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Abstract

The direct focussed helium ion beam milling of solid state nanogears down to 20 nm in diameter is presented. Sapphire is the supporting surface to release the heat created by this milling process. For this resist free process, the He+ dosing was first calibrated to limit the lateral fusion in the deposited nanomaterial during the sculpturing of the teeth on this sapphire surface. 25 nm in diameter solid state nanogear were fabricated in a 20 nm in thickness Au nanomaterial, in a multilayer and in a graphene monolayer having a van der Waals thickness compatible with a single molecule-gears for transmission of rotation. Optimizing again the He+ dosing on a transmission electron microscope grid, free standing graphene monolayer nanogear were also sculptured down to 40 nm in diameter.

Keywords: Focused He ion beam, scanning helium microscope, heat generation, solid state nanogear, graphene

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

1. Introduction

Gears are essential elementary devices for mechanical machinery. Their miniaturization is crucial for portability, fast mechanical response and energy consumption minimization of those miniature machines. Handicraft, workshop machining tools, 3D printing, optical microlithography, focused charged particles beam nanolithography with a resist leads to the nanofabrication of supported minute solid state nanogears down to 50 nm in diameter with a minimum of 6 teeth for electrons and 100 nm for helium ions beam [1]. Wafer surface supporting material, material of the nanogears themselves and nanolithography resist selections are also parts of the fabrication process optimization [1]. Starting from the bottom, single molecule-gears [2] and trains of molecule-gears [3] have also been demonstrated in the 1 nm diameter scale with 6 molecular teeth and even 3 in the simple case of PF3 like molecule-gears nanodomains [4].

Between 1 nm and 50 nm in diameter, there is a known gap in solid state nanogear fabrication worth to explore both for fundamental reasons like friction measurements at the nanoscale [5] and for applications like the fabrication of miniature mechanical calculator immune to radiations [1] or the measure of the motive power of a single molecule motor [6]. For this gap, results coming from resist-based nanolithography are limited down to 50 nm in diameter by proximity effects [7] because the teeth are basically not showing up due for example to backscattered electrons. To avoid those effects, direct writing using Ga+ focused ion beam was already practiced for the 500 nm in diameter gear node [8]. More recently 20 nm in diameter solid state nanodisks were also milled in Au nanomaterials using an He+ focused ion beam [9].

In this paper, we demonstrate how a well master He+ focused ion beam dose leads to the direct writing nanofabrication of 6 teeth solid state nanogears with a diameter of 25 nm and well-shaped teeth. This is demonstrated on a sapphire wafer using a 20 nm gold layer, a graphene multilayer and a graphene monolayer also physiosorbed on the sapphire atomically clean surface and on a transmission electron microscope (TEM) grid. Reaching the graphene monolayer thickness is here important for the objective of having a compatible van der Waals thickness between the solid state nanogear and the molecule-gear to ease the transmission of rotation from one to the other [6]. In section 2, our experimental characterization of the lateral fusion effect created by the He+ focused irradiation is described to determine the optimal He+

dose for milling the nanogear teeth. In section 3, 25 nm 6 teeth solid state nanogear sculptured in a gold layer and in graphene multilayers are demonstrated. In section 4, nanogears are He+ fabricating in a graphene monolayer deposited also on the sapphire wafer surface and on a TEM grid for comparison. Discussion of those results is also presented in conclusion.

