Investigating the thermal stability of metallic and non-metallic nanoparticles using a novel graphene oxide-based transmission electron microscopy heating-membrane

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Abstract

In recent years, graphene has been explored as a heating membrane for studying high-temperature dynamics inside the transmission electron microscope (TEM) due to several limitations with the existing silicon nitride-based membrane. However, the transfer of monolayer graphene films for TEM experiments is challenging and requires many complicated steps with a minimum success rate. This work developed a novel in situ heating platform by combining the graphene oxide (GO) flakes in the pre-patterned chips. The isolated GO flake was self-suspended between the metal electrodes by a simple drop-casting process. The GO was reduced and characterized using Raman and electron energy-loss spectroscopy. Furthermore, a GO-based heater was used to investigate the thermal stability of gold and silica nanoparticles. The gold nanoparticles evaporated non-uniformly and left an empty carbon shell, while silica disappeared uniformly by etching carbon support. We successfully demonstrated a GO flake as a heating membrane to study high temperature thermal dynamic reactions: melting/evaporation, agglomeration, Rayleigh instability, and formation/or removal of carbon in the nanoparticles.

Supplementary material for this article is available online

Keywords: in situ electron microscopy, graphene heater, gold nanoparticle, silica nanoparticle, graphene etching, carbon shell, KCC-1

(Some figures may appear in colour only in the online journal)

Introduction

To study dynamical reactions of nanomaterials at high temperatures, specially designed environmental transmission electron microscope (TEM) and in situ TEM holders are commonly used. The in situ TEM experiments directly visualize the various...
dynamic phenomena with atomic resolution and help to develop
a clear understanding of the structure, morphology, and chemical
can be achieved using stable in water. In previous works, the graphitization of
hydrophilic, thus allowing the GO dispersion to be more
method, controllable morphologies, and chemistry of GO
folds with the availability of scalable and easy synthesis
process. The successful growth of graphene does not guarantee
its effective integration into devices. The final steps to place
graphene on a target substrate are delicate, as the transfer
steps involve various manual interventions and chemicals
These factors prohibit its use in commercial
We developed a low-cost and facile method for setting up
a graphene oxide-based in situ heater. Graphene oxide (GO),
a graphene derivative, can be synthesized by chemical oxi-
dation and exfoliation of graphite flakes to obtain different
morphologies, sizes, and chemistries (oxygen functionalities)
In recent years, the applications of GO exploded ten-
folds with the availability of scalable and easy synthesis
methods, controllable morphologies, and chemistry of GO
flakes. Moreover, the chemical groups on GO make it more
hydrophilic, thus allowing the GO dispersion to be more
stable in water. In previous works, the graphitization of
amorphous carbon and graphene oxide was achieved using
current-induced annealing in vacuum. In this work, the isolated GO flake was used as a support platform for suspending nanomaterials and studying dynamic heating experiments inside a TEM. Using current-induced Joule heating, the GO flake was reduced, as confirmed by Raman and EELS spectroscopy. Further, the thermal stability and high-temperature reactions of Au and silica nanoparticles supported on GO flakes were examined at high resolution.

