The final publication is available at

https://doi.org/10.1002/cssc.202300123

Additional Information

ARTICLE

Fast microwave assisted synthesis, calcination and functionalization of a silica mesoporous nanomaterial: UVM-7

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We report here, for the first time, the use of a solid state microwave source for the synthesis, calcination and functionalisation of a UVM-7 based hybrid mesoporous silica material. The synthesis of the UVM-7 material is obtained in 2 minutes at low power (50 W) and temperature (341 K) by the combination of a microwave irradiation and the atrane route. Moreover, it has been successfully calcined and functionalized in just 13 and 4 minutes respectively with microwave assisted procedures. The products obtained in every step of the synthesis have been characterized using X-ray diffraction, nitrogen adsorption-desorption and transmission electron microscopy techniques, showing analogous properties to the material synthesized under conventional protocol but in much shorter times. Finally, we carried out a total synthesis comprising each individually optimized step, giving the final functionalized material in a time as low as 4 hours including work-up, by contrast to a typical synthesis that comprises several days. Savings higher than one order or magnitude are obtained in time and energy. Our example is a proof of concept of the potential use of solid state microwave generators for the ultrafast on-command preparation of hybrid nanomaterials due to their accurate control and accelerating properties.

Introduction

Microwave-assisted synthesis (MAS) has been applied to chemical reactions in the last decades because it offers several advantages when compared with conventional synthesis.[1,2] Among the many reported benefits, it is worth highlighting the rapid volumetric heating of the solution, the homogeneity of the heating, besides a remarkable efficiency and economic performance that makes this kind of energy environmentally friendly.[3,4] Moreover, the fast synthesis and ease of use makes this technique the most suitable to screen a wide range of experimental conditions or to scale-up processes.[5] When applied to the synthesis of materials, all these assets results in homogeneous nucleation, shorter crystallization times and faster supersaturation of the solution, producing very homogeneous materials, with a narrow particle size distribution, uniform morphology and in higher yields when compared to conventional heating.[6]

Although there is a lower number of examples of the application of microwaves (MW) to materials in comparison to organic synthesis, MAS has been successfully applied to the synthesis of many nanomaterials.[7–9] Some of the examples are referred to the synthesis of mesoporous silica materials using surfactants or copolymers as templates, such as MCM-41, SBA-15, SBA-16, and many others porous related materials.[10] This kind of mesoporous silicas are still very attractive to scientists due to their unique properties like porosity (mesopores with diameters between 2 and 50 nm), high surface areas and morphology, what make them suitable for different applications such as catalysis,[11] sensing,[12, 13] and drug delivery[14] among others. In particular, UVM-7 type solid materials are of special interest, as they show a bimodal porous structure formed by mesopores and textural macropores between particles which improve their applicability.[15–17] Despite microwaves hugely increase reaction rates, the overall process of a microwave-assisted syntheses containing a microwave assisted step is not always as fast as they are supposed to be. In most cases, microwave irradiation is only applied to one step of the whole synthesis process,[18,19] and there are only a few examples of MW applied to the extraction of the template,[20–22] but no references of calcination processes. Some inconveniences associated to use microwaves can be that synthesising the desired solid can delay for several hours of irradiation, apart from work-up[23] or that microwave-assisted synthesised materials possess structural properties different to those obtained conventionally, not always improving them.[24]

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†Electronic Supplementary Information (ESI) available: Experimental conditions and further solid characterization, including N_2 isotherms, XRD and TEM images. See DOI: 10.1039/x0xx00000x

The source of microwaves most frequently used is the magnetron. A magnetron is basically a vacuum tube in which the electrons, produced under a magnetic field, are forced to modify their flow producing microwave radiation. Despite the high power, low cost and simplicity of such devices, magnetrons present significant limitations such as the difficulty to control power, use of high voltage supply, and limited life time.[25] Magnetrons work under ON-OFF cycles, thus alternating none with high power radiation in order to reach the desired average power. More recently, a new technology based on semiconductors named solid state (SS) sources emerged as a feasible alternative to magnetrons.[26] Besides an improved efficiency in converting electric power to microwave energy, these sources provide tuneable parameters, allowing an accurate control of power, frequency, and phase of the generated microwaves. Despite these compelling advantages, their relative novelty and comparatively high costs have reduced their implementation in microwave devices to date.

