High-quality mesoporous SiO₂ nanospheres via a confined jet impingement continuous microchannel reactor

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Abstract

High surface area mesoporous silica (SiO_2) nanospheres has been considered an ideal material for the catalytic, adsorption and drug delivery. However, synthesis of ultra-high specific surface area mesoporous silica nanoparticles with well-defined sphere structure and small particle size (< 200 nm) is still challenging. Here, a two-stream confined jet impingement continuous microchannel reactor is proposed to produce novel mesoporous silica nanospheres (MSNs) with ultra-high specific surface area (SSA) and abundant worm-like meso-porosity. The as-obtained MSNs with worm-like mesoporous structure were produced with average particle diameter of $142 \sim 207$ nm, high SSA of $1347 \sim 1854$ m^2/g , total pore volume of $0.86 \sim 1.23$ cm^3/g and pore diameter of $2.6 \sim 3.3$ nm. Moreover, the shear force field in the microchannel reactor on the mesoscopic structure of MSNs was simulated by mesoscopic kinetics. Additionally, MSNs was used as the silicon source to synthesize lithium silicate (Li_4SiO_4), which enhanced carbon dioxide (CO_2) adsorption of 27.18 wt% at 650°C .

Introduction

High specific surface area (SSA) nanomaterials, mainly include mesoporous silica nanoparticles (MSNs)^{1–3} and mesoporous carbon nanoparticles⁴, have attracted much attention due to their advantageous properties, e.g., as large pore size, high SSA, tunable pore structure and controlled skeleton composition^{5–7}. Especially, MSNs in combination with the lowest surface energy and closed packing nature, offer better hydrothermal stability, higher hardness and chemical properties⁸. The mesopores and short channels in MSNs can effectively increase the density of highly active sites and facilitate molecular diffusion⁹. For all these reasons, MSNs with small particle size but relatively larger pore size are supposed to be an ideal application candidate, such as catalysis^{10,11}, adsorption^{12,13}, energy storage and conversion^{14,15}, and biomedicine^{16,17}. However, the MSNs preparation with rich pore structure on a scale and maintaining effective control over their morphology and particle size smaller than 200 nm remains a major challenge¹⁸.

Generally, cetyltrimethyl-ammonium boromide (CTAB) was used as the most common pore forming agent for MSNs preparation^{19–21}. The critical point is that it is mostly like to result in the mesopores with an average pore size smaller than the hydrodynamic diameter of common metal ions, which prevents the entry of metal active substances into the pore channels for adsorption and immobilization. Therefore, it is of great importance and interest to develop a simple new method for the preparation of larger pore sizes (> 2.5 nm) while maintaining effective control over the morphology and particle size of MSNs.

The associative structures in aqueous solution of CTAB in TEOS/ethanol/ NH_4OH solution and dynamic evolution process of the nucleation and growth were studied by mesoscopic dynamics (MesoDyn) simulations. These simulations have provided useful insights about the effect of shear for the formation of MSNs. And our idea is the use of microchannel reactor for the reinforcement and control of the shear

condition during nucleation process to synthesize new worm-like mesoporous silica nanomaterials with ultra-high specific surface area and large pore volume at room temperature.

Herein, we report a simple, rapid and scalable method to synthesize ultra-high SSA MSNs with well-defined mesoporous spherical structure and large pore volume by using a two-stream confined jet impingement continuous microchannel reactor (CJI-CMR)^{22–24}. Taken together with soft-templating CTAB, CJI-CMR was used for mass transfer intensification in reactors during hydrolysis/condensation of TEOS in ethanol/NH₄OH solution and vigorous magnetic stirring were utilized in a one-pot synthesis process of novel MSNs at room conditions. By changing the shear strength of microchannel reactor in the early stage of synthesis, the structure of the CTAB micelle could be changed. Thus, after removing template molecules, MSNs with excellent water/ethanol dispersibility, uniform sizes (142 ~ 207 nm), and tunable perpendicular mesopores of (2.6 ~ 3.3 nm), high SSA (1347 ~ 1854 m²/g), large pore volume (0.86 ~ 1.23 cm³/g) were obtained. A new type of Li₄SiO₄, with mesoporous spherical structures from the MSNs, was synthesized. Due to the very unique mesoporous spherical structure of Li₄SiO₄, this new Li₄SiO₄ could possess novel features, such as high CO₂ capacity at medium high temperature, fast CO₂ capture kinetics, and excellent cycling stability.

