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One-dimensional organization of copper nanoparticles by chemical reduction of lipid-copper hybrid nanofibers

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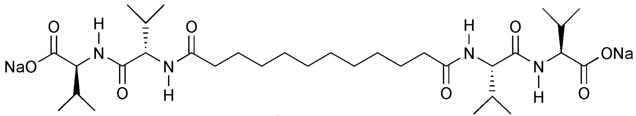
One-dimensional organization of copper nanoparticles has been achieved by chemical reduction using lipid-copper hybrid nanofibers as a template; the reduction of copper ions and the resulting formation of copper clusters occurred at intervals of 2–5 nm along the nanofibers.

Inorganic nanostructures have attracted much attention due to recent exploitation of novel chemical and physical properties as well as potential application as a nanodevice. In particular, a wide variety of studies have allowed us to afford well-defined nanoparticles of metal and semiconductor with limited size distribution.[1–5] Thus, two- or three-dimensional organization of the nanoparticles is now becoming one of the hottest topics in terms of “bottom-up” nanotechnology,[6–9] although there are a few reports on their one-dimensional (1-D) organization. To the best of our knowledge, four kinds of methodology have mainly been developed for 1-D organization, including the linear self-assembly of gold nanoparticles carrying polynucleotide chains,[10] the electrostatic interaction of cation-charged nanoparticles on the anion-charged DNA strand at the air–water interface,[11] template synthesis using mesoporous materials,[12] and the linear assembly of gold nanoparticles at the step edge of amorphous carbon.[13]

We describe here for the first time a novel and facile method for providing 1-D organized copper nanoparticles at intervals of 2–5 nm. To date we have prepared a variety of self-assembled high-axial-ratio nanostructures from peptide lipids.[14] We recently found that peptide bolaamphiphile-copper hybrid nanofibers of 15 nm width and several micrometers long are obtainable through coordination-directed self-assembly in water.[15] The reduction of copper ions using hybrid nanofibers as a template should give 1-D organized copper nanostructures along the lipid layer since these hybrid nanofibers consist of the coordinated copper cations and lipid layers. The reduction with relatively strong reagents like sodium borohydride results in the formation of large aggregates of copper or copper oxide of several hundred micrometers in size. The strong reagents allow a number of copper clusters to induce aggregation of the clusters rapidly. Therefore, we employed hydrazine as a mild reducing agent to avoid the aggregation.

By mixing 2, 20, and 50 mM aqueous solutions of copper acetate and a sodium salt of peptide bolaamphiphile **C(10)[Val$_2$]$_2$**, we prepared colloidal dispersions consisting of lipid-copper hybrid nanofibers. To the dispersions, aqueous solutions of 5–10 equivalents of hydrazine were then added with stirring in an Ar atmosphere. If the concentration of the colloidal dispersions is 1 mM or 10 mM, the copper reduction gives only aggregates of copper or copper oxide. When we employed 25 mM dispersions, we obtained a dark-gray colloid solution which we subjected to transmission electron microscopy (TEM) and energy-dispersive X-ray (EDX) analysis (JEOL 1010).



C(10)[Val$_2$]$_2$

We measured FT-IR spectra of the dehydrated hybrid nanofibers and the dark-gray colloid obtained after reduction. The resulting FT–IR data shows features suggesting that in the dark-gray colloid the copper ions in the original hybrid nanofibers are fully reduced and eventually the sodium salts of the lipids are re-generated. The hybrid nanofibers produce an IR band at 1422 cm^{-1} assignable to the symmetric C=O stretching band of a carboxylate anion, indicating that the carboxylate anions are coordinated to copper(II) ions.[16] The dark-gray colloid obtained after reduction gives an IR band at 1410 cm^{-1}, indicating the absence of coordinated carboxylate anions. The absence of the IR band around 620 cm^{-1} excludes the possibility of copper(I) oxide formation.[17] The obtained dark-gray colloid proved to be very stable even in air for several months, although copper nanostructures are generally known to be easily re-oxidized in air. The protection of the copper nanostructures by sodium salts of the lipid will be responsible for the present stability.

