Probing the beam-induced heating effect inside a transmission electron microscope by nanoparticle labels

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Abstract
Beam-induced heating effect on nanoscale samples is a crucial question, as it strongly influences the interpretation of observed unusual behaviours. This question is currently under debate without a convincing conclusion. Here, using silver nitride (Ag\textsubscript{3}N) nanoparticles as temperature labels, we perform an investigation on this heating effect inside a transmission electron microscope (TEM) under normal imaging conditions. Combined with experimental measurements and semi-quantitative calculations, a temperature increase of more than 100 K is estimated and confirmed in the graphite carbon nitride (g-C\textsubscript{3}N\textsubscript{4}) films. Strong temperature gradients are found to exist in the single-end fixed g-C\textsubscript{3}N\textsubscript{4} films. The influencing factors of heat accumulation are also investigated and discussed. Findings in this study may shed some light on the understanding of the abnormal behaviours of nano-objects observed inside TEM.

1 | INTRODUCTION

Transmission electron microscope (TEM) is one of the most powerful equipments used to characterise materials for their structures, phases, compositions, and properties. The elastic or inelastic interactions between high-energy electrons and specimen atoms enable precise determination of atom arrangements and elemental distributions, providing deep insight into the material structures and related properties. In terms of these interactions, significant side-effects usually co-occur during TEM observation and imaging, including sputtering [1], amorphisation [2], ionisation [3], carbonisation [4], local heating [5], and so forth. Among all these side-effects, the electron-beam-induced local heating is quite elusive, as it is currently neither able to directly measure the precise temperature increase inside the local nanometre-sized specimen nor able to quantitatively determine how much energy has been transformed into heat and kept inside the specimen. Although there are ways to minimise the beam-heating effect, for example, using a quite low-dose beam to image together with a substrate with very high thermal conductivity, beam-induced abnormal phenomena are still frequently observed on nanometre-sized objects during imaging [5–7]. It reflects that the local heating effect may hardly be avoided in many cases. Thereby, a temperature increase could exist and bring considerable interference in understanding the intrinsic properties of the samples from the observed unusual behaviours, especially for metastable and low-dimension functional materials [8, 9]. As early as the 1980s, Iijima et al. showed that Au nanoparticles deposited on a carbon substrate could be excited during TEM observation [10]. The geometric shapes of the Au nanoparticles fluctuated frequently when they were irradiated by the electron beam. This phenomenon was identified as quasi-melting and further similar experiments demonstrated that the electron-beam-induced temperature effect was a key
reason accounting for the phenomenon. Aside from such notable shape changes, the temperature effect is also very often doubted to play a role in many other behaviours observed in TEM, for example, the abnormal deformation behaviours of nanoscale metals, semiconductors and oxides [11], the phase transitions in nanowires and nano-belts [12], the reconstruction and recrystallisations in amorphous nanoparticles [13, 14].

Generally, the electron-beam-induced temperature increase mainly depends on two aspects, that is, the used beam intensity and voltage that govern the input energy to the specimen, and the supporting substrate that determines the heat dissipation. Li et al. estimated that an electron beam having an energy between 500 and 2 keV could cause a temperature rise up to a few hundred degrees on an organic specimen [15]. Egerton et al. indicated that materials with low thermal conductivity (e.g. 0.2–2 W/mK) could be melted or thermally degraded even under a relatively low beam density [16]. Yokota et al. found that AlSi nanoclusters could be easily melted during TEM imaging due to electron thermal spikes in the particles and poor thermal conduction away from the particles [17]. In a recent study, Asoro et al. reported that even for metal nanoparticles supported on carbon films, a temperature increase of 58 K was estimated to be induced by the electron beam during normal imaging [18]. All these investigations imply that the temperature effect during TEM imaging is somehow inevitable. Unfortunately, from current studies, it is hard to make a conclusion on how severe the temperature effect is and what influence will appear subsequently. As a result, the temperature effect is often argued in the interpretations of new phenomena observed in TEM but usually without a convincing conclusion.

