Supporting informations

Facile Growth of Well-dispersed and Ultra-small MoS₂ Nanodots in Ordered Mesoporous Silica Nanoparticles

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1. Experimental section

1.1 Materials. Ammonium tetrathiomolybdate ((NH₄)₂MoS₄), aminopropyltriethoxysilane (APTES), and tetraethyl orthosilicate (TEOS) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Rhodamine 6G (R6G) were bought from Molecular Probes (Life Technologies, USA). Cetyltrimethylammonium bromide (CTAB), Hydrazine hydrate (N₂H₄·H₂O, 50%), N,N-Dimethylformamide (DMF), sodium hydrate (NaOH), and other reagents, if not specified, were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). All the chemicals were used without further purification.

2.2 Synthesis of different nanoparticles. MSN and aminated MSN (MSN-NH₂) were firstly prepared by a common method. Typically, TEOS (500 ml) was slowly added into aqueous NaOH (14.5 mM, 48 ml) solution which had dissolved 100 mg CTAB at 80 °C (for the preparation of MSN-NH₂, this process was followed by adding 80 µl APTES-ethanol solution (1/4, v/v)). Then the solution was kept at 80 °C and stirred for 2 h. The solid product was collected by centrifugation, water washing, and freeze-drying. To remove CTAB from the pores, the product was repeatedly refluxed and washed in a mixture of methanol and NH₄NO₃ (2 mg/ml) at 70 °C. UsMSND@MSN was synthesized by a facile one-step solvothermal reduction. Typically, 5 mg $(NH_4)_2MoS_4$ and 20 mg MSN were dispersed in 8 ml DMF by stirring at room temperature for 10 min, and then 50 µl N₂H₄·H₂O (50%) was added. The resulting solution was ultrasonicated for 15 min with the aim of effective dispersion of $(NH_4)_2MoS_4$ and N_2H_4 ·H₂O into the mesochannels. After that, the solution was transferred into an autoclave and heated at 200 °C for 12 h. The vellowish-brown powder was collected by centrifugation, water/ethanol washing, and freeze-drying. To completely remove residual solvent DMF and the other impurities, the product was dialyzed (MWCO = 10000) against water for two days. The obtained UsMSND@MSN was dispersed in water or other physiological media for further usage. For the synthesis of pure UsMSND, UsMSND@MSN was strirred in the hydrofluoric acid solution for 2 h to remove the SiO₂ by evaporating the produced SiF₄ and the excessive HF. After diluted with water, the mixture was dialyzed against water (MW cutoff = 500) for about 4 days. Finally, the solid in the dialysis bag was recovered as UsMSND.

2.3 Physicochemical characterizations. Transmission electron microscopy (TEM), high-resolution TEM, and energy dispersive X-ray (EDX) spectroscopy/mapping experiments were performed on JEM-2010 instruments (JEOL, Japan) with an acceleration voltage of 200 kV. XPS results were obtained on a RBD-upgraded PHI-5000C ESCA system (Perkin Elmer, USA) with Al K α radiation (hv = 1486.6 eV) as the X-ray source for excitation. Small-angle X-ray scattering (SAXS) and X-ray diffraction (XRD) patterns were taken on a Nanostar U SAXS system

(Bruker, Germany) using Cu Kα radiation (40 kV, 35 mA) and on a PANalytical X'pert PRO diffractometer (PANalytical, Holland) with Cu Kα radiation at a scan rate of 4°/min in the 2θ range 10 - 80°, respectively. UV-vis analysis was carried on a UV-vis absorption spectrometer (UV759, China). Fluorescence excitation/emission spectra were recorded on a Cary Eclipse fluorescence spectrophotometer (Varian, USA). Raman spectra were obtained on a Labram-1B (Dilor, France) with a 632.8 nm wavelength incident laser light. FTIR spectroscopy in the range of 400 - 4000 cm⁻¹ was obtained on a Nicolet-670 FTIR spectrometer using the smearing method. N₂ adsorption desorption isotherms at 77 K and pore size distribution curves were measured using Tristar 3000 systems. Optical photographs were taken using a sensitive Nikon camera. The UsMSND@MSN solution was exposed upon daylight or a 254 nm UV-lamp for the pictures.

