Sorting Transition-Metal Dichalcogenide Nanotubes by Centrifugation

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Supporting Information

ABSTRACT: Tungsten disulfide (WS$_2$) nanotubes are cylindrical, multiwall nanotubes with various diameters and wall numbers. They can exhibit various unique properties depending on their structures and thus preparing samples with uniform structures is important for understanding their basic properties and applications. However, most synthesis methods have difficulty to prepare uniform samples, and thus, a purification method to extract nanotubes with a selected diameter and wall number must be developed. Here, we demonstrate a solution-based purification of WS$_2$ nanotubes using a surfactant solution. Stable dispersions of nanotubes were prepared using nonionic surfactants, which enabled us to sort the diameters and wall numbers of the nanotubes through a centrifugation process. By optimizing the conditions, we successfully obtained thin nanotubes with a mean diameter of 32 nm and mean wall number of 13 with relatively small distributions. Finally, we clarified the relationships between the structure and optical properties of the nanotubes.

Transition-metal dichalcogenide (TMDC, MX$_2$, M = Mo, W; X = S, Se) nanotubes are cylindrical multiwall nanotubes of TMDC sheets, namely, TMDC nanotubes. Since their discovery in 1992,1 TMDC nanotubes have attracted much attention due to their great potential for applications, such as high-strength polymer composite films,2−4 torsional devices,5 field effect transistors,6−7 and thermoelectric devices.8 The performance of such applications depends on the structures of the nanotubes, such as the diameter and number of walls. Thin nanotubes with a small diameter and few walls have great advantages for applications.5,9 For instance, nanotubes with a small diameter can improve mechanical properties because they can endure a larger breaking strain.5 Additionally, theoretical studies suggested that small diameter nanotubes have a one-dimensional band structure due to quantum confinement,10 and we can tune the bandgap and enhance carrier mobility.11 However, the one-dimensional nature of TMDC nanotubes has not been revealed yet because of difficulties in the synthesis of thin nanotubes with a uniform diameter and wall number.12−15 It is important to develop a technique to prepare nanotubes with thin diameters in a relatively small distribution.

In the case of nanomaterials, such as carbon nanotubes and layered materials, we occasionally use solution-based sorting techniques to extract a nanomaterial with a selected structure from synthesized samples containing materials with a wide variety of different structures.16−18 Stable dispersions in solutions are the most important factor for sorting. There have been extensive studies on stable dispersions of these nanomaterials;19,20 however, with regard to TMDC nanotubes, there is no report of a successful stable dispersion except for chemical approaches using covalent functionalization11 and defect formation,21 which damage the original properties of the TMDC nanotubes. Recently, it was reported that nonionic surfactants can disperse MoS$_2$ sheets in an aqueous solution by effectively lowering the density of the surfactant-wrapped MoS$_2$.23 Therefore, a nonionic surfactant can be a good candidate to achieve stable dispersions of TMDC nanotubes in aqueous solutions.

In this study, we demonstrate a method to prepare stable dispersions of WS$_2$ nanotubes in aqueous solutions. Through a comparison between various dispersants, we found that nonionic surfactants are the most appropriate surfactants for dispersions of WS$_2$ nanotubes. A stable dispersion enables us to extract nanotubes with small diameters by precise centrifugation control. The diameter and wall number can be tuned by changing the applied g-force, and we successfully obtained thin nanotubes with a mean diameter of 32 nm and mean wall number of 13 with relatively small distributions.

EXPERIMENTAL METHODS

To obtain a stable dispersion of WS$_2$ nanotubes in an aqueous solution, effective surfactants for the WS$_2$ nanotubes were
The dispersibility of the WS$_2$ nanotubes was estimated using the exciton transition of the WS$_2$ nanotubes. As shown in Figure 1B, the optical absorption at $\sim$650 nm, which is attributed to the A-exciton peak position, was observed for the dispersions using nonionic surfactants. The blueshift of the peak position suggests that thinner nanotubes with improved homogeneity were extracted. The relative narrowing of the bandwidth of the A-exciton optical absorption and the blueshift of the peak position suggest the extraction of thinner nanotubes. The color of the dispersions was changed before and after centrifugation (Supporting Information, Figure S1). The color of the pristine sample was dark, whereas that of the centrifuged sample was yellow. This color change can be reflected in the optical absorption. Figure 2A shows the optical absorption spectra of the WS$_2$ nanotubes obtained at different g-forces. We observed a clear blueshift in the A-exciton peak position with the increase in the g-force (Figure 2B). This blueshift is similar to that observed for the thickness sorting of TMDC sheets. The narrowing of the bandwidth of the A-exciton optical absorption and the blueshift of the peak position suggest the extraction of thinner nanotubes with improved homogeneity by centrifugation.

