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*Published in:*  
Optics Letters

*DOI:*  
[10.1364/OL.41.003627](https://doi.org/10.1364/OL.41.003627)

Published: 01/08/2016

*Document Version*  
Peer-reviewed accepted author manuscript, also known as Final accepted manuscript or Post-print

*Please cite the original version:*  
Karimi, N., Kunwar, P., Hassinen, J., Ras, R. H. A., & Toivonen, J. (2016). Micropatterning of silver nanoclusters embedded in polyvinyl alcohol films. *Optics Letters*, 41(15), 3627-3630. <https://doi.org/10.1364/OL.41.003627>

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# Micropatterning of Silver Nanoclusters Embedded in Polyvinyl Alcohol Films

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Received XX Month XXXX; revised XX Month, XXXX; accepted XX Month XXXX; posted XX Month XXXX (Doc. ID XXXXX); published XX Month XXXX

**Direct laser writing has been utilized to fabricate highly photostable fluorescent nanocluster microstructures in organic polymer poly(methacrylic acid), where the carboxyl functional group is reported to play a vital role in nanocluster stabilization. In this paper, we demonstrate that not only polymer containing carboxyl functional group, but also polymer comprising hydroxyl group, namely polyvinyl alcohol (PVA) can act as an appropriate stabilizer matrix for laser-induced synthesis and patterning of silver nanoclusters. The as-formed nanoclusters in PVA film exhibit broadband emission and photostability comparable to the nanoclusters formed in poly(methacrylic acid) polymer. As PVA is widely used, non-toxic, biocompatible and biodegradable polymer; the technique of patterning fluorescent nanoclusters in PVA thin films is expected to find numerous applications in fields like fluorescence imaging, biolabeling, and sensing. © 2015 Optical Society of America**

**OCIS codes:** (220.0220) Optical design and fabrication; (220.4610) Optical fabrication; (220.4000) Microstructure fabrication; (210.0120) Optical data storage; (160.0160) Materials; (160.5470) Polymers; (250.5230) Photoluminescence; (160.2540) Fluorescent and luminescent materials.

<http://dx.doi.org/10.1364/OL.99.099999>

Metal nanoclusters (NCs) have attracted significant interest as they exhibit different physical, chemical and electronic properties compared to metal nanoparticles or bulk metal [1]. Composed of a few to a few hundred atoms, they provide a missing link between isolated metal atoms and nanoparticles [2,3]. Nanoclusters exhibit molecule-like properties such as discrete electronic transitions and intense fluorescence [1-4]. Due to the bright fluorescence with excellent photostability, metal NCs, such as gold and silver NCs, can be utilized for many applications including single-molecule studies, fluorescence imaging, fluorescence sensing, optical data storage, and labeling [1,3-5].

Silver NCs are often synthesized by dissolving silver salt in a solvent, followed by the reduction of silver ions to the zero-valent state. The reduction of silver ions can be achieved by using chemical reductants [6,7],  $\gamma$ -rays [8], ultrasound [9], ultraviolet [10] or visible light [11,12]. However, the synthesis of NCs is usually difficult, as they strongly tend to aggregate. The aggregation results in the formation of larger particles that no longer exhibit molecule-like properties such as fluorescence [13-15]. Therefore, in order to preserve these attractive properties of NCs, it is necessary to stabilize their growth. The stabilization can be accomplished by reducing the silver ions in encapsulating scaffolds such as polymers [13], dendrimers [16] and DNA [17,18]. The role of stabilizing molecules in the properties of NCs is significant, as they alter the electronic structure of the complex [19]. The encapsulated NCs exhibit more stability against photobleaching in comparison with organic dyes [4,13,20]. Hence, due to their photostability, low toxicity and biocompatibility, silver NCs synthesized in organic matrices could be excellent substitutes for organic dyes and semiconductor quantum dots in biolabeling applications [1,3-5]. Multi-photon direct laser writing (DLW), a technique for the fabrication of three-dimensional micro/nanostructures in photosensitive materials [21,22], has also shown to be a promising technique to form and stabilize silver NCs. Using multi-photon DLW, silver NCs microstructures have been fabricated in glass [23], zeolites [24], and poly(methacrylic acid) (PMAA) films [13]. However, multi-photon DLW requires an expensive excitation source such as a femtosecond or picosecond laser that delivers a high laser pulse intensity. On the contrary, single photon DLW utilizes low-cost continuous wave (CW) lasers and is also shown to form silver nanoclusters in PMAA films with intensity much lower compared to multi-photon DLW. Thus, the use of single photon DLW greatly reduces the expenses and complexity of the technique [25,26].