Experimental methods
GO flakes were synthesized using a modified Hummers method
A GO dispersion (in water) was used for these experiments without sonication. A diluted GO dispersion was drop-cast onto pre-fabricated in situ TEM electrical chips
Using an optical microscope, individual GO flakes suspended
between electrodes were identified. Next, the chips were trans-
ferred to an Aduro Protochips holder and subsequently to the
TEM. The whole setup was appropriately grounded to avoid
failure of the GO flakes (due to parasitic static charges present in the system). In situ experiments were performed on a Thermo Fisher Scientific Tecnai Twin TEM, operating at low voltage (80–120 keV) under low dose conditions (to reduce beam
damage). A Gatan Orius charge-coupled detector (CCD) camera
was used to record images and videos. Videos were captured
using the Snagit screen recorder. Subsequently, the same chips
were transferred to a Thermo Fisher Scientific image-corrected
Titan TEM, operating at 80 keV, to collect high-resolution
micrographs and the electron energy loss spectra (EELS).
Raman spectra were collected from the GO flakes using a
WITEC Alpha300RA. They were acquired at a low dose (0.5
mW) with a laser source of 532 nm, at 100x magnification.
Scanning electron microscopy (SEM) image was collected with
a Thermo Fisher Scientific Nova Nano, at 5 kV. A Park Systems
XE-100 atomic force microscope (AFM) was used to collect the
topography and thickness details of the GO flakes. The samples
for AFM, SEM and Raman analysis were prepared by drop-
casting the GO dispersion onto a pre-cleaned SiO2/Si wafer.
The Au nanoparticles (diameter: 15 nm) dispersion was
obtained from Aurion, The Netherlands. These particles were
washed with water twice by centrifugation at 13000 rpm
(10 min). Subsequently, after each cycle, the sediments were re-dispersed in water. Silica nanoparticles (KCC-1) were prepared by a modified microwave-assisted hydrothermal
synthesis. The silica nanoparticles (dispersed in ethanol) were drop-cast onto a TEM grid and GO membrane for TEM
investigation.

Results
Suspended graphene oxide-based chips
An as-prepared GO stock-dispersion (200 μg ml⁻¹) was
diluted to ultra-low concentration of 0.5 μg ml⁻¹ in water (see
figure 1(a)). To prepare the suspended GO-based devices, one
microliter of the diluted dispersion was pipetted onto the
chips (inset image in figure 1(b)) with a 3–5 μm window and
allowed to dry in air. We prepared tens of these devices with
just a few microliters of the dispersed GO flakes were easily removed by tuning the laser source (of the
Raman instrument) to high power. Then, the devices
were transferred to the TEM column on an Aduro Protochips
holder. TEM and SEM images of the GO-1 device are shown
in figures 1(c) and (d). AFM and SEM images of the as-
produced GO flakes are provided in the supplementary
information. After drop-casting the GO flakes on a blank
wafer, we allowed it to dry in the fumehood. Most of the GO
flakes were flat. SEM images of as-synthesized GO flakes are
shown in figures S1(a)–S1(b) (available online at stacks.iop.
org/NANO/33/255701/mmedia). The AFM scan confirmed
the planar morphology. Most flakes were more than 3 μm
wide and 1.5–5 nm thick, corresponding to 1–4 graphene
flakes.
oxide layers, as shown in the line profiles in figures S1(c)–S1(d). More than 70% of the flakes were less than 3 ± 0.2 nm thick.

Electrical characterization of the GO flakes was performed in a two-probe configuration inside the ultrahigh vacuum of the TEM column, without electron beam irradiation. The electrical resistance of the as-prepared GO devices was of the order of a few MΩ owing to the highly disordered structure and the presence of various functional groups [19]. In our initial setup, many GO devices failed due to residual electrical charges in the TEM holder (see in figure S2). This issue was sorted out by grounding the holder and electrical supply unit before connecting the device to the holder. The resistance of the GO-1 device was around 23 MΩ. More than ten devices were characterized, and most of these had a resistance between 2–70 MΩ. The GO flake was gradually heated by increasing the direct current that passed through it. Here, a ramping rate of 1–10 μA s⁻¹ was used during the entire cycle. Within the first few seconds (as seen in figure 1(f)), the resistance dropped more than 98% due to Joule heating of the GO and the metal-GO contacts [28]. Upon the current-induced reduction of the GO flake, the electrical conductance improved. The I–V curves indicate a linear response of the GO flakes before and after the reduction process (figure 1(e)). The resistance was around 112 kΩ at 50 μA current and dropped linearly with increasing current (see figure 1(f)). When the current was ramped gradually to 350 μA and 650 μA, the resistance plummeted to 9.2 kΩ and 4.0 kΩ, respectively. Three other devices, with similar flake sizes, were selected and subjected to current-induced annealing at 670 μA, 1.0 mA, and 1.2 mA, respectively. The Raman and EELS spectra of these devices are presented in figure 2. The EELS spectra were collected in situ, while for the Raman, the devices were analyzed ex situ.

