole ring vibrations (*i.e.* C=C/C-C stretching vibrations and ring breathing with contributions from C=C/C-C and C-N) are visible at ~ 1590, 1490 and 1360 cm⁻¹. The peaks at ~1240 and 1070 cm⁻¹ are ascribed to C-H in-plane bending vibrations, whereas the peaks below 980 cm⁻¹ can be assigned to C-H out-of-plane bending vibrations. The small band at ~ 1710 cm⁻¹ is associated to

C=O stretching vibrations, which agrees with the presence of oxygen-containing groups, as indicated by the elemental analysis (11.7 wt % O). In the case of the N-containing carbons, the FT-IR bands become broader and overlap due to the strong absorption of carbon. However, bands associated to ring vibrations can still be identified at 1350–1650 cm^{-1} , as well as out-of-plane C-H deformation modes below 980 cm^{-1} . These results indicate that aromatic rings involving N species are present in the composites. The decrease in the intensity of these bands, as the carbonization temperature increases, suggests the gradual removal of nitrogen functionalities. Figure 7c also shows the spectrum for the calcined SBA-15 sample. This exhibits a broad band at 2600–3800 cm^{-1} caused by O-H stretching and an overlapping sharp peak at 3750 cm^{-1} due to the stretching modes of isolated OH groups [31]. Interestingly, the silica-carbon composites do not exhibit any IR signal in this region, which evidences that the silica surface is fully coated by carbon.

The N 1s signal was measured by XPS to obtain a better insight into the nature of the N functional groups and the changes that occurred during carbonization. Figure 8a shows the N 1s core-level spectra corresponding to polypyrrole (PPy), the N-doped carbons obtained by removing the silica framework from the SCN-500 and SCN-800 samples, and the carbon resulting from the pyrolysis of polypyrrole at 800 °C (CP). It can be seen that the XPS spectrum of polypyrrole (used as a reference material) contains only one peak centred at 399.7 eV, which can be assigned to pyrrolic nitrogen (N-5) [20]. In the case of the bulk carbonized polypyrrole two intense peaks centred at 398.1 eV and 400.7 eV, and a small one at 403.1 eV can be distinguished corresponding to pyridinic nitrogen (N-6), and N-oxides of pyridine-N respectively [32]. The pyridine-N-oxide (N-X) band is probably caused by the oxidation of the sample from its exposure to the ambient, and it represents only 3% of the different N moieties [32,33].

The peak centred at 400.7 eV can be attributed to quaternary-N (N-Q), which is the most stable N species under high-temperature pyrolysis conditions [32]. In the case of the carbon-coated silica pores, deconvolution of the N 1s envelope gives peaks with the following binding energies: a) ~398.2 eV, b) 400.0 eV, c) 401.0 eV and d) ~403.1 eV, which can be assigned respectively to: a) pyridinic-N (N-6), b) pyrrolic-/pyridonic-N (N-5), c) quaternary-N (N-Q) and d) N-oxides of pyridine-N (N-X). It can be seen that the carbonization temperature has a strong influence on the relative amounts of each of the surface nitrogen functionalities present in the carbon. Thus, for the sample carbonized at 500°C the distribution of the nitrogen species is: a) $\approx$ 32% of N-6, b) $\approx$ 56 % of N-5 and c) $\approx$ 10 % of N-Q. In contrast, the sample obtained at 800°C exhibits the **following distribution:** a) $\approx$ 29 % of N-6, b) $\approx$ 6 % of N-5 and c) $\approx$ 61 % of N-Q. These results show that, as the carbonization temperature increases, the N-5 (pyrrolic/pyridonic-N) groups gradually disappear, leaving N-6 and N-Q as the principal species, *i.e.* the most stable functionalities at high temperatures. Thus, in the case of the sample obtained at 800°C the main nitrogen functional groups attached to the carbon consist of N atoms located inside six-membered rings (N-Q) and at the periphery of the graphene layers (N-6) [32,33].

