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Synthesis and sorting of inorganic nanotubes

Tungsten disulfide (WS_2) nanotubes, which were discovered in 1992 [1], are one of inorganic nanotubes with a cylindrical multiwall structure of WS_2 sheets. WS_2 nanotubes are semiconducting nanomaterials regardless of how they are rolled and have advantages in semiconductor applications compared to carbon nanotubes containing metallic nanotubes that cause bottleneck for semiconductor applications. The band structure of WS_2 nanotubes depends on the nanotube structure such as the diameter and wall number. Especially, theoretical studies expected that the band structure of small diameter WS_2 nanotubes is distinct from that of the two-dimensional WS_2 due to a curvature effect along the rolled WS_2 sheets, which provides the unique properties such as the tunability of the band gap, carrier mobility, and thermoelectric properties. Thus, it is important to clarify the physical properties of the small diameter nanotubes or its structure dependence experimentally. However, the production of small diameter nanotubes is still challenging and relatively large diameter nanotubes (usually ~100 nm) have been used in various applications including field effect transistors [2,3] and thermoelectric devices [4]. Thus, techniques to prepare WS_2 nanotubes with the uniform structure and small diameter are highly desired.

In this study, we report two approaches to prepare such structure-controlled inorganic nanotubes. One is the post-synthetic sorting of WS_2 nanotubes using a solution process, which is often used for the purification of nanomaterials. The solution process is not usually used for WS_2 nanotubes due to their less solubility in solvent. Here we investigate how to disperse WS_2 nanotubes using surfactants and applied the obtained dispersion to the centrifugation process. The other approach is the synthesis of small diameter nanotubes from solution-synthesized precursor nanowires. WS_2 nanotubes are synthesized from tungsten oxide nanowire precursors [5]. Thus, the use of small diameter precursors mostly results in the production of small diameter nanotubes. The solvothermal synthesis is known to have advantages in the production of small diameter precursors [6], but there are few studies using the synthesized WS_2 nanotubes and thus the properties are little known. Here we investigate the suitable synthetic condition and clarify the utility of the synthesized sample for macroscopic transistor channels.

The sorting of WS_2 nanotubes was performed through the centrifugation process of the dispersion. Through a systematic investigation using various surfactants, we found that non-ionic surfactants that have hydrophobic and non-ionic hydrophilic parts in the molecule are suitable for dispersion of WS_2 nanotubes. Stable dispersion enables us to sort the diameter and wall numbers by changing the *g*-forces during centrifugation. Thus, we successfully obtained the WS_2 nanotubes with a mean diameter of 32 nm and mean wall number of 13. The sorted sample has narrow diameter distributions and small diameters in comparison to the original pristine sample (124 nm in mean diameter) (Figure 1a, [7]). Furthermore, we found that the optical absorption wavelength shifts depending on the applied *g*-forces (Figure 1b, [7]). This spectral shift correlates to the nanotube structure, which allow us to estimate the structure of WS_2 nanotubes from the optical measurements.

The synthesis of WS_2 nanotubes was performed via the solvothermal synthesis of tungsten oxide nanowires from WCl_6, followed by the sulfurization of the nanowires. The formation of WS_2 nanotubes was optimized by changing the temperature during sulfurization. We found the proper temperature range, where the nanowires are converted to WS_2 nanotubes without the collapse of the original small-diameter structures. Thus, we successfully obtained relatively small diameter WS_2 nanotubes with a mean diameter of 20 nm and mean wall number of 9 (Figure 2a, [8]). Furthermore, to investigate the utility as semiconductor applications, transistor characteristics of the synthesized WS_2 nanotubes were measured using an ionic-liquid gated transistor configuration. The transistors of the network film exhibited clear ambipolar operation with an on/off ratio $>10^3$ and mobility of >1 cm^2 V^{-1} s^{-1} (Figure 2b, [8]). We discuss effect of the nanotube structure on the transistor performance.

We believe that this study will accelerate the use of inorganic nanotubes with relatively small diameters and narrow structure distributions for the investigation of the unique nature of one-dimensional tube-like.