The Raman spectra were collected from the suspended GO flake as-prepared and three different reduced GO flakes (RGOs) (figure 2(a)). All presented the characteristic G-, D- and 2D-peaks of carbon materials. Very low 2D and intense D peaks confirmed a highly disordered structure and the presence of various functional groups in the GO flakes [29–32]. Furthermore, its G peak was wide and centred at 1597 cm⁻¹. The degree of oxidation/reduction of the flakes was accessed by calculating the I₈/I₆ ratios. The I₆/I₈ values are listed in table S1; data from the literature for the reduced GO flakes is also summarized. The I₆/I₈ intensity ratio of GO is higher than 1, validating the presence of defects. The RGO-1 device was reduced at a maximum current of 670 μA. Although the I₈/I₆ of RGO-1 did not change significantly, the peak shift and the upturn in the intensity of the 2D peak were observed. For samples RGO-2 and RGO-3, a higher amount of current was used (for reduction). The higher the current and the higher the Joule heating temperature, the better the GO flake reduction is [33]. I₈/I₆ dropped significantly for RGO-2 and RGO-3 (see table S1) due to the complete removal of functional groups and the improvement in the crystallinity of the graphene flakes.

The electron energy loss peaks around 284 eV and 290 eV are associated with the transition of electrons to empty π states and empty σ* states, respectively, linked to the C
K-edge. EELS can also access the chemistry and bonding of reduced GO, as reported in the literature [18, 21]. The peak at 540 eV is the O K-edge, associated with oxygen-rich functional groups present in GO. As seen in figure 2(b), the shape and intensity of the C K-edge and O K-edge peaks changed after the current-induced reduction of GO. The π" peak roughly represents the content of sp²-bonded carbon atoms. The absence of π" peak and the appearance of an O K-edge peak in the EELS spectrum validate the prepared GO from the red-dotted lines in figure 3 represent temperature boundaries. Previously, a similar heating profile was observed for graphene-based heaters [14]. Initially, the evaporation of particles was observed at the top of the TEM image (panels I and II in figure 3). Some amorphous residues remained on the RGO flake after the Au nanoparticles evaporation in panels III and IV (see figure 3). The residues might originate from the sample preparation steps. However, both Au nanoparticles and amorphous residues disappeared when the current increased to 1520 μA (current density: 0.6 × 10⁷ A cm⁻²). At this point, the temperature was higher than 1000 °C at the centre of the flake (panel VI, figure 3).

We also directly heated Au nanoparticles on the same GO support before and after reduction, as shown in figure S3. For the GO-Au nanoparticles system, figures S3(a) and S3(b) display TEM images before and after evaporation of Au nanoparticles. Here, the reduction and heating coincided. The resistance versus current curve of the GO-Au nanoparticles system is shown in figure S3(c). The resistance plummeted from 8.1 MΩ to 2.4 kΩ due to in situ reduction of GO. After the first GO reduction and Au evaporation cycle, the nanoparticles were re-deposited onto the same device. TEM images of the RGO-Au nanoparticle system are shown in figure S3(d). Heating only occurred during the second cycle, when the Au nanoparticles evaporated (figure S3(e)). As observed in figure S3(f), no substantial resistance drop was observed for the RGO heater. The GO and RGO heaters can be used for in situ thermal studies. However, RGO-based heaters are preferred due to fewer variations in resistance during experiments and the absence of functional groups. To identify the evaporation temperature of Au nanoparticles, ex situ experiments were performed by heating the RGO-Au nanoparticle devices inside a vacuum-tube furnace. The devices were annealed at 900 °C, 950 °C, 1000 °C, and 1050 °C in the furnace (<5 mTorr). As seen in figures S4(a)–S4(d), no significant changes were observed in the first RGO-Au nanoparticle device after treatment at 900 °C and 950 °C. In the case of the
annealed devices at 1000 °C (see figures S4(e) and S4(f)), evaporation occurred except for a few large particles. Meanwhile, thermal annealing of the RGO-Au nanoparticle device at 1050 °C resulted in complete evaporation of Au nanoparticles, as seen in figures S4(g)–S4(h).

