

Laser direct write of silver nanoparticles from solution onto glass substrates for surface-enhanced Raman spectroscopy

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A solution based laser direct write technique for patterning of glass substrates with silver nanoparticles is presented. Photoreduction of an AgNO_3 solution, by nanosecond UV laser pulses, produces a source solution of silver particles. A glass substrate is then inserted into this solution and the laser is scanned over its surface. Laser-induced fragmentation of the silver particles in the solution, assisted by the melting of the glass surface, produces coatings of silver nanoparticles in the laser-irradiated regions. Strong enhancement of the Raman signal from a dilute Rhodamine 6G analyte confirmed that these substrates are suitable for surface-enhanced Raman measurements.

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The synthesis of nanosized noble metal particles has become an important branch of research due to their interesting optical, chemical, and electronic^{1,2} properties. For example, Ag nanoparticles are of particular interest due to their surface-enhanced Raman effect,³ which can increase the sensitivity of Raman measurements by orders of magnitude, even allowing single molecule detection. However, the magnitude of the enhancement is strongly affected by the precise nanostructure; thus, research is on going to produce reliable, repeatable nanostructured surfaces.^{4,5} Typically, nanostructured silver substrates for performing surface-enhanced Raman spectroscopy (SERS) are prepared by chemical means from citrate reduced Ag colloids.⁶ However, patterning silver only onto selected areas of a substrate, an important capability for using SERS in future lab-on-chip technologies or for facile integration into industrial processes, is challenging using this method. The laser direct writing of materials has been studied extensively, often using the matrix assisted pulsed laser evaporation transfer technique⁷ or by directly machining microstructures.⁸ However, reports of the laser writing of nanoparticles are rare⁹ and typically involve the precoating of the substrate with a layer of a material to allow photocatalysis to occur at an interface.¹⁰

In this letter we introduce a method for directly writing Ag nanoparticles using a pulsed laser, from a solution containing larger Ag particles onto low-cost glass substrates at low macroscopic temperatures. This process is rapid, requires no pretreatment of the substrate, and involves no complex chemistry. Once produced, the effectiveness of these arrays as substrates for performing SERS is investigated.

The initial silver nanoparticle solutions were synthesized by a UV photoreduction technique using the pulses from a Lambda-Physik LPX 210i excimer laser operating at 248 nm, with a pulse duration of 25 ns. 4 ml of a 0.01M AgNO_3 solution was placed in an open fused silica vessel, with a rectangular cross section, mounted on an X-Y translation stage. 90 mJ laser pulses were focused to produce a rectangular spot of area 0.4 cm² and fluence of 225 mJ/cm². The laser spot was raster scanned over the whole area of the

vessel once every 15 s. A laser shot repetition rate of 20 Hz was used throughout the experiments.

During the initial UV photoreduction of the AgNO_3 solution, a progressive color change was observed. Initially, the solution was clear and colorless. After around 5 min of irradiation a yellow-brown coloration was observed. This coloration is attributed to surface plasmon resonance (SPR) absorption of silver nanoparticles.^{11,12} After 6 min, the solution appeared gray-brown and became more opaque to the eye, likely due to scattering from larger particulates. After 10 min, the solution was gray and cloudy in appearance, apart from the area currently exposed to the laser beam, where a transient yellow-brown coloration was observed. This transient coloration quickly vanished as the laser beam passed. Figure 1(a) shows a scanning electron microscope (SEM) image of the material collected from the solution onto a silicon substrate after the 10 min irradiation. Particulates with sizes in the range 50–500 nm were observed. These particulates were confirmed to be metallic silver by energy dispersive x-ray analysis and electron diffraction measurements in the transmission electron microscope (results not shown here.)

