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Light-assisted nucleation of silver nanowires during polyol synthesis

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A B S T R A C T

This report describes the effect of light irradiation on the synthesis of silver nanowires by the well-known polyol method. High quality nanowires are produced in high yields when the reaction suspension is irradiated with 400–500 nm light during the nucleation stage. These studies suggest that light accelerates the formation of the nanoparticle seeds most appropriate for nanowire growth.

1. Introduction

The unique optical properties of silver nanoparticles (NPs) arise from surface plasmon resonances (SPR) and give these structures enormous potential application in a wide area including sensing and spectroscopy [1–8]. SPR is especially sensitive to the size and shape of the NPs but also to their metallic composition, dielectric environment, and distance between NPs when they aggregate [9–12]. Therefore it is crucial to be able to synthesize NPs with well-controlled size and shape in order to fine-tune their optical properties for future applications.

Many methods have been developed for the controlled growth of silver NPs of various shape and dimension, such as triangles [13–15], cubes [16,17], rods and nanowires [18–24], using both thermal and photonic stimuli as well as capping agents/surfactants. Among these, nanowires (NWs) are interesting materials in the field of plasmonics, employed as sub-diffraction limited waveguides [1,25–27], resonators [28], and photonic crystals [29]. One of the most frequently used methods of silver NW synthesis is the polyol process in ethylene glycol (EG), which provides high quality NWs with a diameter below 100 nm and a length over 10 μm [21,22]. In this method one of the crucial factors is the proper choice of the kind and amount of surfactant, poly(vinylpyrrolidone) (PVP), to bind to and pacify a specific crystal facet. While the protecting agent thus plays a critical role during the growth phase, it should not be forgotten that the initial nucleation of the appropriate seed particle also influences the ability to obtain a NP of the desired shape. In this paper, we demonstrate that light irradiation during the nucleation phase of the polyol synthesis strongly influences seed particle formation and the subsequent growth of silver NWs.

2. Experimental

Silver nitrate (99.9999%), PVP (Mw ∼ 40,000), sodium chloride (>98%), and ethylene glycol (anhydrous, 99.8%) were purchased from Sigma–Aldrich and used without further purification.

We followed the polyol method in reference 16 in our synthesis protocol. For typical synthesis, 5 ml of EG was first refluxed at 160 °C for 60 min under a dry argon flow, followed by addition of 3 ml of an EG solution of silver nitrate (0.1 M) and 3 ml of an EG solution of PVP (0.6 M) drop-wise at a typical rate of 150–300 μl/min (10–20 min total time for injection). After the injection, the solution was refluxed at 160 °C for another hour in air without gas flow. Since the polyol process used in this study is sensitive to the water

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content in the reaction solution, all the solutions were prepared directly in syringes in order to avoid absorbing extra water from air. To study light effect on the synthesis, the reaction suspension was irradiated using a Halogen lamp (100 W, Olympus). UV (<400 nm) and near-infrared light (>800 nm) were rejected with optical filters. In order to select wavelength of the irradiations, a band pass filter (transmit between 400 and 500 nm) or a long pass filter (transmit over 500 nm) were used. In typical experiments, half the power of the lamp was used and the whole reaction suspension was irradiated (irradiation area of ∼60 cm^2).

To measure extinction spectra of the reaction solution during the synthesis, a few hundreds ml of the suspension was taken and immediately cooled down in ice water in order to quench the reaction. UV–vis spectroscopy was conducted using a Lamda40 spectrophotometer (Perkin Elmer).

Transmission electron microscopy (TEM)-studies were performed using Jeol 4000EX (accelerating voltage 400 kV, point-to-point resolution 0.17 nm). Specimens for TEM were made by grinding of the material in methanol followed by deposition of obtained suspension on the conventional holey carbon film.

3. Results and discussion

Fig. 1 displays TEM images of the products formed under two different conditions, i.e. under white light illumination and in dark conditions. NWs are produced when the reaction suspension is exposed to white light (between 400 and 800 nm) during the reaction (Fig. 1a). The NWs typically have a diameter of ∼100 nm with lengths up to 30 μm [see the optical transmission image in Ref. 1]. The NWs grow along the {1 1 2} direction with {1 0 0} side facets (Fig. 1b). The ends of NWs are likely faceted by (1 1 1) and (1 0 0). Single-crystal nanocubes are also produced as a side product. In contrast, the same reaction in dark produces no NWs but NPs with a wide range of size from tens to a few hundreds of nm as shown in Fig. 1c.

