FABRICATION OF 3D POLYMER-METAL NANO-COMPOSITES IN A SINGLE STEP BY TWO-PHOTON INDUCED POLYMERISATION AND METAL SALT REDUCTION

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Abstract

Fabrication of 3D polymer-metal nano-composites in a single step by two-photon induced polymerisation and metal salt reduction has been demonstrated in this study. Two kinds of composites, SU8-Au and IPL-Au, based on different mechanisms of polymerisation, have been fabricated and compared. To the best of our knowledge, this is the first demonstration of IPL-Au nano-composites being fabricated by two-photon lithography. Extra photoninitator is needed for the fabrication of IPL-Au composites, to provide extra free radicals to sustain the two reactions processing at the same time. The distribution of the generated Au nanoparticles in IPL matrix is more uniform than that in SU8 matrix. The technique demonstrated in this study can have great application in metamaterial fabrication.

Keywords

Nano-composites, two-photon lithography, gold nanostructures, nanofabrication, polymerisation, metal salt reduction, metamaterials

1. Introduction

Metamaterials are novel artificial multi-material constructs with sub-wavelength-sized periodic structures containing both conducting (metal) and dielectric (polymer) components. Their unique but previously unachievable properties have promoted lots of extraordinary applications (Cai, Chettiar et al. 2007; Engheta 2007; Choi, Lee et al. 2011; Soukoulis and Wegener 2011). The current techniques for metamaterials manufacturing are mainly based on traditional microchip patterning techniques, e.g. photolithography combined with metal deposition, that are expensive, multistep and slow (Liu, Zhu et al. 2012; Moser and Rockstuhl 2012). Two-photon lithography, which uses a focused ultrafast laser beam to penetrate into photo-reactive polymer resin and scans in true 3D, can overcome this limitation and fabricate micro/nano structures in arbitrary 3D with around 100 nm resolution in a fast and cost-efficient way (Lee, Yang et al. 2006; Maruo and Fourkas 2008; Park, Yang et al. 2009; Malinauskas, Farsari et al. 2013). Both polymeric structures and metallic structures have been manufactured respectively by two-photon induced polymerisation and metal salt reduction (Tanaka, Ishikawa et al. 2006; Kaehr and Shear 2008; Seidlits, Schmidt et al. 2009; Xu, Xia et al. 2010; Greiner, Richter et al. 2012; Ishikawa and Tanaka 2012). Early work of fabricating metallic structures in a polymeric matrix by two-photon associated processing has been demonstrated by Prasad et al (Shukla, Furlani et al. 2010; Shukla, Vidal et al. 2011; Vora, Kang et al. 2012). The great potential applications urge us to expand current capabilities and especially in enriching materials available for various needs.

The mechanism of photopolymerisation can be generally divided into two groups – free radical-based polymerisation and ionic-based polymerisation (Lee, Kim et al. 2008). In the current study, two-photon induced polymerisation based on both mechanisms has been compared, using two commercial resins – SU8 and IPL. SU-8 is a commonly used epoxy-based resin, and the polymerisation is based on the ionic mechanism. The commercially available SU8 resin contains a small amount of photoinitiator(s), optimized for traditional UV lithographic applications. The contained initiator(s) may vary due to different suppliers. IPL is a free radical-based commercial photo-reactive resin, developed by Nanoscribe GmbH for two-photon polymerisation. The as-purchased IPL resin contains <5% initiator. We demonstrate in this paper that two kinds of polymer-metal nano-composites – SU8-Au and IPL-Au – can be fabricated in a single step by two-photon induced polymerisation and metal salt reduction. To the best of our knowledge, this is the first demonstration of IPL-Au nano-composites being fabricated by two-photon lithography.

2. Experimental

Nano-composites were fabricated using a commercial two-photon lithography system – Nanoscribe Photonic Professional GT. The system uses a fiber laser at a wavelength of 780 nm, pulse frequency of 80 MHz and pulse duration of 120 fs. Laser beam is focused by an oil immersion objective (63x, NA = 1.4, WD = 190 µm). Micro/nano patterns are formed by moving the laser beam using a high speed X-Y galvo-scanner or shifting the sample position using a piezo X-Y-Z stage. All the patterns shown in this paper are formed by using the galvo mode at a writing speed of 10,000 µm/s and the laser power in the range of 25 mW to 50 mW.

Gold chloride hydrate powder ($HAuCl_4 \cdot xH_2O$) purchased from Sigma-Aldrich was used as source for metallic component. Monomer SU8 and IPL were purchased from Gersteltec and Nanoscribe, respectively. Photoinitiators were sourced from Sigma-Aldrich.