To probe into this question, we here perform an in-situ investigation using silver nitride (Ag₂N)-decorated graphite carbon nitride (g-C₃N₄) samples as a model. The decomposition of the Ag₂N nanoparticles can serve as temperature labels, providing a direct profile of the temperature distribution in the g-C₃N₄ film induced by electron irradiation.

2 | EXPERIMENTAL SECTION

2.1 | Materials preparation

Ag₃N nanoparticles were synthesised by dissolving silver nitrate (AgNO₃) in concentrated ammonia solution [19, 20]. Typically, 0.25 g AgNO₃ was added into 50 ml deionised water and magnetically stirred for 30 min to form the AgNO₃ solution. Then, a 50 ml sodium hydroxide (NaOH) solution (0.1 M) was added to the AgNO₃ solution dropwise. The amount of NaOH was superfluous and thus silver oxide (Ag₂O) nanoparticles precipitated during the reaction. After the reaction, the turbid liquid was centrifuged and washed to obtain Ag₂O particles. Ag₂N nanoparticles were acquired by adding the Ag₂O particles into superfluous ammonia water. The g-C₃N₄ films were bought from Aladdin Company. Ag₃N-decorated g-C₃N₄ samples were obtained by mixing the Ag₃N nanoparticles with g-C₃N₄ films in an ammonia solution.

2.2 | TEM characterisation and in-situ heating

A 300 kV TEM (FEI, Titan) was used to conduct the experiment with a beam intensity of 1.6 × 10⁴ A/m². The temperatures at which Ag₃N nanoparticles decomposed were calibrated using a heating holder (Protochips Aduro™) with electrical chip (E-chip). The E-chip contained hole-arrays as observation windows, and holey carbon films were overlaid on the windows to support the nano-specimens. By controlling the applied current, the heating temperature of the E-chip can be precisely programmed. As the nominal ramp rate of the E-chip is 1000 K/ms, the retardation of the temperature increase during heating can thus be neglected [21].

3 | RESULTS AND DISCUSSION

Figure 1(a) shows the topography of a typical Ag₃N-decorated g-C₃N₄ sample. Figure 1(b) shows the energy dispersive X-ray spectrum of the film. The strong peaks of carbon (C) and nitrogen (N) elements demonstrate the integrality of the g-C₃N₄ film. Notably, C signal is influenced by other sources such as the supporting substrate, so the signal ratio of C to N elements varies and cannot represent the component proportion of the g-C₃N₄ film. The C signal is influenced by other sources such as the supporting substrate, so the signal ratio of C to N elements varies and cannot represent the component proportion of the g-C₃N₄ film. Figure 1(c) shows a high-resolution TEM image of an Ag₃N nanoparticle. From the fast Fourier transform pattern shown in Figure 1(d), the crystalline structure of Ag₃N can be identified and confirmed by the (0 –2 2), (2 –2 2) and (2 0 0) planes [22] with zone axis [0 1 1].
It is observed that the Ag₃N nanoparticles on the g-C₃N₄ film cannot sustain for a long time during TEM imaging. More Ag₃N-decorated g-C₃N₄ film samples are checked during different electron-beam conditions, and it is found that under a beam intensity of 1.6 × 10⁴ A/m², decomposition of the Ag₃N nanoparticles can gradually occur. Figures 2(a)–(j) show a typical decomposition process of the Ag₃N nanoparticles with diverse sizes. As can be seen, several Ag₃N nanoparticles start to decompose much earlier and faster than the others. However, all the Ag₃N nanoparticles vanish eventually under continuous irradiation, leaving only the g-C₃N₄ frames. These asynchronous decomposition processes imply that the electron-beam-induced heat accumulation is uneven in the g-C₃N₄ film. Thereby, the sequence of the vanishing process of the Ag₃N nanoparticles gives direct information of the distribution of the beam-induced heating effect.

