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Comprehensive Understanding on Synthesis and Formation Mechanism of Dendritic Mesoporous Silica Nanospheres

Pan Hao#, Bo Peng#, Bing-Qian Shan, Tai-Qun Yang* and Kun Zhang*

Abstract: The interest in the design and controlled fabrication of dendritic mesoporous silica nanospheres (DMSNs) emanates from their widespread applications in drug-delivery carriers, catalysis and nanodevices owing to their unique open three-dimensional dendritic superstructures with large pore channels and highly accessible internal surface areas. A variety of synthesis strategies have been reported, but there is no basic consensus on the elucidation of pore structure and the underlying formation mechanism of DMSNs. Although all the DMSNs show a certain degree of similarity in structure, do they follow the same synthesis mechanism? What are the exact pore structures of DMSNs? How did the bimodal pore size distributions kinetically evolve in the self-assembly? Can the relative fractions of small mesopores and dendritic large pores be precisely adjusted? In this review, by carefully analysing their structures and deeply understanding their formation mechanism of each reported DMSNs, and coupling with our research results on this topic, we conclude that indeed all the DMSNs have the same mesostructures and follows the same dynamically self-assembly mechanism using microemulsion droplets as super templates in the early reaction stage, even without the oil phase.

1. Introduction

The high porosity and accessible surface modification of bulk mesoporous silica (in particular MCM-41 and SBA-15 two kinds of ordered mesoporous materials) have opened a new route to the formation of porous supports with high performance catalysts and a potential platform for advanced biomolecule carriers for targeted and controlled drug delivery systems. Because the liquid crystal templating (LCT) principle of the synthesis is quite simple, a variety of sol-gel processes have been developed to synthesize ordered mesostructured silica frameworks with highly tunable porosities and morphologies using varied surfactants as templates including cationic, anionic and nonionic surfactants. Thus, the past three decades have witnessed the rapid development of mesoporous silica materials with diverse topologies and architectures.

The application-driven design of porous materials confirms that the synthesis of mesoporous
silica nanoparticles (MSNs) with short diffusion length and/or with wide pores are more appealed in the field of nanocatalysis and drug delivery.9-15 The sol-gel soft-templating synthesis of MSNs is the best and easiest method, which was first reported by the groups of Cai,16 Mann17 and Ostafin18. Then the term MSNs was popularized by Victor Lin to represent mesoporous silica nanospheres.5, 19-22 Subsequently, the groups of Bein,23-26 Mou,27-29 Tatsumi30-33 and Kuroda34-39 followed this line to carry out the extensive research works. Several important reviews written by some of them cover different aspects of mesoporous silica nanoparticles, such as preparation, characterization and formation mechanism, and applications (in particular targeted drug delivery system) are available in the literature.5, 9, 20-22, 40-49 It is worth noting that, if without the addition of the micelle organic swelling agents, the common surfactant templated MSNs have pores smaller than 3.0 nm,50 which significantly limits their wide use as metal nanoparticles and enzyme immobilizing supports, and multifunctional drug delivery nanocarriers. Therefore, an enlargement of their mesopore size is desired to extend their applications in the different fields. Consequently, the scientific community started to look for a new generation of mesoporous materials with both short diffusion length and wide pores targeting for improved accessibility and molecular transport.

**Figure 1.** Schematic illustration of dendritic mesoporous silica nanospheres (DMSNs) with the unique branching architecture, which is reminiscent of natural mineral dendrimer and artificial organic dendrimer.

In this line of thinking, DMSNs with unique open three-dimensional dendritic superstructures (in some cases, also called hierarchical pore systems) have intensively been developed and have attracted rapidly growing attention since the 2010s. Compared with conventional MSNs with two dimensional hexagonal ordered mesopores (pore symmetry: *p6mm*) and uniform pore sizes, DMSNs have unique three- dimensional disordered superstructures with many permeable center-radial large pore channels and high pore volumes.51-54 So far, corresponding to synthetic systems, several terms have been used to describe its morphology such as fibrous, nanoflowers, radial wrinkle structure and stellar shape etc. The different morphological terminologies used indeed indicate that the mesostructures and formation mechanism of DMSNs have not been fully revealed. Since the intrinsic branching architecture of DMSNs is reminiscent of natural mineral dendrimer and artificial organic dendrimer, the nomenclature of dendritic mesoporous silica nanospheres could be well-accepted (Figure 1).55-58 However, there exists an urgent need to compare the various methods for their preparation, and not least to describe in detail the properties of the materials as well as to establish a firm link between structure and
function. In this report, based on our continuous and long-term studies in the past decade, we summarize recent findings on this topic and the content of review is organized as follows: the emergence and evolution of DMSNs are first discussed in a brief introduction; in the second section, we present a state-of-the-art progress in the strategies for the preparing DMSNs, with emphasis on the elucidation of mesostructural characteristics and physicochemical properties of DMSNs. In addition, by carefully analyzing the structure and synthetic mechanism of each reported DMSNs, combined with our studies on this topic, all the synthesis of DMSNs in the documented records is systematically classified into three main groups, including the micro-emulsion templating (MET) approach, the organosilane assisted co-condensation (OAC) method and the spherical micelle self-aggregated assembly (SMSAA) strategy, and the simplest and reproducible way for the DMSNs is highlighted by comparing the advantages and disadvantages of each method; in the third part, several typical examples are presented to show the unique nanoconfinement effect of spherical mesopores in DMSNs, which could be used as an ideal nanoreactor or platform for the preparation of highly efficient heterogeneous nanocatalysts and the fabrication of photoluminescent (PL) materials. Most interestingly, in this part, by clustering of nonconjugated organic functional groups in the spherical mesopores of DMSNs, the first PL MSNs with tunable colors and high quantum yield (QE) was reported by simple post-grafting technique in the absence of metals, which completely subverts one's understanding on the origin of photoluminescence emission of metal nanoclusters (NCs) and other related quantum dots. Last, but not least, opinions and challenges for future progress of these materials are addressed. We sincerely expected that this summary and in-depth discussion on the formation mechanism of DMSNs could give materials scientists and chemists more inspirations to accelerate the DMSNs family's booming development in related interdisciplinary research.

2. Typical Synthetic Strategies of DMSNs

Differing from the synthesis of MCM-41 with ordered mesostructures, the preparation of DMSNs are complex, and the conventional soft-templating methods are not suitable due to the complex dynamic self-assembly of negative silicate species and surfactants on molecular scale. So far, more than 20 synthetic methods have been reported to synthesize the DMSNs with the 3D center radial pore structure. According to the common characteristics of their synthesis, whether oil-phase organosilane reagent is used, they are classified into three main categories as such, and also are summarized in the Table 1:

1. Micro-emulsion templating (MET) approach, also called biphase stratification approach, emphasizing the self-assembly of silicate species with surfactant at the interface of immiscible phases of water and oil.

2. Organosilane assisted co-condensation (OAC) method, featuring the use of customer-tailored organotrialkoxysilane with special organic functional groups.