Similar techniques of laser reduction have been used to fabricate metallic structures made of nanoparticles, for example, printing of Cu electrodes using direct laser patterning, fabrication of three dimensional gold microstructures and disconnected three-dimensional silver nanostructures [27-29]. However, these studies

do not report the formation of fluorescent nanoclusters. For the formation of nanoclusters, an encapsulating agent such as PMAA polymer is necessary. PMAA is a well-known stabilizing agent for encapsulating brightly fluorescent silver nanoclusters both in solution and thin film. The PMAA polymer has a strong affinity for silver ions and silver surfaces due to the presence of carboxyl functional group. Therefore, it is believed that the presence of carboxyl functional group in this polymer prevents the growth of nanoclusters to large nanoparticles [9,13].

In this paper, we demonstrate the formation and stabilization of photostable fluorescent Ag NCs for the first time in polyvinyl alcohol (PVA) films using the single photon DLW technique. PVA contains hydroxyl functional groups instead of carboxyl functional groups in PMAA. Further, PVA is cost-effective and widely used polymer with excellent film-forming ability [30,31], and features such as biocompatibility, biodegradability, and non-toxicity make PVA an attractive material for biomedical and pharmaceutical applications [30,32,33]. PVA has also been used to stabilize metal nanoparticles [34-36]. However, we used a focused laser beam to photo-reduce silver ions to form nanoclusters locally within a spin-coated PVA polymer film. The silver NCs were studied using fluorescence microscopy and spectroscopy to obtain detailed information about their fluorescence properties and photostability. Furthermore, we characterized the laser written structures in detail using atomic force microscopy (AFM). Our findings show that Ag NCs stabilized in PVA films emit broadband fluorescence at visible wavelengths with excellent photostability.

For the experiments, we prepared 3 w-% of PVA aqueous solution by dissolving the PVA powder (Sigma-Aldrich), with molecular weight between 89000 and 98000 g/mol in water. Varied amounts of silver nitrate (Sigma-Aldrich,  $\geq 99\%$ ) was mixed with the PVA solution to obtain Ag/PVA samples with different concentrations (from 21 w/w to 62 w/w). These values correspond to 5% and 16% when expressed in terms of ratio of number of Ag atoms to number of hydroxide (OH). The mixtures were then spin-coated on glass substrates to obtain thin films of PVA containing silver. The films were exposed to the writing laser beam with wavelength ( $\lambda_{dlw}$ ) of 405 nm using a DLW setup [13,25] where the sample was scanned against the fixed laser beam. We acquired fluorescence images and emission spectra of the written structures through a custom built microscope and spectrometer, described in our earlier work [13]. Additionally, topography of the structures was studied using a Veeco Dimension 5000 AFM with a Nanoscope V controller. The AFM was also used to estimate the thickness of the PVA films by scanning the tip perpendicular to a scratch made by a scalpel.

We obtained significantly bright fluorescence from the areas of Ag/PVA samples that were irradiated with the laser beam. Figure 1(a) illustrates the fluorescence image of an array of lines fabricated with laser intensity ( $I_{dlw}$ ) of 6 MW/cm<sup>2</sup>, and scanning speed of 5  $\mu$ m/s in a Ag/PVA sample with 10% Ag/OH ratio. The fluorescence image was obtained by exciting the written structures with a LED light source of wavelength ( $\lambda_{exc}$ ) of 470 nm and excitation intensity ( $I_{exc}$ ) of 100 W/cm<sup>2</sup>, which is considerably lower than  $I_{dlw}$ . The bright fluorescence emitted from the exposed areas compared to the unexposed regions is attributed to the formation and stabilization of silver NCs through the DLW. This contrast can be also seen in the fluorescence

intensity profile plotted across the fabricated lines (Figure 1(b)), with an average line breadth of 500 nm.

