Graphene-assisted preparation of large-scale single-crystal Ag(111) nanoparticle arrays for surface-enhanced Raman scattering

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Abstract
Surface plasmon resonance (SPR) of metal nanostructures has broad application prospects in the fields of sensing, energy, catalysis and optics. This paper reports a graphene-assisted method for preparing large-scale single-crystal Ag(111) nanoparticle (NP) arrays based on the ion implantation technique. By surface periodic patterning treatment and annealing of the implanted sample, regularly arranged Ag NPs can be prepared on the sample surface. A new application for graphene is proposed, that is, as a perfect barrier layer to prevent metal atoms from evaporating or diffusing. All the Ag NPs show (111) crystal orientation. Besides, the Ag atoms are covered by graphene immediately when they precipitate from the substrate, which can prevent them from being oxidized. On the basis of this structure, as one of the applications of the metal SPR, we have measured the surface-enhanced Raman scattering effect and found that the G peak of the Raman spectrum of the graphene achieved about 20 times enhancement.

Supplementary material for this article is available online

Keywords: ion implantation, annealing, graphene, Ag nanoparticles, surface-enhanced Raman scattering

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

1. Introduction
Surface plasmon resonance (SPR) refers to the resonance of incident light with the vibration of free electron masses on the surface of metal nanostructures [1–4]. Noble metal nanoparticles (NPs), such as Ag, Au and Pt, have a strong local SPR effect, and have broad applications in the fields of sensing, energy, catalysis and optics [5–13]. They can exhibit strong spectral absorption in the ultraviolet, visible and infrared bands. The peak of the absorption spectrum depends on the microstructural characteristics of the NPs, such as the composition, shape, size and structure [4]. Among them, Ag
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Figure 1. (a–d) Sketch of the graphene-assisted preparation of large-area Ag NPs. (a) Ag\textsuperscript{+} implantation. (b) Transferring monolayer graphene onto the substrate. (c) Annealing at 1050 °C for 15 min. During annealing, Ag atoms will diffuse to the surface of the substrate and aggregate to form Ag NPs. (d) Finally, Ag NPs were obtained on the surface of the substrate. (e) Optical image of the Ag NPs. (f) SEM image of the Ag NPs. (g) SEM image of a single Ag NP. Graphene folds can be clearly seen around the Ag NP.

NPs have attracted extensive research attention due to their advantages of antibacterial properties, easy functionalization, and low cost [11, 12]. Recently, in waste water processing, studies have found that Ag NPs have an important role in monitoring heavy metal ions and catalyzing the degradation of organic pollutants [7]. At present, there are many ways to prepare metal NPs, such as electron beam lithography, chemical synthesis, plant extraction, annealing of deposited metal films, nanoimprint lithography and ion implantation followed by annealing [13–23].

Metal ion implantation followed by annealing is one of the common methods for preparing metal NPs [20–23]. During annealing, the metal atoms implanted into the substrate will aggregate to form metal NPs. This method can obtain metal NPs over a large area. However, because of the lack of a barrier layer to prevent metal evaporation, the metal atoms are easy to be evaporated once they precipitate out of the substrate during annealing. Therefore, the annealing conditions are usually controlled to form NPs inside the substrate instead. Because they are inside the substrate, the metal NPs cannot be combined with the surface materials or structures to achieve certain functionalities, such as the enhancement of absorption in a photodetector by surface NPs. Besides, the metal NPs are irregular in arrangement and usually small in size (tens of nanometers).

Graphene, as the first two-dimensional material, has attracted worldwide attention for its many excellent properties since its ‘discovery’ in 2004 [24]. Graphene has ultra-high mechanical strength [25] and atomic impermeability [26], which makes it a potential material as an evaporation barrier.