Results And Discussion

The overall synthesis procedures of MSNs by the two-stream CIJ-CMR are depicted in Fig. 1a. For nanoparticles synthesized with the concentration of CTAB of 8.55 mmol/L and the injection flow rate of 60 mL/min, SEM image (Fig. 1b) shows that the MSNs are uniform in both morphology and size. The HRTEM image (Fig. 1e) of MSNs exhibits the typical spherical morphology and light worm-like mesoporous structure. The particle diameter distribution chart of MSNs (**Fig. S1c**) shows the particle diameter was distributed from 61 nm to 320 nm with an average size of 178 nm. For comparison, the morphology of nanoparticles synthesized by magnetic stirring and HSM methods are irregular ellipsoidal morphology (Fig. 1c and 1f) and two-dimensional sheet structure (Fig. 1d and 1g), respectively. CJI-CMR method shows superior control ability on morphology.

The silica nanospheres prepared via CJI-CMR method were further characterized by nitrogen adsorption and desorption. The SSA, average pore diameter and pore volume of silica nanoparticles prepared by the CJI-CMR method were calculated to be 1022 m²/g, 3.6 nm, and 1.10 cm³/g, respectively. The pore size distribution diagram (**Fig. S1a**) exhibits a single peak appears in the mesopore. The adsorption isotherm (**Fig. S1a**) shows that there is a hysteresis phenomenon, which corresponding to IV adsorption equilibrium isotherm. The SSA of the MSNs prepared by the magnetic stirring method is 1581 m²/g, the average pore diameter is 3.7 nm, and the pore volume is 1.57 cm³/g. The pore size distribution diagram (**Fig. S1b**) shows that the MSNs prepared by the stirring method are in two peaks appear in the mesoporous region at about 2.5 nm and the macroporous region at 67.7 nm. The nitrogen adsorption isotherm shows similar IV adsorption equilibrium isotherm.

Overall, the mesoporous silica nanospheres prepared by the CJI-CMR method show better sphericity, better dispersion and more uniform mesopore size due to kinetics enhancement for nucleation process. Nanoparticles prepared by magnetic stirring method tend to be agglomerated but have a higher specific surface area. The high-shear method has a poor spherical morphology and mainly forms two-dimensional sheet-like nanosheets. Therefore, the CJI-CMR method and the magnetic stirring method are combined to prepare high SSA SiO_2 with a single mesopore size. The nucleation of the mesoporous silica nanospheres is controlled by the CJI-CMR method, and the crystallization and aging process of the mesoporous silica nanospheres are controlled by magnetic stirring. Based on these results, the CJI-CMR method was opted and used in the following experiments.

In this study, the MSN shell thickness can be tuned by simply changing the concentration of CTAB and the flow rate. The precursor solution A and the precursor solution B with various concentration of CTAB were injected at the same flow rate of 40 mL/min, 60 mL/min, 80 mL/min and 100 mL/min, respectively. When the CTAB concentration was 4.27 mmol/L, 12.80 mmol/L, 17.06 mmol/L, and 21.33 mmol/L, the diameter of silica nanospheres decreases with the increase of stream injection speed from 40 to 100 mL/min. Interestingly, the particle diameter of silica nanospheres increased with the increase of injection speed when the concentration of CTAB was 8.55 mmol/L (Fig. 2a). This phenomenon is studied and discussed in the subsequent simulation section. When the CTAB concentration is 4.27 mmol/L, 8.55 mmol/L, or 17.06 mmol/L, the specific surface area of silica nanospheres increases as the injection speed increases. At the same injection speed, the specific surface area of silica nanospheres first increased and then decreased with the concentration of CTAB (Fig. 2b).