S-doped composites

The composites obtained by carbonizing the polythiophene inside the silica pores have sulphur contents ranging from 0.9 to 6.1 wt %. As can be seen in Table 1, the amount of sulphur decreases sharply as the carbonization temperature rises from 500 °C to 800 °C. Thus, for the KIT-6 based composites, the percentage of sulphur varies from 6.1 wt % (KCS-500) to 1.9 wt % (KCS-800). As in the case of the nitrogen functional groups (see above), this change occurs because, as the carbonization temperature increases, sulphur is preferentially removed and consequently, the S/C ratio

diminishes [23,34]. The nature of the sulphur-containing functional groups present on the surface of the carbonaceous matter was investigated by means of FT-IR and XPS spectroscopy. Figure 7b shows the FT-IR spectra for polythiophene and the carbon coating the silica pores (*i.e.* CS(S)-500 and CS(S)-800). The FT-IR spectrum corresponding to polythiophene shows peaks characteristic of this polymer: i) C-H out-of-plane bending vibrations at 650–730 cm^{-1} , ii) C-S stretching vibrations in the 800–930 cm^{-1} range [35], iii) C-H in plane bending vibrations at $\sim 1260 \text{ cm}^{-1}$ [36], and iii) thiophene ring vibrations (*i.e.* C=C/C-C stretching vibrations and ring breathing) at ~ 1640 , 1520, 1450 and 1360 cm^{-1} . As in the case of polypyrrole, C=O stretching vibrations can be appreciated at ~ 1681 – 1780 cm^{-1} . The S-doped carbon samples show the same bands but with a reduced intensity in spite of the fact that there is a broadening of the bands due to the strong absorption of carbon. This indicates that sulphur species are present in the carbon samples. Figure 7d shows that, like the silica-(N-doped carbon) composites, the silica-(S-doped carbon) samples do not exhibit a FT-IR peak corresponding to isolated OH groups characteristic of silica. This suggests that the silica surface is fully coated by S-doped carbon. The presence of a low intensity band attributed to O-H stretching vibrations (3000–3700 cm^{-1}) may be due to the oxygen functionalities (phenol), generated by the oxidative polymerization of 2-thiophenemethanol inside the silica pores.

Additional information about the nature of the sulphur functional groups was obtained by X-ray photoelectron spectroscopy. The S 2p core level spectra corresponding to polythiophene (PTh), the S-doped carbon coating the silica pores (CS(S)-500 and CS(S)-800), and carbonized polythiophene (CPTh) at 800 °C are presented in Figure 8b. The XPS spectrum for polythiophene exhibits a doublet at 163.9 and 165.2 eV, which can be assigned to thiophene-like sulphur [37]. The XPS spectrum

corresponding to carbonized polythiophene (C-PTh) is composed of two doublets: a) a lower energy doublet (164.0 and 165.3 eV) which can be ascribed to -C-S-C- sulphide bridges, and b) a high energy doublet (167.2 and 168.5 eV) which is consistent with $\text{-C-S(O)}_2\text{-C-}$ sulphone bridges [38]. These sulphone bridges represent only $\sim 5\%$ of the total sulphur content, indicating that most of the sulphur present in the C-PTh sample (13.8 wt %) is in the form of sulphide bridges. In the case of S-doped carbons, the S 2p spectrum of the CS(S)-500 sample exhibits only one doublet which is ascribed to sulphide bridges. In contrast, the CS(S)-800 sample contains two doublets associated to -C-S-C- sulphide bridges and $\text{-C-S(O)}_2\text{-C-}$ sulphone bridges like the C-PTh sample. However, the sulphone bridges in the CS(S)-800 sample represent only a very small percentage of the total amount of sulphur ($\sim 4\%$). Therefore, most of the S heteroatoms must be forming sulphide bridges.

