

Small Structures Fabricated Using Ash-Forming Biological Materials as Templates

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Different ash-forming biological materials such as gills of mushrooms, cotton wool, silk fiber, spider silk, dog's hair, and human hair were examined as templates to fabricate small structures. Ashes obtained from gills of mushrooms, silk fiber, and spider silk were miniaturized replicas of the original materials, whereas ashes from dog's hair and human hair were tubes. These materials were successfully coated with different inorganic materials by interface-selective sol–gel polymerization. Calcining coated materials yielded structures composed of ash and coated inorganic materials such as silica, titania, copper oxide, aluminum oxide, and iron oxide. Fully calcined ashes from native materials and materials coated with silica were usually 1/3 and 1/5 as large as their original materials, respectively. Silica–ash hybrid materials were much more rigid than ash materials. Incompletely calcined human hairs formed tubes with thick carbonized walls, and their inside morphologies suggested that medulla in human hairs might be responsible for tube formation. Preparation of complex tubular structures was possible as tied hairs did not break during calcination. Results in this study showed biological materials were useful as templates for fabricating inorganic structures regardless of ash formation.

Introduction

Small structures with complicated architectures are of great interest. There are numerous such small materials in biological systems, and mimicking them must be one of the most promising methods to fabricate small structures with complicated architectures.^{1–3}

If biological materials can be coated with another material and selectively removed afterward, one might be able to prepare replicas of them. Techniques to coat and selectively remove biological materials are indispensable to prepared structures in this approach.

Because biological materials are mainly composed of organic materials that can be usually removed by thermal decomposition, calcining biological materials coated with inorganic materials should be an efficient method to prepare replicas of them.

The most useful method to coat small materials with inorganic materials should be sol–gel coating carried out in aqueous media.⁴ In typical sol–gel coating, inorganic sol particles undergo surface preferred gelation to form an inorganic coat on the templates. However, examples of coating biological materials by sol–gel coating are rare.⁵ This is probably because most biological materials are negatively charged at moderate conditions, which is not ideal for sol–gel coating that is accomplished by taking advantage of electrostatic attraction between negatively charged sol particles and positively charged templates. Also, ashes from biological materials might have been considered to disturb formation of replicas in this method.

We have recently reported interface-selective sol–gel polymerization that was useful to coat different templates regardless of charges on them.⁶ Reaction conditions in that method were so mild that living microorganisms were coated without being sacrificed.

In this study, we are describing small structures fabricated by calcining ash-forming biological materials that were coated with different inorganic materials by interface-selective sol–gel polymerization.

Experimental Section

Materials. The edible mushroom, *Ganoderma lucidum*, was purchased from a grocery store. Cotton wool and silk fiber were purchased from a general store. Spider silk was obtained by collecting available spider webs. Human hairs were donated from three Korean individuals (43, 40, and 12 years old) and dog's hairs were taken from a poodle. Precursors were purchased from Gelest and Aldrich and used as received. Tetrakis[2-(2-methoxyethoxy)ethoxy]silane (TMEES), aluminum(III) tri[2-(2-methoxyethoxy)ethoxide]-(TMEAL), titanium(IV) bis(ammonium lactate)-dihydroxide (TBAL), iron(III) acetylacetonate (IAA), and copper(II) methoxyethoxyethoxide (CMEE) were precursors used in this study. All other chemicals were purchased from Aldrich and used as received.

Coating and Calcination. Biological templates were weighed in a glass vial, and distilled water was added. The mixture was allowed to stand at room temperature for several hours and then appropriate precursors were added. Weights of added precursors were typically 10% of those of biological templates. The pH of the mixture was adjusted to 9 using a

