Photoconversion of Copper Flakes to Nanowires with Ultrashort Pulse Laser Irradiation

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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] Colloidal chemists have obtained excellent controlled nanosized particles for several spherical metal and semiconductor compositions, which has led to the discovery of the quantum size effect in colloidal nanocrystals.[2] 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.[3−5] In particular, the laser-induced ablation method has become an increasingly popular approach for making nanoparticles from the viewpoint of the concise procedure and application of a variety of materials.[6−11] The ripple structures have been observed on the surface of the metal and semiconductor caused by the interferences between the scattering incident laser field and the surface plasmon-polariton waves (SPWs).[11,12] However, until now, there has been no observation of nanowire formation in a colloidal suspension by pulsed laser irradiation and the mechanism of its appearance has not been fully understood. We recently reported the first experimental evidence of the periodic nanostructures embedded in silica glass after irradiation by a single focused beam of a femtosecond Ti:sapphire laser.[13] The phenomenon is 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. Here, we report the first observation of the photoconversion from copper flakes to nanowires and nanospheres formation via ultrafast pulse laser irradiation. This phenomenon has provided two distinct surface plasmon resonances based on the characteristic shape. The observed copper nanowires of 50 nm diameter are fragmented from the initial flakes as a result of the interference between the light field and the SPWs. Beyond the fundamental issues of basic science, applications are possible in the areas of an optical polarization control, an electroconductive nanomaterial, and a catalytic metal.

We used commercially available 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, 4.8 mg, was mixed with 6 mL of 99% ethanol filled in a rectangular quartz vessel of $1 \times 1 \times 3.5$ cm^3. The laser radiation in Gaussian mode produced by a regenerative amplified mode-locked Ti:sapphire laser (Cyber Laser Inc., 215 fs pulse duration, 1 kHz repetition rate) operating at a wavelength of 780 nm was focused via a 10× (numerical aperture = 0.25) microscope objective into the ethanol-suspended copper flakes placed on a magnetic stirrer. The polarization of the laser light was set linear by a half-wave plate placed on the incident beam before the focusing optics. Before laser irradiation, the suspension was deaerated by bubbling nitrogen gas into it for 15 min. To keep as many copper flakes as possible suspended in ethanol, we continuously stirred the solution. The beam was focused in the suspension with a beam waist diameter and laser energy fluence estimated at ∼4 μm and 3.5×10^3 J/cm^2, respectively. After laser irradiation, absorption spectra of the suspension were measured by a spectrophotometer (JASCO, V-570). After ethanol evaporation at room temperature, the laser-dissociated copper particles were analyzed by a scanning electron microscope (JEOL, JSM-6700F) and a transmission electron microscope (Hitachi, HF-2000). All of the experiments were carried out at ambient temperature.

Figure 1A shows the sequence of absorption spectra of the suspension, taken as a function of laser irradiation time. Minor absorption was observed for the dilute suspension of copper flakes in the wavelength region from 330 to 800 nm before the femtosecond laser irradiation, whereas there were

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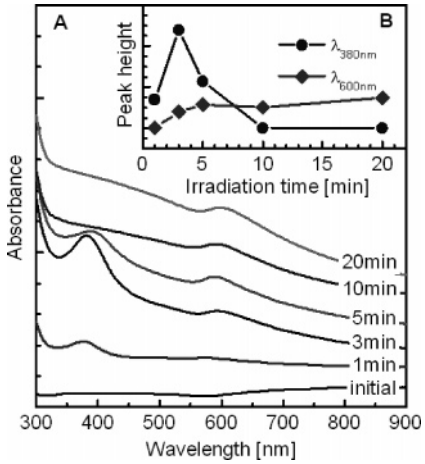

Figure 1. (A) Sequence absorption spectra taken as a function of laser irradiation time at a pulse energy fluence of 3.5×10^3 J/cm^2. Each curve is shifted with respect to the next longer irradiation time. (B) Peak height profiles of the corresponding absorption at $\lambda = 380$ and 600 nm as a function of laser irradiation time.

two apparent surface plasmon peaks in the absorbance ($\lambda_{abs} = 380$ and 600 nm) during laser irradiation.