Having demonstrated that the UV photoreduction of the AgNO_3 solution produces silver particles in solution, these particles were used as a source of silver for laser writing onto glass substrates. The photoreduction was repeated, but after a set time into the process (varied between 0 and 10 min) pre-cleaned glass substrates (standard borosilicate microscope cover glasses) were placed into the vessel and the irradiation was continued for an additional 5 min, scanning over half of the surface of each substrate, through the solution. It should be noted that sedimentation of the source silver particulates was observed to occur around 6 h after synthesis, so during the treatment process little sedimentation of the particulates is expected. After the laser treatment, the samples were removed from the solution and washed in deionized water. The surface morphology of each sample was then examined in an environmental scanning electron microscope (E-SEM) (FEI Quanta 200F), operating in low-vacuum mode to avoid charging of the insulating substrates. For the samples inserted into the solution between 0 and 5 min of irradiation (i.e., before any visible color change), significant cracking

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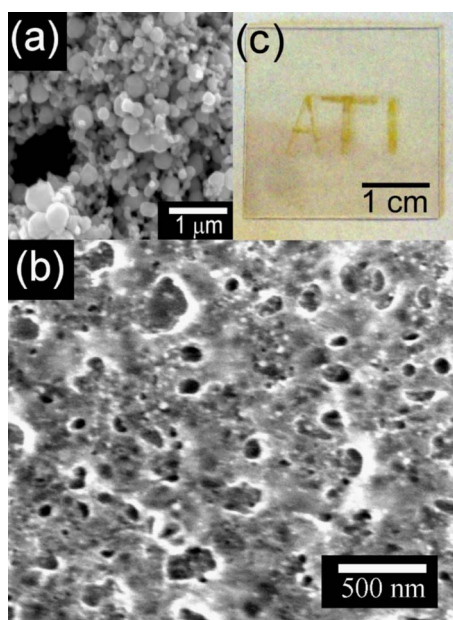


FIG. 1. (Color online) (a) SEM image of the silver particles present in the solution after 10 min of photoreduction. (b) E-SEM image of the laser-irradiated area of a glass substrate exposed to a fluence of 225 mJ/cm^2 . The substrate was inserted into the solution after 10 min of photoreduction. (c) Photograph demonstrating that silver decoration only occurs at the laser-irradiated areas. The yellow discoloration is due to absorption by silver surface plasmons.

and surface damage to the glass were observed. Visually, the glass appeared opaque with a slight brown tinge. For the samples placed into the solution after 8 min or more, the surface took on a strong yellow color only at the laser-irradiated areas. Figure 1(b) shows an E-SEM image of the laser-irradiated area of a glass substrate inserted into the solution after 10 min of photoreduction. The glass surface has become much rougher than the untreated areas, with evidence that melting has occurred. The irradiated areas are also decorated with small silver nanoparticles, which appear as bright dots in the image. No such features were observed in the untreated regions of the glass. Having demonstrated that it is possible to selectively decorate a sample, a predefined pattern can now be written onto to a glass substrate by irradiating through a mask or by restricting the laser spot and translating the X - Y stage. Figure 1(c) shows the initials of the Advanced Technology Institute (ATI) written in silver nanoparticles onto a glass substrate.

After examining the surface morphology, the optical absorption spectrum of each sample was then measured using a Cary 5000 UV-visible-near infrared spectrometer. A constant background, obtained from an untreated glass sample, is removed from each spectrum. Figure 2 shows optical absorption spectra obtained from the laser treated areas of glass substrates inserted into AgNO_3 solutions after (a) 0 min, (b) 3 min, (c) 8 min, and (d) 10 min of photo-reduction. Supporting the observations from the SEM, the samples introduced after 0 and 3 min show significant absorption across the spectrum, which we attribute to scattering due to the significant surface damage and a high density of cracks. There is some evidence from spectra (a) and (b) of a weak silver SPR peak located at $\sim 430 \text{ nm}$. For the samples introduced later into the process [spectra (c) and (d)], a strong silver SPR peak is easily observed at 439 nm for both samples. The long-wavelength scattering from these samples

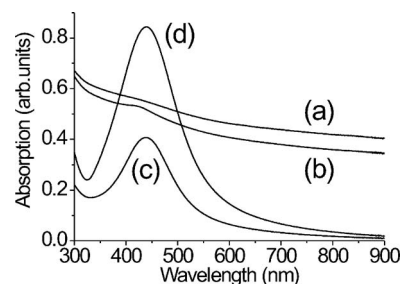


FIG. 2. Optical absorption spectra obtained from the laser treated areas of glass substrates inserted into AgNO_3 solutions after (a) 0 min, (b) 3 min, (c) 8 min, and (d) 10 min of photoreduction.

is similar to that of the untreated glass, showing that there is little large scale modification to the glass surface.