2. Results and discussion

2.1. Determining the He+ dose for a direct sculpturing of the teeth

For reference and following our initial approach [9], we have first thermally prepared a 20 nm in thickness Au(111) gold layer on an atomically flat c(0001) sapphire (Shinkosha Co., Kanagawa, Japan) 5 mm × 10 mm in lateral dimension wafer. For graphene, the multi-layers and its mono-layer version were scotch-taped on this sapphire and on a TEM grid surfaces. Our Orion Plus helium ion microscope (HIM) (Zeiss, Peabody, USA) operates at an acceleration voltage of 30 keV to irradiate focussed He^+ beams at the surface of the sapphire wafer. HIM images were recorded with doses of 0.7 - 7×10^{10} ions/cm^2 to reduce possible irradiation damages of the surface. The spatial lateral extension of our He^+ beam is between 0.35 nm to 0.5 nm in diameter. The irradiation was achieved by using the internal Orion patterning software with a minimum 1 nm pixel spacing. A constant beam current of 0.4 pA was used for all the experiments. We take care of the stability of the He^+ emitting trimer on the tip of the Orion microscope. This is an important point since a direct milling is requiring doses larger than the standard lower than 10^{18} ions/cm^2 He+ nanolithography process using for example an inorganic resist like AlOx [7].

In the following, doses between 5.0×10^{18} ions/cm^2 and 5.0×10^{21} ions/cm^2 have been used. Doses larger than 10^{22} ions/cm^2 renders the emitting tip atomic structure unstable and dose below 10^{18} ions/cm^2 are generally not operant for a direct milling on gold and graphene nanomaterials. The dwell time per pixel was adjusted to achieve the required dose. We have used a sapphire wafer to ease the heat dissipation generated by He+ irradiations at high doses [9]. One example of a 25 nm in diameter gold nanodisk with a central hole for its rotation axle is presented in Fig. 1. The milling of the central hole was obtained by localizing the He+ exactly in the centre of the Fig. 1a disk during 20 s. The optimization of this duration is important to avoid the complete fusion of the nanodisk [9]. Already in the Fig. 1b low dose HIM image, the edge of the nanodisk has changed as compared to the Fig. 1a one after the central hole milling.

Sculpturing teeth at the edge of a nanodisk is more demanding in irradiation strategy than the milling of a single central hole. To optimize this irradiation, we have first sculptured two successive rectangles (10 nm x 20 nm) by changing systematically their distance first in the 20 nm gold layer and then in graphene. The results are presented in Fig. 2 where each almost rectangular milled area is resulting from 10 lines of 20 pixels irradiation. With a 1 nm pixel spacing, this is equivalent to irradiate 200 times a very small rectangular area of the sapphire sample. The Fig. 2 curves have nearly the same slope in linear scale when the two rectangular milled areas are well separated (20 nm in the longitudinal direction). The purple dotted lines in all the Fig. 2 curves corresponds to an ideal sculpturing conditions where the bridge is formed by two rectangles milled respecting the 20 nm rectangle centre to centre distance in the longitudinal direction. When the rectangles become closer, the obtained bridge distance deviates from linear because of lateral proximity effect induced by lateral heat diffusion in the nanomaterial. A shift up of the experimental curves above the dashed line indicates that the dose is too small to mill the rectangular areas and the bridge becomes larger. The value of up or down shifts depends on the stopping cross-section of the nanomaterial used [10], on the heat diffusion towards the sapphire surface and of lateral propagation of the resulting fusion front. For the 20 nm Au nanomaterial, the under exposed red curve Fig. 2b demonstrates that playing with lateral fusion leads to the minimum 6 teeth solid state nanogears of about 25 nm in diameter. For graphene multilayer (Fig. 2c) or single layer (Fig. 2d)), the control by the dose of the lateral fusion front was more delicate leading only to 30 nm graphene nanogears (see below).

