LASER RE-GROWTH OF SINGLE CRYSTALLINE GOLD FLAKES ASSISTED BY HOT ELECTRON CATALYSIS

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Abstract

Despite recent growing interest in Plasmon-mediated growth of nanostructures, re-growth of gold flakes on amorphous materials such as glass is yet to be reported. Herein, we present simple route to fabricate gold flakes on top of glass coverslip and detail the process of re-growth by taking advantage of the intrinsic properties of the flake itself. Single crystalline gold flakes in regular shape of triangular and hexagonal structure was obtained. An experimental setup equipped with home-made microscope was fabricated to visualize the gold flakes. Experiments were run under different configuration and images were acquired. We numerically analyzed the images and comparison was made before and after illumination. Finally, recommendations are given for future development.

Keywords: Gold flake, nanocrystal, surface plasmon, hot electrons, nanoantenna.

1.0 Introduction

Noble metal nanoparticle has continued to attract huge interest due to their very fascinating optical and plasmonic properties, particularly gold and silver [1]. The Gold nanoparticle is a promising material for novel application in near-infrared plasmonic application such as plasmonic nanoantennas and optical nanocircuitry [2]. One of the most interesting properties of gold nanoparticle is that, its exhibits optical resonance within the visible wavelength range and it's sensitive to change in size and shape [3]. Single crystalline gold flakes can be model as plasmonic nanoantennas which are metal nanostructures with free electrons that can easily be driven by an external electromagnetic field [1]. Plasmonics is anticipated to bridge the gap between microscale dielectric systems and nanoscale electronics by providing promising devices with extremely small footprints at extremely very fast speed with low energy consumption compared to electronics [4]. One of these promising devices is the nanoscale antenna operating at optical frequencies called plasmonic nanoantenna [2], it can provide enhanced, controllable and extraordinary light matter interaction as well as strong coupling between far-field and localized surface Plasmon sources [2],[3]. Focused-ion beam milling of metallic thin film is the conventional way of fabricating plasmonic nanostructures, these metallic thin films suffers surface roughness which in turn result into high losses [6]. This trade-off between localization and losses jeopardize the chance for a wide range of application of plasmonics in wave-guiding, photodetection, photovoltaic and nanoresonators[3]. However, to overcome this setback, ultra smooth films such as single crystalline gold flakes can be used. When this gold flakes undergoes laser illumination, energetic hot electrons are generated. In fact, it is indeed an intrinsic property of any plasmonic nanoparticle under laser illumination [6], [22]. Despite recent advancement, the number of optically excited hot electrons and how to isolate them for novel application remain elusive. As inspired by [7], sophisticated hot electrons techniques can be use to grow a material with continuous crystal lattice and with no grain boundaries (single crystalline). In this work, we demonstrate laser re-growth of single crystalline gold flakes by taking advantage of the hot electron release upon laser excitation to catalyze the chemical reaction.

2.0 Experimental

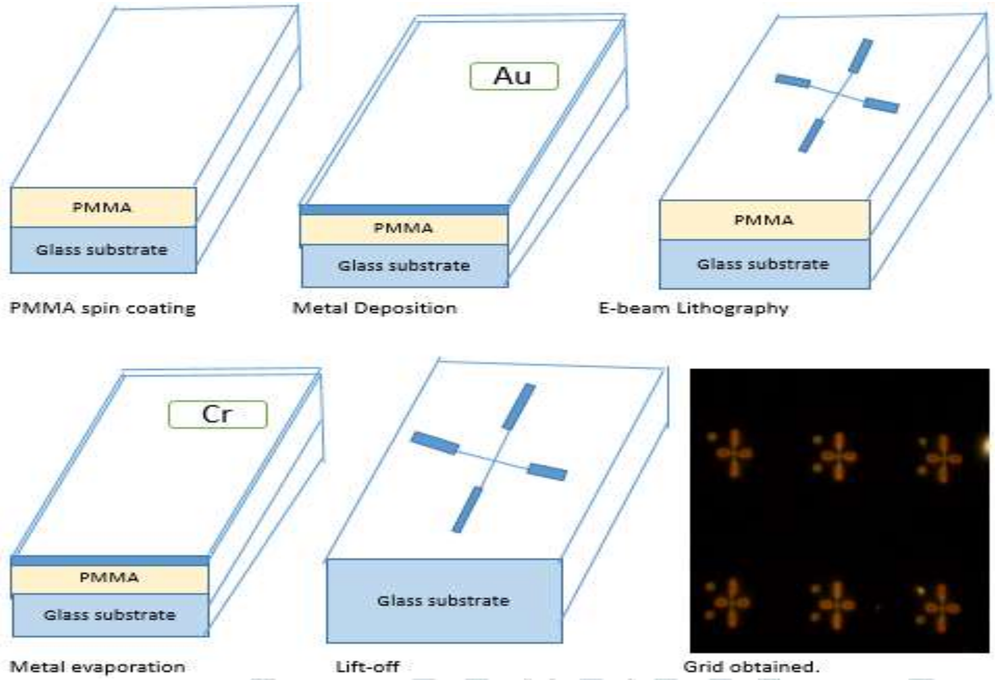
Here, the experiments consist of four stages namely; gold flake synthesis, grid fabrication, building the optical setup and sample preparation.

