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Formation of ferroelectrically defined Ag nanoarray patterns

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ABSTRACT

In order to produce the most effective Ag nanoarrays for plasmon enhanced fluorescence and Raman scattering made using ferroelectric substrates, the optimum conditions for the creation of arrays must be identified. We study here Ag nanopattern arrays formed using ferroelectric lithography based on periodically proton exchanged (PPE) template methods. We examine different conditions in regard to deposition of Ag nanoparticles and analyze the plasmon enhanced signal from the resulting nanoarray. We apply FLIM (fluorescence lifetime imaging) to assess different Ag nanoarray preparation conditions on fluorescence emission from selected fluorophores. In addition, we apply Raman and luminescence spectroscopy with AFM (atomic force microscopy) to study the plasmon enhancement of luminescence and Raman from the Ag nanoarrays.

Keywords: Raman, SERS, Spectroscopy, nanoscale, Li niobate, nanoarray, lithography

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1. INTRODUCTION

Nanostructures made from metals such as silver under the correct conditions create plasmons. These plasmons are created when light creates a collective oscillation of the conduction electrons on the surface of the metal [1-7]. The properties of plasmonic-active nanostructures is dependent on size, shape, and dielectric environment and other factors. Plasmonic materials with specific architectures are of interest in a variety of applications ranging from sensing to enhanced fluorescence [1,3,5,6]. One approach to creating controlled designs of plasmonic nanomaterials is via self-assembly [8], which has been applied to produce a wide range of materials with nanometer sized features such as one dimensional quantum wires or zero dimensional quantum dots [9-15].

Ferroelectric lithography is a method based on patterning the spontaneous polarisation inside ferroelectric crystals so to engineer static electric field distributions, suitable for driving bottom-up assembly and nanodeposition at the surface of ferroelectric templates [16]. Besides electric field poling [17] the spontaneous polarization in materials such as LiNbO₃, can be modified through the chemical process of proton exchange [18,19]. Proton exchange-based and other ferroelectric lithography-based methods have been applied to direct self-assembly of silver (Ag) nanoparticles [15,19-25]. Studies have showed that metallic nanoparticle deposition from an aqueous solution onto +Z charged regions of periodically poled LiNbO₃ nanodomain patterns can be achieved [19-25]. The nanopatterned features created using Ag nanoparticles possessed a size variation between 2–10 nm in diameter and height [24]. Photochemical reduction on LiNbO₃ has been shown under certain conditions to result in nanowires which form along the domain wall [26]. These nanowires have been shown to be conducting, and such high aspect ratio functional nanowires could be of technological relevance [27]. Liu et al., have shown that the deposition can also occur on the +Z surface, and Dunn and Tiwari have demonstrated photochemical reduction on both +Z and -Z surfaces [24,28]. Tiwari and Dunn have pointed out that when the power of the irradiation is taken into account, the results can be described consistently and Sun et al. have further reported on the dependence of the wavelength and intensity of the light and of the concentration of the solution [29].

Chemical patterning potentially offers a method to create substrates that support reproducible surface enhanced Raman scattering spectroscopy (SERS) via arrays of nanopatterns made from silver nanoparticles [3,5]. Damm et al. demonstrated using a molecular probe 4-Aminothiophenol (4-ABT) absorbed onto a silver nanostructured array that SERS can be obtained. The authors showed that the observed SERS spectra exhibit peaks arising from b_2 modes, which occur for plasmon enhanced Raman scattering from 4-ABT, in place of a_1 modes, which occur in normal Raman scattering [5]. Damm et al. applied ferroelectric lithography to generate a nanopattern array consisting of assembled silver nanoparticles [3,5]. They demonstrated that such nanoarrays are plasmon active supporting both plasmon enhanced Raman and luminescence. Fluorescence studies showed that the nanopatterned array supported surface enhanced luminescence. In order to produce the most effective Ag nanoarrays for plasmon-enhanced fluorescence and Raman scattering by using ferroelectric substrates, the optimum conditions for the creation of arrays need to be identified. We study here Ag nanopattern arrays formed using ferroelectric lithography based on periodically proton exchanged (PPE) template methods [30]. We consider different conditions in regard to the deposition of Ag nanoparticles and examine the resulting nanoarrays. We apply FLIM (fluorescence lifetime imaging) to assess the impact of different Ag nanoarray preparation conditions on fluorescence emission from selected fluorophores. In addition we apply Raman and luminescence spectroscopy with AFM (atomic force microscopy) to study the plasmonic enhancement of luminescence and Raman from the Ag nanoarrays.