To further investigate the origin of the fluorescence emitted from the written structures in Ag/PVA films, we acquired emission spectra from the written structures on samples with different Ag/PVA concentration (5% to 12.5% Ag/OH ratio). The Ag/PVA samples with ratio of more than 12.5% exhibited undesired crystallization of silver nitrate and were omitted from the studies. The crystallization most likely happened due to supersaturated solution of AgNO<sub>3</sub> in PVA solution. For all the experiments, the writing conditions, i.e. laser writing intensity and the scanning speed were fixed to 6 MW/cm<sup>2</sup> and 5  $\mu$ m/s, respectively. Fluorescence emission spectra were recorded by exciting the written structures with a 473 nm laser beam having excitation power of 300 W/cm<sup>2</sup>. Figure 2 shows the broad emission spectra of the structures with an emission maximum at around 550 nm. The cutoff at wavelengths shorter than 500 nm is due to the emission filter used in order to block the excitation light. In the spectra, we also observed sharp peaks at around 510 nm. This is attributed to an enhanced Raman scattering effect due to strong charge-transfer interactions of NCs with the surrounding polymer molecules and is discussed in detail in our earlier publications [13,37]. Figure 2 also indicates that the fluorescence intensity increases with increasing silver concentration: the highest and lowest intensities were achieved for Ag/PVA samples with 12.5% and 5% Ag/OH ratio, respectively. The inset image of Figure 2 illustrates the concentration dependence of the fluorescence intensity at 560 nm. Moreover, we were unable to write structures in the sample with no silver content. These findings show that the fluorescence is primarily related to the presence of silver in the polymer [13,25]. The fluorescence from the written structures exhibit very similar characteristics to nanoclusters formed at solution [12,38] and PMAA thin films [13,25]. Most importantly, the fluorescence from the written structures strongly depends on the silver concentration.

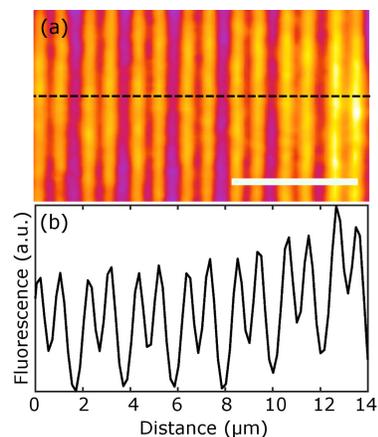


Fig. 1. a) Fluorescence image of laser written lines in Ag/PVA sample with 10% Ag/OH ratio ( $I_{dlw} = 6$  MW/cm<sup>2</sup>,  $\lambda_{dlw} = 405$  nm,  $I_{exc} = 100$  W/cm<sup>2</sup>,  $\lambda_{exc} = 470$  nm). Scale bar = 5  $\mu$ m. (b) Fluorescence intensity profile across the dashed line marked in (a).

Silver nanoparticles larger than 2 nm exhibit collective oscillations of conduction electrons upon interaction with light and typically do not possess fluorescence. There are

few reports about strong photoluminescence of silver nanoparticles, however, it is assumed in the reports that the fluorescence is likely produced from surface bound nanoclusters or angstrom-size domains within nanoparticles [39,40]. Since the fluorescence from the written structures strongly depends on the silver concentration and large silver nanoparticles are not fluorescent, we conclude that silver nanoclusters having size less than 2 nm are the main source of fluorescence in our laser written PVA structures. Since the fluorescence from the written structures strongly depends on the silver concentration and large silver nanoparticles are not fluorescent, we conclude that silver nanoclusters having size less than 2 nm are the main source of fluorescence in our laser written PVA structures.