2.0.1 Gold flake synthesis

Our colloidal synthesis is based on the well known ethylene glycol method which makes use of the ethylene glycol as an organic environment for the colloidal synthesis. The recipe is adopted as exactly reported by [8]. This method is the simplest route to fabricate gold flakes as it involves only two ingredients; the gold precursor (HAuCl4) and the ethylene glycol. [8], [9] and [10] have demonstrated that gold flakes can be grown on top of any inorganic substrate such as silicon nitride, silicon wafer and glass. But to the best of our knowledge re-growth of gold flakes on top of glass cover slip has never been reported.

2.0.2 Grid fabrication

In order to clearly locate and identify the gold flakes, we wish to drop-cast the flakes on top of grid land mark fabricated by electron beam lithography as exactly inspired by [10], [11]. About 180nm thick layer of polymethylcrylate (PPMA 200k) was first spin-coated on a clean substrate and then followed by 50K PPMA. Soft baking was carried out at 60C for 10mins in order to evaporate the solvent and ensure uniform resist thickness. The substrate was gold sputtered in a high vacuum deposition chamber to make it conductive. The resist is exposed to electron beam at 20kev with a dose of 340$\mu c/cm^2$ through standard electron beam lithography. The sample is well calibrated before writing the alignment arrays. We now developed with MIBKAR600-56; a chromium layer was thermally evaporated with the help of a vacuum deposition chamber in evaporator machine. Chromium is preferred over other metals due to its ability to promote adhesion. The unexposed resist was then removed via lift-off with aid of a remover (ARP600-71); the figure below summarized the steps.



Figure(1): shows the steps for grid fabrication, the process is first spin coating, metal deposition, e-beam lithography, metal evaporation, lift-off and finally the grid is obtained.

2.0.3 Building the optical setup

Here, we designed an optical setup on which the experiment is conducted. A home-made microscope was fabricated to visualize the gold flakes under illumination. A beam expender is used in order to fill the numerical aperture of the objective as shown in figure (1). A white light source is also introduced to enable Kohler illumination with the help of beam splitter such that the resolution is greatly enhanced. A set of wave-plate is used to control the polarization and a high numerical aperture objective 40/0.28 is used to focus the beam. A dark field objective makes the image of the sample on the charged-couple device (CCD) camera. The sample is place in between the two objectives with help of sample holder supported on a moving stage which enabled side-ways movement with nanometer precision. A camera equipped with thorlab software is fixed on one end for display and acquisition of the image. Figure (1.1) below illustrate the schematic diagram of the optical setup.