The fluctuation of the surface plasmon peaks are considerably weaker as compared to the background interband transition that predominates the high-energy wing ($\lambda < 320$ nm) of the spectra.[7] We also observed an increase in the intensity of the surface plasmon absorption for the spherical particles at $\lambda_{abs} = 600$ nm with a concomitant growth of a new peak at $\lambda_{abs} = 380$ nm (Figure 1B). Indeed, the surface plasmon absorption of 10 nm spherical copper nanoparticles is located at 560 nm, which can be predicted by Mie theory with no free electron density correction.[14] After 10 min, the peak at 380 nm completely disappeared. In the case of long pulse laser irradiation, these unexplained peaks have not been observed.[7] Scanning electron images (SEIs), when correlated with the time-dependent absorption spectroscopic observations, show that the initial copper flakes (size ≈ 5 μm, thickness ≈ 0.1 μm) were converted to nanowires after the femtosecond laser irradiation between 1 and 5 min (Figure 2B−D). During initial stages of the nanowire formation, both flakes and wires can be seen (Figure 2B). The diameter of the nanowire increases with laser-irradiation time. The growth rate of the diameter of nanowires increases with the pulse repetition rate from 10.2 to 54.2 nm/min. After 10 min irradiation, nearly all of the nanowires are converted to nanospheres 10−70 nm in diameter (images E and F of Figure 2). Transition electron microscopy (TEM) observations indicated that the nanowires and nanospheres were polycrystalline and crystalline, respectively (Figure 3). In addition, the nanowire and nanosphere were composed of Cu_2O and metallic Cu, respectively, on the basis of the electron diffraction pattern. Namely, although a portion of nanowire surface was oxidized to Cu_2O, nanosphere was nearly single-crystal Cu metal.

These data clearly show that the copper nanospheres are dissociated from the initial flakes via nanowires formation. This photoconversion is also indicated in the absorption

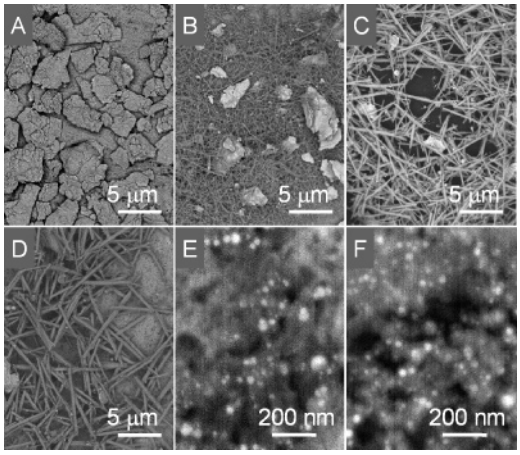

Figure 2. SEM images indicating the morphology changes (A) before irradiation and after (B) 1, (C) 3, (D) 5, (E) 10, and (F) 20 min of the femtosecond laser irradiation.

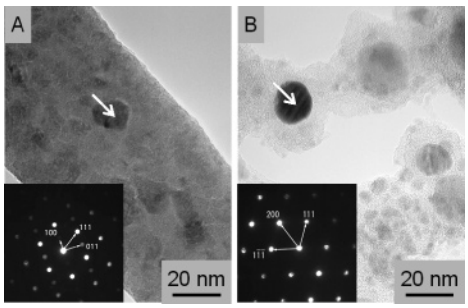

Figure 3. TEM observations of the nanowire and nanosphere after (A) 3 and (B) 10 min of the femtosecond laser irradiation. Inset shows the electron diffraction (ED) pattern at the arrowed point. The ED indicates that the observed area was composed of (A) Cu_2O and (B) metallic Cu, respectively.

spectral changes. Namely, the absorption peaking at $\lambda_{abs} = 380$ nm can be assigned to the transverse surface plasmon resonance of copper nanowires. It is well-known that the surface plasmon resonance frequencies depend not only on the size but also the shape of particles. In the case of the copper nanorods, the surface plasmon peak shifts to blue with an increasing aspect ratio of the particles,[15] which is about 60 after 1 min of femtosecond laser irradiation at 1 kHz repetition rate. We have identified three distinctive stages in copper flake fragmentation by femtosecond laser irradiation: (a) initial flake fragmentation, (b) growth of nanowire, and (c) nanosphere formation. The nanowires are generated by the initial flakes fragmentation via interference between light field and the electric field of the SPWs. Indeed, the nanowire formation could not be observed using a circularly polarized beam just after the laser irradiation. On the other hand, the grown nanowires could also be observed after 1 month (Figure 4). There are two different mechanisms of the nanowire formation: (1) fragmentation of initial flake and (2) nanoparticle growth in a certain direction. Further investigations are needed to understand the nanowire formation mechanism.

