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Laser Guidance Deposition Technique for Patterning Microstructures Made of Nanoparticles with Varying Surface Functionality

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ABSTRACT

We present results on patterning microstructures using laser-guidance deposition of nanoparticles from particle-in-solvent suspensions. A laser beam axially confines and propels the particles inside a hollow optical fiber towards a substrate. Confining is provided by the gradient forces arising from light refraction or electrical forces on polarizable particles. The driving force results from the momentum conservation of photons scattered on particles. Polystyrene particles (100 and 400 nm in diameter) and gold particles (from 8 to 50 nm) with different surface organic functionality serve as a constructive material for fabrication of microstrips. In the experiments, the laser power varies from 0.1 to 1.6 W. The microstrips produced under different deposition conditions are studied using optical microscopy and atomic force microscopy. It was found that deposited polystyrene and gold particles form nanoclusters consisting of at least several particles. If deposited at an appropriate rate, such nanoclusters form multilayer microstrips of high particle density. The typical width of the microstrips ranges from less than 10 microns to 100 microns. This technique allows us to fabricate parallel arrays made of colloidal particles with different surface functionality, which seems to be an especially attractive approach for developing novel chemical and biological microsensors.

INTRODUCTION

The need for and popularity of chemical and biological sensors have created a requirement for new techniques that could pattern organic and biological particles/molecules with the feature size of submicro- or nanometer scales without losing their chemical and biological functionality. Photolithography and electron-beam lithography are the most popular patterning techniques, which are at the heart of modern-day microfabrication, nanotechnology and molecular electronics. All such techniques require a resistive film and harsh chemical etching [1], which makes them unsuitable for patterning nanoparticles or molecules with organic or biological functionalities. Other newly developed techniques, such as “Dip-Pen” nanolithography (DPN), can directly transport particles and molecules to a substrate from the AFM tip allowing patterning on nanometer scale [1]. However, the amount of materials such techniques can transport is small, while transportation efficiency is relatively low. Microcontact printing, which uses an elastomer stamp, can fabricate heterogeneous structures of the micron-size and larger dimensions, but has a limited potential for a mixed functionality surface fabrication [2]. As a complement to many existing micro- and nanopatterning techniques, we present a patterning technique called Laser Guided Direct Writing (LGDW) that can directly trap and pattern nanoparticles onto selected substrates often without losing particle’s functionality.

The LGDW technique, developed at Michigan Technological University, uses optical forces arising from scattered and refracted light at particle interfaces to both axially confine and propel particles through a hollow optical fiber by a laser beam [3]. One of the advantages of this patterning technique is its ability to transport to a substrate a wide variety of materials: metal particles, polystyrene beads, liquid droplets, as well as living biomaterials such as cells and proteins [4]. Virtually any material (inorganic, organic and bio-) can be deposited on any substrate, including flexible substrates, with micron-scale precision [5]. Complex structures can be formed by repeatedly depositing individual

particles with sizes ranging from 10 nm to 10 μm on translated substrates [6]. We use this technique to make microstructures for potential chemical and biological sensor applications. Polystyrene beads (100 and 400 nm in diameter) and gold nanoparticles (from 8 to 50 nm) with different organic functionality on the surface are selected as constructive materials for such structures.

EXPERIMENT

The LGDW system is shown schematically in Fig. 1. It is comprised of a CW laser (wavelength 532 nm), focusing lens, mounted hollow optical fiber or aperture, substrate mounted on the xyz-translator, and mist aerosol generator. The mist of liquid droplets is produced from a starting liquid precursor or colloid suspension by a modified commercial ultrasonic nebulizer [4, 6]. The regulated airflow delivers the droplets to the fiber entrance or aperture. The laser beam is focused with a low numerical aperture lens through the mist to couple with the fiber or aperture and to funnel the droplets into the entrance for transporting them to the substrate. There are two laser-induced optical forces acting on the trapped droplets. One is the force from the back-scattered light, usually known as radiation pressure, which will propel the droplets forward along the laser beam. The other force arises from the refracted light, referred as the gradient force, which points in the direction of the laser beam intensity gradient; it confines droplets axially.