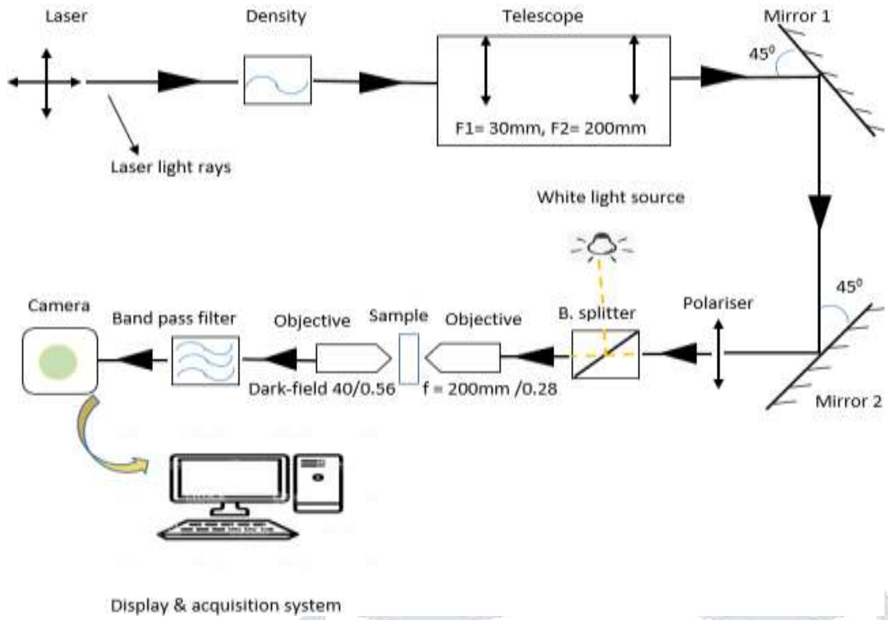
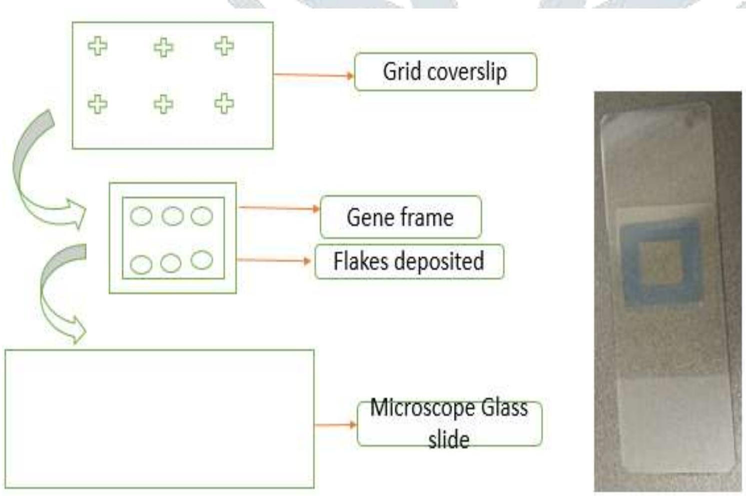


Figure (2) shows the schematic diagram of the setup.

2.0.4 Sample preparation

The microscope glass slide was first clean by immersing it in ultrasonic bath for about 15 minutes and then repeatedly cleans with acetone and rinse with ethanol to completely remove impurities and other contaminants which may be present. Gene frame (an adhesive tape) is fixed on the glass slide for easy release of the cover slip and to prevent leaving behind any sticky residue. The gold flakes are then drop-casted on the slide and sealed with grid fabricated above, evaporation is done at 60^{o}C for 15mins. At some point bubbles formation was observed instead of the flakes, we attribute this drawback to the hydrophobic and hydrophilic nature of the glass slide and to the nature of the surface treatment of the glass slide. Sometimes the solution spreads evenly as soon as drop-casted but sometimes it beads into tiny droplets. To overcome this setback, we employ the service of plasma cleaner as recommend in [12], in advance to the conventional wet cleaning of using acetone and ethanol. Finally, the glass surface is modified, activated and transformed into hydrophilic.



(a) Procedures for sample preparation (b) sample prepared

Figure (3) illustrate how the sample is prepared

We now move to the setup to first observe the formation of the gold flakes before running the experiment. The figure below illustrates the formation and distribution of the flakes as captured by the fabricated home-made microscope.

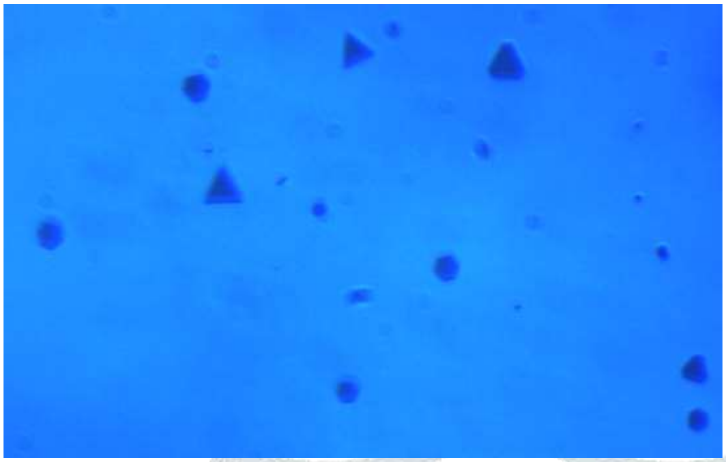


Figure (4) shows formation and distribution of gold flakes on the glass slide.

