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Nanoscale assembly of lanthanum silica with dense and porous interfacial structures

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This work reports on the nanoscale assembly of hybrid lanthanum oxide and silica structures, which form patterns of interfacial dense and porous networks. It was found that increasing the molar ratio of lanthanum nitrate to tetraethyl orthosilicate (TEOS) in an acid catalysed sol-gel process alters the expected microporous metal oxide silica structure to a predominantly mesoporous structure above a critical lanthanum concentration. This change manifests itself by the formation of a lanthanum silicate phase, which results from the reaction of lanthanum oxide nanoparticles with the silica matrix. This process converts the microporous silica into the denser silicate phase. Above a lanthanum to silica ratio of 0.15, the combination of growth and microporous silica consumption results in the formation of nanoscale hybrid lanthanum oxides, with the inter-nano-domain spacing forming mesoporous volume. As the size of these nano-domains increases with concentration, so does the mesoporous volume. The absence of lanthanum hydroxide (La(OH)$_3$) suggests the formation of La$_2$O$_3$ surrounded by lanthanum silicate.

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ilica is an extremely versatile material widely used for tailoring structures such as amorphous micro- and mesoporous structures[1–3], crystalline materials such as zeolites[4,5] and self-assembly materials such as mesoporous hollow spheres[6] to name a few. The flexibility of silica derived sol-gel methods using colloidal precursors in tandem with further processing techniques has spurred the designing of novel silica structures. For instance, microporous silica structures are intrinsically linked to weakly branched fractal dimensions, which contain a high concentration of uncondensed silanol (Si-OH) species[7–9]. In addition, the use of organic templates[10–12], metal oxides[13,14], or both[15], led to the manipulation of sol-gel chemistry and the production of a wide variety of porous structures in silica materials.

Embedding metal oxides into silica matrices to produce microporous structures has received the concerted attention of the scientific community, including nickel oxides[16,17], cobalt oxides[15,18,19], iron oxides[20], palladium oxides[21,22], binary palladium cobalt oxides[23], as well as many others[24–27]. A feature of these reports is that the metal oxide remains homogeneously dispersed as nanoparticles in the silica matrices. In addition, Uhlmann et al.[28] showed that the pore sizes of the interfaces of cobalt oxide and silica were around 3 Å, slightly smaller than the pore sizes (3–5 Å) in pure silica structures. In some formulations, even cobalt oxide to silica molar fractions as high as 1 : 1 still delivered microporous structures[13]. All these reports have limited the calcination temperature to no more than 630°C, to avoid the densification of the silica and/or formation of metal oxide silicates. Transition metals have been the preferred route in producing metal oxide silica porous structures.