As seen in figure 4 (panel I), the Au nanoparticles had a cubic lattice arrangement. In the as-received condition, no surface passivation layer was observed. When the RGO device was heated (via Joule heating), both Au nanoparticles and RGO underwent structural rearrangements at a temperature close to the melting point of Au. Reorientation was also clear by comparing panels I and II of figure 4 and their respective FFT images, in figures S5(a) and S5(b). Moreover, a thin carbon nanoshell formed around the Au nanoparticle. From panels I to III in figure 4, the Au nanoparticle underwent a transformation from a crystalline to a disordered phase. No lattice fringes were noticed, and the shape of the particle changed. A previous report observed significant superheating in a nanoparticle covered with graphitic shells [31]. With a slight increase in temperature of the device, a significant reduction in the size of particles was noted (panel IV, figure 4). Possibly, this occurred due to the evaporation of the surface Au atoms from defect sites and broken carbon nanoshell. In figure 4 (panels IV to IX), the size dropped slowly from 15 to a few nm, before complete evaporation. Interestingly, the evaporation of Au atoms was nonuniform. It was slower for Au atoms adjacent to the carbon shells than atoms on free edges. Figure 4 (panel IX) shows the empty carbon nanoshell after the complete evaporation of the Au nanoparticle. A similar behavior was observed for almost all Au nanoparticles at lower magnification and doses, as seen in figure S6. After the panel IV in figure S6, the experiment was stopped, and the remaining particles in the bottom left corner were analyzed. As seen in figures S6(b)–(c), empty and partially filled carbon nanoshells were present.

Figure 3. Time series TEM images of Au nanoparticles deposited on a RGO device. The images of the nanoparticles evaporation are labelled as panels I–VI sequentially. The red-dotted lines show the temperature distribution during the current-driven heating of the RGO device.
Silica nanoparticles thermal stability

TEM images of as-prepared silica nanoparticles on a RGO flake are shown in figures 5(a)–(c). Their diameter ranges between 35 and 50 nm. The silica nanoparticles are uniformly dispersed in the RGO suspended between the two electrodes (see figure 5(a)). In the high-magnification TEM image (figure 5(c)), the porous morphology of the silica nanoparticles is observed. Some of the nanoparticles have a hollow interior, while others are solid.

Figure 4. Panels: I–IX: time-series HRTEM images of the melting and evaporation of a single Au nanoparticle during the current ramping of the RGO support.

Figure 5. (a)–(c) TEM images of silica nanoparticles supported on the RGO heating membrane at low, medium and high magnifications, respectively.
particles are also attached together by Van der Waals forces, surface impurities or functional groups. Both ex situ and in situ studies were performed to determine the melting/evaporation temperature of silica nanoparticles.

Similar to the previous case, when the current was ramped through the RGO heater, many high temperature-induced behaviours were detected. As soon as the temperature of the RGO increased above 1500 °C, the silica nanoparticles started to agglomerate (figure 6). The temperature of the heater rose slowly until the silica nanoparticles started melting and fusing. From panels I and II (figure 6), it is clear that a chain-like structure formed initially. Furthermore, this chain continuously changed shape due to thermal instability. Eventually, to minimize surface free energy and maximize surface-to-volume ratio at high temperature, the chain-like structure disintegrated into two spherical particles. Before the particle formation, necking of the chain-like structure was witnessed (see panel IV and V, figure 6), and the silica’s porous texture disappeared. Upon heating further, the size of the particles reduced until complete evaporation occurred (panels V–IX, figure 6). As the maximum temperature developed at the centre of RGO flakes, the particles far from the electrode evaporated first, then those close to it. All the particles in the red circle of figure 6 behaved similarly.

Firstly, there is the formation of a chain-like structure, and then disintegration occurs into spherical particles, and finally, evaporation.