We now choose flake with well define shape and size to grow; we first capture the image in order to have prior information about the size and shape before re-growth. After that, we center-focused the characterized laser beam on the flake as can be seen in the figure below:

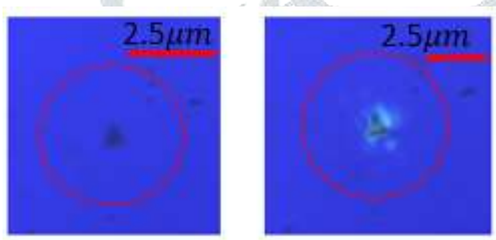


Figure (5): (a) Gold flake to be grown, (b) Gold flake with beam center-focused on it.

During illumination, the laser is blocked from reaching the camera in order to prevent saturation. Experiments were run under different conditions by changing the polarization and laser power (type), the laser used in this experiment were said to be continuous wave(c-w) single pulse laser. We consistently adjust the geometry of the setup until the best configuration was found and adopted throughout the experiment. A 1*m*w red laser is used for the experiment and a density filter to unsaturate the beam, Images were taken at 1 hour interval to get insight on how the growth evolves with time. The laser is circularly polarized to ensure uniform intensity distribution within the flake, insights from this experiment shows that the circular polarization could be the best and so adopted throughout subsequent experiment.

3.0 Result and discussion

The nature of gold flakes obtained via the colloidal synthesis above is shown in figure (3.7). The flat features of the flakes are due to the stable behavior of $HAucl4$. Although twinned and truncated triangular gold flakes were observed but in general triangular and hexagonal gold flakes with sharp edges dominate the by-product. The size ranges fromaround2 to 5μm as can be seen in figure (6) below. Secondly, the flake has uniform size within one flake and this makes the fabrication process easier as opined by [16]. Our investigation details the route to induce photochemical reaction by taking advantage of the intrinsic properties of the gold flake itself. Figure (6) below summarized seven different experiments conducted under similar conditions. However, throughout this experiment only slight change in size but no occurrence of any shape transformation was observed. We assumed that, the laser power is not sufficient enough to delocalize the Plasmon that in turn produces hot electrons to trigger the chemical reaction. We then decide to carry out an overnight experiment but we lost the flake, the next day due to drift in alignment and some particles accelerating from one point to another. Ideally, the focus should be kept constant so as to have uniform contrast of the image before and after illumination but the drift in alignment makes it almost practically impossible when allowed to run over long time. We now numerically analyzed the images captured during step growth, before and after re-growth to determine whether there are small changes as can be clearly seen in the figure (6 & 7). One can notice slight numerical increase in size but the numbers aren't significant enough, this is due to low laser power. However, this is the laser at our disposal. We envisaged that, if the laser is replaced with a more powerful one such as green lasers, picosecond laser or femtosecond laser significant rapid growth could be observed. It is also obvious that, colloidal synthesis of nanoparticle suffers some major drawback such as flakes aggregation, precipitates formation, Flake twinning which causes loss of large flake area and tendency for large flakes to roll off in solutions. In general, chemical synthesis of metal nanoparticle is a simplest process which only requires mixing of chemical reagents at certain well-defined conditions. But this can be tricky due to influence of external conditions which prevent chemical reaction from taking place or affect the morphology of the metals synthesized. Much attention may be given to the concentration of the reactants but the PH value and temperature also have strong impact on the chemical reaction. The cleaning is also a big issue as it can easily alter the chemistry, many cleaning processes were proved more efficient than the wet cleaning such as; Piranha ($H2O2$) which not only remove organic matter but also slightly etches the glass surface and increases the negative charges of the glass and attenuated KOH is also widely used and it completely remove contaminants.