In this work, we have proposed a graphene-assisted method for preparing large-scale Ag NPs based on ion implantation technique. Ag\textsuperscript{+} implantation followed by annealing is used to prepare Ag NPs on the SiO\textsubscript{2}/Si substrate. Graphene was proved to be a good barrier layer to prevent metal atoms from evaporating. Therefore, in the experiment, the annealing temperature can be adjusted within a large range, which could be even higher than the melting point of the metal. The ultrahigh mechanical strength of graphene plays an important role. Besides, by the surface periodic patterning treatment (SPPT) of the substrate, the obtained Ag NPs can be regularly arranged and form Ag nanoparticle arrays (Ag NAs). The obtained Ag NPs are analyzed by optical, scanning electron microscope (SEM), atomic force microscope (AFM), x-ray diffraction (XRD) measurements and x-ray photoelectron spectroscopy (XPS). This method basically solves all the problems mentioned above of metal NPs prepared by the conventional ion implantation technique, and realizes efficient preparation of Ag NAs over a large area, with a regular arrangement and uniform size. The obtained Ag NPs are all single crystalline and show (111) crystal orientation. Furthermore, Ag oxidation has always been a major obstacle to the application of Ag NPs in SPR. This method solves the problem of long-term storage of Ag NPs. When the Ag NPs are prepared, they are wrapped by graphene which blocks the air and prevents Ag from being oxidized. Apart from Ag, this method can achieve the preparation of a variety of metal NPs. On the basis of this structure, just as one example of the applications of SPR, we measured the surface-enhanced Raman scattering (SERS) effect of the NP\textsubscript{S}. The G peak of the Raman spectrum of graphene achieved about 20 times enhancement.

2. Results and discussion

2.1. Preparation of large-scale Ag NPs

Figures 1(a–d) show the preparation method. The substrate we used is heavily doped Si with 300 nm SiO\textsubscript{2}. Ag atoms are first implanted into the shallow surface of the substrate (~22 nm, supporting information, figure S1 (available online at stacks.iop.org/NANO/32/025301/mmedia)) by Ag\textsuperscript{+} implantation. After that, monolayer graphene is transferred onto the substrate followed by an annealing process. Annealing is an important part of this technique. During annealing, Ag atoms will diffuse in the substrate and precipitate from the substrate when the temperature is cooling down. Since no substance

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Figure 2. (a) Transferring SiO$_2$ NPs. (b) Dry etching of the substrate. (c) Transferring monolayer graphene. (d) Annealing at 1050 °C for 15 min to obtain regularly arranged Ag NAs. (e) SEM image of SiO$_2$ NPs after transferring onto the substrate. (f) SEM image of the cylindrical mesa on the substrate. This image was observed at an angle of 75 degrees. (g) Optical images of Ag NPs prepared on the substrates with and without SPPT, respectively.

can pass through graphene (except H$^+$) [26], when Ag atom precipitates out of the substrate, it will be contained by the graphene at the graphene-substrate interface. Graphene’s ultra-high mechanical strength and flexibility make it not torn by Ag vapor even if it has only one atomic layer. Therefore, the annealing temperature (~1050 °C) can be much higher than the melting point of nano-silver. Higher annealing temperature will obtain better lattice and larger sized Ag NPs. Without graphene, the Ag atoms will evaporate completely and no Ag NPs are observed (figure S2, supporting information). By changing the annealing temperature, the average size of the Ag NPs can be adjusted. It was found that the average size of the Ag NPs will increase as the annealing temperature rises (figure S8, supporting information). Figure 1(e) is an optical image of the final Ag NPs at 1000 magnification. The white spots in the image are the Ag NPs. Figure 1(f) is a SEM image of Ag NPs. Figure 1(g) is a SEM image of a single Ag NP with a diameter of about 150 nm. We can clearly see that graphene is supported by the Ag NP, thus graphene folds are forming around the Ag NP. We also noticed that there are many small-size Ag NPs around the big one, which means that the implanted Ag atoms in a certain area will not completely agglomerate into a Ag NP. Not limited to Ag, we also prepared Cu NPs using the same method (figure s3, supporting information).

The result is interesting. Although we have always stressed that graphene has ultra-high mechanical strength, but how to reflect the mechanical strength of graphene? Although there have been reports about graphene used as barrier layers [27, 28], as far as we know, the use of graphene to prevent the evaporation of metal atoms has not been reported. Before our experimental results are obtained, it is difficult to imagine that a material with single-layer atomic can perfectly block the evaporation of metal atoms at such a high temperature. This result shows that graphene has application prospects in preventing the evaporation or diffusion of metal atoms. Compared with conventional method [20–23], with graphene barrier, we can easily obtain Ag NPs on the substrate surface rather than inside the substrate. Thus, the SPR effect of the Ag NPs can be better combined with other materials on the substrate surface.