Based in our past experience in the synthesis of mesoporous materials, and being aware of the reported procedures of MAS of this type of solids, we hypothesised that solid state generators of microwaves could be a suitable energy source for the fast and complete production (synthesis, calcination and functionalization) of a UVM-7 type mesoporous material, thanks to the accurate control on the synthetic parameters provided by this type of MW source. We report here the first microwave-assisted total synthesis of a hybrid mesoporous silica material. This solid could be successfully obtained thanks to the optimization of each individual stage of the synthesis under MW irradiation. To the best of our knowledge, this represents the very first calcination of a mesoporous solid under microwave irradiation without the aid of oxidant reagents. Furthermore, we have discussed the influence of the MW source, irradiation power and time in the size, shape, aggregation, and porosity of the samples.

Results and discussion

UVM-7 synthesis

Taking as starting point our previous experience in the atrane route for the synthesis of mesoporous materials, and considering the reported procedures for the synthesis of silica nanomaterials under microwave irradiation,[10] we wanted to check if microwaves could help to some extent the synthesis of
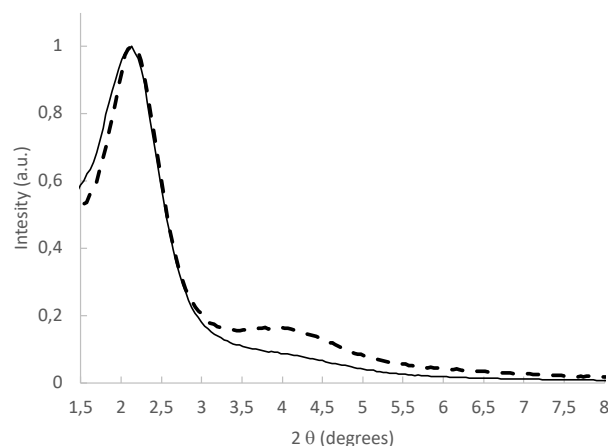
**Figure 1** XRD patterns of SS1 calcined sample (solid line) and Conv (dashed line)

UVM-7 type solids. In particular, we were interested in study the influence of the synthesis parameters (power, and time) in the final properties of the solids. In this way, different experimental conditions (from 50 to 200W and from 30 to 120 seconds) were tried in the SS source of microwave obtaining the samples SS1 to SS7. The experimental conditions and porous features are summarized in Table 1. In all cases it is observed the apparition of a white solid during the reaction in agreement with the formation of silica. These results confirms that the use solid state generators of microwaves can be a suitable approach to increase the hydrolysis and condensation reaction rates in the sol-gel process.

A solid produced under conventional conditions, without microwaves (Conv),[27] was also synthesised for comparative purposes.

The solids were characterised by standard procedures. X-ray diffraction (XRD) pattern of the SS1 material is shown in Figure 1. It displays a typical low angle diffraction pattern with one well defined intense peak round 2° (2θ), and another broad signal of relatively low intensity in the range of about 3.5-4.0° (2θ), what matched well with the typical diffractogram of UVM-7. The XRD peaks can be associated to the (1 0 0) and the overlapped (1 1 0) and (2 0 0) reflections of a hexagonal lattice, respectively. These patterns are characteristic of hexagonal disordered mesoporous materials, and they are related with the presence of an inner ordered mesoporous system within the particles.

Table 1. Summary of the most remarkable experimental conditions and textural properties of UVM-7 type mesoporous materials synthesized under different solvothermal conditions. SS refers to solid state source and Conv refers to the conventional synthesis conditions (without microwaves).

Sample ref.	MW Source	Power (W)	Time (s)	S_{BET} (m²/g)	Mesopore size (nm)	Mesopore Volume (cm³/g)	Macropore size (nm)	Macropore Volume (cm³/g)
SS1	Solid State	50	120	980	2.7	0.81	43.1	1.52
SS2	Solid State	100	60	1000	2.6	0.82	55.1	0.64
SS3	Solid State	200	30	1062	2.6	0.88	43.4	0.36
SS4 (6)	Solid State	50	105	939	2.5	0.72	49.3	0.62
SS5 (8)	Solid State	75	60	945	2.5	0.72	56.0	0.71
SS6 (9)	Solid State	75	70	966	2.4	0.73	51.0	0.85
SS7 (10)	Solid State	75	80	1064	2.4	0.73	57.5	1.17
Conv	None	-	-	969	2.7	0.78	49.9	1.44
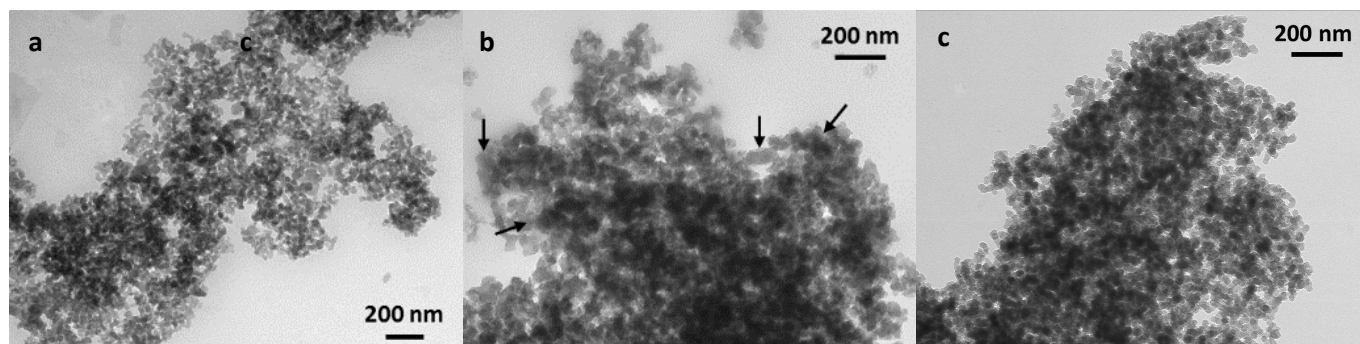
Figure 2 Representative TEM images of selected calcined UVM-7 type materials (a) SS1, (b) SS8, and (c) Conv.

