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Continuous synthesis of nanostructured silica based materials in a gas-liquid segmented flow tubular reactor[†]

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synthesis of advanced nanostructured materials.

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A continuous synthesis of several spherical silica structures – by means of a gas–liquid segmented flow tubular reactor – is reported. Specifically, as proof of concept, we showed that 300–400 nm mesoporous core–shell spheres (SiO₂@mSiO₂), mesoporous spheres (mSiO₂) as well gold-encapsulated spheres (Au@SiO₂) can be effectively produced in a continuous manner in a tubular reactor. Thus, the successful conversion of classical batch methods to continuous processes opens new possibilities for the up-scaled

Introduction

The synthesis of advanced porous materials is receiving great scientific attention, especially due to their application as catalysts and support materials.¹ In the last few decades, large families of different materials have been synthesized and studied, although very often the possibility of tailoring the material features – by tuning the morphology, particle size, and porosity, for instance – remains a major challenge. Conventionally, batch processes are applied to synthesize porous nanostructured materials.² However, in many cases, the batch process presents several disadvantages, *i.e.* inhomogeneous mixing, temperature gradients and reproducibility issues,³ which hinder the scaling-up of the synthetic process is often desirable.

Tubular reactors (TRs) and segmented flow tubular reactors (SFTRs) have been frequently employed to produce, in a continuous manner, nano/microcrystals and colloids.⁴ The basic principle of a TR set-up can be seen as the continuous mixing of (mostly liquids) reagents, which are afterwards pumped through a tube until the reaction is completed. In the case of SFTRs, an additional immiscible phase (typically a gas) is injected to form a regular gas–liquid slug pattern, thus ensuring a better homogeneity within each liquid droplet.^{3a,5} The tube diameter commonly employed in TR set-ups is larger (>1 mm) than the channels present in microtubular reactors or microfluidic

devices; for this reason, the typical production volumes achievable through such devices are higher compared to the so called "lab on a chip" technologies.⁶ On a lab scale, several (nanostructured) materials, *i.e.* monodisperse titania,^{4c,5e,7} silica^{7a,8} and carbonate^{4e} beads, have been produced by means of TRs. Additionally, through the use of multi-stage TRs, the syntheses of more complex nanostructures such as CdSe/ZnS, Au/Ag, SiO₂/TiO₂ or Au/Ag/Au were described.⁹

Silica spheres - or the more advanced dense silica core mesoporous silica shell (SiO2@mSiO2) spheres - represent one of the most popular examples of colloidal nanostructured materials produced via sol-gel methods. The synthesis of monodisperse silica spheres was firstly reported in 1956 by Kolbe.^{2d} Stöber^{2e} further optimized this system, developing the synthesis of spherical silica particles with diameters up to the micrometer range (1.5 µm) under controlled reaction conditions via the ammonia-catalyzed condensation of silicon alkoxides in several water/alcohol mixtures. Giesche^{8a,10} carried out the synthesis of particles with sizes up to 3.0 µm in a continuous manner, via a two-step-growth process. Applying a similar method, Kaiser^{2c} reported the batch synthesis of fully mesoporous silica spheres. Büchel and Unger^{2a} described the synthesis of solid core mesoporous shell silica spheres through a two-step batch process. These core-shell spheres have found, in the last decades, a large variety of applications and they are currently investigated in several areas including catalysis¹¹ and drug delivery.¹² Moreover, they are frequently used as hard template materials to prepare hollow carbon spheres¹³ through nanocasting methods.

Our group has recently used $SiO_2(\underline{a})mSiO_2$ silica spheres (prepared *via* a classical batch process) as exotemplates for the synthesis of hollow graphitic spheres, which were subsequently employed as catalyst support for the oxygen reduction

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Paper

reaction in PEM fuel cells.^{2b,14} In order to increase the production volumes of silica SiO₂@mSiO₂ spheres, and, more in general, as a proof-of-concept, we developed a method for the conversion of the previously used batch synthesis to a continuous synthesis. In the following we demonstrate, through the synthesis of a series of representative silica-based structures, that several different batch synthesis protocols could be transferred – by means of a simple SFTR – to continuous synthetic processes.

