Morphological Control to Kneed Gold Nanowire through Initial Mixing in Polyol Process

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Various kneed gold nanowires with unique morphology were prepared by reducing hydrogen tetrachloroaurate through polyol process in the presence of polyvinylpyrrolidone (PVP). The kneed nanowires were ca. 150 nm in thickness and ca. 14 μm in length. Initial injection and dropping rate of hydrogen tetrachloroaurate ($HAuCl_4$) and PVP solutions into ethylene glycol were keys to induce formation of kneed gold nanowires.

One-dimensional (1D) nanostructure such as nanowires, rods, belts are expected to play an important role as both interconnects and functional units in fabricating electronic, optoelectronic, electrochemical, and electromechanical devices with nanoscale dimensions.[1] Especially, gold nanoparticles with 1D nanostructure are expected application to optoelectric device.[2] Therefore, it is demanded to investigate academically noble 1D nanostructure for more morphological research and industrial application. To control morphology to 1D nanostructure in wet chemical process, hard (carbon nanotube, alumina porous materials) and soft (surfactants) templates are generally employed.[3] With respect to a method using polymer, it is possible to control novel and various morphologies which are not discovered through template method.[4] The chemical reduction rate of metal particles in polyols can be determined by the reaction scheme involved in the nucleation and growth steps of crystallization, thereby morphological control of novel and uniform nanostructures could be easy with use of polymer in polyol.[5]

In the present study, the polyol process was modified to control the shape of gold nanoparticles. The shape changed from spherical nanoparticle to nanowire through unique technique, where ethylene glycol solutions including $HAuCl_4$ and PVP were partly injected into preheated ethylene glycol, and then the $HAuCl_4$ and PVP solutions were simultaneously added dropwise. To our knowledge, this is the first report that describes morphological control to kneed gold nanowires in wet chemical processes.

$HAuCl_4 \cdot 4H_2O$ and PVP (MW 40,000) were used as gold precursor and as protecting agent, respectively. Ethylene glycol was utilized as solvent and reduction agent. The ethylene glycol (5 mL) was preheated up to 155 °C. $HAuCl_4$ was dissolved at 0.05 M in ethylene glycol (1 mL). PVP was added in ethylene glycol (1 mL) at the weight ratio of PVP/$HAuCl_4$ = 1.1. First, the $HAuCl_4$ and PVP solutions (0.03 or 0.05 mL each) were added into the preheated ethylene glycol in initial step, and then the residual solutions were dropped at the injection rate of 0.1 mL/min. After addition, the total solution was aged at 155 °C under vigorous stirring for 20 min. The obtained gold products were washed with ethanol several times and redispersed in ethanol for characterization. The products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and UV–visible spectroscopy.

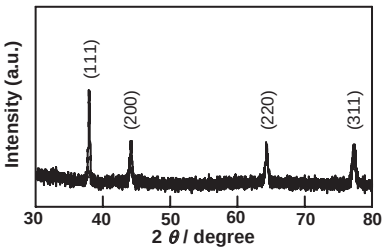

Figure 1. XRD pattern of the gold.

Figure 1 shows XRD pattern of the gold which obtained by initial injection of $HAuCl_4$ and PVP by 0.03 mL. The peaks are assigned as (111), (200), (220), and (311) reflection lines. Bragg reflections were present which indexed on the basis of the face-centered cubic (FCC) gold structure (JCPDS, 04-0784). Inconsistent diffractions, caused by crystallographic impurities were not detected. The XRD pattern clearly shows the generation of crystallized gold by reducing in ethylene glycol.

Figure 2a shows kneed nanowires with various angle and length, whereas spherical particles with large scale were rarely observed. The nanowires were ca. 150 nm in thickness and extremely elongated to ca. 14 μm in length. The average aspect ratio was 93. The initial amounts of the $HAuCl_4$ and PVP solutions were changed. When the initial addition amount increased to 0.05 mL each for the solutions, the gold products were heterogeneous in shape and size as shown in Figure 2b. The morphologies of the products were general nanowires and simple kneed nanowires. When the initial amount was 0.05 mL, the nanowires had ca. 10-μm length and ca. 110-nm diameter. The nanowires had lower aspect ratio by 91. A large number of nanowires were obtained compared with that of 0.03 mL. This result suggests that the formation of nanowires strongly depends on the initial mixing of the reacting agents. We assumed that kneed nanowires occur by the secondary nucleation. When the initial injection amount is large, nanowires were short and straight. Conversely, there is a large opportunity of the secondary nucleation with decreasing initial injection amount. Therefore, the nanowire may elongate owing to easy nucleation at the ends of wires.[6]

When selected area electron diffraction (SAED) pattern for the kneed nanowire was characterized, the ED pattern revealed that the kneed nanowire was single crystal as shown in Figure 3.

