FAVLCE growth of well-dispersed and ultra-small MoS₂ nanodots in ordered mesoporous silica nanoparticles
Facile growth of well-dispersed and ultra-small MoS$_2$ nanodots in ordered mesoporous silica nanoparticles†

Yi Wang,$^{a}$ Shanshan Wang,$^{b}$ Chengyi Li,$^{a}$ Min Qian,$^{a}$ Juan Bu,$^{c}$ Jianxin Wang$^{a}$ and Rongqin Huang$^{a,a}$

A facile one-step solvothermal method was developed for the homogeneously confined growth of ultra-small (~1.5 nm) and monodispersed 2H phase MoS$_2$ nanodots into mesoporous silica nanoparticles (MSNs).

Two-dimensional (2D) layered nanomaterials, such as graphene and transition metal dichalcogenide (TMD) nanosheets have been of interest in research since their discovery due to their unusual physical and chemical properties as well as their promising applications in catalysis, energy storage, optoelectronics and biomedicine.$^{1-4}$ As a special derivation of 2D nanomaterials, small-sized 2D nanomaterials with a diameter below 10 nm (nanodots or quantum dots) are more fascinating compared to intrinsic 2D layers owing to their extra properties and broader applications as a result of stronger quantum confinement and edge effects.$^{5-7}$ Therefore, many efforts have been devoted to engineering nanodots of 2D layered nanomaterials. For graphene, the technologies available for nanodot preparation are relatively prosperous, including various “top-down” and “bottom-up” methods.$^{8,9}$ However, more important 2D TMD nanodots, such as MoS$_2$, with direct band gaps, are often prepared using the “top-down” method with labor-intensive exfoliation and breakdown of 2D nanosheets.$^{10,11}$ What’s worse, these nanodots are still large in size and have a wide distribution. The synthesis of ultra-small MoS$_2$ nanodots whose band gap, together with their electronic and optical properties, can be further broadened are seldom exploited. Therefore, on one hand, it is of fundamental importance and great urgency to develop a facile method to prepare ultra-small MoS$_2$ nanodots.

On the other hand, the incorporation of optical nanodots into ordered mesoporous frameworks is now attracting significant attention because of the advantages of both the optical properties of the guest species and the large surface areas of the host mesoporous materials.$^{11,14}$ However, the facile incorporation of well-dispersed optical nanodots into ordered mesoporous frameworks is still a considerable challenge. Recently, Zhao et al. reported a direct co-assembly strategy to incorporate sub-5 nm graphitic pencil nanodots into ordered mesoporous materials for excellent optoelectronic performance, which would open up new possibilities for practical applications of nanodot-enabled ordered mesoporous structures.$^{15}$ Therefore, the development of a simple method to incorporate much more functional MoS$_2$ nanodots into ordered mesoporous materials is still in great demand.

In this work, we developed a simple “bottom-up” method to directly grow well-dispersed and ultra-small MoS$_2$ nanodots into MSNs (UsMSND@MSN). The prepared UsMSND@MSN can inherit the traditional virtues of MSNs. Meanwhile, it can serve as a precursor for large-scale preparation of ultra-small MoS$_2$ nanodots with about 3–5 unit cells. And it could also be used as an optical mesoporous material for deep ultraviolet (UV) photoluminescence emission.

UsMSND@MSN was synthesized by firstly stirring MSNs in ammonium tetrathiomolybdate [(NH$_4$)$_2$MoS$_4$]-DMF solution, which spurred (NH$_4$)$_2$MoS$_4$ to be adsorbed into the ordered mesochannels of the MSNs, and then using one-step solvothermal reduction, which resulted in the confined growth (incorporation) of well-dispersed UsMSND in the MSNs. TEM images showed that the prepared UsMSND@MSN formed uniform nanoparticles with a size of 115 ± 15 nm, similar to the MSNs. In contrast, a rough dot-like surface was observed on every UsMSND@MSN nanoparticle, implying that they were composed of ultra-small nanoparticles (Fig. 1A). Correspondingly, the EDX pattern revealed the emergence of Mo and S elements with an atomic ratio of 1.3/2.0