Similar diffractograms are obtained for the rest of materials (SS2-7).

XRD does not offer information about the intrananoparticles macropores formed. Much detailed information about the bimodal porous structure of UVM-7 materials can be obtained with the aid of TEM images (Figure 2). In this case, significant differences between solids radiated for different powers appeared. All the solids are basically made up of a continuous network formed by small mesoporous nanoparticles (12-17 nm) between which a non-ordered system of large textural pores (at the edge of large-mesopores and macropores) is formed. The homogeneity of the material obtained in such a short period of time (a few minutes) can be assigned to the accurate control of the power and the continuous irradiation that offer SS MW sources. However, even considering these benefits the power can influence seriously the final structures. If the selected power is too high (over 50 W for the reagent amounts employed in this article), higher size particles were formed, even when microwave radiation time was reduced (Figure 2b).

The formation of larger particles at higher power is not directly related with a solution overheat, because the final reaction temperature registered in the experiments (round 70 °C) was similar in all cases. We hypothesise that, as a result of microwave irradiation, the reactivity of the silatrane precursors increased, making them to condensate and to aggregate nanoparticles in close proximity. The initial silica-based nuclei can act as dipoles in the mixture solution under the effect of the electric field of microwave radiation. Then, under exposure to higher microwave power, the obtained nuclei polarize and aggregate to form larger nanoparticles.[28]

The commented structure of the solids and the effect of the applied microwave power on the porosity of the samples can be further understood by attending to N_2 adsorption-desorption isotherms (see Figure 3 and Table 1). In all cases, the isotherms show the characteristic bimodal pore system of UVM-7 type materials, composed by two well-differentiated adsorption steps. The first one, occurring at relatively low relative pressures ($0.2 < P/P_0 < 0.4$), and characteristic of type IV isotherms, is related to capillary condensation in the mesopores of the particles. Its shape, sharp and without hysteresis loop, suggests these mesopores are uniform and cylindrical. The second step, occurring at high relative pressures ($P/P_0 > 0.8$), corresponds to the filling of the large mesopores or macropores formed between primary nanoparticles. In this case, the

presence of a narrow hysteresis loop indicates macropores are non-cylindrical or less homogeneous, as expected for textural pores. Therefore, adsorption-desorption isotherms results are consistent with TEM and XRD observations. When high microwave irradiation powers are employed, the formation of larger particles causes interparticle pores to reduce in number and to increase in size, thus decreasing the amount of N_2 volume adsorbed during the second adsorption step.

As the physicochemical parameters discussed above have shown, an accurate control of the microwave power is a key parameter regarding the control of the final material obtained. A SS source of microwaves in combination with the atrane route allowed us to obtain UVM-7 materials in a very reproducible way, with similar characteristics to the materials conventionally aged overnight in absence of microwaves.

