Direct Laser Writing of Microstructures on Gold Nanoparticle/PMMA Composites

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ABSTRACT

By using the efficient photon-thermal energy conversion property of gold nanoparticles, a direct laser writing method was developed to fabricate microstructures including microtunnels, and holes on gold nanoparticle/polymer composite thin films. The complete decomposition of the polymer led to the formation of the microholes, while the microtunnels were formed as a result of a subsurface layer explosion of decomposed small molecules that occurred in the nanocomposite film.

Keywords: nanocomposite, photo-thermal conversion, gold nanoparticles, microfabarication, direct laser writing

1 INSTRUCTION

Direct laser writing on organic solids is based on laser ablation of organic materials and can be used for various applications, such as MEMS [1] and microfluidic fabrication [2], etc. However, the precision of micropattern fabrication and the efficiency of laser consumption are still subject to improvement. The extraordinary light absorption and thermal conversion ability of noble metal nanoparticles make them perfectly suitable for this application. It has been demonstrated that the gold nanoparticles can be heated up to melting temperature by a pulsed laser source [3] and the photon capture cross-sections of gold nanoparticles is about 4 to 5 orders of magnitude larger than regular dye molecules [4]. In this study, the possibility of using gold nanoparticles to enhance the absorption of the polymer matrix and microstructure fabrication on a polymer/gold nanoparticle composite was investigated.

2 EXPERIMENTS

2.1 Film Preparation

30wt% of poly(methyl methacrylate) (PMMA) solution was prepared by dissolving PMMA powder (Aldrich, average molecular weight of 120000 g/mol) in tetrahydrofuran (THF). Oleylamine-protected gold nanoparticles were synthesized according to a reported procedure [5]. The nanoparticles were dissolved in THF at appropriate concentrations. Then the gold nanoparticle solution was added into PMMA solution and the mixture was sonicated for 5 min to obtain a good dispersion. The gold nanoparticle/PMMA solution was cast by a drawdown bar (Paul N. Gardner Company, Inc) at 50 mils. Films with an approximate thickness of 250 μm were obtained after drying at least overnight in ambient conditions.

2.2 Transmission Electron Microscopy

Gold nanoparticles solution in THF was dropped onto a meshed copper grid and dried by a gentle nitrogen flow. The prepared grid was then investigated by a FEI Tecnai F30 Transmission Electron Microscopy (TEM).

A cross section of a gold nanoparticle/PMMA nanocomposite film (1.5wt% loading of gold nanoparticles) was prepared using an FEI 200 TEM Focused Ion Beam instrument with a “lift-out” technique refined by Giannuzzi et al [6].

2.3 UV-Vis Spectroscopy Analysis

The UV-Vis absorption spectrum of gold nanoparticles in THF was collected by a Cary 300 UV-VIS spectrophotometer. An accessory for thin film samples was used to collect the spectra of dried composite films.

2.4 Thermal Gravimetric Analysis

A gold nanoparticle/PMMA composite film was cut into small pieces. A piece that weighs about 10mg was analyzed by TGA Q2050 (TA instrument) with an increment of 20℃/min.

2.5 Laser Irradiation

A continuous wave Nd:YAG laser with a beam size of 0.3 mm (Crystalaser LC) was used to irradiate the films to create different features. The output power of the laser can be continuously adjusted from 8.5 mw to 100 mw. The micro-holes were formed by directly irradiating the film surface for a certain time without moving the film. The microtunnels were created by moving the film linearly under irradiation of laser with a power of 30 or 50 mw. The linear movement of the film was controlled by a syringe pump (Kd Scientific) with a speed of 300 um/min.

2.6 Scanning Electron Microscopy

The specimens were observed by a JEOL 6400 SEM at an accelerating voltage of 5 kV. The specimens were coated with a Pd film by an Emitech Magnetron Sputter Coater before imaging in order to avoid electric charge build-up.

3 RESULTS AND DISCUSSION

3.1 Gold Nanoparticle Dispersion

Gold nanoparticles with oleylamine protective ligands were used to prepare the polymer nanocomposite. As shown in Figure 1, oleylamine protected nanoparticles are relatively uniform in size, and the average diameter is around 8 nanometers.

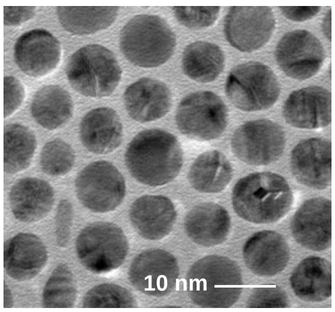

Figure 1. TEM image of oleylamine protected gold nanoparticles (Reprinted from ref. 7, copyright 2006, with permission from Wiley-VCH verlag GmbH & Co. KGaA)

It is well known that a good dispersion of nanoparticles in polymer matrix is difficult due to their high tendency to form aggregates. In our study, well dispersed gold nanoparticles in PMMA matrix was observed as shown in the TEM image (Figure 2) of a cross section of dry gold nanoparticle/PMMA composite film.

