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Fabricating an Ordered Array of Silver Nanoparticles *via* the Nanosphere Lithography Technique

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The challenge of new technology is to produce inventive optical nanogratings, optical nanofilters, solar cell nanoabsorbers, antireflective surface coatings, and nanoelectronics by generating consistent patterns of various sizes and shapes of nanostructure on the smooth and solid surfaces. Nanosphere lithography (NSL) is a cost-effective and easy-to-implement technology that can be used to produce a diverse range of highly ordered nanoparticle-array structures. In this work, physical vapour deposition is used to grow large periodic arrays of silver nanoparticles and nanorings on patterned glass and silicon substrates. To achieve this, a single layer of self-assembled polystyrene nanospheres is firstly applied to the substrate to serve as a mask, and silver is then deposited through the mask. The spacing between the nanospheres can be adjusted by changing the diameter of the polystyrene nanospheres, which affects how the silver is deposited as nanodots or nanorings. The optical transmittance spectra of glass arrays can show significant variation depending on the specific nanostructure that is created. Regarding localized surface-plasmon resonance, nanorings display a red shift and a widening in the plasmon band. Possible uses for the resonance effect of the nanostructure are discussed.

Key words: nanosphere lithography, self-assembly, doctor blade, nanodots, nanorings, plasmonics.

Завданням нової технології є створення спритних оптичних дифракційних наноґратниць, оптичних нанофільтрів, нанопоглиначів для сонячних елементів, просвітлювальних поверхневих покриттів і наноелектроніки

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шляхом ґенерації послідовних зразків наноструктур різного розміру та форми на гладких і твердих поверхнях. Наносферна літографія (НСЛ) — це економічно ефективна та проста в реалізації технологія, яка може бути використана для створення різноманітних високовпорядкованих масивних структур наночастинок. У цій роботі фізичне осадження з газової фази було використано для вирощування великих періодичних масивів наночастинок срібла і нанодротиків на візерунчастих скляних і кремнійових підкладинках. Для цього на підкладинку спочатку наносять один шар самоскладаних полістирольних наносфер, який слугує маскою, а потім осаджують срібло через маску. Віддаль між наносферами можна реґулювати, змінюючи діяметер полістирольних наносфер, що впливає на спосіб нанесення срібла у вигляді наноцяток або нанокілець. Спектри оптичного пропускання скляних масивів можуть демонструвати значну варіяцію залежно від конкретної наноструктури, яка створюється. Щодо локалізованого поверхневого плазмонного резонансу, нанокільця демонструють червоний зсув і розширення плазмонної смуги. Обговорюються можливі застосування резонансного ефекту наноструктури.

Ключові слова: наносферна літографія, самоскладання, скребок-лопатка, наноцятки, нанокільця, плазмоніка.

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1. INTRODUCTION

The development of efficient manufacturing techniques, particularly at the nanoscale, has always been an arduous task. Despite advancements in technology, it remains difficult to discover an affordable and replicable method for creating nanoscale structures [1, 2]. Scientists are intrigued by the possibility of manipulating the properties of materials by selecting and interacting with individual particles. This has led to a growing interest in arranging nanoparticles into complex periodic nanostructures [3]. The unique optical properties of metal nanostructures are due to their smaller size and the replacement of continuous energy levels (density of states) with discrete energy levels, which are dependent on the size and shape of the nanostructures [4, 5]. These energy levels have an impact on the electronic structure and can result in novel optical effects [6]. According to the Drude model, metals possess free conduction electrons, and the plasmonic response refers to the collective excitation of the free electrons in relation to the positive ion cores [7, 8]. When electrons at the interface of a metal and a dielectric (including air) oscillate and couple with an electromagnetic field, surface plasmon polaritons (SPP) can be generated and move along the surface [9]. If the SPP is confined to a nanometre level, a localized surface plasmon resonance is created, which strengthens the electromagnetic field around metallic nanostructures [10]. The detection of electromagnetic field enhancement can be achieved using various techniques such as light absorption, Raman signal enhancement, photoluminescence, and fluorescence [11].