Gold chloride powder was first dissolved in solvent before mixing with monomer resin. Ethanol was used in the mixture of IPL with Au, and 1,4-Dioxane was used in the mixture of SU8 with Au. Then a drop of mixture was loaded on a clean cover slip for two-photon processing. After laser exposure, the cover slip was soaked in a suitable solvent (developer) to remove the unsolidified resins. The fabrication procedure is illustrated in Figure 1.

Structures were imaged by a desktop Scanning Electron Microscopy (SEM) system - Hitachi TM3030. The chemical compositions were analysed by an Energy-dispersive X-ray Spectroscopy (EDX) system - Bruker Quantax 70 - integrated within the Hitachi SEM.

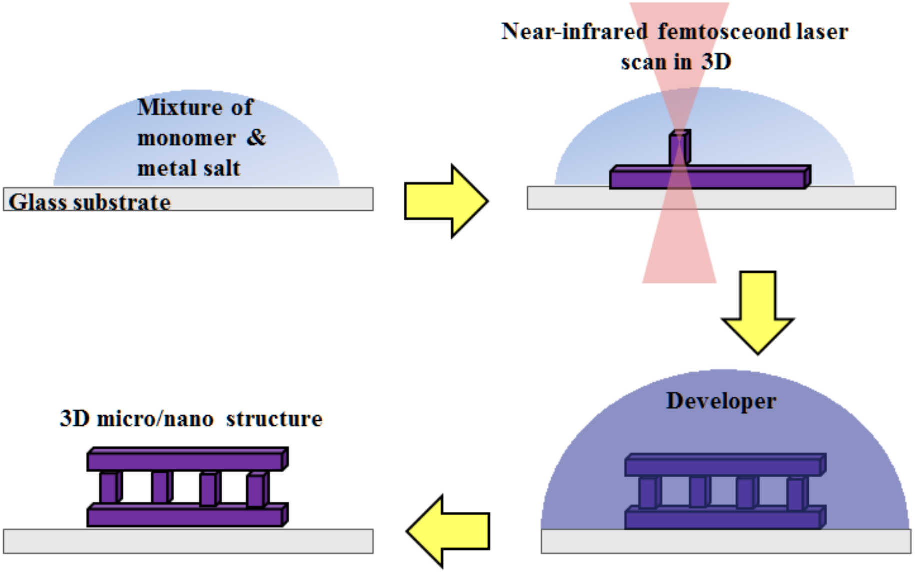


Figure 1: Illustration of fabrication steps.

3. Results and discussion

Fabricating nano-composites in a single step by two-photon induced polymerisation and metal salt reduction is illustrated in Figure 2. A near-infrared femtosecond laser beam is focused into a photo-reactive resin containing the mixture of monomer and metal salt. A photoinitiator is excited by the simultaneous absorption of two photons, which can trigger local chemical reactions, including monomer cross linking and metal salt reduction. In this way, both polymer and metal nanoparticles can be formed. Due to high surface tension, the generated metal nanoparticles tend to aggregate into large ones. The local monomer cross linking may serve as a matrix, thus reduce the diffusion-related metal aggregation. These two simultaneous chemical reactions may compete with each other, leading to different morphology.