Lanthanides have also been used to produce porous silica materials but to a lesser extent than transition metals. In some cases lanthanum was coated on nanoporous SBA-15[29] or on silica layers[30], whilst in other cases the combination of lanthanum niobate silica has formed pillared structures[31] or lanthanum phosphate silica has produced mesoporous materials[32]. Célérier et al.[33] produced mesoporous lanthanum silicate materials for use in solid oxide fuel cells (SOFC) due to their high ionic conductivity at low temperatures, and their ability to form mesoporous materials which impose minimal resistance to fluidic species. In this instance, materials exhibited a large increase in the pore size distribution by forming a lanthanum silicate phase (La$_{9.33}$Si$_6$O$_{26}$). However, no mechanism for the deviation in the pore size distribution was proposed, which is vital to achieve fine tuning of the system. The deviation from conventional micro- to mesoporous structures requires further understanding for metal doped silica materials, as in many cases the formation of metal oxide silicates require high calcination temperatures (>850°C)[34].
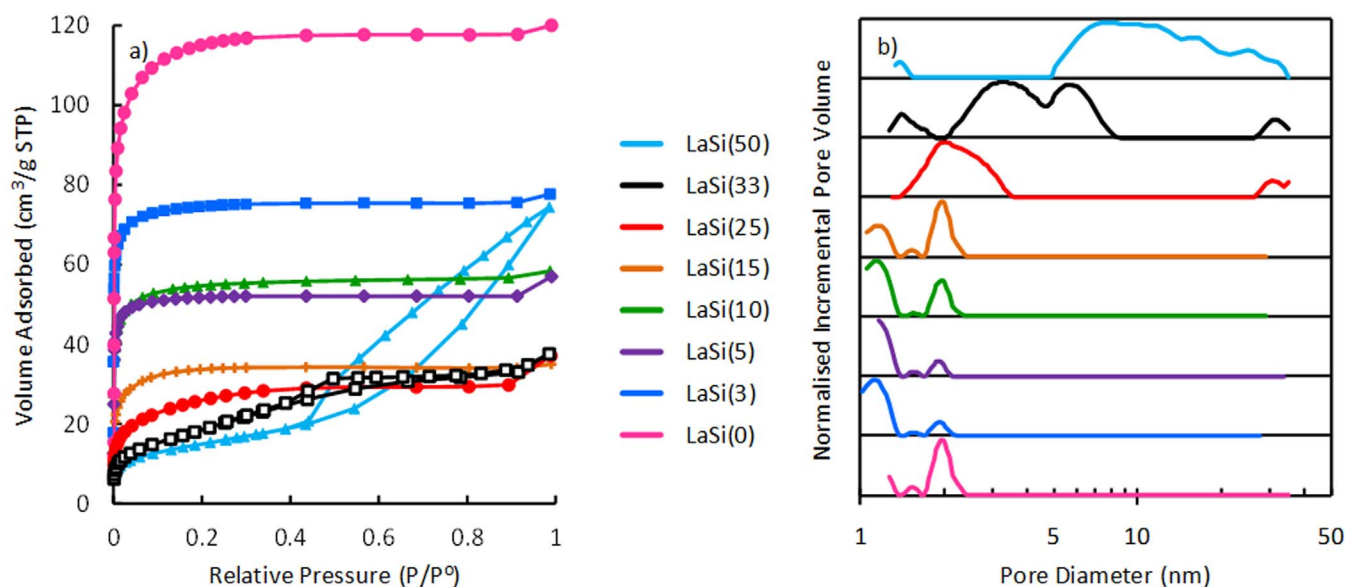
Figure 1 | (a) N$_2$ adsorption-desorption isotherms and (b) Pore size distribution calculated by density functional theory for the lanthanum silica xerogels calcined at 500°C.

The present study focuses on the effect of the concentration of lanthanum within the silica to determine the mechanism behind porosity alteration over the calcination process. Results of porosity measurements show the formation of mesoporous structures above a critical lanthanum concentration, which departs from results found with transition metal dopants. Characterisation of the chemical structure of the materials determined that the lanthanum forms nanoscale oxides, encased by a silicate layer within an amorphous silica matrix. A mechanistic model is proposed to explain the effects of material synthesis on the resultant structure.

Results and Discussion

In order to investigate the structural effect of lanthanum embedded in the silica matrix, xerogel samples were analysed via N$_2$ adsorption. Figure 1a shows representative isotherms of the xerogel samples calcined at 500°C. The LaSi(0) xerogel (i.e. pure silica) shows a type I isotherm which is characteristic of microporous materials. It also displays the largest adsorbed volume of all the samples. The addition of small amounts of lanthanum (LaSi(0.03), (0.05)) results in a more right-angled isotherm at lower nitrogen partial pressures which corresponds to a shift to a narrower pore size distribution (PSD) at lower pore sizes, as seen in Figure 1b. This is likely due to the acidification of solution with the addition of lanthanum nitrate[33,35], a classic method to increase the microporosity of silica in sol-gel theory. Furthermore, a substantial reduction in the volume of nitrogen adsorbed per xerogel mass is evident.

The trend of decreasing micropore volume with increasing lanthanum content continues to higher lanthanum concentrations until a transition point is reached (La/Si > 0.15) whereby the isotherms shift to type IV; thus forming mesoporous networks. This is clearly demonstrated in Figure 1b, with microporous volume decreasing, and mesoporous volume increasing proportionally to lanthanum

concentration above La/Si = 0.15. Table 1 further emphasises the trends in the isotherms and pore size distributions, showing a loss in both the BET surface area and pore volume with increasing lanthanum concentration. This is true for all concentrations except for LaSi(50), whereby pore volume increases due to the large mesoporous volume that has formed.

Figure 2a shows the FTIR spectra of the dried lanthanum silica xerogels, with the typical silica (SiO$_2$) vibrations located at 800, 1080 and 1220 cm^{-1} assigned to siloxane (Si-O-Si)[36] and 960 cm^{-1} to silanol (Si-OH)[37] bonds for non-doped silica, LaSi(0). The integration of lanthanum nitrate into the silica during the sol-gel synthesis results in the emergence of multiple sharp nitrate peaks at 1455, 1425, 1325, 1300, 1050, 1040, 870, 810, 780, 740, 715 cm^{-1} (Figure 2a). Upon calcination at 500°C, there is a significant reduction in the intensity of the nitrate peaks (Figure 2b), attributed to the partial decomposition of the lanthanum nitrate species[38,39]. The silanol peak at 960 cm^{-1} is no longer visible at 500°C for the LaSi(0) xerogels, becoming embedded as a shoulder in the broader siloxane peak from 1080 to 1220 cm^{-1}. This is a direct result of the condensation reactions occurring during the heat treatment, a process which occurs by the forming of siloxane species at the expense of silanol groups.