2.1. Micro-emulsion templating approach

Because of the variety and ease of control, the substructures of microemulsions were used as templates to control the synthesis of mesoporous silica materials with different morphology and
mesostructure. In 2008, Okuyama and his coworkers first reported the synthesis of spherical mesoporous silica particles with tunable pore size and tunable outer particle diameter in the nanometer range in a water/oil phase using cationic surfactant CTABr as a template (Fig. 2a-b). This method involves the simultaneous hydrolytic condensation of tetraethylorthosilicate to form silica and polymerization of styrene into polystyrene (PS) in the presence of octane as oil phase, and subsequent removal of PS by high temperature calcination in the air resulted in the formation of DMSNs with large pores, where PS beads actually acts as hard templates (Fig. 2c). By varying the conditions of the dispersed phase, e.g., the ratio of octane/water, the styrene concentration, the pH, and temperature during preparation, the pore size (4-15 nm) and grain diameter (20-80 nm) of the prepared MSNs can be precisely tuned. While further research investigated by Holmberg suggested that the MSNs synthesized at the same condition free of styrene possessed the same mesostructures (Fig. 2d-e), indicating that the polystyrene (PS) beads formed by polymerization of styrene were not the only template for the formation of DMSNs with large pores. In turn, the authors concluded that the microemulsion spontaneously formed at the interface of water and oil played the main role to control the formation of DMSNs with hierarchical pores (Fig. 2f). This conclusion was further supported by subsequent research of Ernawati and his coworkers.

Table 1. Summary of synthetic strategies and physical properties of varied (DMSNs).

<table>
<thead>
<tr>
<th>Synthetic strategy</th>
<th>Main feature</th>
<th>Solvent</th>
<th>Particle size (nm)</th>
<th>Pore size (nm)</th>
<th>$S_{BET}^a$ (m$^2$/g)</th>
<th>$V_{t}^b$ (ml/g)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil-water mixed</td>
<td></td>
<td>octane</td>
<td>20-80</td>
<td>4-15</td>
<td>600</td>
<td>1.0-1.5</td>
<td>59</td>
</tr>
<tr>
<td>Micro-emulsion</td>
<td></td>
<td>Cyclohexane</td>
<td>250-450</td>
<td>4.6</td>
<td>641</td>
<td>-</td>
<td>62</td>
</tr>
<tr>
<td>templating (MET)</td>
<td></td>
<td>1-octadecene, decahydronaphthalene, or cyclohexane</td>
<td>110-280</td>
<td>2.8-13.0</td>
<td>&lt;700</td>
<td>0.6-1.7</td>
<td>69</td>
</tr>
<tr>
<td>also called</td>
<td></td>
<td>Ethyl ether</td>
<td>150-600</td>
<td>2.7</td>
<td>1078</td>
<td>1.0</td>
<td>76</td>
</tr>
<tr>
<td>biphase stratification approach $^{51,59-90}$</td>
<td></td>
<td>Chlorobenzene</td>
<td>180</td>
<td>45</td>
<td>554</td>
<td>2.59</td>
<td>71</td>
</tr>
<tr>
<td>Organosilane</td>
<td>The interfacial assembling is related to the specific nature of the used organotrialkoxysilane</td>
<td>water</td>
<td>50</td>
<td>4.0</td>
<td>519</td>
<td>0.25</td>
<td>91</td>
</tr>
<tr>
<td>assisted co-</td>
<td></td>
<td>water</td>
<td>&lt;70</td>
<td>2.4</td>
<td>953</td>
<td>1.5</td>
<td>92</td>
</tr>
<tr>
<td>condensation (OAC)</td>
<td></td>
<td>water</td>
<td>30</td>
<td>6.2</td>
<td>614</td>
<td>2.2</td>
<td>93</td>
</tr>
<tr>
<td>method $^{91-94}$</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Spherical micelle</td>
<td>The reaction occurs in single aqueous phase in pH ca. 7</td>
<td>water</td>
<td>50-300</td>
<td>3.0/15-20</td>
<td>&lt;600</td>
<td>1.4-2.1</td>
<td>95</td>
</tr>
</tbody>
</table>

$^a$ Specific surface area, BET method

$^b$ Total pore volume, BJH method
Following the same principle of MET mechanism, but free of organic polymer monomers, Polshettiwar and his coworkers reported the synthesis of dendritic silica nanoparticles with fibrous morphologies (or center-radial wrinkle structures) under microwave-assisted hydrothermal conditions, which was named KCC-1,\(^{62}\) which triggered a boom in the synthesis of DMSNs. But, the early proposed formation mechanism was too simple to understand its formation mechanism (Fig. 3A). More comprehensive studies on the formation mechanism of KCC-1 were carried out by Febriyanti.\(^{66}\) The morphology of KCC-1 was defined as a bicontinuous concentric lamellar morphology (Fig. 3B-E) through a sophisticated TEM technique by the detailed comparison of the gray value intensity profiles of the TEM images of different type of MSNs, and they concluded that the reverse micelle in the reaction media and the polysiloxane species with varied Si–O–Si chain length played the important role for the assembly of DMSNs (Fig. 3F). Further in-depth investigations by Polshettiwar and his coworkers showed that the formation of KCC-1 was just attributed to the structural evolution of microemulsion template.\(^{64, 65}\)

**Figure 2.** SEM (a) and TEM (b) images and proposed mechanism (c) of mesoporous silica nanoparticles prepared by Okuyama and his coworkers with styrene.\(^{59}\) Reproduced with permission from ref. 59. Copyright 2009 Elsevier Ltd. And TEM (d) and SEM (e) images and proposed mechanism (f) of mesoporous silica nanoparticles prepared by Holmberg without styrene.\(^{60}\) Reproduced with permission from ref. 60. Copyright 2016 Elsevier Ltd.
Figure 3. (A) Schematic of silica nanosphere (KCC-1) formation proposed by Basset.\textsuperscript{62} CPB: cetylpyridinium bromide, TEOS: tetraethyl orthosilicate. Reproduced with permission from ref. 62. Copyright 2010 Wiley-VCH, and (B) SEM and (C) TEM images of KCC-1 with their respective illustration drawn in (D) and (E), respectively. (F) Self-assembly of the silicate oligomer for the formation of bicontinuous morphology (The ABA silicate oligomer consists of two A blocks (blue) separated by a B block (red), where the A block consists of O–H groups in the terminal and the B block is the Si–O–Si chain of the oligomers. This pattern is similar to ABA triblock copolymer chains where A and B blocks are formed from different monomers. When B blocks of the polysiloxane have a range of chain lengths, a bicontinuous structure is formed).\textsuperscript{66} Reproduced with permission from ref. 66. Copyright 2016 American Chemical Society.

