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Nanoscale Soldering of Metal Nanoparticles for Construction of Higher-Order Structures

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Metal nanoparticles exhibiting remarkable size-dependent properties are regarded as important "parts" of nano-devices.[1] To construct the nanodevices from the "parts", it is necessary to interconnect the parts together. In recent years, much endeavor has been invested to align size-selected metal nanoparticles as two- and three-dimensional crystals by taking advantage of interactions between metal nanoparticles covered with ligands.[1h] Evidently, these metal nanoparticles do not have any ohmic contact. On the other hand, networks of copper particles, having ohmic contacts mutually, have been prepared by chemical reduction of a metal salt into metal nanoparticles in a micelle, although the size of the networks is hardly controlled.[1i,j]

In this regard, it is necessary to develop a method of creating ohmic contacts among different metal nanoparticles in a controlled manner. If nanoparticles of one kind possess a strong absorption band whose energy coincides with the photon energy of a laser, the nanoparticles can be heated above the melting point into liquidlike nanoparticles under irradiation of the laser.[2] On the other hand, nanoparticles of the other kind which do not have any strong absorption band in this energy range remain as solidlike nanoparticles even under the laser irradiation. Without doubt, the liquidlike nanoparticles join the solidlike nanoparticles as "nano-solders". Choosing the wavelength of the laser, one can liquify any nanoparticle one desires, in principle. In the present study, we demonstrated the feasibility of this concept to join platinum nanoparticles (solidlike) by gold nanoparticles (liquidlike). Using electron microscopy and optical absorption spectroscopy we investigated the geometrical structures and the formation mechanism of networked nanoparticles.

First we prepared surfactant-free gold and platinum nanoparticles in pure water by laser ablation at 1064 nm of gold and platinum metal plates, respectively, in separate vessels (SF-LAS (surfactant-free formation by laser ablation in solution) method).[3] The optical absorption spectrum of water containing gold nanoparticles thus prepared (denoted as "gold nanoparticle solution" hereafter) exhibits the characteristic peak of the surface plasmon band at 520 nm.[4] The average diameter of gold nanoparticles was obtained by electron microscopy to be ~20.0 nm at the laser fluence of 2.4 J pulse^{-1} cm^{-2}. The concentration of gold atoms present in the solution in the form of nanoparticles was estimated to be 0.30 mM. On the other hand, surfactant-free platinum nanoparticles in water were prepared in a separate vessel under identical conditions. The optical absorption spectrum of the platinum nanoparticle solution shows a structureless broad band extending toward the V−UV wavelength range. The average diameter of the platinum nanoparticles was obtained to be 6.0 nm at the laser fluence of 2.4 J pulse^{-1} cm^{-2}. The concentration of platinum atoms in the form of nanoparticles was 0.35 mM in the present study. After mixing the gold nanoparticle solution with the platinum nanoparticle solution at a given molar ratio, the mixed solution was irradiated with the pulsed laser. In practice, a solution in an optical cell made of silica was illuminated with the second harmonic (532 nm) of a Quanta-ray GCR-170 Nd:YAG pulsed laser operating at 10 Hz, which is close to the wavelength of the surface plasmon peak (~520 nm) of the gold nanoparticles. The laser was focused on a spot as large as 0.023 cm^2 on the solution surface by a lens having a focal length of 250 mm. The laser beam was focused into a small region in the solution so that the number of the gold nanoparticles in the focusing region is limited. Practically, the products by the laser irradiation were homogeneously distributed in the solution by a magnetic stirrer.

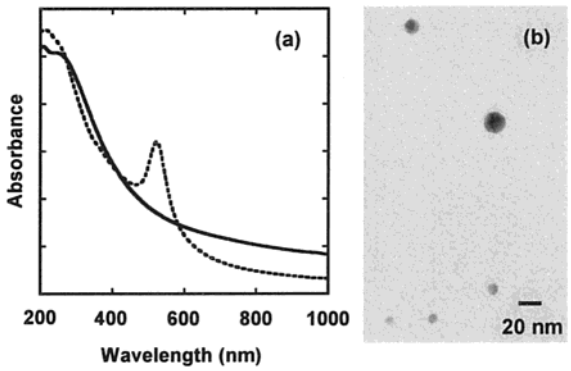

Figure 1. (a) Optical absorption spectra of a mixed solution of gold and platinum nanoparticles produced before (dotted line) and after (solid line) irradiation of a 532-nm laser having the fluence of 2.2 J pulse^{-1} cm^{-2}. (b) Electron micrograph of gold and platinum nanoparticles before laser irradiation.