Many nanodevices are constructed through surface nanopatterning, which can be achieved with great efficiency through template-based surface nanopatterning techniques. Diverse surface nanopatterns can be created using these processes [12, 13]. As a result of the progress in nanotechnology and nanoscience, scientists across different disciplines have gained great proficiency in dealing with nanostructures [14]. This has enabled them to explore the exceptional properties that arise from the nanoscale dimension [15]. There has been a surge in interest in the manufacturing of nanostructures due to this development. Materials scientists, physicists, biologists, and chemists find that the costly and inefficient method of maskless lithography is not a practical solution. The creation and preparation of the mask are the main reasons why mask-assisted lithography is limited to microelectronics facilities and cannot be expanded successfully [16].

Different nanostructuring methods are available to pattern unique nanostructures, such as nanorings, nanodots, nanotubes, nanospheres, and nanopillars on substrate surfaces. Nanopatterning has brought about numerous benefits, which have had a favourable effect on a significant number of nanogap devices, including vacuum sensors, photodetectors, diodes, transistors, OLEDs, sensors, and memristors [17]. The techniques used for this purpose primarily comprise electron-beam lithography, nanoimprinting, scanning probe microscope writing techniques, focused ion beam lithography, and replica moulding processes [18, 19]. However, the surface modification process for these techniques can be sophisticated [19]. When compared to other nanopatterning techniques, the NSL method is a cost-effective approach that saves time and allows for the production of large, well-organized arrays of nanostructures without requiring expensive equipment [20, 21].

The intricacy of the interactions between nanoparticles and the various physicochemical phenomena that occur during assembly are significant factors contributing to the challenges involved in assembling colloidal nanoparticles into a well-defined nanocrystals lattice structure [3]. NSL relies on self-assembled monolayers of spherical nanoparticles as a mask. The ability of colloidal particles to become trapped at gas-liquid or liquid-liquid interfaces significantly affects self-assembly at the gas-liquid interface. This confinement is due to a combination of electrostatic and capillary forces, as well as the hydrophobic properties of the nanospheres' surfaces [22]. Various techniques such as doctor blade [23], spin coating [24], Langmuir–Blodgett [25], drop casting [26], and dip-coating [27] can be used to create self-assembled monolayers. The spherical nanoparticles are arranged in hexagonal close-packed (h.c.p.) arrays through a convective self-assembly mechanism that is caused by the interaction between the nanoparticles and the solvent used in the process [28, 29].

The low-cost fabrication technique of Ag nanoflower arrays growing on the photoresist surface has been demonstrated for surface-enhanced Raman spectroscopy [30]. Considering that the photoresist material is not conductive, this method of fabricating a patterned substrate might not be suitable for certain applications, such as solar cells, where materials with good electrical conductivity are required for efficiently collecting and transporting the generated electrical charges.

This article explains a method for organizing Ag NPs into precise patterns, like nanodots and nanorings. The process involves using two-dimensional scaffolds made of suspended polystyrene nanospheres to guide the nanoparticles' arrangement. The convective self-assembly approach offers a protected and pliable $2D$ space for the polystyrene nanospheres to form ordered scaffolds on a surface. These scaffolds have a hexagonal pattern of polystyrene nanospheres that serve as a template for the Ag NPs. This technique allows for the creation of ordered nanoparticle arrays with unique optical and structural characteristics that can be localized over a few tens of microns. The convective self-assembly mechanism is a practical way to design and produce various devices with ordered nanoparticle arrays.