Very recently, based on a simple adjustment of the water-surfactant-oil ternary phase diagram, the more detailed investigations on the formation mechanism of KCC-1 were elegantly studied by Lee and his coworker following the same recipe of KCC-1. Note that the obtained DMSNs herein was named as wrinkled silica nanoparticles (WSNs).\textsuperscript{67, 68} It is well known that the phase behavior of the ternary systems (the so-called “Winsor system”) is determined by surfactant concentration and the Winsor value $R$, which is a variable depending on temperature, salinity, and affinity of each component. They confirmed that WSNs were preferentially generated in the bicontinuous microemulsion phase of the Winsor III system, and that the particle size of the wrinkled silica nanoparticles (WSNs) and the connective morphology of the WSMs can be precisely controlled by deliberately tune the volume ratio of water/oil with alkyl alcohols as co-solvent (Fig. 4). In addition, these authors first showed that WSNs intrinsically had a bi-modal pore size distributions with a very sharp peak in the 2-4 nm range and a broad peak in the 15-50 nm range, and the smaller pores were embedded in the wall of WSNs, which was attributed to the emulsion rupture-inversion at the early nucleation process. (Fig. 4b), suggesting a completely different formation mechanism from classical MCM-41.\textsuperscript{104}
Later, Zhao and his collaborators have developed a new biphase stratification approach for the synthesis of novel 3D-DMSNs with multigenerational and hierarchical dendrimer-like center-radial mesopore channels (Fig. 5), and it was also successfully expanded to prepare uniform core-shell mesoporous structures with varied functional cores (such as Au nanoparticles and Ag nanotubes) and 3D-dendritic mesopores radial channels.69 In this report, a complex interfacial emulsion, ‘funneling’ gradient assembly and growth mechanism was proposed to elucidate the formation mechanism of DMSNs, which highlighted the interfacial emulsion as a driving force to form oil@water hemimicelles, exclusive composite micelles on the solid nuclei, ‘funneling’ gradient assembly and growth of the mesostructures. Very recently, in the final collected sample, Yu and his coworkers found the presence of isolated cone-shaped structures, which could be used as building subunits to assemble DMSNs, whose shape is reminiscent of funnel-like shape in the model of biphase stratification approach (Fig. 6A-D).51 It is importantly noted that both groups commented that the final mesostructure of DMSNs was sensitive to the stirring rate of reaction media as discussed by other groups,71, 88, 72 which indicates the rationality of MET mechanism.
Figure 5. (A) Synthesis process of the 3D-Dendritic MSNNs and mechanism of interfacial growth, (a) nucleation process of the 3D-dendritic MSNSs; (b) growth process of the first generation of the 3D-dendritic MSNSs; (c) changing the upper oil phase; (d) growth process of the second generation of the 3D-dendritic MSNSs; (e–h) the mechanism of one single mesopore-channel growth with swelling. TEM (B-D) and SEM (E-G) images of the extracted 3D-dendritic MSNSs with one (B, E), two (C, E), and three generations (D, G) prepared via the biphasic stratification approach. All scale bars in TEM and SEM images are 200 nm. Reproduced with permission from ref. 69. Copyright 2014 American Chemical Society.

Figure 6. A picture of a dahlia photographed by C. Xu at Tasmania (A). TEM images at low magnification (B), high magnification (C), an ET slice (D) and proposed formation mechanism (E) of MSN-CC. Reproduced with permission from ref. 71. Copyright 2015 Wiley-VCH.
Indeed, at the early time of mesoporous materials birth, the studies using microemulsion system as a supertemplate for the synthesis of MSNs have been extensively investigated, in particular in the acidic conditions.\textsuperscript{105-107} However, the synthesis under alkaline conditions has not attracted enough attentions except the Cai’s group.\textsuperscript{73, 74, 108} By employing a non-stable interface of biphasic oil-water system (OWTP) and adjusting the molar ratios of oil/water and the alkalinity of the OWTP system using diethyl ether as a co-solvent, Cai and his coworkers first reported the preparation of mesostructured silicas with diversified particle morphologies. By systematic investigations, they established a detailed reaction phase diagram to direct the synthesis of MSNs, and a variety of morphology of the collected products was reported. In fact, in these original papers, one of the obtained nanoparticles (NPs) was first vividly named as radiolarian-like mesoporous silica (RMS), analogous to the shape of coronavirus. Indeed, it is the first example of DMSNs. In viewpoint of historical evolution, the contribution of Cai and his coworkers on this new rising field have been neglected.\textsuperscript{73, 74} In addition, in their reports, two common features for the synthesis of DMSNs were also carefully depicted: RMS showed an interesting bi-modal pore size distributions with a smaller mesopores (centered at $\sim 3$ nm) and the larger ones of $\sim 34$ nm; its synthesis was very sensitive to the volume ratio of water/diethyl ether and the stirring rate of reaction media.\textsuperscript{73, 74} These intriguing experimental observations were attributed to the dynamic self-assembly of micelles at the unstable oil-water interface. The sequential researches by He and his coworkers further blossomed this field,\textsuperscript{76, 109} they noted that, the use of diethyl ether with low boiling point of 34 $^\circ$C was necessary for the formation of dendritic pores due to the ethyl ether gasification.\textsuperscript{64} Thereafter, a huge amount of experimental evidences proved that any non-immiscible water-oil biphase system was effective for the synthesis of DMSNs, such as toluene,\textsuperscript{77} trialkylenzenes,\textsuperscript{78, 79} ethyl acetate,\textsuperscript{80} N,N-dimethylecylamine,\textsuperscript{81} benzyl acetate,\textsuperscript{82} aldehyde,\textsuperscript{83} etc., which evidences the universality of MET mechanism for the synthesis of DMSNs.

To sum up, water-surfactant-oil ternary systems have various phase behaviors and substructures that depend on their chemical composition and component ratio, the substructures of which can be used as super-templates for the synthesis of DMSNs. MET mechanism provides an example for constructing hierarchical porous silica NPs with varied morphologies and tunable mesostructures probably involving dynamic self-assembly of spherical micelles at the unstable interface of microemulsion droplets.\textsuperscript{64, 110} Due to its intrinsic dynamic nature of microemulsion droplet, several common features for the synthesis of DMSNs were observed: (1) the mesostructure and morphology can be precisely tailored with the variation of volume ratio of water to oil; (2) the successful fabrication of DMSNs is very sensitive to the stirring rate of reaction media, which significantly affects the stability of microemulsion droplets; and (3) the obtained DMSNs generally exhibited bi-modal size distributions. However, several
disadvantages of MET methods should be marked: (1) reproducible synthesis is not readily accessible due to the sensitivity of reaction parameters to stability of microemulsion nanodroplets; (2) the large quantity use of organic oils is not good for environment and cost-expensive, which limits the large scale synthesis of DMSNs.