In our experiments with dielectric functional beads, polystyrene beads with a diameter of 100 nm and 400nm (Duke Scientific Co.) were selected to deposit through fibers onto glass. Avidin was attached onto the polystyrene surface by incubating avidin with the beads in phosphate buffered saline (PBS) [7]. A suspension of the processed beads in water with given concentrations were then prepared, converted into mist by a 2-MHz nebulizer and deposited onto silanized glass slides by the LGDW. After deposition, the silanized glass slides were rinsed in the 3% bovine serum albumin (BSA) solution and then immersed in a solution of fluorescein-biotin (Molecular Probes). A spectrofluorimeter (ISA Instruments SA, Inc.) was used to detect the fluorescent peak at 520 nm on the slides. Alkanethiol stabilized gold powder $CH_3(CH_2)_7S$-Au (obtained from the University of Michigan) was suspended in toluene at a concentration of 5 mg/mL. The fabricated microstructures were evaluated by optical microscopy and AFM (Dimension 3000, Digital Instruments). AFM images were taken at a scan rate of 1 - 2Hz with scan sizes from 1 μm×1 μm to 20 μm × 20 μm, using TappingMode™ etched silicon probes (TESP) cantilevers.

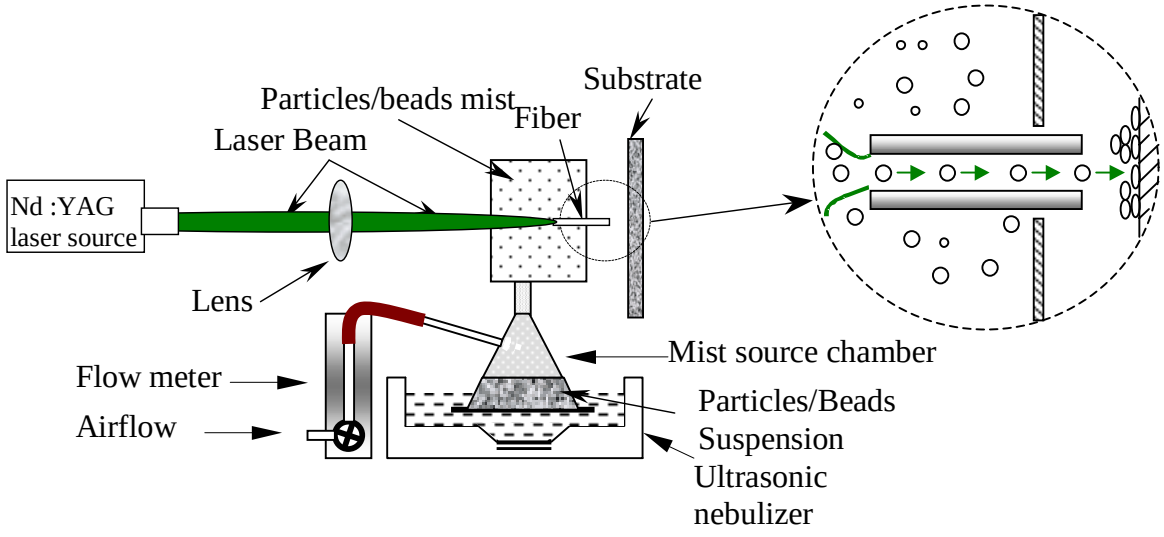
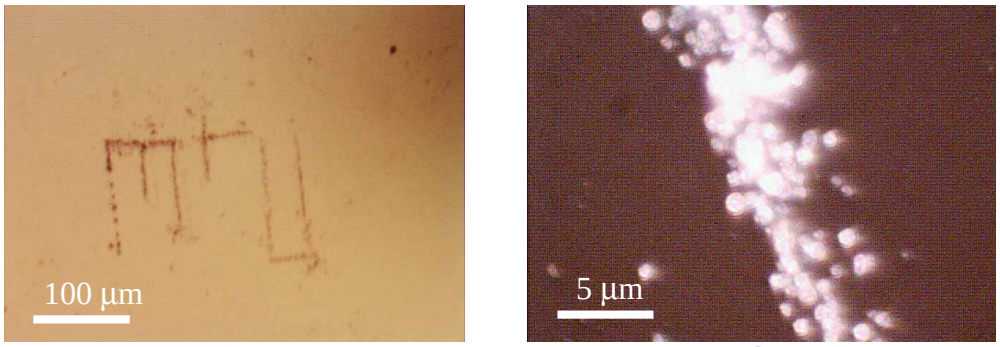


