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Photo-conversion and evolution of one-dimensional Cu nanoparticles under femtosecond laser irradiation

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Abstract

Metal nanowires with electric conductive properties can be useful for optical polarization control medium and electro-conductive nanomaterial. We report on metallic Cu nanowires with a length of 1.0 μm and a diameter of 85 nm which were successfully photo-converted from commercial scale-like Cu particles, dispersed in a methanol solution, by using femtosecond laser irradiation. The growth mechanism of Cu nanowires under laser irradiation was suggested to be a nucleation growth process.

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Keywords: Metal nanowire; Ultrashort pulse laser; Nucleation growth process; Polarization

1. Introduction

In recent decades, increasing interest has focused on the femtosecond (fs) laser field due to its unique characteristics based on the nonlinear optical effects deriving from ultrashort pulse width and high peak power density [1,2]. Especially, by connecting the femtosecond laser technology with nanotechnology, an effective approach was provided to prepare and modify nanoparticles in micro-devices [3–11]. A great success has been achieved in forming zero dimensional nanoparticles by using intense ultrashort light pulses radiation. We have successfully fabricated a colorful micro-pattern composed of Au or Ag nanoparticles inside a glass matrix [7–9]. El-sayed and coworkers reported the evolution of nanoparticles under both femtosecond and nanosecond laser irradiation [10,11]. However, the shape-controlled nanoparticles have been synthesized by the various 'bottom-up' approaches based on a thermal process. Femtosecond laser technology was then adopted to fabricate one-dimensional nanoparticles, e.g. nanowires and nanorods in wet chemical conditions, however the mechanism of the evolution of the nanorods and nanowires in the intense laser fields has been little considered. The limited prior exploration for preparing one-dimensional nanoparticles by a femtosecond laser was concentrated on their fabrication on the materials' surface. Jia et al. reported ZnSe nanowires' growth induced by the femtosecond laser. Yet the nanowires grew only on the ablation crater located on the surface of ZnSe wafer [12,13]. Mazur and coworkers reported the production of submicrometer-sized spikes that consisted of the silicon on the silicon wafer after irradiating a silicon surface with a femtosecond laser [14,15]. Thus 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 plasmons (materials) in the nanoscale. So in this present study we

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report the preparation and the evolution of copper nanowires, dispersed in a methanol solution, from commercial copper flakes by femtosecond irradiation. It was found that the structure and morphology of Cu nanowires were dependent on irradiation time, which allowed us to investigate their structure and morphology evolution in the solution. By observing the morphology transformation of nanowires with time, the mechanism of Cu nanowires growth with ultrashort pulse laser irradiation in the solution was investigated. Other starting materials, e.g. Cu microspheres, were also tested to fabricate nanowires under the same experimental condition to verify the mechanism and procedure of nanowires' growth by another process.

2. Experimental methods

Copper flakes with a size and thickness of 5 and 0.1 μm, respectively, were purchased from Fukuda Metal Foil & Powder Co. Methanol from Wako Pure Chemicals Ltd. was used to prepare 1% (weight) copper flakes suspension. The quartz vessel of 1 cm × 1 cm × 3.5 cm for the reaction was purchased from TOSOH Quartz Corp. The vessels were thoroughly washed by aqua regia and then rinsed by pure water and ethanol several times. A small amount of the copper flakes, 4.8 mg, was mixed with 6 mL of 99.8% methanol and contained in a spectrophotometer vessel.

The linearly polarized laser radiation, in Gaussian mode, produced by the 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 = 0.30) microscope objective into the methanol-suspended copper flakes. The beam was focused in the suspension with a beam waist diameter and laser energy fluence estimated at ~3.2 μm and 2.5×10^3 J/cm^2, respectively. The morphology of Cu nanorods and nanowires, with the different growth time, were observed with a field-emission scanning electron microscopy (FE-SEM, JSM-7400F, and JEOL). The UV–vis pattern was measured on the P400-2-UV–vis system (BAS Inc.). The structures and chemical state of nanowires were measured by a transmission electron microscope (TEM, HF-2000, Hitachi) and a field-emission electron probe micro-analyzer (FE-EPMA, JXA-8500F, and JEOL), respectively.