2. EXPERIMENTS

The Ag nanopattern arrays reported here were made using periodically proton exchanged (PPE) templates. The methodology to create the nanopattern arrays has been outlined previously [19,22]. Briefly, the silver is deposited under ultraviolet (UV) light irradiation by photochemical reduction in solution along the boundaries between ferroelectric regions of the substrate (see Fig. 1a-i and 1a-ii) where the electric field magnitude is at a maximum, creating nanopatterned arrays. The samples were cleaned prior to deposition of silver by sonication for 10 minutes each in isopropanol, acetone, and Milli-Q water. After 150 μl of 10^{-2} M concentration AgNO_3 solution was pipetted onto the substrate, the samples were illuminated with UV light. The photogenerated electrons led to selective deposition of Ag particles on the ferroelectric template through a reduction reaction [19]. The sample was subsequently rinsed in Milli-Q water for 1 min and blown dry with compressed nitrogen. Two probe molecules were used to investigate the plasmon properties of the nanoarrays. A monolayer of Rhodamine 6G (Rh6G) was prepared by dipping the Ag sample in a 0.01 mM H_2O solution for 24 hours, following 5 minutes in H_2O to wash off any excess probe molecules. A reference sample for FLIM measurements was prepared with a 0.01 mM drop placed onto a glass coverslip and left to dry. A monolayer of $[\text{Ru}(\text{bpy})_2(\text{Qbpy})]^{2+}$ (Rubpy) was prepared by dipping the samples in 6 mM MeOH solution for 10 min, following 1 min in methanol to wash off any excess molecules. The samples were illuminated with visible light through a 50x objective lens and the Raman scattering signals were collected at a backscattered angle and directed onto a charge coupled device (CCD) via a monochromator [3-7]. The setup for the Raman scattering studies on the PPE sample used a laser power of 25 mW and an excitation wavelength $\lambda_{\text{ex}} = 532\text{nm}$.

3. RESULTS AND DISCUSSION

Ag nanoarrays created using PPE templates are shown in Figure 1. The AFM topography image of Figure 1a shows the presence of multiple Ag nanoarray patterns. The Ag nanoarrays are c.a. 1000 nm wide and 50 nm high. The length of the Ag nanoarrays patterns is much greater than 10 μm . The Ag linear structures possess additional nanosized fine-structure arising from the presence of small (c.a. 20 nm) sized Ag nanoparticles that self-assemble to form the larger Ag nanowires. The resulting nanoarrays consist of well-defined Ag boundaries. The optical absorption spectrum of the Ag nanoarray patterns is shown in Figure 1b. It shows a broad absorption with a peak at c.a. 550 nm. The amount and height of the silver deposition can be controlled by varying the concentration of the AgNO_3 solution. The images show a silver nanopattern made with 10^{-5} M AgNO_3 , since at this concentration the sample has well defined linear periodic patterns.

Figure 1d is a zoomed-in high resolution image of the sample, clearly showing that the location of the nanoparticles is very specific and controlled (i.e. no nanoparticles can be observed between the nanowires).

