Monolayer single crystal two-dimensional quantum dots *via* ultrathin cutting and exfoliating

Yang Hao^{1,2†}, Wen Su^{3†}, Lingxiang Hou^{1,2}, Xueping Cui^{1,2}, Shaozhi Wang^{1,2}, Pengxin Zhan^{1,2}, Ye Zou^{1,2}, Louzhen Fan^{3*} and Jian Zheng^{1,2*}

ABSTRACT Two-dimensional (2D) atomically thin quantum dots (QDs) possess extraordinary electrical and optical properties. However, fabricating high quality 2D QDs *via* a universal and reliable technique remains a challenge. Here, we report a simple strategy to prepare high quality, monolayer single crystal 2D QDs *via* ultrathin cutting 2D bulk single crystals by ultramicrotome, followed by an exfoliation process. The as-prepared 2D QDs have pristine surface, high quality, high monolayer yield and high photoluminescence quantum yield (the highest photoluminescence quantum yield of WS₂ is 18%), which can be used as promising, low toxic, biocompatible, and good cell-permeability fluorescent labeling agents for *in vitro* imaging.

Keywords: two-dimension, single crystal, quantum dots, ultrathin cutting, photoluminescence quantum yield

INTRODUCTION

Two-dimensional (2D) materials possess compelling electronic, optical and mechanical properties [1–8] arising from the unique combination of atomic-scale thickness, tunable band gap, and high surface areas [9–12]. Quantum dots (QDs) with diameters less than 10 nm demonstrate unique electronic and optical properties due to the confinement of charge carriers in all spatial dimensions [13–17]. When the lateral size of a 2D material reduces to less than 10 nm to form 2D QDs, the synergistic effects of quantum confinement and prominent edge effects will engender [18–20]. In recent years, 2D QDs have been applied in various fields, especially in optoelectronics, such as bioimaging, light-emitting devices and photodetectors [21]. Photoluminescence (PL) quantum yield (QY) is an essential metric of optoelec-

tronic applications, which is closely related to the purity and quality of materials and directly dictates the maximum device efficiency [22]. Therefore, it is crucial to produce 2D QDs with high quality for exploring their intrinsic properties and applications.

2D QDs are generally produced *via* two strategies, top-down and bottom-up. The top-down method produces 2D QDs by cleavage of relevant large bulk precursors through thermal plasma jet method, microwave irradiation and ball milling [21], which usually inevitably contain nanosheets with lateral size of more than few hundred nanometers. And the size cannot be effectively reduced by further sonication, which hinders the yield of 2D QDs. The later is commonly conducted in organic solvents using chemical methods to synthesize 2D QDs and get the 2D QDs with low quality, which always are wrapped by insulated ligands, and followed by tedious post-treatment under rigorous conditions [23–26]. Recently, a facile method was reported to prepare high quality 2D QDs with a maximum PL QY of 7%, by cryo-mediated liquid-phase exfoliation and fracturing process [27]. However, the yield of QDs (1%) and the value of PL QY are far from desired target. Therefore it is essential to purpose a facile and reliable method to fabricate high quality 2D QDs.

Herein, we report a universal strategy to prepare monolayer single crystal 2D QDs, which involves directly ultrathin cutting 2D bulk single crystal, such as MoS₂, WS₂, MoSe₂, WSe₂, SnS₂, SnSe₂, TaS₂, TaSe₂, TiS₂ and TiSe₂, by ultramicrotome at room temperature, followed by exfoliation. This is the first time to prepare monolayer single crystal 2D QDs *via* mechanical cutting, which is simple and universal without high temperature, con-

¹ Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

² University of the Chinese Academy of Sciences, Beijing 100049, China

³ College of Chemistry, Beijing Normal University, Beijing 100875, China

[†] These authors contributed equally to this paper.

* Corresponding authors (emails: zhengjian@iccas.ac.cn (Zheng J); lzf@bnu.edu.cn (Fang L))

centrated acids and strong oxidizing agents. With this strategy, the 2D QDs can easily inherit the high quality of 2D single crystals, since no other organic or impurity elements are introduced. To date, the yield of monolayer single crystal 2D QDs (40%) is the highest, and the as-prepared WS₂ 2D QDs show the highest PL QY of 18%. The 2D QDs are successfully applied as promising, low toxic, biocompatible, and good cell-permeability fluorescent labeling agents for *in vitro* imaging.

