Three-Dimensional Writing of Copper Nanoparticles in a Polymer Matrix with Two-Color Laser Beams

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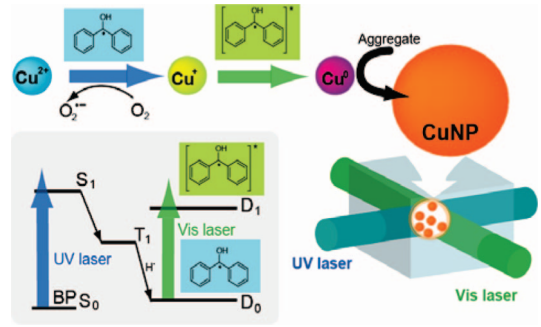
Metal nanoparticle (NP)/polymer composites have recently attracted much interest, covering the broad range of applications such as elecdtronic, optical, magnetic devices, and improved plastics, because the composition of NPs and polymers enhances the properties including conductivity, sustainability, and permeability with respect to neat materials.[1,2] The three-dimensional (3D) processing is a promissing sterategy to realize the super dense processing and optical devices which exhibit unique properties.[3–5] Thus, the direct 3D fabrication of NP arrays in the polymer matrices is the attracting technique due to its potential applications to dense 3D wiring for flexible microelectronics, photonic-crystal waveguides, and other photonic devices.[6,7]

The two-photon-induced microfabrication, in which the two-photon mentioned here is of the same wavelength and derived from the same femtosecond laser, has been applied for constructing 3D NP arrays in the polymer matrices.[7–9] The potential problem of the method is the high density of photon, which possibly causes some undesired damage to the matrix.[8] The multicolor laser processing (photoprocessing using the two or more lasers with different wavelengths) is the choice for the nondestructive 3D processing because the multicolor laser-induced reactive species such as excited radicals and molecules in the higher excited states can be selectively generated in the cross-point of the laser beams (Scheme 1). The photochemical reactions proceed through a stepwise two-photon absorption so that the reaction can be achieved by the low-density photon. This advantage enables the nondestructive fabrication of a 3D array of metal NP in soft materials, which is easily ablated by the irradiation of high-power and/or high-density photon. Another potential benefit is that the very strong reducing power of some reactive species makes it possible to fabricate the metal NP, which cannot be done by the conventional one-photon technique. However, there have been no report about successful fabrication of 3D NP array using the multicolor laser processing.

Scheme 1. Mechanism of the Multicolor Laser Processing is As Follows: UV Laser Excites BP to Generate BP in the Triplet Excited State (BP(T_1)); BP(T_1) Abstracts Hydrogen from the PVA To Form the Benzophenone Ketyl Radical (BPH$^\bullet$) and PVA Radical; BPH$^\bullet$ Excited by the Vis Laser To Form BPH$^\bullet$(D_1)



We have now succeeded the 3D writing of NP using the two-color two-laser for the first time. Previously, we tried to fabricate gold nanoparticles (AuNP) in a polyvinyl alcohol (PVA) film by employing the excited benzophenone ketyl radical (BPH$^\bullet$(D_1)) as the reducing agent, while the 3-D fabrication can not be achieved.[10] The enhancement of AuNP formation by the two-color, two-laser irradiation was small and not sufficient.

The developments in the present work were as follows. The problem in the previous study was the employment of a pulse laser. BPH$^\bullet$ has a strong absorption at around 350 nm, so the 355 nm laser with a high photon density excites the BPH$^\bullet$ within a laser pulse to generate the BPH$^\bullet$(D_1). To achieve the strict control of absorbed photon numbers, we employed continuous wave (CW) lasers here. The other problem was the reactivity of the gold ions. Thus, we selected to fabricate the 3D CuNP array in the present study. The reduction of Cu^{2+} to Cu^0 in the PVA film during the one-photon process is inefficient because the reduction potential of Cu^+ is highly negative (−2.94 V vs SCE)[11,12] and the Cu^+ is very easily oxidized by oxygen molecules back to Cu^{2+} in ambient air.[13]

Our strategy for the 3D writing of CuNP array is shown in Scheme 1. The PVA film containing BP and Cu^{2+} (film) were prepared. The PVA shows a good transmittance at the wavelength of the lasers and works as a hydrogen donor.

