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Laser-Driven Silver Nanowire Formation: Effect of Femtosecond Laser Pulse Polarization *

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We report our laser-driven method used to make large quantities of straight thin silver nanowires, and experimentally demonstrate that femtosecond laser pulse polarization has a prominent effect on formation of non-spherical shapes of nanoscale particles. Further, our experiment directly reveals that the underlying mechanism is plasmon-plasmon interaction, which can be controlled by polarization and plays a decisive role in this non-synthetic method for metal nanowire formation.

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In recent years, laser-driven methods have been used extensively for metal nanoparticle preparation.[1−3] However, there have been few reports on non-spherical metal nanoparticle (for example, metal nanowire in thickness of smaller than 20 nm) formation. Laser ablation in aqueous solution (LAAS) has been known as a laser-driven method of preparing biosensing-friendly metal nanoparticles, owing to that it is free of toxic precursors from chemical reduction reactions.[4] So far the effects of laser pulse fluence,[1,2] central wavelength,[5,6] temporal pulse width,[7] and surfactant properties[2,8] on the particle formation have been investigated, all of which mainly concern with the particle size and production rate. However, the effect of laser polarization has not been fully identified and morphologies other than near-spherical shape have rarely been reported (except for occasional cases with relatively small quantities made in a less controllable way). Meanwhile chemical reduction methods with light-illumination and thermal refluxing have been used to produce metal nanowires[9,10] and nanoprisms,[9−11] all of which need precursors. In this Letter, we report well-controlled precursor-free thin nanowires made and identify polarization-induced plasmon-plasmon interaction as the formation mechanism.

Among previous efforts of laser-driven methods, laser ablation in a polymer-like matrix has been used to make wire-like well-aligned aggregated silver nanoparticles.[12] Here we present individual thin nanowires that have flat surfaces and no traces of aggregation exist. Although light-assisted thermal process has been used to produce nanowires,[10] a light-driven (see our discussion on the different roles of photons for the two methods in latter paragraphs) method is still missing from the list of established techniques of thin metal nanowire preparation. Herein we report such a progress. Our method combines the advantages of femtosecond laser pulses and capping agents.

We focused femtosecond laser pulses onto silver plates, which were immersed in aqueous solution, to produce silver nanoparticles. The 0.2-mm-thick pure silver (99.99%) plates were prepared by mechanical polishing and then cleaned three times with deionized water. For each experiment one silver plate was placed on the bottom of a culture dish, which was filled with aqueous capping agents in deionized water. The solution's thickness above the silver plate was 4 mm. Our laser beam had a central wavelength of 800 nm, a repetition rate of 250 kHz and a pulse duration of 80 fs (from a RegA-9050 Ti:sapphire laser amplifier, Coherent Inc.). It had a $1/e$ amplitude radius of 2.7 mm and was focused using an optical convex lens with a focal length of 50.8 mm onto the top surface of the silver plates. Throughout our experiment each plate was ablated for 10 min, during which the whole culture dish was laterally translated underneath the laser spot smoothly to ensure uniform ablation so that any texturing effect was avoided. The silver nanoparticle suspensions were thus made.

In the above experiments, capping agents of 0.3 mM sodium citrate ($Na_3C_6H_5O_7$, Alfa Aesar) and 0.1 mM polyvinylpyrrolidone (PVP, Aldrich), which have been successfully used in chemical reduction methods,[9] were added into deionized water (Milli-Q,

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Millipore Co.) to make a mixed solution before laser ablation. The major effect of PVP, a water soluble polymer which coats the surfaces of the silver particles, is to prevent the produced silver nanoparticles from aggregating. The role of sodium citrate is such that citrate anions selectively attach to the (111) facet of the tiny silver particles and allow the silver particle to grow only within the (111) plane.[10,11,13]

To characterize the nanoparticles, we took transmission electron microscope (TEM) images with a JEM-2010 (JEOL, 200 kV). The samples were routinely prepared by depositing a drop of suspension containing silver nanoparticles onto a copper mesh coated with carbon film and letting them dry completely in an electronic drying cabinet. Care was taken such that room light did not reach the samples during their drying process.

Our result shows that, at a laser power of 470 mW, silver nanowires were produced (Figs. 1(a) and 2(d)), which is quite unique compared with the previous results reported for LAAS. The previous results were mainly near-spherical particles. We carefully analyzed our data and contemplated that the formation of the silver nanowires is related to the laser polarization, which broke the spatial symmetry and led to the particle growth along a pre-defined direction.

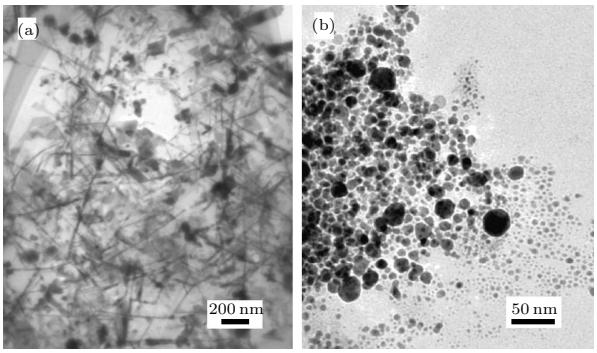

Fig. 1. Effect of laser polarization on shape. (a) TEM image of typical nanowires formed with linearly polarized laser pulses. (b) TEM image of typical near-spherical nanoparticles formed with the same condition as (a) but circularly polarized laser pulses.

