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Letters

Convergent Electron Beam Induced Growth of Copper Nanostructures: Evidence of the Importance of a Soft Template

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In a transmission electron microscope, CuCl particles were irradiated by a convergent electron beam (CEB, 200 kV, 200 pA/cm^2, beam diameter of ca. 1−2 μm) to induce growth of copper nanostructures. Upon CEB irradiation, Cu nanoparticles (5−20 nm in diameter) were formed from commercial CuCl. Using synthesized CuCl encapsulated in permethylpolysilane, growth of polycrystalline copper nanowires (50−200 nm in diameter and up to 30 μm in length) was observed. Evolution of Cu nanoparticles from the synthesized CuCl was observed from the positions with apparent incomplete encapsulation. The effect of polymer encapsulation, acting as a soft template, is shown to be important to influence the nanostructure growth. The observation supports the vapor−solid reaction growth model.

In syntheses of one-dimensional metal nanowires, template-assisted solution growth is frequently employed to control the growth.[1] Recently, we developed a new nonsolution reaction strategy, vapor−solid reaction growth (VSRG), to prepare nanosized metals.[2,3] The reaction employed a vapor-phase permethylpolysilane (PMPS) oligomer, such as $(Me_3Si)_4Si$, to reduce a solid-phase halide of Mo, W, and Cu.[2] Controlling the physical shape of the product has been achieved by employing a polymer as the soft template. For example, when $(Me_3Si)_4Si$ was employed to reduce CuCl in the presence of poly(dimethylsiloxane) (PDMS), cablelike Cu nanowires were formed.[3] In this report, we demonstrate the importance of the polymeric soft template in influencing the growth in a solvent-free environment. To show the differences, reduction of CuCl

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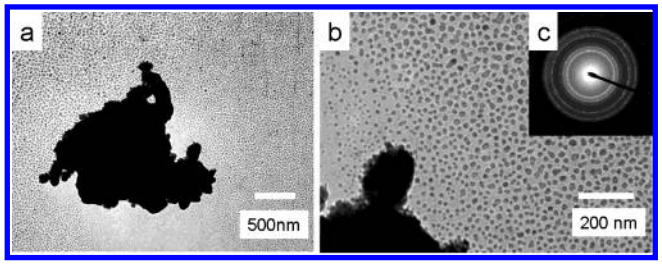

Figure 1. (a) Commercially supplied CuCl particle after direct CEB irradiation (200 pA/cm^2, beam diameter of ca. 1 μm, 30 s). (b) Enlarged view of the selected area in image a. (c) ED pattern of the selected area containing Cu nanoparticles only.

with and without a polymer encapsulation is performed and recorded in situ inside a transmission electron microscope (TEM). The TEM instrument provides an excellent controlled setting for metal complex reduction by electron beam (e-beam)[4] and a platform for direct shape transformation observation.

Dispersed aggregates (0.1−50 μm in diameter) of commercially supplied CuCl particles on a TEM grid were inserted in the TEM for study. A CuCl particle (ca. 2 μm in size) was selected and irradiated under a convergent electron beam (CEB) (200 kV, 200 pA/cm^2, beam diameter of ca. 1 μm). The TEM images of the particle after 30 s of irradiation are shown in Figure 1. Growth of nanoparticles (10−20 nm in diameter) extensively around the CuCl aggregate is observed. From the ring pattern of a selective area electron diffraction (SAED) study of the nanoparticles, Figure 1c, the crystal structure was determined to be cubic with a lattice parameter *a* of 0.36 nm. These results are consistent with the data of Cu metal.[5] The number and the size of the nanoparticles increased after extended irradiation. This e-beam-induced process, a combination of reduction and crystal growth, is analogous to the reduction of CuCl by $(Me_3Si)_4Si$.[2] The growth process can be rationalized by a common model, reduction of CuCl into Cu atoms, migration, coalescence, and nucleation of the atoms into clusters, followed by incorporation of more atoms or clusters into the growing crystals.

In contrast to the above observation, the presence of a soft-template material in the e-beam-induced CuCl reduction shows a significant influence on the nanostructure development. Synthesized CuCl particles (0.1−50 μm in diameter), reduced from $CuCl_2$ by $(Me_3Si)_4Si$, were placed on a TEM grid. Inside the TEM instrument, an area on the grid consisting of two aggregates **A** and **B**, with original diameters of ca. 8 μm each and spaced 1 μm apart, was selected for CEB (beam diameter, ca. 2 μm) irradiation. In Figure 2a, the results of CEB irradiation on **A** and **B** are shown in zones 1 and 2, respectively. The original positions of **A** and **B** are marked as points 1 and 2. After an initial observation, the aggregates were exposed to the CEB together as the beam intensity increased from 30 to 200 pA/cm^2. **A** was irradiated for 30 s at the point marked 1. The image suggests that it transformed completely into nanowires with diameters of 50−200 nm and lengths of up to 30 μm. This differs significantly from the observation in Figure 1 mentioned above. Using energy-dispersive X-ray spectroscopy (EDS), the elemental compositions are determined, as shown in Figure 2b,c. Figure 2b demonstrates that the original **A** before CEB is CuCl, while Figure 2c suggests that the nanowire generated from **A** after CEB is Cu with a very low Cl concentration.

