

Polymer Chain-Guided Arrangement of Gold Nanoparticles

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Here we show a new method for arranging Au nanoparticles along polymer chains. The method contains a polymer complex formation between a thiolated poly(ethylene oxide) chain bound on the Au surface and the added polymers. When poly(acrylic acid) was added, the Au particles formed a network arrangement. The Au particles lined up excellently when a rigid chondroitin sulfate c sodium salt was added to the solution.

One of the aims of nanotechnology is to control the size and morphology of nanoparticles and nanostructured materials, and another aim is to fabricate them in an ordered structure. Various organized surfactant assemblies and polymer films have been used for these purposes.^{1,2} Further miniaturization of such materials is a key demand, and new bottom-up methods to produce nanowires are required. M. P. Pileni and coworkers prepared a copper network from copper dodecyl sulfate solution.^{1,3} If it is possible to place or form electrically conducting metal nanowires at desired places on a solid surface, it will certainly be a breakthrough technology for the nanocircuit. Metal nanowires have been attracting attention in that sense. M. Brust and coworkers reported templated gold nanowire self-assembly on carbon substrate,⁴ and D. Fitzmaurice and coworkers studied carbon nanotube templated self-assembly.⁵ The latter authors obtained gold nanowires by thermal processing of aligned nanoparticles at 300 °C. DNA-templated preparations of nanowires were also studied by W. E. Ford and coworkers⁶ and T. E. Mallouk and co-workers.⁷

When we attempt to transform nanoparticles to nanowires, the first difficulty we encounter is the colloidal agglomeration of metal particles in solvent. The method most often used to avoid this has been to cover the Au surface with various commercially available alkyl mercaptanes⁴ immediately after the Au particles are prepared. Because most long-chain mercaptanes are water-insoluble, most investigations using mercaptane-protected Au nanoparticles are conducted in organic solvents such as toluene. However, the Au nanoparticles are usually prepared by the reduction of water-soluble HAuCl₄. Therefore, the use of water-soluble mercaptanes to protect Au in water may be desirable because it allows us to avoid harmful organic solvents in the preparations of Au particles or wires. Yonezawa and coworkers reported an arrangement of cationic surfactant-protected Au nanoparticles on DNA.⁸ They used the electrostatic interaction between cationic surfactant/Au and anionic DNA.

In this report, we utilized thiolated poly(ethylene oxide)s (PEGSH) of various molecular weights to protect Au nanoparticles prepared in aqueous solutions. Since the PEGSHs are water-soluble and electrically neutral, we do not need to worry about the excess electrostatic repulsion between the particles.

The PEGSHs were prepared by thiolation of the corresponding poly(ethylene oxide)s (PEG) using previously reported methods.⁹⁻¹¹ Poly(ethylene glycol) (PEG) of molecular weights

(MW) 300, 600, 1000, 2000, 4000 and 6000 was used. Poly(acrylic acid) (MW: 450,000) was the product of Poly-science Inc., USA. Chondroitin sulfate C sodium salt (MW: 10,000–15,000) was purchased from Wako Chemicals Co., Japan. All other chemicals were of guaranteed reagent grade. Au nanoparticles were prepared by the reduction of HAuCl₄ with sodium citrate. The color of the solution changed from yellow to reddish. A JEOL 2010 transmission electron microscope (TEM) was used to obtain electron micrographs of the nanoparticles.

The influences of the PEGSH on the agglomeration of Au nanoparticles were studied first. After the Au nanoparticles were prepared in water, various PEGSH solutions were added to this solution, and their transmission electron micrograms (TEM) were taken. Contrary to our expectation, it became clear that the addition of PEGSH at a low molecular weight, such as PEGSH300, promoted the colloidal flocculation and fused some of the nanoparticles. This may be attributable to bridging of Au particles by PEGSH molecules or to the reaction between two free SH groups of PEGSH on the neighboring Au particles to disulfide, because the collision of SH groups of PEGSH with short chain lengths is highly probable. On the other hand, the PEGSH of high molecular weight prevented the agglomeration of the Au nanoparticles, as is shown in the figures below. This may be due to long and flexible PEGSH molecules bound on the Au particles. The mean distance between Au particles in the aggregates increased with the molecular weight of PEGSH, but it became almost constant when the molecular weight is larger than 1,000. This may be explained by the decrease in the amount of PEGSH bound on Au surface with the increase in the molecular weight of PEGSH. It is then apparent that PEGSHs with high molecular weight are necessary to stabilize Au nanoparticles in water.

We next studied the influences that other polymers known to interact with PEG chain have on the PEGSH-covered Au nanoparticles.