As the injection speed increases, both of the particle size and size distribution range of the silica nanospheres gradually decreases (**Fig.S2, S4-S6**). Throughout the processing window, the average particle diameter of silica nanospheres are less than 207 nm. The increase in total fluid jet velocity brings greater collision energy between the two streams and thinner laminar inner layer of the pipeline, which leading to a more uniform mass transfer forming smaller and more homogeneous fluid cells. Therefore, the particle size of the formed silica nanospheres becomes smaller and more uniform with the total fluid injection speed increases. Moreover, the micro-mixing rate gradually approaches the rate at which TEOS hydrolyzes to generate silica nanospheres. The influence of mixing on the precipitation reaction process gradually decreases, the distribution of supersaturation becomes more uniform, and the average particle size of the silica nanospheres decrease gradually.

At the same total fluid injection speed, with the increase of CTAB concentration, the average particle size of silica nanospheres gradually increases, and the distribution range of particle size moves closer to a larger numerical region. The average particle diameter and its distribution rise significantly as the CTAB concentration increases at beginning, indicating that the TEOS hydrolysis rate is speeding up. When CTAB are further increased, the influence of perforating agent concentration on particles is diminished (**Fig S8**). This phenomenon can be explained by liquid crystal templates theory²⁵⁻²⁷. The concentration of CTAB can directly affect the morphology of the liquid crystal template. When the concentration of CTAB close to the critical micelle concentration (cmc), due to its own structural orientation, the spherical

liquid crystal template will gradually increase by self-assemble. With the increase of CTAB concentration, the system tends to form the columnar liquid crystal template.

For the CTAB concentration at 8.55 mol/L, the above rules are different in each group. Under this CTAB concentration, the diameter of the silica nanospheres increases as the injection speed increases (**Fig S3**). In addition, the particles exhibited the narrowest size distribution. The silica nanospheres smaller than 120 nm disappear completely. At the same time, as the total fluid injection speed increases, the value of the diameter of the silica nanospheres shifts to the area with larger coordinate values.

Nitrogen adsorption-desorption test was performed on silica nanospheres with CTAB concentrations of 4.27 mmol/L, 8.55 mmol/L, or 17.06 mmol/L. It can be obtained that the average pore diameter of each silica nanosphere is 2.8–3.3 nm, the pore volume is 0.86–1.26 cm³/g and the S_{BET} is 1347–1854 m²/g (**Fig.S7, Table S2, Fig. 2b**). Notedly, the specific surface area of silica nanospheres increases with the increase of the total fluid injection speed, and the specific surface area of silica can be effectively controlled by the CJI-CMR method. Among them, the specific surface area of silica nanospheres can reach up to 1854 m²/g. Compared with other methods for preparing ultra-high specific surface area worm-hole structure silica nanospheres, the CJI-CMR method can be used to quickly prepare worm-hole structure silica nanospheres with larger specific surface area while maintaining small particle diameter (**Table S3**). The average particle diameter of the worm-like mesoporous silica nanospheres prepared by the CJI-CMR method is easily < 200 nm and it is valuable for the worm-like mesoporous silica nanospheres to be used for biological drug loading and carbon dioxide adsorption. By comparing by other methods (**Table.S4**), the MSNs prepared by the CJI-CMR method has the advantage of the maximum specific surface area, maximum hole volume capacity, larger aperture, faster preparation speed, and minimum particle diameter.