The heat treatment of the LaSi(0.33) xerogel (Figure 2c) shows a significant effect in the reduction of nitrates, which decompose and leave the lanthanum silica matrix as the calcination temperature increases. Similarly, as the calcination temperature increases, the FTIR spectrum exhibits the emergence of a peak at 950 cm^{-1}. This peak is distinctly different in shape to the traditional silanol peak at 960 cm^{-1}, as can be seen by comparison with LaSi(0) in Figure 2b, and emerges at temperatures above 200°C. Furthermore, this peak becomes more intense at higher lanthanum concentrations (Figure 2b). This peak has widely been reported to originate from the SiO$_4^{4-}$ ion, which comprises part of the lanthanum silicate
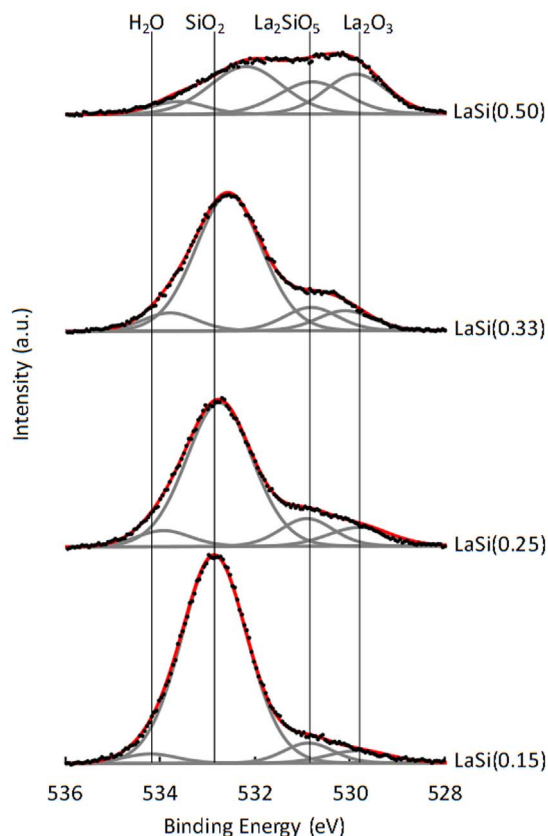
Table 1 | BET surface area and pore volume of all lanthanum silica xerogels

