

Multi-layered Copper Foil Reinforced by Co-deposition of Single-Walled Carbon Nanotube based on Electroplating Technique

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Abstract

For the realization of high-performance power electronics, further improvements to thermal and electrical conductivities are required. Although much effort has been put into revealing the excellent physical properties of SWCNTs in conventional Cu-based materials, the aggregation/bundles of SWCNTs induced by strong van der Waals interaction complicates the preparation of Cu/SWCNT and has been still challenging to solve. In this work, we tried to prepare Cu/SWCNT composites using an electroplating technique based on co-deposition. Utilizing not only cationic surfactant trimethyloctadecylammonium chloride (STAC) but also an atomization process involving shear stress, SWCNTs were successfully immobilized inside a Cu metal matrix to form a Cu/SWCNT sheet without significant loss of crystallinity for SWCNTs, which was confirmed by using Raman spectroscopy. A multi-layered Cu-Cu/SWCNT-Cu foil with an intermediate thickness of 4 μm exhibited higher mechanical properties of 519 MPa strength and approximately 10% elongation compared to that of an electroplated Cu foil without SWCNTs. This is probably because cross-linking SWCNTs strongly immobilized between Cu crystals suppressed further crack generation by increasing fracture resistance. The obtained results indicate that this electroplating method is a promising way to prepare Cu/SWCNT composites.

1. Introduction

The development of metal/single-walled carbon nanotube (SWCNTs) composites in which CNTs are homogeneously dispersed have attracted much attention as excellent thermal and electrical conductors.^{1,2} The motivation comes from not only the physical properties but also the greater mechanical properties such as Young's modulus (~1000 GPa) and tensile strength (~37 GPa) compared with steel. The introduction of SWCNT inside a Cu metal matrix has been studied as a high-performance heat dissipation material and an ultralight electric wire.^{3,4} There is, however, the critical issue that SWCNTs undergo aggregation/bundles by strong van der Waals interaction making homogeneous dispersion difficult.⁵ Strategies for the developments of metal/SWCNTs are mainly classified into the following: roll-to-roll⁶⁻⁸ and metallurgical method^{9,10} followed by heat treatment. On the other hand, we have produced Cu/multi-walled carbon nanotube (MWCNTs) composite substrates by using an electroplating technique.¹¹⁻¹³

During the preparation, the immobilization of MWCNTs on the substrate by metal electrodeposition takes place and the dispersibility of MWCNTs in an electroplating bath significantly determines its amount in the matrix. Although sodium dodecyl sulfate (SDS), sodium dodecyl benzene sulphonate (SDBS), and sodium deoxycholate (DOC) function as a dispersant in pure water (pH 7)⁵, they do not work in acid-based electroplating baths. In this study, the effect of dispersibility on the deposition morphology of Cu/SWCNT in acid-based electroplating baths was studied. In addition, we prepared multi-layered Cu-Cu/SWCNT-Cu foils and investigated their mechanical properties.

2. Experimental details

0.1 g L⁻¹ single walled carbon nanotube (SWCNT, Tuball; OCSiAl) with approximately 1.8 nm-diameter and 10 μm-length was dispersed in deionized water using 0.3 mM trimethyloctadecylammonium chloride (STAC) as the dispersant. Prior to the dispersion, an Fe catalyst used for SWCNT synthesis was removed by using a diluted HCl solution. For atomization of bundles formed by strong van der Waals interaction, a wet-type jet mill (Nanovater; YOSHIDA KIKAI Co., Ltd.) was applied one to one hundred times. The atomization degree was investigated by using a laser diffraction particle size analyzer (SALD-7000; SHIMADZU). High resolution observation of the SWCNTs was performed by a field emission electron microscope (TEM; JEM-2100F, JEOL Co., Ltd.). The suspension was added to a Cu electroplating bath consisting of 0.85 M CuSO₄ + 0.55 M H₂SO₄ without a brightening (leveling) agent and then ultrasonically agitated for 15 min. Co-deposition of Cu/SWCNT was conducted without stirring at room temperature under a constant current density of 20 mA cm⁻² for 22.5 min corresponding to 27 C cm⁻² and 2 μm thickness, respectively (Figure S1).

