

## Morphological control of nanoparticles by femtosecond laser irradiation

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We report on the fabrication and evolution of metal nanowires with a length of 5  $\mu\text{m}$  and a diameter of 100 nm which were successfully photo-converted from scale-like copper micro-flakes, dispersed in an alcohol solution, under ultrashort pulse laser irradiation and a subsequent aging treatment. The dependence of the observed copper nanowires on the conditions of the laser irradiation and aging treatment, and the influence of the surrounding solvent were also investigated. The photoinduced morphology changes are unusual and their optical properties are striking. These previously unknown metal nanowires have a very high aspect ratio, and are created by nuclear growth mechanisms.

**Key words:** Morphology control, Copper nanowires, Femtosecond laser.

### Introduction

The size and shape of nanoscale materials provide excellent control over many of the physical and chemical properties, including electrical and thermal conductivity, luminescence, and catalytic activity [1]. In particular, there is intense interest in the synthesis and morphological control of nanosized metal and semiconductor particles, which exhibit surprising and novel phenomena based on the unique property called the quantum size effect. In the last decade, composite materials containing copper nanoparticles found various applications in different fields of science and technology [2-5]. However various "bottom-up" approaches for preparing copper nanoparticles have been found: they have a disadvantage in terms of the purity of the final products because nanoparticles are unusually sensitive to impurities.

The laser ablation technique has been employed in nanoparticle synthesis because of its many advantages, such as the applicability to various target materials in an ambient atmosphere. Recently, various shape-controlled nanoparticles, such as nanowires [6], nanotubes [7], and composite nanostructures [8], have been fabricated by this technique. In particular, pulsed laser ablation in a liquid has become an increasingly popular approach for preparing nanoparticles from the viewpoint of the concise procedure and ease of handling [9, 10].

In a previous study, we have applied a laser ablation technique to the preparation of one-dimensional copper nanoparticles from micro-flakes using femtosecond laser pulse radiation in an ethanol solution at room temperature

[11]. It should be interesting to investigate the preparation and evolution of nanowires under intense ultrashort light fields, which might reveal the interaction between the photons and the excited surface plasmons on the nanoscale.

In this study, we report the morphological control of copper nanoparticles, dispersed in various alcohol solutions, under femtosecond laser irradiation. It was found that the structure and morphology of copper nanowires depended on the surrounding solvent, which allowed us to investigate their structure and morphological evolution in the solution. We have also confirmed that the formation of the copper nanowires was dependent on the incident light polarization. The phenomenon was interpreted in terms of the interaction between the electric field of the incident light wave and the induced surface plasmon wave. Other starting materials, e.g. copper microspheres and copper sheet, were also tested to fabricate nanowires under the same experimental conditions to verify the mechanism and procedure of nanowires' growth by another process. By observing the morphological transformation of nanowires after femtosecond laser irradiation and subsequent aging treatment, the growth mechanism of copper nanowires was investigated. Beyond the fundamental issues of basic science, applications are possible in the areas of optical polarization control, an electro-conductive nanomaterial, and a probe for Scanning Probe Microscope (SPM).

### Experimental

We used copper flakes produced by a chemical reduction method, which were 5  $\mu\text{m}$  in size and 100 nm thick. A small amount of the copper flakes, 0.36 mg, was mixed with 4.5 ml of 99.5% alcohol (methanol, ethanol, and propanol) in a rectangular quartz vessel of  $1 \times 1 \times 5 \text{ cm}^3$ . The laser radiation in Gaussian mode produced by a regenerative amplified mode-locked Ti:sapphire laser