2.2. Organosilane assisted co-condensation (OAC) method

Silanes are silicon chemicals that possess a hydrolytic sensitive center that can react with inorganic substrate to form stable covalent bonds and have an organic substitution that alters the physical interactions of treated substrates. Depending on the structure of silanes, there are two type of silane coupling agents. Most of the widely used organosilanes have one organic substituent and three hydrolysable substituents (also called monopodal silanes). The general formula for this type of silane coupling agent is as such: R-(CH₂)n-Si-X₃. X is a hydrolysable group typically alkoxy, acyloxy, halogen or amine. The R group is a non-hydrolyzable organic radical that may possess a function of imparting desired characteristics. The other type of silane is a bridged silsesquioxanes with the formula of X₃Si-R-SiX₃ (dipodal silanes). The most common organic groups in the dipodal silanes introduced are disulfides, diamines or benzene etc. In fact, the bridged silsesquioxane precursors are first used to synthesize the periodic mesoporous organosilicas (PMOs), and using the same synthetic principle of PMOs, the synthesis of DMSNs would be possible.¹³ In order to distinguish DMSNs prepared by MET method, the obtained MSNs were named as dendritic-like mesoporous organosilica nanospheres (DMOSNs).

Freire’s group first reported the preparation of DMOSNs by one-pot soft-templating co-condensation strategy with hydrophobic tridecafluoroctyltriethoxysilane (F13) as organosilane and TEOS as silicon source (Fig. 7a-c). The authors demonstrated that the morphology and mesostructure of DMOSNs was strongly dependent on the amount of used organosilane F13. Indeed, the preparation of DMSNs is an unexpected result, wherein the objective was to develop a methodology to generate superhydrophobic and superoleophobic fabrics functionalized with F13-MSNs. A more sophisticated OAC approach was developed by Paula and his coworkers using dual organosilanes of phenyltriethoxysilane (PTES) and 3-(trihydroxysilyl)propylmethyl-phosphonate (THSPMP) as silicon sources,⁹² by simply adjusting the molar ratio of organosilane to TEOS, the well-defined and monodispersed dendritic-like mesoporous organosilica nanospheres (DMOSNs) with radial ultra-large porous structure and particle size of ~ 60 nm could be readily obtained (Fig. 7d-f).
Recently, following the similar synthetic principle, Shi and his coworker reported the facile synthesis of DMOSNs with bis [3-(triethoxysilyl) propyl] tetrasulfide (BTES) as organosilane by one-pot co-condensation strategy.\textsuperscript{93} They discovered that the hydrophobic CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}-S-S-S-S-CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2} fragment in BTES were preferentially located at the interface of CTAC micelles, which cooperatively directed the self-assembly of micelles triggered by adsorption of anionic silicate species (Fig. 8). Very interestingly, the obtained DMOSNs also exhibited bi-modal pore size distributions (Fig. 8g), similar to that of DMSNs synthesized by MET mechanism. Very recently, our experimental results also evidenced that the use of more hydrophobic organosilanes, such as 1, 2-bis(triethoxysilyl)ethane (BTSE) and 1,4-bis(triethoxysilyl)-benzene (BTSB), promoted the formation of DMONs,\textsuperscript{111} suggesting the unique role of hydrophobic organosilanes for tuning the synthesis of DMOSNs. Most recently, Yang and his coworkers demonstrated that the reaction time determines the compositional and structural properties of DMOSNs: For the aqueous phase route, prolonged reaction time is beneficial for improving the organosilica content, but leads to the loss of porous structure; In contrast, for the water/oil biphasic route, prolonging the reaction time causes the reduction of organic content in the products, but facilitates the formation of well-defined dendritic mesoporous structure.\textsuperscript{103}
Figure 8. a) Schematic representation for the molecularly organic–inorganic hybrid composition of thioether-bridged DMOSNs. b) The proposed M/P-CA strategy to enlarge the micelle size of CTAC by incorporating the hydrophobic long organic chains of as-hydrolyzed BTES into the hydrophobic part of initially formed CTAC micelles. And corresponding TEM images (d and f) of DMOSNs at different magnifications (inset of f: the pore shape of DMOSNs). Bright-field (c) and dark-field (e) STEM images of DMOSNs. N$_2$ adsorption-desorption isotherm (g) and (inset of g) the corresponding pore size distribution of DMOSNs. Reproduced with permission from ref. 93. Copyright 2015 Wiley-VCH.

As a short summary, the only difference of single phase OAC method, is the use of hydrophobic organosilanes to substitute the oil phase of water-oil binary system of the MET methodology, which indicates that the organosilane involves the self-assembly of micelle and inorganic silicates. We propose that OAC method indeed follows the same synthetic principle with MET method, where unhydrolyzed or partially hydrolyzed hydrophobic organosilanes were used as oil phase for the spontaneous formation of microemulsion nanodroplets. This conclusion was evidenced by recent discovery of Wang and his coworkers. They demonstrated that the added (3-chloropropyl)trimethoxysilane (CPTMS) played key roles in controlling the size and maintaining the metastable state of the water nanodroplets through insertion of hydrophobic tail of ClCH$_2$-(CH$_2$)$_2$-Si(-O-)$_3$ fragment, and subsequently induced the formation of silica nanotubes (NBs). Compared to multi-step post-synthetic grafting technique, the one-pot OAC method for the synthesis of DMSNs with customer-tailored application is simple and reproducible. However,
very rare examples were reported for the synthesis of DMSNs by this method due to the limitation of commercially available organosilanes. Additionally, the incorporation of organic functional groups onto the pore wall prohibits the subsequent post-synthetic modification, thereby limiting the widespread use of this group of nanomaterials.

2.3. Spherical micelle self-aggregated assembly (SMSAA) strategy

Although two strategies of MET and OAC are seemingly completely different, they indeed follow the same microemulsion template mechanism, which has been evidenced by solid experimental data. But at present, considering of several pivotal aspects of synthesis with environmental concerns, involving a large quantity of toxic and/or highly inflammable organic solvent and the deliberate choice of silane coupling agents, the development of facile and green synthetic methods is particularly appealed. In 2011, using the surfactant cetyltrimethylammonium tosylate (CTATos) as a new template at ultralow concentration, we firstly reported the eco-efficient synthesis of a family of ordered mesoporous silica with varied topology, including hexagonal, cubic and rectangular phase. The key of this method is the deliberate use of the surfactant CTATos with strong affinity of tosylate (Tos\(^{-}\)) as a counter anion. Because Tos\(^{-}\) lies to the end of the typical anion lyotropic series, the critical micelle concentration (CMC) of cationic surfactant is significantly reduced, and adsorption of Tos\(^{-}\) onto the surface of cationic micelles by regulating the interfacial charge density leads to the diversity of mesostructures. Subsequently, inspired by Bein’s pioneering research for the preparation of MSNs using triethanolamine (TEAH\(_3\)) as quenching molecules for the growth of NPs, the dual roles of quenching agent and alkaline source was introduced in our reaction system with CTATos as surfactant template. As expectedly, the conventional MSNs with worm-like morphology were obtained. However, the large quantity use of small organic amines (SOAs) is not environment friendly, since the subsequent recovery and removal of these SOAs normally requires complicated chemical processes, for example, the high-temperature combustion that destroys these high-cost components, producing hazardous (NO\(_x\)) as well as greenhouse gases (CO\(_2\)).