3. Results and discussion

Without atomization of SWCNT bundles formed by strong van der Waals interaction, it is difficult to reveal the characteristics of SWCNTs such as tensile strength and Young's modulus on composite materials. Although the introduction of hydrophilicity groups such as sulfone groups, carboxyl groups, and amino groups by a chemical method is an effective way to achieve dispersion, it induces defects and thereby inevitably results in decrease in electrical conductivity due to the reduction of sp² carbon. The use of DOC is widely known as a good dispersant.⁵ Because an acid-based solution below pH 3 results in a gel due to the addition of DOC, we therefore searched for

a suitable surfactant and finally found that STAC acts as a dispersant for SWCNTs even in the Cu electroplating bath (0.85 M CuSO₄ + 0.55 M H₂SO₄). For more atomization, we considered combining with mechanical atomization.¹⁴

Figure 1a displays the particle size distribution of SWCNTs in the electroplating bath before and after mechanical atomization, showing dispersibility. Using a 0.3 mM STAC, the suspension became visually stable and it did not separate until 24 h without mechanical atomization, but the SWCNT settled out after that (not shown here). By performing the process 100 times, bundles were successfully raveled though a slight amount of aggregation was observed and good dispersibility was maintained after 96 h (4 days). This is supported by Raman spectroscopic analysis and HR-TEM observation: the *G*⁻ feature¹⁵ (1590 cm⁻¹) originating from in-plane vibration along the circumferential axis was emphasized and the diameter of the bundle decreased from 24.6 nm to 4.6 nm, which is very close to the nominal value (1.8±0.4 nm). The crystallinity denoted as the intensity ratio of D band to G band (*I*_D/*I*_G) was little changed even after the atomization (Figure S2). We prepared a multi-layered Cu foil with high mechanical strength using the finely disintegrated SWCNT (Figure 2). The structure of the multilayer consists of Cu/Cu-SWCNT/Cu and the thickness is 4/2/4 μm (total: 10 μm). In the case of using SWCNT without atomization, it was clear that SWCNTs are co-deposited with Cu (Figure 2b). Considering the results of ζ potentials, STAC surfactants give a positive charge to the SWCNT due to the adsorption of the quaternary ammonium cation formed by the dissociation, and thereby promoting co-deposition of SWCNTs due to the resulting attractive force between the cathode (substrate) and SWCNT during electroplating (Figure S3). As for using SWCNT with an atomization treatment, however, we could not detect the SWCNT from FE-SEM image (inset) though the G band suggests the existence of a CNT was observed at Raman spectra of middle layer surface. This is because

the size of the finely dispersed SWCNTs exceeds detection limit of FE-SEM. Multi-layered Cu foils show flexibility regardless of the atomization treatment.

The mechanical properties of the multi-layered Cu foil were evaluated (Figure 3). Electroplated pure Cu foil without a SWCNT showed lower tensile strength of 301 MPa than that of the Cu/SWCNT-Cu/Cu composite without atomization treatment. By using disintegrated SWCNTs, 413 MPa was attained, which also indicates the existence of SWCNTs inside middle layer. The influence of the thickness of the SWCNT/Cu middle layer on the mechanical properties were investigated in which the total thickness was unified to 10 μm . Compared to the system with a middle layer of 2 μm , significantly improved properties of 519 MPa strength and an approximately 10% elongation rate were achieved at 4 μm -Cu/SWCNT middle layer. In the cross-sectional FE-SEM image of the fractured part in the multi-layered composite (4 μm), SWCNTs were observed. It is considered that cross-linking SWCNT strongly immobilized at the Cu surface suppressed further crack generation by increasing fracture resistance (Figure 3c). **The significance in this study is the preparation method with only one step process by co-deposition of Cu and SWCNTs even using an aqueous-based electroplating bath. The developed method does not require high temperature and high pressure unlike a metallurgical method and can be employed under room temperature and normal pressure, which is great advantage when considering industrial manufacturing process.¹⁶ We can immobilize CNTs by co-deposition regardless of type of metal as an underlayer. As well as underlayer, it is applicable to other co-deposited metal.¹⁷** The optimization of diameter and length of the SWCNT should be effective to upgrade the mechanical properties.

4. Summary

The mechanical properties of multi-layered Cu foil composites were reinforced by co-electrodeposition of SWCNTs. When used in conjunction with an atomization process and surfactants (dispersants) to disintegrate the SWCNT bundle, increased toughness was granted to the Cu foil: tensile strength and elongation percentage were successfully improved up to 1.7 and 3.9-folds, respectively compared to electroplated pure Cu foil.