2.2. Solid state nanogear direct sculpturing with 6 teeth

Using the Fig. 2 lateral proximity effect calibration and maintaining constant the He+ beam flux, the dose was determined to fabricate 6 teeth around a nanodisk plus its central hole for its central rotation axle. Without a resist, a direct milling with He+ ions has the advantage to suppress multiple back-scattering effects which can impact the nanolithography process away from the focused beam location [7]. But it is requiring a larger irradiation dose than the one used with a nanolithography resist. As a consequence, the high local temperature increase induced by the chemical reactions and vaporization of materials under the He+ very local irradiation has to be limited laterally to avoid the propagation of the fusion front away from the local irradiation spot. Sapphire is a very good support for ion milling because local heat is evacuated quite fast [9]. The dose used to nano-sculpture the Fig. 3 presented solid state nanogear in gold and multi-layers graphene nanomaterials were optimized according to the Fig. 2 dosing curves with no re-optimization of the dose. It indicates that the large number of local irradiation step performed per tooth around an initial milled nanodisk are not perturbing this nanodisk global structure. The right ordinates in the Fig.2 calibration indicate the expected relation between the bridge distance and the expected overall final solid state nanogear radius with 6 teeth. The Fig. 3a gold nanogear radius is about 25 nm for a 10 nm bridge distance according to the Fig. 2b curve for a 5.0×10^{18} ions/cm^2 dose. Notice that a possible better optimized milling strategy will be to pre-sculpture the nanodisk and then to mill the teeth afterwards since the direct He+ milling is suppressing backscattering effects from the supporting substrate (Supporting information).

2.3. Graphene monolayer nanogears sculpturing

For a single graphene monolayer physiosorbed on a sapphire surface, the calibration dosing curve is also presented in Fig. 2. Using a 5×10^{19} ions/cm^2 dose, the milling results obtained with a graphene monolayer on sapphire are located exactly on the purple dotted line (Fig. 2b). On contrary, the milling results on a graphene multilayer with the same dose shift up above this purple line (Fig.2b) confirming how a larger dose is here required to compensate for heat dissipation in this multilayer structure.

Fig. 4 is presenting the corresponding HIM image of a nano-sculptured 6 teeth graphene monolayer nanogear. Notice that the sculpturing of a single graphene monolayer nanodisk is crucial for the prospect of rotating a single molecule-gear 1 nm in diameter using a nanoscale solid state nanogear. The van der Waals equivalent height between the two must match for an efficient transfer of rotation from the micron to the atomic scale via a solid state nanogear [6]. The overall nanogear diameter is 48 nm corresponding nicely to the Fig. 2c expected radius for a 15 nm bridge distance using a 2.5×10^{19} ions/cm^2 dose. The Fig. 4 HIM contrast is very low for determining the edge structure of the nanogear. Then, we have also performed the He+ milling experiment on a TEM grid to beneficiate from a better resolution of a TEM microscope. After depositing the graphene monolayer on a TEM grid, a new irradiation calibration curve was first established as presented in Fig. 5. A comparison between the Fig. 2c and Fig. 5b curves indicates that the ideal milling conditions given by the dotted line are reached by a smaller 2.0×10^{18} ions/cm^2 dose for a suspended graphene monolayer as compared to the 5.0×10^{19} ions/cm^2 sapphire supported one because heat flow to the substrate is suppressed for a supported monolayer.

The resulting milling of nanogears with the doses determined from Fig. 5 is presented in Fig. 6. The TEM grid imposes that only ½ of the nanogear is sculptured to avoid its detachment from its original graphene monolayer free-standing support. One ½ nanogear sculptured in this suspended graphene is visible on the down left of the Fig. 6 TEM image with 3 teeth as expected and its central hole. Its overall diameter is 43 nm corresponding to the Fig. 5 expected 22 nm radius for a 15 nm bridge distance using a 2.0×10^{18} ions/cm^2 dose (right scale Fig. 5b). The two others TEM imaged nanogears are not very well defined. The top left one is not completely milled and the top right one almost fully fused. In such TEM grid milling experiments, heat releasing is not facilitated since there is no underneath supporting surface. Therefore, the heat produced by the milling process is difficult to dissipate. This is the case of the top right nanogear whose fusion front almost completely destroyed even the nanodisk structure. On the contrary and for the top left one, the milling was performed too closed to a grid mesh edge and the nanodisk basic structure of the nanogear is not completely milled.