In order to further explain the effect of total injection speed and CTAB concentration on the specific surface area and the morphologies of silica nanospheres. The MesoDyn mesoscopic simulator was used to simulate the effect of total injection speed and CTAB concentration. The picture of (**Fig. 3a**) shows that CTAB-T (hydrophobic part) composes the core of the micelle, and CTAB-H (hydrophilic part) is wrapped by TEOS. This part constitutes the precursor colloidal particles of the silica nanospheres. CTAB-T (hydrophobic part) mainly constitutes the microporous structure of silica nanospheres, and CTAB-H (hydrophilic part) mainly constitutes the mesoporous structure of silica nanospheres. Therefore, the specific surface area of the mesoporous silica nanospheres could be adjusted by the concentration of CTAB. Since TEOS micelles were wrapped in ethanol solution to isolate ammonia and water, it can effectively slow down the hydrolysis of TEOS and leave time capacity for the regulation of the nano-spherical morphology of silica. By changing the volume concentration of CTAB (0.03 %, 0.06 %, 0.12 %, and 0.24 %), TEOS micelles became large balls which progressively more uniform in size, and finally decomposed into non-uniform small balls (**Fig. 4f-4g**). At a lower concentration of CTAB, the main effect of the group is to make the TEOS colloidal particles more uniform in size; at a higher concentration, the main effect of the ball group is to participate in the composition of the TEOS colloidal particles (**Fig.S7a-S7d, 3d and 3e**). In addition, as the volume concentration of CTAB increases, CTAB can be the faster the

formation time of TEOS in the gel nucleus, and make TEOS form a stable form in less time (**Fig S7c, S7d, 3d and 3e**). The results of simulation are consistent with the experimental results (**Fig S2-S6**).

The formation of silica nanospheres mainly includes the formation of nuclei and the growth of nuclei crystals. Therefore, the morphology and properties of silica nanospheres depend on the mixing efficiency, thermodynamics and kinetics in the process of TEOS hydrolysis. The picture of order parameters is divided into three stages (**Fig. 3b**), which can correspond to the three stages of LaMer's model (**Fig. 3c**)²⁵. The first stage (I) corresponds to the formation of micelle precursors, with little change in sequence parameters, indicating minimal density fluctuations and aggregate formation. Corresponding to the process in which the degree of supersaturation increases as the reactant monomer is continuously delivered to the reaction system at the beginning of the TEOS hydrolysis reaction. In the second stage (II), from 600 to 2000-time step, the order parameter increased significantly in a relatively short time frame (1400-time step), indicating that the rapid formation of large micelles is considered to be the key to determining the primary morphology of the association structure in the solution. Correspondingly, the TEOS hydrolysis process reaches the supersaturation degree of the nucleation threshold of sodium silica crystals, and the nucleation starts. Both nucleation and growth of nucleation will increase the consumption rate of monomer. As a result, the supersaturation drops very quickly to a level below nucleation threshold. Therefore, the nucleation is completed very quickly, which is the same as the "burst nucleation" in the LaMer's model (the second stage (II)). The third stage (III) involves a slow process in which micelles are adjusted to minimize their energy until they reach equilibrium. Corresponding to the process of stirring and aging after TEOS hydrolysis and nucleation, the growth of nanocrystals continuously consumes monomers and supplies monomers at a controlled rate to maintain low supersaturation below nucleation threshold, thereby ensuring no nucleation process (the third stage (III)).

The method to simulate the CJI-CMR method to control the nucleation process of silica nanospheres: when the CTAB volume concentration is 0.01 %, the different total fluid injection speeds are described by the mesoscopic simulation of increasing different shear rates (0.0001 ns^{-1} , 0.0002 ns^{-1} , 0.0004 ns^{-1} and 0.0008 ns^{-1}) in the second stage (II). With the increase of the shear rate, TEOS micelles gradually from small micelles to large micelles, changing from chaotic to uniform (**Fig. 3j-3k**). As the shear rate increases, TEOS micelles gradually change from small micelles to larger micelles, and large micelles gradually become smaller micelles. The final result is that the micelles change from chaos to uniform. The particle size distribution range of micelles becomes smaller. This phenomenon is consistent with the experimental results. It shows that the nucleation of silica nanospheres can be controlled by the CJI-CMR method.

The method to simulate the magnetic stirring method to control the crystallization and aging process of silica nanospheres: when the CTAB volume concentration is 0.01%, the different Stirring speeds are described by the mesoscopic simulation of increasing different shear rates (0.0001 ns^{-1} , 0.0002 ns^{-1} , 0.0004 ns^{-1} and 0.0008 ns^{-1}) in the third stage (III). With the increase of the shear rate, TEOS micelles gradually from small micelles to large micelles, changing from chaotic to uniform (**Fig. 3n and 3o**). When

the shear rate is too high, the shearing effect will change TEOS micelles from spherical to rod-shaped (Fig. 3n and 3v). Therefore, it is possible to control the silica nanoparticles to maintain a spherical structure by magnetic stirring at a lower speed, and to reduce the particle size distribution of the silica nanoparticles. This phenomenon has been consistent with the experimental results.