An illustration of the synthesis scheme for nitrogen and sulphur doped silica-carbon composites is provided in Figure 9. The synthesis procedure is similar for both materials and comprises the following steps: a) calcination of the as-synthesized silica (SBA-15 or KIT-6), b) impregnation with the carbon precursor (polypyrrole or polythiophene) and c) carbonization. The composite has a thin carbon layer that covers the pores of silica. This carbon layer contains a large number of S or N functional groups attached to the graphene layers, as illustrated in Figure 9. The results obtained reveal that, whereas nitrogen is incorporated into aromatic rings in the form of pyridine and in quaternary positions, most of the sulphur forms sulphide bridges between adjacent graphene layers.

Conclusions

In summary, we have presented a simple synthesis strategy for preparing nitrogen and sulphur doped silica-carbon composites with a thin functionalized carbon layer (~ two graphene sheets thick) coating the pores of mesostructured silica materials (SBA-15 and KIT-6). The silica-carbon composites retain the textural properties of the original silica, *i.e.* a large surface area (up 570 m²·g⁻¹) and a porosity made up of mesopores (8–11 nm). The deposited carbon is homogeneously distributed within the silica pores and forms a uniform layer. With an appropriate precursor the carbon layer can be made to have a large number of nitrogen (up to 4.2 wt %) or sulphur (up 6.1 wt %) functional groups that are attached to the graphene layer. The functionalized composites when carbonized at low temperatures (*i.e.* 500 °C) exhibit a higher surface area and heteroatom content than those obtained at 800 °C. In both cases the mesostructure is retained. The nitrogen contained in the N-doped carbon composites is incorporated into the aromatic rings in pyridine (N-6) and quaternary (N-Q) positions, whereas the sulphur in the S-doped composites mainly forms sulphide bridges (–C–S–C–) which connect the aromatic rings. Removal of the silica from the composites gives rise to templated carbons that exhibit a large surface area and pore volume, in addition to a large amount of nitrogen in the case of N-doped templated carbons (6.7 wt % N) and sulphur in the case of S-doped templated carbons (3.9 wt % S).

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References

- [1] F.Hoffmann, M.Cornelius, J.Morell, M.Fröba, *Angew. Chem. Int. Ed.* 45 (2006) 3216–3251.

- [2] D.Trong On, D.splantier–Giscard, C.Danumah, S.Kaliaguine, Appl.Catal.A: Gen. 253 (2003) 545–602.
- [3] C.H.Huang, K.P.Chang, H.D.Ou, Y.C.Chiang, C.F.Wang, Microp.Mesop.Mat. 141 (2011) 102–109.
- [4] W.Shaobin, Microp.Mesop.Mat. 117 (2009) 1–9.
- [5] J.Lei, J.Fan, C.Z.Yu, L.Y.Zhang, S.Y.Jiang, B.Tu, D.Y.Zhao, Microp.Mesop.Mat. 73 (2004) 121–128.
- [6] J.Lee, J.Kim, T.Hyeon, Adv.Mater. 18 (2006) 2073–2094.
- [7] M.Sevilla, S.Álvarez, T.A.Centeno, A.B.Fuertes, F.Stoeckli, Electrochim.Acta 52 (2007) 3207–3215.
- [8] M.Sevilla, A.B.Fuertes, J.Colloid Interface Sci. 366 (2012) 147–154.
- [9] M.Sevilla, P.Valle–Vigón, P.Tartaj, A.B.Fuertes, Carbon 47 (2009) 2519–2527.
- [10] Z.Wu, D.Zhao, Chem.Comm. 47 (2011) 3332–3338.
- [11] Y.Zhang, F.L.–Y.Lam, X.Hu, Z.Yan, Chem.Comm. (2008) 5131–5133.
- [12] C.He, F.Lam, X.Hu, Adsorption 13 (2007) 281–290.
- [13] H.Nishihara, Y.Fukura, K.Inde, K.Tsuji, M.Takeuchi, T.Kyotani, Carbon 46 (2008) 48–53.
- [14] Z.Yang, Y.Xia, R.Mokaya, J.Mater.Chem. 16 (2006) 3417–3425.
- [15] Z.Wu, J.Pang, Y.Lu, Nanoscale 1 (2009) 245–249.
- [16] T.Yokoi, S.Seo, N.Chino, A.Shimajima, T.Okubo, Microp.Mesop.Mat. 124 (2008) 123–130.
- [17] P.Valle–Vigón, M.Sevilla, A.B.Fuertes, Microp.Mesop.Mat. 134 (2010) 165–174.
- [18] A.Stein, Z.Wang, M.A.Fierke, Adv.Mater. 21 (2009) 265–293.
- [19] J.Kim, M.Choi, R.Ryoo, Bull.Korean Chem.Soc. 29 (2008) 413–416.
- [20] M.Sevilla, P.Valle–Vigón, A.B.Fuertes, Adv.Funct.Mater. 21 (2011) 2781–2787.
- [21] Y.F.Jia, B.Xiao, K.M.Thomas, Langmuir 18 (2001) 470–478.
- [22] H.I.Lee, S.H.Joo, J.H.Kim, D.J.You, J.M.Kim, J.N.Park, H.Chang, C.Pak, J.Mater.Chem. 19 (2009).
- [23] Y.Shin, G.E.Fryxell, W.Um, K.Parker, S.V.Mattigod, R.Skaggs, Adv.Funct.Mater. 17 (2007) 2897–2901.