EXPERIMENTAL SECTION

Materials

N-methyl-2-pyrrolidone (NMP, 99.5%, anhydrous), *o*-dichlorobenzene, hexane, chloroform, acetone, ethanol, isopropanol, methanol were purchased from Sigma Aldrich. Bulk molybdenum (IV) sulfide (MoS₂), tungsten (IV) disulfide (WS₂), molybdenum diselenide (MoSe₂), tungsten diselenide (WSe₂), selenium (IV) sulfide (SnS₂), selenium diselenide (SnSe₂), tantalum (IV) disulfide (TaS₂), tantalum diselenide (TaSe₂), titanium (IV) disulfide (TiS₂) and titanium diselenide (TiSe₂) were purchased from Sigma Aldrich.

Methods

The ultrathin section and manufacture process mainly included the following three steps: first of all, the bulk 2D materials were cut by the ultramicrotome (Lycra ultramicrotome; manufacturer: RMC, model: Powder Tome) with a cutting feed step of less than or equal to 5 nm per second at room temperature and the quasi 2D QD powders were collected. Then the quasi 2D QD powders were dispersed into the solvent NMP or *o*-dichlorobenzene and experienced strong magnetic stirring and liquid-exfoliation with the assistance of bath ultrasonication. Finally the mixed dispersion was centrifuged at 12,000 rpm (rounds per minute) for 20 min, 5 to 7 times to remove non-exfoliated materials. The high dispersity and small size of QDs make it difficult to extract them from NMP, even using the high-speed centrifugation and/or solvent evaporation method. Therefore, after the addition of hexane (poor solvent) and then chloroform (less polar solvent), the 2D QDs dispersion can be easily precipitated through centrifugation. Then the achieved 2D QDs were re-dispersed in methanol or other solvents.

For the bioimaging experiment, HeLa cells (1.0×10^4) were incubated on glass cover slides loaded in 24-well culture plates containing 500 μ L of Dulbecco's modified Eagle's medium (DMEM) for 12 h. The medium was then replaced with fresh Opti-MEM (500 μ L) containing MoS₂

QDs and cultivated for 4 h. After that, each well was washed twice by phosphate buffered saline (PBS) (0.1 mol L⁻¹, pH 7.4) and fresh DMEM medium (500 μ L) was added to the culture for another 24 h. The MoS₂ QDs-transfected HeLa cells were then detected by a confocal microscope (CLS, FV1200, Olympus, Japan or at Olympus Fluoview FV1000).

For the atomic force microscopy (AFM) characterization, the 2D QDs solution was directly dropped onto a new Si/SiO₂ substrate, which would be first dried naturally at room temperature and then further treated in a vacuum oven at 70°C for 5 h to completely eliminate the influence of residual solvents. The 2D QDs solution was diluted and then dropped onto ultrathin carbon then vacuum-dried at 70°C for transmission electron microscopy (TEM) and high resolution TEM (HRTEM) test. The X-ray photoelectron spectroscopy (XPS) and Raman spectrum samples were prepared by dropping the 2D QDs solutions onto Si/SiO₂ substrates, respectively and drying in vacuum oven.

Characterization

AFM image was acquired using a Bruker MultiMode 8 AFM using SCANASYSTAIR cantilevers with a nominal tip radius of 2 nm in scanasyst mode. TEM images were acquired by employing HR-TEM (JEOL JEM-2100F). XPS was conducted using an ESCALab220i-XL electron spectrometer from VG Scientific with 300 W Al K α radiation. The ultraviolet-visible (UV-vis) absorption spectra and fluorescence spectrum were measured using a Jasco-570 spectrophotometer and PF6600 Steady state fluorescence spectrometer. The fluorescence QY and excited stated lifetime were measured by an FLS980 Transient fluorescence spectrometer. Raman measurement was performed with a 532 nm laser under ambient conditions (inVia-Reflex). Optical images were captured with a Nikon Eclipse LV100D. The fluorescence microscope characterization was performed using a fluorescence microscope equipped with a mercury lamp as the excitation light source.

