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Light-assisted nucleation of silver nanowires during polyol synthesis

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ABSTRACT

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 $\sim$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 $\sim$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

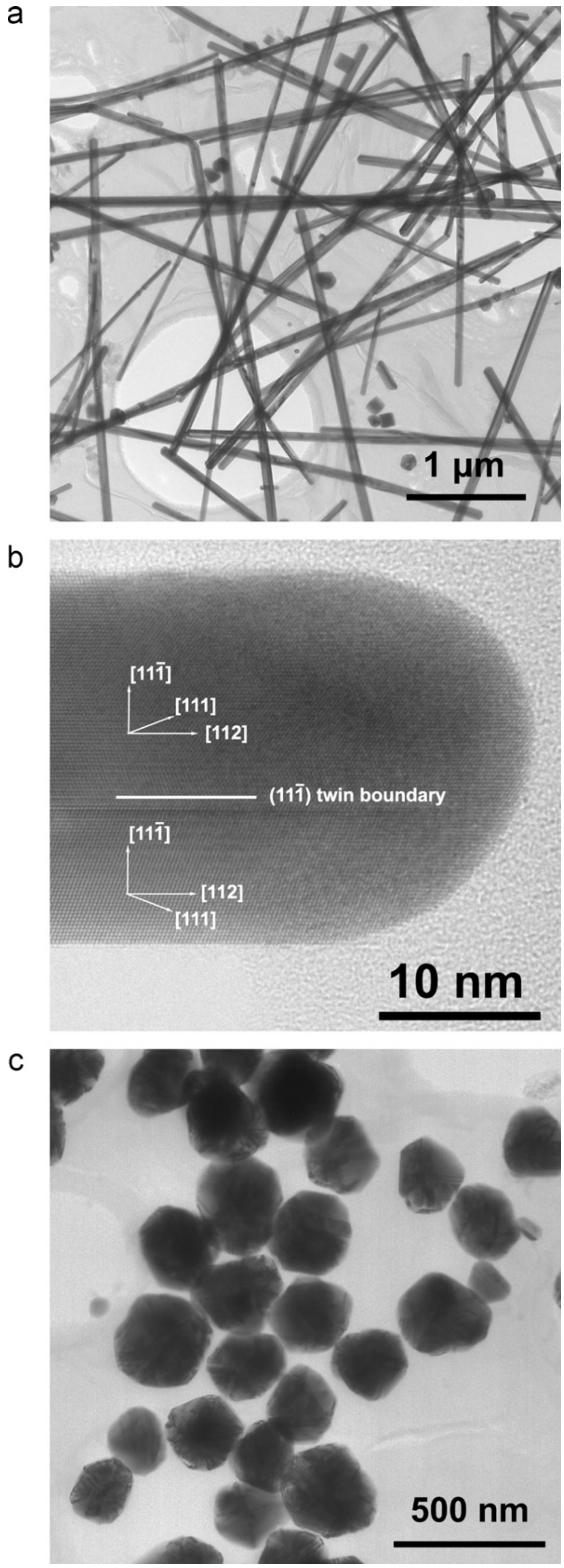

Fig. 1. (a) A TEM image of the final products of the polyol synthesis carried out with white light irradiation. (b) A high-resolution TEM image of a nanowire showing twin boundary and the growth direction. (c) A TEM image of the final products of the synthesis in dark.