3. Conclusion

The direct milling of solid state nanogears down to 20 nm in diameter have been presented. The He+ beam dosing was first calibrated to limit the lateral fusion during the sculpturing process on an atomic scale sapphire surface. Sapphire was selected as a support to release the heat created by the He+ focussed ion beam milling process used. Optimizing again the dosing, free standing graphene monolayer nanogear were also nanofabricated down to 40 nm in diameter. Other irradiation strategies have also been explored to refine for example the teeth shape. On the sapphire surface, those solid state nanogears are certainly still chemically bonded from point to point to the sapphire surface while they are free standing on the TEM grid. It remains now to optimize a nanoscale technique to transfer those graphene nanogears from their native sapphire surface to a proper ultra-clean metallic surface where they can be manipulated in mechanically interaction with a single molecule-gear as recently explored using molecular mechanic calculations [6].

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

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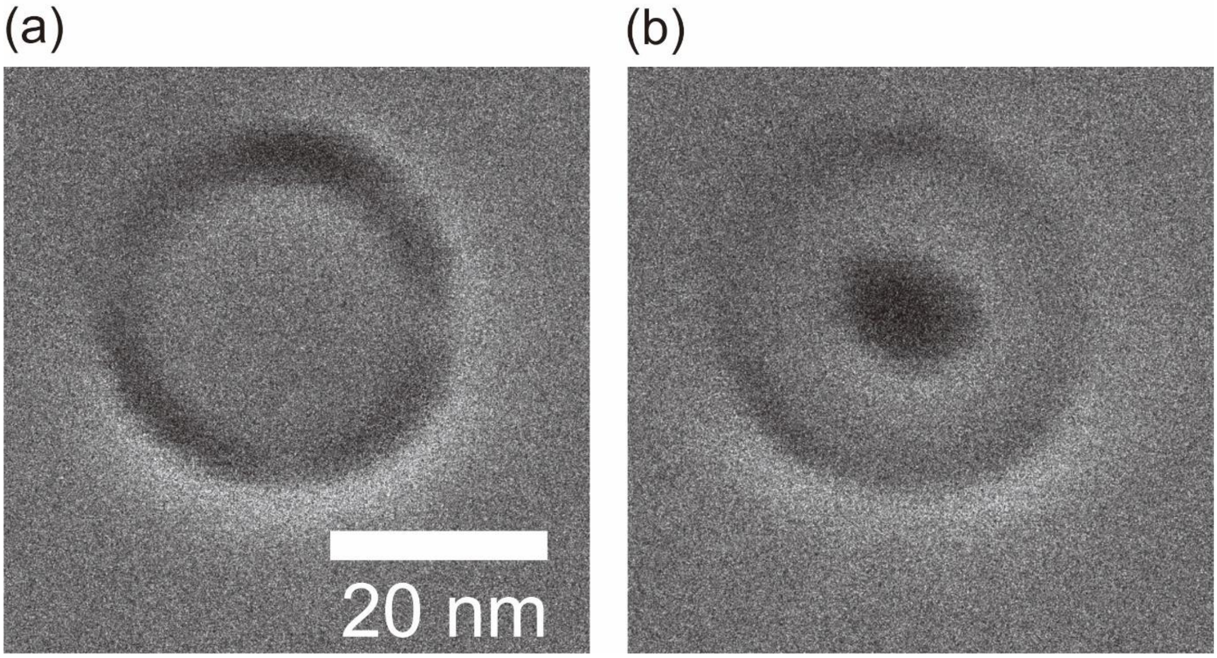

Figure 1. HIM images of the same 25 nm in diameter gold nanodisk before (a) and after (b) its central hole. It was nanofabricated using a focused He^+ focused ion beam with a 5.0 $\times 10^{21}$ ions/cm^2 irradiation dose on a 20 nm thick Au(111) layer deposited on an atomically flat sapphire sample surface. In (a), the edge sharpness at the boarder of the nanodisk is around 2 nm. In (b), this end sharpness is now10 nm due to the heat created by the milling of the central hole.