	LaSi(x)							
	0	3	5	10	15	25	33	50
BET (m^2/g)	345	223	155	166	103	86	69	53
PV (cm^3/g)	0.182	0.12	0.078	0.088	0.053	0.046	0.051	0.093
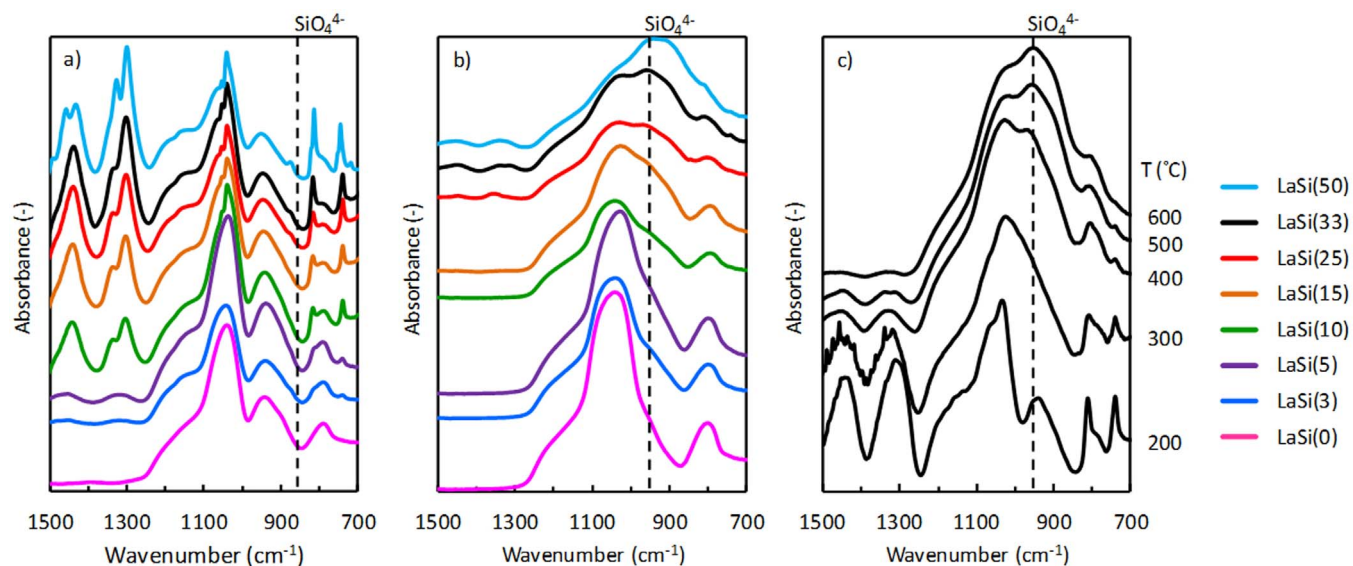
Figure 2 | Infrared spectra for xerogels with a lanthanum to silica molar ratio of $0 \leq La/Si \leq 0.5$ heated to (a) 60°C, (b) 500°C, and (c) LaSi(0.33) as a function of temperature.
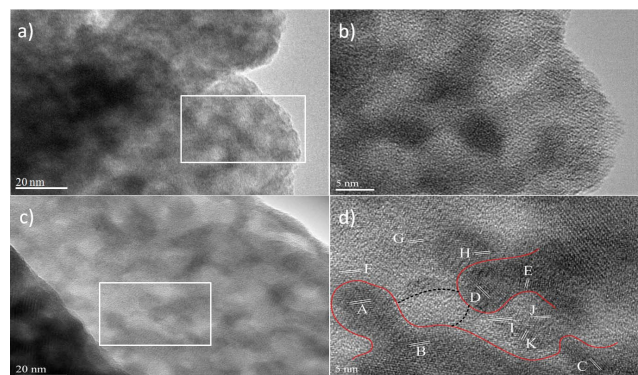
species, a phase which forms at elevated temperatures due to the diffusion of La_2O_3 and silica[33,40–42]. As nitrates are decomposed during calcination, the thermodynamic propensity is for the formation of lanthanum oxides, thus suggesting the formation of metal oxide particles in silica, as reported elsewhere for cobalt and cobalt iron oxides[13,19,43,44].

X-ray photoelectron spectroscopy (XPS) was carried out to gain a more thorough understanding of the chemical formation of the lanthanum silica xerogels. The XPS spectra in Figure 3 displays the O1s region of the xerogel for samples LaSi(0.15) to LaSi(0.50) calcined at 500°C. Deconvolution of the LaSi(0.15) spectra shows a large peak present at 532.8 eV, commonly associated with SiO_2[41]. As the concentration of lanthanum increases in the xerogels, the binding energy of the SiO_2 peak decreases, consistent with results published elsewhere[41]. Deconvolution of the shoulder at lower binding energy shows a peak at approximately 529.8 eV which is assigned to La_2O_3[41,45–48]. Furthermore, the deconvolution reveals the presence of a peak between the SiO_2 and La_2O_3 species, at 530.8 eV, which has been extensively reported as lanthanum silicate[41,45,47], thus confirming the results from the FTIR spectra in Figure 2b and c. Deconvolution of the lanthanum oxide and lanthanum silicate species within the O1s region matches well with deconvolution within the La3d region confirming the results.

TEM images of the xerogels were taken to investigate the presence of nano-domains composed of lanthanum oxide and lanthanum silicate. Figure 4a shows a representative image of the LaSi(0.33) xerogel. The presence of particulate aggregates can be seen, particularly in Figure 4b, which are similar to the nanoscale assembly that was reported by Célérier et al.[33] for the formation of lanthanum

Figure 3 | Deconvoluted, baseline corrected XPS spectra of the O 1 s region in the xerogel with lanthanum concentration LaSi(0.33) calcined at 500°C.

