

Plasmon assisted two-photon direct laser writing of micro-structures composed of chiral Ag nanoparticles

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ABSTRACT

We present an approach to produce micropatterns of metallic nanoparticles (NPs) that preserve key optical properties of the individual NPs. The technique uses a photothermal reaction induced by two-photon direct laser writing. The studied NP property is plasmon chirality, which was obtained via chemical conjugation of Ag NPs with chiral ligands: *N*-(tert-butoxycarbonyl)-L-cysteine methyl ester. The ligand cleavage initiated by a femtosecond pulsed laser induced thermal reaction results in a significant change in dispersibility of the nanocrystals, thereby enabling a solvent selective development process after photo-patterning. We analyzed the optical chirality of the Ag NP films before and after micropatterning by two-photon lithography. We show that this patterning technique allows the patterned film to maintain this predefined optical property. In contrast, we show the disadvantage of the common use of a photo-acid generator for the cleavage of solubilizing groups via protonation. In this case, the ligand protonation results in the loss of the chiral behavior.

Keywords: two-photon lithography, metallic nanoparticles, chirality, bottom-up approach, top-down approach.

1 INTRODUCTION

Localized surface plasmons (LSPs) are electromagnetic waves that propagate along the interface between a metallic nanoparticle and a dielectric material. The tightly confined electromagnetic field of LSPs decays exponentially away from the metal surface, resulting in evanescent wave characteristics; thus, distance from metallic NPs (MNPs) is known to play an important role in inducing or enhancing optical effects by LSP resonance (LSPR) [1-4]. Several recent papers have demonstrated plasmonic enhancement of optical effects including optical circular dichroism (CD) when achiral metallic particles exhibit chiral response at plasmonic frequency [5-8]. This enhancement has been attributed to several factors but strongly depends on the precise tailored optical properties of MNPs to meet specific

requirements for each of these applications. It is also well known that local heating of the environment can be generated efficiently via LSPR absorption by MNPs [9-11]. Here, we show how two-photon excited LSPR can lead to the thermal cleavage of the ligands adsorbed on the surface of metallic nanoparticles. The overall process is initiated by a nonlinear optical process in which the Ag NPs absorb two photons simultaneously. The electron gas thermalizes internally by electron-electron coupling producing a distribution of electrons which are not in thermal equilibrium [12]. These “hot electrons” then equilibrate with the lattice by electron-phonon coupling [13-16]. The heat released initiates the photothermal cleavage of the functionalized ligands for patterning the Ag NPs [17]. Furthermore, we demonstrate that ligand-induced chirality of MNPs is preserved in the fabricated patterns. Preservation of pre-tailored optical properties of a medium upon irradiation for photolithography can be of key importance for many practical applications. As an example, it is crucial to keep chirality of building blocks when a planar chiral metamaterial is fabricated by photopatterning of these building blocks. In this case the resulting optical activity of the material can be greatly enhanced.

Recently, several groups took advantage of two-photon lithography for fabrication of solid state films by *in-situ* growth of MNPs in polymer template [18-21]. However, this approach results in limited loading of MNPs in patterned area. Furthermore, optical properties of *in-situ* grown MNPs are very difficult to control in a reliable and reproducible fashion and they often lose their unique localized surface plasmon quality due to aggregation and sintering into larger particles with bulk-like properties. We have recently reported a method to photo-pattern semiconductor nanocrystals (NCs) via conventional photolithographic technique [22, 23]. In this technique, the original ligand on the nanocrystal is replaced by a *tert*-butyl *N*-(2-mercaptoethyl) carbamate ligand. This modification allows release of the *tert*-butoxycarbonyl (*t*-BOC) group of this carbamate ligand upon irradiation by UV light in the presence of a photoacid generator (PAG). Formation of the shortened ligand, accompanied by a drastic change of the dispersibility of the nanocrystals, enables a solvent-

selective development process after photopatterning. We also demonstrated that this deprotection of *t*-BOC is possible through thermal decomposition at an appropriate temperature [24]. Hence, we chose photothermal deprotection reaction of *t*-BOC initiated by nonlinear excited localized surface plasmon resonance of MNPs to achieve patterning without use of a photosensitizer. Because PAG-initiated deprotection must be carried out in the complete dark, our new method can be much more convenient for practical applications.

2 MATERIALS AND METHODS

In this work we achieve subwavelength laser patterns via two-photon lithography of MNPs assisted by hot electron-induced photothermal reaction which preserve the chirality of the individual Ag NPs. The developed photothermal patternable material is used to demonstrate this technique. Such material is composed of Ag NPs functionalized with the *t*-BOC thermally cleavable functional ligand. This ligand possess short alkyl groups and highly soluble moieties, allowing low cost solution casting. Therefore, the strategy is based the use of a *t*-BOC protected ligand for MNP so that the thermally cleavable groups can be removed by plasmon-assisted photothermal reaction.