Isolated silica nanoparticles were also analysed and one of these is marked by a solid red arrow, in figure 6. During heating, the isolated silica nanoparticles acted differently from the agglomerated ones. No movement and aggregation of isolated particles was recorded; this might be due to anchoring of

Figure 6. (a) Time series TEM images (panel I–IX) of thermal annealing of silica nanoparticles loaded onto the RGO heater.
nanoparticles on the flake’s surface defects [7, 20, 32]. However, isolated particles also lost their porous morphology (due to surface atoms diffusion at elevated temperature) originating dense spheres, as observed by the almost 20% reduction in their size (see panels III and IV in figure 6). Due to the structural instability of the isolated nanoparticles close to the melting point, their size dropped continuously from 50 nm to less than 10 nm, as observed in panels I–VII. Finally, this particle disappeared at $t = 460$ s due to complete evaporation, as shown in figure 6 (panel VIII). At the end of the evaporation of silica nanoparticles, we noticed irregular-shaped pores in the carbon lattice. Pores with different sizes and shapes were recorded, as seen in figures S7(a) and S7(b). The smallest pore (18 nm) was observed after the complete evaporation of an isolated particle (see pore marked by the red arrow in figure S7(a)).

The ex situ thermal stability of the silica nanoparticles was inspected by heating the chips inside a vacuum (<5 mTorr) tube furnace at 1100 °C. The TEM micrographs were collected from the same chip, before and after the ex situ heat treatment, as shown in figures S8(a) and S8(b). The silica nanoparticles were very stable at this temperature, with no melting or fusion of the particles. Moreover, the silica nanoparticles maintained their porous morphology (figure S8(c)). Next, thermal gravimetric analysis (TGA) of these nanoparticles was carried out between temperatures of 25 °C–1500 °C (heating rate of 10 °C min$^{-1}$) under an Ar flow. Even at a temperature as high as 1500 °C, a mass loss of less than 5% was recorded (figure S8(d)), attributed to the removal of organic impurities or adsorbed water [26]. These ex situ results demonstrated the excellent thermal stability of the silica nanoparticles (KCC-1).

Discussion

In this work, GO-based and RGO-based heaters were developed and used for in situ thermal experiments inside a TEM. The electron beam-induced knockout damage on GO flakes was minimized by limiting the accelerating voltage to 80–120 kV. We prepared tens of devices from a few microliters of dispersion, and only 1–2 μl was sufficient to craft a single device. In the first step, current-induced Joule heating originated the heating and reduction of GO. Initially, GO had very high electrical resistance brought down to more than 90% by localized heating. The resistance decreased rapidly with a slight increase in current. With a further rise in current density of the heater, the resistance decreased gradually and linearly. The current induced heating led to the removal of functional groups, as reported in the literature [19, 33]. Furthermore, with Raman spectroscopy and EELS, the improved carbon content bonded with sp2, and the crystallinity of graphene were established. $I_D/I_G$ ratio plunged significantly from 1 to 0.34, confirming the reduction of GO to RGO. In the EELS spectra, the oxygen peak also vanished completely. Additionally, the thermal investigation of the Au and silica nanoparticles was carried out using the RGO-based heater, as shown in figure 7. It was found that the RGO heater had radial heat distribution. Moreover, the maximum temperature was achieved in the centre of the suspended RGO flake, while close to the electrode, the temperature was lower due to heat dissipation through metal electrodes to the silicon chip [3, 12].

In order to determine the temperature, we compared the current density used in our GO heater with those reported in the literature. As described by Huang et al., the temperature in a carbon nanotube or graphene layer is around 1700 °C–2000 °C inside an electron microscope for a current density greater than $1 \times 10^7$ A cm$^{-2}$ [29, 30]. Here, for complete graphitization of the GO flake and melting/evaporation of silica nanoparticles, a current density greater than $1.0 \times 10^7$ A cm$^{-2}$ was used. The Raman and EELS spectra of the GO heater were compared with the electrically or thermally reduced GO samples as reported in the literature; the temperature was around 1500 °C–2400 °C for the graphitization of the amorphous carbon or graphene oxide and forming the ordered structure. The intensity ratio of Raman peaks from D and G ($I_D/I_G$) band decreased to 0.34 for the RGO samples after the current induced reduction. As observed by Song et al., Li et al and Dez-Betru et al, to obtain the $I_D/I_G$ ratio of less than 0.35 for thermally reduced graphene oxide samples, a temperature of more than 1700 °C–2000 °C was required [34–36]. Furthermore, Asaka et al and Barreiro et al showed the graphitization of amorphous carbon on the surface of multi-walled carbon nanotube and graphene at approximately 2000 °C and 1600 °C, respectively, during Joule heating experiments inside TEM [14, 22]. These previous research provided good information regarding the temperature rise during our Joule heating experiments.
Upon Joule heating of RGO, nonuniform distribution of heat resulted in melting/evaporation of Au particles in the centre first and then at the edges of RGO flake. The melting point of the bulk Au is 1064 °C. The melting point is known to decrease with the reduction in size for nanoparticles [37]. In this work, evaporation of Au nanoparticles occurred above 950 °C as confirmed by ex situ and in situ studies. In recent work, Liu et al found that melting/evaporation of prism-shaped Au nanoparticles took place at 875 °C using commercial heating chips [38]. Hobbs calculations showed that the temperature rise due to electron beam-induced heating is negligible in highly conductive samples [39].

