Holographic patterning of fluorescent microstructures comprising silver nanoclusters

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Abstract: Metal nanoclusters, which exhibit extraordinary physical and chemical properties that are different from their bulk counterparts, are highly promising nanomaterials for photonics. Recently, the use of two-photon excitation to fabricate silver nanoclusters in polymers was reported but still lacks speed and flexibility which are imperative for applications such as labeling and spectroscopy. Here, we demonstrate the fabrication of fluorescent nanocluster microstructures using spatially phase-shaped laser beams. Using an incident power of 60 mW and exposure time of 8 s, we found that the smallest line-width of the fluorescent microstructures is 478 nm, which is comparable to the line-width achieved with a two-photon laser scanning approach. As a proof-of-principle demonstration, the technique is used to fabricate fluorescent micro-labels that could be used in anti-counterfeiting applications.

OCIS codes: (090.0090) Holography; (300.0300) Spectroscopy; (310.0310) Thin films; (220.0220) Optical design and fabrication; (210.0210) Optical data storage; (160.0160) Materials; (250.5230) Photoluminescence; (160.2540) Fluorescent and luminescent materials.

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1. Introduction

Noble metal nanoclusters (NCs) are extremely small nanomaterials (< 2 nm) consisting of few atoms to roughly a hundred atoms [1]. They act as a missing link between the properties of metal atoms and larger metal nanoparticles. At such a small length scale, the free electrons in the metal NCs are spatially confined to discrete energy levels that leads to molecular properties such as strong fluorescence [1,2]. The ultrasmall size and fluorescence properties of NCs have been used for various applications such as detection of metal ions, nucleic acids and proteins, cancer cell imaging, labeling and data storage [1].

In particular, silver NCs have received significant attention within the past few years as they act as an excellent fluorophores with attractive features such as ultrabright emission, photostability and subnanometer size. Stabilizing silver NCs and retaining their enhanced functionality is challenging due to oxidation of silver; however, significant effort has been made to synthesize stable silver NCs [3]. The synthesis of silver NCs requires reduction of silver ions by chemical, electrochemical, radiolytic, sonochemical or photoreduction methods and stabilization in a scaffold that restricts the growth of NCs, thereby preventing the formation of larger nanoparticles. Different synthetic polymers, microgels, DNA, dendrimers and small molecules can act as the stabilizing scaffold [1,4–6]. Moreover, direct laser writing (DLW) has been used to produce highly photostable silver NCs in glass and zeolites [7–9]. Recently, the applicability of multiphoton and single-photon absorption-based DLW of two-dimensional silver NC microstructures in poly(methacrylic acid) matrix has been demonstrated [10,11].

Multiphoton DLW is a well-established technique for fabricating microstructures [12]. This technique utilizes a tightly focused ultrashort-pulsed high intensity laser beam to induce

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multiphoton absorption into a layer of photoresist resulting in polymerization chain reaction [12–16]. The multiphoton-based DLW method is capable of fabricating polymeric three-dimensional microstructures in photoresist with a resolution down to 120 nm [13]. However, the serial nature of point-by-point scanning is time-consuming and significantly hinders the potential of nanostructuring to applications where speed and scalability are crucial [17]. Moreover, the probability that the multiphoton absorption will occur, is extremely small. Hence the use of a high-intensity femtosecond laser source such as Ti:sapphire is inevitable [10,12,13]. Single-photon DLW can surmount the limitation of using expensive laser sources in DLW of two-dimensional structures. The technique is based on a low-cost continuous wave (CW) laser and was recently proven to be sufficient in fabricating fluorescent NC microstructures at much lower laser intensities than in multi-photon DLW [11]. The single photon DLW technique is also limited in efficiency by serial point-by-point scanning; however, the decrease in laser intensity in single-photon DLW allows simple, fast and a cost-effective parallel fabrication of microstructures [17].