RESULTS AND DISCUSSION

Fig. 1a shows the fabrication procedure of 2D QDs in this study. Firstly, 2D bulk single crystals (Fig. S1) were perpendicular ultrathin cut by ultramicrotome with a cutting feed step of ≤ 5 nm s⁻¹ at room temperature to prepare the quasi 2D QDs, i.e., 2D nanoribbons with about 5 nm width, random length and thickness (Figs S2, S3 in the Supplementary information). Then, these nanoribbons were soaked in *o*-dichlorobenzene or NMP, followed by

Figure 1 (a) Schematic illustration of the process for preparing 2D QDs. (b) TEM image of MoS₂ QDs with the scale bar of 20 nm. (c) HRTEM image of a MoS₂ QD with the scale bar of 2 nm (insets: FFT patterns, scale bar of 50 1/nm). (d) AFM image of MoS₂ QDs, scale bar of 500 nm. (e) Raman spectra of bulk single crystal MoS₂ (black line) and MoS₂ QDs (red line). (f, g) XPS spectra of MoS₂ QDs.

strong magnetic stirring and sonication. Finally, 2D QDs were separated by high-speed centrifugation and dispersed in other solvent, such as methanol, ethanol, isopropanol, even deionized water. Ultrathin cutting not only directly obtains nanoribbons with sizes close to QDs but also avoids excessive tens-to-hundreds-nanometers nanosheets. In previous reports, these tens-to-hundreds-nanometers nanosheets are hardly further reduced in size by sonication, which is the main factor limiting the yield of QDs, because the scission will quit when the strain force of ultrasonication falls below the critical value for nano materials disruption [28]. However, the length of nanoribbons with about 5 nm width can be easily trimmed downsize to the same size of width to form QDs by

sonication. Furthermore, the nanoribbons with this size are inclined to be exfoliated into monolayer by sonication, due to the relatively weak van der Waals force between layers. Monolayer single crystal 2D QDs with uniform size were finally obtained.

Characterization of 2D QDs

The TEM image reveals the sizes of 2D QDs. Taking MoS₂ QDs for example, the lateral sizes are in the range of 3 to 6 nm with nearly circular shape, as shown in Fig. 1b. HRTEM (Fig. 1c) of a single MoS₂ QD shows the single crystal feature, evidenced by the hexagonal lattice structure with lattice spacing of 2.7 Å matching to the (100) planes of MoS₂ single crystal. The corresponding

fast Fourier transform (FFT) pattern (insets in Fig. 1c) also confirms its single-crystalline characteristic. The thicknesses of the MoS₂ QDs are in the range of 0.7 to 1.8 nm, corresponding to one to two layers, consistent with the AFM results (Fig. 1d and Fig. S4a, b). The yield of monolayer MoS₂ QDs reaches 40% (Fig. S4c), higher than previous reports. We also fabricated other 2D single crystal QDs successfully, such as MoSe₂, WS₂, WSe₂, SnS₂, SnSe₂, TaS₂, TaSe₂, TiS₂ and TiSe₂. Their suspensions in NMP are shown in Fig. S5. The corresponding HRTEM images confirm their single-crystalline feature with the lateral sizes in the range of 3 to 6 nm similar to the MoS₂ QDs, as shown in Fig. 2.

Taking MoS₂ QDs as example, the structure and performance were analyzed. In Fig. 1e, the Raman spectra of the bulk single crystal and QD MoS₂ reveal peaks of A_{1g} and E_{2g}¹ modes, respectively. Compared with the peaks of

bulk single crystal MoS₂, A_{1g} (out-of-plane optical vibration of S atoms) and E_{2g}¹ (in-plane optical vibration of the Mo–S bond in opposite directions) peaks of the QDs slightly red-shift with similar intensity. The A_{1g} peak shifts from 411.4 to 407.86 cm^{−1}, and the E_{2g}¹ peak shifts from 386.6 to 383.1 cm^{−1}, due to the reductions of thickness and lateral size [15,29]. The intensity ratio of A_{1g}/E_{2g}¹ is ~ 1.18, revealing the high quality of the QDs without massive defects [30]. This phenomenon indicates that the as-prepared MoS₂ QDs are thinned to mono- or bi-layers. Similar tendency were found in the case of MoSe₂, WS₂ and WSe₂ QDs (Fig. S6). XPS was performed to further identify the chemical composition and phase state characteristics of the MoS₂ QDs. As shown in Fig. 1f, g, the as-prepared MoS₂ QDs is pure (no octahedral (1T) MoS₂ and other elements) with extremely low defects, which is distinctly different and unique compared with

