Polarization-dependent Memory of Light via Ultrashort Pulse Laser Irradiation

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Abstract — The remarkable phenomena in ultrafast light-matter interactions manifested as an evolution of one-dimensional metal nanoparticles in liquid ablation are observed. The polycrystalline copper nanowires with a length of 1.0 µm and a diameter of 85 nm are successfully formed only under the linear-polarized laser irradiation. The growth mechanism of copper nanowires under the femtosecond laser irradiation was suggested to be a nucleation growth process. The formation mechanism of copper nanowires can be interpreted in terms of a created pattern via coupling between photon and surface plasmon waves; consequently a material could memorize the direction of the light polarization.

1. INTRODUCTION

The size and shape of nanoscale materials provide important control over many of the physics and chemical properties, including electric and thermal conductivity, luminescence, and catalytic activity [1]. In particular, there is intense interest in synthesis and morphology control of nanosized metal and semiconductor particles, which exhibit surprises and novel phenomena based on the unique properties called the quantum size effect [2]. In the last decade, composite materials containing copper nanoparticles found various applications in different fields of science and technology [3–6]. However, various “bottom-up” approaches for making anisotropic-shaped colloidal nanoparticles have been found, with most of these solution methods being based on a thermal process. On the other hand, “top-down” approaches have been developed for producing metal and semiconductor nanowires, nanobelts, and nanoprisms [7–9]. We recently reported the periodic nanostructures composed of oxygen depleted regions of 20 nm size with periods as small as 140 nm inside silica glass, are aligned perpendicular to the laser polarization [10]. The phenomenon could be interpreted in terms of interference between the incident laser light field and the generated bulk electron plasma waves, resulting in the periodic modulation of electron plasma concentration and the structural changes in transparent material. More recently, we have applied this nonlinear interaction between the photons and the plasmons in the nanoscale to preparation of one-dimensional copper nanoparticles from micro-flakes by using femtosecond laser pulses radiation in an ethanol solution at room temperature [11]. A photo-initiated process via femtosecond pulse-induced nucleation in alcohol suspension of copper flakes, followed by thermal treatments for growth into copper nanowires, was investigated. Polycrystalline copper nanowires with a length of 1.0 µm and a diameter of 85 nm were successfully formed under linearly polarized laser irradiation, compared to nanospheres under circularly polarized laser beam. Single crystalline copper nanospheres with a diameter of 10 nm have been kept the metallic state after long time laser irradiation and subsequent thermal treatment due to covering of the amorphous carbon layer which was formed by the photodissociation of the surrounding solvent. The structure and morphology of copper nanoparticles depended on surrounding solvent, which allowed us to investigate their structure and morphology evolution in various solutions. The polarization-dependent growth mechanism of copper nanowires was also proposed.

2. ONE-DIMENSIONAL COPPER NANOPARTICLES GROWTH

We used copper flakes produced by the chemical reduction method, which are 5 µm in size and 100 nm thick. A small amount of the copper flakes 0.36 mg, was mixed with 4.5 mL of alcohol (methanol, ethanol, and propanol) filled in a rectangular quartz vessel of 1 × 1 × 5 cm\textsuperscript{3}. The
laser radiation in Gaussian mode produced by a regenerative amplified mode-locked Ti:sapphire laser (Cyber Laser Inc., 230fs pulse width, 1kHz repetition rate) operating at a wavelength of 780 nm was focused via a 20× (numerical aperture = 0.40) microscope objective into the alcohol-suspended copper flakes placed on a magnetic stirrer. The polarization of the laser light was set linear or circular by a half-wave or a quarter-wave plate placed on the incident beam before the focusing optics. To keep as many copper flakes as possible suspended in a solution, we continuously stirred the suspension. The beam was focused in the suspension with a beam waist diameter and laser energy fluence estimated at ∼4 µm and $2.4 \times 10^3$ J/cm², respectively. After laser irradiation, the suspensions were left at rest in a temperature-controlled bath having a constant temperature of 40 or 60°C.

Figure 1: SEM images indicating the morphology changes of initial copper flakes (a) after linearly (b) and circularly (c) polarized femtosecond laser irradiation for 5 minutes, followed by and subsequent aging treatment at room temperature for 5 days.

Figure 2: SEM images of the copper nanoparticles after linearly polarized femtosecond laser irradiation for 5 minutes and subsequent aging treatment at 40°C (a)∼(c) and 60°C (d)∼(f). Aging time is 12 hours (a), (d), 24 hours (b), (e), and 120 hours (c), (f), respectively.