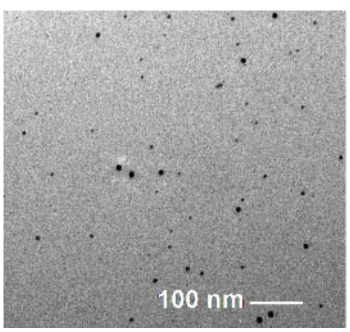

Figure 2. TEM images of the cross section areas of a nanocomposite film with 1.5wt% of gold nanoparticles. (Reprinted from ref. 7, copyright 2006, with permission from Wiley-VCH verlag GmbH & Co. KGaA)

In addition, UV-Vis results (Figure 3) show that the dried composite film exhibited a strong absorption band at 532 nm, arising from the surface plasmon resonance (SPR) of gold nanoparticles. This SPR band wavelength is the same as that observed from nanoparticles dispersed in solution, suggesting that the nanoparticles are not aggregated in the composite film. The results from TEM and UV-Vis analysis demonstrated that a good dispersion of gold nanoparticles in a polymer matrix can be achieved by appropriate selection of protective ligands of gold nanoparticle and processing conditions.

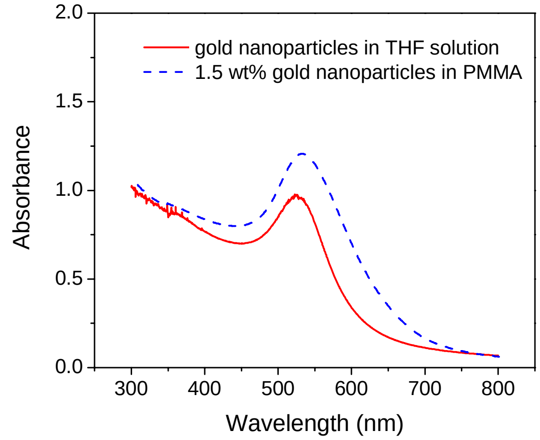

Figure 3. UV-Vis spectrum of gold nanoparticles in THF solution (solid line) and in PMMA (dashed line)

3.2 Thermal Decomposition

The thermal decomposition condition of the nanocomposite films was studied by thermal gravimetric analysis. The derivative thermogravimetry results were obtained by taking the derivative of weight loss with respective to degree of temperature. The curve shape (solid line in Figure 4) of a pure PMMA film is similar to the one reported in the literature for the PMMA prepared from a free radical polymerization [8]. It has three distinct weight loss stages, around 200, 290 and 390℃, corresponding to the scissions of irregular head to head linkage, the scissions of chain end vinyl groups and the random carbon-carbon scissions, respectively. Among the three stages, the random carbon-carbon scissions cause the largest weight loss. About 60% of composite was decomposed at this stage (390℃). The intermediate products mainly decompose to generate monomers.

The decomposition curve of gold nanoparticle/PMMA composites has the similar profiles as the pure PMMA film. However, with the addition of 1.5 wt% of gold nanoparticles, the decomposition rate and weight loss was decreased less than 10% compared to pure PMMA in the second stage, while an increased weight loss was observed at higher temperature. The postponed decomposition in the second stage suggests a possible stabilization of polymer end chains by gold nanoparticles. The complete decomposition of pure PMMA or composites with gold nanoparticles occurred at almost the same temperature, around 450℃

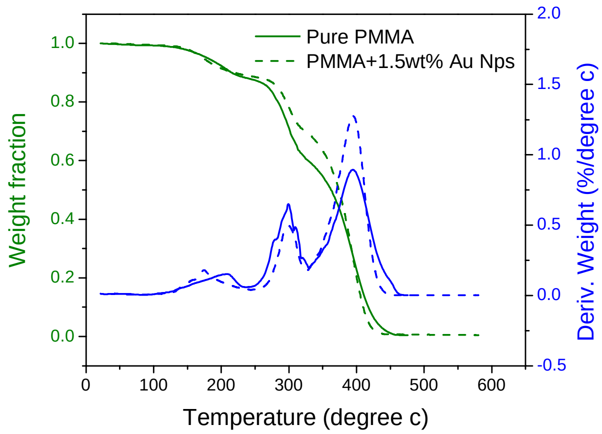

Figure 4. TGA results for pure PMMA and PMMA/gold nanoparticle composite films

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3.3 Microstructure Fabrication