The results described above have shown how the combination of irradiated power and time are key parameter to obtain the desired morphology of the UVM-7 materials. Although the global energy provided to solids SS1-3 was the same (SS1 (50 W, 2 min), SS2 (100 W, 1 min), and SS3 (200 W, 0.5 min)), their structural parameters were pretty different (see Table 1). When the power increased, particles obtained were larger and fewer in number, thus reducing the volume of the pores formed between these particles. Attending to pore volume parameters, the most affected one by this effect, it decreased from 1.52 cm^3/g in SS1, to 0.64 cm^3/g in SS2 and finally to 0.36 cm^3/g in
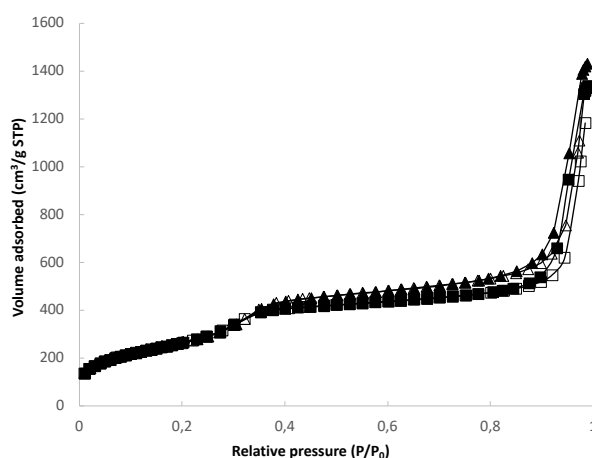
Figure 3 Nitrogen adsorption-desorption isotherms of calcined samples. Triangle SS1, square Conv. Empty adsorption, solid desorption.

SS3. That suggest that the power could be relevant in the particle growth when the rest of parameters (i.e. temperature or energy) are maintained. However further studies in the synthesis of other materials and synthesis conditions would be necessary to understand in a conclusive way this effect.

Synthesis repeatability

In order to evaluate the repeatability of the synthesis procedure, it was repeated six times. The experimental conditions were exactly the same in all cases, irradiating the same amount of reagents mixture with a solid state microwave source for 2 minutes at 50 W power. The homogeneity between samples prepared with microwaves is noticeable attending to XRD and nitrogen adsorption-desorption measurements (Table 2 and Figures S1 and S2). The relative variation in the peak position of the 100 peak shows a relative variation lower than 1% (2.14±0.02). We can observe that the synthesis is more robust for the parameters related with mesopores and the total surface, with variations lower than 6%. It indicates that the inner template mediated structure of the particles is the same in all cases, as no variations in the angle of the most intense diffraction peak are observed. This value agrees with the narrow variation observed for the peak position of XRD. By contrast, the process related with the formation of the macropores is more sensitive to slight variations in the synthesis and fluctuates in each batch. Furthermore, TEM images show how every solid is formed by the aggregation of small homogenous particles, leading to a bimodal pore system (see Figure S3). Neither aggregates nor larger particles are observed in any case. In conclusion, all these evidences support the fact that a more reproducible UVM-7 type of solid with well-defined parameters can be produced when microwave SS sources are employed.

The repeatability obtained under microwave assisted method was compared with the reproducibility from other UVM-7 solids previously synthesised in bibliography using conventional synthesis (a list of the data source can be found in the supplementary material Table S1). Pore sizes, pore volumes and BET surface areas present less disperse values, thus indicating MW assisted synthesis is a good method for obtaining well defined solids, more similar to each other than those provided under conventional conditions.

Table 2 Summary of physicochemical parameters obtained by XRD and nitrogen adsorption-desorption techniques.

| Parameter	SS MW*	Conventional*
S_{BET} (m^2/g)	940 ± 33 (3.5)	971 ± 87 (8.9)
Mesopore size (nm)	2.5 ± 0.1 (2.7)	2.7 ± 0.1 (4.1)
Mesopore volume (cm^3/g)	0.72 ± 0.04 (5.9)	0.79 ± 0.12 (15)
Macropore size (nm)	52 ± 6 (11)	42 ± 7 (16)
Macropore volume (cm^3/g)	0.95 ± 0.33 (35)	1.10 ± 0.32 (29)

*Mean ± standard deviation (relative variation %)

UVM-7 Calcination

As a second step towards the fast synthesis of the hybrid material, the application of microwaves to the calcination of the UVM-7 as made material was studied. Conventional calcination in a muffle of CTAB in silica mesoporous solids requires 5 h at 550 °C plus the time needed to heat up (about 3h) and cool down the oven. Thus, calcination of silica mesoporous materials needs one workday to have them ready to use. To the best of our knowledge, reported microwave methodologies for template removal from mesoporous solids requires acids,[22] organic solvents[20] or combination of conventional and microwave oven,[21] but no method reported to date has been able to fully calcine the solid in such a simple way. A special calcination chamber was prepared for template removal in a microwave cavity (Figure 6.b). This is based in a ceramic material highly susceptible to microwaves and resistant to high temperatures. In a short period of time, the susceptor efficiently transformed microwaves into heat and allowed to reach temperatures higher than 700 °C. Moreover, the susceptor was in direct contact with a porcelain crucible, containing the sample, and both (crucible and susceptor) were placed into a porous alumina chamber, which acted as insulator to prevent temperature loss.