To facilitate checking the heat distribution, eight Ag₃N nanoparticles are statistically selected and their size evolutions are recorded by measuring their projection areas from the TEM image sequence. Since most of the nanoparticles keep spherical during size reduction, the change on the projection area of the nanoparticles can thus be used as a direct indicator for monitoring the evolution of the particle sizes. Figure 3 collects the measured projection areas as a function of irradiation time. Two stages can easily be identified in the evolution trends of particles 2, 3, 4, 6, 7, and 8, that is, a first stage showing a flat trend with nearly unchanged particle sizes, and a second stage showing drastic size decrease. In the first stage, the particle sizes change a little during the initial irradiation. This is possibly ascribed to the shape/structure relaxation of the pristine nanoparticles that are staying at metastable state. In the second stage, continuous size reduction appears, indicating the start of structural decomposition induced by strong heat accumulation. Notably, nanoparticles marked by 1 and 5, which are located at the edge, present a much earlier start of decomposition than the others. Their absence of the first stage implies that the beam-induced heating effect on nanoparticles located at the film edge is much more severe due to the weak heat dissipation into surroundings. These findings prove that the decomposition of Ag₃N nanoparticles is dominated by the beam-induced heating effect but not the beam-sputtering effect.

Bulk Ag₃N is known to decompose at a temperature around 400 K [23]. However, the decomposition temperature of Ag₃N nanoparticles may change due to the size effect [24]. To verify the decomposition temperature of the Ag₃N nanoparticles, a heating holder was used to carry out a calibration. Holey carbon films are applied as supporting substrate instead of g-C₃N₄ films, as they have a much higher thermal conductivity, and this can be helpful to relieve thermal retardation. Using the same beam intensity of 1.6 × 10⁴ A/m², it is found that the Ag₃N nanoparticles can sustain a heating temperature below 380 K. When the heating temperature is increased to above 380 K, the Ag₃N nanoparticles start to decompose as shown in Figure 4(a). To double-check the accuracy of the heating E-chip, bismuth (Bi) nanoparticles are used to make a comparison. By heating the E-chip to 515 K, sublimation of Bi nanoparticles is achieved and shown in Figure 4(b). Based on our previous work [21] dealing with the sublimation speed, the change rate of Bi nanoparticle radius $dr/dt$ can be calculated by

$$
\frac{dr}{dt} = \frac{1}{4} V_0 \sqrt{\frac{8RT}{\pi M_r}} \left( \frac{P_r - P_\infty}{kT} \right)
$$

$R$ is the gas constant (8.314 J·mol⁻¹·K⁻¹), $T$ is the thermodynamic temperature, $k$ is the Boltzmann constant (1.38 × 10⁻²³ J·K⁻¹) and $V_0$ and $M_r$ are the molecular volume and weight of
Bi nanocrystal, respectively. $P_\infty$ is the equilibrium vapour pressure over a flat surface that, for bulk Bi, follows the empirical vapour pressure equation from experiments.

$$\log P_\infty = A + \frac{B}{T} + C \log T + DT + ET^2$$

where $A$, $B$, $C$, $D$ and $E$ are the fitting constants [25]. For a certain temperature, the equilibrium vapour pressure over a flat surface is a constant. Nanoparticles sublimation is supposed to follow Kelvin's law with an exponential form, and the equilibrium vapour pressure over the curved surface of Bi nanocrystal $P_r$ can be written as

$$P_r = P_\infty \exp \left( \frac{2\gamma M_r}{\pi T \rho R} \right)$$

$\gamma$ is the surface energy (490 mJ m$^{-2}$ for Bi), $\rho$ is the density.

Figure 5 shows the calculated sublimation rate with the temperature for Bi nanoparticles having an initial radius of 2, 5, 10, 20 and 50 nm at various temperatures. The sublimation process is size-dependent and with a certain temperature, the smaller the particle radius is, the easier or faster it sublimates.