To overcome the serial scanning issue in DLW, microlens arrays [18], axicon lenses [19], and pixelated instruments such as digital mirror devices [20] and spatial light modulators (SLM) [21–23] were used. Among these methods, the liquid crystal-based SLM is the most flexible and is realized in many applications like optical trapping [24], laser pulse shaping [25], and imaging [26]. Moreover, it has also been practically utilized in DLW [17,27]. In this approach, a suitable phase is pre-calculated and then encoded by the SLM to the incident laser beam just before the light impinges on the photoresist. Usually, the phase of a desired intensity distribution at the focal plane is calculated by Gerchberg-Saxton (GS) algorithm [28]. Then, the objective lens simply projects the shaped light intensities in the sample plane [17,27].

In this article, we demonstrate the parallel fabrication of fluorescent NC microstructures that is based on spatial light modulation of a continuous wave laser. This fabrication technique is fast and cost-efficient, and precludes the use of a scanning procedure. The as-formed NCs in microstructures produced by this technique are comparable to the results of serial scanning [10,11], i.e., the nanoclusters are highly photostable and exhibit a broadband emission at visible wavelength ranging from 500 to 800 nm with a maximum at 545 nm. Furthermore, we fabricated a fluorescent silver nanocluster-based micro-label that can be used in different applications like security and authenticity marking.

2. Sample preparation

Aqueous solutions of silver nitrate ($AgNO_3$) and poly(methacrylic acid) (PMAA) were mixed to obtain a solution having 1.5 w-% PMAA and Ag/MAA ratio of 50%, corresponding to one Ag^+ per two MAA units. The borosilicate coverslips (22 mm × 22 mm × 0.17 mm) were cleaned with ethanol and blow-dried prior to spin coating. Samples were prepared by spin coating the solution onto coverslips at 1500 revolutions per minute (rpm) for 120 s. Subsequently, the spin coated samples were dried in vacuum for 12 h. The Rhodamine samples were used for photostability test. In order to prepare these samples, 10 nM Rhodamine 6G was mixed with 1.5 w-% aqueous PMAA polymer and the solution was spin coated onto the precleaned coverslips.

3. Experimental

The Ag@PMAA samples were irradiated using a parallel laser writing setup shown in Fig. 1. A CW 532 nm laser diode (Millennia Pro, Spectra Physics) was used as excitation source. An attenuator (A) was used to adjust the intensity of incident laser beam, which was expanded and collimated by lenses L1 and L2. Mirror M1 directed the laser beam towards the half-wave plate (Thorlabs) aligned to match the polarization of the incoming beam to the orientation of the liquid crystals of the SLM (HES 6010 BB-HR, Holoeye). A computer generated hologram, created by HOLOEYE spatial light application software, was externally fed to the SLM to modulate the phase pattern of the impinging laser beam. The reflected beam, which contains the additional phase information was incident on a second unity collimator (L3 and

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L4). An iris was used as spatial filter to discriminate the first order diffraction from the other unwanted diffraction orders from the SLM. Mirror M2 guides the beam towards the dichroic (FF535-SDi01, Semrock), which allowed the encoded beam to pass towards the oil immersion objective lens (Leica, NA of 1.4, 100 ×). The objective lens is used to focus and project the patterned beam into the sample which is mounted on a stage. The fabrication process was viewed in real-time with a bright field microscope (dichroic mirror (DM), exposure beam blocking filter (F), camera (C), objective (O), sample and stage (S) and light emitting diode (LED)) incorporated in the setup. A custom-built fluorescence microscope and spectroscope, described elsewhere [10], was used to image the fluorescent NC microstructures and to record the emission spectra obtained from the microstructures. The absorption spectrum was recorded with a spectrophotometer (Perkin Elmer Lambda 950). In order to obtain the final absorption spectrum of the silver nanoclusters in the written structures, the spectrum from the unexposed part of sample was also measured and subtracted from the spectrum of written structures.