2. EXPERIMENTAL DETAILS

The diagrammatic representation of the doctor-blade apparatus has been illustrated in Fig. 1, *a*, which employs the convective self-assembly process of nanospheres as shown in Fig. 1, *b*. The process involves the assembly of a single layer of polystyrene nanospheres with a diameter of 750 nm on a hydrophilic substrate. The substrate is first fixed onto a motorized stage to regulate its speed, and the current ex-

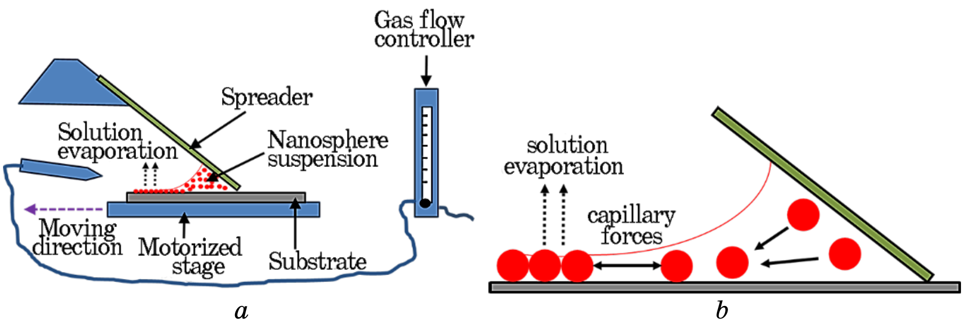


Fig. 1. Schematic representation of (*a*) doctor-blade setup; (*b*) convective self-assembly mechanism.

periments speed is optimized to be 5 millimetres per second, while a glass slide is utilized to spread the nanospheres. As the stage begins to move, the nanosphere suspension is pulled along the substrate, and N_2 gas is utilized to regulate the suspensions evaporation by blowing it across the suspensions end. By purging the atmosphere, N_2 gas controls suspension evaporation and creates a regulated environment with lower humidity levels. Additionally, it gently disperses agglomerated or weakly connected polystyrene nanospheres, permitting the formation of a monolayer film that is uniform and stable.

The formation of the nanosphere suspension monolayer can be affected by various factors such as concentration, stage speed, and solution dilution, and this process can be monitored using an optical microscope to control the evaporation rate of the solution. To adjust the distance between polystyrene nanospheres and control their diameters, oxygen plasma etching was employed. An electric field is applied to a mixture of oxygen and argon gas in a vacuum chamber, which results in the formation of plasma. Positive oxygen ions and electrons are produced by the electric field and are accelerated toward the substrate by the plasma. In the polystyrene nanospheres, the carbon and hydrogen atoms chemically interact with the oxygen ions to produce the carbon–oxygen and hydrogen–oxygen bonds. The polystyrene nanospheres can degrade (etch) as a result of this process. The resulting monolayer was utilized as a mask to generate structures such as metal nanodots and nanorings. Once the nanosphere template was formed, a 50-nm thin film of Ag was deposited onto a patterned substrate. The nanosphere mask was removed by chemical etching, accomplished by sonicating the substrate in toluene for 2 minutes by using an ultrasonic bath with very low power to avoid removing the deposited Ag nanodots and nanorings from the substrate. The formation of Ag nanodots and nanorings utilizing the nanosphere lithography technique is schematically illustrated in Fig. 2.

3. RESULTS AND DISCUSSION

A photograph representing a single layer of polystyrene nanospheres with a thickness of 750 nanometres was displayed in Fig. 3. These nanospheres have been assembled on both glass and silicon substrates. It is evident from the picture that the convective self-assembly process [24] can be employed to fabricate nanospheres on a substrate of significant size.

Top and side views of a 750-nanometer single-layer nanosphere are displayed in Fig. 4, *a* and Fig. 4, *b*, respectively. These nanospheres have formed on the substrate through the self-assembly process of the polystyrene nanospheres, resulting in the creation of a uniform and crystal-like structure.

