New approach to preparing one-dimensional Au nanowires utilizing a helical structure constructed by schizophyllan†‡

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Three methods for the preparation of Au nanowires using SPG as a template are presented: in particular, the reshaping of 1D-aligned Au nanoparticles linked to the SPG structure yields 1D-aligned Au nanowires using chemical reduction after photo-induced dissociation, and this new method is very powerful for creating continuous Au nanowire structures.

1. Introduction

A recent challenge in nanotechnology is the preparation of metal nanowires that could act as circuitry components in future nanoscale devices.[1] In particular, Au nanowires have attracted a great deal of interest because of their excellent electrical conductivity and stability in oxidizing environments.[2] So far, several methods for the creation of Au nanowires have already been reported. Examples include those based on surfactant-directed growth from spherical seeds, sacrificial silver nano-objects or those made using porous materials as templates.[3]

Biomolecules exhibit various unique higher-order structures, so that some of them should act as fascinating templates for creating nanowires.[4] In particular, DNAs and proteins have been regarded as the most attractive templates because of their unique self-assembling capabilities in addition to their well-regulated higher-order structures. Those properties cannot be easily replicated by artificial polymers or molecular assemblies. In fact, the recognition capabilities inherent in DNAs or proteins have been incorporated into nanodevice structures to sense specific chemical species or to align nanocomponents.[5] Although patterning DNA and protein-assembled nanowires in device conformations is relatively straightforward due to their robust and reproducible recognition functions,[6] it is necessary for those nanowires to be conductive in order to function as electronic devices and sensors.[7]

Schizophyllan (SPG) is a natural polysaccharide produced by the fungus *Schizophyllum commune* and it shows considerable anti-cancer activity in xenograph models and clinical practice. Its repeating unit consists of three β-(1-3)-glucoses and one β-(1-6) glucose side chain linked at every third main-chain glucose (Fig. 1).[8] SPG adopts a triple helix (t-SPG) in nature, but can be dissociated into a single chain (s-SPG) by dissolving in polar organic solvents such as dimethyl sulfoxide (DMSO).[9] The s-SPG chain can revert to the original triple helix by exchanging the organic solvents for water. It is already known that the 2-OH side along the main-chain glucoses is more hydrophobic, whereas the 6-OH or the side glucose face is more hydrophilic.[10] Therefore, one may imagine that a one-dimensional hydrophobic cavity is created inside the SPG triple helix, like a one-dimensional cyclodextrin array. Taking these unique properties of SPG into consideration, we have demonstrated that when the renaturing process from s-SPG to t-SPG is carried out in the presence of hydrophobic polymers such as carbon nanotubes,[11] poly(aniline),[12] poly(thiophene)[13] and poly(silane),[14] they can be entrapped in the cavity with the aid of hydrophobic forces to give water-soluble one-dimensional composites. Recently, we found that Au nanoparticles can also be aligned in a one-dimensional architecture by wrapping them in the helical structure constructed by SPG.[15] One may expect that if this one-dimensional architecture of Au nanoparticles is melted, they would fuse to one another, leading to the creation of Au nanowires.

Several schemes for the creation of Au nanowires have been reported utilizing chemical reduction of $HAuCl_4$ in the presence of an anionic one-dimensional template, onto which Au ions can be deposited by electrostatic interactions.[16] An alternative is to use a one-dimensional Au nanoparticle array. It is

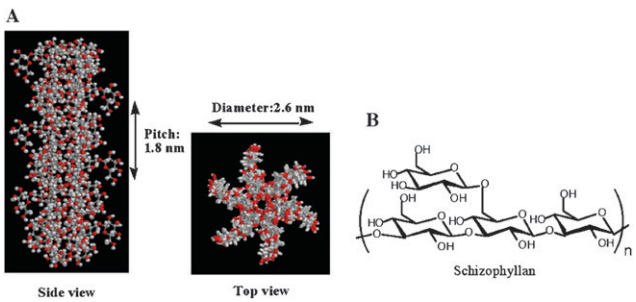

Fig. 1 Calculated models of schizophyllan (SPG) triple helix (A), repeating units of SPG (B).

