



Article Efficient Preparation of Small-Sized Transition Metal Dichalcogenide Nanosheets by Polymer-Assisted Ball Milling

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Abstract: Two-dimensional (2D) transition metal dichalcogenide nanosheets (TMDC NSs) have attracted growing interest due to their unique structure and properties. Although various methods have been developed to prepare TMDC NSs, there is still a great need for a novel strategy combining simplicity, generality, and high efficiency. In this study, we developed a novel polymer-assisted ball milling method for the efficient preparation of TMDC NSs with small sizes. The use of polymers can enhance the interaction of milling balls and TMDC materials, facilitate the exfoliation process, and prevent the exfoliated nanosheets from aggregating. The WSe₂ NSs prepared by carboxymethyl cellulose sodium (CMC)-assisted ball milling have small lateral sizes (8~40 nm) with a high yield (~60%). The influence of the experimental conditions (polymer, milling time, and rotation speed) on the size and yield of the nanosheets was studied. Moreover, the present approach is also effective in producing other TMDC NSs, such as MoS₂, WS₂, and MoSe₂. This study demonstrates that polymer-assisted ball milling is a simple, general, and effective method for the preparation of small-sized TMDC NSs.

Keywords: high yield; polymer-assisted; ball milling; TMDC nanosheets

1. Introduction

2D TMDCs have a unique layered structure in which the layers interact with each other by weak van der Waals force rather than by strong chemical bonding, which makes them different from other materials [1–4]. 2D TMDCs usually have the general formula of MX₂, in which transition metal (M) atoms and chalcogen (X) atoms form an X-M-X 'sandwich' structure, such as MoS₂, MoSe₂, WS₂, WSe₂, TiS₂, or TiSe₂ [1,5]. Since the interaction between TMDC layers is weak, few-layer or single-layer TMDC NSs can be obtained by physical or chemical exfoliation. These dimension changes in 2D TMDCs cause significant variations in their electronic structures and have a great impact on their physical and chemical properties [2,3]. For example, ultrathin MoS₂ NSs have high carrier mobility, enhanced photoluminescence, and high catalytic activity [6–9]. The size and aggregation of TMDC nanosheets also strongly influence the lubrication property in solid lubricants [10–12]. Moreover, when the lateral size of TMDC NSs is significantly reduced, typically at less than 20 nm, their properties are influenced by quantum confinement effects [13,14], which make small TMDC NSs promising nanomaterials for applications in optoelectronics, catalysis, energy storage, and biomedicine [3,5,15].

Over the last few decades, various methods have been developed to control the dimensions of TMDC NSs [2,4,16]. Bottom-up methods, such as chemical vapor deposition (CVD) and colloidal synthesis, can be used to synthesize TMDC NSs with various compositions and structures, for which high temperatures and rigorous reaction conditions are usually needed [17–19]. As well as bottom-up routes, top-down methods that involve exfoliating bulk TMDCs have also attracted great attention. Novoselov et al. developed a



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). micromechanical exfoliation method for TMDC NSs by using Scotch tape [20]. Although high-quality TMDC NSs can be prepared by using this method, low yield and tedious work limit its use. Chemical exfoliation by alkaline metal intercalation is an efficient top-down approach to prepare ultrathin TMDC NSs [21–23]. However, the intercalation reactions usually need to be carried out in strict oxygen-free and water-free conditions, and the as-prepared TMDC NSs often have altered crystal structures with the formation of abundant defects. Ultrasonication-assisted liquid phase exfoliation (LPE) is another popular method that has been extensively explored for the preparation of TMDC NSs due to its simplicity and generality [24,25]. However, the efficiency of LPE is relatively low, especially for the preparation of TMDC NSs with small sizes [24–26]. Ball milling is another topdown method to produce TMDC NSs with the potential for large-scale production [27–30]. Compared with the normal force-dominated LPE method, ball milling utilizes both shear force and normal force provided by the milling balls to exfoliate and pulverize the layered TMDCs [31,32]. Similar to the LPE method, the low yield of nanosheets is also a common issue due to the limited milling ball-material contact interface and the reaggregation of nanosheets during ball milling. Although sonication-assisted exfoliation has been used together with ball milling, the improvement of the yield is still limited and the operation becomes complicated [28,33,34]. Therefore, a novel method for highly efficient preparation of small TMDC NSs with high yield and simplicity is still needed.

In this report, we develop a polymer-assisted ball milling strategy for the efficient preparation of TMDC NSs with small sizes (Scheme 1). By using carboxymethyl cellulose sodium (CMC) as a solid intermedium in the ball milling process, WSe₂ NSs with different average sizes from about 8 nm to 40 nm were successfully prepared with a total yield of over 60%. The influence of the polymer, rotation speed, and milling time on the size and yield of WSe₂ NSs was studied. This method provides polymer surface modification during preparation, which gives the as-prepared WSe₂ NSs good colloidal stability. Moreover, this method can also be used to prepare other TMDC NSs, such as MoS₂, MoSe₂, and WS₂. Our study demonstrates a novel method for the preparation of small-sized TMDC NSs with high yields by using polymer-assisted ball milling, which is efficient, simple, general, and scalable.



Scheme 1. Preparation of small TMDC NSs by polymer-assisted ball milling.

