Edited by Kun'ichi Miyazawa

FULLERENE NANO-WHISKERS

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Chapter 1

INTRODUCTION TO FULLERENE NANOWHISKERS

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Fine fibrous precipitates of C_{60} were discovered in 2001 in a colloidal solution of lead zirconate titanate containing C_{60}. Those fine solid fibers of C_{60} were identified as single-crystal C_{60} nanofibers and named "C_{60} nanowhiskers." The synthetic method of preparing C_{60} nanowhiskers — the liquid–liquid interfacial precipitation method — was soon developed and has been widely used to prepare various fullerene nanowhiskers of C_{70}, C_{60} derivatives, and C_{60}. The liquid–liquid interfacial precipitation method is applicable to preparing tubular fullerene nanofibers (fullerene nanotubes), C_{60} nanosheets, and low-dimensional fullerene nanomaterials containing various metals and chemicals. This introductory chapter gives an overview of the synthetic method, the crystallographic structure, and the mechanical, thermal, electrical, and chemical properties of fullerene nanowhiskers and fullerene nanotubes and their application.

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1.1 WHAT IS A FULLERENE NANOWHISKER?

Lead zirconate titanate (PZT) is a well-known ferroelectric ceramic material widely used in sensors and actuators. PZT thin films are often used in microelectromechanical systems such as microcantilevers.[1] Since the non-ferroelectric pyrochlore phase of PZT appears at low-temperature calcination, it was necessary to find a method to suppress the formation of the pyrochlore phase.

It was known that the vacuum annealing of pyrolized amorphous PZT gel enhances the growth of the perovskite phase by suppressing the formation of the pyrochlore phase.[2] Hence, C_{60} was expected to act as a scavenger for oxygen and suppress the formation of the pyrochlore phase. In fact, it was found that the temperature at which the perovskite phase is formed can be lowered to 400°C from 600°C when a PZT sol containing C_{60} is used to fabricate PZT thin films.[3]

Furthermore, we noticed fine fibrous precipitates formed in the C_{60}-added PZT sol as shown in Fig. 1.1. These fibrous precipitates were found to be single-crystal nanofibers composed of C_{60} and were named "C_{60} nanowhiskers" (C_{60}NWs).[4]

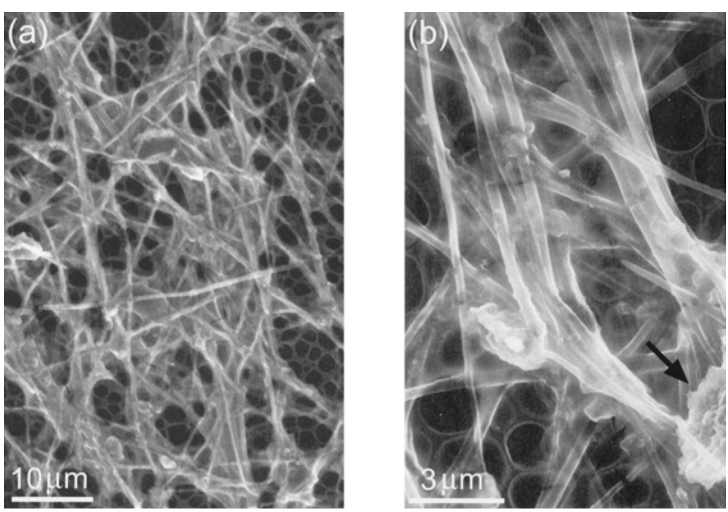

Figure 1.1 (a) Scanning electron microscopy (SEM) image of the C_{60}NWs formed in a PZT sol containing C_{60}. The arrowed part of (b) shows a piece of PZT gel.[4]

The term "C_{60} whisker" was first used by Yosida in 1992.[5] However, the reported C_{60} whisker had a diameter greater than 1 μm and a rugged surface.

A synthetic method for preparing C_{60}NWs with smooth surfaces was soon developed after the discovery of C_{60}NWs. This method was named "liquid–liquid interfacial precipitation method" (LLIP method).[6] Figure 1.2 shows an example of C_{60}NWs synthesized by the LLIP method.