A TEM image and the EDX profile of the dark-gray colloid after reduction are shown in Fig. 1. We found relatively large aggregates, denoted by the arrow A, with sizes ranging from several hundreds of nm to several μm, which coexist with apparently fragile fibrous structures denoted by the arrow B. EDX measurement also supports the co-existence of copper nanostructures with sodium salts of the lipids. The peaks

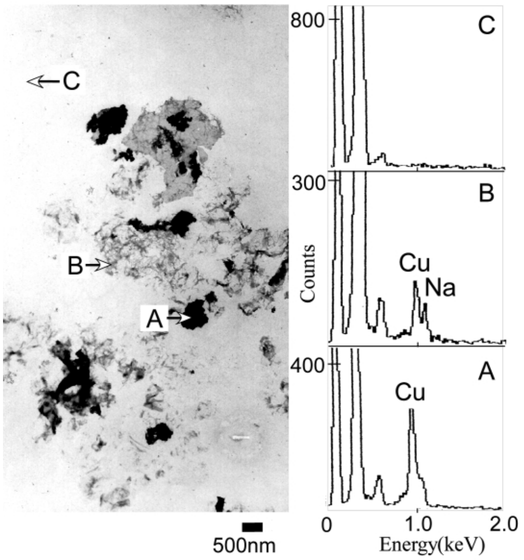


Fig. 1 (a) TEM image of the dark-gray colloid after reduction and (b) EDX profile of the part labelled by A, B, and C.

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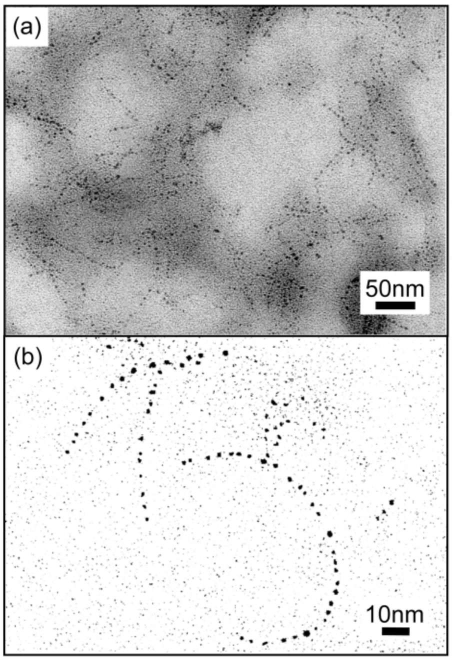

Fig. 2 (a) TEM image of the dark-gray colloid and (b) high-magnification of one-dimensional organization.

corresponding to copper (Cu) can be observable both in the position A and B, but not in position C as a reference. Thus, both the aggregates (A) and the fibrous structures (B) were found to include copper. In addition, position B shows an elemental peak corresponding to sodium (Na). If copper ions coordinating to carboxylates of the lipids are completely reduced, the lipids should require a sodium ion as a counter cation.

High-magnification TEM images of the dark-gray colloid are also shown in Fig. 2. A number of copper nanoparticles of 1–3 nm diameter are observed aligning one-dimensionally along the line of maximum lengths of 200 nm. Interestingly, we found that the distances between the nanoparticles are kept at intervals of 2–5 nm. These copper nanoparticles should be aligned on each nanofiber structure made of the sodium salts of the lipids. Low contrast images around the copper nanoparticles show their existence (Fig. 2a). The fringes can be clearly observable for each nanoparticle and the distance between them is 0.181 nm, corresponding to a (200) face of the copper since bulk copper with fcc lattice shows the lattice parameter a = 0.361 nm.[18]

Fig. 3 indicates a possible formation mechanism for the 1-D organization of copper nanoparticles along lipid-copper hybrid nanofibers. One copper nanoparticle of about 1.5 nm diameter is comprised of 55 copper atoms.[2,19] There would be 15 copper cations along the short axis of the nanofibers 15 nm wide (Fig. 3a) since one copper cation coordinates to two carboxylate anions. Therefore, 60 copper atoms localizing within 15 nm (width) × 2 nm (length) are held together to form copper nanoparticles with about 1.5 nm diameter, forming the 1-D organization at intervals of 2 nm (Fig. 3a,b). This situation is well compatible with the experimental fact that copper nanoparticles of 1–3 nm are aligned at intervals of 2–5 nm.

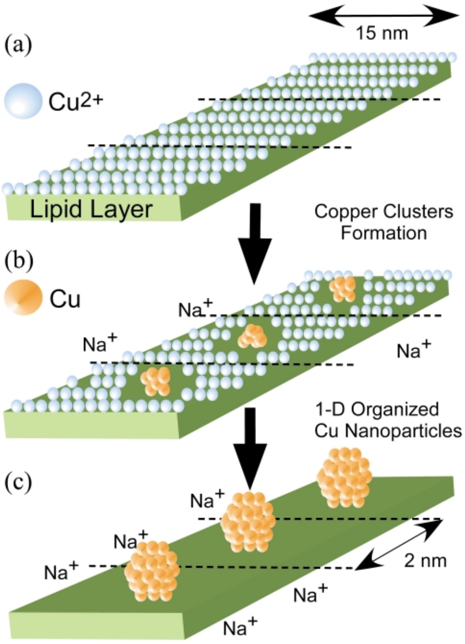

Fig. 3 Schematic illustration of 1-D organization of copper nanoparticles using lipid-copper hybrid nanofibers as a template.

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