The typical procedure of laser irradiation was as follows: 6.0 mL copper flakes suspension in the quartz vessel was placed on the magnetic stirrer, keeping continuous stirring during the procedure. Then the laser beam was focused in the centre of vessel with the constant irradiation time (1, 5, 10, 20 and

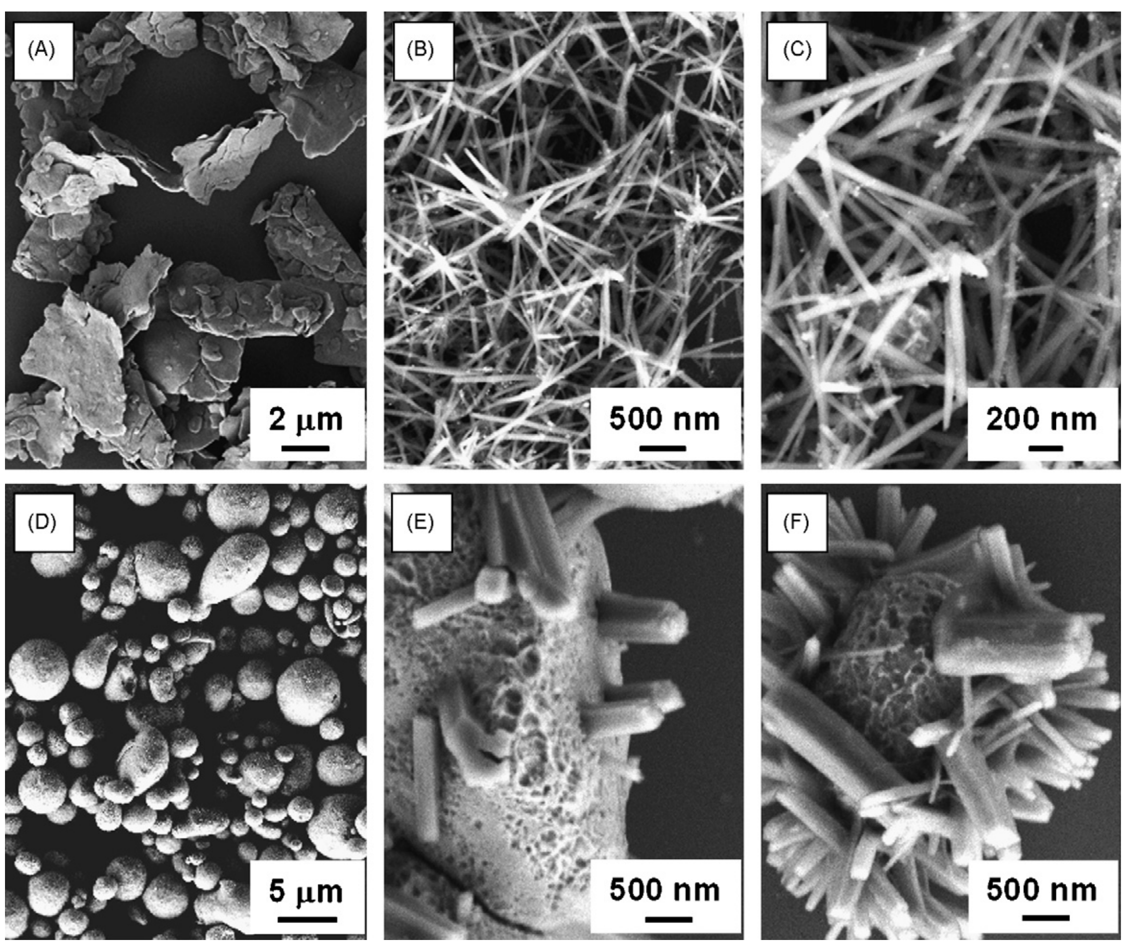

Fig. 1. Typical FE-SEM images of micro-flakes before fs laser irradiation (A) and nanowires observed after 10 min fs laser irradiation. The images are shown in two different scales. Low-magnification image (B) and high-magnification image (C) for the same area. FE-SEM images of microspheres before laser irradiation (D) and rectangle-like nanowires prepared with the different irradiation time: (E) 10 min and (F) 20 min are also shown.