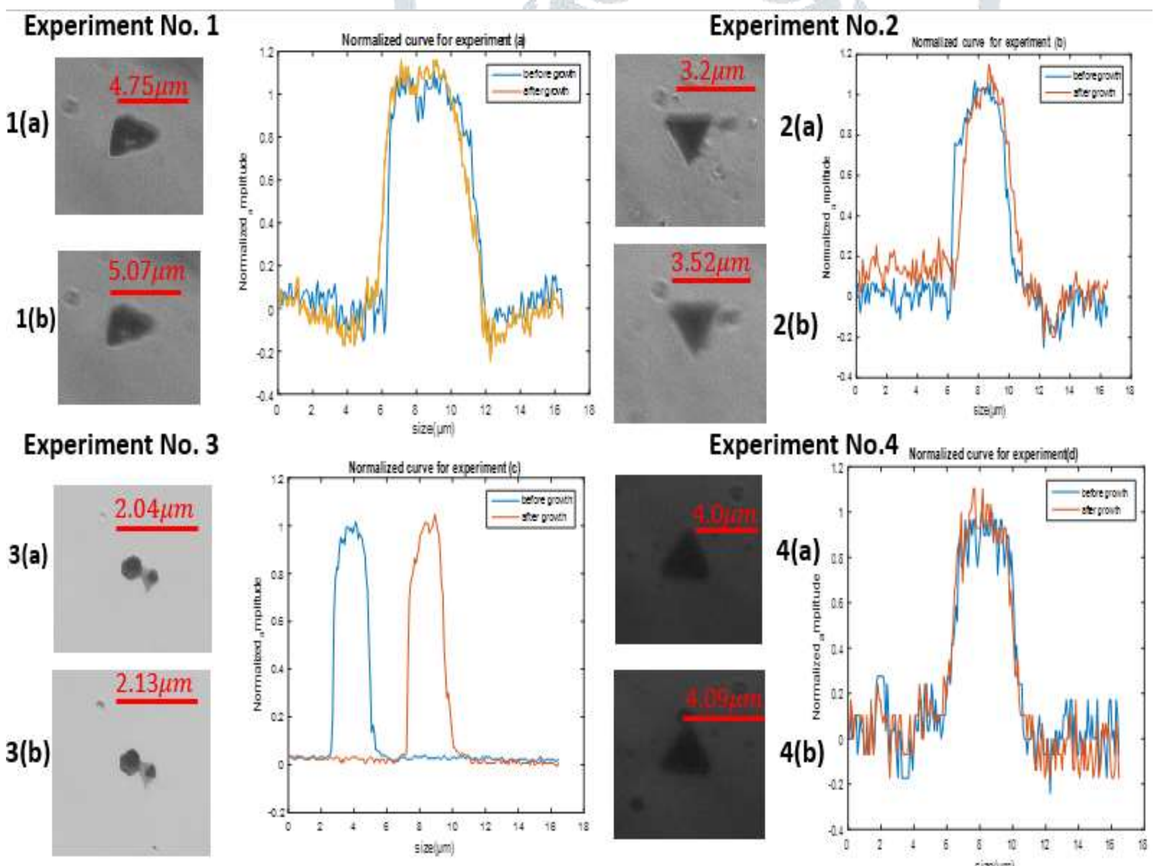


Figure (6): 1(a) triangular gold flake of size 4.75µm before illumination, 1(b) same flake with size 5.07µm after 7 hours of illumination with 1mW 632nm red laser(c-w) and their corresponding size curve sub plotted for comparison. 2(a) Gold flake of size 3.2µm before illumination, 2(b) same flake after 7hours of illumination with 1mW 632nm red laser(c-w) and by the side is a normalized curve sub plotted to compare their size before and after. 3(a) is a hexagonal gold flake of size 2.04µm identified before illumination, 3(b) the same flake with size 2.13µm after 7hours of illumination with same laser as above. By the right is also their size curve normalized to ease comparison before and after illumination. 4(a) triangular gold flake of size 2.13µm before illumination, 4(b) is the same flake after 7hours of illumination with their normalized size curve for comparison.

4.0 Conclusion

It has been shown that, Gold flakes can be fabricated and grown ontop of a glass coverslip. The experiment was carried out at ambient temperature and therefore defects such as air impurities can easily alter the chemistry. This paper intends to reveal a simplest route to induce photo-chemical reaction in gold nanocrystal via the intrinsic properties of the nanocrystal itself. It also inspire a strategy to utilize hot electrons in exploiting the potential of noble metal nanoparticle whose plasmonic resonances can be tailored. With this recipe long time stable gold nanoparticles are obtained but less density of flakes were observed. The gold flakes obtained have well-defined crystal orientation, enormous aspect ratio and constant thickness within one flake, a feature which facilitate nanostructure fabrication. By comparison, the process of gold nanoparticle formation by the well-known reduction techniques as reported by Turkevich and Frens can yield much better result. However, the method proposed here is cheap, easy to implement as it requires no specialize instrumentation while one has the freedom of chosen particular flake to be grown.

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