Figure 4 | Representative TEM image of LaSi(0.33) xerogel calcined at (a) 500°C and c) 1000°C. (b) and d) are high resolution images from within the boxes of a) and c) respectively.
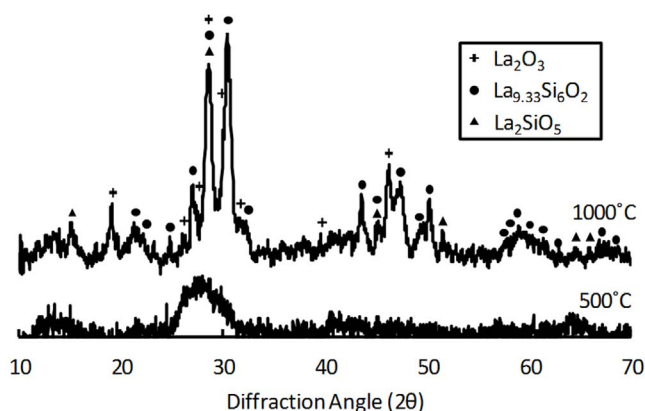
Figure 5 | XRD of LaSi(33) calcined at 1000°C.

silicates at high temperatures. Determination of the phases present in these nanoscale domains is difficult due to their amorphous nature (confirmed by XRD in Figure 5). Thus, to determine the phase of the various components in the TEM image, the LaSi(33) sample was heated to 1000°C to induce crystallinity. It can be seen in Figure 4c that the structure of the xerogel is very similar to that calcined at 500°C. High resolution TEM exhibits the presence of multiple crystalline phases (Figure 4d), those that are labelled are presented in Table 2. The red line bordering the dark areas indicates the interface between lanthanum oxide and lanthanum silicate, while the enclosed space between the dashed black line and the red line is amorphous, and is proposed to be unreacted microporous silica.

Figure 5 shows the XRD patterns of the LaSi(33) xerogel calcined at 500 and 1000°C. The xerogel calcined at 500°C exhibits a largely amorphous structure. Four broad peaks are present attributed to amorphous silica ($2\theta = 27°$) and lanthanum oxide/lanthanum silicate crystallites ($2\theta = 13°$, $43°$ and $64°$). The 1000°C pattern shows numerous crystalline peaks, all of which were assigned to La_2O_3 (JCPDS cards 05-0602, 22-0369), La_2SiO_5 (JCPDS card 40-0234) and $La_{9.33}Si_6O_{26}$ (JCPDS card 49-0443), with La_2O_3 and $La_{9.33}Si_6O_{26}$ constituting the majority of the crystalline material. This corresponds to the TEM image shown in Figure 4d.

With further analysis of the XPS spectra (Figure 3), it is observed that the shoulder present in the LaSi(0.15) xerogel increases in intensity proportionally to the lanthanum concentration. However, the shape of the shoulder also changes, from a gradual tailing off in intensity at the lower binding energy side of the shoulder for the LaSi(0.15) sample to the formation of a distinct peak at low binding energies for the LaSi(0.50) sample. This deviation suggests a variation in the ratios of lanthanum oxide to lanthanum silicate. The ratio of these deconvoluted peak areas is displayed in Figure 6. It can be seen that the ratio of lanthanum oxide to lanthanum silicate increases linearly with lanthanum concentration. Assuming the formation of

nano-domains containing both La_2O_3 and lanthanum silicate of a constant composition, this suggests that the average particle size is increasing proportional to the lanthanum concentration.

The TEM micrograph suggests the formation of lanthanum oxide nano-domains surrounded by lanthanum silicate. It is proposed that at low lanthanum concentrations ($\leq$LaSi(0.15)) the reaction between La_2O_3 and silica converts microporous silica into a dense lanthanum silicate. This is supported by the emergence and growth of a peak at 950 cm^{-1} in the FTIR spectrum of lanthanum doped xerogels (Figure 2b) and the decrease in microporous volume of lanthanum doped xerogels (Figure 1a). In addition, studies have shown that transition metal oxides that are incorporated within microporous silica are accessible by ambient water molecules, due to the hydrophilic nature of the silica matrix[18]. Exposure of La_2O_3 to water results in a spontaneous reaction to produce lanthanum hydroxide ($La(OH)_3$), a compound which does not appear within the infrared or XRD analyses as expected. This further indicates that the La_2O_3 phase must be fully enclosed within a dense silicate material at its interface, such that ambient moisture cannot contact the La_2O_3. Hence, these results strongly suggest the formation of a lanthanum nano-phase constituted by La_2O_3 encased by lanthanum silicate.