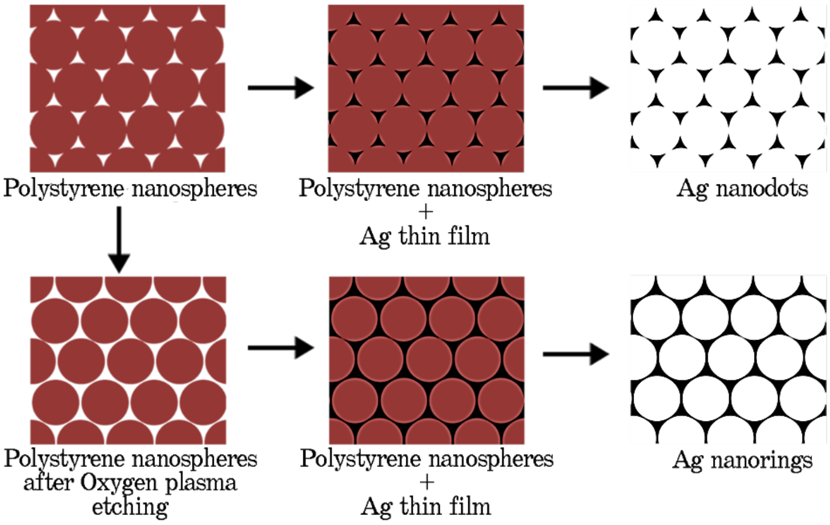


Fig. 2. Schematic representation of nanodots and nanorings periodic array formation.

In Figure 1, *b*, the experimental setup is depicted with a magnified view of the substrate and the spreader, which demonstrate the three processes controlling the formation of a monolayer array [28]: capillary forces, which draw liquid from the rest of the solution to the dry regions; convective transfer of nanospheres from the remainder of the

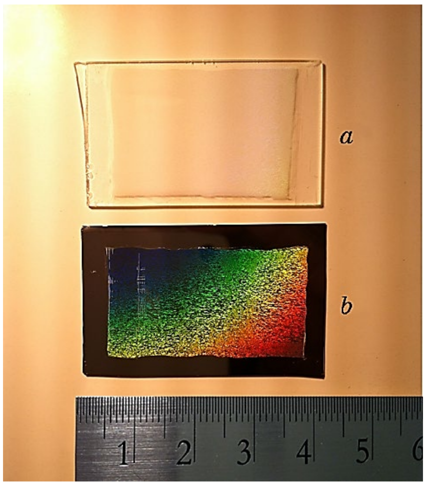
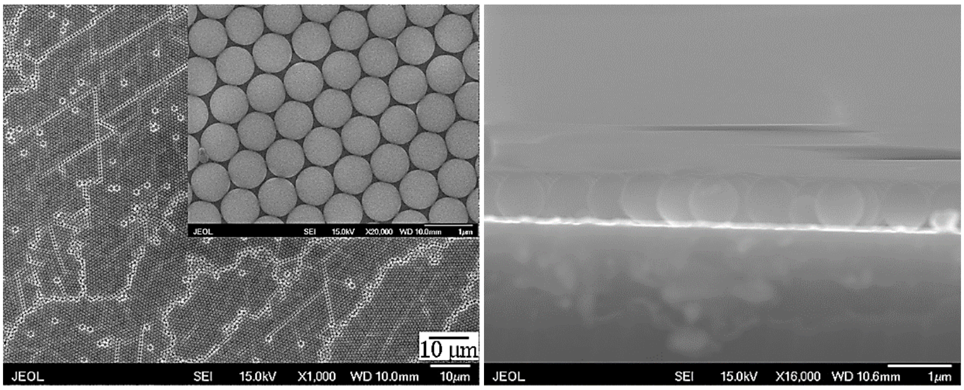


Fig. 3. Polystyrene nanospheres deposited on (*a*) glass and (*b*) silicon substrates.



a *b*

Fig. 4. SEM image of a 750-nm single-layer polystyrene nanosphere with a uniform crystal-like structure (*a*) top view (the inset shows a magnified image of the top view) (*b*) side view.

solution to the thin wetting film; and water evaporation. A pressure difference is formed when the solution drop is positioned along the angle of the spreader. This difference induces a capillary effect, which transfers a portion of the solution from the main drop to the dry zone, resulting in the formation of a thin wetting layer [22], as illustrated in Fig. 1, *b*. The nanospheres can seek out the configuration with the lowest energy by freely flowing all over the substrate [22].