It should be pointed out that the graphene we used is commercial polycrystalline graphene grown on Cu foil. Meanwhile, the transfer process may lead to some graphene breakage. Therefore, at the grain boundaries or broken sites, graphene cannot effectively block the evaporation of Ag atoms, leading to no Ag NPs formed at some nominally area covered by graphene. This problem can be solved by some methods. We found that multiple transfer of monolayer graphene can significantly reduce the area without Ag NPs (figure S4, supporting information). At the same time, there have been many reports about the growth of large-area single-crystal graphene [29, 30]. Therefore, we believe the use of single-crystal graphene may help solve this problem. In addition, we found that the wrinkles of graphene will affect the appearance of Ag NPs, and Ag NPs are more likely to appear in the wrinkles of graphene (figure S7, supporting information).

2.2. Regular arrangement of Ag NPs

One of the problems in the conventional preparation of metal NPs by annealing is the failure to form regular arrangement. However, in this work, the Ag NPs can be periodically aligned by the SPPT. As shown in figures 2(a)–(d), we transferred SiO$_2$ nanospheres on the surface of the sample. The diameter of SiO$_2$ nanospheres is about 600 nm. The water environment used in the transfer process facilitates the SiO$_2$ nanospheres to regularly arrange themselves via energy-driven self-assembly. Therefore, the obtained SiO$_2$ nanospheres will show a regular arrangement as shown in figure 1(e). After that, we used SiO$_2$ nanospheres as masks to dry etch the sample, and divided the surface of the sample into many cylindrical mesas (figure 1(f)). The etching depth is about 40 nm, which is deeper than the implanted depth, so the implanted region is completely separated into many 600-nm diameter circular regions, each of which is independent of each other. After the SPPT, we transferred graphene and annealed the sample. Interestingly, the
obtained Ag NPs show a regular alignment the same as the SiO$_2$ nanospheres. Figure 2(g) shows the Ag NPs obtained on the substrates with and without SPPT.

Figures 3(a) and (b) are the SEM images of the Ag NAs. It can be seen that the arrangement of Ag NPs is the same as that of SiO$_2$ nanospheres in figure 2(e). They are all regular hexagonal. The distance between two adjacent Ag NPs is about 600 nm (white dotted line in figure 3(a)), which is consistent with the diameter of SiO$_2$ nanospheres, proving that the regular arrangement of Ag NPs is caused by the periodic cylindrical mesas on the substrate surface. In order to obtain the information about the relative positions of Ag NPs and cylindrical mesas, we removed the graphene by oxygen plasma. As shown in figure 3(c), the circle marked by the black dotted line is the position of the cylindrical mesa. All the Ag NPs are located at the center of the cylindrical mesas, which means that the Ag atoms in each cylindrical mesa form a single Ag NP. Figure 3(d) is the three-dimensional sketch of the Ag NAs. Figures 3(e) and (f) are the AFM images of Ag NAs before (e) and after (f) removal of graphene by oxygen plasma etching.

At the same time, we found that the size of the Ag NPs prepared on the substrate with SPPT is more uniform. We have calculated the size distribution of Ag NPs shown in figures S5(a) and (b) (supporting information). The size of the area shown in figures S5(a) and (b) is consistent. Since Ag NPs are not strictly circular, we calculate the width of each Ag NP, i.e. the projection length in the x-axis direction. It can be seen in figure 4(a) that with SPPT, the size of the Ag NPs is more consistent and is concentrated around 144 nm. This is
because after SPPT, the diameter of each cylindrical mesa is basically the same, so the implanted dose of Ag atoms in each cylindrical mesa is almost the same. Therefore, the diameter of the Ag NPs formed on each cylindrical mesa is almost the same. This phenomenon also gives us an inspiration that we can control the size of the Ag NPs by controlling the implanted dose and the diameter of the cylindrical mesa. We roughly calculated that the yield of Ag NPs was about 64.9% (Supporting Information). In other words, about 64.9% of the implanted Ag atoms will agglomerate to form the large-size Ag NPs we want, and the remaining Ag atoms may not precipitate from the substrate, or form many small-size Ag NPs on the substrate surface around the large-size NPs, similar to the situation shown in figure 1(g).