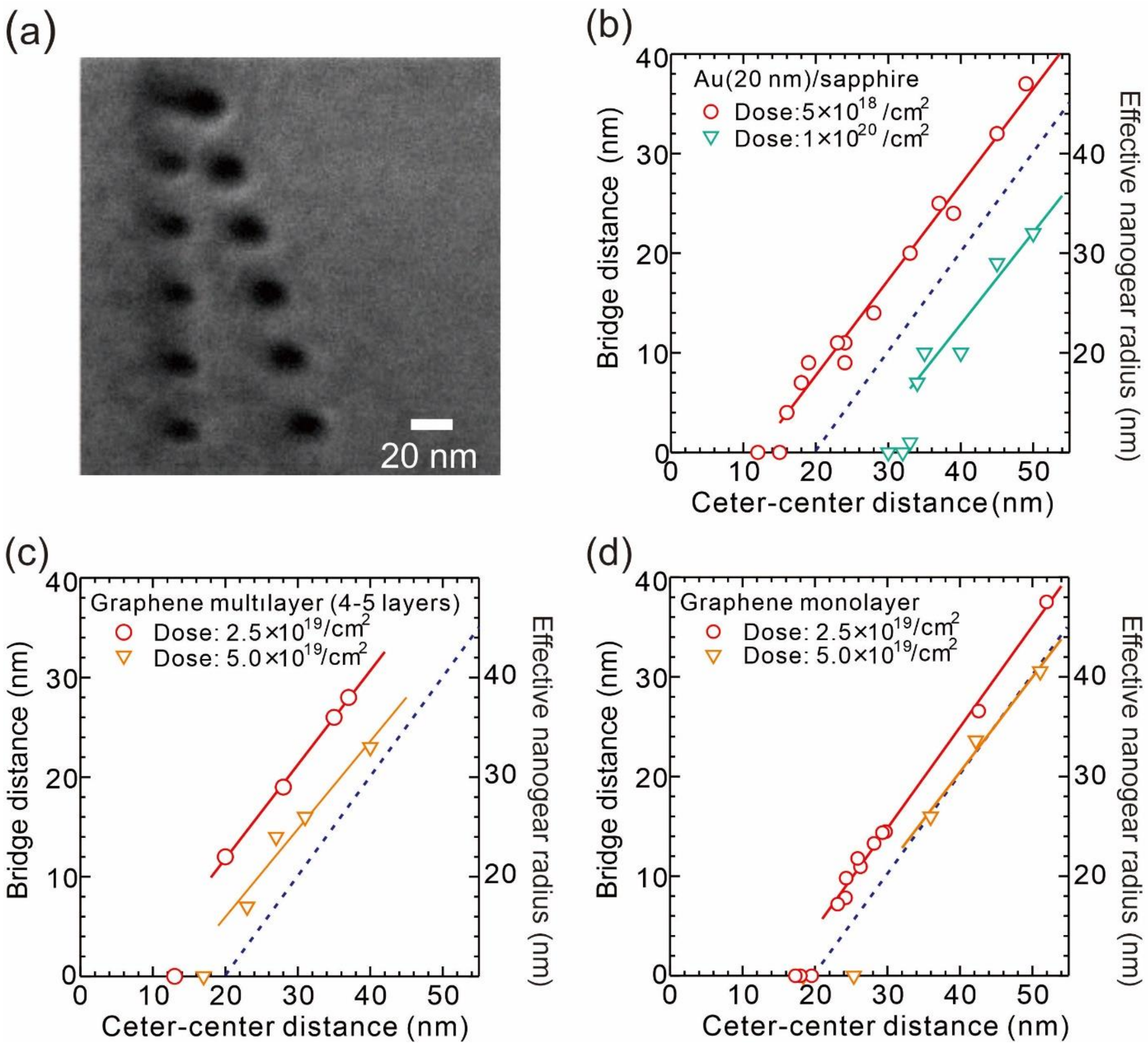

Figure 2. (a) a low dose HIM image of a series of two rectangular patterns (10 x 20 nm^2) sculptures by a focused He^+ ion beam as a function of the distance between two center positions. The relationship between the center-center distance and bridge distance for (b) Au layers (20 nm), (c) a graphene multilayer (4-5 layers) and (d) a graphene monolayer. The right ordinate scale for (b), (c) and (d) is giving the effective nanogear diameter awaited depending on the measured bridge distance.