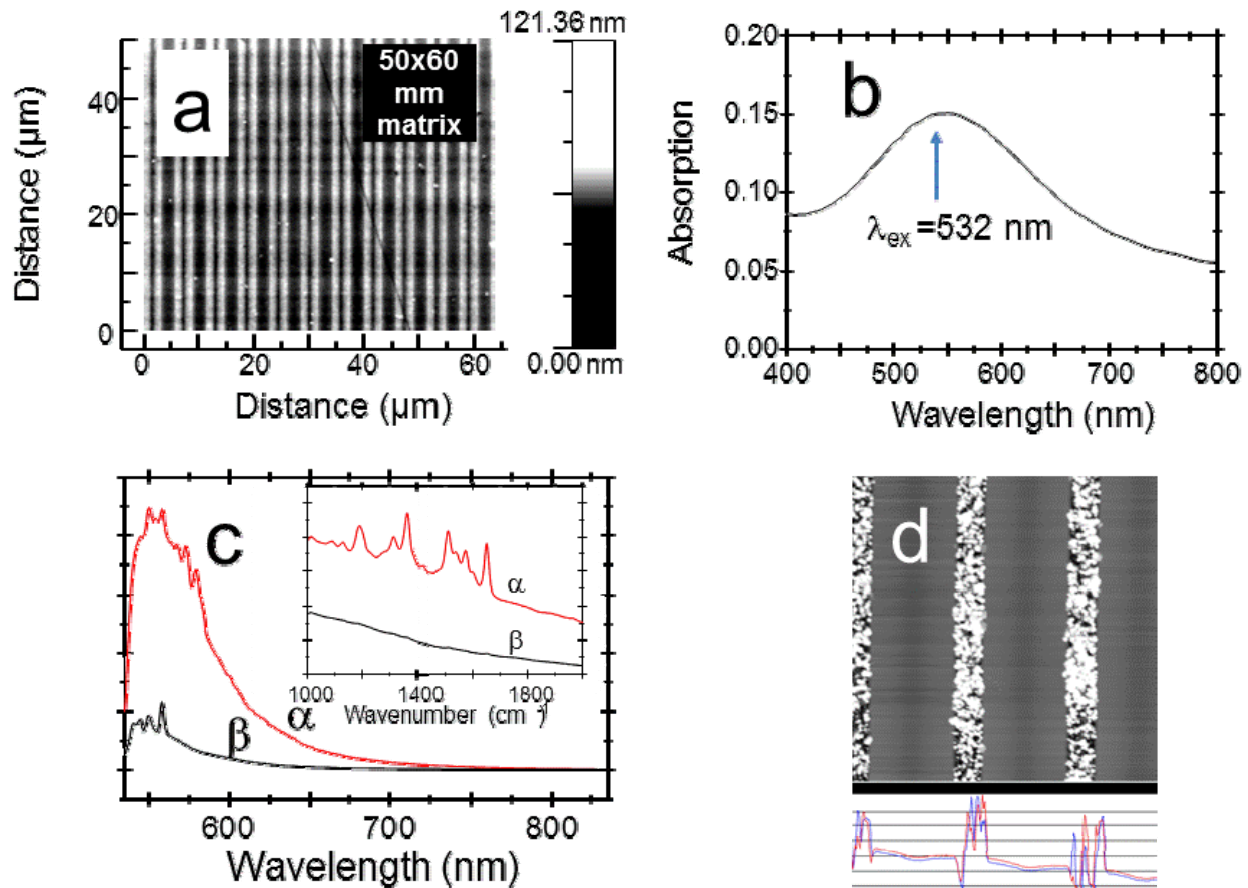


Figure 1. a) AFM topography image of the substrate showing the presence of arrays of Ag nanowire like structures. b) optical absorption image of the Ag nanoarray substrate. c) shows luminescence from the probe molecule from the probe molecule on Ag nanoarray (α) and glass (β). Inset shows the resulting Raman from the probe molecule on Ag nanoarray (α) and glass (β). d) High resolution AFM image of sample.

Raman scattering and luminescence spectroscopy using a Rh6G probe molecule attached to the nanoarray substrate were performed. Rh6G has an emission at c.a. 550 nm. When excited at 532 nm, Rh6G exhibits fluorescent emission and Raman scattering in the same spectral region. Previous studies have showed that these probe molecules enable surface enhanced Raman scattering (SERS) and luminescence (SEL) [ref]. The Raman scattering spectrum is shown in Fig. 2c- α i.e. SERS is observed for the probe molecules on the silver. The broad background comes from luminescence from the probe molecules. Figure 2c shows that the luminescence intensity increases when the probe molecule is on the Ag nanoarray compared to glass therefore SEL is observed along with SERS for this system as the luminescence signal on the glass is weaker than on the silver plasmonic enhancement of the emission must have occurred i.e. SEL.