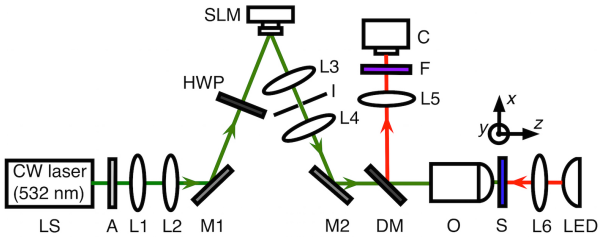

Fig. 1. Experimental setup for parallel DLW of silver nanocluster microstructures. The components are laser source (LS), attenuator (A), lens (L1, L2, L3, L4, L5, and L6), mirrors (M1 and M2), half wave plate (HWP), spatial light modulator (SLM), iris (I), dichroic mirror (DM), exposure beam blocking filter (F), camera (C), objective (O), sample and stage (S) and light emitting diode (LED).

4. Results and discussions

We investigated the performance of the technique by fabricating microstructures and estimating their line-widths from the fluorescence microscopy images. We utilized parallel laser writing to pattern a micro-star with a laser power of 90 mW after SLM, wavelength of 532 nm and exposure time of 6 s. The laser power is measured after the SLM in all the cases unless otherwise mentioned. A bright field and a fluorescence microscopy image of the written structure is shown in Fig. 2(a) and 2(b). A light emitting diode (LED) with excitation wavelength of 470 nm and excitation intensity of 2 MW/m^2 was used to produce the fluorescence image. The structure fluoresces from the area exposed to the writing beam due to the formation of the silver NCs, likely by laser-induced reduction of silver ions in PMAA polymer. In our previous report, we have shown that similar silver nanoclusters can be formed using multiphoton DLW [10].

Figure 2(c) shows the variation of the line-width of silver nanocluster microstructures written using different laser writing parameters. These line-widths were estimated from the fluorescence images of micro-stars written with varying laser power and exposure time. Fluorescence intensity profiles were plotted from several micro-stars, along red dashed lines as shown in Fig. 2(b). The full-width at half-maxima of these line profiles were derived and then averaged to obtain the correct line-width. Clearly, Fig. 2(c) depicts that the threshold of the exposure time for writing a structure is 8 s for a 60 mW writing power. This time decreases to 2 s for 90 mW. This short exposure time demonstrates the fast fabrication capability of this technique compared to conventional serial scanning. The line-widths of the written structures increase with increasing exposure time for all constant power and increase with laser power, when the exposure time is kept constant. Furthermore, the smallest line-width of 478 nm is measured from the fluorescent microstructure written with laser writing power of 60 mW and exposure time of 8 s. However, the smallest line-width of the

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fluorescent nanocluster microstructures written with two-photon DLW in silver containing polymer thin films was 380 ± 40 nm; hence the parallel writing technique is comparable to the performance of a serial scanning approach in terms of resolution [10].

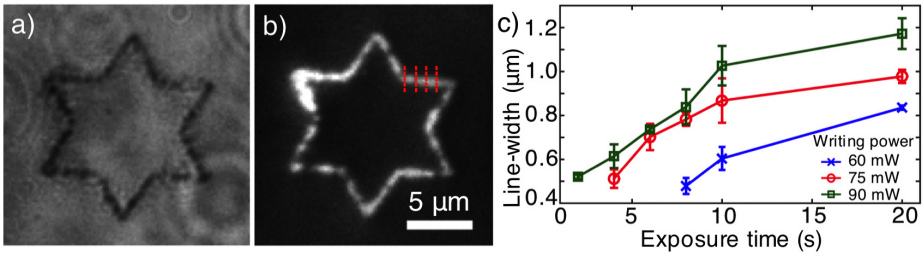

Fig. 2. (a) Bright field and (b) corresponding fluorescence microscopy image of a micro-star written with parallel DLW. The fluorescence image was recorded using LED light of intensity of 2 MW/m^2 and excitation wavelength of 470 nm. Line-width of micro-star was estimated by plotting the fluorescence intensity profile along the dashed red lines. (c) Measured line-widths of the written structures with different laser powers as a function of exposure time.