The difference in the reactions with/without light is already present at the nucleation stage (the first 10–20 min in which the injection of $AgNO_3$ and PVP solutions occurs). While the color of the suspension turns yellow a few minutes after starting the injection, and becomes grayish in around 5 min in both conditions, transmission electron microscope (TEM) studies show that a radically different nucleation occurs. Fig. 2 displays TEM images of NPs in the suspension taken at 10 min (Fig. 2a and c) and 15 min (Fig. 2b and d) after starting the injection (rate of 300 μl/min), with and without light illumination, respectively. Under light irradiation, many multiply twinned particles are obtained, containing {1 1 1} twin boundaries (Fig. 2a). Besides these twinned crystals, single-crystal nanocubes and twinned rods are also found. At 15 min, the reaction suspension contains mainly twinned rods and single-crystal cubes, with fewer twinned NPs (Fig. 2b). The TEM images in Fig. 2a and b show that the rods also exhibit {1 1 1} twinning along their longitudinal axis.

The same reaction without light irradiation (in the dark) shows a strikingly different result as displayed in Fig. 2c and d. The NPs are much larger and more polydispersed both in shape and size. NP size ranges from a few tens to a hundred nm at 10 min (Fig. 2c) and most of the NPs contain many random boundaries. The NPs are larger after 15 min (Fig. 2d) but none of them converted into NWs during the further growth phase (Fig. 1b).

As mentioned, in both light and dark conditions the color of the initial suspension becomes yellowish within a minute of starting the injection of the silver nitrate and PVP EG solutions, indicating that small silver NPs were generated in both cases. However the TEM results clearly show that these NPs are likely to be multiple-twinned/single-crystal NPs in the presence of light, and

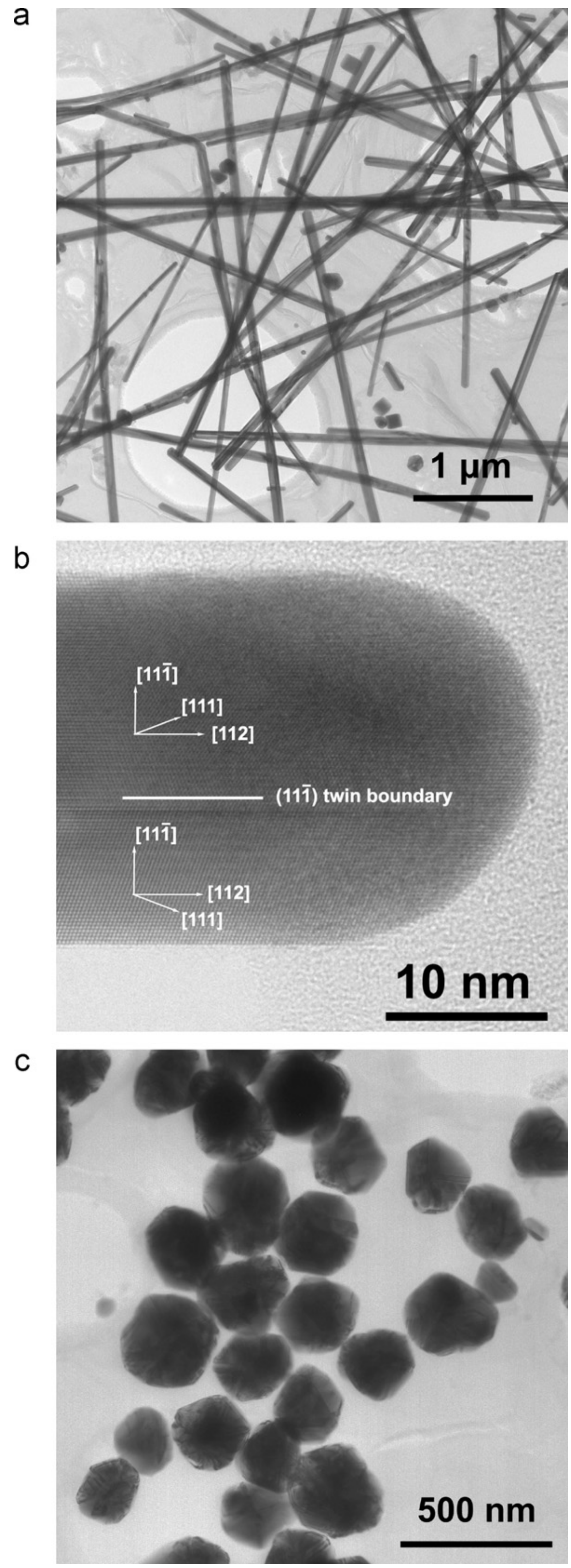

Fig. 1. (a) A TEM image of the final products of the polyol synthesis carried out with white light irradiation. (b) A high-resolution TEM image of a nanowire showing twin boundary and the growth direction. (c) A TEM image of the final products of the synthesis in dark.