$^a$ Department of Pharmaceutics, School of Pharmacy, Key Laboratory of Smart Drug Delivery, Ministry of Education, Fudan University, Shanghai 201203, China.
$^b$ Center of Analysis and Measurement, Fudan University, Shanghai 200433, China.
$^c$ Department of Macromolecular Science, State Key Laboratory of Molecular Engineering of Polymers, Fudan University, Shanghai 200433, China.
$^†$ Electronic supplementary information (ESI) available: Experimental methods, STEM images, TEM images, HRTEM images, Raman spectra, FT-IR spectra, N$_2$ adsorption–desorption isotherms and FL spectra. See DOI: 10.1039/c6cc04076d
alongside the typical Si and O elements from the MSNs. Thus the incorporated nanoparticles could be described as \( \text{MoS}_2 \) with S defects.\(^{16} \) The STEM image clearly showed these ultra-small nanodots, deduced by the obvious contrast between Si and Mo (Fig. 1B and Fig. S1, ESI\(^+\)). The HR-STEM image revealed that the ultra-small nanodots were incorporated into the ordered mesoporous network of the MSNs, which was also proved by the magnified TEM image and the high stability of the growth (Fig. 1C and Fig. S2, ESI\(^+\)). The HRTEM image showed that these closely confined UsMSND were crystallized as observed from the obvious lattice fringes (Fig. 1D). To identify this incorporated lattice, Fourier-transformation (FT) was performed to obtain diffraction patterns and a reconstructed image, which suggested that the MoS\(_2\) nanocrystals had (103) faces with a \( d \)-spacing of 0.23 nm (Fig. 1C and D).\(^{12} \) Moreover, to confirm the interesting structure and the well-dispersed incorporation, TEM and STEM images, and corresponding EDX-mappings of the individual UsMSND@MSN particles (Fig. 1E–J) were carefully performed, which clearly showed that the Mo and S from the incorporated UsMSND were well-distributed within the MSNs with Si and O framework.

The composition and structure of the UsMSND@MSN were also investigated. X-ray photoelectron spectroscopy (XPS) showed that UsMSND@MSN was composed of 27.7 at% Si, 69.7 at% O, 1.1 at% Mo, and 1.5 at% S elements (Fig. 2A), consistent with the EDX results. The deconvoluted Mo 3d and S 2p spectra gave four well-resolved peaks at 162.1 eV, 163.5 eV, 229.5 eV and 232.6 eV (Fig. 2B), corresponding to S 2p\(_{3/2}\), S 2p\(_{1/2}\), Mo 3d\(_{5/2}\), and Mo 3d\(_{3/2}\), respectively, which could be attributed to the binding energies of Mo\(^{4+}\) and S\(^{2-}\) in the 2H phase of the superficially confined MoS\(_2\).\(^{17} \) The presence of a silica tetrahedron framework peak and a surface silanol peak at 103.1 eV and 532.6 eV, respectively, revealed no obvious bonding between the MSNs and the MoS\(_2\) nanoparticles.\(^{16,15} \) The SAXS pattern of UsMSND@MSN exhibited two resolved diffraction peaks with a reciprocal spacing, \( 1/d_{hk} \), ratio of approximately 1 : \( \sqrt{3} \) (Fig. 2D).