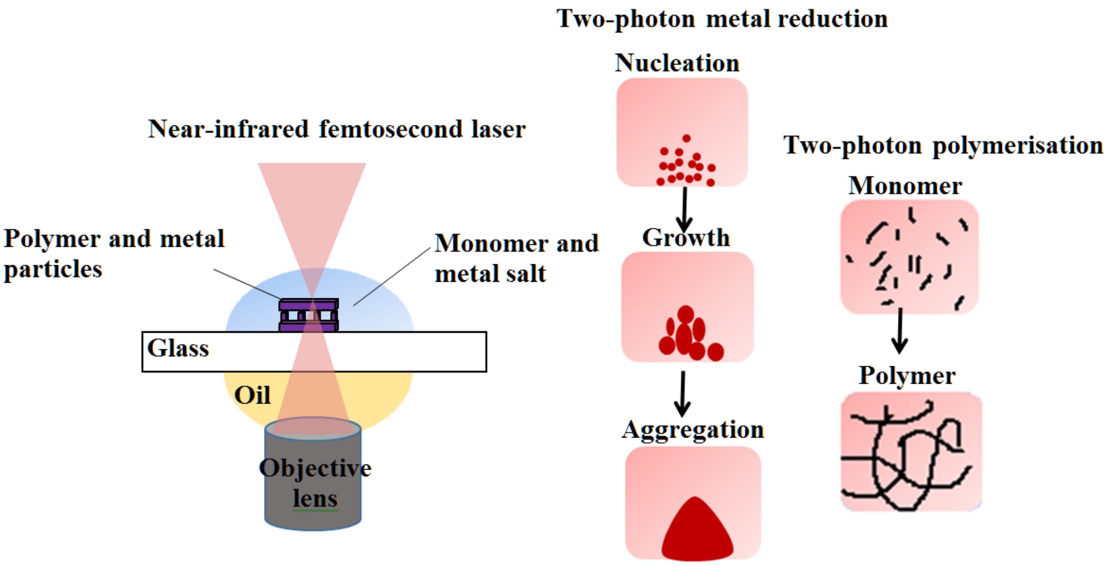


Figure 2: Illustration of fabricating nano-composites in a single step by two-photon induced polymerisation and metal salt reduction

- **Nano-composite of SU8 and Au**

The mixture of gold chloride and SU8 was exposed to laser at energy of 30 mW and a scanning speed of 10,000 µm/s. A SU8-Au hybrid pattern is shown in Figure 3. The grey lines were made of SU8, and the white dots were Au nanoparticle aggregations, with the sizes ranging from dozens of nanometers up to 1 micrometer. The mechanism of simultaneous Au salt reduction and SU8 ionic polymerization has been discussed before (Shukla, Furlani et al. 2010; Shukla, Vidal et al. 2011). Compared to the patterns produced by Prasad et al (Shukla, Furlani et al. 2010; Shukla, Vidal et al. 2011), the aggregation of Au nanoparticles at some positions is more predominant for our case. This phenomenon could be associated with the different photoinitiators used. Our SU8 sourced from Gersteltec contains no antimony and we have not added any extra initiators for the current study, while the SU8 used by Prasad et al which was sourced from Microchem includes antimony ($Ar_2I^+SbF_6^-$). As the exact initiators in our SU8 are not clear, it is difficult to identify how they affected the aggregation of *in-situ* generated nanoparticles.

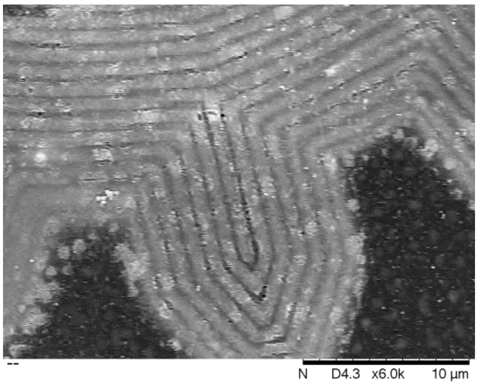
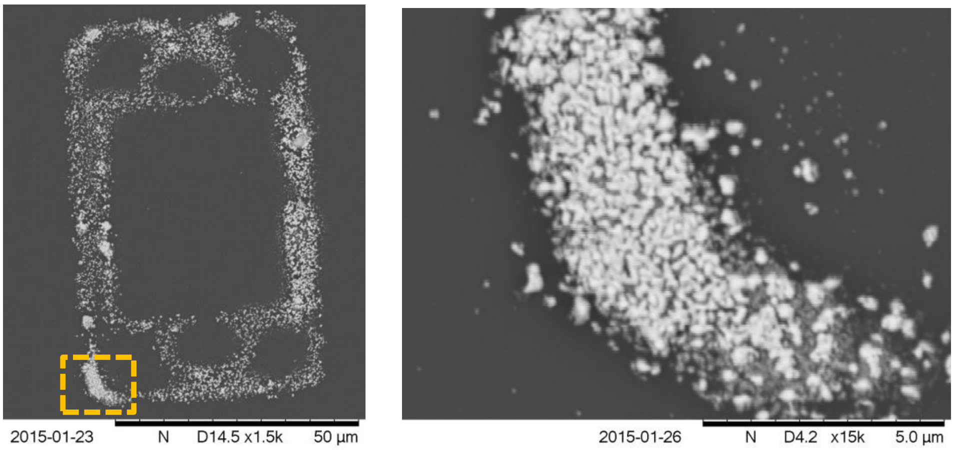


Figure 3: SEM image of SU8-Au nano-composite. The grey lines were made of SU8, and the white dots embedded in the grey lines were Au nanoparticle aggregations.