After plasmonic excitation, the relaxation of the hot electrons is responsible for the thermal cleavage of the ligands on the MNPs assemblies. The non-linear two-photon absorption of the spin coated Ag NP drives the thermal cleavage of the functional ligands on their surface by local heating. The short ligands remain after *t*-BOC cleavage are expected to provide densely packed MNPs in

solid state films by efficiently decreasing the interparticle gap, providing collective plasmons at longer wavelengths. More importantly, after *t*-BOC cleavage, the MNPs are no longer dispersible in common solvents. Thus, solvent development removes unexposed regions and leaves behind the patterned regions. Therefore the photothermal reaction assisted via two-photon writing provides a route towards subwavelength structures without extrinsic additives.

All chemicals were purchased from Aldrich, and used without further purification. The Ag NPs were synthesized using an established procedure from the literature [25]. The typical resident dodecanoic acid ligands were then replaced with the chiral *t*-BOC protected ligand which contains both a chiral center and a thermally cleavable group: *N*-(*tert*-butoxycarbonyl)-L-cysteine methyl ester [22, 24]. The ligand exchange proceeds easily because the thiol-terminated ligand binds much more strongly to the silver surface than carboxylic acids or amines [22]. From now on the *N*-(*tert*-butoxycarbonyl)-L-cysteine methyl ester protected Ag NPs are called *t*-BOC Ag NPs, and its deprotected form deprotected Ag NPs, the chemical structures are illustrated in Figure 1. The Ag NPs are spherical with a mean diameter of 9.3 ± 0.9 nm. From absorption spectroscopy we observed that the *t*-BOC Ag NPs in chloroform have a specific surface plasmon resonance band at 410 nm. But, as expected due to the strong near-field interactions between NPs, the plasmonic absorption spectrum shifts toward the red and broadens in solid state films [26, 27] (Figure 2). As a matter of fact, the dense assemblies of Ag NPs offer efficient light trapping which can enhance the photo-patterning using NIR laser.

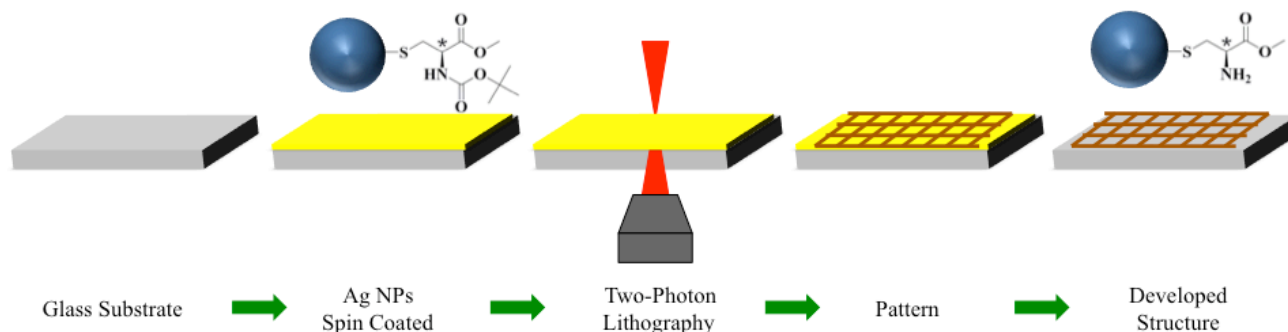


Figure 1. Schematic sequence of two-photon thermal lithography using functionalized chiral Ag NPs.

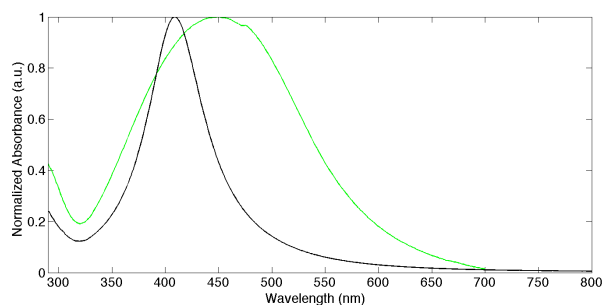


Figure 2. Absorption spectra of *t*-BOC Ag NPs solution in chloroform (black line) and *t*-BOC Ag NP film (green line).

The absorbance spectrum of the Ag NPs shows no substantial plasmonic absorption at NIR and beyond. Thus, a femtosecond pulsed laser at 800nm with a repetition rate of 76MHz was chosen to achieve two-photon lithography at a wavelength where negligible single-photon absorption occurs. To photopattern the films by two-photon absorption process, the *t*-BOC protected Ag NPs were dispersed in chloroform (50 mg/mL), and spin coated onto a glass substrate to produce a 150 nm film. The femtosecond pulsed beam was introduced into an inverted microscope and focused onto the spin coated Ag NPs film through an objective lens. The samples were scanned in the (*x,y*)-plane in the focus of the beam by a computer-controlled piezo stage synchronized with a photoacoustic modulator working as a shutter to obtain the desired design. Finally, the written patterns were immersion developed in 4:1 chloroform:ethanol by volume.

