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Micropatterning of silver nanoclusters embedded in polyvinyl alcohol films

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Direct laser writing has been utilized to fabricate highly photostable fluorescent nanocluster microstructures in an organic polymer poly(methacrylic acid), where the carboxyl functional group is reported to play a vital role in nanocluster stabilization. In this Letter, we demonstrate that not only the polymer containing the carboxyl functional group, but also the polymer comprising the 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 the PVA film exhibit broadband emission and photostability comparable to the nanoclusters formed in the poly(methacrylic acid) polymer. As PVA is a widely used, nontoxic, 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. © 2016 Optical Society of America

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Metal nanoclusters (NCs) have attracted significant interest, as they exhibit different physical, chemical, and electronic properties compared to metal nanoparticles or bulk metals [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], γ-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 NC 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 intensities 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, the printing of Cu electrodes using direct laser patterning and the 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 a PMAA polymer is necessary. PMAA is a well-known stabilizing agent for encapsulating brightly fluorescent silver nanoclusters both in solutions and thin films. The PMAA polymer has a strong affinity for silver

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ions and silver surfaces due to the presence of a carboxyl functional group. Therefore, it is believed that the presence of a carboxyl functional group in this polymer prevents the growth of nanoclusters into large nanoparticles [9,13].

In this Letter, 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 the carboxyl functional groups found in PMAA. Further, PVA is a 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 PVA powder (Sigma-Aldrich) with a molecular weight between 89,000 and 98, 000 g/mol in water. Varied amounts of silver nitrate (Sigma-Aldrich, ≥99%) were mixed with the PVA solution to obtain Ag/PVA samples with different concentrations (from 21 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 hydroxides (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 a wavelength ($\lambda_{\rm dlw}$) 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, the 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 a laser intensity ($I_{\rm dlw}$) of 6 $\rm MW/cm^2$ and a scanning speed of 5 µm/s in an Ag/PVA sample with a 10% Ag/OH ratio. The fluorescence image was obtained by exciting the written structures with an LED light source with a wavelength ($\lambda_{\rm exc}$) of 470 nm and an excitation intensity ($I_{\rm exc}$) of 100 $\rm W/cm^2$, which is considerably lower than $I_{\rm dlw}$. 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 [Fig. 1(b)], with an average line breadth of 500 nm.

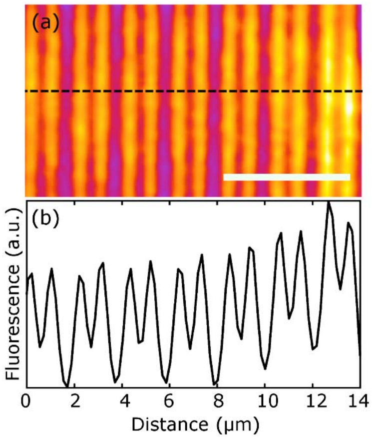

Fig. 1. (a) Fluorescence image of laser written lines in an Ag/PVA sample with 10% Ag/OH ratio ($I_{\rm dlw} = 6\ {\rm MW/cm^2}$, $\lambda_{dlw} = 405\ {\rm nm}$, $I_{\rm exc} = 100\ {\rm W/cm^2}$, $\lambda_{\rm exc} = 470\ {\rm nm}$). Scale bar = 5 µm. (b) Fluorescence intensity profile across the dashed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

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 concentrations (5% to 12.5% Ag/OH ratio). The Ag/PVA samples with ratios of more than 12.5% exhibited undesired crystallization of silver nitrate and were omitted from the studies. The crystallization most likely happened due to the supersaturated solution of $\rm AgNO_3$ in the PVA solution. For all the experiments, the writing conditions, i.e., the laser writing intensity and the scanning speed, were fixed to 6 $\rm MW/cm^2$ and 5 µm/s, respectively. Fluorescence emission spectra were recorded by exciting the written structures with a 473 nm laser beam having an excitation power of 300 $\rm W/cm^2$. 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 the increasing silver concentration: the highest and lowest intensities were achieved for Ag/PVA

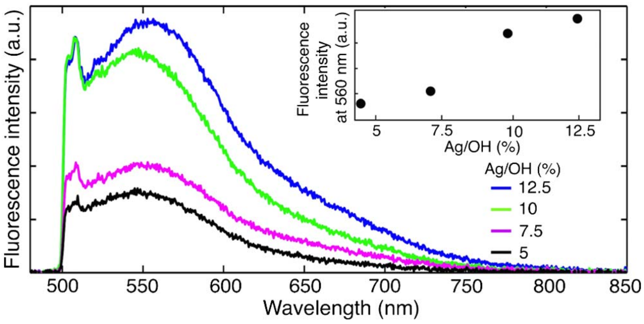

Fig. 2. Fluorescence emission spectra of laser written silver NCs in Ag/PVA films with Ag/OH ratios of 5% to 12.5% ($\lambda_{\rm exc} = 473$ nm). The inset image illustrates the dependence of the fluorescence intensity on the Ag concentration at 560 nm.

samples with 12.5% and 5% Ag/OH ratios, respectively. The inset image of Fig. 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 in the solution [12,38] and PMAA thin films [13,25]. Most importantly, the fluorescence from the written structures strongly depends on the silver concentration.