Particles with an aspect ratio (length to diameter) of greater than 3 are defined as fibers.[7] Fullerene nanowhiskers (FNWs) are crystal thin solid fibers that are composed of all species of fullerene molecules, i.e., C_{60}, C_{70}, endohedral fullerenes, fullerene derivative molecules with functional groups, and so forth. FNWs have diameters less than 1000 nm and are usually single crystals.

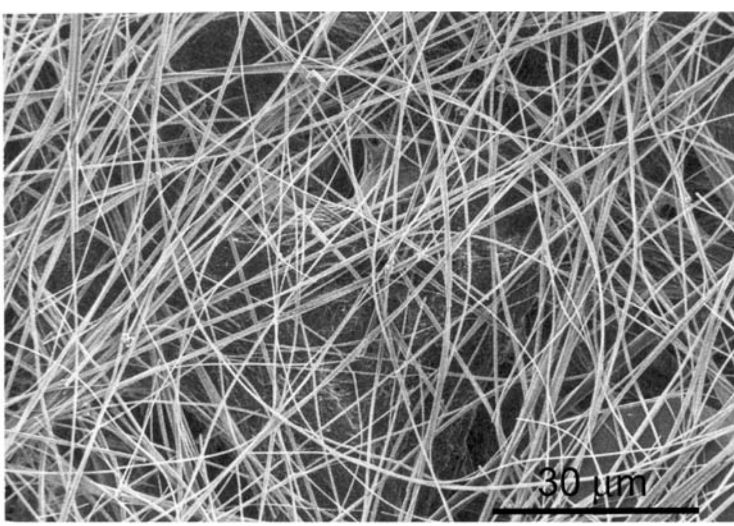

Figure 1.2 SEM image of the C_{60}NWs synthesized by the liquid–liquid interfacial precipitation method.

On the other hand, fullerene nanotubes (FNTs) are thin fibers with tubular morphology and have diameters of less than 1000 nm. FNTs are literally composed of fullerene molecules and can take single-crystal, polycrystalline, or amorphous structures.

FNWs and FNTs can be collectively called "fullerene nanofibers" according to the above definition of fibers. The term "fullerene nanowhisker" is sometimes also called "fullerene nanorod." Although the terms "fullerene nanorod," "fullerene nanowire," "fullerene nanoribbon," "fullerene nanobelt," and so forth are occasionally used, they can all be classified into the category of "fullerene nanofiber."

This introductory chapter reviews the synthetic method and the crystallographic, mechanical, thermal, electrical, and chemical properties of FNWs and FNTs. This chapter also discusses various other forms of fullerene nanomaterials such as fullerene nanosheets.

1.2 THE LLIP METHOD

Fullerene nanofibers (FNFs) with various components and compositions can be synthesized by using the LLIP method, where a poor solvent of fullerene is added to a good solvent solution of fullerene. The mixing order of two liquids can be changed. Alcohols such as ethanol, isopropyl alcohol (IPA), and isobutyl alcohol are often used as the poor solvents, while toluene, *m*-xylene, benzene, CCl_4, and so forth are used as the good solvents of fullerenes. The liquid–liquid interface formed between a fullerene-saturated good solvent and a poor solvent provides the heterogeneous nucleation sites of fullerene crystals; i.e., the poor solvent plays the role of a nucleation agent.

An example using the LLIP method to synthesize C_{60}NWs is as follows:[6] 5 mL of toluene solution saturated with C_{60} is put in a transparent glass bottle, and 5 mL of IPA is slowly added to the toluene solution to form a liquid–liquid interface. The solution temperature is usually set to be lower than 21°C. Fine C_{60} crystals nucleate at the liquid–liquid interface. The glass bottle is capped and stored for a few minutes or more to grow the C_{60}NWs in an incubator. Figure 1.3 shows a transmission electron microscopy (TEM) image of a C_{60}NW synthesized by using the LLIP method.