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Figure captions

Figure 1. (a) Particle size distribution of SWCNT in deionized water cationic with 0.3 mM surfactant (STAC) after atomization at several conditions. HR-TEM (b) images and Raman spectra (c) of SWCNT before and after the atomization (100 times).

Figure 2. (a) FE-SEM images of electrodeposited Cu and Cu/SWCNT composite at each layer. (b) Photographs of the composite foil. Cu film (4 μm) was formed on a SUS304 substrate and then co-deposition of Cu/SWCNT (2 μm) was conducted. Finally, Cu electroplating (4 μm) was performed to prepare multi-layered Cu foil followed by exfoliation from the SUS.

Figure 3. (a) Stress-strain curves of electroplated Cu foil and multi-layered Cu foil prepared by co-electrodeposition. (b) Influence of Cu/SWCNT (middle layer) thickness on strength of Cu-based foils. Tension rate in this evaluation was set to 1 mm min^{-1} . (c) Schematic illustration of improved mechanism of mechanical properties for the multi-layered Cu foils. Inset: cross-sectional FE-SEM image of fractured part of after the mechanical test.

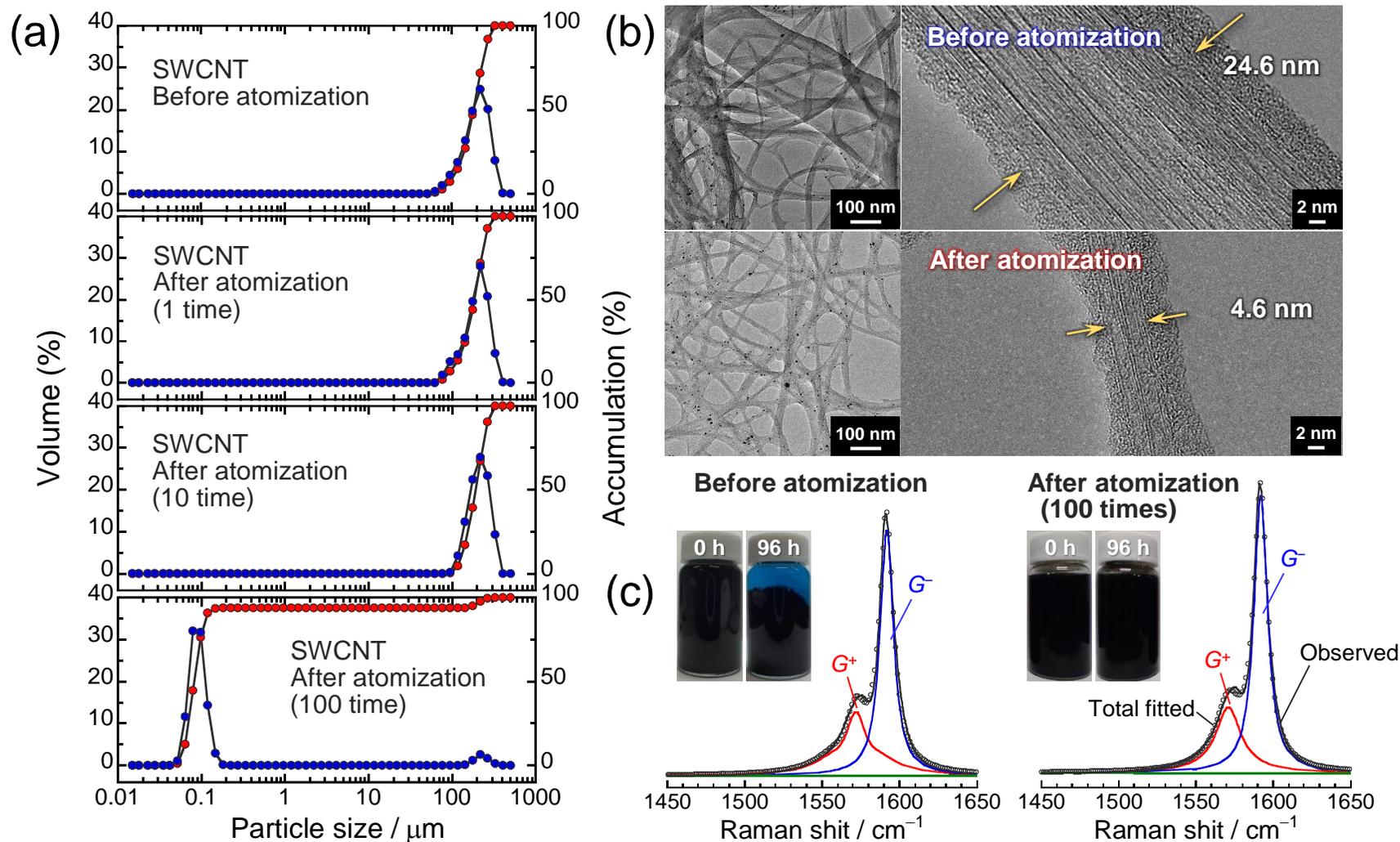


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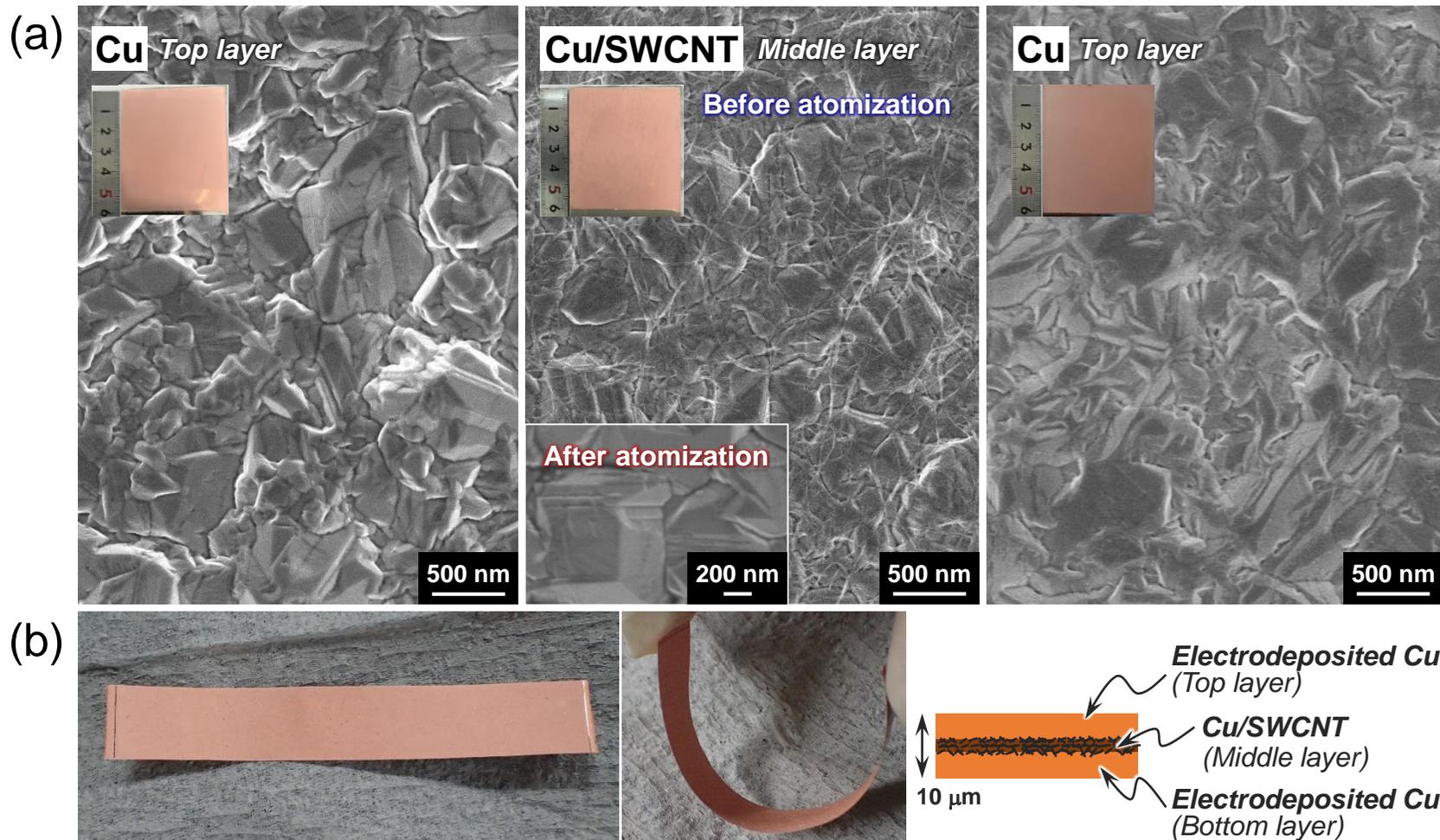