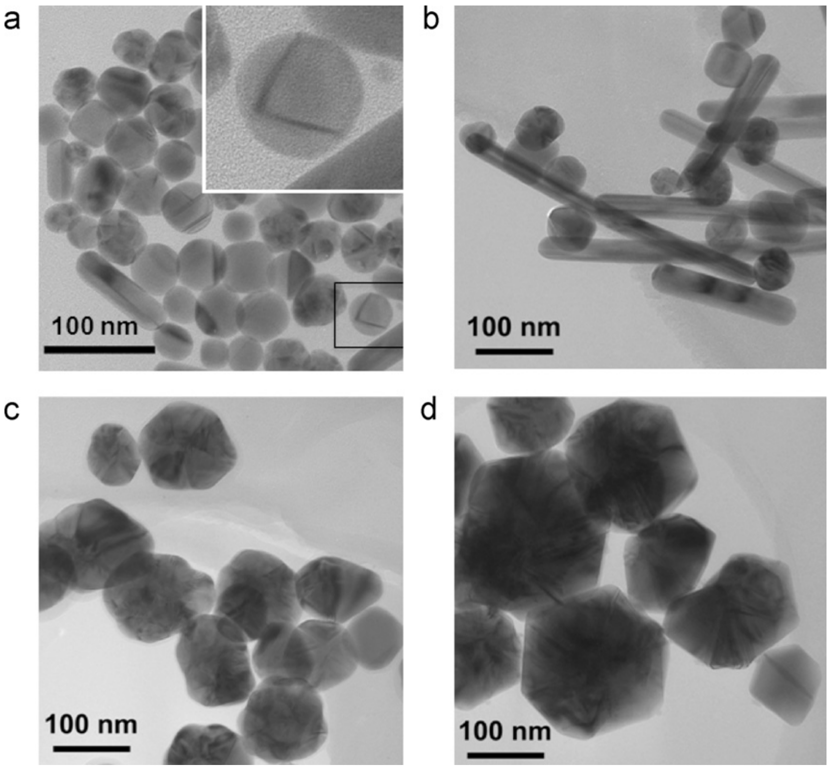

Fig. 2. TEM images of particles in suspension during the nucleation stage: under white light irradiation at 10 min (a) and 15 min (b) after starting the injection; in the dark at 10 min (c) and15 min (d) after starting the injection.

NPs without any specific shape in dark conditions. It is important to note that light illumination only has an effect during the nucleation phase (injection during the first 10–20 min of the reaction). The subsequent NW growth (or its absence) is not effected by light/dark conditions. All this evidence suggests that light causes nucleation of specific NP structures which favour further growth of NWs in the polyol method.

The reaction was found to be sensitive to specific light wavelengths as well. Fig. 3 shows excitation spectra of the final products of the reaction with irradiation by white light (400–800 nm), by light with wavelength >500 nm, and without light during the nucleation stage, respectively. Only with white light irradiation does the spectrum of the final suspension show the broad excitation band typical of NW formation (magenta in Fig. 3) due to the longitudinal (along the length of the NW) and transverse (normal to the long axis) SPR bands of NWs as well as those of other side products (e.g. variously sized nanocubes). In contrast, both reactions in the dark and with irradiation with >500 nm light result in a final suspension with a narrower excitation peak centered at ~450 nm. This peak corresponds to NPs without any specific shapes and in the size range shown in Figs. 1b and 2d, with the width of the band being due to the polydispersity of NP size and shape produced. These studies show that a clear difference in reaction products (e.g. significant NW production) only occurs if irradiation by light of 400–500 nm is present during the injection phase.

This was confirmed by the fact that irradiation by 400–500 nm light only provided an even higher yield of NW formation (close to 100%) than for broad-band illumination. This suggests that the excitation of the SPR band of the initially formed/forming NPs during the first minutes of injection (the yellow suspension, maximum of the excitation band ~430 nm (Fig. 3)) is one of the key factors leading to efficient NW growth.

For comparison, we studied the effect of light irradiation on two alternative polyol syntheses of silver NWs. The first was a polyol synthesis with pre-seeding proposed by Chen et al. [22]. Briefly, silver nitrate was added and refluxed in EG at 160 °C for 15 min prior to adding more silver nitrate and PVP for growth. This reaction allows NW growth even in dark conditions, suggesting that the pre-seeding produces the appropriate nucleation for further growth into NWs. Secondly we confirmed that NWs could be cre-

