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# Direct observation of zipper-like wall-to-wall coalescence of double-wall carbon nanotubes

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ABSTRACT

In situ transmission electron microscope (TEM) observation has become a fairly powerful characterization method to uniquely provide the real-time information on the dynamics and kinetics of physical and chemical transformations at the nanometer scale. Here, we report a development of a high-temperature-compatible specimen heating holder equipped with a micro-sized carbon nanotube (CNT) network heater. The CNT network heater can heat samples up to extremely high temperature, as high as >2000 °C, while minimizing the spatial drift of the samples induced by the heating. This has directly led to a real-time imaging of a purely thermally-driven nano-welding process between two parallel-aligned double-wall carbon nanotubes (DWCNTs) using low-voltage TEM (80 keV); a single larger-diameter DWCNT was formed after the reaction and the reaction rate was determined. This technique developed is basically applicable to the in situ TEM study of various thermal-driven solid-phase dynamical changes/reactions and should provide more significant insight on nanoscience and nanothermodynamics.



## 1. Introduction

The study of structural transformations and the related dynamical processes occurring under extremely high temperature (1000 – 3000 °C) have attracted widespread attention due to the presence of underlying novel chemistry [1–3]. Because the high temperature can easily induce a direct bond breaking and formation, the high-temperature-driven reactions have realized formation of novel nanomaterials that are difficult to synthesize by using conventional reactions. For instance, a high-temperature-driven fusion reaction of carbon nanotubes (CNTs) have provided bi-cable structures and various junction structures of CNTs [4,5], and high-temperature fusion reactions in CNTs has realized selective formation of ultrathin boron nitride nanotubes [6], graphene nanoribbons [7], and metal atomic wires [8]. Furthermore, high-temperature annealing of graphene has enabled controlled formation of sharp zigzag and armchair edges [9]. Further development of the high-temperature reactions therefore will open opportunities to explore novel chemistry leading to creation of various materials.

Real-time observation of the high-temperature reactions using in situ TEM have provided a basis for studies on the novel chemistry at extremely high temperature since 1970 [10,11]. In contrast to other structural characterization methods, such as X-ray diffraction, in situ TEM observation provides us real-time and atomic-level structural information in real space, which is essential to understand the kinetics and mechanism of the high-temperature reactions [12–14]. In fact, in situ high-temperature TEM observation has already

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revealed the detailed formation process of diamond nanocrystals [1,15], kinetics of top-down fullerene formation mechanism [16], and nucleation and growth process of CNTs [17].

However, in situ TEM observation at extremely high temperature is still challenging. Using an ordinal commercially available specimen-heating holder, the maximum temperature on TEM observations is so far limited to ca. 1000 °C [13,17–20]. Furthermore, a large spatial drift induced by high-temperature heating prevents researchers from performing a detailed structural characterization on account of limited quality of images and difficulties in following a sample location [18–20]. Therefore, the development of a reliable and high-temperature-compatible (at least up to 2000 °C) specimen-heating holder is of great importance toward improving our knowledge base on the high-temperature reactions of nanomaterials.

Here, we report the development of a new home-made specimen heating technique for in situ TEM applicable to extremely high temperature. The key point here is to utilize CNT networks as a micro-sized heater and sample stage simultaneously, which enables us to achieve the maximum temperature of about 3000 °C while maintaining a small heating-induced spatial drift of the samples. By using the developed technique together with low-voltage TEM (80 keV), we observed, for the first time, detailed reaction dynamics of intrinsic thermal wall-to-wall coaleacence of double-wall carbon nanotubes (DWCNTs) at ~2000 °C, revealing a zipping mechanism with a determined rate.

