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In situ transmission electron microscopy studies of nanomaterials' structure-property relationships (review article)

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Abstract

In situ transmission electron microscopy (TEM)-based experiments have shown to be powerful and reliable ways to study nanomaterials. By combining high-resolution TEM characterization and property measurements on a unique platform, scientists can get deep insights of structure-property relationship at the nanoscale. Modern dedicated TEM holders with precise manipulating capability have opened a new realm of possibilities of what can be done under the microscope. This paper aims to highlights the past, present and future of these exciting methods based on in situ TEM in the last decade. The topics of interest include tensile testing of carbon nanotubes, compression testing of nanostructures, and phase transformations in metallic nanoparticles. The key points of all experiments discussed are that the measurement data are acquired on an individual nanostructure level under ultimately high spatial resolution achievable in TEM, and thus can directly be linked to the dynamic structural and physical states of a given nanomaterial. The success of these in situ TEM based analysis should clear up discrepancies in experimental data obtained from indirect measurements of nanomaterials' properties in literature, and allow engineers to design new devices/products corresponding to the real nanomaterials' potentials.

Keywords: Transmission electron microscopy, Nanomaterials, Structure-property relationship, In situ method

1. Introduction

Properties of nanostructured materials have been subjected to numerous studies in the past three decades. Most attentions have been focused on the prospects of nanomaterials' unusual properties. For instance, nanoscale particles are believed to have enhanced strength due to limited number of defects as compared to their bulk counterparts. Tubular forms of a graphite sheet, namely carbon nanotubes, have boasted ballistic electrical transport properties, ultra-high strength, and superplasticity. [1-3] While thousands of research papers have been reported in diverse areas and fields, only limited numbers of industrial applications have emerged. On the one hand, this is due to the difficulty to synthesize uniform shapes and sizes as well as to manipulate nanostructures to the level that mass-production can be realized. On the other hand, property measurement data available in literatures often appear to be scattered among different research groups, depending on different measurement

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techniques and interpretations of their results. These uncertainties have confused practical engineers and prevented major investment in the nanotechnology related industries.

The disagreements of measured properties shown in literature are due to inadequate instruments' capabilities to provide exact analysis of physical and chemical properties of a given nanomaterial, in particular on the individual structural level. In the past, property measurements are performed using techniques with no direct access to the nanomaterial internal structure, such as scanning electron microscopy (SEM) and atomic force microscopy (AFM) [4-7]. These instruments do not provide direct correlation between structure and property of the investigated nanomaterials. For instance, carbon nanotubes and their derivatives that are measured by AFM or SEM-based techniques would show indifferent topographies among a single-walled carbon nanotube (SWNT), a small bundle of SWNTs, filled SWNTs, or a multi-walled carbon nanotube (MWNT). This would lead to different conclusions, and therefore misleading published results.

To date, transmission electron microscope (TEM) may perhaps be the only instrument that can provide high-spatial resolution images of materials, while allowing their mechanical or electrical properties to be measured simultaneously. Unlike typical light microscopes, TEM operates on the basis of electron waves that pass through the sample. With small wavelengths of electrons, TEM provides extremely high resolution images, allowing researchers to inspect objects to the order of a few angstroms (10^{-10} nm). Because of possibilities to achieve high magnifications and high resolutions, TEM has been serving as a vital tool in nanomaterial research. With additions of electron diffraction, energy dispersive X-ray, and electron energy loss spectroscopy capabilities, sets of information on materials' crystallography, chemistry and existing defects, can also be analyzed.

While conventional TEM operations allow researchers to inspect structural details of materials (which normally are the products of synthesis processes or results of experiments that have been done outside the microscope), recent advances in electron microscopy allow ones to conduct experiments inside the TEM's column, called an "in situ TEM" technique. Tremendous efforts and extreme engineering have been made to build dedicated TEM holders during the last decade. The difficulties in this field arise from the limited space within the TEM column. In particular, the pole pieces (where sample has to be placed in between) have an extremely narrow gap of approximately 0.2 mm [8]. Furthermore, the instrument's small depth of focus limits operators from moving a sample around and away from the back focal plane of the electromagnetic lens too much; thus, precise control is needed to manipulate the sample. To date, custom-made holders that incorporate piezoelectric manipulators, precise electrical contacts, and even load cells have been developed. Companies like Nanofactory Instrument AB, Sweden, and Hysitron Incorporation, USA, have been helping to push the design and development forward. Figure 1 shows commercialized TEM holders from these companies.