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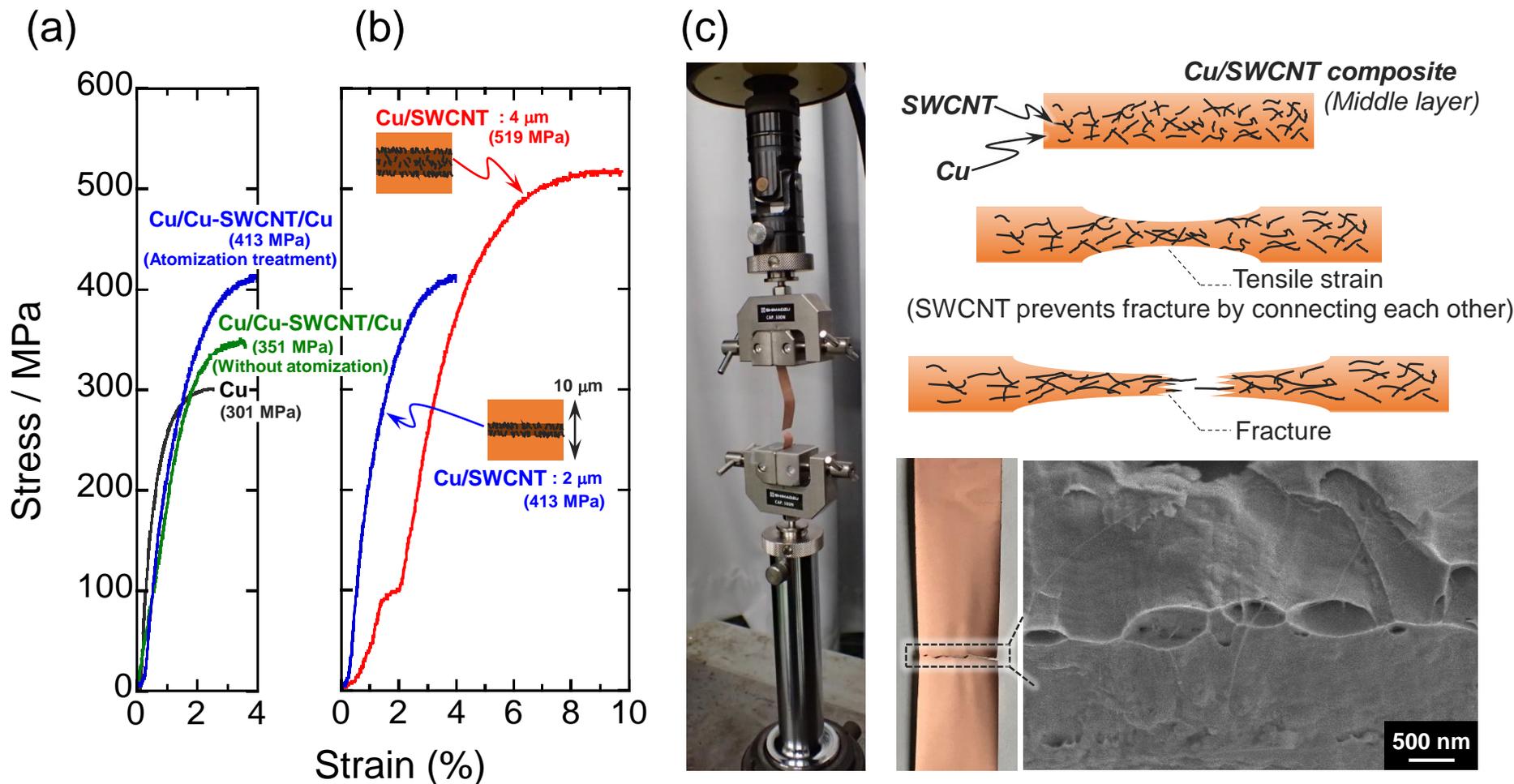


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