References

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Figures

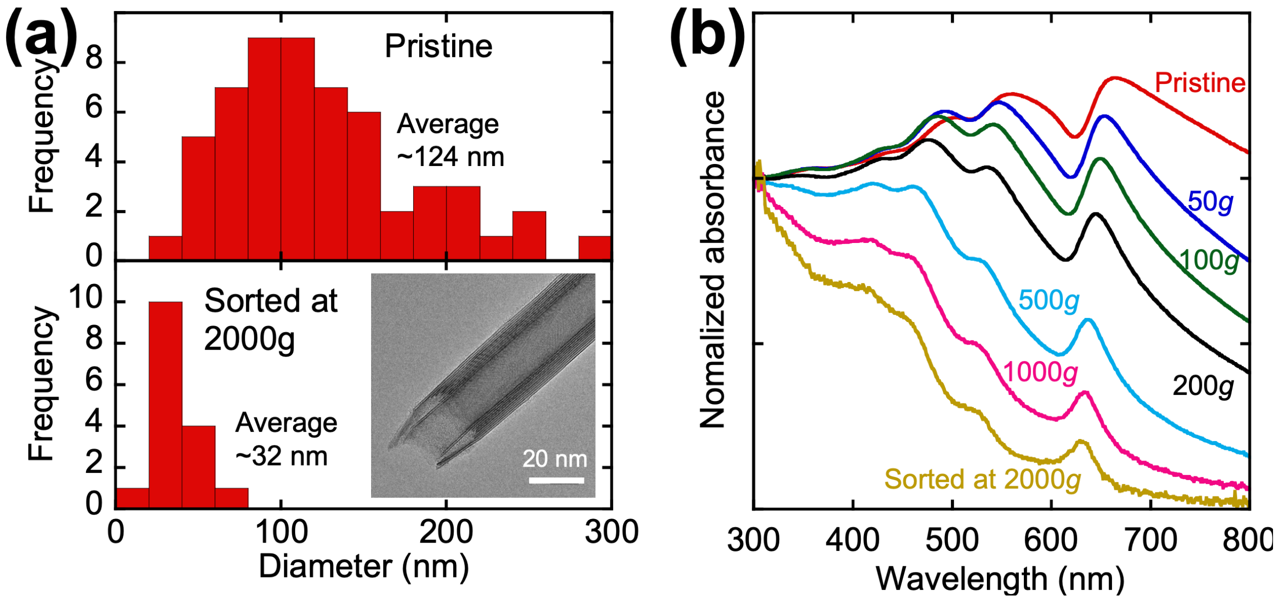

Figure 1: Sorting of inorganic nanotubes. (a) Diameter distribution of the pristine (top) and sorted WS_2 nanotubes (bottom). The inset represents a typical TEM image of the sorted WS_2 nanotubes. (b) Optical absorption spectra of the pristine and sorted WS_2 nanotubes.

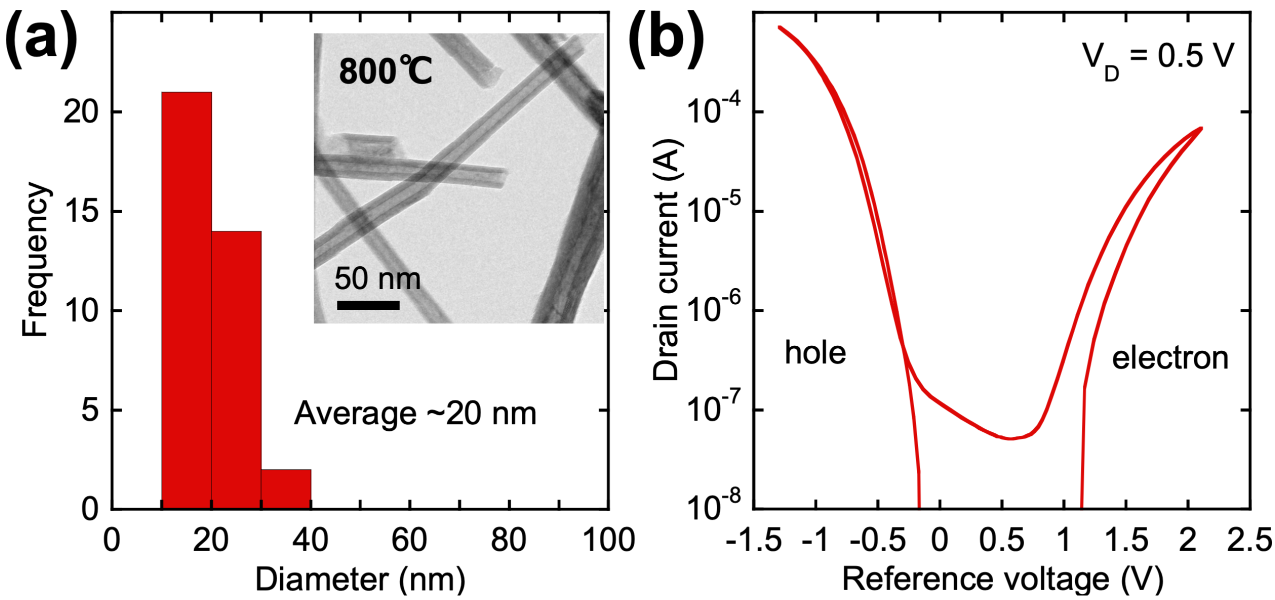

Figure 2: Synthesis of inorganic nanotubes. (a) Diameter distribution of the synthesized WS_2 nanotubes. The inset represents a typical TEM image of the synthesized WS_2 nanotubes. (b) Transistor characteristics of the network film of the synthesized WS_2 nanotubes.