Through the above simulation process, it can be obtained that as the concentration of CTAB increases, the particle diameter of the silica nanospheres, firstly, shows that the large micelles become smaller, the small micelles become larger, and the particle diameter becomes uniform. Then the uniform particles slowly aggregate into a large spherical particle. When the concentration of CTAB is large enough, the large spherical particles will decompose the small spherical particles. By changing the injection speed of the total fluid and increasing the magnetic stirring process, the particle diameter distribution will be narrowed. The results indicate that faster mixing can lead to a higher crystallization rate and smaller particles with a narrower particle size distribution, other research groups also got the same result. This result can explain the experimental results that the average particle size of silica nanospheres decreases with the increase of the total injection speed (Fig. 2a, S2-6).

When the CTAB concentration is 8.55 mmol/mL, the average diameter of the silica nanospheres increases with the increase of the total injection speed. The reason could be conclude that this concentration is precisely the concentration at which CTAB is more likely to accumulate in large micelles. Under such conditions, as the total injection speed increases, the system tends to form homogeneous micelles which resulting in narrowed particle size distribution. And the average particle size of the mesoporous silica nanospheres increases with the increase of the total injection speed (Fig. 2a, S3). Confirmed by TEM images, all silica nanoparticles smaller than 120 nm is disappeared. The larger the volume of the mesoporous silica particles, the more micropores and mesoporous structures contained, and the larger the specific surface area. Therefore, when the CTAB concentration was exactly 8.55 mmol/L, the mesoporous silica nanospheres obtained the largest specific surface area. When the CTAB concentration increased to 17.06 mmol/L, the TEOS micelles collapsed into heterogeneous micelles due to the excessive CTAB concentration. This leads to an increase in spheres smaller than 120 nm and an increase in the range of particle size distribution. Therefore, the specific surface area of the mesoporous silica nanospheres prepared at CTAB concentration of 17.06 mmol/L was lower than that of the silica nanospheres prepared at CTAB concentration of 4.27 mmol/L (**Fig.S2, S5**). As the total liquid injection speed increases, the particle diameter of the mesoporous silica nanospheres gradually narrowed, which accounting for the gradual increase in the specific surface area of the mesoporous silica nanospheres at the same CTAB concentration.

MSNs with a SSA of 1854 m²/g, a pore volume of 1.22 cm³/g, an average pore size of 3.3 nm and a particle size of 197 nm were used as the silicon source, and LiNO₃ was used as the lithium source to prepare Li₄SiO₄ (named 2-(HS1854)-Li₄SiO₄, Fig. 4a) to adsorb carbon dioxide. The high SSA mesoporous silica nanospheres prepared by the same method as silicon source Si:Li is 1:4 (molar ratio) Li₄SiO₄, named 4-(HS1854)-Li₄SiO₄. Using SBA-15 as the silicon source, and the same method was used

to prepare Li_4SiO_4 with Si: Li molar ratio is 1:2 and 1:4, named 2-(SBA-15)- Li_4SiO_4 and named 4-(HS1854)- Li_4SiO_4 , respectively.