Rh6G probe molecules were added to the substrate. The luminescence properties were subsequently probed by FLIM. The luminescence image from a ($\text{LiNbO}_3 + \text{Ag nanowires} + \text{Rh6G}$) sample is shown in Figure 2a. A larger view of the FLIM image is shown in Figure 2b. The luminescence arises from defined regions (shown in blue), while no luminescence arises from the black region. The blue regions show clear boundaries and shape profiles that match up well with the profiles seen in the AFM image for the Ag nanoarray shown in Figure 1. This indicates that the luminescence

originates from regions of the sample where Ag is situated. The average lifetime from the luminescence is less than 1 ns. Figure 2c shows the decay trace for the probe molecule on glass (black line) and for the probe molecule on the Ag nanoarray (red line). The decay trace for the probe molecule on Ag nanoarray is much faster as expected when a molecule is in contact with a silver surface. The FLIM image shows luminescence that arises from the probe molecule that forms a c.a. monolayer on the silver. Shown in Figure 2d is a profile of luminescence intensity as a function of distance taken from the FLIM data shown in Figure 2a. The plot shows regular spikes in luminescence intensity that occur at set distances over the sample surface. The dimensions of these spikes correlate well with the position of the Ag nanoarrays as inferred from the AFM images.

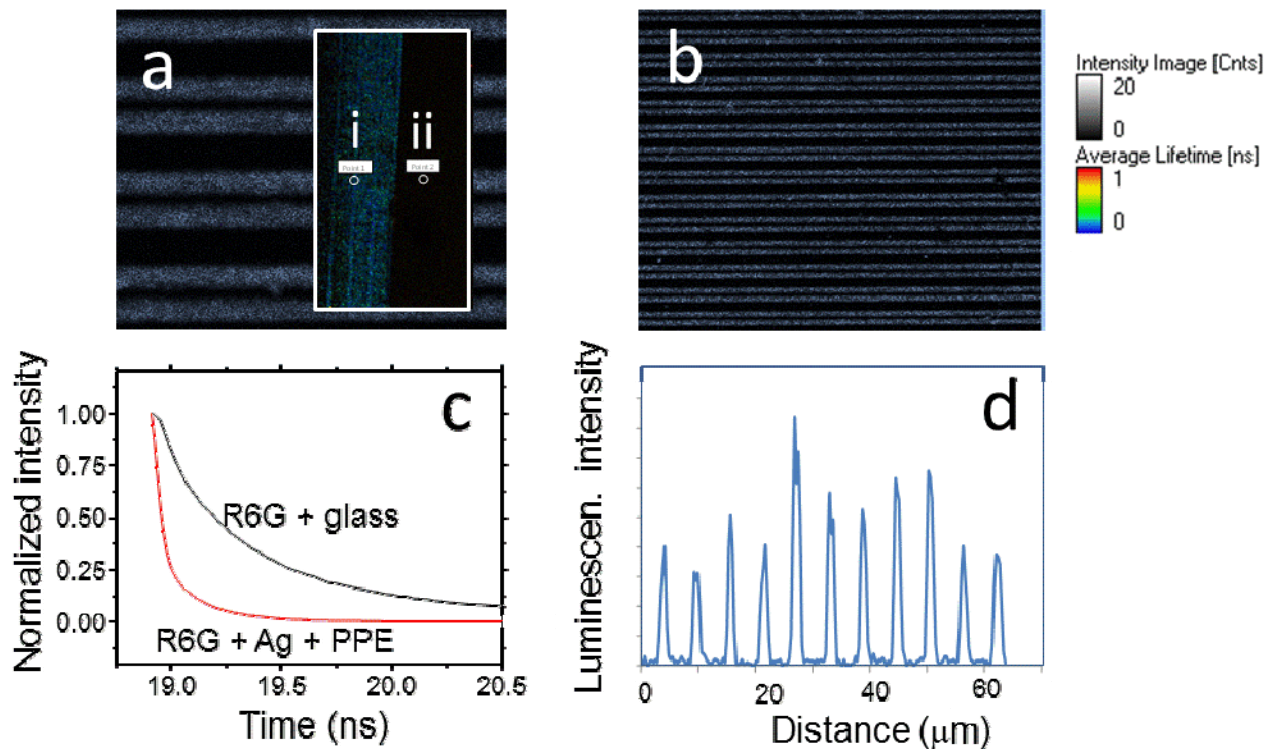


Figure 2. a) FLIM image of the nanoarray substrate + Rh6G showing the presence of arrays of Ag nanowire like structures. Insert shows a zoomed in view of a region about a single wire like structure, caption i refers to on the wire (blue region) and ii off the wire (black region). b) expanded view of a). c) Lifetime plot of the probe molecule on glass and on the Ag nanoarray. D) plot of luminescence intensity with distance.

Varying the concentration of the AgNO_3 solution from 10^{-5} M AgNO_3 was studied. The effect of over addition of Ag nanoparticles above the optimum level was explored. Figure 3a shows FLIM image for an Ag nanoarray with more Ag nanoparticles added (1×10^{-4} and 5×10^{-4} M) than was used to build the Ag nanoarray shown in Figure 2. The image shows the presence of luminescence randomly occurring on the substrate in areas between well-defined and regular Ag regions. These well-defined Ag regions are similar to the Ag wire-like structures shown in Figure 2. When the Ag nanoparticle concentration is increased further, more areas appear to give rise to random luminescence. Figure 3d shows the corresponding FLIM image with increased numbers of Ag nanoparticles present between the wire like structures. These studies demonstrate that a careful control over the concentration of Ag nanoparticles is needed in order to optimize the nanoarray. Over exposure of Ag nanoparticles ie too many nanoparticles present results in nanoparticles placing

themselves onto the substrate surface – away from the preferred charged regions that have been lithographically prepared.