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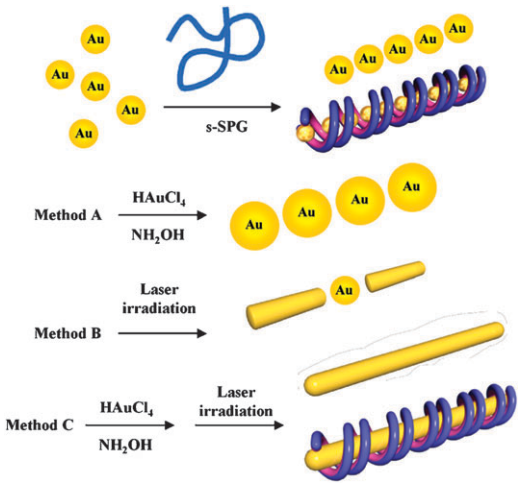
† Dedicated to Professor George Gokel on the occasion of his 60th birthday.
‡ The HTML version of this article has been enhanced with additional colour images.



Scheme 1 The conceptual process for creation of Au nanowires from 1D-aligned Au nanoparticles.

expected that irradiation of near-IR light on the nanoparticle array would induce the fusion of neighbouring Au nanoparticles,[17] leading to the creation of Au nanowires. It is well-known that photoinduced dissociation using near-IR light of functional molecules from complexes can constitute a core technique for active drug- or gene-delivery systems because it is essential to minimize the damage of biofunctional materials, such as proteins, DNA and antibodies.[18]

Herein, we focused our attention on the transformation of one-dimensional Au nanoparticles created with the aid of SPG into Au nanowires, where we expected that SPG would act not only as a one-dimensional template for preorganization of the Au nanoparticles but also for facilitation of Au nanoparticle fusion. An important goal of the present work is the use of high information content molecules and nanoparticles to self-assemble and self-organize nanowire interconnects using near-IR light followed by chemical reduction of $HAuCl_4$ in solution. This is a new method by which Au nanowires are formed under visual monitoring (Scheme 1).

2. Experimental

Materials

SPG was kindly supplied by Mitsui Sugar Co., Japan. The molecular weight and the number of repeating units were evaluated to be 1.5×10^5 and 231, respectively. Dimethyl sulfoxide (DMSO) was obtained from Kishida Chemical Co. and used for all experiments without further purification. Au nanoparticles (5 nm diameter) were purchased as an aqueous solution of bare gold nanoparticles (without surfactant stabilizer; BB International). TEM images were acquired using JEOL TEM-2010 (acceleration voltage: 120 kV). The TEM grid was dried under reduced pressure for 6 h before TEM observation. AFM images were acquired in air using a Topo METRIX SPM 2100 (noncontact mode). The sample was cast on mica and dried for 6 h under reduced pressure before AFM observation.

Preparation of one-dimensionally aligned Au nanoparticles

An aqueous solution of dispersed Au nanoparticles was mixed with a DMSO solution containing s-SPG ($M_w = 150\,000$). At this stage, the mixed solution consisted of 2 mL of the aqueous solution containing Au nanoparticles (1250 particles with 5 nm diameter) and 400 μL of the DMSO solution containing polysaccharide (50 mg mL^{-1}). The mixture was centrifuged (9000 rpm) for 1 h and the supernatant which contained unreacted s-SPG and Au nanoparticles was pipetted off. The precipitated SPG-Au composites were separated and then dispersed into fresh water (1.6 mL). Repeating this process three times, excess s-SPG was removed and the solvent was replaced by water.

Preparation of Au nanowires using method A (chemical reduction)

The resulting aqueous solution containing the SPG–Au composites (5000 particles per mL, 2.0 mL) was then treated with $HAuCl_4$ (1.0 M, 1.0 mL) and hydroxylamine (NH_2OH, 1.0 M, 1.0 mL) at room temperature for 20 s. The resultant solution was dialyzed with distilled water through a cellulose membrane (molecular weight cut-off (MWCO) = 500). By this dialysis process excess $HAuCl_4$ and NH_2OH could be removed completely.