2. Results and Discussion

2.1. WSe₂ NSs Prepared by CMC-Assisted Ball Milling

As illustrated in Scheme 1, polymers are mixed with bulk TMDC materials in a steel jar to assist the dry ball milling process. The shear force provided by the steel balls leads to the exfoliation of the layered materials, while the normal force fragments the nanosheets. During ball milling, the polymers act as an intermedium to transfer the impact from steel balls to TMDC materials and enhance the interaction between steel balls and TMDC materials. Moreover, the polymer molecules can adsorb on the surface of TMDC NSs and reduce their reaggregation, which also improves the exfoliation efficiency. Polymerassisted ball milling not only decreases the thickness and lateral size of layered TMDCs but also produces homogeneous TMDC–polymer composites. Without further ultrasonication treatment, the as-prepared TMDC NSs can easily disperse in water and form stable colloidal dispersions. TMDC NS aqueous dispersions were first centrifuged at low speed to remove the large aggregates, and the supernatant was further centrifuged at different speeds to obtain TMDC NSs with different sizes.

CMC was first explored to prepare WSe₂ NSs by ball milling. As a carboxymethyl functionalized cellulose, CMC is an abundant, cheap, and environmentally friendly material and has been extensively used in various industrial applications [35]. After ball milling, CMC-WSe₂ NSs composites can easily form aqueous dispersions due to the electrostatic repulsion force provided by CMC. After gradient centrifugation at different rotation speeds, a series of small WSe₂ NSs were obtained and named as WSe₂-Low (10,000 rpm), WSe₂-Medium (16,000 rpm), and WSe₂-High (21,000 rpm), respectively. TEM was used to investigate the morphology of WSe₂ NSs. Figure 1a–c and Figure S1 show that WSe₂ NSs have uniform sheet-like morphology with average sizes of 39.66 ± 13.63 nm (WSe₂-Low), 20.02 ± 6.28 nm (WSe₂-Medium), and 7.90 ± 3.11 nm (WSe₂-High), respectively. As shown by the HRTEM images in Figure 1d–f, WSe₂ NSs have a clear crystalline structure and the lattice spacing of 2.8 Å can be assigned to the (100) plane of 2H-WSe₂ [36]. The six-fold SAED patterns (Figure 1g–i) indicate that the WSe₂ NSs with different sizes have the same hexagonal symmetry structure, suggesting no significant change in the structure during the ball milling process.



Figure 1. (**a**–**c**) TEM, (**d**–**f**) HRTEM, and (**g**–**i**) SAED images of WSe₂ NSs with different sizes prepared by CMC–assisted ball milling at different centrifugation speeds: (**a**,**d**,**g**) WSe₂–Low (10,000 rpm for 1 h), (**b**,**e**,**h**) WSe₂–Medium (16,000 rpm for 1.5 h), (**c**,**f**,**i**) WSe₂–High (21,000 rpm for 4 h). Scale bars: 200 nm for (**a**–**c**), 2 nm for (**d**–**f**), and 5 1/nm for (**g**–**i**).

Atomic force microscopy (AFM) was used to investigate the thickness of WSe₂ NSs. AFM images (Figures 2 and S2) show that the average thickness of WSe₂ NSs gradually decreases from 8–10 nm (WSe₂-Low) to 2–3 nm (WSe₂-High) according to the increase in centrifugation speed from 10,000 rpm to 21,000 rpm. Hence, small-sized WSe₂ NSs with different thicknesses can be obtained by varying the rotation speed during gradient centrifugation. Since CMC molecules can still absorb on the surface of WSe₂ NSs after purification, the apparent thickness of WSe₂ NSs detected by AFM may be a little higher than the exact true values.



Figure 2. (**a**–**c**) AFM images and (**d**–**f**) corresponding height profiles of WSe₂ NSs with different sizes prepared by CMC–assisted ball milling after gradient centrifugation: (**a**,**d**) Wse₂–Low, (**b**,**e**) Wse₂–Medium, (**c**,**f**) Wse₂–High. Scale bar: 200 nm.

The structure, composition, and properties of the WSe₂ NSs were further studied. As shown by the XRD patterns in Figure 3a, diffraction peaks at 13.6°, 31.4°, 37.8°, and 47.4° belong to the (002), (100), (103), and (105) planes according to the standard diffraction data of WSe₂ (JCPDS, 38-1388). The broadening and weakening of these diffraction lines originate from the size and thickness reduction of WSe₂ NSs after ball milling [37,38]. XPS was used to investigate the chemical state of the as-prepared WSe₂ NSs. As shown by the core-level XPS spectra of W in Figure 3b, the doublet peaks near 33 eV and 35 eV belong to W^{4+} 4f_{7/2} and W^{4+} 4f_{5/2} of 2H-WSe₂, while the binding energy peak located at about 38 eV can be ascribed to W^{4+} 5p_{3/2} [39]. The absence of doublet peaks for W^{6+} between 36 and 38 eV indicates that no WOx formed during ball milling [40]. As illustrated in Figure 3c, the doublet peaks near 55 eV and 56 eV belong to Se $3d_{5/2}$ and Se $3d_{3/2}$ of 2H-WSe₂ [41]. Similarly, WSe₂ NSs with other sizes (WSe₂-Low and WSe₂-High) have the same chemical states of W and Se as WSe₂-Medium (Supplementary Materials Figure S3), which implies that WSe₂ NSs were prepared by polymer-assisted ball milling mainly through physical exfoliation and fragmentation rather than the mechanochemical way. Raman spectra of WSe₂ NSs (Figure 3d) show that the characteristic peak located at about 250 cm⁻¹ can be ascribed to the degenerate A_{1g} (out-of-plane) and E^{1}_{2g} (in-plane) vibrational modes, suggesting the few-layer structure of WSe₂ NSs [39,41]. UV-vis-NIR spectra of WSe₂ NSs (Figure 3e) indicate that the absorption peaks near 750 nm blueshift with the size and thickness reduction, similar to previous reports [42,43]. As the FT-IR spectra of WSe₂ NSs depict in Figure 3d, IR absorption bands at 3430 cm⁻¹ and 1630 cm⁻¹ can be assigned to