Figure 1. Schematic of Laser Guided Direct Writing system



(a) (b)

Figure 2. (a) "MTU" pattern made of 400-nm polystyrene beads by LGDW on a silanized glass substrate (laser power 300 mW, hollow fiber 6 mm long and 20 μm ID, the distance 10 μm between the fiber end and substrate). (b) Optical image of a line in (a) at higher magnification.

RESULTS

Deposition of polystyrene beads

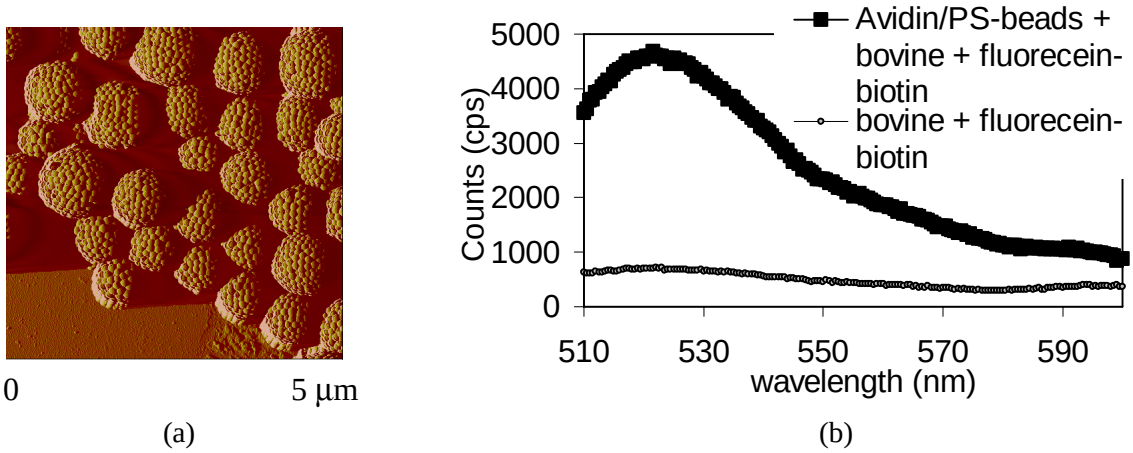
Polystyrene beads, commercially available in a wide range of sizes, have the ability to carry proteins on their surface. We explore patterning of polystyrene-protein particles for potential biosensor applications; some of the preliminary patterns are shown in Fig. 2.

The MTU letters in Fig. 2a are made of 400 nm polystyrene beads. The lines are patterned by repeatedly moving the substrate forward and backward along one direction. As seen in Fig. 2b, the lines are about 5 micron wide, i.e., equal to ten beads placed side by side. Similar patterns were also obtained with 100 nm polystyrene beads (not shown). We found that the deposition precision depends on several parameters including the intensity of the laser beam, size of droplets generated by the nebulizer, solvent type, and distance between hollow fiber end and substrate. Under optimal operational conditions, the deposition precision can approach the 1-micron range [4].

The patterns of 100 and 400 nm polystyrene beads fabricated in our experiments were composed of not individual beads but clusters resulting from transporting and depositing polystyrene-in-water droplets produced during the atomization of the initial water-polystyrene suspension. We believe that the number of beads in each droplet is proportional to the bead concentration. An AFM image of 100-nm polystyrene bead clusters deposited on a silanized glass substrate at laser power 300 mW is shown in Fig. 3a. As seen, the area density of the beads is practically independent of the cluster size; additionally, the beads are not distributed randomly, but form chains oriented predominantly in one direction (close to vertical in Fig. 3a). Both regular arrangement of beads in clusters and a spherical shape of the clusters imply on the role of capillary forces in patterning of regularly-shaped polystyrene particle clusters. It is not clear however, whether water evaporates before or after the droplets reached the substrate in this example. The higher the laser power the more probable the former.