## 2. Development and fabrication of high-temperature-compatible TEM specimen-heating holder equipped with a CNT network heater

Fig. 1a shows the head part of the TEM specimen-heating holder presently developed, which mainly constitutes of a copper tip, a built-in $Si/SiO_2$ sample substrate and electrical connections. There are two pairs (outer and inner) of thin Pt/Ti electrodes patterned onto the $Si/SiO_2$ substrate. Each pair is separated by a micro-sized slit as shown in Fig. 1b, which allows electron beams to penetrate the substrate. We placed a CNTs network with the same size of the silt (ca. $3 \times 50$ μm) between the two electrodes as a micro-sized heater simply by dielectrophoresis where CNTs are preferentially deposited between electrodes in pairs [21]. On account of these experimental configurations, we can observe samples supported on the CNT network by TEM and characterize structural changes under a wide range of temperature driven by current-induced Joule heating as schemed in Fig. 1c. The network structure of CNTs can support various nanomaterials in an almost free-standing way, which allows one to observe nanomaterials without being affected by underlying support materials. We also employed Au nanoparticles (an average diameter of 40 nm) on the CNT network as nanometer-sized thermometers. Melting of the Au nanoparticles can be used to roughly estimate the local temperature, where the average diameter (ca. 40 nm) of the nanoparticles is large enough to safely avoid size effect of the phase change of Au. Melting temperature of Au nanoparticles with diameter of

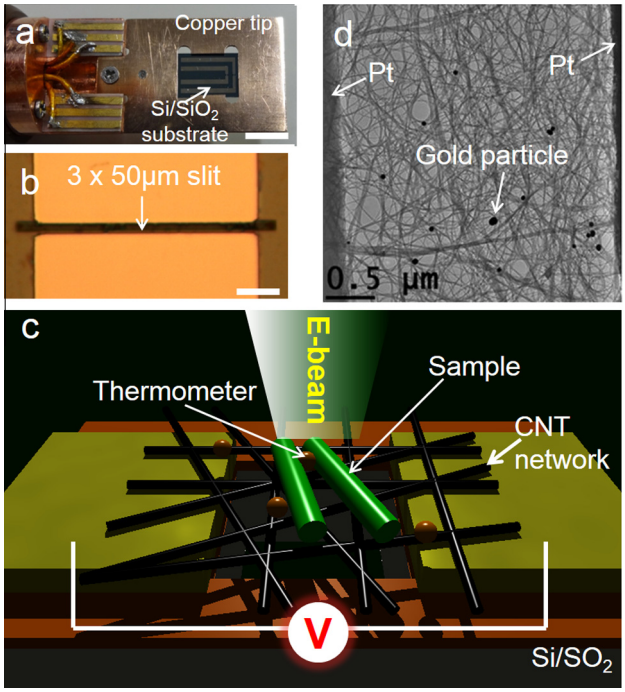


**Fig. 1 – Configuration of the developed specimen-heating holder equipped with a micro-sized CNT network heater. (a) A picture showing the head part of our home-made heating holder. (b) An optical image near the slit region. (c) A schematic of the working principle of high temperature in situ heating TEM. (d) Low-magnification TEM image of the prepared CNT network with deposited gold particles. Scale bars in (a) and (b) are 5 mm and 10 μm, respectively. (A colour version of this figure can be viewed online.)**

20 nm is already almost identical to that of bulk Au [22], and the melting of Au particles was confirmed by shape changes of gold particles and a disappearance of diffraction spots. Fig. 1d is a typical low-magnification TEM image of the CNT network heater, where Au particles (black spots) are seen over the network. Prior to any heating experiments, we performed $H_2$ plasma treatment to remove amorphous impurities attached on the outer surface of CNTs (see SI Fig. S1).

## 3. Performance of the CNT network heater for in situ TEM imaging

### 3.1. *Reduced spatial drift upon high temperature heating*

To obtain information on the heating-induced spatial drift of the samples supported on CNT network, we have measured the spatial drift at various temperatures and conditions. The heating-induced spatial drift terminates typically within 1–2 min after starting the flash heating up to ca. 1000 °C. For example, the spatial drift terminates within 130 s with the total spatial drift of typically 1.47 μm (see SI Fig. S2), which means that the samples can be heated up to ~1000 °C at a heating rate of about 500 °C $min^{-1}$with a small spatial drift rate of about 11 nm $s^{-1}$. After 20 min heating at 1000 °C, we found that the average drift rate of the samples was 0.013 nm $s^{-1}$ (see SI Fig. S3); one of the smallest values ever