Different experimental conditions were tried to optimize the calcination procedure (Table 3). UVM-7 was also calcined using the standard conditions (in a conventional oven at 550 °C) for comparative purposes. Due to the size and shape of the crucibles employed, 200 mg of UVM-7 were calcined each time. The uncalcined and calcined samples are white, but during the calcination, the solid becomes black due to the formation of carbon derived from the decomposition of the surfactant. Thus, the colour of the material is a convenient naked eye method for the monitoring of the calcination. The presence of a black or brown colour in the solid is indicative that the calcination is incomplete. Conversely, to protect the inner porous structure, temperatures above 600°C are undesired because at higher temperatures the porous structure starts a collapsing process.

After a preliminary screening process the white colour of the solid confirmed that our system was able to calcinate the material in less than 20 minutes (200W) and a further detailed studied was defined to optimize the synthesis conditions (see Table 3). Assays with an irradiation time of 10 minutes revealed that the calcination was not complete (CSS1). By contrast, when the irradiation was increased to 15 minutes the calcination was complete but the temperature reached 760 °C (CSS2). Seeming that not a single power would provide the desired conditions to fully calcine the sample without exceeding temperature, in the successive experiments a power ramp was applied (CSS3-CSS5): the initial high power part (200 W) was used to quickly increase
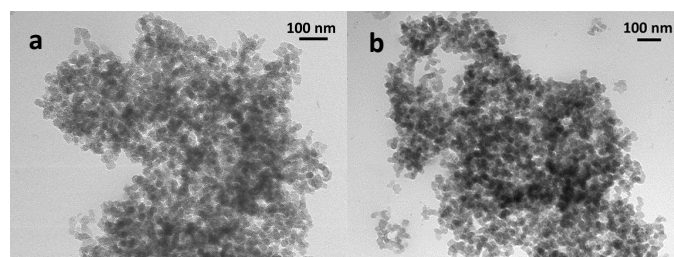
Figure 4 Representative TEM images of UVM-7 calcined (a) in a conventional muffle or (b) in a solid-state microwave (CSS5).

the temperature and decompose CTABr, whereas the low power step (150 W) was used to keep the temperature constant, compensating temperature losses over time. This procedure kept an optimal temperature in the cavity and provided organic matter time enough to properly calcine. Time was a key point: long times (CSS3) provided a white material but overcame the desired temperature, whereas shorter times (CSS4) did not complete the calcination yielding a brownish solid. Finally, a two steps power ramp of 8 minutes at 200 W and 5 minutes at 150 W (CSS5) resulted as optimal.

Table 3 Experimental conditions tested for UVM-7 calcination in a solid-state microwave.

Sample	Power (time) W (min)	T_f (°C)	Appearance
CSS1	200 (10)	620	Not totally white
CSS2	200 (15)	760	White
CSS3	200 (7) + 150 (7)	715	White
CSS4	200 (8) + 150 (4)	540	Not totally white
CSS5	200 (8) + 150 (5)	575	White

Once the heating ramp was selected, N_2 adsorption-desorption isotherms and TEM images were taken to evaluate and compare their structure. According to Table 4 the physical properties of the UVM-7 calcined in a conventional muffle are practically identical to those of the solid calcined in a solid-state microwave with the optimized power ramp. No differences between both methods can be outlined attending just to the isotherms. Therefore, TEM images (see Fig. 4) were also taken, showing a similar result: no substantial changes affecting the double pore system of the solid occurred after calcination either in a muffle or in the microwave.

Table 4 Physicochemical properties of UVM-7 type mesoporous materials calcined in a conventional muffle (conv.) or in a SS microwave (CSS6).

Sample ref.	S_{BET} (m²/g)	Mesopore size (nm)	Mesopore Volume (cm³/g)	Macropore size (nm)	Macropore Volume (cm³/g)
CSS5	902	2.6	0.75	47.7	1.06
Conv.	956	2.6	0.76	47.6	0.96

Attending to the good results obtained, we can conclude that solid-state sources can be successfully employed to calcine UVM-7 mesoporous solids. In a total time of just 13 minutes, we were able to calcine UVM-7 under microwave irradiation, a much shorter time than the 5.5 h required under conventional heating in a muffle.
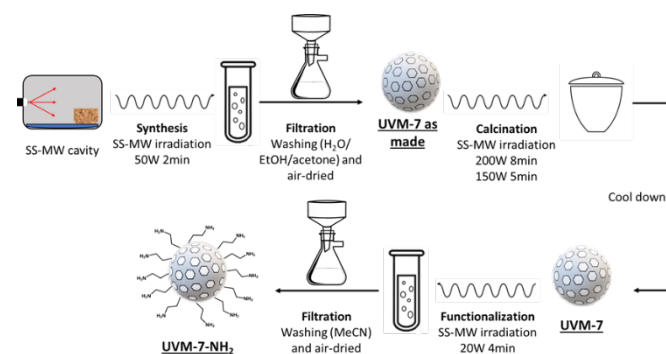
UVM-7 Functionalization