Thermogravimetric analyzer (TGA) was used to measure the dynamic adsorption performance at $10^\circ\text{C}/\text{min}$ and $30\text{--}800^\circ\text{C}$ under pure carbon dioxide atmosphere. The adsorption isotherms of 2-(HS1854)- Li_4SiO_4 and 2-(SBA-15)- Li_4SiO_4 at 500°C , 550°C , 600°C , 650°C and 700°C were measured respectively. Through dynamic temperature swing adsorption, it can be found that Li_4SiO_4 prepared with UHMSNs was better than Li_4SiO_4 prepared with SBA-15 as the silicon source, and has better medium and high temperature ($500\text{--}680^\circ\text{C}$) absorption for CO_2 under the same molar ratio of silicon to lithium. 2-(HS1854)- Li_4SiO_4 has better CO_2 adsorption performance at 500°C – 680°C than 2-(SBA-15)- Li_4SiO_4 (Fig. 4b). The corresponding maximum values of dynamic temperature swing adsorption of CO_2 , with 2-(HS1854)- Li_4SiO_4 , 2-(SBA-15)- Li_4SiO_4 , 4-(HS1854)- Li_4SiO_4 and 4-(SBA-15)- Li_4SiO_4 , are 27.18wt% (696°C), 10.61 wt% (712°C), 32.41 wt% (712°C) and 30.55 wt% (719°C) respectively (Fig. 4b). 2-(HS1854)- Li_4SiO_4 and 2-(SBA-15)- Li_4SiO_4 are used for the CO_2 isotherm adsorption test at 500, 550, 600, 650 and 700°C . The adsorption capacity of 2-(HS1854)- Li_4SiO_4 for CO_2 is 15.2wt% at 500°C , and the adsorption capacity of 2-(SBA-15)- Li_4SiO_4 is 0 wt%. The maximum adsorption capacity of 2-(HS1854)- Li_4SiO_4 for CO_2 is 27.1 wt%, but only 6 wt% for 2-(SBA-15)- Li_4SiO_4 for CO_2 . (Fig. 4c).

Therefore, when MSNs are used as the silicon source, a better CO_2 adsorption effect can be achieved at a lower silicon-to-lithium ratio, The HMSNs prepared as a silicon source are better than SBA-15 at $500\text{--}700^\circ\text{C}$, with the same silicon-to-lithium ratio.

The adsorption isotherms of 2-(HS1854)- Li_4SiO_4 and 2-(SBA-15)- Li_4SiO_4 at various temperatures are fitted by $y = A\exp(-k_1x) + B\exp(-k_2x) + C$, to obtain their respective kinetic parameters. In this equation, y represents the adsorption capacity in the form of mass percentage, which is the adsorption time in S, and k_1 and k_2 are the carbon dioxide adsorption kinetic constants and diffusion kinetic constants. The adsorption kinetic constants and diffusion kinetic constants of 2-(HS1854)- Li_4SiO_4 and 2-(SBA-15)- Li_4SiO_4 both increase with the increase of temperature (**Table S5**). By comparing the kinetic constants of 2-(HS1854)- Li_4SiO_4 and 2-(SBA-15)- Li_4SiO_4 at the same temperature, it can be known that the adsorption kinetic constants and diffusion kinetics of HS1854-Li: Si = 2:1 is larger than 2-(SBA-15)- Li_4SiO_4 . 2-(HS1854)- Li_4SiO_4 has the largest adsorption capacity for CO_2 at 650°C , its

The FESEM showed that the morphology of 2-(HS1854)- Li_4SiO_4 was petal hollow microspheres with an average particle size of $3.5\text{ }\mu\text{m}$ (Fig. 4e). 2-(SBA-15)- Li_4SiO_4 , 4-(SBA-15)- Li_4SiO_4 , and 4-(HS1854)- Li_4SiO_4 were worm-like, two-position flake-like and smooth spherical structures, respectively (**Fig.S8**). Compared with the silicon source, the specific surface area and pore volume of 2-(HS1854)- Li_4SiO_4 were extremely small, while the average pore size became larger, and the values were $1.75\text{ m}^2/\text{g}$, $0.0042\text{ cm}^3/\text{g}$, and 21.8 nm , respectively. Among four kinds of Li_4SiO_4 , 2-(HS1854)- Li_4SiO_4 has the largest pore size, pore volume and specific surface area (**Table S6**). Therefore, 2-(HS1854)- Li_4SiO_4 shows better adsorption performance