According to the basic principle of sol-gel chemistry, hydrolysis of the Si-OR bond in TEOS could be catalyzed by both acid and base, thus in theory, for classic \(\{S^+I^-\}\) synthetic route under alkaline conditions (wherein \(S^+\) means the cationic surfactant with positive charges and \(I^-\) denotes the silicate species with negative charges), the use of just trace amount of base will initiate the hydrolysis of TEOS, and neutral pH value favors the maximum condensation. Obviously, the higher pH value, the stronger electrostatic interactions between \(S^+\) and \(I^-\), which accelerates the assembly between surfactant and silica. Thus, in conventional synthesis of MSNs, the reaction was generally performed at high pH value (generally above pH = 11). Fully taking account of the kinetics of hydrolysis and condensation of TEOS, by precise pH adjustments of the reaction mixture, we first achieved the massive synthesis of DMSNs with dendritic pore channels in kilogram (kg) scale using SOAs of catalyst quantity as alkali source (extremely low molar of SOAs/TEOS ratio less than 0.026), and by various adjustments of reaction parameters, including the pH of the reaction mixture, the characteristics of surfactants or copolymers used, as well as the concentrations and the sources of silica, the diversity of MSNs.
with controlled particle size and varied morphology such as raspberry-like (RB) and worm-like channel morphologies, were also obtained (Fig. 9).\textsuperscript{122}

Compared to the reported MAT and OAC strategies, our method is very simple, just containing TEOS/CTATos/TEAH\textsubscript{3}/Water ternary components, and the reaction takes place under very mild conditions (at 80 °C for 2 h) with low water/silica ratio of 80 at extremely low surfactant concentration (CTATos/TEOS = 0.06), and most importantly form the viewpoint of green synthesis, free of any exotic organic solvent is used,\textsuperscript{95} which is very similar to the synthesis of standard silica NPs by classic Stöber method.\textsuperscript{123} This may answer why our synthetic strategies have been widely adapted and expanded in a very short times.\textsuperscript{100}

In order to take great advantages of the review paper for propagations, the optimal synthetic details for DMSNs is described as follow: 1458.0 g of tetraethylorthosilicate (TEOS), 192.0 g of cetyltrimethyl-ammonium (CTA\textsuperscript{+}) tosylate, and 34.7 g of TEAH\textsubscript{3} was dissolved in 10 L of water. The final molar ratio of mother liquor is 1.0SiO\textsubscript{2}:0.06CTATos:0.026TEAH\textsubscript{3}:80H\textsubscript{2}O. The reaction was carried out at 80 °C for 2 hours. The final pH was ca. 7. After filtration and drying at 100 °C for 2 hours, 460 g of final products was collected (93% yield for SiO\textsubscript{2} and the surfactant). The obtained DMSNs exhibit typical dendritic morphology, and very interestingly, the characterization by N\textsubscript{2} adsorption shows a bimodal pore size distributions in ~2.6 nm and ~15 nm, respectively, to certain degree, implying the relevance to the mechanism with MET and OAC methods.

A three-step formation mechanism based on self-assembly and ion competition at the electrical palisade of micelles is proposed as follow: (I) the formation of partly silicated single micelles, which was also discovered by Wiesner and Zhao,\textsuperscript{124, 125} and (II) block formation using these micelles as primary building unit, and (III) block aggregation into dendritic morphology (Fig. 9a). At the single micelle level, the curvature of the organic–inorganic electrical interface was affected by the counterions (X\textsuperscript{-}) remaining in the material. This can be described as \{(1+n)S\textsuperscript{+}, nX\textsuperscript{-}, I\textsuperscript{-}\}. The pivotal role of the counterions in forming the pore network is rationalized by the much lower affinity of Br\textsuperscript{-} than Tos\textsuperscript{-} for the electrical palisade of the CTA\textsuperscript{+} micelles. Tos\textsuperscript{-} competes more strongly against the adsorption of silicate oligomers on the micelles than Br\textsuperscript{-} which is more favored at low pH value, answering the formation of DMSNs at extremely low SOA concentrations. Indeed, the silanolate density (I \textsuperscript{-}) is too small to displace Tos\textsuperscript{-} anions efficiently. We named this phenomenon “weak templating” interactions. In contrast, high SOA concentrations (pH \approx 10) and high silanolate density result in stronger templating conditions, yielding MSNs with a more organized 1D worm-like array of the pore channels, like MCM-41 and SBA-15 silicas.
Figure 9. (a) Scale-up synthesis with tunable mesostructures via mono-micelle templating self-assembly strategy, and SEM (b, d, f) and TEM (c, e, g) images of samples synthesized with different small organic amines (SOAs) of triethyleneamine (b, c), triethanolamine (d, e), and 2-amino-2-(hydroxymethyl) propane-1, 3-diol (f, g). Reproduced with permission from ref. 95. Copyright 2013 American Chemical Society.

Because self-assembly takes place between polymerized silicate oligomers and individual or single surfactant micelles, we named this synthetic strategy as spherical micelle self-aggregated assembly (SMSAA) mechanism, highlighting the key role of the surfactant counterions and pH value to tune the morphology of MSNs using single spherical micelles as primary building unit. The imperfect-centered dendritic morphology indicates that the nucleation and growth processes via a block-by-block aggregation, wherein the block as secondary building unit was composed of primary building units of single micelles. Similar experimental phenomena was observed in the synthesis of silicate-1 zeolite. The mesochannel morphology is controlled by the template counterion and the SOA concentration, which was determined by weaker or tighter templating interaction between silicate species and single micelles.

To further prove the competing adsorption role of counter anions on the positive micelles to negative silicate species, the anionic surfactants, such as, sodium dodecyl benzene sulfonate (SDBS), sodium dodecyl sulfate (SDS), sodium laurate (SL) and sodium stearate (SS), were introduced to synthesize DMSNs in the presence of conventional cationic CTABr surfactants (Fig. 11). In current cationic-anionic surfactant dual-templating strategy, the anionic surfactant has a much higher affinity than the Tos\(^-\) anion for the electrical palisade of the CTA\(^+\) micelles due to the very strong hydrophobic forces between the long carbon chains. The presence of the anionic surfactant in the mixed surfactant micelles strongly counteracts the competitive adsorption of silicate oligomers (I\(^-\)) on
the mixed CTA\(^+\) micelles due to the electrostatic repulsion relative to the single cationic CTA\(^+\) micelles. Thus, following the same SMSAA mechanism mentioned above, DMSNs was finally collected. Moreover, by finely tuning the molar ratio of dual-templates, MSNs with varied morphology, including silkworm cocoon-like (SW-MSNs) and mono-lamellar vesicle (V-MSNs), were also synthesized (Fig. 10a, bottom). Again, the common feature for DMSNs with dual size pore distributions of ~ 4.0 nm and ~ 21 nm was also observed (Fig. 10a). With chaotic treatment of TEM image of individual DMSNs nanosphere (Fig. 10b), the blocks composing of single micelles in size of ~4.0 nm could be distinguishably observed, like ‘the single micelles filling in the dendritic channels’, which clearly answers the origin of smaller pore size distribution for all the DMSNs on N\(_2\) adsorption (Fig. 10c).