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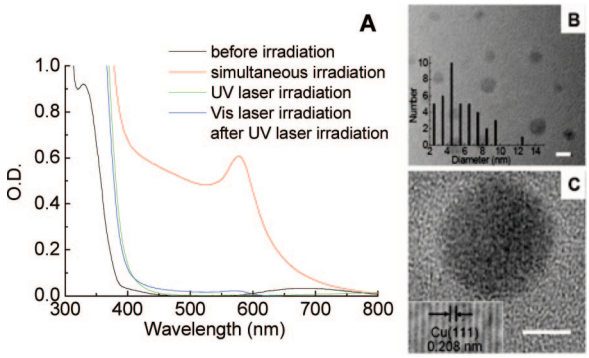

Figure 1. UV–vis−near-IR absorption spectra of the films before and after the lasers irradiation for 30 min (UV laser (363.8 nm, 3 mW) and Vis laser (514.5 nm, 50 mW)) (A). The TEM images of the film after the simultaneous irradiation for 30 min and the size distribution of CuNP (B). The HRTEM image of CuNPs (C). Inset shows the magnified image. The scale bar is 5 nm.

The UV laser (363.8 nm) and Vis laser (514.5 nm) were placed in order to form cross-point in the film. The UV laser excited the BP to generate the BP in the triplet excited state ($BP(T_1)$). $BP(T_1)$ abstracts hydrogen from PVA to form $BPH^{\bullet}$ and the PVA radical. In the cross-point, the simultaneously irradiating Vis laser excites $BPH^{\bullet}$ to generate $BPH^{\bullet}(D_1)$.[14–17] If only $BPH^{\bullet}(D_1)$ completes the reduction of Cu ions to the Cu atoms (Cu^0), the CuNP should be fabricated only at the cross-point of the two laser beams.

First, difference of CuNP-formation efficiency after UV laser irradiation and simultaneous irradiation of UV and Vis lasers (simultaneous irradiation) was investigated. The UV–vis absorption spectra of the film after the UV laser irradiation or simultaneous irradiation (UV laser (363.8 nm, 3 mW) and Vis laser (514.5 nm, 50 mW)) are shown in Figure 1A. The intensity of the surface plasmon resonance (SPR) band of CuNP was quite weak after the UV laser irradiation and the absorption of Cu^{2+} at around 690 nm decreased. On the contrary, after the simultaneous irradiation, the strong SPR band of CuNP was observed remarkably.[13,18] When the UV and Vis lasers were irradiated separately (i.e., Vis laser was irradiated after the UV laser irradiation), the intensity of the SPR band was still weak compared with that after the simultaneous irradiation. Additionally, no formation of CuNP was observed in the absence of BP. These facts indicate that the $BPH^{\bullet}(D_1)$ formed by the two-color, two-laser excitation plays an important role in the formation of CuNP. We attempted a 2D micropatterning. A clear and highly resolved 2D pattern was observed only after the simultaneous irradiation (see the Supporting Information).

The CuNPs were characterized using XRD (see the Supporting Informaiton) and TEM. The TEM images of the film after the simultaneous irradiation are shown in images B and C in Figure 1. The TEM images revealed that the randomly dispersed spherical CuNPs were formed by the simultaneous irradiation. The average diameter of the CuNP was about 5 nm. The crystal lattice fringes are spaced 0.208 nm apart, which agreed with the lattice spacing of the (111) plane of the Cu crystal. The CuNPs were not observed in the UV laser irradiated film.