Figure 2 HRTEM images of 2D QDs. (a) MoSe₂, (b) WS₂, (c) WSe₂, (d) SnS₂, (e) SnSe₂, (f) TaS₂, (g) TaSe₂, (h) TiS₂, and (i) TiSe₂ with the scale bar of 2 nm.

the QDs prepared by traditional chemical process. Similarly, the XPS spectra of MoSe₂, WS₂ and WSe₂ QDs exhibit consistent trends (Fig. S7).

Optical features of 2D QDs

The optical properties of the obtained 2D QDs were investigated by UV-vis absorption, fluorescence microscopy and PL spectroscopy. As shown in Fig. 3a, the UV-vis spectrum of MoS₂ QDs with 5 nm lateral size shows only one weak shoulder peak at 362 nm, with absorption edge near 420 nm, attributed to the excitonic features of MoS₂ QDs [31,32]. Other 2D QDs all reveal similar absorption spectra, as shown in Fig. S8. In previous reports, the bandgap of MoS₂ changes with layers [33], i.e., bulk MoS₂ is an indirect semiconductor with a bandgap of 1.2 eV, whereas monolayer MoS₂ is a direct gap semiconductor with a bandgap of 1.8 eV. Herein, the bandgap energies of the MoS₂ QDs was calculated using the Equation $E_g^{\text{opt}} = 1240/\lambda_{\text{edge}}$, where λ_{edge} is the onset value of the first excitonic absorption peaks in the direction of longer wavelengths. The calculated bandgap energy of MoS₂ QDs is 3.08 eV, which is large than that of bulk or large-size monolayer MoS₂ [34,35]. Simultaneously, ultraviolet photoelectron spectroscopy (UPS) was employed to determine the valence band (VB) of different size MoS₂ QDs, and the conduction band (CB) was obtained by subtracting the bandgap from the VB. Therefore, the VB and CB levels are -6.25 and -3.17 eV, respectively (Fig. 3a, b).

Bulk 2D MoS₂ as indirect band gap semiconductor, has no PL. However, for the cut MoS₂ quasi QDs (nanor-

ibbons), when excited with 400–480 nm (blue) or 490–570 nm (green) light, green or red luminescence was clearly observed due to the quantum confinement size effects, indicating that the PL was sufficiently strong to be imaged (Fig. S9). Excitation-dependent steady state PL behavior phenomenon was observed in MoS₂ QDs. As shown in Fig. 3c, the PL peak red shifts (from 465 to 501 nm) with increasing excitation wavelength (from 300 to 400 nm). Under irradiation with UV light at 360 nm, the MoS₂ QDs solution emits blue light (inset in Fig. 3c). The excitation-dependent fluorescence emission is similar to previous reports [36,37], which may be attributed to the presence of several trap states, the hot fluorescence from the K point of the Brillouin zone and the polydispersity of the MoS₂ QDs [38,39]. This phenomenon also appears in other 2D QDs (Fig. S10).

Time-resolved PL measurement was performed to further investigate the exciton recombination dynamics of these 2D QDs. As shown in Fig. 3d, the time-resolved PL spectrum of MoS₂ QDs can be fitted by multi-exponential decay function. According to the result of multi-exponential function fitting [40], MoS₂ QDs have a much elongated PL lifetime of 7.80 ns, which is in sharp contrast with the reported PL studies on pure monolayer MoS₂, whose PL decay time is a few hundred picoseconds [41]. The longer PL decay time signifies that the native defects are extremely low in the MoS₂ QDs, consistent with the TEM and XPS results. The PL lifetimes of other 2D QDs are shown in Fig. S11, which all are few nanoseconds.