**Figure 10.** (a) Dual template synergistically controlled micelle self-aggregated model to understand the formation mechanism of dendritic MSNs; (b) Pore networks of the typical dendritic MSNs by TEM observation. Red, green and brown circles indicate the small, intermediate and large pores using monomicelles, bimicelles and aggregated micelles as the templates or structure building units, respectively. (Inset 1, pore networks of classical amorphous silica sol particles; Inset 2, the hexagonal pore array of MCM-41 or SBA-15.); (c) Pore size distribution (PSD) of typical dendritic MSNs synthesized by using the dual-templating strategy in the presence of the anionic sodium stearate (SS) surfactant calculated by the BJH method from both desorption branches.\(^{122}\) Reproduced with permission from ref. 122. Copyright 2017 The Royal Society of Chemistry.
Figure 11. From (A1) a Dahlia-like DMSN to (A2) a Pomegranate-like MSN and (B) a Kinetic Micelle Filling Mechanism, The dahlia-like DMSNs (B1) are first assembled by an anion-assisted approach through lamellar building blocks. By gradually filling the large dendritic pores with composite micelles, we obtained a series of intermediate structures (B2) and small-pore MSNs with the dendritic pores completely filled (B3). Objects are drawn not to scale; TEM images (C-F) of MSNs at fixed reaction temperature of 80 °C and FC2/CTAB molar ratio of 1 at various reaction time of (C) 0.3, (D) 1, (E) 2, and (F) 5 h. Reproduced with permission from ref. 100. Copyright 2018 American Chemical Society.

More investigations followed this concept showed that not only other anionic surfactant and small organic anion (such as fluorocarbon anions,99-102 sodium salicylate,97, 98, 127), but also nonionic surfactant could play the same role for the synthesis of DMSNs.128 Among of these reports, Yu and his coworker performed much more elegant researches, not only in the synthesis and application of DMSNs (especially in biomedical field), but also for completely new and in-depth understanding on the dynamic structural changes.71, 100 A new micelle filling mechanism was proposed in these study to reveal the dynamical structure change from a dahlia-like morphology to pomegranate-like morphology (Fig. 11), based on this mechanism, the final structures of DMSNs with a bimodal pore size distributions were rationally elucidated: the silica-coated micelles are heterogeneously nucleated on a preformed large dendritic pore surface due to further condensation between silanol groups, and subsequent surfactant removal, results in the formation of small mesopores (nanocasted by single spherical micelles in Fig. 11 B2) and large dendritic pores (Fig. 11 B1), and the extent of micelles filled into the dendritic large pores finally determines the final fractions of small mesopores in DMSNs.100

By combing other reported mechanisms, a universal spherical micelle self-aggregated assembly (SMSAA) mechanism was proposed to understand the formation mechanism for the synthesis of MSNs by precisely tuning the electrostatic interactions between silicate species and single micelles (Fig. 12).128 Depending on the
strength of interfacial charge shielding, three types of MSNs with varied kinetically controlled heterogeneous structures were synthesized. At high pH value in the presence of the conventional surfactant of CTABr, generally called modified Stöber method, traditional MCM-41 and MSNs were finally obtained due to very strong electrostatic interaction of \( \{S^+I^-\} \), where the primary building unit (PBU) could be spherical micelles or rod-, or worm-like micelles (Fig. 12, route I). At the medium strength of \( \{S^+I^-\} \) interactions, DMSNs with dendritic networks were synthesized in the presence of dual surfactants or the special surfactant counter anions with high hydrophobicity (Fig. 12, route II), where the silica partly coated single spherical micelles were used as PBU, i.e., so called SMSAA mechanism. Obviously, the respective size of bimodal porosity of smaller mesopores and dendritic large pores, and their relative fractions were determined by the strength of \( \{S^+I^-\} \) interactions. At very weak interaction in route III, for example, if the nonionic 4-Nonylphenol branched ethoxylated surfactant (Tergitol NP-7) or polyoxyethylene(20)sorbitanmonoleate (Tween-80), was used as co-templates, DMSNs only show dendritic large pores without small mesopores (Fig. 12, route III). Although the detailed formation process of dendritic large pores is still in debate, a common consensus on SMSAA mechanism using silica partly coated single spherical micelles as PBU has been reached, and the fraction and accessibility of small mesopores located inside dendritic large pores is strongly dependent on the coverage of silica coating of single spherical micelles, i.e., the strength of \( \{S^+I^-\} \) electrostatic interactions during the self-assembly processes.\(^\text{95, 122, 100}\)

Compared with MET and OAC method with spontaneously formed microemulsion droplets as supertemplates, intuitively, SMSAA methodology should follow a completely different mechanism for the synthesis of DMSNs because of the absence of oil phase. However, a common feature for all the synthesis of DMSNs is neglected since the used hydrophobic TEOS as silica sources could be acted as oil component to form the immiscible oil/water biphases, especially at the early stage of reaction. Thus, now the question is coming up whether all the DMSNs follow the same synthetic principles? Very recently, both experimental and theoretical studies evidenced that ternary solutions containing one hydro trope (such as ethanol) and two immiscible fluids, both being soluble in the hydro trope at any proportion, showed unexpected solubilization power and the presence of ‘detergentless’ micelles or microemulsions in such mixtures,\(^\text{130-134}\) a phenomena that is called the ‘pre-Ouzo’ structure effect. The spontaneous formation of fine emulsions with a remarkable stability provides a supertemplate for the synthesis of DMSNs in the early reaction stage, answering the intermediate or dynamic nature of DMSNs with dendritic larger pores.\(^\text{100, 111}\) Recently, by just a simple premixing of three components tetraethoxysilane-water-ethanol (TEOS-H\(_2\)O-EtOH), we first reported the MSNs were synthesized even in the absence of organic surfactant templates. The formation of mesoporosity is attributed to the leaching or dissolution and recondensation of the unreacted silicon species contained in the ‘pre-Ouzo’ structure, which was spontaneously preformed in the ternary TEOS–H\(_2\)O–EtOH system as a metastable microemulsion self-template.\(^\text{135}\) Thus we concluded that, even in the absence of organic additive (or oil phase), in the TEOS (or partially hydrolyzed TEOS)/Ethanol/Water ternary system, especially at the very early stage of reaction, the spontaneously formed microemulsion droplets by the ‘pre-Ouzo’effect could act as the supertemplate
to direct the formation of dendritic large pores, and with the reaction proceeding, the silica partly coated spherical micelles are deposited onto the supertemplate of microemulsion droplets, consequently leading to the formation of DMSNs with bimodal pore size distributions. In a word, DMSNs is indeed a product or the result of a two-level template collaborative self-assembly process of microemulsion droplets and micelle templates. However, more details on the influence of ‘pre-Ouzo’ effect to mesostructures of DMSNs need more investigations in the near future. It is important to note that even though the ‘pre-Ouzo’ effect was intensively studied in surfactant chemistry, the application of the pre-Ouzo effect for the synthesis and mechanistic understanding on the mesoporous silica and even Stöber silica NPs was seldom investigated, which should be developed to one of the most cutting-edge research directions in nanomaterials science. Well to sum up, all three types of methods for the synthesis of DMSNs, including MET, OAC and SMSAA protocols, follow the same synthetic principle, answering their unique structure features of bimodal pore size distributions and dendritic pore networks in an individual nanosphere.