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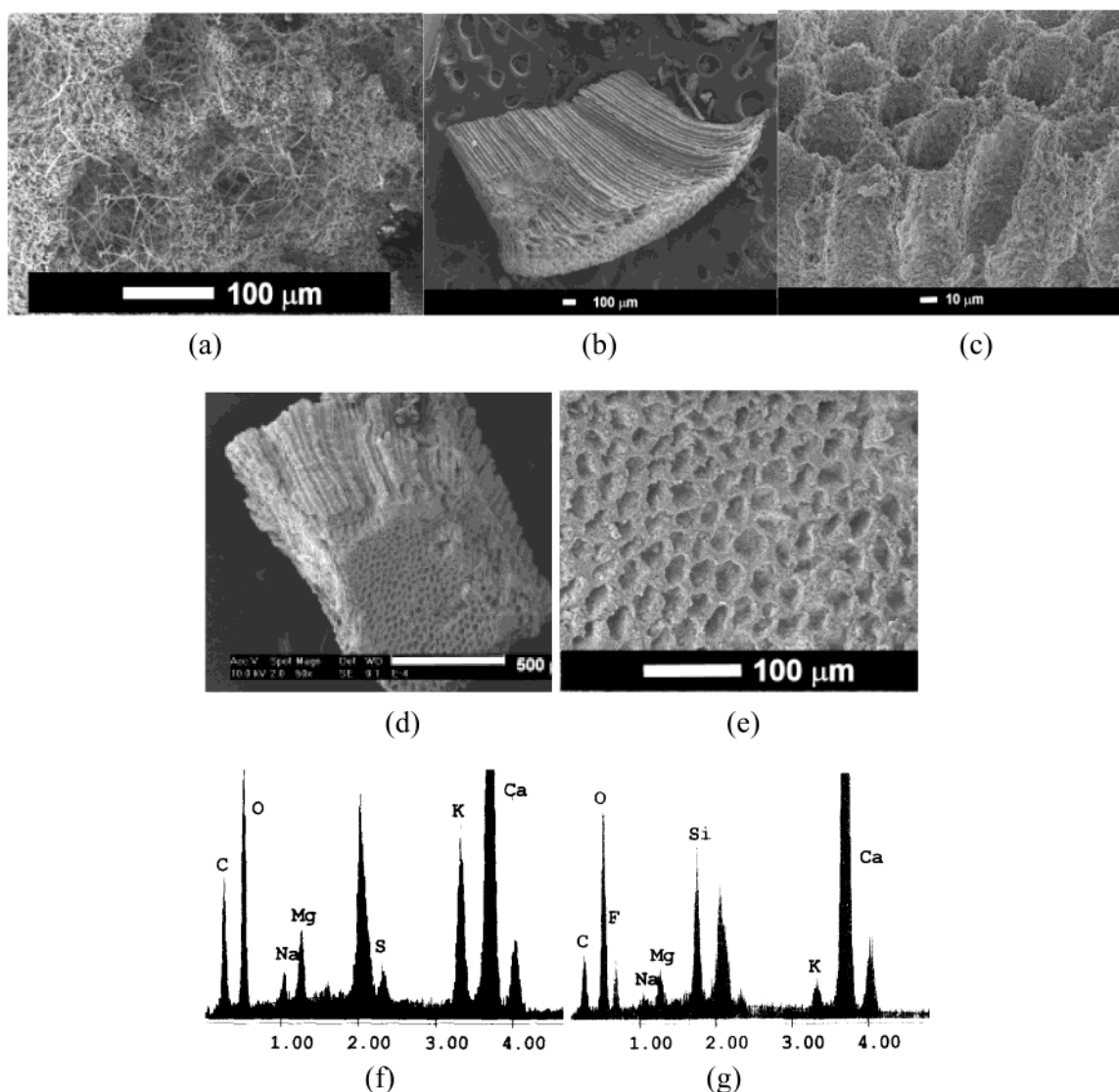


Figure 1. SEM images of (a) gills of *Ganoderma lucidum*, (b) ash of gills of *G. lucidum*, (c) magnified surface of Figure 1b, (d) silica-ash structure obtained by calcining gills of *G. lucidum* coated with silica, (e) magnified surface of Figure 1d, (f) EDX spectrum of the structure in Figure 1b, (g) EDX spectrum of the structure in Figure 1d. X axes in f and g are in electronvolts (eV).

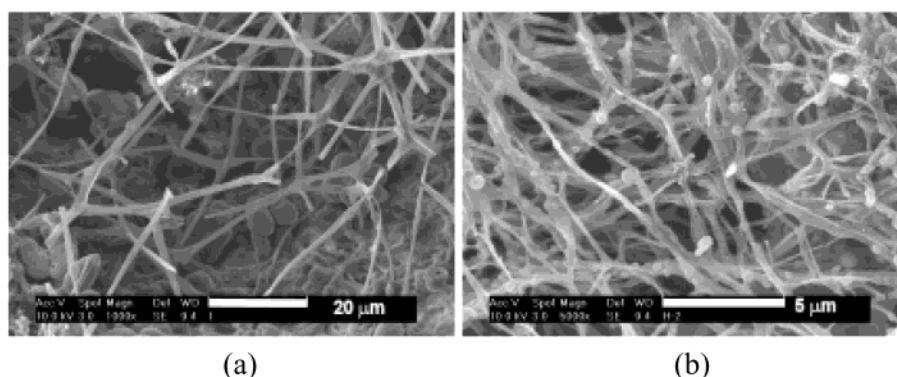


Figure 2. SEM images of (a) spores and hyphae in gills of *G. lucidum* shown in Figure 1a and (b) replica of spores and hyphae in gills of *G. lucidum* in silica-ash structure shown in Figure 1b.

dilute aqueous NaOH solution when IAA was used. IAA was added to the mixtures as saturated solutions in either THF, DMSO, or DMF. A small amount (0.001 wt % of water) of cetyltrimethylammonium bromide was added when TBAL was used. The reaction mixtures were allowed to stand overnight at room temperature and then washed thoroughly

with water and ethanol. The coated products were dried in the air and then calcined in a furnace. The temperature of the furnace was raised at a ramp of 2 °C/min from room temperature to 450 °C. For full calcination, samples were recovered 24 h after the temperature reached 450 °C, and partially calcined samples were obtained by recovering the