- 1 [24] D.Zhao, Q.Huo, J.Feng, B.F.Chmelka, G.D.Stucky, J.Am.Chem.Soc. 120 (1998)
2 6024–6036.
- 3 [25] F.Kleitz, S.H.Choi, R.Ryoo, Chem.Comm. (2003) 2136–2137.
- 4
- 5 [26] A.B.Fuertes, Macromol.Rapid Commun. 26 (2005) 1055–1059.
- 6
- 7 [27] M.Kruk, M.Jaroniec, A.Sayari, Langmuir 13 (1997) 6267–6273.
- 8
- 9 [28] M.Mandal, M.Kruk, Chem.Mater. 24 (2011) 149–154.
- 10
- 11 [29] Y.Shin, G.E.Fryxell, C.A.Johnson II, M.M.Haley, Chem.Mater. 20 (2007) 981–
12 986.
- 13
- 14 [30] R.G.Davidson, T.G.Turner, Synth.Met. 72 (1995) 121–128.
- 15
- 16 [31] A.Zecchina, S.Bordiga, G.Spoto, L.Marchese, G.Petrini, G.Leofanti, M.Padovan,
17 J.Phys.Chem. 96 (1992) 4991–4997.
- 18
- 19 [32] J.R.Pels, F.Kapteijn, J.A.Moulijn, Q.Zhu, K.M.Thomas, Carbon 33 (1995) 1641–
20 1653.
- 21
- 22 [33] M.Lezanska, P.Pietrzyk, Z.Sojka, J.Phys.Chem.C 114 (2010) 1208–1216.
- 23
- 24 [34] M.Sevilla, A.B.Fuertes, Microp. Mesop. Mat. 158 (2012) 318–323.
- 25
- 26 [35] X.G.Li, J.Li, M.R.Huang, Chem.Eur.J. 15 (2009) 6446–6455.
- 27
- 28 [36] G.Socrates, Infrared and Raman Characteristic Group Frequencies, Wiley, New
29 York, 2005.
- 30
- 31 [37] W.S.Baker, J.W.Long, R.M.Stroud, D.R.Rolison, J.Non-Cryst.Solids 350 (2004)
32 80–87.
- 33
- 34 [38] D.J.Malik, A.W.Trochimczuk, A.Jyo, W.Tylus, Carbon 46 (2008) 310–319.
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Table 1. Physical properties of the silica materials (calcined at 550 °C) and functionalized silica-carbon composites (carbonized at 500 and 800 °C).