Functionalization of mesoporous materials with different chemical groups is a key point after calcination, as it provides the solid of the desired functionality to be applied in different fields. Taking into consideration all the chemical groups that can be attached to the surface by using the commercially available trialcoxysilanes, amine group is probably the most used to

functionalize silica solids. Amine groups have been widely applied as silica coating as they interact with proteins,[29] metals[30] and some gases.[31] Thus, APTES was selected as the target molecule to optimize microwave-assisted surface functionalization, and to compare it with the modification produced by conventional methodology.

Typical conditions reported in bibliography for the functionalization with APTES required a mixture of 6 mmol of APTES *per* g SiO_2, stirred at room temperature in 30 mL of the desired solvent for 5.5 h.[32] When using this conventional methodology, a total content of 3.55 mmol of $-NH_2$ *per* g SiO_2 was calculated attending to thermogravimetry data. This value agrees with others previously reported in bibliography.[15] On the other hand, when the same mixture was placed in the solid-state microwave and irradiated at very low power (20 W) for only 4 minutes, the $-NH_2$ content functionalized onto the particles turned out to be 1.8 mmol of $-NH_2$ *per* g SiO_2. Although this is roughly half of the functionalization provided by conventional method, this might be due to the absence of stirring during microwave process, thus avoiding the dispersion of the particles and thereby decreasing the functionalization achieved. In any case, as a proof of concept, microwaves were able to reach a functionalization of 50 % in only 4 minutes. This amount is enough in most cases, as it is easy to find in the bibliography values of $-NH_2$ content similar to 1.8 mmol of $-NH_2$ *per* gram of SiO_2.[33]

UVM-7 total synthesis (synthesis, calcination and functionalization)

Once the solid-state microwave experimental conditions were optimized for each single step concerning a typical synthesis of UVM-7 (synthesis, calcination and functionalization), a complete synthesis of UVM-7 via solid-state irradiation was tested. We considered that, if we were able to consecutively apply every step in such a fast way, the final material UVM-7 would be ready for its application in less than 20 minutes of irradiation. Therefore, we carried out the complete synthesis, which considering the intermediate steps of washing, filtration, drying, and cooling down, took around 4 hours to yield the final material (see Figure 5). This amount of time is negligible when compared with the 3 days needed when using the conventional method.

Figure 5 Representative scheme of total UVM-7 synthesis (synthesis, calcination and functionalization) by means of a solid-state microwave.

Once prepared, X-ray powder diffraction and TEM techniques were used to confirm the mesoporous structure from the UVM-7 in every step. The XRD pattern (See Figure S4) of the three solids showed the low-angle reflection indexed as a (1 0 0) Bragg reflection and the overlapped (1 1 0) and (2 0 0) reflections characteristic of UVM-7 materials. Moreover, it can be observed how, after calcination, the main peak slightly shifts to lower angles due to condensation of silanol groups. Therefore, diffractograms proved that, throughout the process, the materials kept their characteristic hexagonal disordered mesoporous structure. When compared with solids synthesised or calcined either conventionally or by microwave assisted methods mentioned above, no remarkable differences where observed between them, thus it can be concluded that microwave irradiation produced nanomaterials structurally analogues to those obtained under conventional techniques in a shorter time. On the other hand, TEM images (see Figure S5) confirmed that the UVM-7 solids were well synthetized, and the mesoporous structure was not affected by microwaves and maintained during the consecutive steps. Finally, Regarding the N_2 adsorption-desorption isotherms, the characteristic bimodal pore system of UVM-7 was maintained during the whole process. Values of 2.5 nm (mesopores) and 48 nm (macropore) were measured. Moreover, a high specific surface value, close to 1000 m^2/g, was found. These values, along with the pore volumes, match with those typical of a conventional UVM-7 and with those obtained in our previous assays. Lastly, the amount of amino groups on the UVM-7 mesoporous hybrid material, estimated by a TGA analysis, was found to be 1.16 mmol of -NH_2 *per* g SiO_2.

Power consumption

Finally, the electricity consumption of each stage (synthesis, calcination and functionalization) was measured for both conventional and microwave assisted methods. From this value, CO_2 emissions were further calculated by considering the values of US Environmental Protections Agency, giving a conversion factor of 433 g CO_2 *per* kWh.[34] This information is summarized in Table 6 for comparative purposes. In general, microwave consumption is notably lower than that required under conventional techniques (0.115 *vs* 6.100 kWh, respectively). Considering the global synthesis pathway, microwave consumption represents a reduction in more than one order of magnitude and a value as low as 2% of that required by conventional techniques. This is mainly due to calcination step. As expected, microwave calcination required a negligible part (2%) of the energy required to achieve the same process in a muffle. Therefore, microwave saved both time and energy in each and every step of the synthesis, allowing the environmentally friendly synthesis, calcination and/or functionalization of silica nanoparticles.