To unambiguously verify our interpretation, we performed a laser polarization-dependence experiment. At 470 mW laser power and the same capping solution we carried out two parallel experiments with one using linearly polarized laser and the other using circularly polarized laser. The typical results are shown in Figs. 1(a) and 1(b), respectively. Large quantities of uniform-thickness nanowires can be seen in Fig. 1(a), with an average width of about 15 nm and an average length of about 300 nm. As a comparison, there are mainly near-spherical nanoparticles shown in Fig. 1(b), with an average diameter of about 20 nm. We examined carefully all the aggregated-particle groups contained in this sample and did not see nanowires, although in reality we do not exclude occasional cases due to complex conditions. Our result clearly revealed the effect of laser polarization on the nanoscale structure formation.

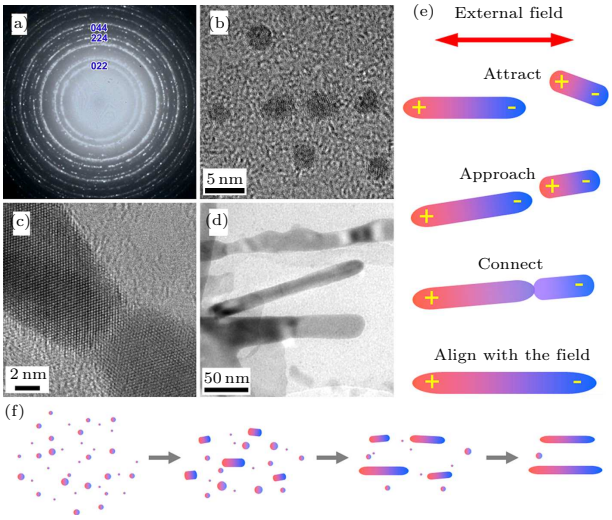

Fig. 2. Mechanism of nanowire formation. (a) Electron diffraction patterns of Fig. 1(a), showing the typical 022, 224 and 044 rings of polycrystalline FCC silver. (b) HRTEM image of separated ultrasmall particles of less than 5 nm. (c) HRTEM image of the connection part of two particles (wires), showing the merging of the two. (d) TEM image of three typical nanowires with the middle one thin, smooth, and straight, the upper one having a noticeable connection, and the lower one growing into a thin film. (e) Schematic showing how plasmon-plasmon interaction induces two nanowires to merge into a single one. The red and blue colors correspond to different charge parities. (f) Schematic diagram of formation of nanowires under linearly polarized laser.

The microscopic mechanism of this polarization effect, i.e. polarization-induced plasmon-plasmon interaction leads to the formation of the nanowires, is illustrated in Fig. 2(e). When laser pulse comes in, electrons in the composing small particles or short wires oscillate collectively in phase with the external field, thus plasmons emerge and sustain within the wires. The laser pulse in our experiment had a beam waist radius of 5 μm ($1/e$ amplitude radius), hence a uniform laser field can be assumed and the plasmons in each individual particle (wire) are coherent with each other. Charge densities oscillate along the same direction and are in phase with each other, even though they are contained in separate particles and differently-oriented wires. When these particles or wires are near to each other, their plasmons inevitably interact with each other, repelling or attracting depending on the charge parities. When the interaction is strong enough, the plasmon-plasmon attraction indeed leads to the formation of connected longer wires (Fig. 2(e)), whereas repulsion hinders the formation of thin films. During the formation of longer wires,

the original particles (wires) have a chance to reorient themselves as depicted in Fig. 2(e). Once the longer wire is formed, a new plasmon mode emerges and the wire itself resists falling apart. When higher laser fluence is used and more tiny particles (see Fig. 2(b)) are generated, the growth rate along directions other than the laser polarization will increase, which leads to the appearance of more thin silver films, as shown in Fig. 2(d).

In Fig. 2(a) we show the electron diffraction pattern of the corresponding selected area in Fig. 1(a), manifesting the typical 022, 224 and 044 rings of polycrystalline FCC (face centered cubic) silver. In Fig. 2(b) we show the high resolution TEM (HRTEM) image of composing ultrasmall particles of less than 5 nm, and in Fig. 2(c) we present the HRTEM image of the connection part of two wires (particles), demonstrating the merging of the two. In Fig. 2(d) we show three typical single nanowires, with the middle one thin and uniform, the upper one having apparent connection, and the lower one growing into a thin belt or film. A schematic depicting the over-all growth process for the nanowires under linearly polarized laser is shown in Fig. 2(f). Images shown in Figs. 2(b) and 2(c) were taken on a Tecnai F20 (200 kV) electron microscope.

The above interpretation is verified by our polarization-dependence experiment, since the only difference that leads to different results is the polarization. Further, with currently available various temporal and special pulse shapers, one can control the plasmon-plasmon interactions by controlling the polarization, making it a relatively general means of controlling nanostructure formation.

It is worthy to note that the net effect of photons here is to help the nanowires grow larger, in sharp contrast to the cases where photons effectively digest the nanorods[14] or nanoparticles.[11] We believe that it is crucial to optimize both laser fluence and concentration of the capping agent, although apparently polarization is the determining factor. It is expected that our method is not limited to silver and other metals,[15,16] and can be applied to alloys.[17] Our further investigation (not shown here) reveals that laser power has a noticeable effect on the nanowire length. With our method, further investigation and optimization of the capping agents, laser pulses properties and ablated materials are expected to result in richer morphology. Ablation angle effect[18] can also be investigated. Our method can produce large quantities of smooth-surface uniform-thickness straight nanowires, which entails more potential applications in many areas such as biosensing, medical treatment, catalysis, etc.

In summary, we have experimentally demonstrated that, for the first time, a laser-driven method can be used to produce large amounts of thin metal nanowires. We have designed and performed a polarization-dependence experiment, which directly reveals a new mechanism for the nanowire formation. In our non-synthetic method plasmon-plasmon interaction plays a decisive role in the nanowire formation, whereby the interaction can be well-controlled by the polarization of femtosecond laser pulses.

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