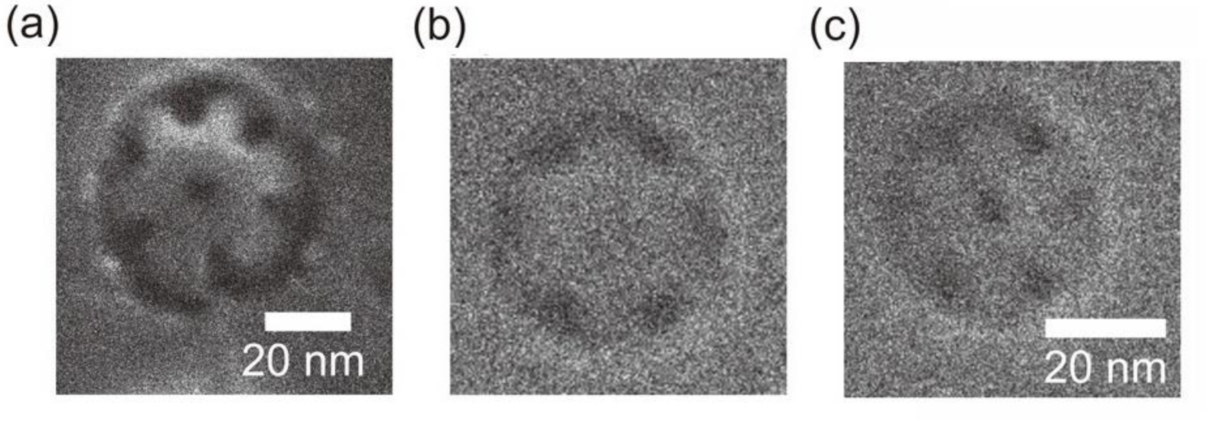

Figure 3. HIM images of a nanogear sculptured using a He^+ ion focused beam irradiation in (a) a 20 nm in thickness gold layer (1.5×10^{19} ions/cm^2), (b) a graphene multilayer (4 - 5 layers thickness) before (2×10^{18} ions/cm^2) and (c) after making the center hole (1×10^{20} ions/cm^2).