To scrutinize the intrinsic characteristic fluorescence

Figure 3 (a) Normalized UV-vis absorption spectra of MoS₂ QDs. (b) UPS data of MoS₂ QDs. (c) Steady state PL spectra of MoS₂ QDs excited at different wavelengths, with the inset showing the digital images of the corresponding QDs under UV light. (d) Transient state fluorescence spectrum of MoS₂ QDs. (e) The normalized temperature-dependent PL spectra of MoS₂ QDs. (f) The plots of PL peak energy of the MoS₂ QDs as a function of temperature. (g) The plots of integrated PL emission intensity of the MoS₂ QDs as a function of temperature. (h) The fluorescence QY of 2D QDs.

property of the MoS_2 QDs, temperature-dependent PL spectra was also recorded. As shown in Fig. 3e and Fig. S12, as the temperature decreases from 297 to 77 K, the integrated PL peak intensity of MoS_2 QDs obvious enhances with a slight blue-shift, which could be well described by traditional empirical Varshni models with the reduced electron-phonon coupling due to the restricted structural vibrations and distortions at the lower temperatures. As shown in Fig. 3f, the emission peaks of MoS_2 QDs change with temperature, which can be fitted by the Equation (S1) (Varshni models in Supplementary information) [42]. According to the fitting results, the band gap of the MoS_2 QDs is 2.42 eV, close to optical band gap and higher than that of bulk MoS_2 . The shift of MoS_2 QDs PL band with the temperature is similar to that of the temperature-dependent band gap shrinkage of bulk material, due to the quantum confinement effect. The temperature-dependent integrated PL of the MoS_2 QDs can be fitted using the Equation (S2) [35], as plotted in Fig. 3g. According to the fitting analyses, the MoS_2 QDs have a relatively large excitation binding energy of 183.3 meV, which is larger than that of many other inorganic QDs and thus contributes to the PL of MoS_2 QDs. This is probably due to quantum confinement effect associated with the high-quality QDs.

The PL QY of the as-prepared 2D QDs was measured by transient fluorescence spectrometer to gain additional insight into the exciton recombination dynamics. The PL QY is substantially lowered by defects in conventional semiconductors, which is a key metric of optoelectronic performance that directly dictates the maximum device efficiency. Graphene-like 2D semiconductors always exhibit poor fluorescence QY (0.01%–6%), for the number of photons radiated from the material is much lower than the number of generated electron-hole pairs. The low QY in these materials is attributed to the defect-mediated nonradiative recombination and biexcitonic recombina-

tion at higher excitation powers [41]. In previous reports, the PL QY of graphene-like 2D materials is typically below 7% [27,43]. However, in this study, the PL QY of 2D QDs is typically above 5%, as shown in Fig. 3h. The fluorescence QYs of MoS_2 , MoSe_2 , WS_2 and SnSe_2 QDs exceed 10%. Among them, WS_2 QDs have the highest PL QY of 18%, to our knowledge, which is the ceiling value of pure and untreated graphene-like 2D materials. The high fluorescence QY indicates that these 2D QDs have low density of defect states and extraordinary electronic quality [43,44].

The excellent fluorescence properties of 2D QDs, i.e., fluorescence QY typically above 10% and nanosecond lifetime of the luminescence, suggest that the as-obtained 2D QDs are potential candidates for optoelectronic and biological applications. To illustrate the potential in biological applications, uptake and bioimaging experiment of MoS_2 QDs was performed with the confocal fluorescence microscope. After incubation with MoS_2 QDs for 10 h, green fluorescence was observed in cytoplasm, indicating the MoS_2 QDs were successfully internalized by the HeLa cells without any other conjugations (Fig. 4). This result suggests that these as-prepared MoS_2 QDs can be used as promising, low toxic, biocompatible, and good cell-permeability fluorescent labeling agents for *in vitro* imaging.