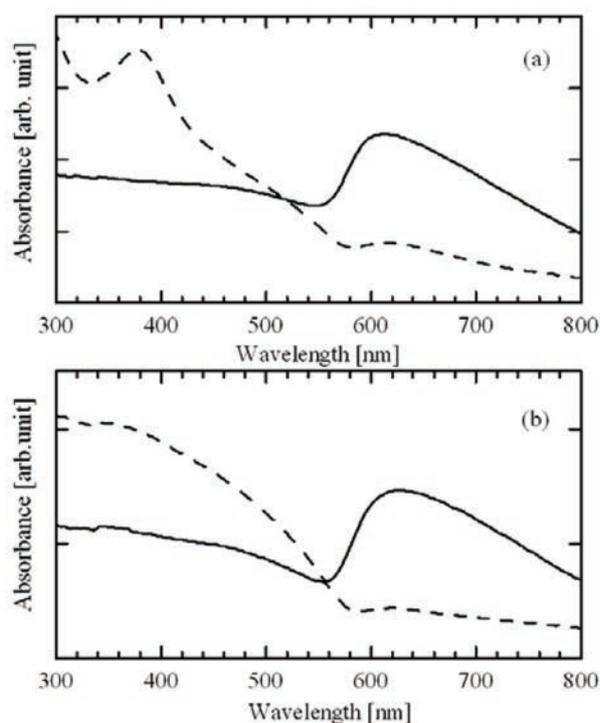
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(Cyber Laser Inc., 230 fs pulse duration, 1 kHz repetition rate) operating at a wavelength of 780 nm was focused via a  $20\times$  (numerical aperture = 0.40) microscope objective lens into the alcohol-suspended copper flakes placed on a magnetic stirrer. The polarization of the laser light was set linear or circular by a half-wave or a quarter-wave plate placed in the incident beam before the focusing optics. To keep as many copper flakes as possible suspended in the solution, we continuously stirred the solution. The beam was focused on the suspension with a beam waist diameter and laser energy fluence estimated at  $\sim 4\ \mu\text{m}$  and  $2.4 \times 10^3\ \text{J}/\text{cm}^2$ , respectively. After laser irradiation, the suspensions were left at rest in a temperature-controlled bath having a constant temperature of 40 or 60 °C. Absorption spectra of the sample suspensions were measured by a spectrophotometer (JASCO, V-570). After solvent evaporation at room temperature, the morphology of the copper particles after femtosecond laser irradiation and the subsequent aging treatment were observed by a field-emission scanning electron microscopy (FE-SEM, JEOL, JSM-6700F) and a transmission electron microscope (TEM, Hitachi, HF-2000).

## Results and Discussion

### One-dimensional copper nanoparticles growth

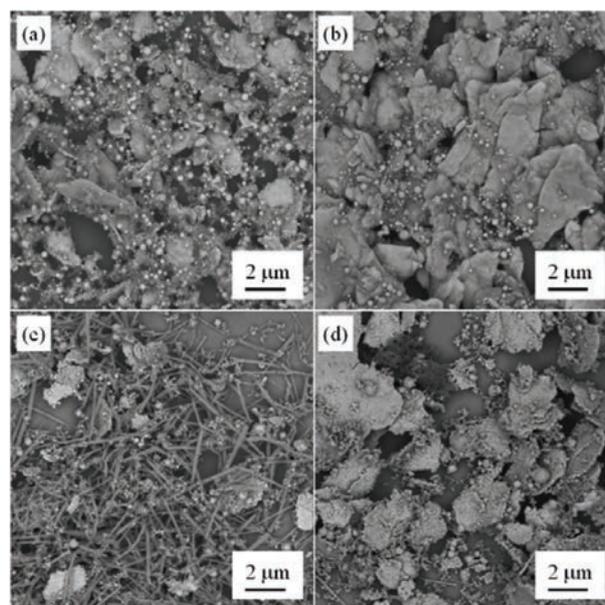
Figure 1 shows the absorption spectra of the copper flakes dispersed in ethanol just after linearly or circularly



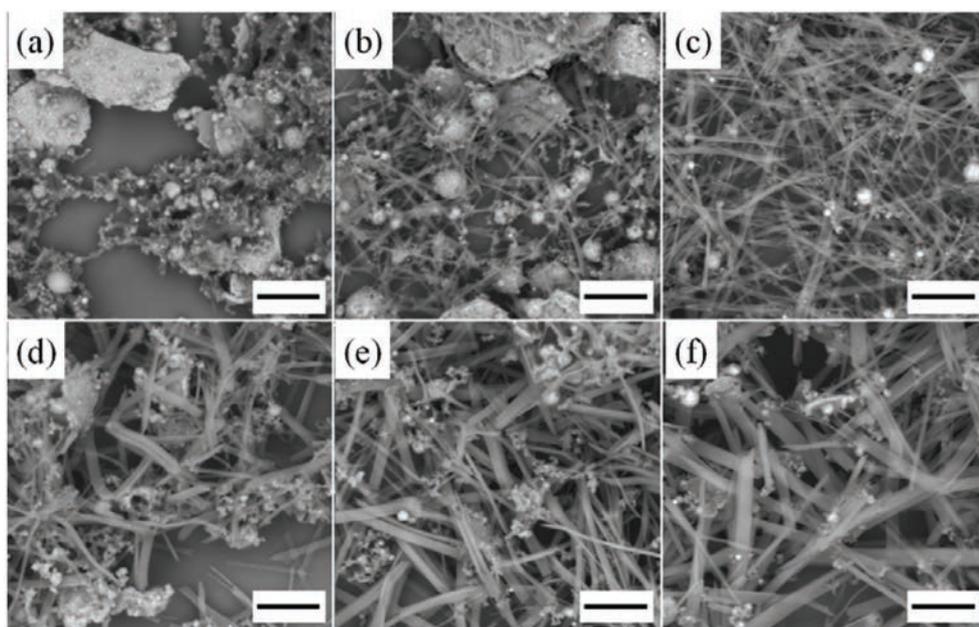
**Fig. 1.** Absorption spectra of the copper flakes dispersed in ethanol just after linearly (a) or circularly (b) polarized femtosecond laser irradiation for 5 minutes (solid line). The absorption spectra after subsequent aging treatment at room temperature for 5 days are also shown (broken line).