Type of material	Sample	Carbonaceous matter (wt %) ^a	N or S and O content ^b			Textural properties		
			N (wt %)	S (wt %)	O (wt %)	S_{BET} ($\text{m}^2\cdot\text{g}^{-1}$)	V_p ($\text{cm}^3\cdot\text{g}^{-1}$) ^c	Pore size (nm) ^d
Silica	SBA-15	–	–	–	–	670	1.25	9.8 (1.4)
	KIT-6	–	–	–	–	680	1.26	11 (0.9)
N-doped Composite	SCN-500	23.7	3.6	–	2.3	480	0.72	8.3 (1.6)
	SCN-800	23.1	1.6	–	2.5	390	0.56	7.6 (1.5)
	KCN-500	25.7	4.2	–	1.1	510	0.82	10.4 (1.0)
	KCN-800	20.1	1.6	–	0.2	440	0.62	8.8 (1.3)
S-doped Composite	SCS-500	26.6	–	5.1	3.1	490	0.69	8.7 (1.6)
	SCS-800	22.9	–	0.9	1.2	340	0.56	8.5 (1.6)
	KCS-500	23.8	–	6.1	1.3	570	0.86	10.3 (0.9)
	KCS-800	20.6	–	1.9	2.7	490	0.74	9.7 (0.8)
Templated Carbons	CN(S)-800	–	6.7	–	11	830	2	4.3
	CS(S)-800	–	–	3.9	5.1	840	1.6	3.9

^a Carbonaceous matter consists not only of pure carbon but also other associated heteroatoms (e. g. H, N, O and/or S).

^b Heteroatoms associated to carbonaceous matter.

^c Pore volume determined at $p/p_0=0.99$.

^d Maximum of pore size distribution, (the full width at half maximum (in nm) of the pore size distribution is given in parentheses).

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Figure 1. SEM micrographs of a) SBA-15, b) SCN-500, c) SCS-500 and d) SCS-800.

Figure 2. Nitrogen sorption isotherms and pore size distributions (insets) of the silica and N- or S-doped silica-carbon composites carbonized at 500 and 800 °C. (a) SBA-15 and N containing SBA-15/carbon composites; (b) KIT-6 and N containing KIT-6/carbon composites; (c) SBA-15 and S-doped SBA-15/carbon composites, and (d) KIT-6 and S-doped KIT-6/carbon composites.

Figure 3. XRD patterns in the low-angle region of the mesostructured SBA-15 silica and the corresponding functionalized silica-carbon composites carbonized at 500 and 800 °C.

Figure 4. TEM micrographs of SBA-15 silica (a); N-doped carbon-silica composites treated up to 500 °C, SCN-500 (b) and 800 °C, SCN-800 (c) and S-doped carbon-silica samples carbonized at 800 °C, SCS-800 (d).

Figure 5. N₂ sorption isotherms (with PSDs inset) of the carbons obtained from the functionalized silica-carbon composites treated at 800 °C.

Figure 6. TEM micrographs of the templated carbons obtained: N-doped carbon, CN(S)-800 (A and B) and S-doped carbon, CS(S)-800 (C and D), obtained by removing the SBA-15 silica from the functionalized carbon-silica composites carbonized at 800 °C.

Figure 7. (a) FT-IR spectra corresponding to N- and S-rich polymers (polypyrrole and polythiophene) and to the resulting doped carbons from the SBA-15/carbon composites. (b) FT-IR spectra of the polymer-silica hybrids, SBA-15/carbon composites doped with N and S and calcined SBA-15.

Figure 8. (a) N 1s core level spectra of PPy, CN(S)-500, CN(S)-800 and CP. (b) S 2p core level spectra of PTh, CS(S)-500, CS(S)-800 and CPTh.

Figure 9. Illustration of the preparation of mesostructured silica-carbon composites with (A) nitrogen and (B) sulphur functional groups.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9. Illustration of the preparation of mesostructured silica-carbon composites with (A) nitrogen and (B) sulphur functional groups.

Functionalization of mesostructured silica-carbon composites

Graphical Abstract

Functionalization of mesostructured silica-carbon composites

Highlights

- Nitrogen- and sulphur-doped mesoporous silica-carbon composites have been prepared.
- The composites retain the structural properties of the mesoporous silica.
- The N or S-doped carbon layer is uniformly deposited within the silica pores.