Having demonstrated that selective deposition is possible, the mechanisms behind the decoration should be discussed. Firstly, although a constant laser pulse energy was used in each run, the duration of the photoreduction prior to inserting of the substrates affects the fluence on the glass. This is due to the increasing absorption of the laser energy by silver particulates in the solution. The modification of noble metal nanoparticles by laser irradiation has been studied in detail previously.^{13,14} For short pulse irradiation, nanoparticles that are larger than a threshold size can be heated by the laser irradiation to temperatures high enough to cause fragmentation and boiling, producing a distribution of hot, smaller clusters. Particles that are smaller than this threshold cool rapidly due to their high surface area to volume ratio, and are hence relatively unaffected by the irradiation. It is suggested that the large particles and aggregates observed in solution after the photoreduction [see Fig. 1(a)] absorb a fraction of the incident laser energy and fragment into smaller particles. This hypothesis is supported by the observation of the transient yellow-brown coloration during continued irradiation of the solutions formed after 10 min of photoreduction. This transient coloration quickly vanished as the laser beam passed, which is likely due to the small clusters coalescing into large particles. However, in the vicinity of the glass substrate these smaller nanoparticles can be stabilized if they stick to the surface. The observed melting of the glass surface [see Fig. 1(b)], by the remaining fraction of the energy that does not get absorbed by the solution, is thought to increase the likelihood of these nanoparticles sticking, as they can become embedded into the molten surface. SEM images of the regions close to the irradiated areas showed the presence of very few nanoparticles, again indicating that melting of the glass surface is important in assisting the attachment of the silver. The yellow coloration observed in the laser treated areas was unaffected by washing the substrates, indicating that the coatings are robust.

As nanoparticles with a strong SPR can be produced, by introducing the glass into the process after around 10 min, the suitability of these substrates for SERS was investigated using a Renishaw Ramanscope, using 514 nm excitation. A dilute solution of Rhodamine 6G (R6G, $\sim 20 \mu\text{M}$) was used as a standard test analyte. The substrates were placed into the analyte solution for 10 min and then removed and blown dry with nitrogen to remove any excess. Figure 3 shows Raman scattering spectra taken from silver decorated glass [spectrum (a)] and untreated glass [spectrum (b)]. The characteristic Raman peaks from R6G could easily be detected in the

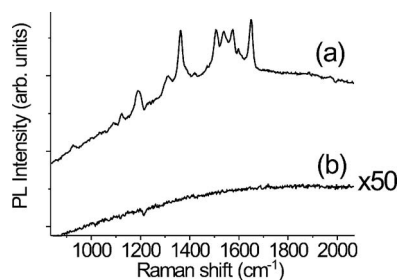


FIG. 3. Raman scattering spectra from (a) silver decorated glass and (b) untreated glass dipped into a dilute R6G solution. The laser treatment in (a) was started after 10 min of photoreduction of the solution.

silver coated areas, but were undetectable on the plain glass. There was also an approximately 100-fold enhancement of the background photoluminescence from the R6G in the silver coated areas. This is attributed to a combination of surface-enhanced fluorescence¹⁵ and the increased surface area of the glass due to the nanoscale roughening introduced by irradiation.

In conclusion, a solution based laser direct write technique for precisely decorating selected areas of glass substrates with silver nanoparticles is presented. The laser-induced fragmentation of silver particles in a source solution into which the substrate is inserted, assisted by the melting of the glass surface, produces robust coatings of silver nanoparticles only at the laser-irradiated regions. This technique produces SERS active coatings of silver particles, with a strong

enhancement of the Raman signal demonstrated, and is readily scalable to pattern large areas. The technique also induces nanoscale roughening of the glass surface, enhancing its effective surface area for collecting analytes.

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