Detailed SEM observations revealed that the diameters of the copper nanowires were about 62, 159, and 270 nm for the number of light pulses of 6×10^4, 180×10^4, and 300×10^4, respectively, and for the pulse energy of 0.4 mJ,

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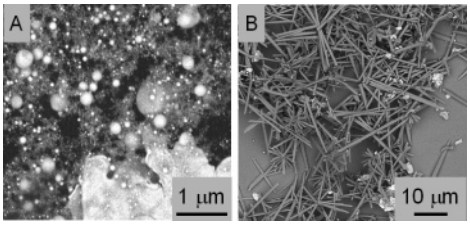

Figure 4. SEM images indicating the morphology changes (A) just after the circular polarized femtosecond laser pulses irradiation and (B) a month later.

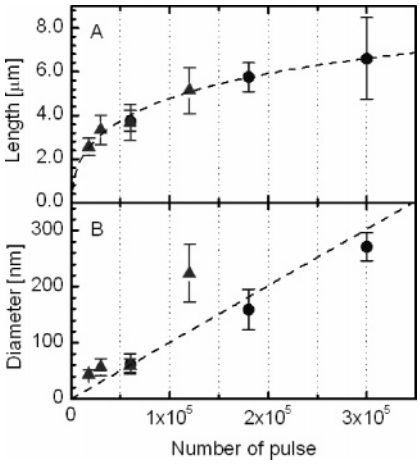

Figure 5. (A) Length and (B) diameter of the nanowire as a function of irradiated number of pulse with intensity of 1.6×10^{16} W/cm^2. Different symbols show the varying of the pulse repetition rate: 100 Hz (▲) and 1 kHz (●), respectively.

corresponding to intensity of 1.6×10^{16} W/cm^2. This indicated a linear dependence of the nanowire diameter on the number of light pulses (Figure 5B). During the nanowire growth stage, the lengths of nanowires slightly increased from 3 μm and eventually were saturated to 6 μm (Figure 5A). The extremely small copper clusters could be also generated by the fragmentation of a portion of nanowire and consumed in this nanowire growth. Finally, nanospheres of 10−70 nm were formed by the fragmentation of nanowires along with the termination in growth of the nanowires. The copper clusters were also formed from either fragmentation or dissolution of the nanospheres. The nanowires act as the sources of nanospheres and clusters.

The following explanation of the copper nanowire formation in the early period of the femtosecond laser irradiation is proposed. At the instant the light pulse impinges on the surface of the initial flakes, multiphoton ionization rapidly occurs without significant ablation. The SPWs with a large electric field parallel to the surface are resonantly excited by light and propagate along the surface. The SPWs could absorb the light wave via inverse Bremsstrahlung heating[16] and couple with the incident light wave only if it propagates in the plane of light polarization.[13] This light-plasma coupling occurs at the flake surface over a narrow region with a depth of the order of the skin depth ($d_p \ll \lambda$). Previous investigations[17] suggested that either preimposed or self-generated deformations on the solid surface strongly affect laser energy absorption. Evidence for small deformations comes from the wide spreading of the reflected radiation observed in experiments.[18] 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 ($n_e = n_c$).[19] Such rippling is generated as a result of interference between the light field and the surface plasmon-polariton wave launched by initial random surface inhomogenities. Positive feedback leads to exponential growth of the periodic surface structures oriented perpendicular to the light polarization, which become frozen within the material. Indeed, the time scale of the nanowire formation is faster than the other bottom-up methods. A detailed mechanism of the fragmentation responsible for the nanowire formation is under investigation.

The photoconversion from copper flake to nanowire and nanosphere via ultrashort pulse laser irradiation is unusual and their optical properties are striking. These previously unknown copper nanowires have a very high aspect ratio. Therefore, the discovery of these copper nanowires and their unusual optical properties could be useful for not only an optical polarization control medium but also an electroconductive nanomaterial.

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