A solid state continuous wave Nd:YAG laser with a beam size of 300 μm and wavelength of 532 nm was used to irradiate gold nanoparticle/PMMA films. As shown in the SEM image (Figure 5 a), without addition of gold nanoparticles, pure PMMA remain intact after 2 minute irradiation. With 0.5wt% of gold nanoparticles added to the polymer, a small deformation appeared on the surface (Figure 5b). By increasing the concentration of gold nanoparticles in the composite film, holes were observed due to the decomposition of PMMA (Figure 5c and d). The dimension of the hole is around 300 μm, approximately corresponding to the laser beam size. In fact, with 1.5w% of gold nanoparticles, it was observed that holes can be created within 2 seconds. As shown in TGA results, complete decomposition of PMMA happened above 390 ℃. Therefore, the formation of holes on the composite film demonstrates that sufficient heat can be converted by gold nanoparticles in the composite. The heat was built up around the nanoparticles, leading to decomposition of PMMA.

One-dimensional microtunnels on the film were further fabricated by controlling the movement of the nanocomposite film samples under laser irradiation, as shown in Figure 6 a-c. A more complicated microfeature was successfully created later by using motorized stages (Figure 6d).This microtunnel structure is different from the channel that used to be obtained from the existing laser direct writing process. From the images of the mechanically opened tunnels (Figure 6b and c), it can be observed that the surface of the composite film was expanded to form the upper wall of the channel. The reason for the microtunnel formation is that the heat inside the film is built up promptly and the polymer decomposes into small molecules, while the temperature of the composite surface is only raised to a small extent due to heat dissipation to the air. The heated surface is more flexible and tends to expand to release the pressure caused by formation of gas molecules inside the film.

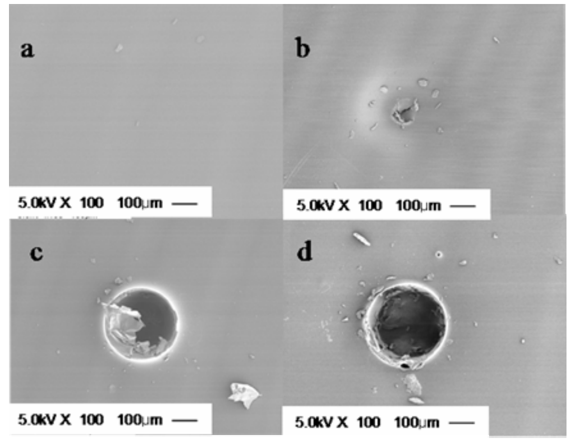

Figure 5. SEM images of holes created by laser irradiation (532 nm) for 2 min on pure PMMA (a) and nanoparticle/PMMA composite films (b-d). The weight ratio of gold nanoparticles in each composite film is: b. 0.5%; c. 1.0%; d. 1.5%, respectively. (Reprinted from ref. 7, copyright 2006, with permission from Wiley-VCH verlag GmbH & Co. KGaA)

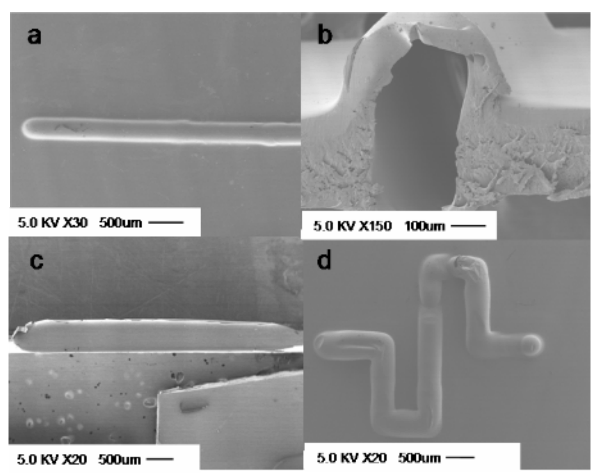

Figure 6. SEM images of microtunnels created by laser writing on a 1.5 wt % nanoparticle/polymer composite film. (a) is a top view of an intact microtunnel, (b) is a side view of a microtunnel, (c) is an image of the exposed inner surface of a microtunnel after the upper wall was removed mechanically, (d) is a image of a complex microtunnel.

4 CONCLUSION

PMMA/gold nanoparticle composite was obtained by disperse oleylamine protective gold nanoparticles into PMMA with a wet solution route. A strong absorption at 532 nm wavelength of the composite film was achieved due to the SPR absorption of gold nanoparticles. The photo-thermal conversion ability of gold nanoparticles allows heat to build up in the sorrounding area. As a result, microholes were created by complete decomposition of PMMA when the composite film was irradiated with a continuous wave laser. By controlling movement of the composite film, microtunnels were fabricated due to subsurface layer decomposition of PMMA.

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