Once the evaporation process takes place, the nanospheres form a monolayer that is packed closely in a hexagonal pattern, which can be seen in the inset image in Fig. 4, *a*. The process is sustained by moving the stage at a steady speed in the opposite direction of the monolayer formation. The formation of a monolayer is dependent on a withdrawal rate of the solution that is proportionate to the rate of water evaporation in the dry region. If the withdrawal rate is slower than the evaporation rate, nanospheres will accumulate and create multilayer arrays dominating the substrate. Conversely, faster withdrawal rates lead to an amorphous deposition with unfilled zones.

The emergence of point, line, and area defects on the substrate is depicted in Fig. 5. The nanospheres have to balance two forces, *i.e.*, adhesion between polystyrene nanospheres and adhesion between polystyrene nanospheres and substrate, as they experience polymer interdiffusion, which is the primary cause of defect formation [31].

An SEM image of modified nanospheres' diameters after undergoing oxygen plasma etching for 2 seconds is shown in Fig. 6. As a result, the nanospheres' diameters reduce from 750 nm to 745 nm, creating gaps between them for thin-film deposition. In the thermal evaporation system, a 200 nm thin film of silver was deposited by utilizing the

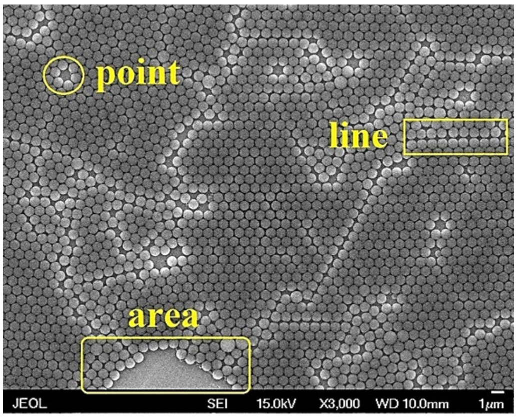


Fig. 5. SEM image of a 750-nm polystyrene nanosphere with a uniform crystal-like structure and some point, line, and area defect formation on the substrate.

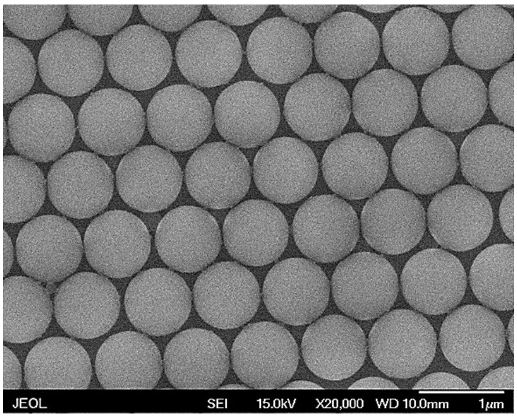
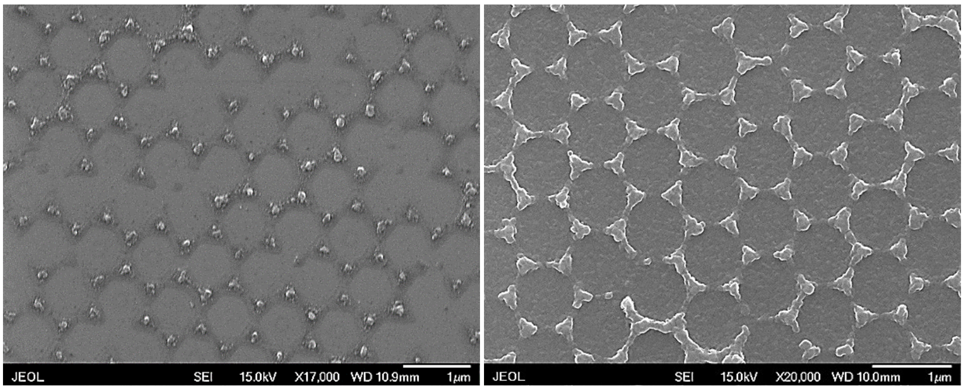


Fig. 6. SEM image of a single-layer polystyrene nanosphere after oxygen plasma etching for 2 seconds.