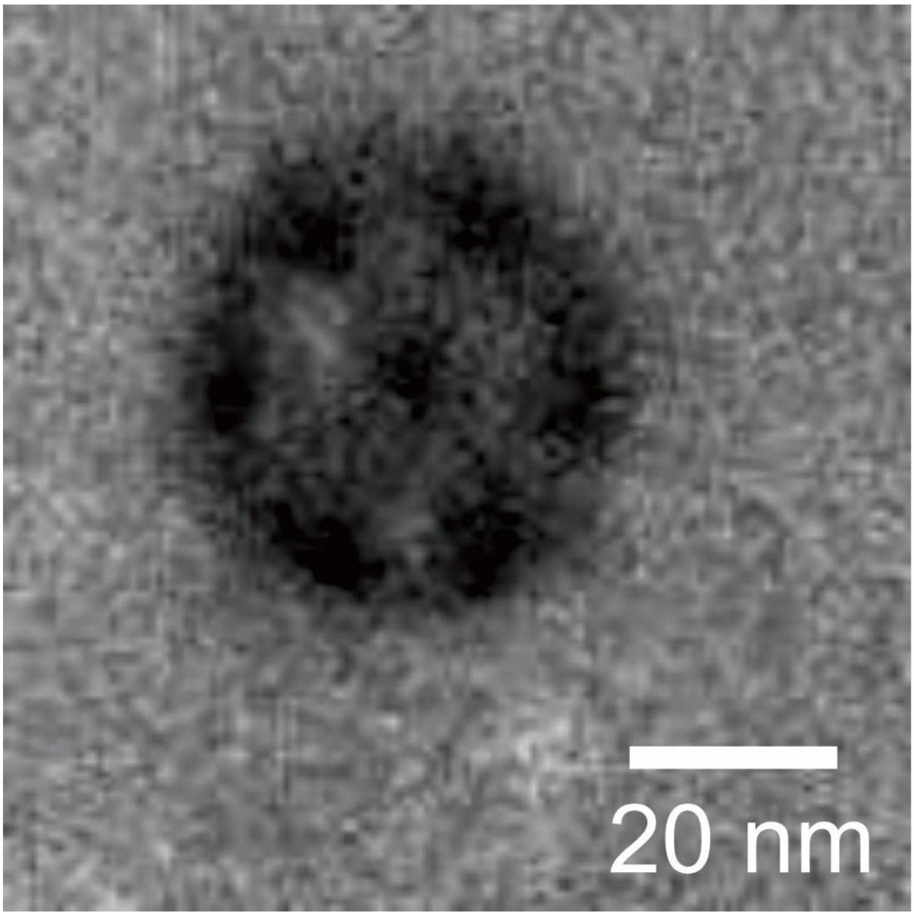

Figure 4. HIM images of a single nanogear milled in a graphene monolayer with also its central hole for the rotation axle by using a dose of $9{\times}10^{18}$ ions/cm^2.

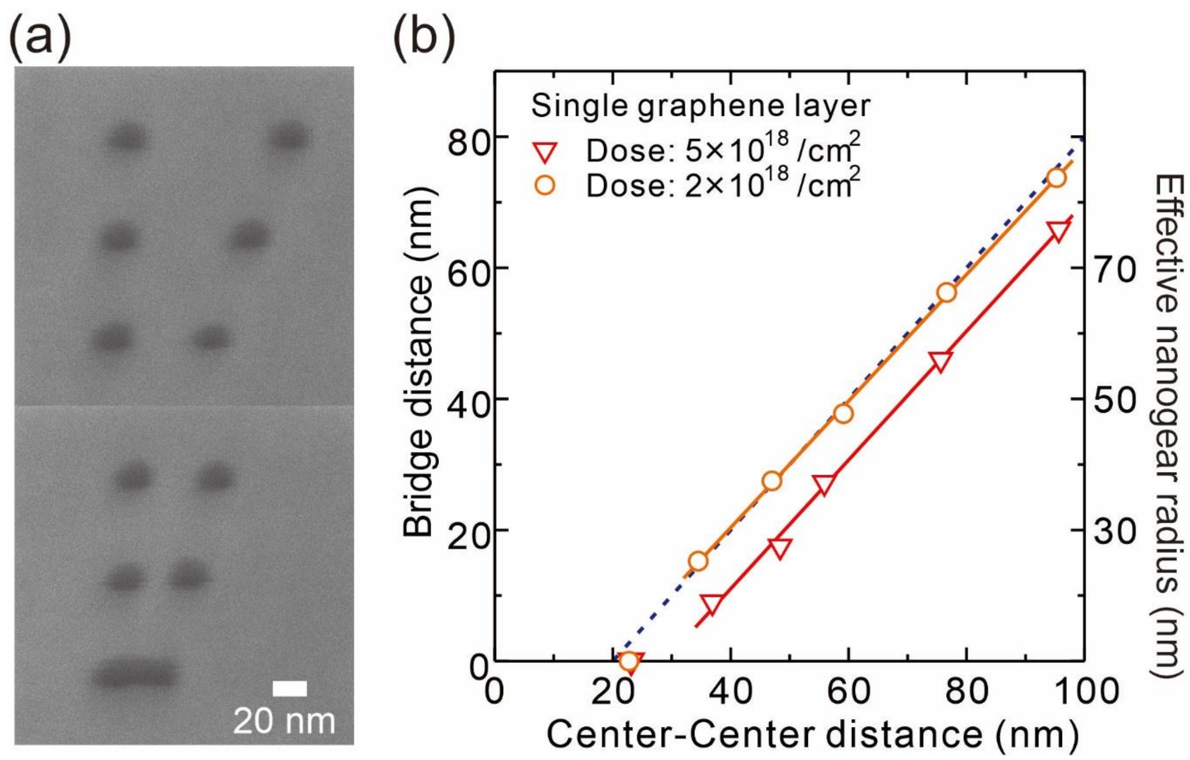

Figure 5. (a) The low dose HIM image of a series of two rectangular patterns on a graphene monolayer suspended on a TEM grid. (b) The relationship between the center-center distance and bridge distance for this suspended graphene monolayer using different He+ doses.