Experimental section

Synthesis set-up

Two liquid solutions were combined in the first T-junction (\emptyset ID 0.33 mm) with constant flow rates achieved *via* a precision-pump and a peristaltic pump (P-500, Pharmacia GE Health care; Minipuls 3, Gilson). The formation of a segmented flow was achieved by the injection (with a constant flow) of nitrogen gas (mass flow controller: EL-FLOW[®] F-201D-FAC-33-V, Bronkhorst), *via* an additional T-junction (\emptyset ID 3 mm). The gas inlet pressure was set to 1.5 bars. For the standard synthesis, the flow rates were set to 60 mL h⁻¹ for the pumps and 120 mL h⁻¹ for the gas. The aging was performed in the tubular reactor consisting of a PTFE tube (\emptyset 3 mm × 4 mm; 60 m in length).

Syntheses of silica spheres, SiO_2@mSiO_2, Au@SiO_2 and mSiO_2 $% \mathcal{O}_{2}$

The synthesis via the modified Stöber process was performed by employing the pumps with two different solutions, as illustrated in Fig. 1. Solution 1 contained ultrapure (Milli-Q water; 18.2 M Ω cm at 25 °C) water and the ammonium hydroxide solution (NH₃(aq); Sigma-Aldrich Co.; 500 mL; 28.0-30.0%), whereas solution 2 contained the silica precursor. Typically, for the synthesis of Stöber silica spheres, solution 1 consisted of 12.48 mL of ethanol (99.7%; denatured with 2.6% toluene), 5.68 mL of water and 0.55 mL of NH₃(aq). Solution 2 was provided with 17.52 mL of denatured ethanol and 1.19 mL of TEOS (Sigma-Aldrich Co.; 250 mL; >99.0%). For the shell deposition, 30 mL of the previously prepared Stöber solution plus 2.53 mL of ethanol, 7.84 mL of water and 0.76 mL of NH₃(aq) were supplied as solution 1. A mixture of 1.62 mL of TEOS, 0.64 mL of OTMS (Sigma-Aldrich; 90%) and 38.87 mL of ethanol was employed as solution 2. To prepare mSiO₂



Fig. 1 Scheme of the SFTR set-up employed for all the syntheses described in this work. The gas-liquid segmentation present in the tube, as well as the SiO_2 more progressive shell growth, is schematically highlighted in the magnified red rectangle.

spheres with a diameter of 320–340 nm, solution 1 contained 9.70 mL of ethanol, 4.47 mL of water and 0.83 mL of $NH_3(aq)$. The required silica source is provided *via* solution 2, which contained 0.79 mL of TEOS, 0.31 mL of OTMS and 13.90 mL of ethanol. Au@SiO₂ particles were synthesized according to the description of Arnal *et al.*^{18*a,c*} Solution 1 contained 24 mL of the as prepared aqueous gold colloids (14 nm; 0.01 mol L⁻¹), which was further diluted with 51.0 mL of ethanol and 3.36 mL of $NH_3(aq)$. Solution 2 contained 2.9 mL of TEOS and 75.5 mL of ethanol. All particles were calcined for 6 h at 550 °C with a heating rate of 2 K min⁻¹.

The corresponding batch syntheses are performed following the procedures reported in the literature (ref. Büchel, Unger *et al.*^{2*a*} for SiO₂ and SiO₂(@mSiO₂, ref. Kaiser and Unger^{2*c*} for mSiO₂).

Transmission electron spectroscopy

The TEM images presented in this work were obtained *via* a Hitachi H-7100 instrument (100 kV). All samples were placed on a Lacy carbon film supported by a copper grid. The dried solid samples were deposited on the Lacey grid without further treatment.

Nitrogen physisorption

The nitrogen sorption measurements were carried out on a Micrometrics ASAP 2010 instrument. Prior to analysis the samples were activated under vacuum for at least 6 h at 200 °C. The measurements were performed at 77.35 K using a static-volumetric method. The empty volume was determined with He. The BET surface area was calculated from the adsorption data in the relative pressure interval from 0.04 to 0.2; the pore size distribution was evaluated implementing the classical Barrett–Joyner–Halenda (BJH) method, applied to the adsorption branch of the isotherm. The total pore volume was estimated from the amount of nitrogen adsorbed at a relative pressure of 0.97.

Results and discussion

Synthesis set-up description

The SFTR setup (Fig. 1) employed in this work consists of three sections. (1) Initially, two different liquid solutions were pumped through a static mixer (T-junction 1) to mix the reactants with solvents and catalysts.