CONCLUSIONS

In summary, 2D single crystal QDs with pristine surface, high quality and high monolayer yield were obtained through ultrathin cutting from bulk 2D single crystals with the assistance of exfoliation. The as-prepared monolayer single crystal 2D QDs have great optical performance, i.e., obvious PL spectra peak, high fluorescence QY and long PL decay times, which are successfully applied in biological imaging. This facile and reliable strategy for preparing 2D QDs is appropriate for multifarious 2D materials to prepare pristine QDs without

Figure 4 (a) Confocal laser scanning microscopy image of living HeLa cells stained with 0.001 mg mL⁻¹ LysoTracker for 20 min. (b) The corresponding image under bright field. (c) Merged image of (a) and (b). All the scale bars are 20 μm.

surfactant covering or chemical intercalation.

Received 22 December 2019; accepted 15 February 2020;
published online 1 April 2020

- 1 Manzeli S, Ovchinnikov D, Pasquier D, *et al.* 2D transition metal dichalcogenides. *Nat Rev Mater*, 2017, 2: 17033
- 2 Xiao Y, Zhou M, Liu J, *et al.* Phase engineering of two-dimensional transition metal dichalcogenides. *Sci China Mater*, 2019, 62: 759–775
- 3 Liu Y, Huang Y, Duan X. van der Waals integration before and beyond two-dimensional materials. *Nature*, 2019, 567: 323–333
- 4 Ren J, Teng C, Cai Z, *et al.* Controlled one step thinning and doping of two-dimensional transition metal dichalcogenides. *Sci China Mater*, 2019, 62: 1837–1845
- 5 Cui X, Kong Z, Gao E, *et al.* Rolling up transition metal dichalcogenide nanoscrolls *via* one drop of ethanol. *Nat Commun*, 2018, 9: 1301
- 6 Kappera R, Voiry D, Yalcin SE, *et al.* Phase-engineered low-resistance contacts for ultrathin MoS₂ transistors. *Nat Mater*, 2014, 13: 1128–1134
- 7 Sun L, Zheng J. Optical visualization of MoS₂ grain boundaries by gold deposition. *Sci China Mater*, 2018, 61: 1154–1158
- 8 Liu T, Liu S, Tu KH, *et al.* Crested two-dimensional transistors. *Nat Nanotechnol*, 2019, 14: 223–226
- 9 Radisavljevic B, Kis A. Mobility engineering and a metal–insulator transition in monolayer MoS₂. *Nat Mater*, 2013, 12: 815–820
- 10 Cai Z, Liu B, Zou X, *et al.* Chemical vapor deposition growth and applications of two-dimensional materials and their heterostructures. *Chem Rev*, 2018, 118: 6091–6133
- 11 Li MY, Shi Y, Cheng CC, *et al.* Epitaxial growth of a monolayer WSe₂–MoS₂ lateral p–n junction with an atomically sharp interface. *Science*, 2015, 349: 524–528
- 12 Zheng J, Zhang H, Dong S, *et al.* High yield exfoliation of two-dimensional chalcogenides using sodium naphthalenide. *Nat Commun*, 2014, 5: 2995
- 13 Zhao G, Hu R, Li J, *et al.* Graphene oxide quantum dots embedded polysulfone membranes with enhanced hydrophilicity, permeability and antifouling performance. *Sci China Mater*, 2019, 62: 1177–1187
- 14 Kagan CR, Lifshitz E, Sargent EH, *et al.* Building devices from colloidal quantum dots. *Science*, 2016, 353: aac5523
- 15 Han C, Zhang Y, Gao P, *et al.* High-yield production of MoS₂ and WS₂ quantum sheets from their bulk materials. *Nano Lett*, 2017, 17: 7767–7772
- 16 Ponomarenko LA, Schedin F, Katsnelson MI, *et al.* Chaotic Dirac billiard in graphene quantum dots. *Science*, 2008, 320: 356–358
- 17 Chuang CHM, Brown PR, Bulović V, *et al.* Improved performance and stability in quantum dot solar cells through band alignment engineering. *Nat Mater*, 2014, 13: 796–801
- 18 Shen J, Zhu Y, Yang X, *et al.* Graphene quantum dots: emergent nanolights for bioimaging, sensors, catalysis and photovoltaic devices. *Chem Commun*, 2012, 48: 3686–3699