When the Au nanoparticles were analyzed at high magnification with an aberration corrected microscope, carbon precipitation on crystalline Au particles was detected. In previous studies, similar formation of the carbon nanoshell has been observed for different metal nanoparticles such as Cu, Ag and Au nanoparticles [40–42]. Because of the appearance of a carbon nanoshell around the Au nanoparticles, no Oswald ripening occurred during the heating experiments. The carbon nanoshells are formed by electron beam-induced disintegration of hydrocarbons molecules and subsequent deposition and graphitization of carbon around the crystalline nanoparticles at elevated temperatures. Sutter et al studied the interaction of Au nanoparticles on an amorphous carbon support, and they reported the formation of carbon layers at temperatures as low as 425 °C subjected to intense electron irradiation [42]. The melting of Au nanoparticles was recorded as observed in figure 4. Previous studies found that, upon heating, pressures as high as 3 GPa were generated due to the encapsulation of nanoparticles inside agraphitic shell [31]. That may be the reason before evaporation started, Au nanoparticles transformed from ordered structures to more disordered ones without significant shape changes [40]. The evaporation of Au nanoparticles began only when the temperature was increased beyond this point. During the evaporation, the carbon nanoshell preserved its shape and structure.

As shown in figure 4, within the last 75 s, particles disappeared completely with a current rise of 40 μA. There were mainly three reasons for the faster evaporation of Au nanoparticles with the same incremental current. As the flake was heated with current induced heating, the temperature rise was not linear with the current increase, rather it was exponential. As reported in literature, the temperature rises exponentially with increasing bias through suspended nanomaterials [43, 44]. During our experiments, the temperature of the system soared continuously with current. That was one reason for the faster disappearance of Au nanoparticles. In the literature, most of the experiments were performed at constant temperature after initiation of evaporation/sublimation. Therefore, the rate of evaporation/sublimation of nanoparticle was slower in those cases [38, 41, 45].

Other factors that affected the evaporation rate of the nanoparticles were size, shape, and defects. Buffet et al found that the melting point of nanoparticles decreased with the drop in size of particles [37]. Further, Li et al observed that 25 nm silver nanoparticles took more than twice the time of 15 nm particles during sublimation at same temperature. Moreover, the sublimation of the nanoparticles was slow and linear, initially. Below 8 nm, the size of the particles dropped rapidly as governed by Kelvin equation and kinetic theory [45]. Electron irradiation and the ultra-high vacuum of the TEM column also affect the structure, shape and size of nanoparticles, as reported by Tanaka et al and Ajayen et al [46, 47] Tanaka et al detailed the disappearance of Pd nanoparticles within 15 s when subjected to strong beam irradiation, without external heating [46]. Even though we tried to minimize the electron beam irradiation, there might exist some effects of electron beam at high magnification. Thus, we believe that a combination of the above factors causes the rapid evaporation of Au nanoparticles.