For the synthesis of Stöber spheres, solution 1 contained water, part of the total volume of ethanol and ammonia (catalyst), whereas solution 2 contained the silica precursor: tetraethylorthosilicate (TEOS) and/or octadecyltrimethoxysilane (OTMS), typically diluted in ethanol. For the synthesis of other silica structures, slight modifications to this configuration were applied. The composition of the two solutions for each experiment is reported in detail in the experimental part. The aging tube was cleaned by pumping a solution of 1 M NaOH through the tube for \sim 1 h, followed by rinsing the tube with ethanol.

The flow rate of the two pumps was always kept equal in order to maximize the mixing efficiency in the first Tee (T-junction 1).

(2) A second T-junction (T-junction 2) is placed along the tube and N2 is injected to form the segmented gas-liquid slug pattern. (3) The liquid-gas slugs are continuously pumped through a long polytetrafluoroethylene tube for a fixed residence time, till the resulting colloidal suspension is collected at the outlet. The segmentation created in the second T-junction is known to give a homogeneous velocity distribution profile within each slug, significantly different from the parabolic profile usually observed in a laminar flow.^{5e} Additionally, the segmentation provides an important internal mixing. The presence of two vortices assures, besides the diffusion driven mixing, a continuous homogenization of the reaction mixture inside each liquid segment, as described in detail by Taylor.^{5a} Although a turbulent flow could potentially offer a comparable internal mixing, in our case, such a flow regime was not achievable because of flow rate restrictions of the employed pumps. A dimensionless number introduced by Bretherton^{5b} is commonly used to identify the characteristics of a gas-liquid segmented flow in a capillary and to estimate the threshold - in this case the maximum tube diameter - above which the formation of segmented flow would not be attainable anymore. If a tube with a diameter larger than the threshold value is used, the buoyancy forces would overcome the surface tension between the liquid droplet and the gas bubble, resulting in a flow where the gas bubbles would just bypass the liquid slugs. In our case (for the calculation details see the ESI⁺) such a critical situation is reached at diameters higher than 3.1 mm. In order to confirm the calculated threshold value, a PTFE tube with an inner diameter of 4 mm was employed as the aging tube. As predicted by the estimate, it was not possible to obtain a segmented flow with the employed reaction mixture of ethanol, water and ammonium hydroxide solution. Therefore, an inner tube diameter of 3 mm was applied in our system, which worked well in sustaining a segmented flow.

Continuous synthesis of mesoporous silica material

The continuous synthesis of silica spheres *via* the Stöber method in a TR has already been described by Giesche,^{8a} and more recently by Gutierrez *et al.* and Khan *et al.*, who performed the same synthesis in a microfluidic reactor.^{3a,8b} In our case, the Stöber synthesis is the first step in the synthesis of SiO₂@mSiO₂ spheres and therefore was the first synthesis we optimized for our setup. In agreement with what had previously been reported by Gutierrez,^{8b} we found the segmented-flow regime crucial to achieve the desirable monodispersity. In addition, we could control the size of the spheres by adjusting the ammonia content in the reaction mixture, as typically done in the batch synthesis. Moreover, we optimized the total residence time to assure the completion of the reaction. All these results are summarized in the ESI.[†]

For the continuous synthesis of SiO_2 @mSiO₂ core-shell spheres, 220 nm large Stöber spheres were used as core. Also for the shell growth, segmentation of the flow is necessary to achieve highly monodisperse silica core-shell particles. It is important to note that both types of syntheses were performed under similar conditions; in order to maintain the same



Fig. 2 (A) TEM micrographs displaying the different synthesized core-shell particles and the respective shell thickness \pm standard deviation under laminar flow (green; c and d), segmented flow conditions (red; a and b) as well as in the batch process (blue; e and f). (B) Shell thickness distribution histograms for core-shell spheres prepared under laminar (green), segmented (red) conditions and in a batch process (blue).

residence time for both experiments (considering that the gas inlet was sealed for the laminar-flow synthesis), the pump flow rates were adjusted accordingly.

