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Growth orientation control of metal nanostructures using linearly polarized light irradiation

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ABSTRACT

Controlled orientation of metal nanostructures on a solid substrate was realized by irradiating a pre-deposited nanoseed layer with linearly polarized light in a growth solution containing metal cations. The resulted nanostructures showed the different transmittance spectra for two orthogonal polarized lights, which indicated an anisotropic growth induced by polarized light. The investigation on the growth conditions demonstrated that the wavelength of the irradiated light and the existence of cetyl cetyltrimethylammonium bromide used as surfactant could affect the anisotropic degree of the oriented nanostructures. It was suggested that the polarized lights enhanced the anisotropic local electric field of Au seed nanoparticles, which resulted in the oriented growth of metal nanostructures during the reduction process in the solution. The approach reported in this work can be used in the device fabrication based on oriented metal nanostructures, such as photocatalysts or optical sensors.

1. Introduction

Metal nanostructures show the unique optical/electrical property known as localized surface plasmon resonance (LSPR), where the incident light to the structures can be captured and the energy is concentrated around them. This light-harvesting nature of metal nanostructures has been investigated for various applications such as photocatalysts, including artificial photosynthesis application [1,2], sensitization of solar cells [3], bio/chemical sensing [4–6], and so on. Using anisotropic metal nanostructures like nanorods is one of the strategies to achieve larger field enhancement or to modulate the plasmon band [7,8]. Many synthetic methods have been investigated to obtain metal nanorods, such as the processes using hard or soft templates [9–11] and the photo-assisted processes [12,13]. These methods are generally based on the synthesis in suspensions, which can produce the nanorods suspended in water or organic solvent inexpensively. However, the additional processes of fixation to substrates [14] and simultaneous orientation control are required when they are used to fabricate solid devices. Some groups performed the growth of gold nanorods directly on substrate surfaces, by fixing seeds on surfaces at first followed by the growth process [15–17]. All of them employed cetyltrimethylammonium bromide (CTAB) as a soft template to achieve the anisotropic growth, but no orientation control was performed. The lithographic techniques like electron beam lithography [18] can be also employed to obtain the oriented nanostructures onto substrates. Although those lithographic techniques are useful as direct ways to obtain the precise nanostructures on substrates, there are problems of expensiveness and time-consuming because of the intrinsic problem of scanning beam irradiation.

In this study, we examined a direct way to obtain the anisotropic metal nanostructures with aligned orientation on solid substrates, by applying the seed-mediated growth processes on the seeds fixed on the substrates, with the help of the irradiation of linearly polarized light. Conventional growth processes of metal nanorods in suspension [10–13] and on substrates [15–17] utilized the anisotropic growth rate depends on crystal faces of seed particles and realized the anisotropic growth. However, the necessity of simultaneous orientation control of grown nanostructures on substrates still remains as next challenge because of the difficulty of fixing nanoparticles on solid substrates with specific direction. Our approach uses anisotropic electron distribution on the surface of seeds induced by polarized light irradiation, not crystal anisotropy, to realize such simultaneous oriented growth on a substrate. Such direction control of the polarization of metal nanostructures has been already harnessed to trap particle and control their position in previous research [19], known as a plasmonic tweezer, while the application for anisotropic growth has not performed yet. Although the photo-induced reduction of metal ions has been utilized to realize anisotropic metal growth [12,13], synthesis of metal nanoparticles [20], and controlling micron-scale metal structures [21], those methods only concerns the reaction rate and excludes the polarization directions from growth mechanisms.

The concept of the anisotropic growth assisted with polarized light is shown in Fig. 1. Anisotropic distribution of electric near-field or hot electrons, on the surfaces of gold seeds induced by the irradiation of