This review article provides past and current developments of TEM-based measurements of nanomaterials' properties. The author aims to demonstrate the usefulness of exciting in situ TEM techniques. The reviewed topics include indirect mechanical property assessments of carbon nanotubes, direct tensile testing of carbon nanotubes, compression testing of nanostructures, and phase transformations in metallic nanoparticles.

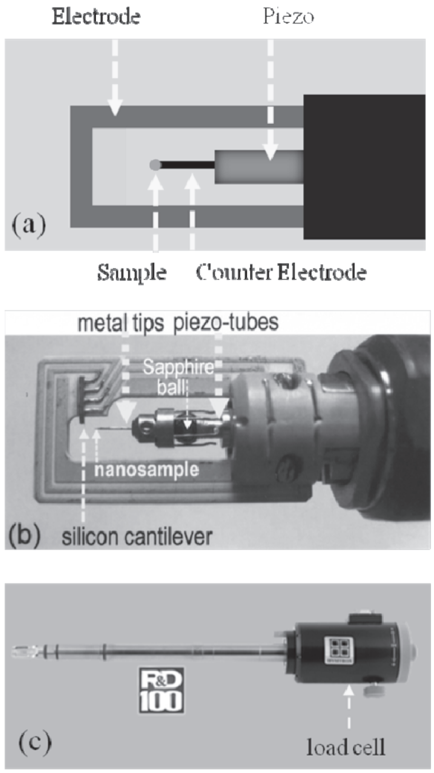

Figure 1 TEM holders for in situ TEM studies (a) schematic representation of main components in custom-designed TEM holder (b) TEM holder incorporating atomic force microscope (AFM) capabilities (c) TEM holder with a load-cell for indentation study ((b) adopted from [9]; (c) adapted from (10))

2. Indirect Property Determinations of Carbon Nanotubes/ Nanowires

2.1 Mechanical Property Assessments through Thermal Vibrations

Carbon nanotubes and metallic nanowires are among highly important one-dimensional structures in early search for promising nanomaterials to have impacts on industrial applications. An early experimental work [11] on mechanical properties of nanostructures such as carbon nanotubes were based on measurements of thermally-actuated vibration amplitudes in TEM. Treacy et al. investigated the vibration of free standing MWNTs at high temperatures [11]. Thermal vibrations of such structures are shown in Figure 2. The vibration amplitude at the tip of MWNTs is related to the thermal vibration energy, which can be approximated through $\langle W_n \rangle = kT$ for each vibration mode, with W_n obeying the Boltzmann distribution. By referring to simple beam mechanic equations, they were able to calculate the Young's modulus of carbon nanotubes, which were found to be in the terapascal (TPa) range.

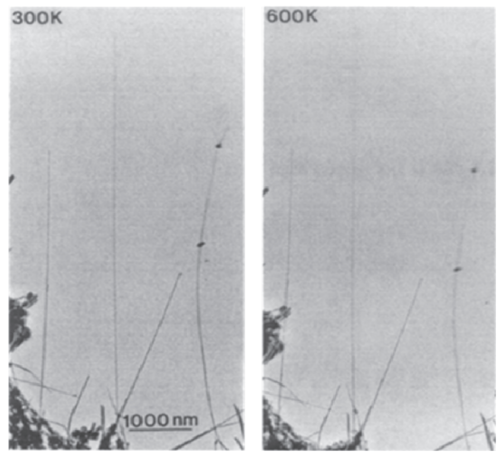

Figure 2 TEM micrograph of free-standing carbon nanotubes showing the blurring at the tips due to thermal vibration at 300K and 600K. [11]

While this technique provides a breakthrough in studying mechanical properties of nanostructures, it has a drawback which is the low accuracy of the measurement. The amplitude of vibration is very small even at high temperature; therefore, the measurement of the vibration is only possible when the specimen is very long.

2.2 Mechanical Property Assessments Through Electrical Induced-Vibrations

Because of uncertainties in thermal vibration amplitude measurements in the technique pioneered by Treacy et al., a new technique to measure mechanical properties of carbon nanotubes was introduced by Poncharal et al. [12]. They built a special TEM holder to allow applications of electrical signals to the sample. The technique is based on the in situ TEM detection of the mechanical resonance vibrations of MWNTs induced by external AC electric field. This technique employs an applied oscillating signal with tunable frequencies to actuate the resonance of the sample.