The difference in monodispersity between the particles prepared applying these two different flow regimes can be appreciated analysing the TEM images (Fig. 2a), where a significant shell thickness heterogeneity among the SiO₂@mSiO₂-laminar particles is observed. The average shell thicknesses (and corresponding standard deviations) of different SiO₂@mSiO₂ spheres, evaluated through the analysis of the TEM images, are reported in Fig. 2, together with the shell thickness typically obtained through the equivalent batch synthesis (SiO₂@mSiO₂-batch). Interestingly, the standard deviations relative to SiO₂@mSiO₂-batch and SiO_2 @mSiO₂-segmented particles are in good agreement as can be seen from the TEM micrographs as well as in the histogram (Fig. 2). Thus, the advantages of the tubular reactor, such as higher productivity and continuous operation can be capitalized on without compromising the product quality. In contrast, the standard deviation of SiO_2 @mSiO₂-laminar spheres is twofold larger (as visible in the sparse distribution histogram in Fig. 2b). Therefore it is clear that internal mixing provided by segmentation is crucial to achieve the desired core–shell structure. Based on these results, the segmented flow pattern was applied for all the following continuous experiments.

As a next step, the possibility of controlling the final shell thickness was investigated. Fig. 3 shows SiO₂@mSiO₂ spheres obtained by varying the total amount of reactants (TEOS and OTMS) fed into the reactor. Thanks to an increase of the final volume fraction of TEOS + OTMS from 1.06% to 2.5% (see Table S1, ESI[†]) it was possible to increase the shell thickness from 18 ± 3 nm to 60 ± 7 nm. To further prove the flexibility of this approach, we extended the synthesis of coreshell spheres to the preparation of completely mesoporous silica spheres through modification of the method (batch synthesis) firstly described by Kaiser.^{2c} By directly mixing TEOS and OTMS (without the presence of non-porous silica core), fully mesoporous silica particles (mSiO₂) with an average diameter of 341 ± 53 nm were obtained.

Once separated and dried, all the silica core-shell particles were calcined (550 $^{\circ}$ C, 6 h) to combust the porogen (octadecyl alky chain of OTMS) and thus form porosity within the silica shell. The textural properties of different SiO₂@mSiO₂ spheres were evaluated by means of N₂ physisorption (Fig. 3).

The increase in adsorbed volume is directly proportional to the thickness of the mesoporous shell, or, in other words, to the ratio of the shell volume over the volume of the non-porous core. The fully mesoporous spheres (mSiO₂) thus represent the limiting case (maximum mesoporosity achievable). The measured BET surface areas ranged from 125 m² g⁻¹ for the 18 nm shell, 282 m² g⁻¹ for the particles with 60 nm thick shells, and up to 626 $m^2 g^{-1}$ for the fully mesoporous spheres (Table S1, ESI[†]). All the samples, except the SiO₂@mSiO₂ spheres with a 18 nm thin shell, have pore sizes of 3-4 nm, as expected for a mesoporous shell formed at a TEOS/OTMS ratio equal to 2.5 (vol/vol).¹⁵ The deviation from this value for the SiO₂@mSiO₂-18 sample might be caused by the very thin shell, which might hinder the complete formation of a structurally stable mesoporous framework. The pore size distribution curves were calculated by applying the BJH (Barrett-Joyner-Halenda) method to the adsorption isotherm branch. The desorption branch, which is recommended by the IUPAC for the pore-size analysis,¹⁷ might be influenced by the presence of measurement artefacts, caused by the ink-bottle shape of the mesopores or capillary instability, and could therefore not be used.

Alternative continuous synthesis approaches to achieve higher yields

At a typical concentration for the $SiO_2 @mSiO_2$ -segmented silica particles of 0.009 g mL^{-1} and under standard conditions



Fig. 3 Textural and physical properties of different silica spheres. (A) Adsorption isotherms and corresponding BJH pore size distribution curves (B) for SiO₂@mSiO₂-18 (blue), SiO₂@mSiO₂-60 (red) and the mSiO₂ (green). (C) TEM images of SiO₂@mSiO₂, mSiO₂ and Au@SiO₂.

(inner diameter 3 mm and 120 min residence time), a productivity of 0.95 g h⁻¹ was achieved (based on sample mass after calcination). An increase in the production rate could only be achieved by elongating the tube and thus increasing the flow rate, or by shortening the residence time to a minimum of around 90 min (Fig. S1, ESI†), which would yield 1.25 g h⁻¹. An increase of the inner diameter of values higher than 3 mm is not feasible, since the segmentation of the flow would break down (see ESI†).