Figure 3: SEM images of copper nanoparticles after femtosecond laser irradiation for 3 minutes (a)∼(c) and 20 minutes (d)∼(f) and subsequent aging treatment for 5 days in ethanol (a), (d), methanol (b), (e), and propanol (c), (f), respectively.

Figure 1 indicates the typical SEM images of the morphology changes of initial copper flakes [Fig. 1(a)] after linearly and circularly polarized femtosecond laser irradiation for 5 minutes and subsequent aging treatment at room temperature for 5 days. In each polarization case, the copper nanospheres and unreacted starting copper-flakes are observed just after laser irradiation, while copper nanowires can be observed after linearly polarized laser irradiation and subsequent aging treatment [Fig. 1(b)]. On the other hand, in the case of circularly polarized laser irradiation, aggregates of copper nanospheres and unreacted starting materials can be observed, namely there is no apparent formation of copper nanowires [Fig. 1(c)]. These results evidently indicate that the formation of the copper nanowires was dependent on the incident light polarization, even though the ablated copper nanospheres just after the laser irradiation were still standing at room temperature for 5 days. We have also confirmed that the one-dimensional growth of copper nanoparticles occurs during the subsequent aging process. Fig. 2 shows SEM images of the copper nanostructures after 5 minutes of the linearly polarized laser irradiation and subsequent aging treatment at 40 and 60°C for several hours. These SEM observations reveal the diameter growth rate of copper nanowires...
increases in the aging temperature [Figs. 2(c), (f)]. In the early stage during aging process at 40°C, nanoscale web-like aggregates of nanoparticles can be observed [Fig. 2(a)]. This phenomenon is similar to the formation of unusual aggregated structures composed of both crystalline and amorphous silicon nanoparticles by the femtosecond laser ablation in the presence of a background gas [12]. These nanoscale web-like aggregates are expected to be evolved into copper nanowires [Figs. 2(a)∼(c)]. Indeed, the inner part of the copper nanowires was composed of polycrystalline metallic cooper [Figs. 4(d)∼(f)]. Detailed SEM observations indicated the diameter of copper nanowires was variable as a function of the aging time. After the subsequent aging treatment for 120 hours, the diameters of copper nanowires were eventually about 68 and 185 nm, and the lengths were about 7.5 and 3.5 μm at the aging temperature of 40 and 60°C, respectively. This indicates that an aspect ratio of the copper nanowires can be controlled by the change of the subsequent aging conditions.

3. SOLVENT EFFECT ON THE COPPER NANOPARTICLES FORMATION

The effect on the formation of copper nanoparticles by the surrounding solvent was also investigated. Although the nanoparticles prepared by 3 minutes of the laser irradiation in an ethanol were almost wire-like, the fraction of nanospheres increased in the laser irradiation time [Figs. 3(a), (d)]. In contrast, the nanoparticles prepared by the same conditions of the laser irradiation in a methanol were observed in the cubic nanostructures [Fig. 3(b)], while the nanorods were formed in the case of the long time laser irradiation (20 minutes) [Fig. 3(e)]. Besides, in the case of long time laser irradiation in ethanol and methanol, the nanospheres still exist after subsequent aging treatment for 5 days [Figs. 3(d), (e)]. However, the one-dimensional growth of the nanoparticles after laser irradiation and subsequent aging treatment occurred in both cases of ethanol and methanol; no morphology change was observed in the case of a propanol [Figs. 3(c), (f)]. Detailed TEM observations of copper nanowires and nanospheres indicate that the nanowires' surface are composed of polycrystalline Cu$_2$O [Figs. 4(a)∼(c)]. Furthermore, the cross-sectional observations clearly demonstrate that nanowires are partially oxidized from the surface to the depth of about 5 nm [Fig. 4(e)]. On the other hand, the inner part of the nanowires was composed of polycrystalline metallic cooper [Figs. 4(d)∼(f)]. Indeed, the electron diffraction patterns of the inner and surface parts indicate that the observed areas were composed of metallic copper [Fig. 4(f)] and Cu$_2$O [Fig. 4(c)], respectively. We have also confirmed that the nanospheres after long time laser irradiation in an ethanol are composed of single crystal of metallic copper. Fig. 5 shows TEM observations of copper nanospheres after femtosecond laser irradiation for 20 minutes in an ethanol. Red and blue arrows in Fig. 5(a) show the analysis points of the electron energy-loss spectroscopy (EELS). The EELS spectra near C-K and Cu-L edge evidently indicate that the copper nanospheres are covered by carbon layer [Figs. 5(b), (c)]. Results of the existence of the many single crystal

