

One-step preparation of positively-charged gold nanoraspberry

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Self-assembling particles were prepared by a new synthetic strategy for a raspberry-like aggregate, based on three-dimensional particle–aniline oligomer–particle repeated sequences; this one-step process, without the need for extra control, organic solvents, or ligand exchange, could further help in the realization of nanoscale electronics and molecular devices.

Metal nanoparticles are of fundamental interest to many researchers because of their controllable grain diameter and their potential applications in emerging areas of nanotechnology due to their unique electronic and optical properties.^{1–3} Their distinguishing shapes and combinations, such as nanobarcodes, nanorods, and nanowires, produce unique functions which are never found with bulk metals.^{4,5} The building of structures in a particle-by-particle fashion simultaneously organizes many particles into self-assembled materials whilst satisfying the requirement for easy control of their chemical reactivity and interparticle connectivity on a single-particle level.⁶

Creating a functionality on the surface of a nanoparticle is desirable for the purpose of particle handling and the construction of functional architectures, however, it is intractable and unavailable due to the necessity of multistep-processing. Gold nanoparticles prepared by ligand exchange, such as cationic thiols, can usually be formed by the following closely-controlled two-step protocol: gold nanoparticles (AuNPs) are synthesized at the aqueous/organic solution interface, and then covered with a thiol molecule in organic media (1st step). The passivation layer is exchanged or modified in a functional compound solution for time periods of over 10 hours (2nd step).^{6–10} The layer thus treated, however, provides only a low-density coverage of functional molecules on the surface of the nanoparticles, so that the nanoparticle must be modified with alkylthiols before the first step.

To construct nano-superstructures, it is necessary to develop nanoparticles as a functional accessory, having not only the desired size, but also a specific reaction and interaction sites with a template molecule. We now present a simple preparation method for positively-charged AuNPs *via* a one-step process without the need for extra control, organic solvents, or ligand exchange. Moreover, the AuNPs have an interesting raspberry-like configuration as a building block for nanoarchitecture. Novel positively-charged AuNPs were prepared using a reducer such as aniline. The simple preparative procedure was as follows. An aqueous aniline solution was added to a 0.03% chloroauric acid aqueous solution

(200 mL), and stirred at 65 °C for 30 min. The resulting solution was then centrifuged at 8500 rpm at 5 °C. The first supernatant was removed. The precipitate was again redispersed in 30 mL of ultrapure water, and then the dispersion was centrifuged using the same conditions described above. These procedures were repeated three times. The resulting precipitate, not including any unreacted species, was stored in a glass bottle at 5 °C. The resulting dispersion was characterized by its zeta potential, submicron particle size analysis, and field emission transmission electron microscopy with an accelerating voltage at 200 kV. The surface of the resulting AuNPs after being dropped and dried on mica was characterized by atomic force microscopy in the tapping mode. Electrical measurements of the AuNPs were carried out as follows: a 20 μ L AuNP dispersion (0.42 g L⁻¹) was dropped onto a comb-shaped Pt microelectrode (2.6 mm², NTT-AT, Japan), and then dried under vacuum for 60 min at 40 °C. The resistance was monitored using a digital multimeter (34970A, Agilent) in the standard two-probe configuration at 25 °C (33% RH).^{11,12}

Fig. 1 shows the TEM image of AuNPs prepared using 5.5 \times 10⁻⁴ mol aniline as a reducer. Above 5.5 \times 10⁻⁵ mol of aniline, a raspberry-like aggregation of AuNPs was formed that possessed a 1.5 nm-mean particle diameter with a 0.23 nm standard deviation. It is well-known that the diameter of a nanoparticle strongly depends not only on the reaction time and temperature, but also on the mixture ratio of the reactants, *i.e.*, aurate and the reducer. Particles synthesized by aniline reduction are a nearly dispersed agglomeration consisting of spheres size-controlled by the initial concentrations of aurate and the reducer. An increase in the amount of reducer leads to a decrease in the diameter of the AuNPs.¹³ The aggregation, consisting of the aurum element determined by elemental analysis, was covered by a misty passivation layer (*ca.* 4.0 nm).

The *in situ* UV spectral analysis followed the time course of the preparation process of the AuNPs in a UV quartz cell. The solution mixture of aurate and aniline was allowed to stand with stirring at 65 °C. During the first stage, the orange-pink colored solution mixture had an absorption at 485 nm, which was attributed to the original color of the respective components and surface plasmon resonance. While a gradual red shift in the peak intensity to 553 nm was observed, a new peak at 700 nm occurred and increased after 20 min. This means that the aurate was reduced to aurum by the aniline, while aniline was oxidized to an oligomer by the aurate, along with the rising temperature. Aggregation was revealed by the thick figure in the AFM observation.