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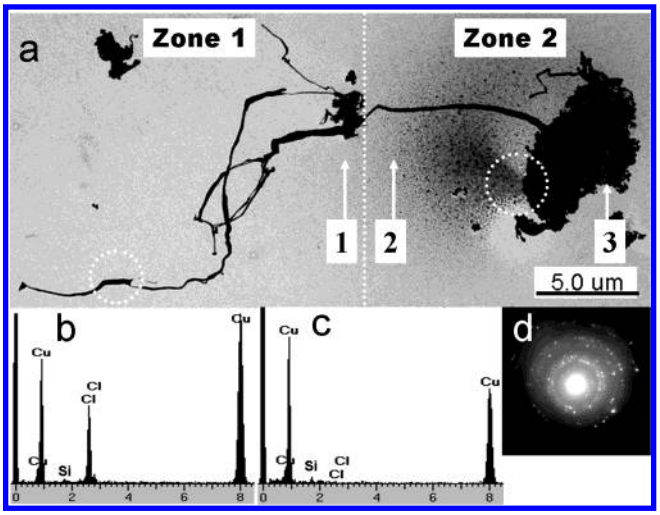


Figure 2. (a) TEM image of synthesized CuCl aggregates **A** and **B** (sizes, ca. 8 μm) after irradiation by the CEB. Points 1 and 2 were the original positions of **A** and **B** and the points of irradiation. **A** was irradiated first to produce nanowires in zone 1. In zone 2, **B** shifted from point 2 to the displayed position at point 3 after irradiation. From the circled area in zone 2, nanoparticles evolved. (b) EDS of **A** before irradiation. (c) EDS of the circled area in zone 1. (d) ED pattern of the circled area in zone 1.

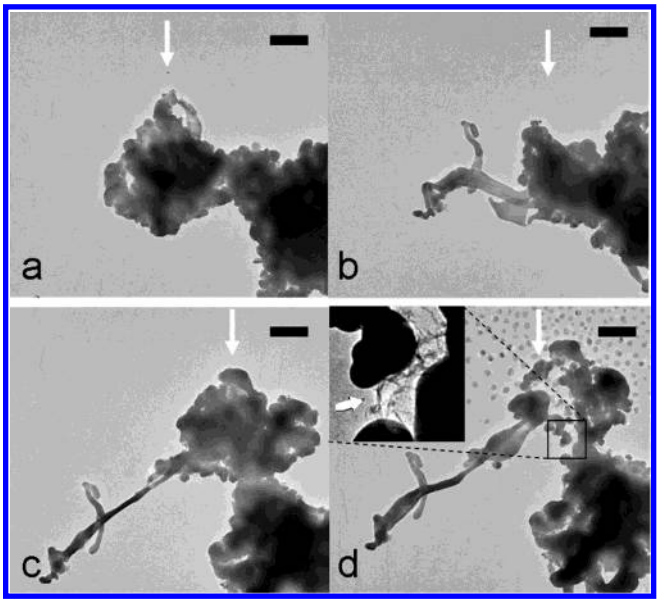
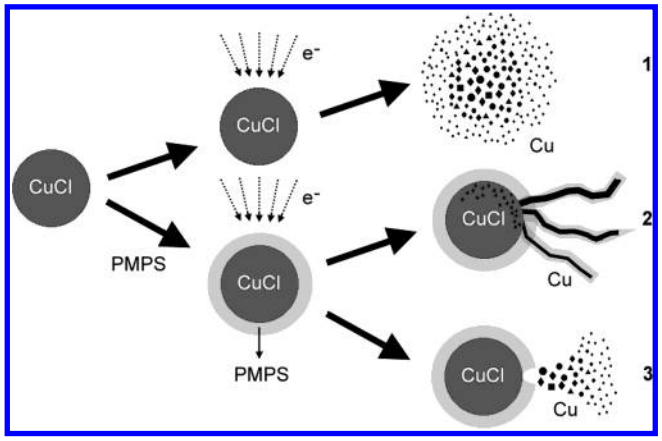


Figure 3. In situ TEM study of copper nanowire growth; scale bar = 500 nm. (a) Synthesized CuCl before irradiation by the CEB at the spot indicated by the arrow. (b) After the first CEB irradiation (see the text for the detailed process). (c) After the fourth CEB irradiation. (d) After the fifth CEB irradiation. The arrow in the inset points to a residual polymeric sheath.