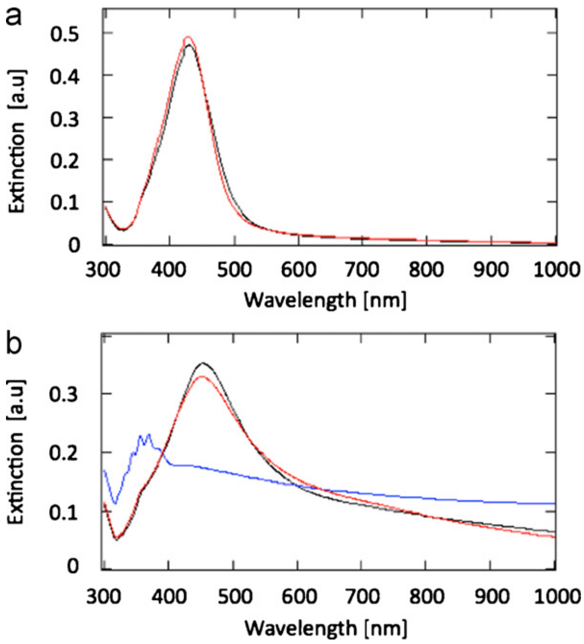

Fig. 3. (a) UV–vis extinction spectra of the suspension at 1 min during the injection with light (red) and in dark (black). (b) UV–vis spectra of the final products of the polyol reaction: with 400–800 nm irradiation during injection (blue); with >500 nm irradiation during injection (red); in the dark (black). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

ated in the dark when chloride ions were present in the reaction, as reported in Refs. [18,19]. In this reaction, AgCl colloids are initially formed, reducing the concentration of free silver ions in the suspension. Ag^+ ions are slowly released from the AgCl colloids via oxygen etching which, in a similar manner to the use of a syringe pump to deliver silver ions used in this study, results in a slowing down of the reduction of silver ions during nucleation.

It is known that multiply twinned NPs are thermodynamically stable, while single-crystal seeds which can grow into e.g. cubes are kinetically stable [24,30]. According to previous reports [16,17,22–24], multiply twinned icosahedron NPs grow into nanowires, whereas single-crystal NPs lead to the formation of nanocubes. The equilibrium between the formations of these types of NPs is crucial to obtain the multiply twined NPs for further growth into NWs. In the two alternative polyol syntheses mentioned above (with pre-seeding and in the presence of chloride ions), the reaction may become suitable for the formation of thermodynamically stable twinned NPs due to the slow nucleation time.

If this is true, one should be able to produce NWs when using a very slow injection rate of silver ions and PVP even without pre-seeding or chloride ions. Indeed, we have confirmed that NWs can be prepared in the dark using the polyol synthesis from Ref. [7] using a very slow injection rate (e.g. less than 50 μl/min). Under these conditions, however, the length of NWs is much shorter and the number of side-products increases, indicating that the very slow injection still allowed too much seed formation in this case.

The light-induced transformation of silver NPs into specific shapes, e.g. plate, dodecahedra, rods, etc. and the role of surface plasmons in this process is well known [13–15]. Xue et al. suggested that SPR could lead to anisotropic charge distribution, which could enhance electron transfer from the metal surface to adsorbed Ag^+ ions and it could favour photo-deposition of Ag atoms on certain crystal facet [15]. A similar effect might be responsible for the influence of light irradiation on the polyol synthesis reported here. The silver NPs in the initial yellow suspension in the first few minutes of the injection seem to be converted quickly into multiply twinned or single crystal NPs by light illumination at their SPR band. Once such NPs are created, they grow into NWs or nanocubes even without light. Thus, light irradiation is a crucial factor to produce suitable nuclei for growth into long NWs using the well-known polyol synthesis. It is worth to mention that intensity of the light illumination is not necessary high for this synthesis. For example, natural light in a room (e.g. fluorescent room lighting) is enough for the formation of nanowires. This indicates that the reaction is very sensitive to light. This irradiation becomes more important for NW production as the nucleation time is decreased (injection rate increased).

4. Conclusions

We demonstrated the effect of light on an established protocol for the polyol synthesis of silver NWs. In dark conditions NWs are not created, while irradiation with light shorter than 500 nm provides a high yield (∼100%) of NW formation. TEM shows significant differences between the NP structure at the nucleation stage with and without light (400–500 nm) illumination. Under light illumination, ∼50 nm NPs with a few twin boundaries and single-crystal NPs are created within 10 min, while multiply twinned NPs are formed in dark. We attribute this finding to light-induced/accelerated transformation via SPR of nucleating NPs into multiply twinned NPs (or single-crystal nanocubes). TEM measurements indicate that the twinned NPs subsequently grow into NWs. A more detailed irradiation wavelength dependence on the nucleation is under investigation; nevertheless, the importance of the excitation of the SPR band of the nucleating NPs is already clear from the requirement of 400–500 nm light. This work encourages us to make use of the nucleating silver NPs to grow NWs at a specific position e.g. on a surface or on top of an AFM cantilever, toward sensing applications.

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