Preparation of Au nanowires using method B (photoinduced dissociation)

The solution containing the 1D-aligned Au nanoparticles was irradiated by the fundamental light of a Q-switched Nd:YAG laser (Continuum Surelite I, 532 nm, pulse duration: 5–7 ns, beam diameter: ~6 mm). The YAG laser irradiation was conducted in a 1.0 cm quartz cell containing 2.0 mL of the solution for 5 min.

Preparation of Au nanowires using method C (photoinduced dissociation followed by chemical reduction)

The solution containing the 1D-aligned Au nanoparticles was irradiated by the fundamental light of a Q-switched Nd:YAG laser (Continuum Surelite I, 532 nm, pulse duration: 5–7 ns, beam diameter: ~6 mm). The YAG laser irradiation was conducted in a 1.0 cm quartz cell containing 2.0 mL of the solution for 5 min. After laser irradiation, the resulting aqueous solution containing the laser-induced fusion of Au nanoparticles (5000 particles per mL, 2.0 mL) was treated with $HAuCl_4$ (1.0 M, 1.0 mL) and hydroxylamine (NH_2OH, 1.0 M, 1.0 mL) as a reducing agent for 10 s. The resultant solution was dialyzed with distilled water through a cellulose membrane (MWCO = 500).

3. Results and discussion

One-dimensionally aligned Au nanoparticles

We first studied whether SPG interacts with Au nanoparticles. To obtain evidence that SPG interacts with Au nanoparticles, the morphology of the composite was analyzed by TEM and AFM. From the TEM image shown in Fig. 2(a), we can identify that Au nanoparticles exist in a one-dimensional alignment, suggesting that the wrapping by s-SPG forces the

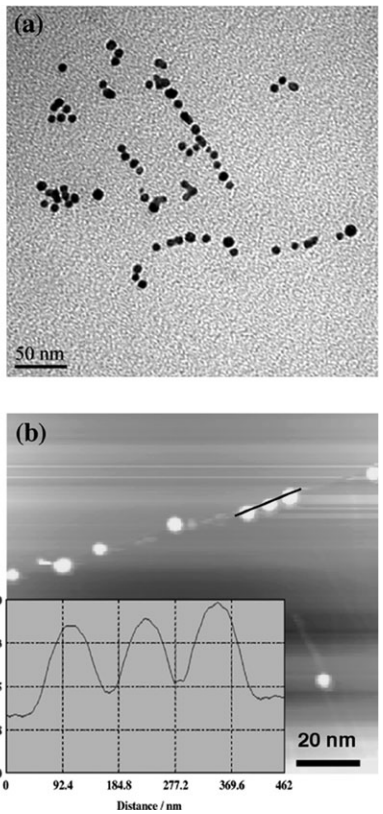


Fig. 2 TEM (a) and AFM (b) images of the SPG–Au composite.

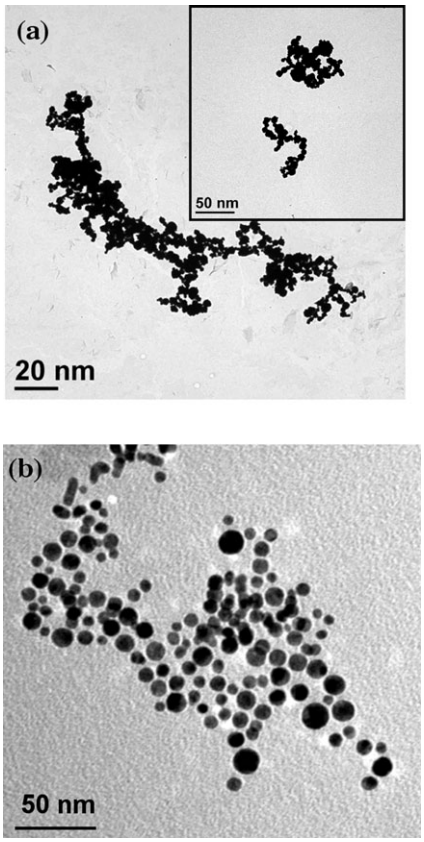


Fig. 3 TEM images of the samples prepared by chemical reduction of $HAuCl_4$ (method A); (a) in the presence of SPG and (b) in the absence of SPG.