the stretching vibration of the hydroxyl group (-OH) and asymmetric vibration of the carboxyl group (COO-) of CMC [44,45], respectively, which suggests the existence of CMC molecules on the surface of WSe₂ NSs. Due to the hydrophilicity and electrostatic repulsion of CMC, WSe₂ NSs are stable in phosphate buffer saline (PBS) and cell culture medium (DMEM) (Supplementary Materials Figure S4), and no obvious precipitation can be observed even after being stored for months in water, which suggests their good colloidal stability in biological environments.



Figure 3. (a) XRD patterns of WSe₂ NSs with different sizes. XPS spectra of WSe₂ NSs (WSe₂–Low) for (b) W 4f and W 5p, and (c) Se 3d. (d) Raman spectra of bulk WSe₂ and WSe₂ NSs with different sizes. (e) UV–vis–NIR absorption spectra and photos of WSe₂ NSs aqueous dispersions (inset). (f) FT–IR spectra of WSe₂ NSs, bulk WSe₂, and CMC.

2.2. The Influence of Experimental Conditions on Polymer-Assisted Ball Milling

The influence of the experimental conditions of ball milling on the size and yield of WSe₂ NSs was studied. Due to the important role of the polymer during ball milling, different polymers were first studied. As shown in Supplementary Materials Figure S5, WSe₂ NSs prepared by using different polymers all have uniform morphology and good dispersity with an average size smaller than 100 nm. Table 1 indicates that the total yield of WSe₂ NSs by CMC-assisted ball milling is 62.68%, while the yields of WSe₂ NSs using F127, PVP, and PEG are 12.34%, 32.08%, and 11.89%, respectively. Moreover, the lateral size of WSe₂ NSs using CMC is much smaller than those using other polymers. The superiority of CMC for the ball milling process may originate from its unique structure. Previous studies have revealed that the hydroxyl and carboxyl groups of polymers, such as alginate, bovine serum albumin, and glycan, have a strong interaction with the surface of TMDC NSs, and the synergy of the repetitive units of the polymers also enhances this interaction [46–48]. Compared with F127, PVP, and PEG, CMC has much more hydroxyl and carboxyl groups, which may provide a stronger interaction between the surface of WSe₂ NSs and polymers and significantly improve the efficiency of ball milling. Milling time and rotation speed during ball milling also play important roles in the morphology and yield of the WSe₂ NSs. As shown in Table 1 and Supplementary Materials Figure S6, the lateral size of WSe₂ NSs generally reduces with increased milling time, while total yields of WSe₂ NSs are nearly the same ($\sim 60\%$), suggesting that the milling time mainly influences the size of WSe₂ NSs

rather than the yield. As shown in Supplementary Materials Figure S7 and Table 1, the size of most WSe₂ NSs decreases from about 60 nm to 30 nm when the rotation speed of the ball mill increases from 400 rpm to 800 rpm. Meanwhile, the total yield of WSe₂ NSs increases from about 30% to 60% once the rotation speed has exceeded 650 rpm. Therefore, both the size and yield of WSe₂ NSs can be easily adjusted by varying the rotation speed and milling time during ball milling, suggesting the controllability of this method.

Table 1. Average lateral size and yield of WSe₂ NSs prepared by polymer-assisted ball milling under different experimental conditions.

Polymer	Speed (rpm)	Time (h)	WSe ₂ -Low	Size (nm)/Yield (%) WSe ₂ -Medium	WSe ₂ -High	Total Yield (%)
CMC	650	12	39.66/26.32	20.02/26.18	7.90/10.18	62.68
F127	650	12	93.20/7.68	72.39/3.84	48.73/0.82	12.34
PVP	650	12	46.29/23.48	19.05/8.39	14.87/0.21	32.08
PEG	650	12	47.05/8.81	37.00/2.21	30.76/0.87	11.89
CMC	650	6	55.04/22.34	35.28/25.60	21.54/14.36	62.30
CMC	650	24	24.06/32.52	12.41/23.72	7.68/3.82	60.06
CMC	400	12	61.05/26.92	51.44/1.32	35.78/0.56	28.80
CMC	800	12	28.26/23.61	15.82/21.34	7.46/13.92	58.87

2.3. The Preparation of other TMDC NSs by Polymer-Assisted Ball Milling

The feasibility of polymer-assisted ball milling for the preparation of other TMDC NSs was investigated. As shown in Figure 4a–c, the MoS₂, MoSe₂, and WS₂ NSs prepared by CMC-assisted ball milling have uniform morphology and good dispersity. These TMDC NSs obtained by medium centrifugation speed (16,000 rpm) have lateral sizes similar to WSe₂-Medium (~20 nm) (Figure S8, Supplementary Materials), suggesting the general applicability of this method. HRTEM images (Figure 4d–f) show that MoS₂, MoSe₂, and WS₂ NSs all have a clear crystalline structure with identical lattice spacings to previous reports [36,46]. The SAED patterns (Figure 4g–i) further indicate the hexagonal symmetry structure of these TMDC NSs, which is characteristic of the crystal structure of the 2H phase [24,36]. As shown in Figure 5 and Supplementary Materials Figure S9, the average thickness of these TMDC NSs is in the range of 4–6 nm, suggesting they have a similar few-layer structure to WSe₂ NSs.