The decomposition temperature of Ag$_3$N nanoparticles is apparently in good agreement with theoretical calculations of the average ionisation potential of the electrons in the atom. $T_m$ and $T_e$ can be described, respectively, as

$$T_m = \left( 560.8/A \right) \frac{E}{me^2} \left( \frac{E}{me^2} + 2 \right)$$

$$T_e = \frac{m}{M} \left( 1 + Z^{2/3} \right) R_b$$

where $E$ is the energy of electrons and $R_b$ is Rydberg energy for hydrogen.

To make a direct comparison, Bi nanoparticles and holey carbon film are also considered in the calculation. It is important to note that, in the experiment, Bi nanoparticles located on the g-C$_3$N$_4$ film or holey carbon film as well as Ag$_3$N nanoparticles located in the g-C$_3$N$_4$ films can decompose easily if heat cannot be dissipated timely. According to the decomposition temperature of Ag$_3$N nanoparticles is believed to be 380 K.
calculation results, nanoparticles show a rapid temperature increase at first, and then the temperature increase becomes very sluggish. The rapidly upward region with several tens of seconds can well explain the existence of nearly stable stage (first stage) for particles inside the g-C$_3$N$_4$ network shown in Figure 3. At this stage, the temperature increment is not high enough for nanoparticles to decompose. With further irradiation, nanoparticles finally get enough heat energy and decompose dramatically. The model is for the perfectly embedded nanoparticles those are in good contact with surroundings. In actual experiments, the various contact conditions between nanoparticles and surrounding films lead to the inconsistent start-point of decomposition. As for particles, those that are supported at the edge of the film, the electron-induced heat cannot be conducted through the surrounding film efficiently and the thermal conductivity used in the above equation cannot be simply treated as the one of film network. Figure 7 gives the temperature increment of Ag$_3$N and Bi nanoparticles in a network having different thermal conductivity after 180 s beam irradiation. The temperature increment is small enough and can be neglected when the thermal conductivity of the film network is larger than 30 W/mK.

To estimate the heat dissipation from the supporting grid, a single-end fixed Ag$_3$N-decorated g-C$_3$N$_4$ film was carefully examined. Figure 8 shows the illustration of the film sample with two monitored regions (red boxes). After 3-min irradiation with a beam intensity of $1.6 \times 10^4$ A/m$^2$, the Ag$_3$N nanoparticles in the two regions show significant discrepancies. In the region nearby the supporting copper (Cu) grid, all the Ag$_3$N nanoparticles can well retain, even for the very small ones. In sharp contrast, the Ag$_3$N nanoparticles in the region that is far away from the supporting Cu grid largely vanish after beam irradiation. This evidence points out that a large temperature gradient should exist in the g-C$_3$N$_4$ film. The key factor causing this temperature gradient is the partially supported Cu grid. Therefore, during TEM imaging, the beam-induced temperature effect should be considered comprehensively, as the thermal conduction between nano-samples and supporting films as well as the thermal conductivity of the supporting film itself indeed plays crucial roles. Moreover, as for those large-scale nanowires and membranes, significant thermal gradients may be induced during TEM imaging. This may cause usual behaviours that do not originate from their intrinsic properties.

4 | CONCLUSION

Using Ag$_3$N nanoparticles as temperature labels, we have explored the temperature effect inside a TEM during normal imaging. The decomposition temperature of the Ag$_3$N nanoparticles is carefully calibrated to be 380 K by heating experiments. During normal imaging, a strong beam-heating effect can be caused, and a semi-quantitative calculation indicates a temperature increase of more than 100 K in the g-C$_3$N$_4$ films due to heat accumulation, which well agrees with the experimental
observation of Ag$_3$N nanoparticle decomposition during imaging. Significant temperature gradients are experimentally verified and demonstrated, possibly providing valuable information in understanding the unusual behaviours in nanomaterials.

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