Figure 4(b) shows the XRD results. We can see that there is only one diffraction peak corresponding to (111) orientation of Ag [31], which proves that nominally all the NPs are (111) orientation. Meanwhile, our annealing temperature (1050 °C) is much higher than the melting point (<960 °C) of nano-silver. It is almost impossible for the obtained Ag NPs to have multiple grains. From the SEM image (figure 1(g)), we also did not observe grain boundaries. Therefore, we can draw the conclusion that all the Ag NPs are Ag (111) single crystals. XPS measurement was also carried out (figure S9, supporting information). Based on the results, no clear Ag oxidation states was found.

In principle, this method can obtain large-area Ag NAs because both proton implantation and graphene or SiO$_2$ nanospheres transfer can realize wafer-scale preparation. Compared with electron beam lithography, this method has advantages in efficiency and cost. Besides, the arrangement period and the size of Ag NPs can be adjusted by changing the diameter of SiO$_2$ nanospheres.

2.3. SERS of the Ag NAs

SERS is an important application of metal SPR. SERS technology overcomes the weakness of conventional Raman signal and can increase the Raman intensity by several orders of magnitude. In order to get a strong enhancement signal, first of all, we need a good substrate. Graphene, as a two-dimensional ultra-thin carbon material, is easy to adsorb molecules and can be said to be a natural substrate. When some molecules are adsorbed on the surface of graphene, the Raman signal of the molecules will be significantly enhanced. Recently, there have been many reports on graphene SERS [32–34]. Metal plasmonic nanostructures can enhance Raman signals by generating strong local electric fields. Therefore, the combination of graphene and noble metal nanostructures can effectively enhance Raman signal. Our technique involves both graphene and Ag NAs. Thus, as one of the applications, we measured the Raman enhancement effect of the Ag NAs.

Figure 5(a) shows the Raman enhancement results of the Ag NAs. Raman spectra of three kinds of graphene were measured respectively. First, we measured the Raman spectrum of graphene before annealing (black curve in figure 5(a), Gr before annealing). Second, there are no Ag NPs formed in some graphene-covered areas after annealing due to the defects or transfer-caused damages of graphene. We also measured the Raman signal in these areas (blue curve in figure 5(a), Gr after annealing). Finally, we measured the Raman signal of graphene with Ag NAs (red curve in figure 5(a), Gr/Ag after annealing). As we can see, the G band has an intensity of 320 counts before annealing, and an intensity of 6700 counts after annealing in the area with Ag NAs, which is increased by about 20 times. This enhancement effect is pronounced. We have also noticed two obvious phenomena. First, the Raman signal of graphene is still enhanced in the region without Ag NPs after annealing. This is mainly due to the fact that Ag atoms do not precipitate completely. Some Ag atoms aggregate inside the substrate to form NPs [22]. Therefore, there are still some Raman enhancement effects in these regions. Second, we found that the D peak of graphene increased significantly after annealing, representing the increase of the amount of graphene defects, which also led to the decrease of the 2D peak. The increase of graphene defects may be due to the deformation of graphene caused by high temperature annealing and precipitation of Ag atoms. A comparison of the SERS effect of our method with other reports [35–37] is shown in table S1 (supporting information). In future research, this sandwich structure (graphene-Ag NPs-SiO$_2$/Si) can be used to enhance
Figure 5. (a) Raman spectra of the graphene. The black curve represents the graphene Raman signal before annealing. The blue curve represents the graphene Raman signal after annealing and without Ag NAs. The red curve represents the graphene Raman signal after annealing and with Ag NAs. (b) The Raman signal of the graphene with Ag NAs before and after ten weeks storage in air. (c) Dark-field optical image of the Ag NAs. (d) The G-peak Raman mapping of the graphene in the region shown in (c).

the Raman signal of some organic molecules (such as Rhodamine). Graphene as the top layer of the sandwich substrate can well adsorb these molecules. We placed the sample in the air for 10 weeks and measured it again. It was found that the Raman signal of graphene can still be enhanced. At the same time, by optical observation, we found the color of the Ag NPs did not change, and they remained silvery white (figure S6, supporting information). Combined with the results, we can conclude that the Ag NPs prepared by this method can be stored for a long time, and graphene protects the Ag NPs from oxidation. Figure 5(d) shows the Raman mapping of G peak for the area shown in figure 5(c). Figure 5(c) is a dark-field optical image of the Ag NAs. From figure 5(d), it can be seen that the Raman enhanced region fits well with the region of the Ag NAs. In figure 5(c), there is a strip region without Ag NAs, and the Raman signal in this region is also significantly weaker in figure 5(d).