To further confirm the successful preparation of the MoS₂, MoSe₂, and WS₂ NSs, structure, composition, and property characterizations were performed. As illustrated in Figure 6a, diffraction peaks at 14.3° (MoS₂), 13.7° (MoSe₂), and 14.3° (WS₂) belong to the (002) plane, respectively, similar to the standard diffraction data. The weakening of (100), (103), and (105) lines may originate from the size and thickness reduction of these TMDC NSs [37]. The doublet peaks in the XPS spectrum of Mo (Figure 6b) near 229 eV and 232 eV correspond to $Mo^{4+} 3d_{5/2}$ and $Mo^{4+} 3d_{3/2}$ of 2H-MoS₂, respectively; and the weak peak near 227 eV corresponds to S 2s [34,49]. The absence of the peak near 237 eV for Mo⁶⁺ 3d suggests no oxidation of MoS_2 [40]. The doublet peaks near 162 eV and 163 eV in Figure 6c can be ascribed to the S $2p_{3/2}$ and S $2p_{1/2}$ of 2H-MoS₂, respectively. In addition, the high-resolution XPS spectra (Supplementary Materials Figure S10) further confirm the successful preparation of 2H phase MoSe₂ NSs and WS₂ NSs, while slight oxidation was found for WS₂ NSs [40]. Raman spectra of MoS₂, MoSe₂, and WS₂ NSs (Figure 6d) reveal the characteristic peaks for MoS_2 (408 cm⁻¹ and 382 cm⁻¹), $MoSe_2$ (241 cm⁻¹ and 287 cm⁻¹), and WS_2 (420 cm⁻¹ and 354 cm^{-1}), which belong to their A_{1g} and E_{2g}^{1} vibrational modes, respectively [33]. Figure 6e shows the UV-vis-NIR spectra of the TMDC NSs aqueous dispersions and their photos under ambient light (inset). The distinct absorption peaks located near 800 nm (MoSe₂), 632 nm (MoS_2) , and 620 nm (WS_2) originate from the A exciton transition, similar to the reports of few-layer TMDC NSs [43,50]. Figure 6f and Figure S11 show the FT-IR spectra of the TMDC NSs and their bulk materials. The IR absorption bands near 3410 cm^{-1} and 1630 cm^{-1} can be assigned to the stretching frequency of OH and COO groups from CMC adsorbed on the surface of the TMDC NSs.



Figure 4. (**a**–**c**) TEM, (**d**–**f**) HRTEM, and (**g**–**i**) SAED images of MoS₂, MoSe₂, and WS₂ NSs prepared by CMC–assisted ball milling: MoS₂ (**a**,**d**,**g**), MoSe₂ (**b**,**e**,**h**), and WS₂ (**e**,**f**,**i**). Scale bars: 200 nm for (**a**–**c**), 2 nm for (**d**–**f**), and 5 1/nm for (**g**–**i**).



Figure 5. AFM images and corresponding height profiles of MoS₂, MoSe₂, and WS₂ NSs prepared by CMC-assisted ball milling: (**a**,**d**) MoS₂, (**b**,**e**) MoSe₂, (**c**,**f**) WS₂. Scale bar: 200 nm.



Figure 6. (a) XRD patterns of MoS₂, MoSe₂, and WS₂ NSs prepared by CMC–assisted ball milling. XPS spectra of MoS₂ NSs for Mo 3d (b) and S 2p (c) core level energy regions. (d) Raman spectra of MoS₂, MoSe₂, and WS₂ NSs. (e) UV–vis–NIR absorption spectra with the photos (inset) and (f) FT–IR spectra of MoS₂, MoSe₂, and WS₂ NSs.

3. Materials and Methods

3.1. Chemicals

WSe₂ powder (99.8%) was purchased from Alfa Aesar. MoS₂ powder (99%), MoSe₂ powder (99.9%), WS₂ powder (99%), Pluronic F-127, and polyvinyl pyrrolidone (PVP) were obtained from Sigma-Aldrich (St. Louis, MO, USA). Carboxymethyl cellulose sodium (CMC) and polyethylene glycol (PEG) were purchased from Aladdin and Macklin, respectively. Ultrapure water (18.2 M Ω , Billerica, MA, USA) was used to prepare aqueous solutions in this study.