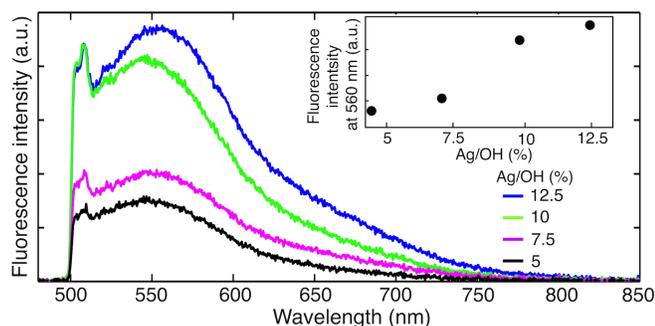


Fig. 2. Fluorescence emission spectra of laser-written silver NCs in Ag/PVA films with Ag/OH ratios of 5% to 12.5% ( $\lambda_{exc} = 473$  nm). The inset image illustrates the dependence of the fluorescence intensity on Ag concentration at 560 nm.

To characterize the microstructures written on the Ag/PVA thin film in detail, we studied the topography of the surface using AFM. Figure 3 shows the AFM images of the structures written with different laser writing intensities and the corresponding line profiles along the region marked by red in the AFM images. The depths observed in line profiles manifests the formation of 3D grooves at the positions of the laser-written structures. The grooves made by laser intensities of 6 MW/cm<sup>2</sup>, 9 MW/cm<sup>2</sup>, and 12 MW/cm<sup>2</sup> had depths of 32 nm, 35 nm, and 38 nm, respectively. Obtained from the AFM analysis of a scratch made by a scalpel, the Ag/PVA film had a thickness of about 58 nm. Comparing the values measured for the depth of the grooves and the film thickness suggests that the DLW process ablates a considerable amount of the material in the exposed areas. However, the fluorescence signal was detected precisely from the regions exposed to the writing laser beam (Figure 1). This result suggests the presence of the silver NCs in the written structures despite the material ablation. Moreover, the line breadths of the structures written with laser intensities of 6 MW/cm<sup>2</sup>, 9 MW/cm<sup>2</sup>, and 12 MW/cm<sup>2</sup> were estimated to be 380 nm, 600 nm, and 700 nm, respectively. Further, the surface roughness of the structures was found to be around 2 nm.

Finally, we investigated the photostability of the fluorescent silver NCs under strong illumination conditions. Microstructures written with  $I_{dlw}$  of 6 MW/cm<sup>2</sup> ( $\lambda_{dlw} = 405$

nm) on Ag/PVA sample with 10% Ag/OH ratio were excited by a 473 nm laser diode, with laser intensities of 60 W/cm<sup>2</sup>, 300 W/cm<sup>2</sup>, and 600 W/cm<sup>2</sup>. Fluorescence spectra were recorded with an interval of 1 s, and the total fluorescence intensity was estimated by integrating the area under each spectrum. The photobleaching curves shown at Figure 4 depict that the written structures bleached to 53%, 30% and 15% of its initial intensity in 300 s when they were irradiated with 60 W/cm<sup>2</sup>, 300 W/cm<sup>2</sup>, and 600 W/cm<sup>2</sup>, respectively.

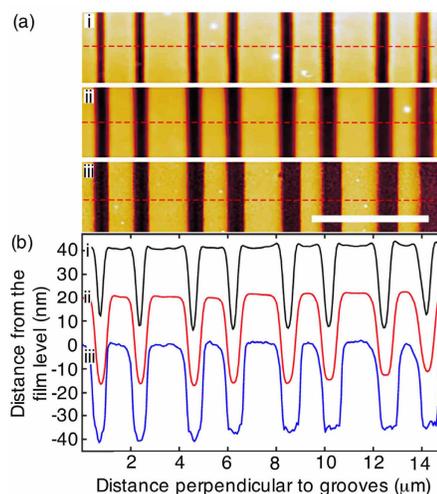


Fig. 3. (a) AFM images of the structures written with  $I_{dlw}$  of (i) 6 MW/cm<sup>2</sup>, (ii) 9 MW/cm<sup>2</sup>, and (iii) 12 MW/cm<sup>2</sup> in Ag/PVA samples with 10% Ag/OH ratio. Scale bar = 5  $\mu$ m. (b) Line-cut topography profiles of the structures across the dashed lines marked in (a). The line width of the grooves measured from the line-cut topography profiles are (i) 380 nm, (ii) 600 nm, and (iii) 700 nm. For clarity, the line profiles of i and ii are vertically shifted by 40 nm and 20 nm, respectively.