A typical spectrum of AuNPs, prepared with an excess of 5.5 \times 10⁻⁴ mol of aniline over the trivalent aurate, with the molar ratio of 30 (to 1.82 \times 10⁻⁵ mol aurate), after ultracentrifuging and stirring of the resulting aniline–AuNPs in an aqueous 0.1 M

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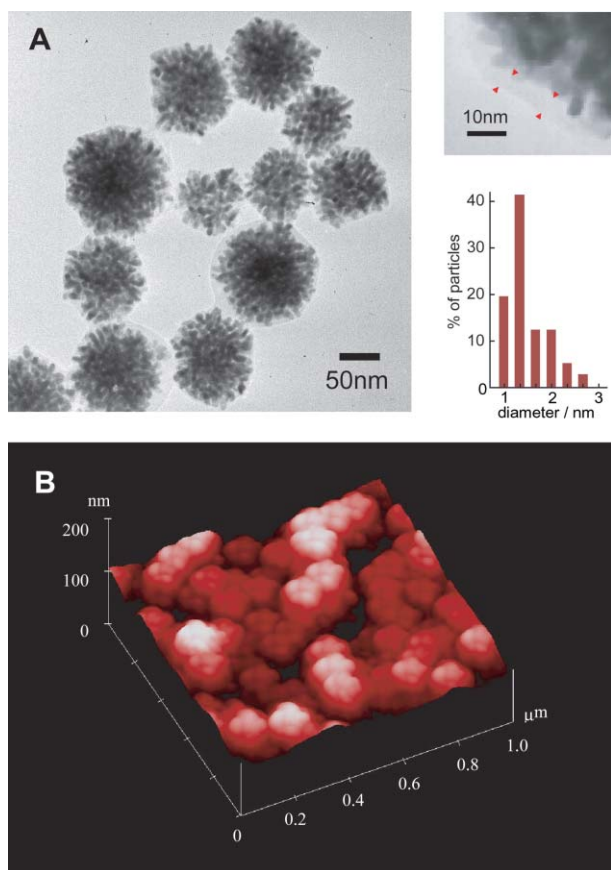


Fig. 1 TEM (A) and AFM images (B) of AuNPs prepared using aniline at the concentration of 5.5×10^{-4} mol after 3 ultracentrifuges at 5°C .

NaOH solution for 12 h, possessed a peak intensity around 543 nm, which was attributable to a surface plasmon resonance that was observed as shown in the inset of Fig. 2a. An about-20 nm red-shift, compared to that of the generally reported AuNPs coated by surfactants (520 nm), indicated, not only that the AuNPs were coated with a monolayer having a larger dielectric

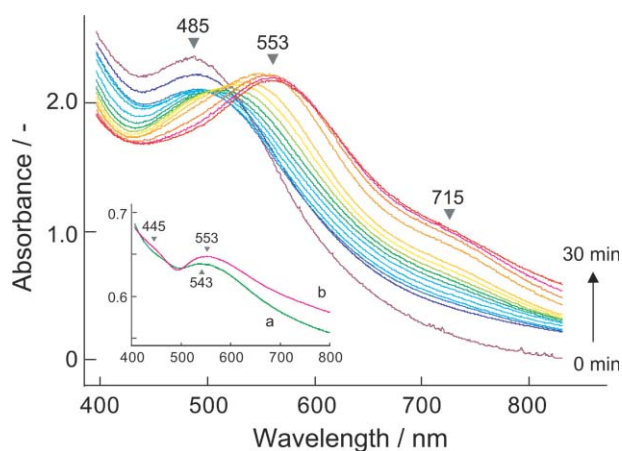


Fig. 2 UV spectra of the production process of AuNPs in a solution mixture of aurate and aniline with stirring at a temperature increasing by 2°C min^{-1} . The inset is the UV spectrum of AuNPs (a) with dedoping in an aqueous 0.1 M NaOH solution, and (b) with doping in an aqueous 0.1 M H_2SO_4 solution after 3 ultracentrifuges.

constant, but also coupling of the surface plasmon between the closely spaced AuNPs, based on the observation of a broadening of the absorbance at 600–800 nm, as reported by Natan *et al.*⁴ Therefore, the broad peak observed at 543 nm would be composed of a few peak intensities due to the oxidized aniline and coupling of the surface plasmon.