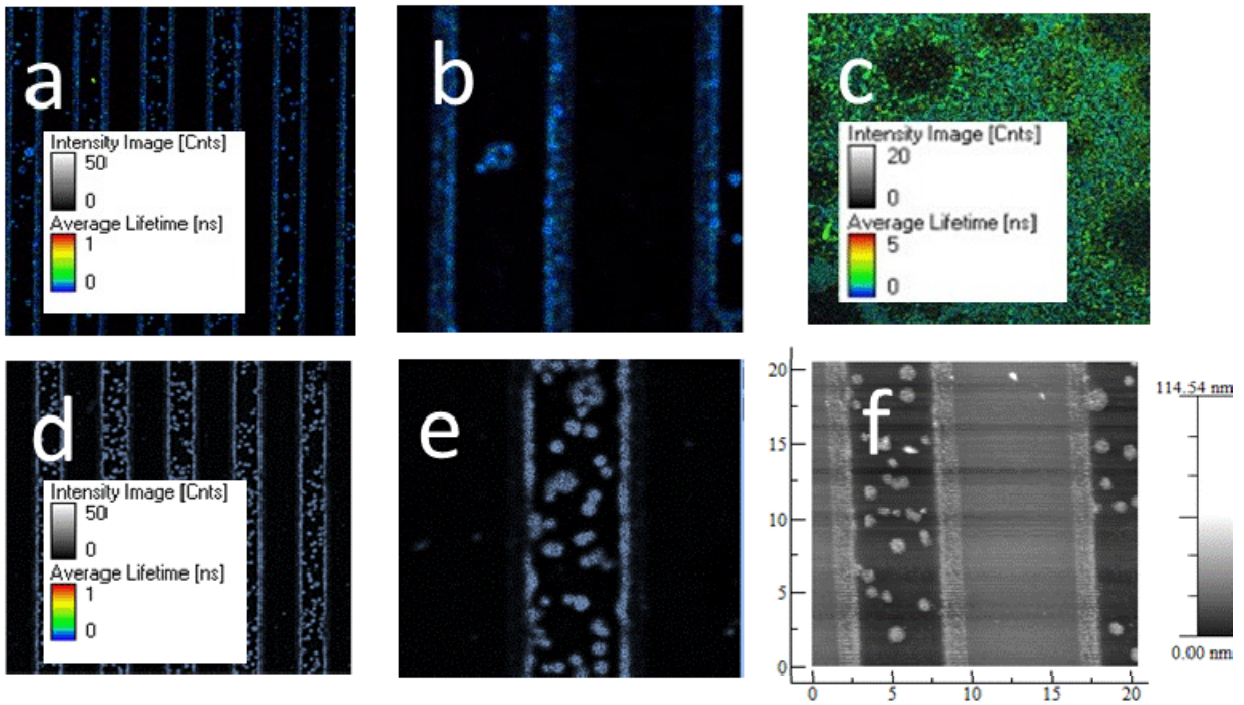


Figure 3. a) FLIM image of nanoarray, with b) a zoomed in view of the same sample. c) FLIM from the probe molecule on glass. d) FLIM image of a nanoarray, e) zoomed in image of the same sample. F) AFM of sample shown in d) and e).

The effect of a reduction of the Ag nanoparticle count above the optimum level was explored i.e. using 1×10^{-6} and 5×10^{-6} M concentrations. Figure 4a shows FLIM image for an Ag nanoarray. The nanowire-like structures form incomplete lines arising from missing silver nanoparticles. Reducing more the silver nanoparticle concentration produces further incompleteness as shown in Figure 4b. AFM topography images (Figure 4c), consistently with FLIM results, shows incomplete wire-like structures.

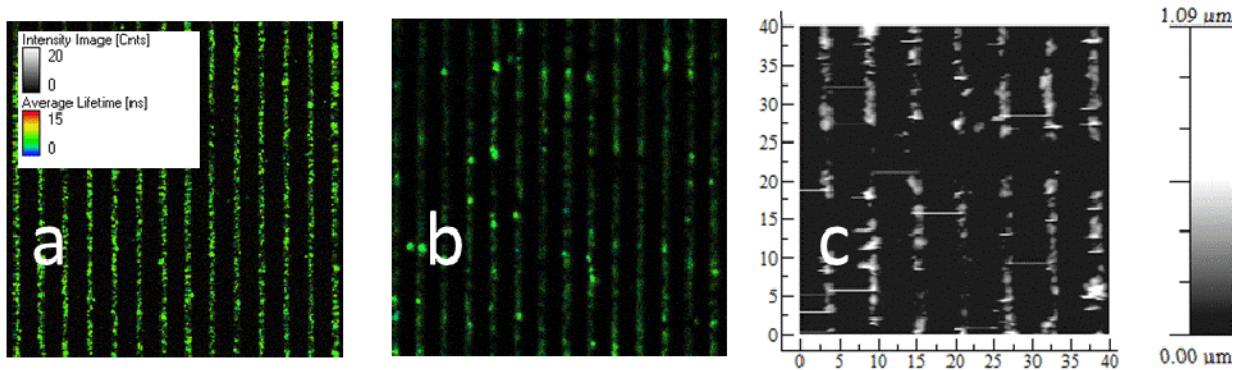


Figure 4. a) FLIM image of nanoarray, b) FLIM image of nanoaray. c) AFM of sample shown in b)

To conclude, we have studied the effect of silver nanoparticle concentration in order to produce the most effective Ag nanoarrays for plasmon enhanced fluorescence and Raman scattering made using lithography based on periodically proton exchanged (PPE) template methods [30]. We examined different conditions in regard to deposition of Ag nanoparticles and analysed the resulting nanoarrays. We apply FLIM (fluorescence lifetime imaging) to assess the impact of different Ag nanoarray preparation conditions on fluorescence emission from selected fluorophores. In addition we applied Raman and luminescence spectroscopy with AFM (atomic force microscopy) to study the plasmonic enhancement of luminescence and Raman from the Ag nanoarrays. We show that in order to optimize the potential of this approach to creating features using nanoparticles care attention to nanoparticle concentration is required. However, once this has been understood very well ordered structures can be produced. Well defined and precise ordering can be achieved using the outlined approach when conditions are optimized. We show here that such optimization can be achieved via control over the specific sample preparation parameters. This approach to creating self-assembled patterned arrays has the potential to be applied in a range of device applications such as in Raman sensing devices where reproducibility of Raman intensity is desired.

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