The nanotube, which behaves like a clamped cantilevered beam, will vibrate when the frequency of the applied oscillating electric force matches its natural resonant frequency (Figure 3). The elastic beam theory was then employed to relate the nanotube's resonant frequency with its dimension and elastic modulus.

The moduli of MWNTs in the experiment by Poncharal et al. were found to be dependent on the diameter, and are in the range between 1 to 0.1 TPa. Not only does this work provide early and rare experimental data on properties of nanomaterials during that time, but it also offered first glimpses of what more can be done with the TEM to study properties of materials at the nanoscale.

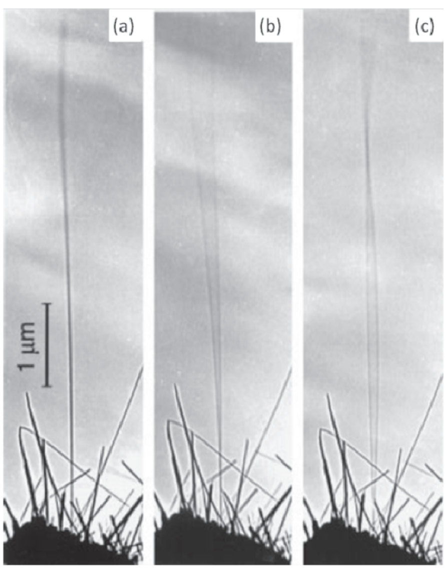

Figure 3 Nanotube response to resonant alternating applied potentials. a) In the absence of a potential b) Resonant excitation of the fundamental mode of vibration (f = 530 kHz), c) Resonant excitation of the second harmonic (f = 3.01 MHz) [12]

3. Direct Tensile Measurements of Carbon Nanotubes

Direct measurements of nanomaterials' mechanical properties were not possible until a major upgrade in the TEM holder's capability had been made by the Nanofactory Instrument AB Company recently. A new special TEM holder was equipped with a piezoelectric-controlled manipulator and a force measurement system. Using such holder, Wang et al. [13] were first to report direct tensile testing of SWNTs. In their experiment they initially picked up MWNTs with a sharp tungsten tip. The tip was then loaded into the TEM holder. Upon inspection in the TEM, a protruding MWNT from the tungsten tip was manipulated until its other end was attached to the other clamping area. To ensure stable clamps on the two tube ends, they performed a "nanowelding process" by focusing electron beam at the clamped ends to enhance adhesion between the MWNT and the tungsten tips. Figure 4 shows schematic representations of this study. A bias of a few hundreds µA was then applied between the tungsten tips causing a shell-by-shell breakdown from the middle of the MWNT. As shown in Figure 4c, the middle section finally transformed into a very thin tube that contained only one layer. The SWNT was pulled while force values were directly recorded using an incorporated force sensor within the holder. The displacement was measured by inspecting the positions of the tungsten tips before and after the test. Wang et al. reported the tensile strength of SWNTs in the range of 25 - 102 GPa [13]. The variations are due to the defects within the structures, which normally include kinks and heptagon-pentagon pairs. The strengths of SWNTs with least defects have been shown to achieve their theoretical limit and are comparable to the values calculated by Mielke et al. using quantum mechanical calculation methods [14].