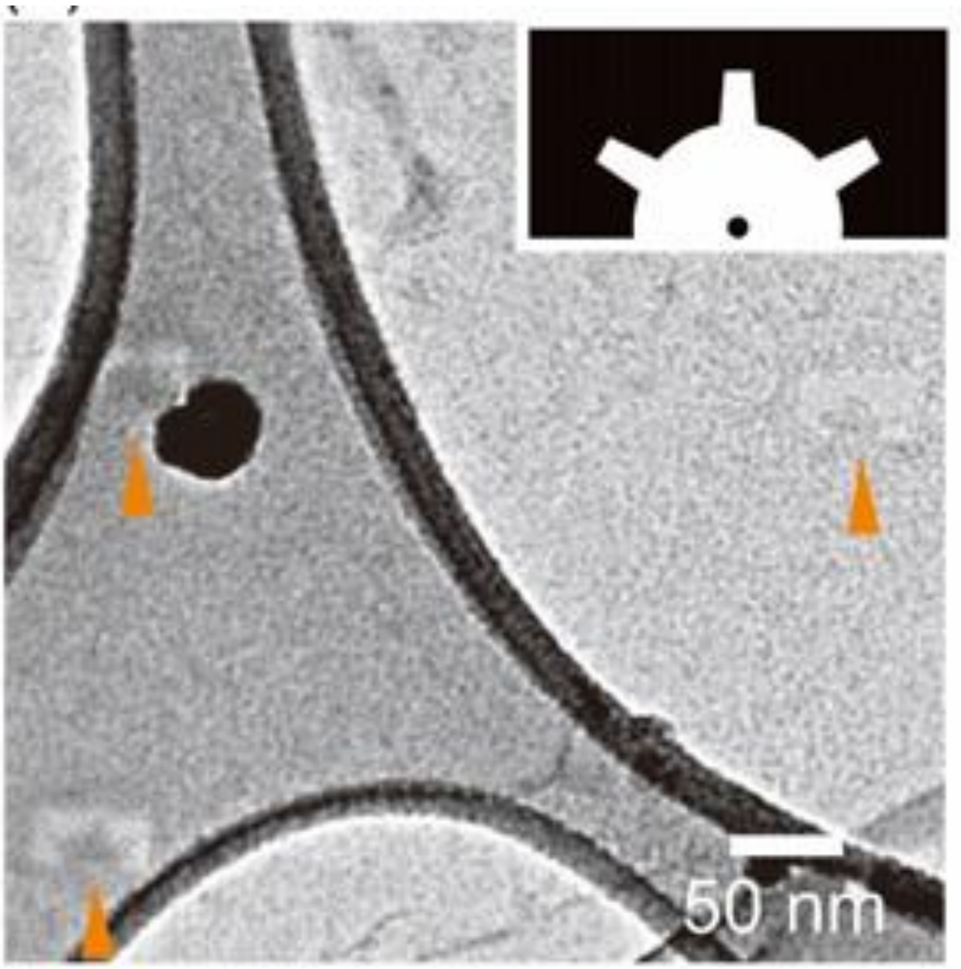

Figure 6. The TEM image of nanopatterns (marked by orange arrows) sculptured by focused He^+ ion beam in a single suspended graphene monolayer on a TEM grid. Inset: Nanopattern where black area is scanned by the He+ focused ion beam. Note that the sample was taken out in air after its Orion He+ ion milling and then moved on the stage of an ultra-high vacuum TEM (JEOL, JEM-2100F, 200 keV).