- 19 Ha HD, Han DJ, Choi JS, *et al.* Dual role of blue luminescent MoS₂ quantum dots in fluorescence resonance energy transfer phenomenon. *Small*, 2014, 10: 3858–3862
- 20 Zhang X, Lai Z, Liu Z, *et al.* A facile and universal top-down method for preparation of monodisperse transition-metal dichalcogenide nanodots. *Angew Chem*, 2015, 127: 5515–5518
- 21 Xu Y, Wang X, Zhang WL, *et al.* Recent progress in two-dimensional inorganic quantum dots. *Chem Soc Rev*, 2018, 47: 586–625
- 22 Hanifi DA, Bronstein ND, Koscher BA, *et al.* Redefining near-unity luminescence in quantum dots with photothermal threshold quantum yield. *Science*, 2019, 363: 1199–1202
- 23 Gu W, Yan Y, Zhang C, *et al.* One-step synthesis of water-soluble MoS₂ quantum dots via a hydrothermal method as a fluorescent probe for hyaluronidase detection. *ACS Appl Mater Interfaces*, 2016, 8: 11272–11279
- 24 Zhang H, Hu B, Sun L, *et al.* Surfactant ligand removal and rational fabrication of inorganically connected quantum dots. *Nano Lett*, 2011, 11: 5356–5361
- 25 Yan Y, Zhang C, Gu W, *et al.* Facile synthesis of water-soluble WS₂ quantum dots for turn-on fluorescent measurement of lipoic acid. *J Phys Chem C*, 2016, 120: 12170–12177
- 26 Liu R, Wu D, Feng X, *et al.* Bottom-up fabrication of photoluminescent graphene quantum dots with uniform morphology. *J Am Chem Soc*, 2011, 133: 15221–15223
- 27 Wang Y, Liu Y, Zhang J, *et al.* Cryo-mediated exfoliation and fracturing of layered materials into 2D quantum dots. *Sci Adv*, 2017, 3: e1701500
- 28 Hennrich F, Krupke R, Arnold K, *et al.* The mechanism of cavitation-induced scission of single-walled carbon nanotubes. *J Phys Chem B*, 2007, 111: 1932–1937
- 29 Gopalakrishnan D, Damien D, Shaijumon MM. MoS₂ quantum dot-interspersed exfoliated MoS₂ nanosheets. *ACS Nano*, 2014, 8: 5297–5303
- 30 Lin Z, Liu Y, Halim U, *et al.* Solution-processable 2D semiconductors for high-performance large-area electronics. *Nature*, 2018, 562: 254–258
- 31 Chikan V, Kelley DF. Size-dependent spectroscopy of MoS₂ nanoclusters. *J Phys Chem B*, 2002, 106: 3794–3804
- 32 Gan ZX, Liu LZ, Wu HY, *et al.* Quantum confinement effects across two-dimensional planes in MoS₂ quantum dots. *Appl Phys Lett*, 2015, 106: 233113
- 33 Radisavljevic B, Radenovic A, Brivio J, *et al.* Single-layer MoS₂ transistors. *Nat Nanotech*, 2011, 6: 147–150
- 34 Wang X, Feng H, Wu Y, *et al.* Controlled synthesis of highly crystalline MoS₂ flakes by chemical vapor deposition. *J Am Chem Soc*, 2013, 135: 5304–5307
- 35 Dumcenco D, Ovchinnikov D, Marinov K, *et al.* Large-area epitaxial monolayer MoS₂. *ACS Nano*, 2015, 9: 4611–4620
- 36 Dong H, Tang S, Hao Y, *et al.* Fluorescent MoS₂ quantum dots: Ultrasonic preparation, up-conversion and down-conversion bioimaging, and photodynamic therapy. *ACS Appl Mater Interfaces*, 2016, 8: 3107–3114
- 37 Yuan F, Yuan T, Sui L, *et al.* Engineering triangular carbon quantum dots with unprecedented narrow bandwidth emission for multicolored LEDs. *Nat Commun*, 2018, 9: 2249
- 38 Ren X, Pang L, Zhang Y, *et al.* One-step hydrothermal synthesis of monolayer MoS₂ quantum dots for highly efficient electrocatalytic hydrogen evolution. *J Mater Chem A*, 2015, 3: 10693–10697
- 39 Li B, Jiang L, Li X, *et al.* Preparation of monolayer MoS₂ quantum dots using temporally shaped femtosecond laser ablation of bulk MoS₂ targets in water. *Sci Rep*, 2017, 7: 11182
- 40 Hao Y, Hao Y, Sun Q, *et al.* Broadband EQE enhancement in organic solar cells with multiple-shaped silver nanoparticles: Optical coupling and interfacial engineering. *Mater Today Energy*, 2017, 3: 84–91
- 41 Amani M, Lien DH, Kiriya D, *et al.* Near-unity photoluminescence