Importantly, the presence of a small amount of Si is observed in Figure 2b,c. This and the observation of a residual shell material (discussed below and shown in Figure 3d) suggest that the CuCl particles were encapsulated in a thin PMPS layer. Electron diffraction (ED) of the nanowire shows a ring pattern (Figure 2d) corresponding to a cubic phase material. The lattice parameter *a* is estimated to be 0.36 nm, consistent with the value of elemental Cu.[5] **B**, originally at point 2, was irradiated together with **A** initially. Upon irradiation, **B** shifted away from the CEB-focused position near points 1 and 2 to a new position at point 3, as shown in zone 2 of Figure 1a. Apparently, a growing nanowire exerted a force on **B** for the movement. Thus, **B** was only briefly irradiated and

Scheme 1. CEB-Induced Growth of Cu Nanostructures from CuCl



largely intact. In addition, evolution of scattered Cu nanoparticles from **B**, close to the original CEB-irradiated position, is observed. The scattering pattern also suggests the presence of a shell material, with an opening to allow the escape of the growing nanoparticles.

An in situ observation of the nanowire growth process was recorded in a series of TEM images (Figure 3). Initially, the beam current was maintained at 20 pA/cm^2 to take the first image, shown in Figure 3a, of a synthesized CuCl particle. The CEB (beam diameter, ca. 1 μm) induced reduction started after the beam current was increased to 200 pA/cm^2 and converged for 1 s at the particle. Then, after the beam spot was spread and the current was reduced to 20 pA/cm^2, the second image, Figure 3b, was taken. Visibly, growth of nanowires was initiated from the particle. The steps, beam converging, spreading, and photographing, were repeated sequentially. These induced further growth of the nanowires, shown in the images recorded in Figure 3c,d. Also, it was noted in other experiments that increasing the beam intensity increased the diameter and the growth rate of the nanowires. Finally, after the reactant, CuCl, was exhausted, the presence of a residual sheath material was observed, as shown in the inset of Figure 3d. Based on the observation and the EDS data, the layer is determined to be a PMPS material encapsulating the synthesized CuCl particles. Also, growth of Cu nanoparticles was observed nearby, probably from Cu-containing species that escaped through openings on the e-beam-damaged sheath.

As described above, the CEB-induced reductions of the commercially supplied CuCl and the synthesized CuCl produce vastly different Cu nanostructures. The observations are summarized in Scheme 1. The first equation describes the evolution of Cu nanoparticles from a commercially supplied template-free CuCl particle. The second equation illustrates the growth of Cu nanowires from a synthesized CuCl particle, encapsulated in PMPS, after CEB irradiation. The third equation shows the evolution and scattering of Cu nanoparticles from a synthesized CuCl particle with a broken sheath. In summary, the PMPS layer, acting as a soft template, is the key factor controlling the nanowire growth. The sheath probably restricts the outflow of CuCl molecules and guides the growth direction. Without a complete coverage, upon the CEB irradiation, CuCl molecules are likely to be dissociated and reduced into Cu nanoclusters, which then combine into nanoparticles.[6] With a complete coverage, the CEB reduction of CuCl probably produces Cu nanoclusters confined within the sheath. These clusters could diffuse and coalesce into Cu crystals only in the sheath-limited space and would then be guided and restricted by the extending sheath into nanowires.[3] Further support of the role of the sheath was observed using Dow Corning DC 976 (a frequently used poly(dimethylsiloxane) high-vacuum grease) to encapsulate commercially supplied CuCl. Upon CEB irradiation, these CuCl aggregates were reduced and grew into Cu nanowires also.

In summary, we have employed transmission electron microscopy to observe the continuous growth process of Cu nanoparticles and nanowires from CEB reduction of CuCl. The observation is analogous to the VSRG of cablelike Cu nanowires and supports the proposed growth model.[3] This preliminary study has shown the importance of how a soft template enclosing the solid reactant could influence the nanostructure growth. Many other reaction variables, such as the position of irradiation, the local reaction conditions, and the selection of soft templates, may significantly influence the nanostructure growth. We anticipate that the technique developed in this study, observing the electron-beam-induced reduction and crystal growth process in situ, will be a powerful tool for understanding nanoscale reaction systems.

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Supporting Information Available: Experimental section. This material is available free of charge via the Internet at http://pubs.acs.org.

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