3.2. Characterization

Transmission electron microscopy (TEM) images were obtained by using a HT7700 at 120 kV (Hitachi, Tokyo, Japan). High-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) images were obtained using field emission electron microscopes (Talos F200x, FEI, 200 kV, Waltham, MA, USA). Atomic force microscopy (AFM) images were acquired on Nanoscope IIIa (Bruker, Billerica, MA, USA). X-ray diffraction (XRD) patterns were recorded on an X-ray diffractometer (D8 Advance A25, Bruker, Billerica, MA, USA) with Cu K α radiation (λ = 1.54178 Å). X-ray photoelectron spectroscopy (XPS) was performed on KRATOS Axis Supra (Shimadzu, Kyoto, Japan) with Al K α (h ν = 1486.6 eV) as the excitation source. Raman characterization was carried out on a micro-Raman spectroscopy system (inVia, Renishaw, Wotton-under-Edge, UK) equipped with a 532 nm laser. Ultraviolet-visible-near infrared (UV-vis-NIR) absorption spectroscopy was performed on a UV-3600 spectrophotometer (Shimadzu, Kyoto, Japan). Fourier transform infrared (FT-IR) spectra were recorded on a FT-IR spectrometer (Perkin Elmer, Waltham, MA, USA). The concentration of TMDC NSs was determined by using an inductively coupled plasma optical emission spectrometer (ICP-OES, Optima 5300DV, Perkin Elmer, Waltham, MA, USA).

3.3. Preparation of WSe₂ NSs by CMC-Assisted Ball Milling

WSe₂ powder (0.1 g) and CMC (1.0 g) were mixed and put into the steel jar of a planetary ball mill (Tianchuang, Changsha, China) for ball milling at 650 rpm ($35 \times g$) for 12 h. Then, 40 mL ultrapure water was added into the jar and mixed. The aqueous suspensions of WSe₂ were first centrifuged at 3000 rpm ($765 \times g$) for 30 min to remove the large aggregates. Then, the supernatant was centrifuged at 10,000 rpm ($8497 \times g$) for 1 h. The sediment was collected and redispersed in water, while the supernatant was further centrifuged at 16,000 rpm ($21,752 \times g$) for 1.5 h. Similarly, the sediment was collected and the supernatant was then centrifuged at 21,000 rpm ($37,471 \times g$) for 4 h. Each sediment was further purified more than three times by centrifugation to remove the redundant CMC. Finally, the sediments were dispersed in ultrapure water and stored at 4 °C. WSe₂ NSs obtained at different centrifugation speeds (low speed at 10,000 rpm ($8497 \times g$), medium speed at 16,000 rpm ($21,752 \times g$), and high speed at 21,000 rpm ($37,471 \times g$)) are referred to as WSe₂-Low, WSe₂-Medium, and WSe₂-High, respectively.

3.4. WSe₂ NSs Prepared by Using Different Polymers during Ball Milling

The preparation of WSe₂ NSs by using different polymers, including F127, PVP, and PEG, has similar experimental conditions to CMC-assisted ball milling. Since the stabilization abilities of different polymers are different, the centrifugation conditions used to purify WSe₂ NSs were adjusted according to the polymer used. For F127, WSe₂ NSs were obtained by gradient centrifugation at 5000 rpm (2124× *g*) for 20 min (WSe₂-Low), 7500 rpm (4779× *g*) for 20 min (WSe₂-Medium), and 10,000 rpm (8497× *g*) for 30 min (WSe₂-High). For PVP, WSe₂ NSs were obtained by gradient centrifugation at 10,000 rpm (8497× *g*) for 1 h (WSe₂-Low), 16,000 rpm (21,752× *g*) for 2 h (WSe₂-Medium), and 21,000 rpm (37471× *g*) for 4 h (WSe₂-High). For PEG, WSe₂ NSs were obtained by gradient centrifugation at 5000 rpm (4779× *g*) for 20 min (WSe₂-Medium), and 10,000 rpm (3000 rpm (2124× *g*) for 20 min (WSe₂-Medium), and 21,000 rpm (37471× *g*) for 4 h (WSe₂-High). For PEG, WSe₂ NSs were obtained by gradient centrifugation at 5000 rpm (2124× *g*) for 30 min (WSe₂-Medium), and 10,000 rpm (8497× *g*) for 30 min (WSe₂-High).

3.5. Preparation of Other TMDC NSs

 MoS_2 , $MoSe_2$, and WS_2 NSs were prepared using similar procedures to the CMCassisted ball milling of WSe_2 NSs, except that the centrifugation conditions were adjusted according to the different materials.

4. Conclusions

In summary, we have developed a novel polymer-assisted ball milling method for the efficient preparation of TMDC NSs with small sizes. The as-prepared WSe₂ NSs by using CMC have small sizes (8–40 nm) with high yield (over 60%), which is not easy to achieve by using other top-down methods. The high efficiency of this method is attributed to the enhanced interaction of the 2D TMDCs and the milling balls because of the polymer used during ball milling. The size and thickness of the WSe₂ NSs can be adjusted by changing the rotation speed and milling time during ball milling and the centrifugation conditions during purification. Moreover, this polymer-assisted ball milling method can also be used to prepare other TMDC NSs, such as MoS₂, WS₂, and MoSe₂. The as-prepared TMDC NSs have good colloidal stability in PBS and cell culture medium. This study provides a highly efficient, simple, general, and scalable method for the preparation of TMDC NSs with small sizes, which may also be used for other 2D materials.