- quantum yield in MoS₂. *Science*, 2015, 350: 1065–1068
- 42 Varshni YP. Temperature dependence of the energy gap in semiconductors. *Physica*, 1967, 34: 149–154
- 43 Yuan L, Huang L. Exciton dynamics and annihilation in WS₂ 2D semiconductors. *Nanoscale*, 2015, 7: 7402–7408
- 44 Mak KF, Lee C, Hone J, *et al.* Atomically thin MoS₂: A new direct-gap semiconductor. *Phys Rev Lett*, 2010, 105: 136805

Acknowledgements This work was supported by the National Natural Science Foundation of China (21573253), the National Key Research and Development Program of China (2017YFA0204700) and the Strategic Priority Research Programme of the Chinese Academy of Sciences (XDB12010000). We thank Yuanping Yi and Qian Peng for analyzing the optical performances.

Author contributions Hao Y performed the experiments, analyzed the data, and wrote the paper. Zheng J and Fan L designed the work, performed the experiments, conceptualized the work, and analyzed the data. Su W performed the bioimaging experiment. Hou L, Cui X, Wang S, Zhan P and Zou Y performed some characterization experiments and analyzed the data.

Conflict of interest The authors declare no conflict of interest.

Supplementary information The supporting data are available in the online version of the paper.

Yang Hao received his BSc degree in material physics from Xi'an University of Technology in 2013. Currently, he is a PhD student under the supervision of Prof. Jian Zheng at the Institute of Chemistry, Chinese Academy of Sciences (ICCAS). His research interests focus on the preparation and photoelectric properties of 2D materials.

Wen Su received her BSc degree in applied chemistry from the Capital Normal University in 2014. Currently, she is a PhD student under the supervision of Prof. Louzhen Fan at Beijing Normal University. Her research interests focus on the synthesis and biomedical applications of fluorescent carbon nanomaterials.

Louzhen Fan is now a professor of the Department of Chemistry, Beijing Normal University. She received her PhD in physical chemistry in 1998 under the supervision of Prof. Daoben Zhu and Prof. Yongfang Li from ICCAS. Her research interests are focused on the synthesis of novel carbon and metal nanomaterials and their applications in biology and energy.

Jian Zheng is now a professor in the Organic Solids Laboratory, ICCAS. He received His PhD in organic chemistry in 2011 under the supervision of Prof. Daoben Zhu and Prof. Yongqi Liu from ICCAS. His research interests are focused on the preparation, organic hybridization and self-assembly of novel 2D materials based on chemical methods and the application and research of 2D materials in the fields of optical, electrical and energy devices.

超薄切片与剥离制备单层单晶二维量子点

郝阳^{1,2†}, 宿雯^{3†}, 侯凌霄^{1,2}, 崔雪萍^{1,2}, 王少芝^{1,2}, 占鹏鑫^{1,2}, 邹业^{1,2}, 范楼珍^{3*}, 郑健^{1,2*}

摘要 二维(2D)原子级薄量子点(QDs)具有非凡的电学和光学性能。但是用于制备高质量2D量子点的通用、可靠技术仍然面临挑战。本文中, 我们报道了一种简单的用超薄切片垂直切割2D块体单晶, 然后通过剥离来制备高质量单层单晶2D量子点的方法。所制备的2D量子点具有原始表面、高质量、高单层产率和高光致发光量子产率(WS₂具有最高的光致发光量子产率18%)。所制备的单层单晶二维量子点可作为一种有前途的低毒、生物相容性好、具有良好细胞通透性的荧光标记试剂。