Figure 4 shows UV–vis absorption spectra of $HAuCl_4$ before formation of gold particles and the kneed gold nanowires. The $HAuCl_4$ solution having yellow color in ethylene glycol shows the absorption band at a short wavelength around 320 nm. Absorption spectra are reflected at different positions of wavelength because of morphological change of gold particles. In general, a spectrum of spherical gold nanoparticle reflects around wavelength of 550 nm, while the peak of $HAuCl_4$ at 320 nm disappears.[7] The absorption spectrum of the kneed

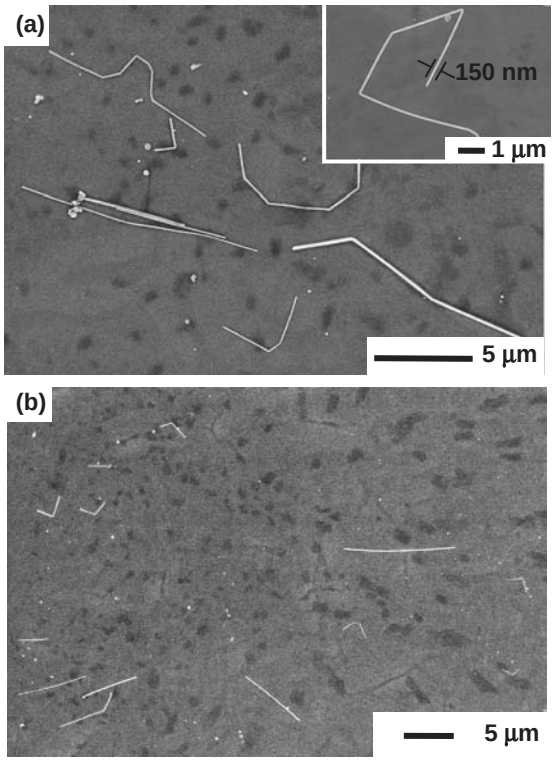

Figure 2. SEM image of gold particles obtained by initial mixing of the $HAuCl_4$ and PVP solutions by (a, b) 0.03 mL and (c) 0.05 mL.

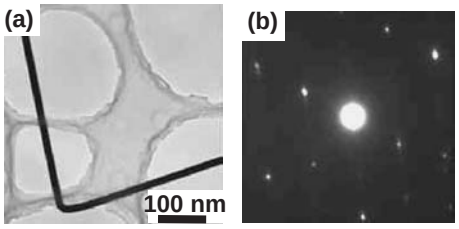

Figure 3. (a) TEM image and (b) SAED pattern of an individual kneed nanowire. The black line in TEM image indicates the kneed nanowire obtained by initial injection mixing of the $HAuCl_4$ and PVP solutions (0.03 mL, respectively).

nanowires appeared around 604 nm. The spectrum was shifted to long wavelength by ca. 50 nm compared to typical reflection position for spherical gold particle. This is due to plasmon resonance from the growth to the nanowires with long length and large scale.

From a series of experiment, when reaction temperature is 145 °C, belt-like particles are formed. Conversely, rod-like particles are major at above 165 °C. These results suggested that shape evolution should be a kinetically controlled growth.

The formation mechanism of the kneed nanowires is assumed as follows. During the processing, nanometer-sized gold particles are formed preferentially by the initial injection, and play a role as seed to grow to nanowires. Subsequently, a small number of gold particles is formed by continuously

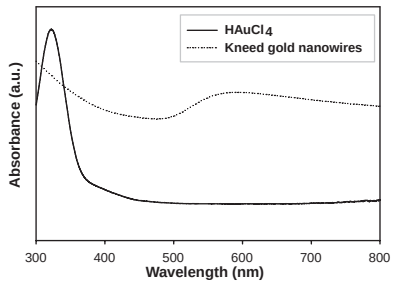

Figure 4. UV–vis absorption spectra of $HAuCl_4$ solution and the kneed gold nanowires obtained by initial mixing of $HAuCl_4$ and PVP solutions by 0.03 mL.

dropping the $HAuCl_4$ and PVP solutions. Continuous dropping helps to digest small gold particles by seed particles. For the role of PVP, PVP molecules could selectively adsorb on various facets of gold through Au–O and Au–N coordination bonds. The selective adsorption of PVP on gold faces affects the crystal growth direction.[8] The nanowires may grow along (111) growth direction via gold diffusion. The strong adsorption of PVP molecules on the (100) surface and the gold atoms may prefer to diffuse to the ends of nanowires owing to their higher chemical potential and reactivity.[9]

In summary, the fabrication of anomalous morphology of the kneed nanowires was strongly influenced by basis of the injection method applying the initial addition and appropriate dropping rate. PVP plays a critical role to lead anisotropic growth. And the initial mixing under adequately precise condition induces to kneed nanowires through secondary nucleation from continuously delivered starting solutions.

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