Supplementary Materials: The following supporting information can be downloaded at: https://www. mdpi.com/article/10.3390/molecules27227810/s1, Figure S1: Large-scale TEM images of WSe2 NSs prepared by CMC-assisted ball milling at 650 rpm for 12 h and centrifuged under different conditions; Figure S2: Large-scale AFM images of WSe2 NSs prepared by CMC-assisted ball milling at 650 rpm for 12 h and centrifuged under different conditions; Figure S3: XPS spectra of WSe2 NSs prepared by CMC-assisted ball milling at 650 rpm for 12 h; Figure S4: Photographs of CMC-WSe2 NSs dispersed in water, PBS, and DMEM for different times; Figure S5: TEM images of WSe2 NSs prepared by ball milling with different polymers under different centrifugal conditions; Figure S6: TEM images of WSe2 NSs prepared by CMC-assisted ball milling for different times after gradient centrifugation; Figure S7: TEM images of WSe2 NSs prepared by CMC-assisted ball milling with different rotation speeds after gradient centrifugation; Figure S8: Size statistics of (a) MoS2, (b) MoSe2, and (c) WS2 NSs prepared by CMC-assisted ball milling; Figure S9: Large-scale AFM images of (a) MoS2, (b) MoSe2, and (c) WS2 NSs prepared by CMC-assisted ball milling; Figure S10: High-resolution XPS spectra of Mo 3d (a) and Se 3d (b) core level energy regions for MoSe2, and W 4f (c) and S 2p (d) core level energy region for WS2; Figure S11: FT-IR spectra of bulk MoS2, MoSe2, and WS2.

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References

- Chhowalla, M.; Shin, H.S.; Eda, G.; Li, L.-J.; Loh, K.P.; Zhang, H. The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets. *Nat. Chem.* 2013, *5*, 263–275. [PubMed]
- Su, J.; Liu, G.; Liu, L.; Chen, J.; Hu, X.; Li, Y.; Li, H.; Zhai, T. Recent Advances in 2D Group VB Transition Metal Chalcogenides. Small 2021, 17, e2005411. [PubMed]
- Manzeli, S.; Ovchinnikov, D.; Pasquier, D.; Yazyev, O.V.; Kis, A. 2D transition metal dichalcogenides. *Nat. Rev. Mater.* 2017, 2, 17033. [CrossRef]
- 4. Kim, Y.; Woo, W.J.; Kim, D.; Lee, S.; Chung, S.M.; Park, J.; Kim, H. Atomic-Layer-Deposition-Based 2D Transition Metal Chalcogenides: Synthesis, Modulation, and Applications. *Adv. Mater.* **2021**, *33*, e2005907. [CrossRef]
- 5. Huang, X.; Zeng, Z.; Zhang, H. Metal dichalcogenide nanosheets: Preparation, properties and applications. *Chem. Soc. Rev.* 2013, 42, 1934–1946.
- Splendiani, A.; Sun, L.; Zhang, Y.B.; Li, T.S.; Kim, J.; Chim, C.Y.; Galli, G.; Wang, F. Emerging Photoluminescence in Monolayer MoS₂. Nano. Lett. 2010, 10, 1271–1275. [CrossRef] [PubMed]
- Mak, K.F.; Lee, C.; Hone, J.; Shan, J.; Heinz, T.F. Atomically Thin MoS₂: A New Direct-Gap Semiconductor. *Phys. Rev. Lett.* 2010, 105, 136805. [CrossRef]
- Radisavljevic, B.; Radenovic, A.; Brivio, J.; Giacometti, V.; Kis, A. Single-layer MoS2 transistors. *Nat. Nanotechnol.* 2011, 6, 147–150. [CrossRef] [PubMed]
- Kibsgaard, J.; Chen, Z.; Reinecke, B.N.; Jaramillo, T.F. Engineering the surface structure of MoS₂ to preferentially expose active edge sites for electrocatalysis. *Nat. Mater.* 2012, *11*, 963–969. [PubMed]
- Liu, Y.; Li, J.; Yi, S.; Ge, X.; Chen, X.; Luo, J. Enhancement of friction performance of fluorinated graphene and molybdenum disulfide coating by microdimple arrays. *Carbon* 2020, *167*, 122–131.
- 11. Liu, Y.; Chen, X.; Li, J.; Luo, J. Enhancement of friction performance enabled by a synergetic effect between graphene oxide and molybdenum disulfide. *Carbon* **2019**, *154*, 266–276.
- 12. Liu, Y.-F.; Liskiewicz, T.; Yerokhin, A.; Korenyi-Both, A.; Zabinski, J.; Lin, M.; Matthews, A.; Voevodin, A.A. Fretting wear behavior of duplex PEO/chameleon coating on Al alloy. *Surf. Coat. Technol.* **2018**, *352*, 238–246. [CrossRef]
- Wang, X.; Sun, G.; Li, N.; Chen, P. Quantum dots derived from two-dimensional materials and their applications for catalysis and energy. *Chem. Soc. Rev.* 2016, 45, 2239–2262. [CrossRef] [PubMed]
- 14. Xu, Y.; Wang, X.; Zhang, W.L.; Lv, F.; Guo, S. Recent progress in two-dimensional inorganic quantum dots. *Chem. Soc. Rev.* 2018, 47, 586–625.
- 15. Li, X.; Shan, J.; Zhang, W.; Su, S.; Yuwen, L.; Wang, L. Recent Advances in Synthesis and Biomedical Applications of Two-Dimensional Transition Metal Dichalcogenide Nanosheets. *Small* **2017**, *13*, 1602660.
- 16. Han, J.H.; Kwak, M.; Kim, Y.; Cheon, J. Recent Advances in the Solution-Based Preparation of Two-Dimensional Layered Transition Metal Chalcogenide Nanostructures. *Chem. Rev.* **2018**, *118*, 6151–6188. [CrossRef] [PubMed]