To clarify this point, we tried to identify the structure of the samples using transmission electron microscopy. Figure 3A shows the typical TEM images of the pristine sample and samples after 500, 1000, and 2000 g (see Supporting Information, Figure S2 for others). Figure 3B shows the histograms of the diameter of the samples shown in Figure 3A (see Supporting Information Figure S3 for others). The pristine and stability. This stability of dispersions using nonionic surfactants was confirmed by multiple measurements. The dispersions using nonionic surfactants were preserved for more than 10 days (Figure 1C). Thus, we concluded that nonionic surfactants are the most appropriate dispersants for WS$_2$ nanotubes.

Such a stable dispersion enables us to apply a solution-based purification. Here, we used a centrifugation technique to separate nanomaterials under the centrifugation force based on the difference in the sedimentation, which reflects the size of the diameter and the number of walls of the nanotubes. First, we adjusted the centrifugation conditions. We chose Triton X-100 among the nonionic surfactants for the following experiments because of its easy thermal removal. The removal of surfactants is important for identifying structures by transmission electron microscopy (TEM) techniques. The dispersions using 1% Triton X-100 were prepared through centrifugation at different g-forces ($50$–$2000$ g) for 60 min using a swinging bucket rotor (50 mL centrifugation tube) and centrifuge, and the top 60% of the supernatant was collected.

We found that the color of dispersion was changed before and after centrifugation (Supporting Information, Figure S1). The color of the pristine sample was dark, whereas that of the centrifuged sample was yellow. This color change can be reflected in the optical absorption. Figure 2A shows the optical absorption spectra of the WS$_2$ nanotubes obtained at different g-forces. We observed a clear blueshift in the A-exciton peak position with the increase in the g-force (Figure 2B). This blueshift is similar to that observed for the thickness sorting of TMDC sheets. The narrowing of the bandwidth of the A-exciton optical absorption and the blueshift of the peak position suggest the extraction of thinner nanotubes with improved homogeneity by centrifugation.

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sample exhibited a wide diameter distribution from 25 to 300 nm. As the g-force increased, the diameter distribution became narrower and the mean diameter became smaller. This fact indicates an improvement in the uniformity of the samples and thinning of the mean diameter of the nanotubes in the sample. The mean diameter decreased as the g-force increased, and then we obtained nanotubes with a mean diameter of 32 nm (Figure 3C). Figure 3D shows the histograms of the wall numbers of the nanotubes contained in the samples after 500, 1000, and 2000g. We found that the wall number also decreased as the g-force increased, and we obtained nanotubes with a mean wall number of 13 (Figure 3E). There is a close correlation between the diameter and wall number (inner diameter) of the centrifuged samples (Supporting Information, Figure S4), and both the distributions became narrow in association with the g-forces (Supporting Information, Figure S5). On the other hand, the length was not sorted through the centrifugation process because the large distribution of length of nanotubes was almost the same before and after centrifugation (Supporting Information, Figure S6). This result means that the diameter and wall number can be sorted without serious shortening of the length.

Figure 2. Optical measurements of the WS₂ nanotubes. (A) Optical absorption spectra of the pristine and centrifuged WS₂ nanotubes. (B) A-exciton wavelength plotted as a function of the g-force.

Figure 3. Structure evaluation of the WS₂ nanotubes. (A, B) Typical TEM images (A) and diameter histogram (B) of the pristine WS₂ nanotubes. Scale bar is 20 nm. (C, D) Typical TEM images (C) and diameter histogram (D) of the centrifuged WS₂ nanotubes. Scale bars are 20 nm. (E) Mean diameter plotted as a function of the g-force. (F) Wall number histogram of the centrifuged WS₂ nanotubes. (G) Mean wall number plotted as a function of the g-force.
Here, we discuss the difference in the dispersibility of the WS2 nanotubes with ionic and nonionic surfactants. The density of surfactant-wrapped WS2 nanotubes can be lowered by adsorption of a surfactant and formation of a hydration layer, which slows their sedimentation rate and stabilizes their dispersion. Since the water in the hydration layer typically has the lowest density among the components, the hydration layer thickness significantly contributes to the decreased density. Nonionic surfactants have a relatively large molecular hydrophilic segment (e.g., poly(ethylene oxides) for the nonionic surfactants used in this study, except for PVP) compared to ionic surfactants, which accompany the thick hydration layer. According to the previous estimation for MoS2 sheets,23 even if the surface coverage by the nonionic surfactant Pluronic (42.5%) is lower than that by ionic SC (94%), the Pluronic surfactant can decrease the density of the surfactant-wrapped MoS2 more than SC because of its thicker hydration layer (20.6 nm) than that of SC (3.3 nm). It is thought that the surfactant wrapping on WS2 nanotubes is similar to that of the sheets because of their relatively large curvature radius. Therefore, a thick hydration layer accompanied by nonionic surfactants would contribute to a stable dispersion of WS2 nanotubes. This physical background could be the reason why the nonionic surfactants are appropriate for stable dispersions of WS2 nanotubes.