Figure 1a shows optical absorption spectra of the mixed solution of gold and platinum nanoparticles produced before (dotted line) and after (solid line) irradiation of a pulsed 532-nm laser having the fluence of 2.2 J pulse^{-1} cm^{-2}, where the molar fraction of gold in the solution was 0.36. The absorption spectrum of the mixed solution before the laser irradiation coincides completely with the spectrum obtained by summing the absorption spectrum of gold nanoparticles and that of platinum nanoparticles with the weight of a given molar fraction. In other words, both the gold and the platinum nanoparticles are dispersed in the mixed solution, and no essential change of the nanoparticles takes place by the simple mixing. In fact, electron micrographs of the nanoparticles show that they are spherical and separated from each other (see Figure 1b). On the other hand, in the absorption spectrum of the mixed solution after the laser irradiation, the characteristic plasmon peak of the gold nanoparticles disappears, and instead a tail portion longer than 600 nm is intensified. It is inferred from these spectral changes that the gold nanoparticles are melted to form alloys with platinum;[2h] otherwise, the gold nanoparticles with a diameter of ~20 nm would give a sharp plasmon peak in the absorption spectrum. This inference is actually proven by the electron micrographs of the

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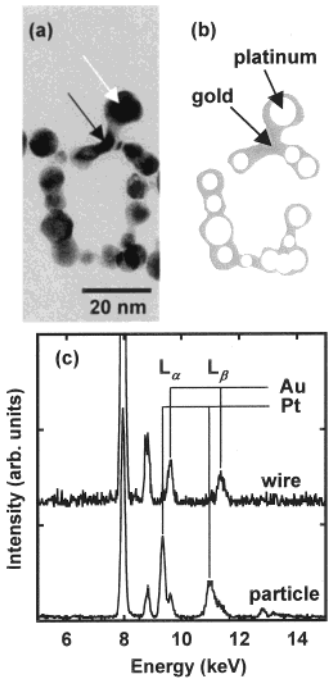

Figure 2. (a) Electron micrograph of platinum and gold nanowebs produced by laser irradiation at 532 nm onto a mixed solution of platinum and gold nanoparticles with a molar ratio of 0.2. (b) Schematic view of the nanoweb shown in panel a. (c) Wavelength dispersive X-ray spectroscopy of a joint and a spherical particle of the nanoweb shown in panel a.

products by the laser irradiation as shown in Figure 2a; joined spherical nanoparticles, "nanowebs", are formed. In addition, the resulting wavelength dispersive X-ray spectroscopy of the nanowebs due to excitation by the electron beam of the electron microscope show that the spherical particles are platinum nanoparticles covered with gold, whereas the joints interconnecting the spherical particles are made of gold (see Figure 2c). The structure of the products (nanowebs) leads us to conclude that gold nanoparticles are melted by the laser irradiation to cover the platinum nanoparticles and to create ohmic joints among the platinum nanoparticles. The nanowebs were found to extend as wide as $0.1-1$ μm.

Under the electron microscope, the nanowebs were found to translate readily on the substrate (collodion-coated copper grid), while maintaining their whole steric geometry. These facts indicate that (1) the nanowebs are not just aggregates of these spherical particles bound by a weak interaction but are jointed strongly together and (2) the nanowebs extend in three dimensions and are weakly held to the collodion substrate.

Optical absorption spectra of the nanowebs at a various molar fractions of gold in the mixed solution show that the tail in the IR region is intensified at an increasing extent as the molar fraction of gold increases. With a further increase, a shoulder at 520 nm appears at the molar ratio of 0.77 and then grows into a distinct peak. The spectra compared with the electron micrographs of the products indicate that the abundance and the length of the nanowebs formed by irradiation of the 532-nm laser increases with an increase in the molar fraction. In addition, spherical gold nanoparticles are included in the nanowebs when the solution contains gold richly. Note that similar nanowebs are formed in water containing only gold nanoparticles. Conversely, complete disappearance of the plasmon peak in a mixed solution of gold and platinum nanoparticles below the molar ratio of 0.56 suggests that pure gold particles do not exist in the solution and that gold and platinum alloy particles are formed by the laser irradiation. The shape of the nanowebs also changes with changing the laser fluence and the number of the laser shots.

When a pulsed 532-nm laser illuminates the mixed solution, only the plasmon band of gold nanoparticles in the solution is excited.[2e−g] The photon energy is transmitted to the internal modes of the nanoparticles as heat. During a single laser pulse, one gold nanoparticle is considered to absorb many photons successively and reaches the temperature as high as the melting point.[2e−g] Gold nanoparticles in the close vicinity of the platinum nanoparticles solder them together as if they acted as "nanosolders". Thus, the nanowebs constructed by the platinum nanoparticles are formed with gold nanojoints. After the single-laser pulse is switched off, the internal energy is transmitted quickly enough to the solution that the nanoparticles are equilibrated with the solution before the next one arrives. The nanoweb formation occurs at every laser pulse. The platinum nanoparticles remain solidlike in the photoexcitation of the gold nanoparticles because the platinum nanoparticles have the optical absorption cross section at 520 nm, smaller by 3 orders of magnitude than gold nanoparticles.

In conclusion, one can prepare, in a controlled manner, nanowebs consisting of platinum nanoparticles soldered by gold under laser irradiation onto a mixed solution of gold and platinum nanoparticles with a proper molecular ratio. The gold and platinum nanowebs thus fabricated should show collective chemical and physical properties and can be employed as promising catalysts, nanoscale electric devices, and so forth.

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