Supporting Figures:



Figure S1. STEM images of UsMSND@MSN. The brightly white dots confined in MSN revealed the ultra small MoS₂ nanoparticles.



Figure S2. TEM image of the strong sonication-treated UsMSND@MSN, which showed that the UsMSND (arrows) was stably confined in MSN, but not loosely stuck on the surfaces.



Figure S3. TEM image of MSN. The insets were the FT and the corresponding inverse FT of the TEM image, respectively. MSN had a hexagonal pore arrangement.



Figure S4. Raman spectra of UsMSND@MSN and bulk MoS2.



Figure S5. N₂ adsorption-desorption isotherms and corresponding pore size distribution curves (inset) of UsMSND@MSN and common MSN, respectively.



Figure S6. (A-D) TEM and HRTEM images of the samples synthesized under different conditions. (A) Without MSN, (B) with the increased $(NH_4)_2MoS_4$, (C) using calcined MSN as carrier, (D) using MSN-NH₂ as carrier with the decreased $(NH_4)_2MoS_4$. The arrow in "C" showed the MoS₂ nanosheets away from MSN, while the arrows in "D" indicated the incorporated ultra-small MoS₂ nanodots.



Figure S7. (A) TEM, (B) HRTEM images and (C, D) corresponding FT patterns of the as-synthesized samples without MSN support. It revealed the formation of highly crystallized MoS₂ nanosheets.



Figure S8. (A, B) TEM and (C) HRTEM images of the as-synthesized samples with the increased $(NH_4)_2MoS_4$. The arrows showed the MoS₂ shell and the dotted line showed the core-shell interface. Meanwhile, the 0.62 nm layered lattices evidenced the plane of MoS₂ nanosheets.



Figure S9. (A-B) TEM images of the as-synthesized samples using the calcined MSN as carrier. The arrows showed the formation of MoS₂ nanosheets away from the MSN.



Figure S10. The band-gap energy calculated according to the UV-vis spectrum, where a is the absorbance, E is the

photon energy and aE is the absorption energy.



Figure S11. FTIR spectra of bulk MoS₂, UsMSND@MSN and MSN, repectively. Since bulk MoS₂ is an infrared inactive material, no obvious peak was observed. The identical vibrations of UsMSND@MSN and MSN proved the absence of unsaturated S atoms (such as -SH) and also any other impurities (such as oxidized carbon nanoparticles produced in the synthesis) in the UsMSND@MSN. This result revealed that: (1) the confined UsMSND was terminated by Mo at its external edge due to the lack of S atoms, and it was ultra-small MoS₂ nanodots with S cavities (defections), in good agreement with EDX and XPS results; (2) it was not the surface states or the carbon impurities that contributed to the fluorescence, which was different from many other reported graphene or MoS₂ nanodots. The unique fluorescence was only attributed to the instrinic states and defect states.



Figure S12. Fluorescence spectra of UsMSND@MSN excited at 210 nm (left) and R6G excited at 535 nm (right) upon the exposure to 250 nm-UV excitation with different time periods. UsMSND@MSN had much stronger resistance to the UV bleaching than the fluorescence dye R6G.



Figure S13. (A) Deep UV fluorescence spectra of empty cuvette, H_2O and UsMSND@MSN solution. The dot line is the simulant big tail of 363 nm emission in case of the frequency doubling interference. (B) Photographs of empty cuvette (a), H_2O (b) and UsMSND@MSN solution (c) excited by daylight and a deep UV lamp, respectively.

Table S1	
Fextual properties of MSN (ion-exchanged sample) and UsMSND@MSN.	

Sample	BET surface area (m ² g ⁻¹)	Total pore volume (cm ³ g ⁻¹)	Pore diameter (D)(nm)	Unit cell (a ₀)(nm)	Wall thickness (t) (nm)
MSN	884	0.95	2.6	4.5	1.9
UsMSND@MSN	530	0.73	2.2ª	6.9	4.7 ^a

 $*d_{100} = \lambda/2\sin\theta_{100}$, $a_0 = 2d_{100}/\sqrt{3}$, $t = a_0 - D$. a: the serrated pore size distribution curve with the most probable pore size of 2.2 nm and the much thicker pore walls also suggested the confined growth of ultra-small MoS₂ nanoparticles into the meso-channels.