polarized femtosecond laser irradiation for 5 minutes. The absorption spectra after a subsequent aging treatment at room temperature for 5 days are also shown. In each polarization case, absorptions peaking at 600 nm due to the surface plasmon resonance of copper nanospheres are observed just after laser irradiation. Indeed, the surface plasmon absorption of 10 nm copper nanospheres is located at 560 nm, which can be predicted by Mie theory with no free electron density correction [12]. An apparent difference in absorption spectra was observed after a subsequent aging treatment for 5 days. In the case of the circularly polarization, the maximum absorption was shifted to the short wavelength region (Fig. 1(b)). This is attributed to the fact that the partial oxidation of copper nanospheres causes the blue shift [13]. On the other hand, a particular absorption peaking at 380 nm was observed after linearly polarized laser irradiation and subsequent aging treatment (Fig. 1(a)).

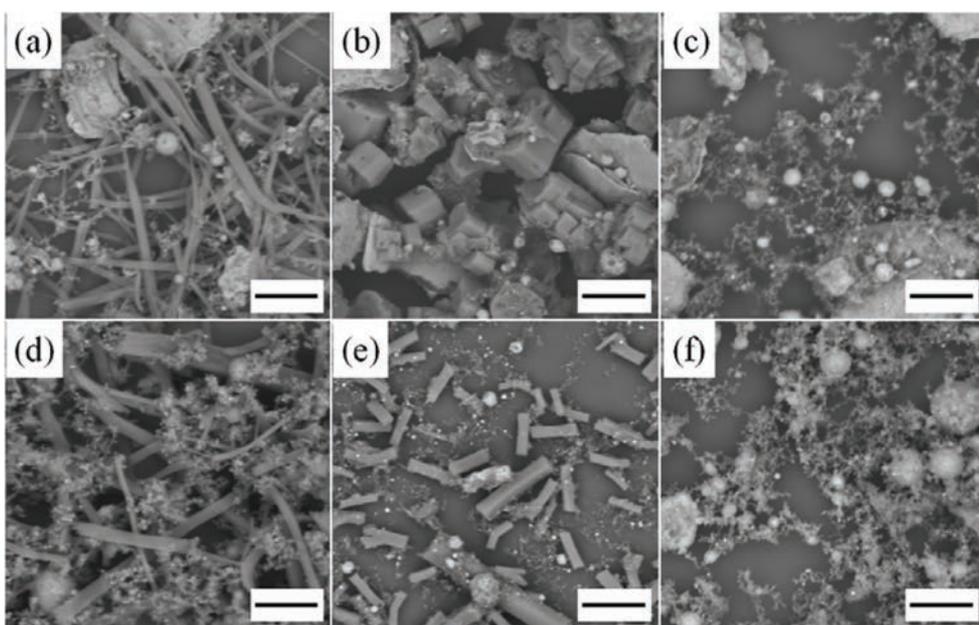
Figure 2 gives the SEM images of copper nanoparticles corresponding to the absorption spectra in Fig. 1. In each polarization case, the copper nanospheres and unreacted starting copper-flakes are observed just after laser irradiation (Fig. 2(a), (b)), while copper nanowires can be observed only after linearly polarized laser irradiation and a subsequent aging treatment (Fig. 2(c)). On the other hand, in the case of circularly polarized laser irradiation, there is no observation of copper nanowires just after laser irradiation and the subsequent aging treatment (Fig. 2(b), (d)). These results evidently indicate that the unknown absorption peaking at 380 nm may be due to the surface plasmon resonance of partially-



**Fig. 2.** SEM images of the copper nanoparticles corresponding to the absorption spectra in Fig. 1. (a) just after linearly polarized laser irradiation and (c) subsequent aging treatment at room temperature for 5 days, (b) just after circularly polarized laser irradiation and (d) subsequent aging treatment at room temperature for 5 days, respectively.



**Fig. 3.** 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 was 12 hours (a), (d), 24 hours (b), (e), and 120 hours (c), (f), respectively. The bar in each figure corresponds to 1 μm.