Figure 12. Interfacial charge shielding (ICS) directs the synthesis of MSNs with varied mesostructures by precisely controlling the interactions between cationic surfactant micelle (S⁺) and negative inorganic silicate species (I⁻): Route I, solo template method using single CTA⁺ surfactant for the synthesis of MSNs and MCM-41 silica at high pH value; Route II, cationic–anionic dual surfactant template approach for dendritic MSNs with 3.0 nm of mesopores using anionic sodium dodecyl sulphate (SDS) surfactant as co-template; Route III: cationic–nonionic dual surfactant templates strategy for dendritic MSNs with large mesopores (> 5.0 nm) using nonionic NP-7 or Tween 80 as co-template. Reproduced with permission from ref. 128. Copyright 2019 The Royal Society of Chemistry.
3. A new generation of nanoreactor for the heterogeneous catalysis and the fabrication of PL materials

Benefiting from the prior accumulations on the synthesis of DMSNs and fundamental understanding the kinetically controlled heterogeneous nature of DMSNs, it is much more effective and conscious for the rational design and fabrication of silica based nanoreactors for their customer-tailored multi-target applications. Even though diversity of synthetic strategies were reported to synthesize DMSNs with varied pore size and morphology, they all exhibit the identical and unique structural feature of bimodal pore size distributions, i.e., the coexistence of small spherical mesopores and large dendritic pores, and their pore sizes and the fractions could be easily adjusted by precisely changing the reaction parameters. Most importantly and very fortunately, these small spherical mesopores nanocasted by partly silica coated micelles are open and diffusion-accessible after the removal of surfactant removal via high-temperature calcination or acid-extraction. This is also the reason that, in some cases, DMSNs are called three dimensional (3D) nanostructured mesoporous silica. One can imagine the dendritic channel of DMSNs as a V-shaped container filled with open hollow spheres by hard sphere close-packing. Importantly noted that the released review papers mainly focused on the discussion of the applications of DMSNs in the drug delivery and biomedicine by just taking full advantage of it’s the size effect of nano-scale particle. In this review, benefiting from its unique structural nanoconfinement of small spherical mesopores in the dendritic networks, we just highlight its applications in nanocatalysis and optical materials.

3.1. Unique nanoconfinement effect for heterogeneous catalysis

By virtue of its native structure advantage, DMSNs was extensively used as a catalytic support for various chemical reaction and can be directly applied for an efficient catalyst through introducing other active metal element into the structure or surface modification. While the catalytic performance actually depends on many factors (such as the quantity, properties, micro-environment of the active site, etc.) and cannot be absolutely attributed to the advantage of the structure, but it is still an ideal platform for the design of metal nanocluster (NCs) based heterogeneous catalysts with high performance, because of the bimodal pore size distributions of DMSNs, especially the small open spherical mesopores which provide an ideal nanoreactor for the encapsulation of metal NCs in size less than 3.0 nm. Even though, by both bottom-up and top-down synthetic strategy using protective molecules as templates, the metal NCs with precise atom numbers could be easily prepared, the protective ligands on NCs core greatly limit the contact of reaction substrate to the catalytic active sites and reduce the chemical reactivity of catalyst. Here, as a typical example, using hierarchical DMSNs as a unique confinement matrix wherein open spherical mesopores with a micelle size (ca. 4.0 nm) nested in the dendritic channels (Fig. 13a, inset), an Au/Ag bimetallic
catalyst is fabricated by a multi-step in situ nanocrystal seeding induced-growth (SIG) strategy, which endows the alloy with an ultra-small size (∼3 nm) and high dispersity (Fig. 13). The obtained Au/Ag bimetallic catalysts show an exceptional superior photocatalytic activity for the reduction of 4-nitrophenol (4-NP), surpassing most reported noble metal nanoparticle catalysts. The excellent photocatalytic activity originates from nanosized quantum effect, which significantly promotes interfacial electron transfer.

Figure 13. Bright-field TEM (a) and high-resolution HAADF-STEM (b) images of 1%AgO/1% Au-DMSNs. Corresponding STEM EDX mapping images of Au/AgO: (c) Au (yellow), (d) Ag (blue) and (e) Au/Ag merge (green), respectively. The inset in (a) shows that DMSNs have small, ill-ordered spherical pores (∼3 nm) nested in the dendritic channel networks. Reproduced with permission from ref. 151. Copyright 2019 The Royal Society of Chemistry.

In another example, Peng and his coworkers conceptually developed a “catalysts in coronas” strategy to make high active nickel (Ni) nanoparticles (NPs) catalyst for methane dry reforming reaction, using DMSNs as a support of Ni NPs (Figure 14). The obtained Ni NPs based catalyst exhibited an excellent catalytic performance with long life time (145h) and high conversion of 76% at 700 °C, which is close to its equilibrium conversion. The authors concluded that, sintering of Ni NPs and coking resistance was aroused from the surface spatial confinement effect where the three-dimensional dendritic layers in the corona posted a steric barrier against migration and aggregation of Ni NPs. These findings shed new lights on the design of other metal- or metal oxide-supported catalysts especially for high-temperature heterogeneous catalytic reactions, such as the gas-phase oxidation and the water gas shifting reaction (WGSR).
3.2. Fabrication of PL materials using non-conjugating organic molecules

Due to the interesting photoluminescence (PL) properties, zero-, one- and two- dimensional quantum nanomaterials attracts much more interests, including noble metal nanoclusters (NCs), semiconductor quantum nanostructures (black phosphorus nanosheet and transition metal dichalcogenides as typical examples), and carbon (or graphene) quantum dots (QDs).\textsuperscript{159, 161-165} However, the green and reproducible synthesis of NCs based QDs with tunable colors is challenging. In addition, even though the nanocluster-centered free-electron model based on the quantum confinement mechanisms have been well accepted, the elucidation and origin of optoelectronic properties are diverse and contradictory over the past decade.\textsuperscript{166-173} More and more experimental evidences have been proved that the distribution of surface protecting ligands (or clustering of surface) on the metal core played a paramount role to tune the optoelectronic properties of noble metal NCs.\textsuperscript{169, 170, 174}