spacing between polystyrene spheres, resulting in hexagonal arrays of nanoscale silver nanodots (Fig. 7, *a*) and nanorings (Fig. 7, *b*) on both substrates before and after etching. The polystyrene nanospheres were removed from the substrate by immersing them in a Toluene ultrasonic bath after silver deposition. The results depicted in Fig. 7 demonstrate that this cost-effective and straightforward method can be used to create highly aligned nanoparticles suitable for optoelectronic [1, 12, 17] and medical applications [7, 32]. The aligned array of silver nanostructures efficiently traps light by scattering it into specific optical modes, leading to a notable increase in optical absorption [33].



a *b*

Fig. 7. SEM image of (*a*) silver nanodots and (*b*) silver nanorings.

The transmittance spectra of silver nanostructure ensembles on a glass substrate have been revealed in Fig. 8. The arrays of silver nanodots and nanorings are denoted by the dashed and solid curves, respectively, and they exhibit localized surface plasmon resonance (SPR) at wavelengths of 502 nm and 520 nm. As the nanoparticle size increases, the plasmon band widens and its intensity decreases, causing the spectral line to shift towards the red due to the retardation effect [4, 34, 35]. Varying the size of nanoparticles allows for the creation of adjustable optical sensors as it causes a shift in the plasmon resonance. This suggests that the spectral response is influenced by the size and shape of the nanostructure. The use of Ag NPs can function as a light-trapping layer on the transparent electrode or within the absorber layer [36] of a solar cell, enhancing the multiple scattering of incoming light [37].

4. CONCLUSION

This paper introduces a timesaving lithographic technique called nanosphere lithography. The process involves using a lithographic mask composed of 2*D* colloidal polystyrene nanospheres, onto which material for evaporation is applied resulting in a range of shaped particles on the substrate. By adjusting the diameter of the nanospheres, nanoparticles in a hexagonal framework can be created. Oxygen plasma etching can be used to modify the size of interstices between the nanospheres in a controllable manner. This approach significantly reduces the cost of fabricating nanostructured samples compared to other lithographic techniques. The present study shows that large-area monolayers of polystyrene nanospheres can be organized with considerable 2*D* colloidal monocrystals, although these colloidal monolayers have structural

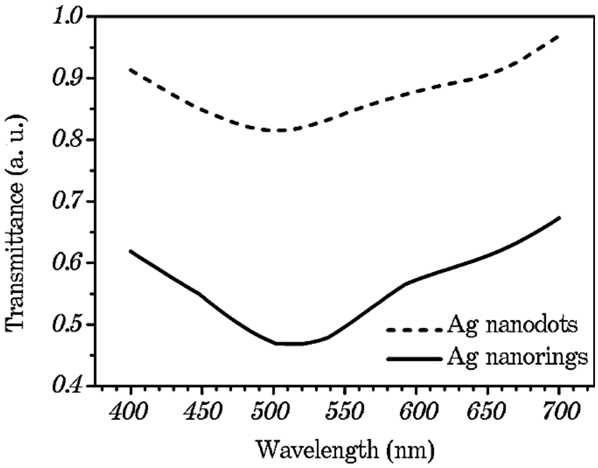


Fig. 8. Optical characterization of Ag nanodots and nanorings arrays.

deficiencies like conventional crystals. To create periodic arrays of nanoparticles like nanodots and nanorings, prepared colloidal masks are used, and a thin layer of silver is applied to the nanospheres mask via thin film deposition, while the crystal arrangement is maintained since this technique has no impact on the inner structure of polystyrene nanospheres. Oxygen plasma etching is used to create masks with not connected packed arrays of polystyrene nanospheres. When silver evaporates through the etched spheres, a layer with spherical mesh holes is formed. These nanoparticle arrays on a large substrate allow a simple optical characterization and can be used to illustrate the practical uses of these arrays. Overall, nanopatterning is an important technique in solar cell production that can enhance their efficiency and performance by allowing researchers to create precise, nanoscale structures that enhance the optical and electronic properties of solar cells.

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