Another factor is the average size of droplets in aerosolized mist. According to ultrasonic atomization models, the diameter of droplets generated by the ultrasonic nebulizer depends on the solution surface tension σ, its mass density ρ, and transducer frequency ω as:

$$d = C\left(\frac{\sigma}{\rho\omega^2}\right)^{1/3} \quad (1)$$



(a) (b)

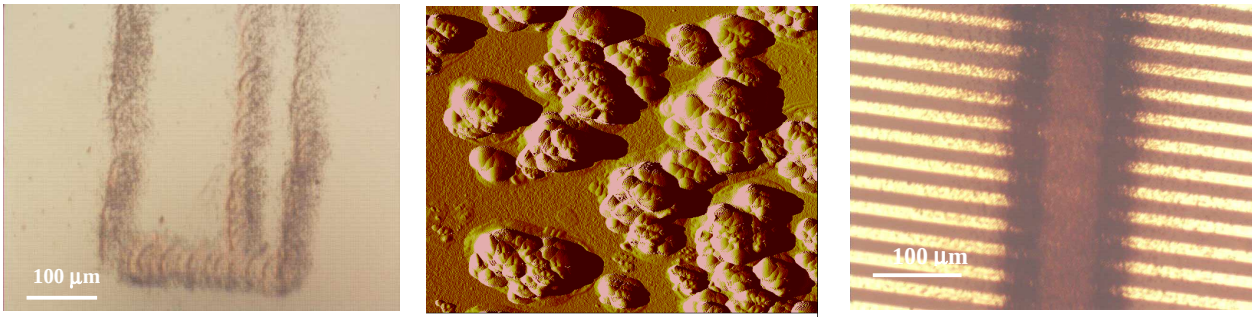
Figure 3. (a) AFM image of 100 nm polystyrene beads patterned on silanized glass substrate at the laser power 300 mW. (b) Fluorescence spectra obtained by spectrofluorimeter emission scan.

where C is a numerical factor between 1 and 5, depending on the model (see, for instance [8]). As seen from the equation, it is the transducer frequency that can affect the droplet size the most. In our study, the frequency is 2 MHz corresponding to about 2-µm mean droplets size. After the solvent evaporates during the deposition process, suspended particles form clusters with less than 1 µm in diameter on the substrate. Since the cluster size depends on the concentration of polystyrene beads, the size can be substantially reduced below 1 µm by diluting the original solutions.

We studied the stability of proteins during the LGDW process by attaching avidin to the 400-nm polystyrene beads, as described in the experiment section above, and measuring fluorescence spectra of the avidin-coated beads after deposition. The beads were deposited on a silanized glass slide at a laser power of 300 mW. Bovine serum albumin served as a blocker to cover the non-deposited slide area, while fluorescein-biotin was used as an indicator to detect the avidin functionality. Since there is very high avidin-biotin affinity, fluorescein-biotin specifically binds to avidin if it maintains its functionality after deposition and can be detected by spectrofluorimetry. The silanized glass substrates before and after deposition were first rinsed by 3% BSA solution, then immersed into fluorecein-biotin solution for 5min, and finally rinsed by PBS. The fluorescence spectra shown in Fig. 3b demonstrate the fluorescence peak at 520 nm only after the avidin-attached beads were deposited, with no sign of protein degradation. This indicates that the laser beam keeps avidin safe during deposition.

Deposition of gold nanoparticles

Gold nanoparticles coated with an organic functionality have potential applications for chemiresistor (CR) sensors [9]. The (CR) sensor miniaturization is, however, a challenge since we need to pattern gold nanoparticles into arrays without losing their ability to monitor changes in the electric properties with analyte sorption. In our experiments, we exploited the LGDW to pattern $CH_3(CH_2)_7S$-Au nanoparticles into uniform microstrips of less than a 100-µm width range. Instead of the hollow fiber, however, we used direct laser beam and controlled resolution by the focused beam spot size. The capability of the LGDW technique in fabrication of multiple arrays and microstructures of complex geometry is demonstrated in Fig. 4. As seen from Fig. 4a, the technique allowed us to produce gold microstrips of less than 100 µm wide. The profile of the deposited microstrips mirrored the radial distribution of gold nanoparticles within the laser beam. The particles preserved their original shapes after deposition if the laser power was less than 100 mW (Fig. 4b). CR sensors could only work if made