Silver nanoparticles larger than 2 nm exhibit collective oscillations of conduction electrons upon interaction with light and typically do not possess fluorescence. There are a few reports about the 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 sizes less than 2 nm are the main source of fluorescence in our laser written microstructures in PVA.

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 the line profiles manifest the formation of three-dimensional grooves at the positions of the laser written structures. The grooves made by laser intensities of 6 $\mathrm{MW/cm^2}$, 9 $\mathrm{MW/cm^2}$, and 12 $\mathrm{MW/cm^2}$ 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 (Fig. 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 $\mathrm{MW/cm^2}$, 9 $\mathrm{MW/cm^2}$, and 12 $\mathrm{MW/cm^2}$ 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.

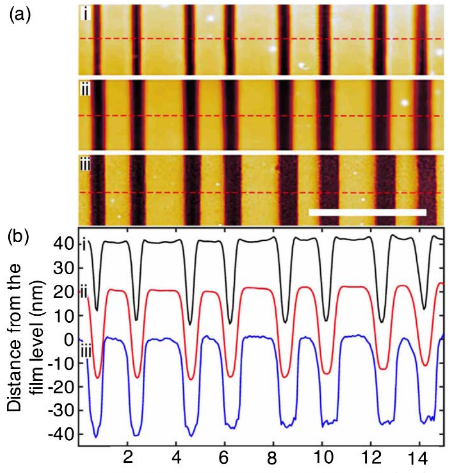

Fig. 3. (a) AFM images of the structures written with I_{dlw} of (a-i) 6 $\mathrm{MW/cm^2}$, (a-ii) 9 $\mathrm{MW/cm^2}$, and (a-iii) 12 $\mathrm{MW/cm^2}$ in Ag/PVA samples with 10% Ag/OH ratio. Scale bar = 5 μm. (b) Line-cut topography profiles of the structures across the dashed lines marked in (a).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

Finally, we investigated the photostability of the fluorescent silver NCs under strong illumination conditions. Microstructures written with I_{dlw} of 6 $\mathrm{MW/cm^2}$ ($\lambda_{\mathrm{dlw}} = 405$ nm) on the Ag/PVA sample with a 10% Ag/OH ratio were excited by a 473 nm laser diode, with laser intensities of 60 $\mathrm{W/cm^2}$, 300 $\mathrm{W/cm^2}$, and 600 $\mathrm{W/cm^2}$. 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 in Fig. 4 depict that the written structures were bleached to 53%, 30%, and 15% of their initial intensity in 300 s when they were irradiated with 60 $\mathrm{W/cm^2}$, 300 $\mathrm{W/cm^2}$, and 600 $\mathrm{W/cm^2}$, 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 (Fig. 4), where a and b are amplitude parameters, t is time, and τ_1 and τ_2 represent bleaching time constants. Table 1 summarizes the acquired values for τ_1 and τ_2 when the 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 τ_1, while the other population shows considerable photostability with a much longer time constant of τ_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 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 $\mathrm{W/cm^2}$ [41]. The photoluminescence property and the photostability

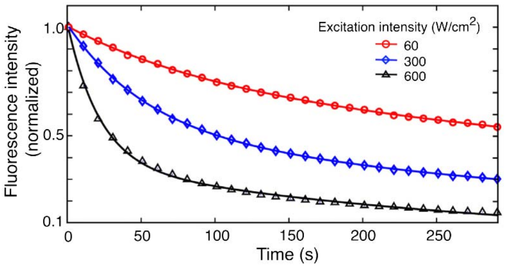

Fig. 4. Fluorescence photobleaching curves corresponding to the structures written with I_{dlw} of 6 $\mathrm{MW/cm^2}$ ($\lambda_{\mathrm{dlw}} = 405$ nm) in Ag/PVA sample with 10% Ag/OH ratio. The sample is excited with a 473 nm laser, and I_{exc} of 60 $\mathrm{W/cm^2}$ (red), 300 $\mathrm{W/cm^2}$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

Table 1. Bleaching Time Constants τ_1 and τ_2 When Written Structures are Excited with a Laser with Three Different Intensities at 473 nm Wavelength

I_{exc} (W/cm^2)	τ_1 (s)	τ_2 (s)
60	103	990
300	52	507
600	23	300

of the as-formed nanoclusters are very similar to that of the silver nanoclusters in PMAA [13]. PVA is widely used industrial polymer offering a cost-efficient matrix for fluorescent nanoclusters.

In conclusion, we have successfully fabricated fluorescent microstructures comprised 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, such as optical data storage, imaging, biolabeling, and sensing.

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