Together with the TEM results of the MSN precursors (Fig. S3, ESI\(^+\)), this could be indexed as typical (100) and (110) reflections of an ordered hexagonal \( P6_{3}m\bar{m} \) mesostructure with a unit cell parameter \( (a_0) \) of 3.73 nm.\(^{20} \) Notably, the calculated \( a_0 \) and pore wall thickness were bigger than that of the MSNs (Table S1, ESI\(^+\)), which could be attributed to the expansion of the framework after the embedding of UsMSND during the solvothermal reaction.\(^{21,22} \) The XRD pattern (Fig. 2D) and Raman spectra (Fig. S4, ESI\(^+\)) of UsMSND@MSN didn’t show any peaks indexed as the bulk MoS\(_2\), which indicated the ultra-small size of the incorporated UsMSND without obvious layer–layer interactions.\(^{10,16} \) \( \text{N}_2 \) adsorption–desorption isotherms and pore diameter distribution curves revealed that the UsMSND@MSN had a BET surface area of 530 m\(^2\) g\(^{-1}\), a pore volume of 0.73 cm\(^3\) g\(^{-1}\), and a main pore size of 2.2 nm (Fig. S5, ESI\(^+\)). These values were a little smaller than
that of the MSNs possibly due to the incorporated MoS\textsubscript{2} nanodots in the meso-structure (Table S1, ESI†). All of these results demonstrated the uniform incorporation of well-dispersed and ultra-small 2H phase MoS\textsubscript{2} nanodots (UsMSND) into MSNs, and this incorporation didn’t obviously affect the porous properties of the MSNs.

The preparation of UsMSND@MSN is simple, and the key is the employment of surface silanol-containing MSNs as carriers, which not only provide enough accessible meso-channels for the anchoring of MoS\textsubscript{4} ions but also prevent the aggregation and overgrowth of the nanosized MoS\textsubscript{2} dots during the solvothermal reduction.\textsuperscript{23} In a parallel control experiment, a direct solvothermal reduction of (NH\textsubscript{4})\textsubscript{2}MoS\textsubscript{4} in DMF solution without MSNs only resulted in highly crystallized MoS\textsubscript{2} nanosheets (Fig. S6A and S7, ESI†). Also, excess addition of (NH\textsubscript{4})\textsubscript{2}MoS\textsubscript{4} in the MSNs caused overloading of the MoS\textsubscript{4}\textsuperscript{2-} species on the surfaces of the MSNs and consequently converted them into core–shell MSN@MoS\textsubscript{2} (Fig. S6B and S8, ESI†). Moreover, using calcined MSNs as carriers, composites with MoS\textsubscript{2} nanosheets positioned away from the MSNs were formed (Fig. S6C and S9, ESI†). This might be because the framework integrity and few surface groups on the calcined MSNs were not able to supply accessible mesochannels and anchoring sites for the nucleation and growth of ultra-small MoS\textsubscript{2} nanodots. This was further proven by using MSN-NH\textsubscript{2} as a carrier, whose electropositive surface groups were much more beneficial for the anchoring of MoS\textsubscript{4} ions. Therefore, UsMSND@MSN-NH\textsubscript{2} can also be obtained under conditions involving less addition of (NH\textsubscript{4})\textsubscript{2}MoS\textsubscript{4} (Fig. S6D, ESI†).

Attributed to the dispersed incorporation of UsMSND into the MSNs, UsMSND@MSN can be used as a precursor for the preparation of ultra-small MoS\textsubscript{2} nanodots. As observed from the TEM and HRTEM images of the Si-extracted UsMSND@MSN (Fig. 3), homogeneous nanodots with ultra-small sizes between 0.6–2.5 nm (equal to about 3–5 unit cells of MoS\textsubscript{2})\textsuperscript{24} can be obtained. They can be indexed as crystallized MoS\textsubscript{2} nanoparticles from typical lattices. Since many efforts have recently been devoted to engineering MoS\textsubscript{2} nanodots by labor-intensive exfoliation, this work gave an extremely simple alternative for the synthesis of well-dispersed and ultra-small MoS\textsubscript{2} nanodots.