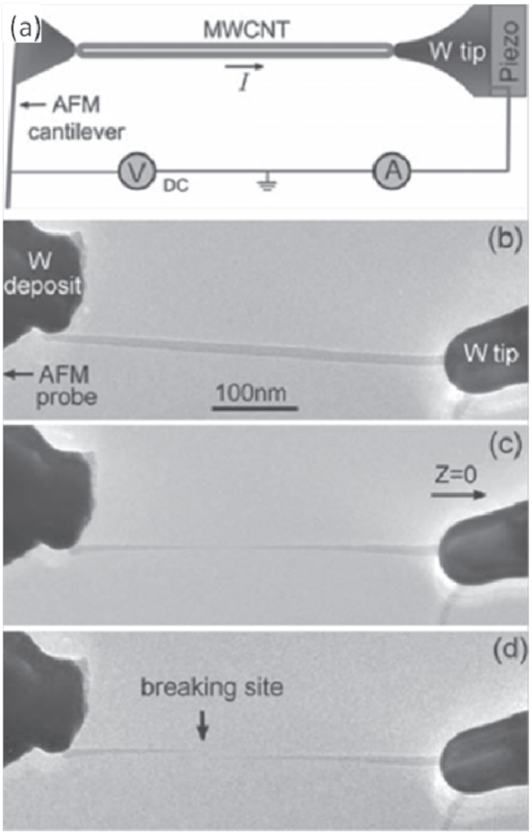

Figure 4 Direct tensile test of carbon nanotubes a) schematic of the experimental measurement inside TEM. b-c) TEM images showing a typical MWNT before and after its middle section transforms into an extremely thin tube under a current flow. d) the tube was tensile stressed and finally broken (adapted from 13)

While theoretical studies predict that nanotubes mechanical properties also depend on their chiralities [14], scientists still need to confirm this notions experimentally. Yet, the study by Wang et al. has shown that actual experimental measurements are clearly catching up with theoretical calculations. Unlike reports made by several groups [4-7, 11-12, 15-16] in the past, this new and direct method to study mechanical properties of nanomaterials has made the analysis of results straightforward and allowed engineers to be able to better perceive the real nanomaterials' potentials.

4. In Situ TEM Nanocompression

4.1 Witnessing Fracture of Nanoparticles

Besides pulling of the nanostructures, in situ TEM nanocompression and nanoindentation have also revealed several new findings in nanomaterial research recently. Using the recently available TEM holder with load cell made by Hisitron Corp., Shan et al. conducted compression tests on individual nanoparticles, while being able to inspect their changes in structures and morphologies, simultaneously [17]. Figure 5 show in situ compression-to-failure test of an individual hollow CdS sphere.

The authors found that their synthesized CdS nanoparticles were hollow and could withstand extreme stresses, approaching the ideal shear strength of CdS. Furthermore, the spherical shells of CdS were able to exhibit considerable deformation to failure (up to 20% of the sphere's diameter). Not only does this experiment show prospects of advanced engineering materials, it also allows scientists to understand the importance of structural hierarchy in controlling mechanical properties of nanoparticles.

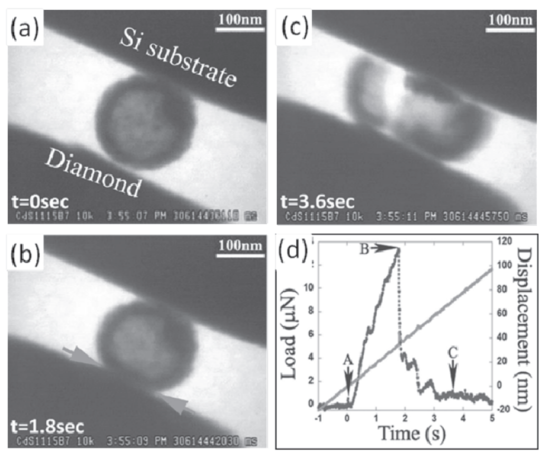

Figure 5 In situ compression-to-failure test of an individual nanocrystalline hollow CdS sphere. (a-c) extracted video frames of the in situ compression test, corresponding to t = 0 s (a), 1.8 s (b), and 3.6 s (c), (d) Load-displacement data from the loading portion of the in situ test versus time (adapted from 17)

4.2 Experimental Proofs for Source-Limited Deformations

It has been widely known for a long time that dislocations within structures play important roles in plastic deformation phenomena in crystalline materials. During the deformation, dislocations are mobile and can be combined with their neighbors. This combination of dislocations gives rise to new multiple sources of dislocations (known as the Frank-Read sources) and causes the materials to further deform [19]. This notion is valid unless the sizes of materials are in the nanoscale. Greer et al. [20] and Nix et al. [21] have proposed that mobile dislocations can escape from the crystal at the nearby surfaces before multiplying and interacting with other dislocations during the deformation process. This leads to a state of dislocation free, causing stiffening in the materials.