![Figure 4: TEM observations of copper nanowires after femtosecond laser irradiation for 3 minutes. Schematic diagrams of the analysis methods are also shown on the left hand side. Two types of observations were carried out: conventional (a)∼(c) and cross-sectional (d)∼(f). The images are shown in two different scales: low magnification images (a), (d) and high magnification images (b), (e) for the same area. Arrows of P1 and P2 in Figures (b) and (e) show the analysis points of the electron diffraction pattern. The electron diffraction patterns of P1 and P2 are shown in (c) and (f), respectively.](image-url)
of metallic copper in the case of long time laser irradiation indicate that these amorphous carbon layer produced by the dissociation of solvent prevents not only the aggregation and growth of nanospheres but also the oxidation. Indeed, hydrogen gas was generated by the photo-dissociation of solvent and act as a reducing gas (Fig. 6). The hydrogen gas generation rate is proportional to the standard enthalpy change of formation of solution. In particular, methanol has a profound inhibitory effect of oxidation. On the other hand, the covering effect by the photo-dissociated amorphous carbon appears prominently in the case of propanol.

4. MECHANISMS OF COPPER NANOWIRE FORMATION

The growth mechanism for one-dimensional copper nanoparticle was considered to be nucleation growth process. We have identified two distinctive stages in copper nanowire formation by femtosecond laser irradiation and subsequent aging treatment: (1) generation of copper nanospheres by the laser ablation on the initial flake surface, (2) growth of copper nanowires due to the aggregation of the ablated copper nanospheres. During the first stages of the laser ablation, the generation of copper nanospheres is affected by the laser polarization because the initial flakes remain stationary with respect to the direction of laser polarization during laser pulse width of 230 femtoseconds. In addition, the hydrogen gas generated by the photo-dissociation of solution prevents the oxidation of nanospheres during femtosecond laser irradiation. The copper nanospheres were ablated from the surface of initial flakes via interference between incident light field and the electric field of the surface plasmon waves (SPWs). The SPWs could couple with the incident light wave only if it propagates in the plane of light polarization [11]. This coupling occurs on the flake surface over a narrow region with a depth of the order of the skin depth \( d_p \ll \lambda \) due to the surface roughness on the initial flakes. Previous investigations suggested that either preimposed or self-generated deformations on the solid surface strongly affect laser energy absorption [13]. Evidence for small deformations comes from the wide spreading of the reflected radiation observed in experiments [14].

Numerical simulations suggested that electron oscillations may grow for a step density profile much faster than the typical time scale of ion motion, leading to an oscillatory “rippling” of the critical surface \( n_e = n_c \) [15]. Such rippling is generated as a result of interference between the light field and the surface plasmon-polariton wave launched by initial random surface inhomogeneities. During the second stages, the copper nanospheres which may be the aggregation of the laser ablated copper atoms and/or clusters could act as a nucleus of the growth of nanowire in alcohol solution. Although a part of the aggregates are oxidized to Cu\(_2\)O, most are kept the metallic state due to covering of the amorphous carbon layer which was formed by the photo-dissociation of the surrounding solvent. Such layer prevents the aggregation and growth of the nanospheres.
amount of the photo-dissociation of solvent is increased with the laser irradiation time and the length of carbon chain. By the competition between the oxidation to Cu$_2$O and the aggregation of metallic copper nanospheres, copper nanoparticles grow one-dimensionally into nanowires which have core-shell structure. In fact, it is well known that in the case of Cu$_2$O crystals, the O$^{2-}$ ions in the (001) facet are more apt to hydrolyze, compared with those in the (111) facet, and the stacking along (001) directions therefore becomes energetically favorable [16]. A detailed mechanism of the copper nanowire formation is under investigation.

5. CONCLUSION

In conclusion we have demonstrated the morphology control of copper nanoparticles by femtosecond laser irradiation in an alcohol solution. The copper nanowires with a core-shell structure are formed depending on the surrounding solvent and laser irradiation time. An aspect ratio of the copper nanowires can be controlled by the change of the subsequent aging conditions. The formation mechanisms of copper nanowires are interpreted in terms of the competition between the oxidation to Cu$_2$O and the aggregation of metallic copper nanospheres. Another puzzling phenomenon is polarization-dependence of copper nanowires formation. Apart from the fundamental importance of the observed phenomenon as the first direct evidence of polarization-dependent memory of light, the observed copper nanowires could be useful for optical polarization control medium, electro-conductive nanomaterial, and probe for SPM.

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