The relationships between the structure of the WS2 nanotubes and the A-exciton peak position were clarified in this study. Figure 4A shows the relationships between the mean diameter, D and A-exciton peak wavelength, λ. Here, we used the wavelength of the samples dispersed in methanol (Supporting Information, Figure S7) that were used in the TEM observation. We found that λ logarithmically increases with the diameter and wall number of the nanotubes, which is consistent with the empirical raw observed in TMDC sheets.17 By fitting the data, we experimentally determined the following relationships between D and λ.

\[
D = 8.02 \times 10^{-10} \exp(\lambda/25.6)
\]

This equation allows us to roughly estimate the diameter of the WS2 nanotubes from the optical measurements. Additionally, λ is related to the bandgap of the WS2 nanotubes, and this equation suggests that the bandgap increases with a decrease in D. This is possibly due to the decrease in the wall number, which results in a decrease in the bandgap, as expected theoretically.25

Applicable g-forces are strongly dependent on the used pristine sample. For this pristine sample, the obtained sample decreased as the g-force increased and became a tiny amount after centrifugation at 1000 and 2000g due to sedimentation of almost all samples. However, even the sample obtained at 200g is still thick compared to the TMDC sheets, when the pristine sample contains thin nanotubes more, higher g-force can be applicable.

Multistage centrifugation26 was performed for comparison (see Supporting Information, Figure S8). Changes in the optical absorption spectra were almost the same as the changes observed in the normal centrifugation (Figure 2A). With regard to the A-exciton peak (Supporting Information, Figure S9) and optical absorption line shapes (Supporting Information, Figure S10), the multistage centrifugation (50g for 60 min + 100g for 60 min + 200g for 60 min + 500g for 60 min) achieved almost the same result as that obtained by the normal centrifugation (1000g for 60 min). Therefore, multistage centrifugation is also available for sorting WS2 nanotubes.

## CONCLUSIONS

In this study, we established how to stably disperse WS2 nanotubes using nonionic surfactants and demonstrated a method to extract WS2 nanotubes with a relatively small diameter and wall number through centrifugation. The nonionic surfactants result in better dispersions than the ionic surfactants. The stable dispersion enabled us to sort WS2 nanotubes using centrifugation techniques. The diameter and wall number of the WS2 nanotubes gradually decreased as the centrifugation g-force increased, and we successfully obtained thin and uniform nanotubes with a mean diameter of 32 nm and mean wall number of 13. Furthermore, we clarified the relationships among the diameter, wall number, and A-exciton peak wavelength, which enabled us to estimate the structure of the WS2 nanotubes from the optical measurements. We believe that the preparation of thin and uniform TMDC nanotubes will play an important role in clarifying the basic properties of WS2 nanotubes and their electronic applications.

## ASSOCIATED CONTENT

1. Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b00745.

Color of the pristine and centrifuged WS2 nanotubes (Figure S1); typical TEM images of the centrifuged WS2 nanotubes (Figure S2); diameter histograms of the
centrifuged WS$_2$ nanotubes (Figure S3); relationship between the diameter and wall number and between the outer diameter and inner diameter of the centrifuged WS$_2$ nanotubes (Figure S4); standard deviation of the structure of the centrifuged WS$_2$ nanotubes (Figure S5); typical SEM images of the pristine and centrifuged WS$_2$ nanotubes (Figure S6); optical measurements of the WS$_2$ nanotubes dispersed in methanol (Figure S7); optical absorption spectra of the pristine and centrifuged WS$_2$ nanotubes through multistage centrifugation (Figure S8); comparison of A-exciton wavelength of the centrifuged WS$_2$ nanotubes (Figure S9); comparison of optical absorption spectra of the centrifuged WS$_2$ nanotubes (Figure S10) (PDF)

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**Notes**
The authors declare no competing financial interest.

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