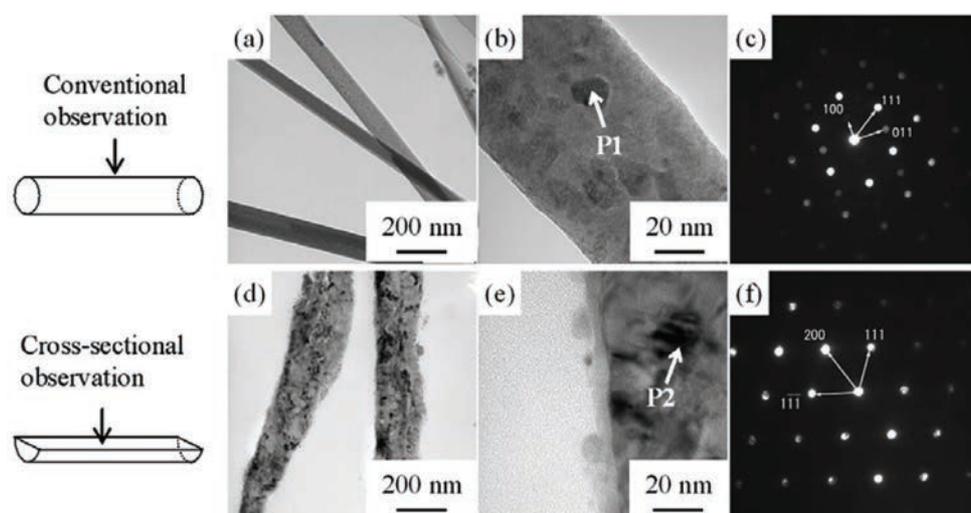


**Fig. 4.** SEM images of copper nanoparticles after femtosecond laser irradiation for 3 minutes (a)-(c) and 20 minutes (d)-(f) and a subsequent aging treatment for 5 days in ethanol (a), (d), methanol (b), (e), and propanol (c), (f), respectively. The bar in each figure corresponds to 1 μm.

oxidized copper nanowires (Fig. 1(a), Fig. 2(c)). Indeed, it is well-known that the surface plasmon resonance frequencies depend not only on the size but also the shape of particles [14]. Further investigations of the simulation based on Mie theory may be needed to understand the absorption spectra of core-shell type nanowire composed of metallic copper and copper oxide.

In addition, the copper nanospheres which may be the aggregation of the laser ablated copper atoms and/or clusters can grow one-dimensionally in ethanol at room

temperature only after linearly polarized laser irradiation. We have also confirmed that the one-dimensional growth of copper nanoparticles occurs during the subsequent aging process. Figure 3 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 with the aging temperature (Fig. 3). In the initial stage during aging process at 40 °C, namely one-



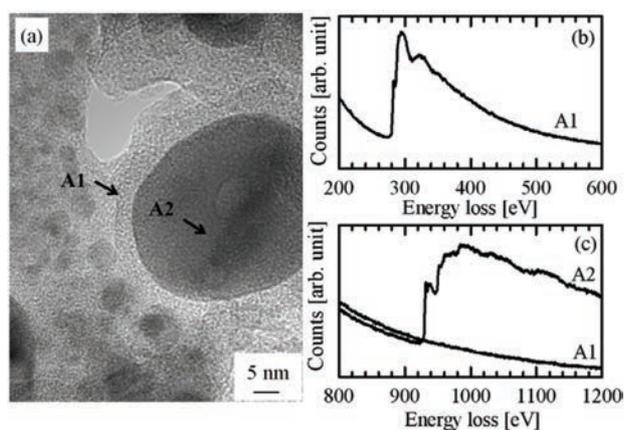
**Fig. 5.** TEM observations of copper nanowires after femtosecond laser irradiation for 3 minutes. Schematic diagrams of the analysis methods are also shown on the left hand side. Two types of observations were carried out: conventional (a)-(c) and cross-sectional (d)-(f). The images are shown at two different scales: low magnification images (a), (d) and high magnification images (b), (e) for the same area. Arrows P1 and P2 in figures (b) and (e) show the analysis points of the electron diffraction patterns. The electron diffraction patterns of P1 and P2 are shown in (c) and (f), respectively.

dimensional growth of copper nanoparticles, nanoscale web-like aggregates of nanoparticles were formed (Fig. 3(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 [15]. These nanoscale web-like aggregates are expected to be evolved into copper nanowires (Fig. 3(a)-(c)). Indeed, the inner part of the copper nanowires was composed of polycrystalline metallic copper (Fig. 5(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  $\mu\text{m}$  at the aging temperatures of 40 and 60  $^{\circ}\text{C}$ , respectively. This indicates that the aspect ratio of the copper nanowires can be controlled by the change of the subsequent aging conditions.