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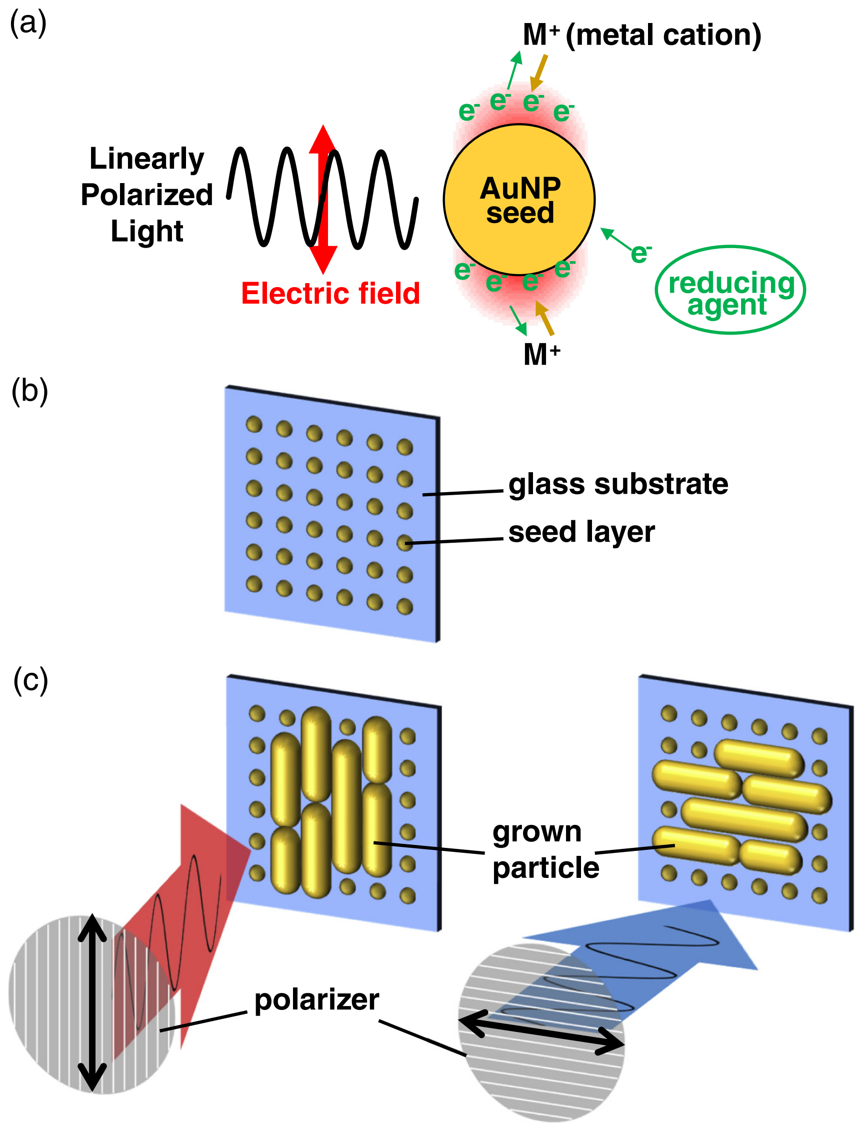

Fig. 1. Schematic illustrations of (a) the estimated mechanism of anisotropic growth by the irradiation of polarized light to (b) metallic seeds fixed on substrate. (c) is the concept of the actual growth experiments to obtain the orientation-aligned metal nanostructures using polarized light, where the direction of electric field, indicated with black arrows, decides the orientation of grown metal. Two orthogonal directions were defined as vertical and horizontal for identification.

polarized light are expected to be a driving force for anisotropic and oriented growth of those seeds, assuming that the growth due to the reduction of metal ions caused by the hot electrons is more active than other region (Fig. 1a,c). This scheme of polarized-light-assisted growth is an approach to realize the oriented growth control of metal nanostructures on the solid substrates directly.

2. Experimental

Firstly soda-lime glasses were cut into 9 mm wide and 26 mm high and were cleaned with continuous sonication in deionized water, acetone, ethanol for 10 min for each cleaning solvent. Subsequently, a seed layer was prepared by deposition of gold onto those glass substrates with 5 nm of nominal thickness using sputtering with a quick coater (SC-701HMCII, SANYU ELECTRON), followed by annealing of them in 580 degrees Celcius for 10 h in an electric furnace (SMF-1, AS ONE), which resulted in the formation of stably-fixed [22,23] and moderately separated gold seeds as shown in Fig. 2 a. Then we examined the influence of the irradiation with polarized light to seeds during the growth, in the growth solution that contains metal ions (0.86 mM of $HAuCl_4$ or 2.4 mM of $AgNO_3$), reducing agent (1.8 mM trisodium citrate), and surfactant (240 μM of CTAB). Although this condition can cause the spontaneous particle formation in room-temperature without light irradiation, the rate is much slower than the growing reaction at the seed surfaces with light irradiation. The concentrations of the growth solutions were chosen to observe significant changes in anisotropic growths. However, in the gold-containing solution, the concentration of gold ions had to be limited because high concentration caused the detachment of gold seeds from the substrates. The incident light was irradiated perpendicularly to the seed-fixed substrates with the power of 10 mW/cm^2 for 1 h. Six band-pass filters (FB450-40, FB500-40, FB550-40, FB600-40, FB650-40 and FB700-40, whose center wavelengths were 450, 500, 550, 600, 650, 700 nm respectively and their FWHMs were 40 nm, Thorlabs Inc.) were used for wavelength selection of the light irradiations. All growth processes were performed in room temperature. We used a xenon light source (LAX-103, ASAHI SPECTRA) as the light source, and analysed the resulted nanostructures by using a field-emission scanning electron microscope (FE-SEM, SU8000, Hitachi High-Technologies) at the operating voltage of 1 kV, and a UV–vis spectrometer (UV-1800, SHIMADZU).