- 17. Najmaei, S.; Liu, Z.; Zhou, W.; Zou, X.; Shi, G.; Lei, S.; Yakobson, B.I.; Idrobo, J.C.; Ajayan, P.M.; Lou, J. Vapour phase growth and grain boundary structure of molybdenum disulphide atomic layers. *Nat. Mater.* **2013**, *12*, 754–759. [PubMed]
- 18. Matte, H.; Gomathi, A.; Manna, A.K.; Late, D.J.; Datta, R.; Pati, S.K.; Rao, C.N.R. MoS₂ and WS₂ Analogues of Graphene. *Angew. Chem. Int. Ed.* **2010**, *49*, 4059–4062.
- Hwang, H.; Kim, H.; Cho, J. MoS₂ Nanoplates Consisting of Disordered Graphene-like Layers for High Rate Lithium Battery Anode Materials. *Nano. Lett.* 2011, 11, 4826–4830. [CrossRef] [PubMed]
- Novoselov, K.S.; Jiang, D.; Schedin, F.; Booth, T.J.; Khotkevich, V.V.; Morozov, S.V.; Geim, A.K. Two-dimensional atomic crystals. Proc. Nat. Acad. Sci. USA 2005, 102, 10451–10453.
- 21. Joensen, P.; Frindt, R.F.; Morrison, S.R. Single-layer MoS₂. Mater. Res. Bull. 1986, 21, 457–461.
- 22. Zeng, Z.; Yin, Z.; Huang, X.; Li, H.; He, Q.; Lu, G.; Boey, F.; Zhang, H. Single-Layer Semiconducting Nanosheets: High-Yield Preparation and Device Fabrication. *Angew. Chem. Int. Ed.* **2011**, *50*, 11093–11097.
- Yuwen, L.; Yu, H.; Yang, X.; Zhou, J.; Zhang, Q.; Zhang, Y.; Luo, Z.; Su, S.; Wang, L. Rapid preparation of single-layer transition metal dichalcogenide nanosheets via ultrasonication enhanced lithium intercalation. *Chem. Commun.* 2016, 52, 529–532. [CrossRef] [PubMed]
- 24. Coleman, J.N.; Lotya, M.; O'Neill, A.; Bergin, S.D.; King, P.J.; Khan, U.; Young, K.; Gaucher, A.; De, S.; Smith, R.J.; et al. Two-Dimensional Nanosheets Produced by Liquid Exfoliation of Layered Materials. *Science* **2011**, *331*, 568–571. [CrossRef]
- Smith, R.J.; King, P.J.; Lotya, M.; Wirtz, C.; Khan, U.; De, S.; O'Neill, A.; Duesberg, G.S.; Grunlan, J.C.; Moriarty, G.; et al. Large-Scale Exfoliation of Inorganic Layered Compounds in Aqueous Surfactant Solutions. *Adv. Mater.* 2011, 23, 3944–3948. [PubMed]
- Zhao, X.; Ma, X.; Sun, J.; Li, D.; Yang, X. Enhanced Catalytic Activities of Surfactant-Assisted Exfoliated WS₂ Nanodots for Hydrogen Evolution. ACS Nano 2016, 10, 2159–2166. [PubMed]
- Zhou, Y.; Xu, L.; Liu, M.; Qi, Z.; Wang, W.; Zhu, J.; Chen, S.; Yu, K.; Su, Y.; Ding, B.; et al. Viscous Solvent-Assisted Planetary Ball Milling for the Scalable Production of Large Ultrathin Two-Dimensional Materials. ACS Nano 2022, 16, 10179–10187. [PubMed]
- Yao, Y.; Lin, Z.; Li, Z.; Song, X.; Moon, K.-S.; Wong, C.-P. Large-scale production of two-dimensional nanosheets. J. Mater. Chem. 2012, 22, 13494–13499.
- 29. Krishnamoorthy, K.; Pazhamalai, P.; Veerasubramani, G.K.; Kim, S.J. Mechanically delaminated few layered MoS₂ nanosheets based high performance wire type solid-state symmetric supercapacitors. *J. Power Sources* **2016**, *321*, 112–119.
- 30. Ashraf, W.; Khan, A.; Bansal, S.; Khanuja, M. Mechanical ball milling: A sustainable route to induce structural transformations in tungsten disulfide for its photocatalytic applications. *Phys. E Low-Dimens. Syst. Nanostructures* **2022**, *140*, 115152.
- 31. Yi, M.; Shen, Z. A review on mechanical exfoliation for the scalable production of graphene. J. Mater. Chem. A 2015, 3, 11700–11715.
- 32. Zhu, T.T.; Zhou, C.H.; Kabwe, F.B.; Wu, Q.Q.; Li, C.S.; Zhang, J.R. Exfoliation of montmorillonite and related properties of clay/polymer nanocomposites. *Appl. Clay Sci.* 2019, 169, 48–66.
- Abdelkader, A.M.; Kinloch, I.A. Mechanochemical Exfoliation of 2D Crystals in Deep Eutectic Solvents. ACS Sustain. Chem. Eng. 2016, 4, 4465–4472.
- Dong, H.; Chen, D.; Wang, K.; Zhang, R. High-Yield Preparation and Electrochemical Properties of Few-Layer MoS₂ Nanosheets by Exfoliating Natural Molybdenite Powders Directly via a Coupled Ultrasonication-Milling Process. *Nanoscale Res. Lett.* 2016, 11, 409. [CrossRef]
- 35. Heinze, T.; Koschella, A. Carboxymethyl Ethers of Cellulose and Starch—A Review. Macromol. Symp. 2005, 223, 13-40.
- Jawaid, A.; Che, J.; Drummy, L.F.; Bultman, J.; Waite, A.; Hsiao, M.S.; Vaia, R.A. Redox Exfoliation of Layered Transition Metal Dichalcogenides. ACS Nano 2017, 11, 635–646. [PubMed]
- 37. Wang, Y.; Liu, Y.; Zhang, J.; Wu, J.; Xu, H.; Wen, X.; Zhang, X.; Tiwary, C.S.; Yang, W.; Vajtai, R.; et al. Cryo-mediated exfoliation and fracturing of layered materials into 2D quantum dots. *Sci. Adv.* **2017**, *3*, e1701500. [PubMed]
- Yuwen, L.; Zhou, J.; Zhang, Y.; Zhang, Q.; Shan, J.; Luo, Z.; Weng, L.; Teng, Z.; Wang, L. Aqueous phase preparation of ultrasmall MoSe2 nanodots for efficient photothermal therapy of cancer cells. *Nanoscale* 2016, *8*, 2720–2726. [PubMed]
- Bang, G.S.; Cho, S.; Son, N.; Shim, G.W.; Cho, B.K.; Choi, S.Y. DNA-Assisted Exfoliation of Tungsten Dichalcogenides and Their Antibacterial Effect. ACS Appl. Mater. Interfaces 2016, 8, 1943–1950. [CrossRef] [PubMed]
- 40. Ambrosi, A.; Sofer, Z.; Pumera, M. 2H→1T phase transition and hydrogen evolution activity of MoS₂, MoSe₂, WS₂ and WSe₂ strongly depends on the MX₂ composition. *Chem. Commun.* **2015**, *51*, 8450–8453.
- Wang, H.; Kong, D.; Johanes, P.; Cha, J.J.; Zheng, G.; Yan, K.; Liu, N.; Cui, Y. MoSe2 and WSe2 Nanofilms with Vertically Aligned Molecular Layers on Curved and Rough Surfaces. *Nano. Lett.* 2013, 13, 3426–3433.
- 42. Del Corro, E.; Terrones, H.; Elias, A.; Fantini, C.; Feng, S.; Nguyen, M.A.; Mallouk, T.E.; Terrones, M.; Pimenta, M.A. Excited excitonic states in 1L, 2L, 3L, and bulk WSe₂ observed by resonant Raman spectroscopy. *ACS Nano* **2014**, *8*, 9629–9635. [PubMed]
- 43. Zhao, W.; Ribeiro, R.M.; Eda, G. Electronic structure and optical signatures of semiconducting transition metal dichalcogenide nanosheets. *Acc. Chem. Res.* 2015, *48*, 91–99. [PubMed]
- Biswal, D.R.; Singh, R.P. Characterisation of carboxymethyl cellulose and polyacrylamide graft copolymer. *Carbohydr. Polym.* 2004, 57, 379–387.
- 45. He, F.; Zhao, D.; Liu, J.; Roberts, C.B. Stabilization of Fe–Pd Nanoparticles with Sodium Carboxymethyl Cellulose for Enhanced Transport and Dechlorination of Trichloroethylene in Soil and Groundwater. *Ind. Eng. Chem. Res.* **2007**, *46*, 29–34.