Silica nanoparticles have been explored as a catalyst support for many applications [48, 49]. Therefore, it is crucial to assess the thermal stability of these nanoparticles at elevated temperatures. Even at a temperature above 1000 °C, these nanoparticles retain their high surface area, chemical properties, morphology, and structure. However, visual inspection of their porous texture at extreme temperature is missing. In this work, the silica nanoparticles were very stable. They retained the porous morphology when subjected to the ex situ heat-treatment at 1100 °C. The particles are synthesized in extreme chemical conditions and subjected to high-temperature calcination during preparation. No evidence of melting/evaporation was detected, and particles retained their shape, size, and location on the RGO heating membrane. The heat-treatment of the silica nanoparticles on an RGO support did not originate the formation of a carbon shell. Moreover, TGA confirmed excellent thermal stability of silica particles, from room temperature to 1500 °C, with no significant weight loss observed [26, 50].

This is the first work of in situ TEM where the melting/evaporation kinetics of high-temperature silica nanoparticles was recorded. By Joule heating of the RGO-silica nanoparticles system t, significant changes in the size and shape of nanoparticles took place followed by the agglomeration of particles. First, silica nanoparticles fused to form an irregular chain-like structure and then transformed into more dense and regular-shaped large particles. Due to Rayleigh’s instability of the elongated chain-like structure, the fragmentation into elliptical particles followed [51]. Next, the disintegrated elliptical particles converted into a spherical shape due to surface atom diffusion. The diameter of the silica nanoparticles dropped evenly due to the uniform evaporation from the surface. Contrary to the case for Au nanoparticles, no carbon shell was detected here; instead, the silica nanoparticles etched the graphene support. Nanometre-sized pores were created in RGO, and this was attributable to a carbothermal reaction between silica and graphene at elevated temperatures. Analogously, Martin et al reported the synthesis of SiC particles from silica and a carbon source, at 1500 °C–1800 °C under vacuum [52]. These conditions were similar to those observed in our work. The carbothermal reaction between silica and carbon is shown in figure S7, where a small crystalline particle was detected at the edge of the hole after the reaction. The spectroscopical and structural
analyses of the crystalline particles were not performed because they were out of the scope of this work. In previous reports, nonmetallic and metallic nanoparticles induced catalytic hydrogenation or oxidation and caused the formation of pores in graphene [53–55]. In our experiments, catalytic hydrogenation and oxidation were not possible due to the absence of gases in the TEM vacuum chamber.

It is unclear what caused the uniform and nonuniform evaporation in silica and Au nanoparticles respectively, inside the ultra-high vacuum of the TEM column at elevated temperature. As reported in the literature, the size, shape, orientation, and surface defects profoundly affect the degree and uniformity of evaporation. The divergent evaporation behaviour of Au and silica nanoparticles was strongly related to the difference in chemical nature and surface morphology [45, 56, 57]. Moreover, no agglomeration of Au nanoparticles was recorded before melting/evaporation [45, 56, 57]. The GO support was successfully in situ populated with Ga-doped ZnS: i. data processing for the extraction of the elastic modulus Nano technology 20 405706.

Data availability statement
All data that support the findings of this study are included within the article (and any supplementary files).

Conflicts of interest
There are no conflicts to declare.

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Conclusions

Here, we demonstrated a simple and cost-effective method to fabricate a GO/RGO-based in situ TEM heater. The heater was manufactured by simply drop-casting a GO dispersion onto the pre-patterned Si chips. The GO/RGO-based heater has several advantages: low cost, extensive heating range (R. T.–1700 °C), electron transparent membrane, good mechanical and thermal stability, and ability to resolve atomically defined images. The GO support was successfully reduced using Joule heating and was subsequently used for heating experiments. Moreover, we investigated the stability of Au and silica nanoparticles at temperatures higher than their melting points. Au nanoparticles being crystalline materials showed nonuniform evaporation while noncrystalline silica nanoparticles evaporated uniformly. Their interaction with carbon also varied greatly, and one stabilized the carbon shell while the other predatorily etched the RGO support. The temperature of suspended RGO was raised to more than 1700 °C as confirmed spectroscopically and by the evaporation of metallic and non-metallic nanoparticles. The device described can be used to analyse a large variety of nanomaterials, is excellent alternative to the current commercial technology, specially because our graphene-based heater can be cleaned quickly and reused.

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