Figure 3 shows the absorption and emission spectra obtained from an area exposed to the writing laser beam. The silver NCs absorb light of wavelength ranging from 300 nm to 700 nm with a maximum located at 435 nm [11]. Absorption spectra of similar characteristics have been reported from solvated Ag@PMAA nanoclusters [5,6]. The emission spectrum of NCs is recorded using a laser diode of wavelength 473 nm and intensity of 2 MW/m^2. The NC shows a broadband emission at visible wavelengths. Considering the maximum wavelength and the shape of the emission spectrum, the fluorescent silver NCs have also similar emission properties to silver NCs in solution [6,29]. A sharp peak is observed at 510 nm of emission spectrum of the silver NCs. This peak is identified as Raman scattering as in our previous studies [10].

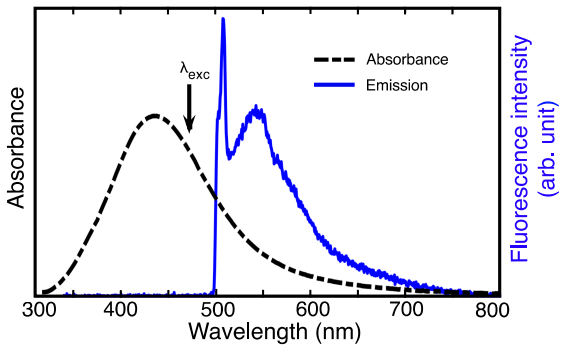

Fig. 3. Absorption (black curve) [11] and emission (blue curve) spectra of silver nanoclusters. Emission spectrum of the nanoclusters is recorded by exciting them with laser light of wavelength 473 nm and intensity of 2 MW/m^2.

Finally, we demonstrate the applicability of this technique by fabricating a fluorescent micro-label using a 532 nm CW laser diode with laser writing power of 90 mW, and exposure time of 6 s in the 50% Ag@PMAA thin film. Figure 4 shows the bright field image and corresponding fluorescence image of the micron scale bar code fabricated using parallel DLW. The fluorescence image was obtained by exciting the written structure with 470 nm LED light source with intensity of 2 MW/m^2. The fabricated pattern does not require additional developmental steps; it can be read immediately using a microscope. The photostability of the NCs in the micro-label are remarkably high compared to that of organic dye Rhodamine 6G. We observed that the organic dye Rhodamine 6G bleached to 2.5% of its

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initial fluorescence intensity in 3 min when the film was irradiated with laser intensity of 2 MW/m^2 and wavelength of 473 nm. However, under similar conditions, the fluorescence intensity from the area containing the microstructures decreased only to 40% of its initial intensity.

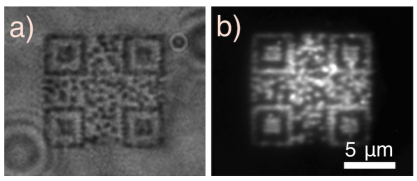

Fig. 4. (a) Bright field and (b) corresponding fluorescence microscopy image of an authenticity marking code written with parallel DLW. Fluorescence image was recorded using LED light of intensity of 2 MW/m^2 and excitation wavelength of 470 nm.

Altogether, the results show that SLM-based parallel writing can be used to fabricate silver NCs with optical properties similar to the silver NCs formed by multiphoton DLW [10]. Moreover, the use of SLM makes this technique fast and cost-efficient compared to DLW of silver NCs. For instance, as reported in our earlier work, the fabrication of micro-label similar to one shown in Fig. 4 takes 100 s using serial scanning methods; however, it takes only 2 s to write a label with similar dimensions using the parallel technique [11]. The quality of fabricated micro-star and micro-label is compromised due to the speckle noise of optical intensity distribution at the sample plane. The speckle noise can be reduced by improving the hologram using different wavefront correction techniques. These correction techniques can use holograms containing the multi-phase information [30] or optimize the holograms utilizing optically reconstructed diffraction-peak intensities [31].

5. Conclusions

To conclude, we have demonstrated the parallel fabrication of fluorescent NC microstructures by spatially modulating the laser beam using SLM. This technique surmounts the problem of relatively time-consuming point-by-point serial nature of laser scanning. To show the applicability of this technique, a fluorescent micro-label was fabricated in a single short exposure. The formed nanoclusters in microstructures are photostable and fluorescent. The fabricated microstructures can be useful in many labelling applications such as authenticity marking and fluorescent tagging.

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