Due to its special confined growth, UsMSND@MSN was also expected to have unique optical properties. As shown in Fig. 4A, UsMSND@MSN, at different concentrations, exhibited three absorption peaks centered at 208.5 nm (where absorbance was linearly related to the concentration with \(R^2 = 0.9999\)), 232 nm and 316 nm. These could be assigned to (1) the excitonic absorption generated by the direct bandgap transition at the \(K\) point with an energy split from valence band spin–orbital coupling,\textsuperscript{25} and (2) the defect level introduced in the incorporated UsMSND with an S cavity (Fig. 4E).\textsuperscript{16} The remarkable blue-shift of the absorption to the deep UV as compared with those of the other MoS\textsubscript{2} nanomaterials suggested that the ultra-small sized UsMSND exhibited a strong quantum confinement effect, which led to an enhanced band gap.\textsuperscript{26} Correspondingly, the direct band-gap energy was calculated to be 4.92 eV by plotting the square root of the absorption energy \((aE)\) vs. the photon energy \((E)\) (Fig. S10, ESI†), which was much larger than that of the bulk MoS\textsubscript{2} (1.2 eV),\textsuperscript{27} monolayer MoS\textsubscript{2} (1.9 eV)\textsuperscript{28} and other reported MoS\textsubscript{2} nanodots (4.26 eV).\textsuperscript{7} The FL spectra showed that UsMSND@MSN could emit ultraviolet (295 nm)
and violet (363 nm) photoluminescence upon excitation by deep UV, and the intensity decreased rapidly with an increase in excitation wavelengths [Fig. 4B], which were typical features of the MoS2 nanodots.29 Nevertheless, being different from common poly-dispersed MoS2 nanodots with excitation-dependent single emission,26,30 the obvious two excitation-independent emissions in UsMSND@MSN might originate from intrinsic states and defect states of the confined UsMSND with advanced monodispersity.11,31 Photoluminescence excitation (PLE) spectra of the 295 nm emission gave a peak at 208.5 nm, due to the intrinsic excitonic absorption in the UV-Vis spectra, which also suggested that the 295 nm emission was mainly due to intrinsic states, while the other one might come from S defects (defect states) [Fig. 4E]. Further evidence for these unique optical properties was found in the FT-IR spectra, from which the surface states or the carbon impurities that possibly contributed to the fluorescence could be excluded [Fig. S11, ESI†].29,32 Attribution to the stable incorporation of UsMSND in the MSNs, UsMSND@MSN could resist UV bleaching [Fig. S12, ESI†]. Meanwhile, originating from the big tail of the 363 nm emission, a yellow concentrated UsMSND@MSN solution could be observed to have blue-violet fluorescence [Fig. 4C, D and Fig. S13, ESI†]. These results suggested that UsMSND@MSN not only had excellent light converting properties as compared to many compound-semiconductor-based QDs, but also could benefit from the porous mesochannels for the anchoring of MoS4/C02− and the Sino-German Research Project (GZ995).

In summary, a UsMSND@MSN composite with homogeneous incorporation of ultra-small and monodispersed 2H phase MoS2 nanodots in MSNs was prepared using the one-step solvothermal reduction method. The key for this method is the employment of MSNs as carriers, which not only provide enough accessible mesochannels for the anchoring of MoS2,2− but also prevent aggregation and overgrowth of the nanosized MoS2 dots during the solvothermal reaction. The prepared UsMSND@MSN can be used as precursor for facile preparation of ultra-small MoS2 nanodots, and it could also emit deep UV photoluminescence due to the strong quantum confinement effect of the incorporated UsMSND with a large direct band-gap energy of 4.92 eV. This work promised a facile route to regulate MoS2 for further applications.

This work was supported by grants from the Key Basic Research Program (2013CB932502) of China (973 Program), National Natural Science Foundation of China (81573002 and 21303022) and the Sino-German Research Project (GZ995).

Notes and references

7 H. D. Ha, D. J. Han, J. S. Choi, M. Park and T. S. Seo, Small, 2014, 10, 3438–3462.