We further studied the photobleaching of nanoclusters by employing a double exponential decay ( $y = a \times \exp(-t/\tau_1) + b \times \exp(-t/\tau_2)$ ) fitting for the bleaching curves (Figure 4), where  $a$  and  $b$  are amplitude parameters,  $t$  is time, and  $\tau_1$  and  $\tau_2$  represent bleaching time constants. Table I summarizes the acquired values for  $\tau_1$  and  $\tau_2$  when structures were excited with the three different intensities. Obtaining two different time constants for the bleaching indicates two different populations of fluorescent NCs. The first population dies out quite fast with the time constant of  $\tau_1$ , while the other population shows considerable photostability with much larger time constant of  $\tau_2$ . Further, we observed that there are no changes in the shape of the recorded fluorescence spectra during the bleaching (data not shown). The bleaching results demonstrate that the fabricated nanoclusters in PVA are remarkably photostable when compared to conventional organic dyes such as Rhodamine 6G under the similar illumination conditions [13,25]. The written NC structures are still brightly fluorescent after hundreds of readouts. It is worth noticing that the illumination conditions in our experiments are harsh compared to normal solar irradiance on Earth which

is about  $0.1 \text{ W/cm}^2$  [41]. The photoluminescence property and photostability of as-formed nanoclusters are very similar to that of silver nanoclusters in PMAA [13]. PVA is widely used industrial polymer offering a cost efficient matrix for fluorescent nanoclusters.

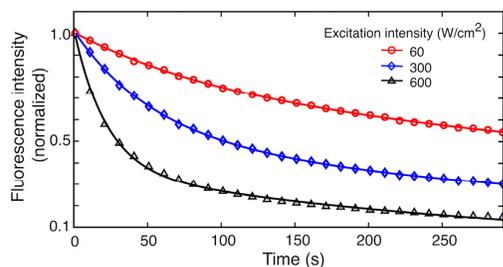


Fig. 4. Fluorescence photobleaching curves corresponding to the structures written with  $I_{dlw}$  of  $6 \text{ MW/cm}^2$  ( $\lambda_{dlw} = 405 \text{ nm}$ ) in Ag/PVA sample with 10% Ag/OH ratio. The sample is excited with a 473 nm laser, and  $I_{exc}$  of  $60 \text{ W/cm}^2$  (red),  $300 \text{ W/cm}^2$  (blue), and  $600 \text{ W/cm}^2$  (black). The solid lines represent double-exponential fits to the data points (open symbols).

**Table 1. Bleaching time constants  $\tau_1$  and  $\tau_2$  when written structures are excited with a laser with three different intensities at 473 nm wavelength**

$I_{exc} (\text{W/cm}^2)$	$\tau_1 (\text{s})$	$\tau_2 (\text{s})$
60	103	990
300	52	507
600	23	300

In conclusion, we have successfully fabricated fluorescent microstructures comprising of silver NCs for the first time in PVA films using DLW with a cost-effective laser diode. The written structures were found to be highly photostable, as compared to previously studied NCs and organic dyes, confirming that PVA film is an appropriate matrix to form and stabilize silver NCs. We anticipate that this technique can be extended to the fabrication of various metal NCs in different polymer matrices for numerous applications like optical data storage, imaging, biolabeling, and sensing.

P.K. is grateful for the support from the Graduate School of Tampere University of Technology. This work made use of the Aalto University Nanomicroscopy Center (Aalto-NMC) premises.

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