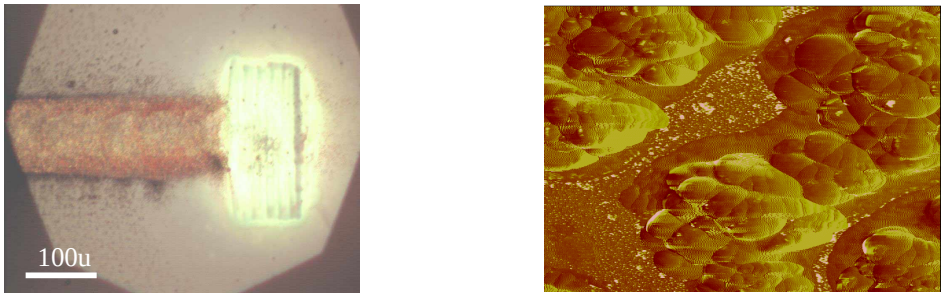
(a) (b) (c)

Figure 4. (a) Optical image of parallel microstrips of gold nanoparticles deposited at laser power 200 mW. (b) AFM image of gold nanoparticles deposited at laser power 100 mW. (c) Optical image of a highly dense microstrip of gold nanoparticles deposited on microelectrodes at laser power 200 mW by multiple deposition process.

of highly dense-packed gold nanoparticles to provide a sufficient surface area for contaminant adsorption and particle's vapor-induced resistivity. As shown in Fig. 4c, repeated deposition allows us to produce a highly dense complex mesoscopic structure.

One of important features of the LGDW is that the microstrips in arrays can be made of different particles or the same particles with different functionality simply by using mists generated from diverse suspensions and producing complex CR sensors. Our experimental results demonstrated that the LGDW technique has the ability to deposit gold nanoparticles into multiple layers of gold clusters. Another important feature is the *in-situ* fabrication capability of the LGDW technique. By using the same laser beam but at a higher power, we could simultaneously melt a part of deposited microstructures producing solid gold electrodes from gold nanoparticles (Fig. 5a).

The preservation of organic functionality on the surface of patterned gold nanoparticles is critical for successful fabrication of the CR sensors. The lasers used in the LGDW not only propel the particles but also heat them up. If overheated, gold nanoparticles loose their sensing properties due to a degraded surface functionality. As the resistivity measurements and AFM inspection of the arrays of gold-thiolate nanoparticles indicated show, we could not exclude some gold melting and/or fusion between the particles that could lead to evaporation of organothiols from the particle surface. An example of such melting is shown in Fig. 5b. Deposited gold nanoparticles with degraded alkanethiols become insensitive to the vapors of organic solvents. Since gold has a maximum absorption at a wavelength of 532 nm, lasers of a lower power (less than 100 mW) and longer wavelength would be preferred to avoid melting problems.



(a) (b)

Figure 5. (a) Optical image of gold nanoparticle microstrip with an additional gold electrode produced by in-situ melting. (b) AFM image of gold nanoparticle clusters deposited at laser power 200 mW showing melting of a substrate at the cluster base.

CONCLUSION

In this study, we demonstrated the ability of the LGDW technique to deposit polystyrene and gold nanoparticles on glass substrates patterning mesoscopic structures. We discussed the features of the technique, which are important for successful fabrication of chemical and biological sensors. We showed that the biological and chemical functionality produced on the surface of nanoparticles could be preserved during the deposition process if appropriate laser source parameters are chosen. The power and potential of the LGDW technique lies in its ability to deposit virtually any material in the form of nanoparticles on a variety of substrates, with micron-scale precision. These advantages are superior to other techniques in fabrication of various multi-array chemical and biological sensors. At the same time, more studies are required to understand better various materials aspects of the LGDW technique essential for microsensors development and fabrication.

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