- 46. Guan, G.; Zhang, S.; Liu, S.; Cai, Y.; Low, M.; Teng, C.P.; Phang, I.Y.; Cheng, Y.; Duei, K.L.; Srinivasan, B.M.; et al. Protein Induces Layer-by-Layer Exfoliation of Transition Metal Dichalcogenides. *J. Am. Chem. Soc.* **2015**, *137*, 6152–6155. [PubMed]
- 47. Zong, L.; Li, M.; Li, C. Bioinspired Coupling of Inorganic Layered Nanomaterials with Marine Polysaccharides for Efficient Aqueous Exfoliation and Smart Actuating Hybrids. *Adv. Mater.* **2017**, *29*, 1604691. [CrossRef]
- 48. Kang, T.W.; Han, J.; Lee, S.; Hwang, I.J.; Jeon, S.J.; Ju, J.M.; Kim, M.J.; Yang, J.K.; Jun, B.; Lee, C.H.; et al. 2D transition metal dichalcogenides with glucan multivalency for antibody-free pathogen recognition. *Nat. Commun.* **2018**, *9*, 2549. [PubMed]
- 49. Eda, G.; Yamaguchi, H.; Voiry, D.; Fujita, T.; Chen, M.; Chhowalla, M. Photoluminescence from Chemically Exfoliated MoS₂. *Nano. Lett.* **2011**, *11*, 5111–5116. [PubMed]
- 50. Zhao, W.; Ghorannevis, Z.; Chu, L.; Toh, M.; Kloc, C.; Tan, P.-H.; Eda, G. Evolution of Electronic Structure in Atomically Thin Sheets of WS₂ and WSe₂. *ACS Nano* **2013**, *7*, 791–797.