At high lanthanum concentrations ($>$LaSi(0.15)) it is proposed that the enhanced size of the nanoscale assembly of lanthanum increase their proximity. The reduction in inter-assembly spacing, in addition to the enhanced consumption of silica, results in the formation of nano-domains, as can be seen in Figure 4. As the lanthanum concentration increases, the nanoscale assembly of lanthanum silicates and oxides continues to increase in size, resulting in the expansion of the inter-nano-domain voids. This effect correlates well with the results in Figure 1b, with the mesoporous volume increasing proportionally to lanthanum concentration. The expansion of the porous network of lanthanum silicate materials over the calcination process has been shown previously by Célérier et al.[33]. This work shows that the underlying mechanism causing the expansion of the porous network is the formation and expansion of lanthanum nano-domains. This study thus provides a platform for porosity optimisation studies for lanthanum silica materials.

Methods

Table 2 | Inter-lattice fringe assignments for LaSi(33) calcined at 1000°C

	d-spacing	reference	Orientation	Phase
A	0.296	0.298	[101]	La_2O_3
B	0.341	0.341	[100]	La_2O_3
C	0.297	0.298	[101]	La_2O_3
D	0.295	0.298	[101]	La_2O_3
E	0.304	0.306	[002]	La_2O_3
F	0.288	0.289	[112]	$La_{9.33}Si_6O_{26}$
G	0.333	0.330	[102]	$La_{9.33}Si_6O_{26}$
H	0.279	0.280	[300]	$La_{9.33}Si_6O_{26}$
I	0.315	0.318	[210]	$La_{9.33}Si_6O_{26}$
J	0.291	0.291	[211]	$La_{9.33}Si_6O_{26}$
K	0.327	0.327	[021]	La_2SiO_5
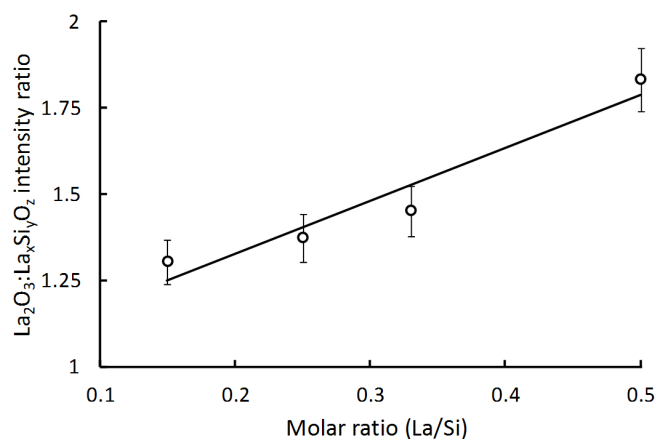
Figure 6 | XPS deconvolution for 0.15 < La/Si < 0.50 samples calcined displaying the lanthanum oxide to lanthanum silicate intensity ratio at 500°C.

Characterisation. Fourier transform infrared (FTIR) spectroscopy was performed using a PerkinElmer Spectrum 400 FT-IR/FT-FIR spectrometer with a diamond/ZnSe crystal. Data was collected between 4000–500 cm^{-1}. Transmission electron microscopy (TEM) was performed using a JEOL 2100 transition electron microscope operating at 200 keV. Samples were prepared by suspending finely crushed xerogels in ethanol and depositing them on a hollow carbon copper grid. X-ray photoelectron spectroscopy (XPS) was performed after xerogel powders were re-crushed to minimise any contaminant formed on the surface layer. A Kratos Axis ULTRA X-ray Photoelectron Spectrometer incorporating a 165 mm hemispherical electron energy analyser was implemented to acquire the data. An Al Kα (1486.6 eV) monochromatic x-ray source was used at a 90° takeoff angle with 0.05 eV step size to obtain XP spectra. Charge compensation was performed by setting the adventitious C1s peak to a binding energy of 284.6 eV. Peak deconvolution of the high-resolution data was carried out using CasaXPS software with a Shirley baseline. Kratos library relative sensitivity factors (RSFs) were used to normalise atomic regions.

N_2 adsorption-desorption isotherms were generated at 77K in a Micromeritics TriStar 3000 volumetric adsorption system. Before analysis, xerogels were degassed for 8 hours at 200°C in a Micromeritics VacPrep061 at a pressure of approximately 0.05 mbar. The pore size distribution (PSD) was calculated via density functional theory assuming cylindrical pores with an oxide surface.

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Acknowledgments

Author contributions

B.B. performed the experimental works, analysed results and wrote the manuscript. J.M., C.R.M., S.S. and J.C.D.d.C. assisted in the analyses of results. S.S. and J.C.D.d.C. reviewed the manuscript prior to submission.

Additional information