Table 6 Comparison of experimental conditions and power consumption of the different steps of UVM-7 whole synthesis (synthesis, calcination and functionalization) under conventional or microwave assisted methods.

	Conventional			Microwave		
	Time (h)	Consumption (kWh)	CO_2 emissions (g CO_2)	Time (min)	Consumption (kWh)	CO_2 emissions (g CO_2)
Synth.	24	0.566	245	2	0.008	3.5
Calcin.	8.5	5.407	2341	13	0.097	42.0
Funtio.	5.5	0.127	55	4	0.010	4.3
Total	35	6.100	2641	19	0.115	49.8

Experimental

Chemicals

All the synthesis reagents were analytically pure and were used without further purification. Tetraethyl orthosilicate (TEOS), triethanolamine ($TEAH_3$), cetyl-trimethylammonium bromide (CTABr), and (3-aminopropyl)triethoxysilane (APTES) were purchased from Sigma Aldrich química (Madrid, Spain). NaOH, acetonitrile and ethanol were purchased from Scharlab S.L.

Physical measurements

All solids were characterized by X-ray powder diffraction (XRD) at low angles (Bruker D8 Advance Diffractometer) using a monochromatic Cu Kαsource operated at 40 kV and 40 mA. Patterns were collected in steps of 0.04° (2θ) over the angular range 1.3–8.3° (2θ) for 1 s *per* step. Transmission electron microscopy (TEM) images were taken with a JEOL-JEM-1010 instrument operated at 100 kV (equipped with digital camera MegaView III and ''ANALYSIS" software). Samples were gently ground in ethanol, and grains were deposited on a holey carbon film supported on a Cu grid. Nitrogen adsorption-desorption isotherms (-196 °C) were recorded on a Micromeritics ASAP 2020 automated analyser. The samples were degassed in situ at 120 °C and 10^{-6} Torr for 15 h prior to analysis. Specific surface areas were calculated from the adsorption data within the low-pressure range using the Brunauer-Emmett-Teller (BET) model. Pore sizes and pore volumes were determined following the Barrett-Joyner-Halenda (BJH) model on the adsorption branch. Thermogravimetric analysis (TGA) were obtained with a SETARAM SETSYS 16–18 instrument (Caluire-et-Cuire, France) under a dry air flow at heating rate of 10 °C min^{-1} up to 1000 °C.

SS-Microwave device and calcination chamber

The SS device used during the whole process consists of a SS source connected through a coaxial cable to the irradiation cavity (see Figure 6.a). The source operates at a maximum power of 200 W selectable in 1 watt increments. The frequency can be selected from 2420 MHz to 2480 MHz in 5 Hz increments to tune the system in order to optimise the absorbed power. During the calcination stage, a special calcination chamber was used (Figure 6.b). It comprises three well differenced parts: an external porous alumina chamber, an intermediate microwave-

absorbent ceramic crucible and an inner commercially available porcelain crucible. The alumina chamber is made up of two blocks with an inner cavity, and thanks to its porous structure acts as an efficient insulator to keep high temperatures inside. The heat is produced by a microwave-absorbent ceramic crucible placed inside. Based in SiC, this ceramic part efficiently transforms microwaves into heat. The heating produced is finally transferred by conduction and convection to a final Haldenwanger porcelain crucible where the sample to calcine is placed.
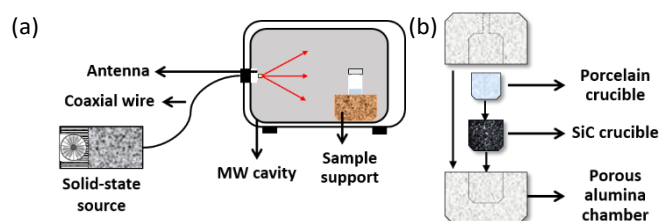
Figure 6 Schematic representation of (a) SS microwave and (b) calcination chamber used during the synthesis of UVM-7 mesoporous material.

Synthesis of UVM-7

The MAS is based in the reported method for UVM-7 preparation following the atrane route.[27] In a general synthesis, 4.12 mL of an atrane mixture containing Si:TEAH$_3$:CTABr in a 1:3.4:0.25 mole ratio were transferred to a microwave glass vial and 10 mL deionized water were added. After capping the vial the mixture was smoothly shaken until homogeneity. The vial was finally placed into the SS microwave oven cavity and irradiated for a given time at the defined power (see the results section for the values employed in each synthesis). As a result, an abundant white solid resulted, and the reaction was immediately stopped by cooling down the vial in an ice bath. Then, it was collected by centrifugation, washed with water and ethanol, and dried in an oven at 40 °C overnight to give as-made UVM-7.