While the above notion sounds plausible, actual experimental evidence of source-limited (finite numbers of combined and regenerated dislocations) deformation only becomes available recently. Using Hysitron Corp's load cell-equipped TEM holder, Shan et al. [18] have shown that submicrometer-diameter Ni crystals can be made dislocation-free upon compression—the phenomenon they referred to as "mechanical annealing". Figure 6 shows in situ TEM compression tests on a Ni nanopillar structure. Figure 6(a) shows the dark-field TEM image of the pillar before compression test. It is clear that large amount of dislocations are present within the structure (which appeared as dark bands in the image). The pillar is then compressed causing dislocation to move and escape through the nearby surfaces. Figure 6(b) shows TEM image of the same pillar after the compression, which is now defect-free (as shown by the uniform contrast in dark-field TEM image). This experiment is so unique in a sense that it provides the proof of source-limited deformation event—an event that only occurs in a very small structure, and by far, can only be witnessed by in situ TEM.

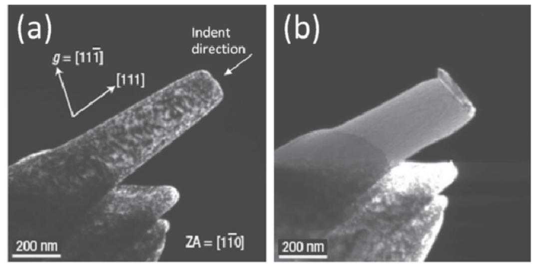

Figure 6 Microfabricated 160-nm-top-diameter Ni pillar (a) Dark-field TEM image of the pillar before the tests showing high initial dislocation density (b) Dark-field TEM image of the same pillar after the first test showing that the pillar is now free of dislocations [18]

5. Phase Transformation of Nanomaterials

Phase-change memory utilized the electric field-induced reversible structural changes between crystalline and amorphous phases to store information in a rapid and nonvolatile manner. Although extensive amounts of research have been carried out in this field, the underlying mechanisms involved in the relationship between structural and electrical properties in phase-change materials are still not well understood. This is because the visualization of electrically-driven structural transition has been experimentally challenging.

Up until only recently have the investigations in phase-change materials been made in greater details. With advanced in situ TEM technique, Golberg et al. have demonstrated real-time visualization of crystalline-amorphous transitions in Fe nanoparticles upon electrical current pulse [9]. Figure 7 shows experimental setups of phase transformation in an Fe nanoparticle encapsulated in a multi-walled CNT. The nanotube is connected to Au and W electrodes. The TEM holder is specially designed so that it allows electrical pulse to pass through to the sample. Figure 7(c-d) show the results of phase-change characteristics of Fe nanoparticles before and after an electrical pulse, respectively. This approach demonstrates the potential to provide new information regarding the dynamic structural and electrical states of phase-change materials at the nanoscale. Further experimental studies are expected to advance the design of future phase-change memory devices.

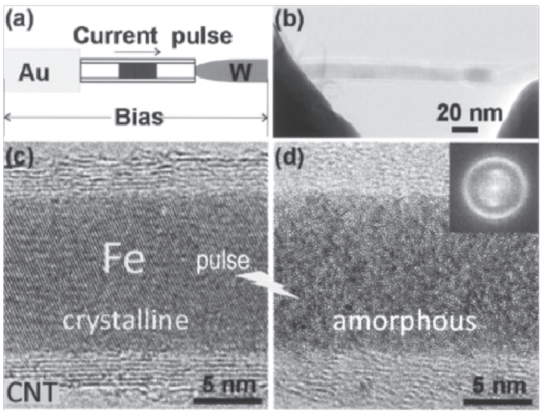

Figure 7 (a) Schematics illustrating a metal filled multi-walled carbon nanotube placed inside the STM-TEM holder and experiencing a short voltage/current pulse; (b) TEM image of the setup; (c) and (d) transformation from a crystalline (c) to amorphous (d) iron wire under an electrical pulse (adapted from 9)

6. Summary and Outlook

To date, in situ TEM technique might be the only Characterization method with appropriate spatial resolution to allow one-to-one correlation between structure and property of nanomaterials. Recent upgrades in TEM holders with specific capabilities allow researchers to discover theoretical strengths, superelacticity, source-limited deformation, and phase-change properties in various materials. In addition to the above-mentioned experimental findings, other properties such as electrical and thermal behaviors of nanomaterials are to be explored for the realization of practical nanoscale devices. Future outlook should also include investigations of structural-optical property relationships, and other combined measurement techniques. For instance, it will be very useful to have the capability to make real-time collections of light absorption and transmission spectra under current flows and/or deformation of materials. To further explore these topics, it will require extreme engineering endeavors ahead to construct TEM holders for such tasks.

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