Inspired by the fundamental understanding on the origin of metal NCs PL dominated by p band intermediate state (PBIS) model, recently, using DMSNs as support, we demonstrated that the self-assembly of organic functions in spherical mesopores by post-grafting technique produced a stable and bright AIE-type luminogen as an emitter for PL emission free of any metals (Fig. 15 a and b).\textsuperscript{175} It is importantly noted that the functional groups of the selectively used organosilanes contains heteroatoms with unpaired lone electrons, such as oxygen (O), nitrogen (N), and sulfur (S), as used protecting ligand molecules for the synthesis of metal NCs. The characterizations of optical absorption and PL emission spectrums showed that the luminescent mesoporous silica nanoparticles functionalized by nonluminescent organosilanes exhibit the same spectroscopic properties as metal NCs, and that their PL properties strongly depends on the nature of organic functional groups: the amino-functionalized DMSNs showed a striking blue-light fluorescence emission at ca. 430 nm, and its excitation and emission spectra completely match, implying an AIE luminogen emission mechanism (Fig. 15c); while the succinic functionalized DMSNs exhibited a remarkable red-color emission at ca. 615 nm (Fig. 15d).
Figure 15. Ligand assembly in the MSNs free of metals and their tunable luminescent properties. Scanning electron microscopy (SEM) (a) and TEM (b) images of as-synthesized fluorescent mesoporous silica nanoparticles. The inset shows the assembly of amino- and carbonyl- groups in the confined nanopores. (The scale bar in a and b is 200 and 100 nm, respectively.) (c) Excitation and emission spectra of aminopropyl-functionalized MSNs. (d) Absorption and emission spectra of propylsuccinic-functionalized MSNs.\(^{175}\)

Note that both single amino and succinic functional groups are nonluminescent. It is reasonable that, in the confined nanospace of DMSNs, the self-assembly of the amino and carboxylate groups, through space electronic interactions, namely, overlapping of the p orbital of lone pair (n) electrons among amino and carbonyl groups, extends the conjugation; thus, the corresponding intense and multiple adsorption bands in a range of 300-500 nm are observed with subsequent PL emissions (Fig. 15c-d). So far, to our best knowledge, this is the first example that simple organic functional-group-modified DMSNs can emit a very strong PL by the self-assembly of targeted molecules with electron-rich heteroatoms in the confined nanopores.\(^{175}\) The successful
synthesis of PL DMSNs, in turn, clearly demonstrates for the first time that the bright PL of few-atom metal nanoclusters originates from the self-assembly of surface ligands, innocent of metal core, providing a direct evidence on the effectiveness and rationality of \( p \) band dominant ligand-centered model for the elucidation of photochemistry and photophysics of low dimensional quantum nanomaterials relative to conventional metal-centered free-electron model.\(^{159}\)

DMSNs are also an ideal matrix for the synthesis of CsPbBr\(_3\) perovskites QDs. Take full advantages of the unique open 3D porous architecture of dendritic mesoporous silica nanospheres (DMSNs) with cage-like spherical nanopores, highly dispersed and pure cubic CsPbX\(_3\) QDs were successfully immobilized onto the mesoporous networks by a combining chemical anchoring and spatial isolation strategy.\(^{165}\) The fabricated CsPbX\(_3\)@HA-DMSNs exhibit excellent luminescence property (tunable emission color and high quantum yield (QY reached a maximum of 55\%)) and enhanced stability (especially for the water resistance capacity) (Fig. 16). The photoluminescence (PL) was sustained without any distinct change after 100 d storage under ambient conditions, even 90\% PL intensity was maintained after continuous UV irradiation for 45 h and no obvious PL reduction was observed when soaked in water for 7 h. Therefore, DMSNs with unique mesostructures provides an alternative candidate for the fabrication of light-emitting material for display devices as a stable support.

**Figure 16.** Spatial and chemical confined ultra-small CsPbBr\(_3\) perovskites QDs in dendritic mesoporous silica nanospheres with enhanced stability for the fabrication of LEED.\(^{165}\) Reproduced with permission from ref. 165. Copyright 2020 Elsevier Ltd.

4. Summary and Concluding Remarks

Obviously, in the surfactant-silica assembly, the complex thermodynamic and kinetic processes of sol-gel chemistry, as well as the adjustment of a large number of reaction parameters (such as the silica source, the surfactant type, the organic additives, the base source, the reaction temperature, the water content, and the pH value of the reaction solution, etc.), cover up the real nature of the DMSNs formation, and different synthetic principles was proposed to understand its formation mechanism, which in turn greatly interferes with the accurate analysis of its real structures of DMSNs. By carefully analyzing the similarities and differences of each preparation approach, as well as
the structural characteristics of the synthesized DMSNs, we draw the conclusion that, all the synthetic strategies for DMSNs follow the same dynamic self-assembly mechanism with a synergetic dual-template role of microemulsion nanodroplets and surfactant micelles, which answers their common structural characteristics of DMSNs with bimodal pore size distributions. Consequently, the posed questions in the abstract could be easily understood, which will guide the more rational synthesis of DMSNs toward the customer-tailored applications. We believe that this elegant synthetic strategy could be easily expanded for the synthesis of other hierarchical nanomaterials with tunable morphology and varied chemical components, such as carbon, transition metal or noble metal crystals and even microporous zeolites.

DMSNs have risen as ideal model nanoreactors for studying heterogeneous catalysis and nanoscale surface chemistry due to its unique confined dimensions. Here, using DMSNs as a model platform, we reveal the electronic mechanisms of how size effect and surface ligands assembly modify their catalytic activity and PL properties, respectively. In addition, we first showed that DMSNs are also an ideal matrix for the trapping of CsPbBr_3 perovskites QDs, which exhibited excellent PL properties with high stability. We confirmed that, in the confined nanospace, surface chemistry is affected by particle size, surface modification and surface ligation states can dominate the physical and chemical performances of nanomaterials. DMSNs could act as a new generation of nanoreactor to generally explore the electronic mechanisms of size dependent catalysis, ligand-induced surface effects on tuning the electronic structures, optical properties, and device performance of nanomaterials.

**Conflicts of interest**

There are no conflicts to declare.

**Acknowledgements**

This work was supported by the NSFC (21872053 and 21573074), the Science and Technology Commission of Shanghai Municipality (19520711400), the CAS key laboratory of Low-Coal Conversion Science & Engineering (KLLCSE-201702) and the JORISS program, the Postdoctoral Science Foundation of China (2018M640360). K.Z. thanks ENS de Lyon for a temporary position as an invited professor in France. This paper is dedicated to Prof. Ming-Yuan HE in the occasion of his 80th birthday. We also thanks for the long-term research cooperation for this topic with Prof. Laurent Bonneviot and Prof. Bélen Albal at ENS-Lyon in France, and Prof. Peng Wu at ECNU in China, since 2004. In addition, we appreciate Prof. Bonneviot and Prof. Wu for their great suggestions on the organization and writing of this review paper.

**Notes and references**

The precise elucidation of mesostructures of dendritic mesoporous silica nanospheres (DMSNs) underlying formation mechanism, is paramount important to further expand the wide applications of DMSNs as a new-rising star materials in catalysis, drug-delivery, biodiagnostic and biomedicine, and optic device and materials, etc.