For comparative purposes, UVM-7 was also synthesized conventionally without applying microwave energy. The preparative procedure followed has been described in detail elsewhere.[27]

Calcination

The template (CTABr) was removed by calcining UVM-7 solid in the SS microwave device (Figure 6.b). This time, the calcination was accomplished by placing 200 mg of as-made UVM-7 into the calcination chamber located in the microwave oven cavity. Optimal calcination conditions were achieved with a two steps heating ramp of 8 min at 200 W and subsequent 5 min at 150 W, after which 100 mg of calcined UVM-7 were recovered. Frequency was adapted during the calcination procedure in order to minimize the reverse power. Temperature at the end of the experiment was measured using a thermographic camera (Optris PI 160).

In order to compare and to validate the microwave calcination methodology, as-made UVM-7 was calcined in an oven under conventional conditions as a control. 500 mg of as-made UVM-7 were placed in a porcelain crucible and then calcined at 550 °C for 5 h in a furnace under static air atmosphere. The target temperature was reached by progressively heating at 3 °C min^{-1}.

Functionalization

Calcined UVM-7 was further functionalized by microwave irradiation. In short, 50 mg of calcined UVM-7 were dispersed in acetonitrile (15 mL) and mixed with APTES (0.3 mmol) in a microwave glass vial. The mixture was shaken for 10 seconds in a vortex, and then placed into the microwave oven cavity. Irradiation at 20 W for 4 minutes reached a final temperature of 70 °C. Afterwards, the vial with the mixture was cooled down in an ice bath. The white solid was collected by centrifugation, washed with acetonitrile and dried in an oven at 40 °C overnight.

Conventional procedure was also carried out as a control. Following a previously reported procedure,[32] the mixture of UVM-7, APTES and acetonitrile was stirred for 5.5 hours at room temperature. The solid was isolated, washed and dried as described above.

Total synthesis

The total synthesis procedure consisted of the sequential application of each individually optimized stage. The method provided the final hybrid nanomaterial after global irradiation time of just 19 min. Considering work-up in every stage, it took barely 4 hours to produce the final functionalised solid.

For the synthesis, 4.12 mL of a atrane mixture containing Si:TEAH$_3$:CTABr in a 1:3.4:0.25 mole ratio were transferred to a microwave glass vial and 10 mL deionized water were added. After capping the vial with a silicone septum and a snap cap, the mixture was smoothly shaken until homogeneity. The vial was irradiated for 2 minutes at 50 W power, producing the formation of an abundant white solid that formed a gel. The white solid was cooled down in an ice bath, collected by vacuum filtration, washed with water, ethanol, and acetone and air-dried for one hour. Then, 200 mg of the as-made UVM-7 were transferred to the porcelain crucible of the calcination chamber, and finally placed inside the microwave oven cavity. The solid was calcined by irradiation for 8 min at 200 W and subsequent 5 min at 150 W, after which 100 mg of calcined UVM-7 were recovered. Once cooled down, 50 mg of calcined UVM-7 were dispersed in acetonitrile (15 mL) and mixed with APTES (0.3 mmol) in a microwave glass vial. The mixture was shaken for 10 seconds in a vortex, and then placed into the microwave oven cavity. Irradiation for 4 minutes at 20 W provided the final hybrid functionalized material, which was collected by centrifugation, washed with acetonitrile and air-dried for one hour.

Conclusions

In summary, the present study has established an extremely rapid synthesis, calcination and functionalization method for UVM-7, which should also be applicable to other materials.

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Several synthesis conditions were tried using solid state sources, and the huge importance of controlling the power was reflected in the properties of the materials produced. In particular, UVM-7 mesoporous silica materials were produced in half gram scale when the mixture of TEOS, TEAH$_3$, CTABr and water was irradiated for only 2 minutes at 50 W power. Moreover, a two-steps power ramp calcination of 13 minutes and a functionalization with APTES in only 4 minutes provided the calcined and modified material, respectively. Finally, a total synthesis procedure comprising all the optimised steps was successfully carried out, providing the final ready-to-use material in around 4 hours 98 % saving in energy. This study represents a proof of concept of the potential of solid state MW sources for the control of chemical processes. This opens the door to the quick and controlled synthesis, calcination or functionalization of many other materials under solvothermal methodology that require very specific and soft irradiation conditions to be produced.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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