3. Conclusion

In this work, a graphene-assisted method for preparing Ag NPs is proposed. Ag atoms are implanted into the shallow surface of the substrate by ion implantation, and are agglomerated to form NPs by annealing. Graphene has been proved to have a good effect of blocking the evaporation of Ag atoms during the annealing process. Large-area single-crystal Ag NPs can be obtained directly on the substrate surface. The atomic impermeability and high mechanical strength of graphene are well demonstrated in the experiment. Through the SPPT on the substrate, the obtained Ag NPs will show regular arrangement. In principle, the size and arrangement of the Ag NP can be precisely controlled. The Ag NPs exhibited a significant SPR effect, and the G peak of the Raman spectrum of the graphene was enhanced by 20 times. After long-term storage, the Raman enhancement effect remains unchanged, which proves that graphene plays a good role in protecting the Ag NPs from oxidation. The XPS results also verify this conclusion. Ag NPs are of great value in the fields of sensing, energy, catalysis. The preparation method reported here can be used to obtain large-area on-chip Ag NAs, which is conducive to integration with light sources (light-emitting diodes or semiconductor lasers) and detectors to fabricate a small sensor chip. At present, there is still room for improvement. By optimizing the graphene transfer process and using high-quality single-crystal graphene, more complete large-area Ag NPs should be obtained.

4. Experimental section

4.1. Preparation of Ag NAs

The Ag atoms is implanted into the substrate (heavily doped n-type Si with 300 nm SiO$_2$ layer) by ion implantation...
technique. The $n$-type Si substrate is doped with phosphorus, and the doping concentration is about $10^{19} \sim 10^{20}/\text{cm}^3$. The Ag source used for ion implantation is solid Ag with purity higher than 99.999%. The graphene used is monolayer graphene grown on the surface of Cu foil by chemical vapor deposition, and the monolayer ratio is higher than 97%.

First, the substrate was cleaned with ethanol (analytically pure), acetone (analytically pure) and DI water. Then, Ag atoms are implanted into the shallow surface of the substrate. The implanted energy is 30 keV corresponding to the implanted depth of about 22 nm, and the implanted dose is $5 \times 10^{15}/\text{cm}^2$. Next, the SPPT process is carried out. After the SPPT, a monolayer graphene is transferred onto the substrate. The graphene is transferred by the common wet transfer process [38]. The Cu etch mask used in the transfer process is a mixed solution of CuSO$_4$:HCl:HO$_2$ = 10 g:50 ml:50 ml. Then, annealing at 1050 °C for 15 min in a H$_2$/Ar (40 sccm/960 sccm) atmosphere. Finally, we obtain Ag NAs on the substrate surface. The preparation experiment of Ag NPs above has been repeated many times, which results prove that it has good reproducibility.

### 4.2. SPPT

First, SiO$_2$ nanospheres are transferred onto the substrate. The transfer step of the SiO$_2$ nanospheres is as follows: 1. Preparing a beaker with deionized water. 2. A solution mixed with SiO$_2$ nanospheres (solid content: 5%) was dropped into the deionized water. Due to the surface tension of water, the SiO$_2$ nanospheres will float on the surface of the water. 3. The substrate is first immersed in water using a pulling machine, and then pulled up. The SiO$_2$ nanospheres will be attached to the surface of the substrate. After transfer, the SiO$_2$ nanospheres are used as masks to dry etch the substrate in order to separate the implanted region into several regularly arranged small regions. The etching depth is about 40 nm. Then, removal of SiO$_2$ nanospheres by ultrasound in deionized water.

### 4.3. Material characterization

The surface morphology of Ag NAs was characterized by optical observation (Olympus BM51 optical microscope), SEM (Zeiss Merlin scanning electron microscope operating at 15 kV) and AFM (Bruker scanning probe microscope, Dimension FastScan). The XRD result is obtained using a Shimadzu x-ray diffractometer (XRD-7000). The Raman spectra were obtained using a Horiba LabRAM HR Evolution Raman microscope (532 nm laser). The XPS measurements were carried out on a Thermo Fisher ESCALAB 250Xi energy spectrometer.

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