Au nanoparticles to arrange into a linear chain. By AFM observation, we can recognize the presence of fibrous structures of *ca.* 6–7 nm in height, which is higher than that of SPG chains themselves (*ca.* 1 nm) (Fig. 2(b)).[15] The result clearly establishes that this unique morphology is created by the Au nanoparticles included in the SPG helical structure.

Attempt to create Au nanowires using method A (chemical reduction)

For creating Au nanowires, chemical reduction of $HAuCl_4$ has frequently been utilized, where $HAuCl_4$ is treated with an appropriate reducing agent in the presence of an anionic one-dimensional template. Our sample was prepared according to method A by treating with $HAuCl_4$ and NH_2OH (for details, see Experimental section). TEM images of the solutions obtained are shown in Fig. 3. The TEM pictures were taken without staining, so that the image would clearly show only the Au nanoparticles. Fig. 3(a) indicates that each Au nanoparticle was increased in size without connecting to its neighbours. The resultant particles have a diameter ranging from 10 to 50 nm, which is consistent with the dimensions expected from the enlargement of the nanoparticle seeds (5 nm diameter). As a reference experiment, we also reduced $HAuCl_4$ in the presence of nanoparticles but in the absence of SPG. In the absence of SPG, we can confirm that the enlarged Au nanoparticles are arranged randomly on the grid without the nanowire-like image (Fig. 3(b)). From these results, we learned that the procedure to yield a continuous Au nanowire using method A suffers from several limitations; that is, $HAuCl_4$ is selectively reduced on the Au nanoparticles, which cannot cause the one-dimensional fusion of Au nanoparticles but only the spherical growth of Au nanoparticles.

Attempt to create Au nanowires using method B (photoinduced particle fusion)

Next, we focused our attention on photoinduced dissociations of Au nanoparticles using near-IR light. The solution containing the 1D-aligned Au nanoparticles was irradiated by the fundamental light of a Q-switched Nd laser for 5 min. The photoinduced morphological change was evaluated by TEM observations. Fig. 4(a) shows a TEM image of the solution after irradiation (5 mJ per pulse, 5 min). As can be seen in the TEM image, the Au nanoparticles are changed into a nanowire-like structure although the continuity is not perfect. As a reference experiment, we prepared a sample without SPG according to the same procedure. However, we could not recognize any significant structure as observed for the s-SPG–Au composite (Fig. 4b). This indicates that the alignment of Au nanoparticles by added SPG facilitates the laser-induced fusion of Au nanoparticles. As one can see from Fig. 3(a), however, the final morphology cannot not satisfactorily be called a "nanowire" because of the presence of several gaps. Thus, we can conclude that laser irradiation of the 1D-aligned Au nanoparticles array is useful but not so powerful as to create complete nanowire structures.

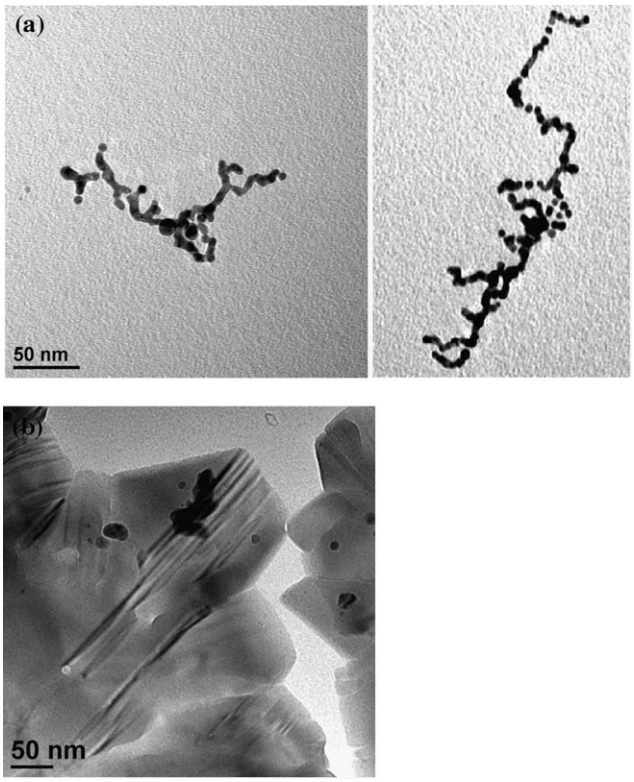


Fig. 4 TEM images of the samples prepared by pulse-laser irradiation; (a) in the presence of SPG and (b) in the absence of SPG.