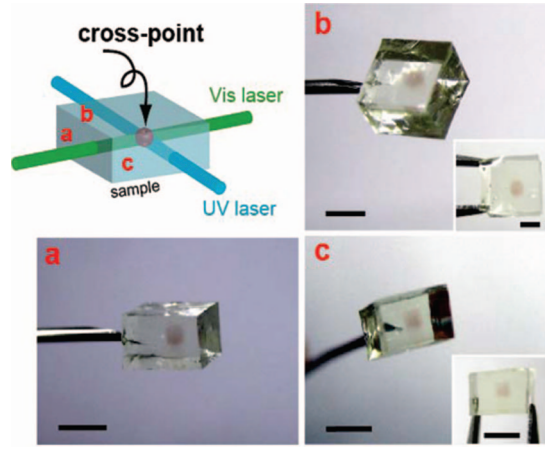

Figure 2. Photographs of the 3D CuNP array fabricated in the PVA film. Two lasers (UV laser (363.8 nm, 0.3−0.6 mW) and Vis laser (514.5 nm, 0.5 W)) were set perpendicular to each other to form the cross-point in the PVA film. The lasers were irradiating for 1 h. The letters in the cartoon of the film correspond to the direction of the photograph. The scale bar is 3 mm.

To confirm the formation mechanism of CuNP, the transient absorption spectra were measured using the laser flash photolysis (see the Supporting Informaiton for details). Although $BP(T_1)$ was inert to Cu^{2+}, the reduction of Cu^{2+} by $BPH^{\bullet}$ was inferred by the decrease of the $BPH^{\bullet}$ lifetime in the presence of Cu^{2+}. Since both $BPH^{\bullet}$ and the PVA radical have a sufficient reducing power (−0.25 and −0.61 V vs SCE, respectively)[19] for Cu^{2+} (−0.072 V vs SCE),[18] Cu^{2+} was reduced by these radicals to form Cu^{+}. The Cu^{+} would not be reduced during these one-photon induced processes (vide supra).[20]

In the previous studies, we investigated the reducing power of $BPH^{\bullet}(D_1)$ and found that $BPH^{\bullet}(D_1)$ can efficiently reduce organic compounds with a highly negative reduction potential, such as 4-methoxybenzonitrile (−2.71 V vs SCE).[15] Although it is difficult to compare the experimental results in solution with the present system, the result would qualitatively support our hypothesis.

The generated Cu^0 are aggregated to form nuclei (i.e., small Cu clusters). It is known that the reduction potential of the metal ions dramatically increased by the adsorption on nuclei.[12,22,23] Although ketyl radical and PVA radical cannot reduce Cu^{+}, they would reduce Cu^{+} adsorbed on the nuclei. Additionally, once the CuNPs were formed, the film

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shows an absorption at the Vis-laser wavelength. The thermal effect induced by the Vis-laser irradiation may accelerate the formation of CuNP. Although the reduction efficiency of Cu^+ by short-lived $BPH^{\bullet}(D_1)$ is low, those processes would accelerate the formation of CuNP.

Finally, we tried to fabricate the 3D array of CuNP in the film. Two laser (UV laser (363.8 nm, 0.3−0.6 mW) and Vis laser (514.5 nm, 0.5 W)) were set perpendicular to each other to form the cross-point in the PVA film. To suppress the formation of $BPH^{\bullet}(D_1)$ by the UV laser, the power was set to low. On the contrary, the Vis laser power was set quite high in order to efficiently excite the $BPH^{\bullet}$ and produce $BPH^{\bullet}(D_1)$. After a 1-h irradiation of the two lasers, a color-change due to the formation of CuNP was observed only at the cross-point of the laser beams (Figure 2 and movie shown in Supporting Informaiton). No ablation was visually observed on the surface of the PVA film.

In conclusion, the breakthrough in the present work are as follows. First, the fabrication of 3D NP array in the polymer matrices using the two-color, two-laser was succeeded for the first time. Second, it was demonstrated that very strong reducing power of $BPH^{\bullet}(D_1)$ makes it possible to fabricate the CuNP in the PVA film, which cannot be done by the one-photon technique. Our method could be applicated to several chemical or physical processes including lithographic fabrication and laser witing techniques. The 3D microfabrication is not demonstrated here due to the limitation of instrument. The 3D microfabrication is now underway.

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Supporting Information Available: Experimental section, characterization of CuNP, transient absorption measurements (PDF); movie (AVI). This material is available free of charge via the Internet at http://pubs.acs.org.

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