A segmented flow pattern for larger diameters could possibly be maintained in a droplet flow reactor, in which the reaction mixture is sequentially distributed as small droplets in an immiscible liquid carrier phase, instead of achieving segmentation with a gaseous phase. However, this would require a fully new optimization protocol, if the synthesis is possible at all. TEOS is soluble in most oil phases, and thus problems by partial or full solubilisation of the TEOS in oil segments are to be expected. Nevertheless, a droplet flow reactor could have some advantages, as higher possible tube diameters and thus higher productivity and the possibility of separating the reaction phase fully from the tube walls, which could reduce the risk of fouling and could lead to enhanced operation times.¹⁶ However, relatively long stable operation can also be achieved by the gas segmented flow. Long-term experiments over 8 h were conducted as part of this study for the synthesis of SiO₂ and SiO₂(@mSiO₂. In both cases continuous operation was possible without problems, while the material quality was maintained. However, silica residues became visible during the cleaning process, which might cause trouble on a longer timescale.

Zhang et al.4g discussed the upscaling of the continuous synthesis of nanocrystals in droplet flow reactors with the immiscible liquid phase and the liquid reactant phase with an inner diameter of up to 3 mm. Restrictions in terms of quality were observed for reactors with inner diameters of 3 mm, which could be overcome by pinching the tube to improve the mixing characteristics. The additional mixing contributions due to shearing and reorientation of the droplets led to the formation of particles with qualities as obtained with smaller diameter reactors. Nevertheless, the narrowing of the tube, below 3 mm, was necessary for increasing the diameters indicating restrictions in a similar diameter range as for the setup herein. In the case of segmentation with a gaseous phase, operation of the tube diameter of up to 3 mm is possible, thanks to the additional mixing contribution induced by friction between the tube wall and the reaction phase.5a

Higher production yields might be achieved following the tubular reactor setup of Giesche^{8a} for the synthesis of multistep growth of silica beads. Here the reagents are initially mixed *via* a vibrating magnetic stirring bar inside a Y-tube. The following aging is performed in a "double helix"-like twisted tube, which was required to prevent accumulation of the silica particles. However, whether transfer of this concept to the synthesis of SiO₂@mSiO₂ particles is possible is still an open question.

Continuous synthesis of Au@SiO2

A modified Stöber process is typically also employed in the synthesis of M(aSiO₂ core-shell particles, where M can be a metal (Au, Ag and Pt, among others) or a metal oxide (Fe₂O₃).¹⁸ The resulting spheres can be further processed to obtain, for instance, yolk-shell particles.^{14,19} To extend our proof of concept, we used our SFTR to cover gold colloidal nanoparticles with a dense (non-porous) silica shell. Initially, PVP-capped (polyvinylpyrrolidone) gold nanoparticles were synthesized in a batch process, following the synthesis described by Turkevich

and Enustun.²⁰ These nanoparticles have a diameter of 14 nm, as can be seen from the TEM images, Fig. 3C, right panels. The gold colloidal suspension, after being diluted with an ethanol/ water mixture, was continuously mixed with the solution containing the silica precursor, and pumped through the aging tube to finally grow the silica shell around the Au colloids. The overall good quality of Au@SiO2 core-shell particles is visible in Fig. 3 and is in complete agreement with what was obtained under batch conditions: every silica sphere contains a single Au colloidal particle, and a surrounding silica shell of 40 nm \pm 5.6, supporting again the notion that continuous processing is possible without compromising the product quality. Although not reported here, the shell thickness can potentially be adjusted by varying the TEOS or ammonia concentrations, as typically done for batch processes. In addition, it would be possible to grow an additional mesoporous shell on Au@SiO2 particles,^{19b} applying the same procedure described above for SiO₂@mSiO₂.

Conclusions

In this work we have described the continuous synthesis of several representative types of silica-based colloidal particles in an SFTR. In particular, we showed that the continuous synthesis of silica spheres (Stöber process), SiO2@mSiO2, mSiO2 and Au@SiO₂, is possible by adapting the methods commonly used in batch processes. Our results prove that several features of the silica spheres, like particle size, shell thickness and mesoporosity, are completely controllable by adjusting the synthetic parameters. We believe that this concept could potentially be extended to other materials (non silica-based sol-gel syntheses) as well as to other cases (by replacing the Au colloidal particles with other metals or metal oxides, for instance). Additionally, two (or multiple) synthesis steps, as the synthesis of SiO_2 and SiO₂@mSiO₂, could easily be combined in a single set-up consisting of two sequential stages. These considerations clearly point out the versatility of the applied system towards the continuous synthesis of advanced materials.

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