at medium and high temperature because of the unique spherical structure and larger mesoporous structure of petal hollow microspheres. The petal-like mesoporous Li_4SiO_4 has a rough petal-like surface, which provides a larger specific surface area and active sites for adsorption sites, and can increase gas disturbance and reduce air film resistance, thereby increasing the adsorption rate. Its large mesoporous structure allows carbon dioxide molecules to easily pass through the spherical shell and enter the inside of the sphere. It can also reduce the high temperature because the reaction rate is too fast to block the pores. Because of the existence of mesopores, CO_2 diffuses easily into the sphere, reducing the concentration of carbon dioxide on the surface, and increasing the concentration difference between carbon dioxide on the surface and the main body of CO_2 , increasing the driving force for mass transfer and increasing the adsorption rate of CO_2 fast. Because 2-(HS1854)- Li_4SiO_4 adsorbs CO_2 too fast at 700°C , the resulting Li_2CO_3 covers the surface of the sphere and blocks the mesoporous structure of the spherical shell. Makes the carbon dioxide unable to reach the inside of the microspheres. The reason why the adsorption performance of 2-(HS1854)- Li_4SiO_4 for carbon dioxide at 650°C is better than that at 700°C . Thus 2-(HS1854)- Li_4SiO_4 better adsorption properties of carbon dioxide than 700°C .

Through XRD analysis, 2-(HS1854)- Li_4SiO_4 produces more Li_4SiO_4 and less by-products than 2-(SBA)- Li_4SiO_4 . Through the Debye-Scherrer equation calculation and analysis, 2-(HS1854)- Li_4SiO_4 has a smaller grain size than 4-(SBA)- Li_4SiO_4 . According to the double-shell model, during the sorption stage, CO_2 diffuses to the surface of Li_4SiO_4 and reacts with Li^+ and O^{2-} to form Li_2CO_3 and Li_2SiO_3 . Li_2SiO_3 forms a solid shell that covers unreacted Li_4SiO_4 . Similarly, Li_2CO_3 forms another shell out-side the Li_2SiO_3 shell²⁸. Therefore, once the external layer was completely formed, Li^+ and O^{2-} had to diffuse throughout the Li_2SiO_3 shell to continue reacting with CO_2 , and the CO_2 also need to diffuse throughout the external Li_2CO_3 layer. It could explain the excellent sorption performance of 2-(HS1854)- Li_4SiO_4 at low temperature, because 2-(HS1854)- Li_4SiO_4 samples have small crystal size and high specific surface area.

Adsorption and desorption of 2-(HS1854)- Li_4SiO_4 isothermally under a pure CO_2 atmosphere were performed 10 times at 650°C . 2-(HS1854)- Li_4SiO_4 as carbon dioxide adsorption showed a good cycle life. In the 10th cycle, the carbon dioxide adsorption capacity was maintained at 26.1 wt% (Fig. 4g). The Li_2CO_3 generated by the 10th cycle, named 10-CYCLE-(HS1854)- Li_2CO_3 . Through XRD analysis, the powder surfaces were mainly Li_2CO_3 and Li_2SiO_3 . According to FESEM analysis, 10-CYCLE-(HS1854)- Li_2CO_3 had a micron spherical structure with a diameter of $5\text{ }\mu\text{m}$ (Fig. 4f). Compared with 2-(HS1854)- Li_4SiO_4 , 10-CYCLE-(HS1854)- Li_2CO_3 had a larger diameter and a smoother spherical surface, which could be contributed to the formation of Li_2CO_3 and Li_2SiO_3 on the surface. This is consistent with the situation described by the double-shell model. Therefore, 2-(HS1854)- Li_4SiO_4 could maintain good spherical structure in shape during the cyclic adsorption of CO_2 and showed higher sorption capacity in the low temperature range of $500\text{--}650^\circ\text{C}$.