3 RESULTS AND DISCUSSION

Figure 3 shows an SEM image of a pattern made via the process described above. To confirm the presence of Ag NPs after patterning, the Energy-dispersive X-ray spectroscopy (EDS) measurement was done, which clearly shows a distinct peak at around 3keV due to the $K\alpha$ fluorescence X-rays of Ag NPs (Figure 3). Different photopatterns were obtained as the average laser power was varied from 1 mW to 35 mW with the speed of writing fixed at 0.05 μ m/ms. In addition, different patterns were obtained with two different microscope objective with numerical aperture (NA) 0.85 and 1. The narrowest line obtained reliably and repeatedly was 500 nm but single lines less than 200 nm wide were also observed. For these conditions, total power of 1 mW and a NA 1 was enough for the two-photon lithography process.

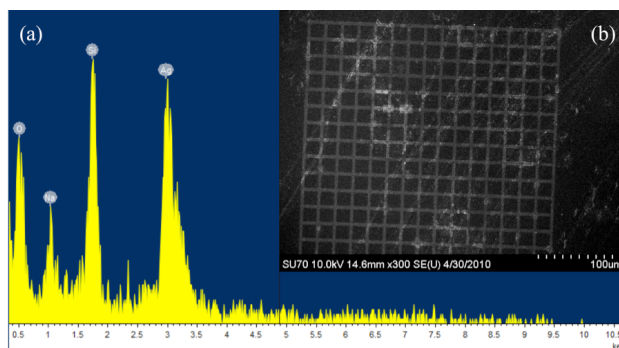


Figure 3. (a) EDS spectrum of the fishnet structure, which confirmed the existence of silver NPs and (b) SEM image of the photopatterned structure.

The width of patterned lines increased in proportion to the incident power, which means that higher laser power provides a photothermal reaction in a broader region because energy sufficient to initiate thermal deprotection was deposited over a broader region.

In addition to the photopatterning of thin films of the Ag NPs, we report preliminary experiments to examine the ligand-induced CD properties of the two resulting films. Specifically, the solid state Ag NPs film was studied with regard to the optical chiral response of the Ag NPs in which chiral ligands are adsorbed to previously achiral nanoparticles. The resulting CD spectra of the Ag NPs films are shown in Figure 4. The dodecanoic acid protected Ag NPs film does not show any CD response due to the absence of chirality of dodecanoic acid as well as of Ag NPs. While there were no significant signal changes observed in the CD spectra of the *N*-(*tert*-butoxycarbonyl)-L-cysteine methyl ester in film state compared to solution, new characteristic CD signals were generated in the range of 300-700 nm when the chiral ligand was attached to the Ag NPs. A new series of CD bands in the visible range, including a band at the plasmonic frequency, makes the chiral Ag NPs suitable for CD-based applications in the visible range [28]. The CD spectrum of *t*-BOC deprotected Ag NPs film showed that the induced chirality is preserved when the film is *t*-BOC deprotected by photothermal reaction, whereas chirality in the wavelength region between 400 and 800 nm vanishes completely when deprotection is realized by means of PAG.

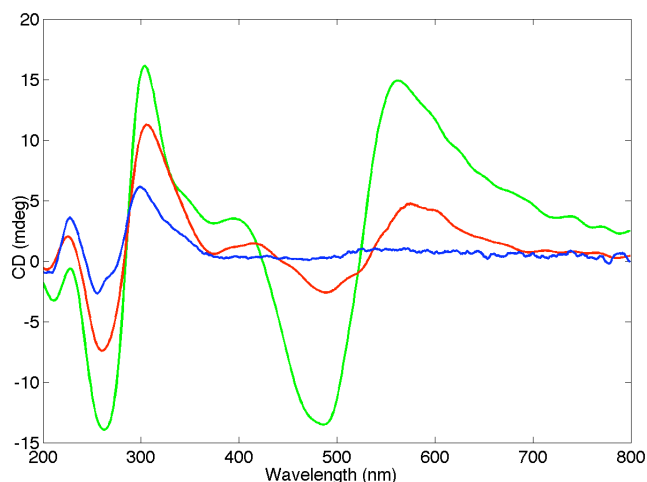


Figure 4. CD spectra: *t*-BOC protected chiral Ag NPs film (green line), *t*-BOC deprotected Ag NPs film (red line), and *t*-BOC deprotected Ag NPs film fabricated under UV with PAG (blue line)

4 CONCLUSION

We demonstrate that two-photon photothermally induced reaction can be used to produce patterned structures of Ag NPs with submicron resolution and optical properties conferred by the nanoparticle constituents. The two-photon absorption process occurs at the localized surface plasmon resonance of Ag NPs. It is the strong two-photon absorption of the Ag NPs that allows this highly localized photochemistry to be initiated in subwavelength domains without addition of any photosensitizer.

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