Poly(acrylic acid) (PAA) is well known to form a polymer complex with poly(ethylene oxide) through hydrogen bonding.¹² After PEGSH was added to Au colloid, PAA was introduced. Increasing the molecular weight of the PEGSH made the group of Au particles thinner and longer. When PEGSH2000 was used, an interesting network was observed (Figure 1). Most particles were separated from each other by PEGSH2000 as mentioned above, but their group formed networks. The interaction between PEGSH and Au, as well as that between PEGSH and PAA, must have gathered Au particles near the long PAA chains. PEGSH might have served as an adhesive agent or a mediator between Au and PAA. However, the exact reason for this network arrangement of the particles is unknown at this stage. Some kinds of dissipative structure may have been formed in the course of drying on the TEM grid. Further detailed study is needed.

Next, the influence of chondroitin sulfate c sodium salt (NaCS) on the PEGSH-covered Au nanoparticles was studied.

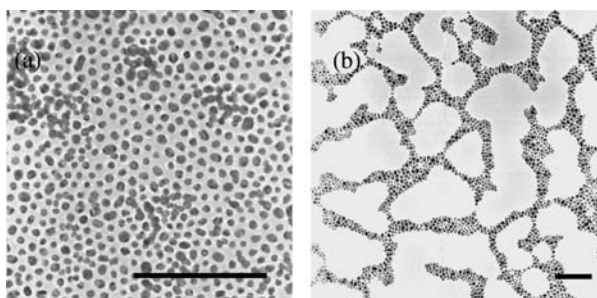


Figure 1. TEM images of Au particles covered with PEGSH2000 in the absence (a) and presence (b) of PAA. $[\text{HAuCl}_4] = 1.0 \times 10^{-5} \text{ M}$, $[\text{PEGSH2000}] = 1.0 \times 10^{-3} \text{ M}$, $[\text{PAA}] = 3.1 \times 10^{-6} \text{ M}$ (based on monomer unit). The bars are 200 nm.

NaCS is a polysaccharide carrying sulfuric acid groups and carboxylic acid groups, which are expected to interact with the PEG chain. NaCS is thought to have a very rigid main chain with a straight conformation because the main chain is composed of bulky 6-membered rings. Figure 2 shows an interesting and clear TEM image of arrays of Au particles arranging in almost straight lines. Moreover, the lines are separated. Though we cannot see the organic polymer chains, this arrangement of particles is thought to reflect the rigid conformation of NaCS. Judging from the molecular weight of NaCS, the length of NaCS chain can be estimated to be 30–40 nm. The linear arrangement of Au particles in Figure 2 cannot be due to a single NaCS chain, but maybe to a long polymer complex formed between NaCS and PEGSH molecules.

In summary, thin or linear arrangements of Au nanoparticles on TEM grid were observed. The arrangement of the particles was 2-dimensional on a solid surface, which is quite different from the results of A. K. Boal and coworkers who observed 3-dimensional assemblies of Au particles in solution.¹³ If it is possible to heat the system to 300 °C without destroying the arrangement on a solid surface, it may be possible to convert the arrays of the Au nanoparticles to nanoribbons or nanowires.^{4,5}

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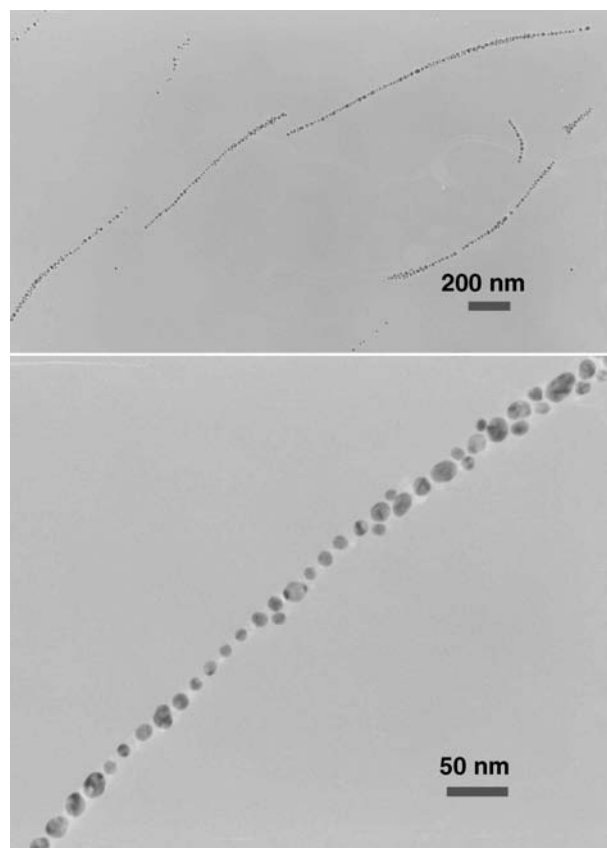


Figure 2. TEM Images of Au particles covered with PEGSH2000 observed in the presence of NaCS. $[\text{HAuCl}_4] = 1.0 \times 10^{-5} \text{ M}$, $[\text{PEGSH2000}] = 1.0 \times 10^{-3} \text{ M}$, $[\text{NaCS}] = 1.0 \times 10^{-6} \text{ M}$.

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