To confirm the composition of the passivation layer, the resulting aniline–AuNPs were stirred in an aqueous 0.1 M H_2SO_4 solution for 12 h. New absorbance peaks were observed at around 445 and over 700 nm in curve b. The dispersibility and electrostatic repulsion of the AuNPs hardly changed before (+25.7 mV) and after (+26.8 mV) the doping process. Therefore, the new absorbance peaks that originated at 445 and over 700 nm, which were not based on the aggregation of the AuNPs, were attributable to the localized (cation radical) and delocalized polaron (free-tail), respectively.^{14,15} This observation shows that a structural change in the oligomeric aniline originated in the acid doping, and it was transformed from an insulating base to a conducting salt-type, while the polyaniline did not exist due to the disappearance of the peak intensity at 715 nm observed during the production process stage after the centrifuging. The difference between spectra (a) and (b) was attributed to the absorbance based on the existence of the aniline oligomer. Consequently, a thick aggregation was postulated as follows: a 4.0 nm-thick passivation layer, indicated by the red arrows in Fig. 1, corresponded to the oxidized aniline formed during the reduction of aurate, the size resulting from the calculated molecular length, which was evaluated by MOPAC using the PM3 approximation, with at least an octamer of aniline (4.1 nm), since the pH 4.1 of the solution mixture constitutes a limiting factor for the growth of the polyaniline. It was assumed that interactions, such as π -stacking, of the respective aniline oligomer, coated adjacent to the AuNPs, leads to the raspberry-like aggregation, and therefore, the overlapping of oligomers acts as a polymer, based on the spectroscopic results in Fig. 3A.

The electrical properties of the aniline–AuNPs, cast on a microelectrode and dried under vacuum in Fig. 3B, significantly

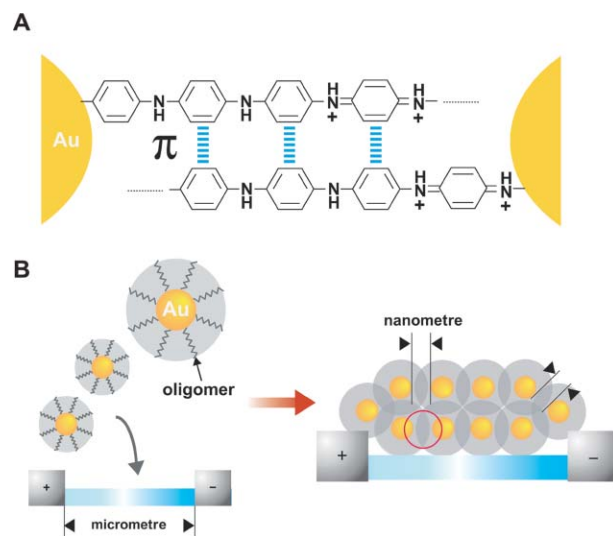


Fig. 3 (A) Illustration of the enlarged view of aniline oligomer between adjacent AuNPs and (B) AuNP film configuration cast on the comb-shaped microelectrode.

changed after the acid doping and dedoping. The doped aniline–AuNPs revealed the good conducting property of $3.1 \times 10^{-2} \text{ S cm}^{-1}$ (as prepared: over $3.2 \times 10^{-8} \text{ S cm}^{-1}$). This is similar to the conductivity of the generally reported salt-type polyaniline.^{16,17} On the other hand, the electrical conductivity of the base-type aniline–AuNPs, dedoped in an aqueous 0.1 M NaOH solution for 12 h, had a dramatically reduced value of over $3.2 \times 10^{-8} \text{ S cm}^{-1}$. This observation means that the molecular bridging of the overlapped aniline oligomers between adjacent AuNPs performs as a nanogap, and sensitively detects the transformation from the conducting (salt-type) to insulating (base) oligomers. Therefore, aniline–AuNPs act as a building block for assembling into a nanosized integrated array system with an easy-fabrication method which uses the simple procedure of dropping the dispersion onto a microelectrode.^{18,19}

In summary, we developed a facile one-step process, without the need for extra control, organic solvents, or ligand exchange, which allows us to obtain positively-charged AuNPs of which the raspberry-aggregation was on a nanoorder level. It is expected that AuNPs prepared using aniline will strongly interact with biomolecules containing carboxylate and phosphate groups. Therefore, this method will also be helpful for investigating and constructing metal nanoparticles, a biomolecule composite and organic polymer materials. Assembling NPs with various properties could help to further realize nanoscale electronics. Especially, the building of aniline–AuNP films on a microelectrode leads to a nanogap electrode, consisting of three-dimensional AuNP–aniline oligomer–AuNP repeated sequences, and it has a significant potential for applications in molecular devices such as chemical, gas, and biosensors.

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