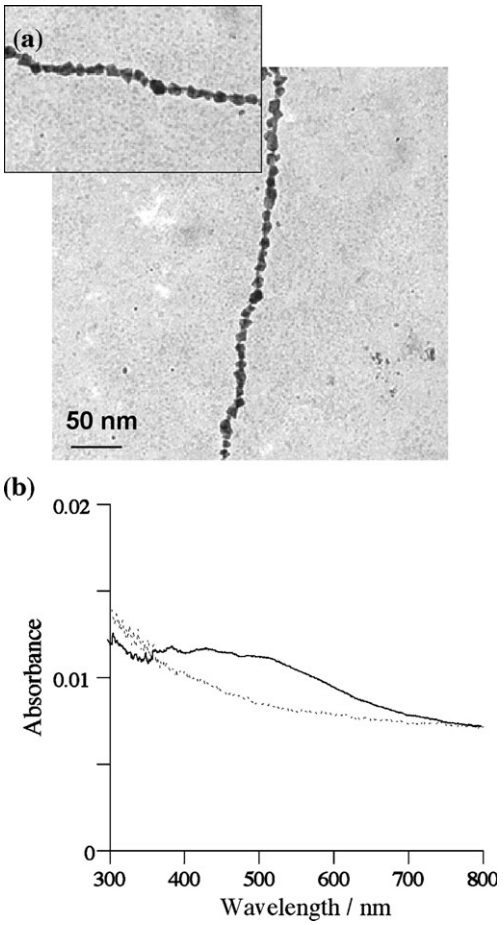


Fig. 5 (a) TEM images showing formation of continuous nanowires and (b) UV–Vis spectra of Au particles aligned by SPG (solid line) and Au nanowires created using chemical reduction of $HAuCl_4$ after pulsed-laser irradiation in aqueous solution at 25 °C; 5 min, 5 mJ per pulse, 532 nm (broken line).

Attempt to create Au nanowires using method C (photoinduced particle fusion followed by chemical reduction)

Here, we expected from method B that if the composite consisting of both disconnected fibers and unreacted Au nanoparticles was treated with $HAuCl_4$ in the presence of NH_2OH, the complete wire structure might be created by filling up the crevice. To test this idea, the solution was first laser-irradiated and then treated with $HAuCl_4$ and NH_2OH, according to the same procedures described above. To evaluate the validity of method C, the morphology of the composite was directly observed by TEM. Fig. 5(a) shows a TEM image of one-dimensional Au nanowires obtained by method C. As can be seen in the TEM image, the isolated Au nanoparticles were no longer present, but changed into apparently continuous Au nanowires. These TEM images are assignable to a morphological change of one-dimensional aligned Au nanoparticles into Au nanowires. We further confirmed the formation of a continuous Au nanowire by using the UV absorbance spectrum. As shown in Fig. 5(b), the obtained solutions show remarkably reduced surface plasmon (SP) bands around 525 nm in the near-IR region, and almost complete disappearance of the SP bands. This spectral change is also assignable to the laser-induced reshaping of aligned Au nanoparticles into interconnected Au nanowires.[10]

Conclusion

We have found that morphological changes of one-dimensionally aligned SPG–Au composites induced by 532 nm laser irradiation could trigger the fusion of Au nanoparticles to prepare discontinuous Au nanowires. Furthermore, using both the near-IR irradiation and a reducing agent led to continuous Au nanowires. It is already reported by us that chemically modified SPG can also act as a 1D template for the creation of Au nanoparticle arrays, where the composite can be easily functionalized through the functional groups introduced into the side glucose groups of SPG.[15] This capability opens up new possibilities not only for novel sensor systems but also for applied electronics, such as patterning the metallization in solution for nanocircuits, which was previously very difficult.

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