- **Nano-composite of IPL and Au**

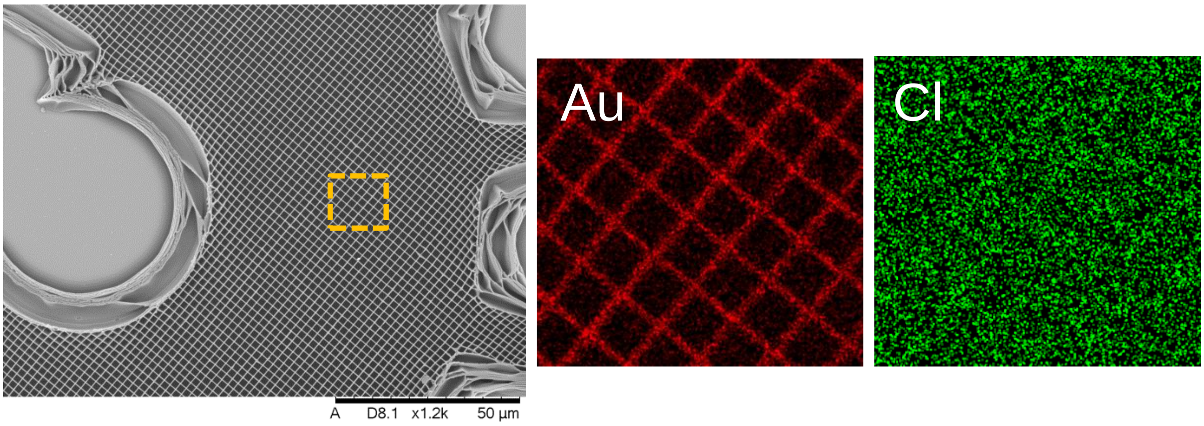
The following study was firstly carried out by testing the sample containing IPL and gold chloride without adding extra initiators. Although commercial IPL is designed for two-photon processing, no polymerisation was observed for the sample containing the mixture. As shown in Figure 4, only Au nanoparticle aggregation is observed. This is because two-photon induced metal ion reduction consumes free radicals generated by initiators. However free radicals are also needed for two-photon induced polymerisation. In the case of lacking sufficient free radicals, part of reactions is suppressed. In current situation, gold ions reduction consumed all the free radicals in the mixture, thus prevented monomers from cross-linking.



(a) (b)

Figure 4: (a) SEM image showing the fabricated pattern using the mixture of IPL with gold chloride without extra initiators; (b) Magnified SEM image showing the section marked in figure (a).

Extra photoinitiator was added to the mixture of IPL and gold chloride, to provide extra free radicals, thus to promote the two reactions – polymerisation and reduction – to happen at the same time. The initiator was chosen due to its high two-photon absorption cross-section at the wavelength of 780 nm - the wavelength of the laser used in this study (Makarov, Drobizhev et al. 2008). Figure 5(a) shows a 10-µm-high micro structure formed by adding a small amount of initiator to the mixture of IPL and gold chloride. The surface morphology of the fabricated micro structure looks no different from the structure formed by using pure IPL, i.e., containing no metallic part. However, EDX analysis shows that Au nanoparticles are well embedded in the IPL matrix. As shown in Figure 5(b), the distribution of Au element corresponds well with the 3D micro structure. However, the distribution of Cl is almost uniform throughout the whole substrate (see Figure 5(c)). EDX analysis proves that gold chloride has been successfully reduced into gold.



(a) (b) (c)

Figure 5: (a) SEM image of IPL-Au nano-composite fabricated using rhodamine B as an extra photoinitator. The pattern is about 10 µm high, with 25 layers. (b) & (C) EDX mapping analysis showing Au and Cl distribution in the area marked in figure (a), which proved that gold chloride has been successfully reduced into gold.

Comparing the two samples shown in Figure 3 and 5, it is obvious that Au nanoparticles distributed more uniformly in the matrix of IPL than that in the matrix of SU8.

The aggregation of Au nanoparticles in SU8 matrix is also observed in the work published by Prasad et al (Shukla, Vidal et al. 2011). Such great difference in surface morphology can be associated with the different polymerisation mechanism. Ionic-based polymerisation (for the case of SU8) tends to generate more heat than radical-based polymerisation (for the case of IPL). The local heat can accelerate the surface diffusion of Au nanoparticles, thus promote aggregation. To fabricate nano-composite with high resolution, radical-based polymerisation is preferred.

4. Conclusions

Two kinds of polymer-metal nano-composites – SU8-Au and IPL-Au – have been fabricated in a single step by two-photon induced polymerisation and metal salt reduction. Extra photoinitiator is needed for the generating the composite of IPL-Au, to provide extra free radicals to sustain the two reactions processing at the same time. The distribution of generated Au nanoparticles in IPL matrix is more uniform than that in SU8 matrix. This phenomenon can be associated with the difference in the local heat generated by radial-based polymerisation (for the case of IPL) and ionic-based polymerisation (for the case of SU8).

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