#### 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 laser irradiation in ethanol were almost wire-like, the fraction of nanospheres increased with the laser irradiation time (Fig. 4(a), 4(d)). In contrast, the nanoparticles prepared by the same conditions of laser irradiation in methanol were observed to be cubic nanostructures (Fig. 4(b)), while nanorods were formed in the case of the long time laser irradiation (20 minutes) (Fig. 4(e)). Besides, in the case of long time laser irradiation in ethanol and methanol, many nanospheres still exist after a subsequent aging treatment for 5 days (Fig. 4(d), (e)). However, the one-dimensional growth of the nanoparticles after laser irradiation and a subsequent

aging treatment occurred in both the cases of ethanol and methanol but no morphological change was observed in the case of using propanol (Fig. 4(c), (f)). A detailed TEM analysis of copper nanowires and nanospheres prepared in ethanol has been performed. Figure 5 shows TEM observations of copper nanowires after femtosecond laser irradiation for 3 minutes. Schematic diagrams of the analysis methods are also shown. The conventional observations indicate that the nanowires' surfaces are composed of polycrystalline  $\text{Cu}_2\text{O}$  (Fig. 5(a)-(c)). Furthermore, the cross-sectional observations clearly demonstrate that nanowires are partially oxidized from the surface to a depth of about 5 nm (Fig. 5(e)). On the other hand, the inner part of the nanowires was composed of polycrystalline metallic copper (Fig. 5(d)-(f)). Indeed, the electron diffraction patterns of the inner and surface parts indicate that the observed areas were composed of metallic copper (Fig. 5(c)) and  $\text{Cu}_2\text{O}$  (Fig. 5(f)), respectively. We have also confirmed that the nanospheres after long time laser irradiation in ethanol are composed of a single crystal of metallic copper. Figure 6 shows TEM observations of copper nanospheres after femtosecond laser irradiation for 20 minutes in ethanol. A1 and A2 arrows in Fig. 6(a) show the analysis points of the electron energy-loss spectroscopy (EELS). The EELS spectra near the C-K and Cu-L edges evidently indicate that the copper nanospheres are covered by a carbon layer (Fig. 6(b), (c)). Results of the existence of the many single crystals of metallic copper in the case of long time laser irradiation indicate that these amorphous carbon layers produced by the fragmentation of solvent prevents not only the aggregation and growth of nanospheres but also their oxidation. This solvent effect on the growth of the copper nanoparticles appears prominently in the case of propanol.



**Fig. 6.** (a) TEM observations of copper nanospheres after femtosecond laser irradiation for 20 minutes in an ethanol. Arrows A1 and A2 in image show the analysis points of the electron energy-loss spectroscopy. The electron energy-loss spectra near C-K (b) and Cu-L edge (c) corresponding to the A1 and A2 arrows are also shown.

### Mechanisms of copper nanowire formation

The growth mechanism for one-dimensional copper nanoparticles was considered to be nucleation growth as follows: when an intense femtosecond laser pulse impinges onto the copper target, the surface is ablated after the excitation of the surface plasmon-polariton wave. This ablation process corresponding to the nucleation is affected by the interaction between the electric field of the light wave and the electric field of the excited surface plasmon-polariton wave on the nanoscale. Indeed, nanowire formation could not be observed using a circularly polarized laser just after the laser irradiation [11]. These ablated nuclei composed of copper atoms and/or nanoclusters are aggregated and act as a source for nanoparticle growth. Although a part of the aggregates are oxidized to  $\text{Cu}_2\text{O}$ , most retain the metallic state due to covering by the amorphous carbon layer which was formed by the fragmentation of the surrounding solvent. Such a layer prevents the aggregation and growth of the nanospheres. The amount of this fragmentation of the solvent is increased with the laser irradiation time and the length of carbon chain. By the competition between the oxidation to  $\text{Cu}_2\text{O}$  and the aggregation of metallic copper nanospheres, copper nanoparticles grow one-dimensionally into nanowires which have a core-shell structure. In fact, it is well known that in the case of  $\text{Cu}_2\text{O}$  crystals, the  $\text{O}^{2-}$  ions in the (001) facet are more apt to hydrolyze, compared with those in the (111) facet, and stacking along (001) directions therefore becomes energetically favorable [16]. A detailed mechanism of the copper nanowire formation is under investigation.

### Conclusions

In conclusion we have demonstrated the morphological control of copper nanoparticles by femtosecond laser irradiation in an alcohol solution. Copper nanowires

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

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