Conclusions

In summary, CJI-CMR has been developed to synthesize mesoporous silica nanospheres with worm-like meso-porosity with large adjustable size and high specific surface area and mesoporous structure. Through the CJI-CMR with a shearing assisted, silica nanospheres with a diameter of < 200 nm can be easily prepared, large and tunable diameter of 142 – 207 nm, high surface area up 1347–1854 m²/g, and large pore volume of 1.26 cm³/g can be obtained. The preciseness of size control and the uniformity of mesoporous silica nanospheres are ensured by the “controlled nucleation” and the following “crystallization and aging” in this strategy. Moreover, the mechanism of this strategy is perfected through mesoscopic simulation. Preparation of carbon dioxide absorbent(2-(HS1854)-Li₄SiO₄) with MSNS, which showed higher sorption capacity in the low temperature range of 500–650°C. In addition, this new 2-(HS1854)-Li₄SiO₄ sorbents exhibited excellent cycling stability. After 10 sorption/desorption cycles, the CO₂ sorption capacity of 2-(HS1854)-Li₄SiO₄ only slightly decreased by 1.1 wt%. MSNs has a large specific surface area, a large pore capacity and a uniform pore structure, making it an excellent nanoreactor. In the process of preparing Li₄SiO₄, it is not only used as a reactant, but also as a reaction vessel. The huge specific surface area and pore volume provide huge space for the reaction to proceed, so that the reaction can also occur under lower lithium source conditions, which can significantly reduce the amount of LiNO₃ used. Considering the continuity of the synthetic route and good controllability, it is expected that the CJI-CMR method can be extended to design other functional nanostructures with multiple components and integrated characteristics for various applications.

Declarations

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Figures

Figure 1

(a) Schematic diagram of synthesis of MSNs by CJI-CMR; (b) the SEM images of synthesis of MSNs by CJI-CMR; the FETEM image of synthesis of MSNs by (c) magnetic stirring and (d) high shear mixing; the HRTEM image of synthesis of MSNs by (e) CJI-CMR (f) magnetic stirring and (g) high shear.

Figure 2

(a) Graph of the particle diameter of silica nanospheres at different concentrations as a function of different injection speeds; (b) Graph of the specific surface area of silica nanospheres at different concentrations as a function of different injection speeds.

Figure 3

(a) Density distribution graph of water, ethanol, TEOS, CTAB-H and CTAB-T; (b) The order parameters diagrams and TEOS density distribution at the volume concentration of CTAB of 0.01 %; (c) Schematic illustration on the change of supersaturation degree as a function of time in LaMer's model; (d) and (e) are the order parameters diagrams with the volume concentration of CTAB of 0.12 % and 0.24%, respectively; (f), (g), (h) and (i) are the TEOS density distribution diagrams with the volume concentration

of CTAB of 0.03 %, 0.06 %, 0.12 % and 0.24 %, respectively; (j), (k), (l) and (m) are the TEOS density distribution diagrams with the share rates of 0.0001 ns-1, 0.0002 ns-1, 0.0004 ns-1 and 0.0008 ns-1 in the stage Ⅱ at volume concentrations of 0.01 %, respectively; (n), (o), (p) and (q) are the TEOS density distribution diagrams with the share rates of 0.0001 ns-1, 0.0002 ns-1, 0.0004 ns-1 and 0.0008 ns-1 in the stage Ⅲ at volume concentrations of 0.01 %, respectively.

Figure 4

Ⅱa) Schematic illustration of the synthesized CO₂ sorbent; (b) Dynamic adsorption curves of CO₂ for 2-(SBA-15)-Li₄SiO₄, 4-(SBA-15)-Li₄SiO₄, 2-(SBA-15)-Li₄SiO₄, and 4-(HS1854)-Li₄SiO₄ at 400-800°C for 10 K/min; (c) CO₂ sorption capacity of 2-(HS1854)-Li₄SiO₄ and 2-(SBA-15)-Li₄SiO₄ at 500 °C, 550 °C, 600 °C, 650 °C and 700 °C under 100 vol% CO₂ for 2 h; (d) Isothermals of the CO₂ sorption on of the four Li₄SiO₄ sorbents at 500 °C, 550 °C, 600 °C, 650 °C and 700 °C under 100 vol% CO₂ for 2 h; (e) the SEM image of synthesis of 2-(HS1854)-Li₄SiO₄; (f) the SEM image of 2-(HS1854)-Li₄SiO₄ after 10 CO₂sorption/desorption cycles; (g) CO₂ sorption/desorption cycling performance of the 2-(HS1854)-Li₄SiO₄ after 10 cycles.

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