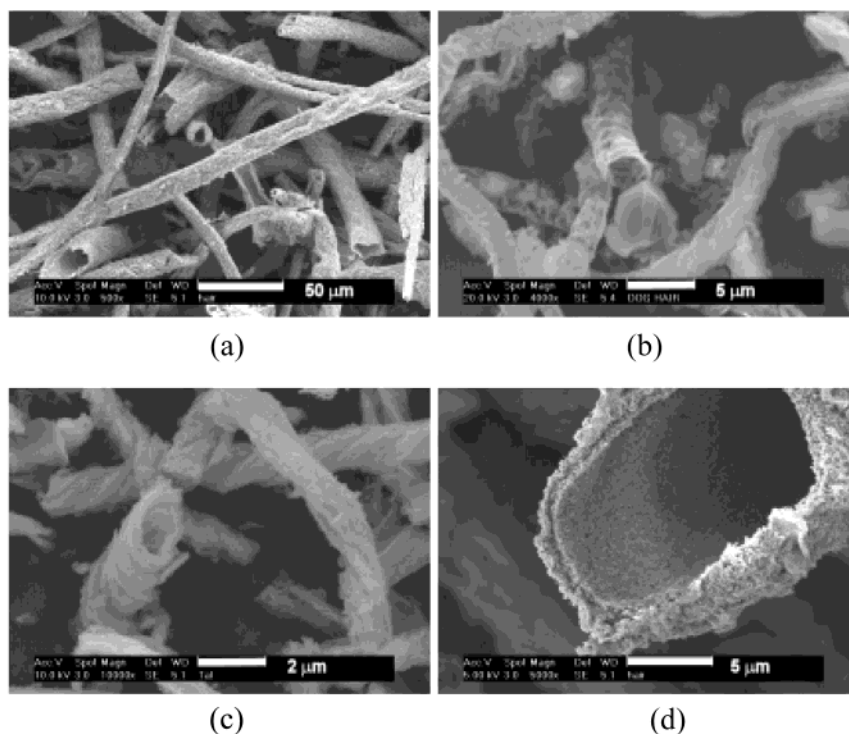


Figure 3. (a) Ash tubes from human hair, (b) ash tubes from dog's hair, (c) ash tubes from cotton wool, (d) magnified image of ash tube from human hair.

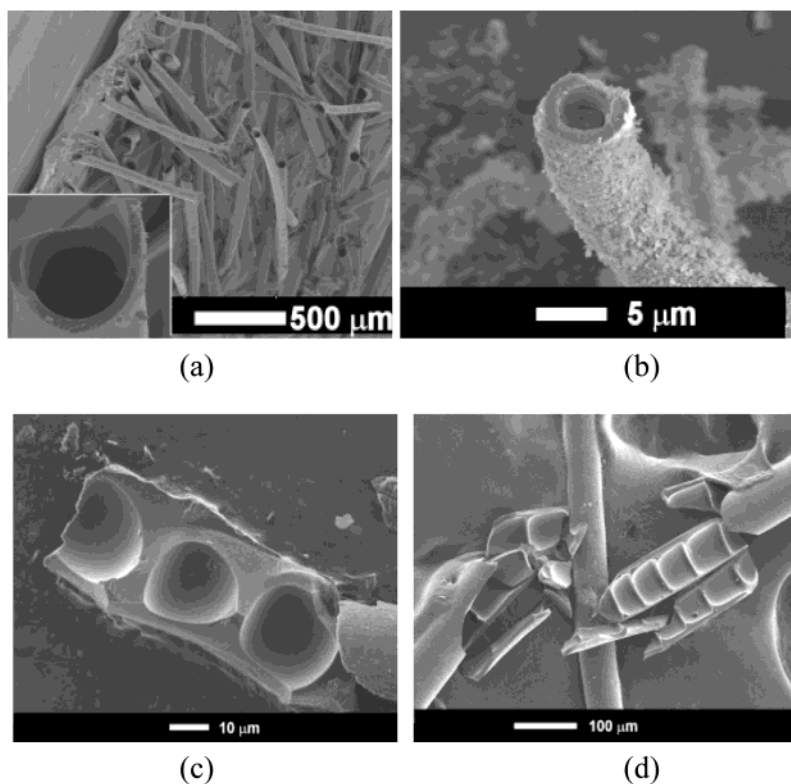


Figure 4. (a) Tubes obtained by calcining human hair incompletely, (b) tubes by calcining dog's hair coated with titania incompletely, (c) inside of human hair in the middle of void formation, and (d) inside of human hair shown in Figure 4a.

samples approximately 2 h after the temperature reached 450 °C. Calcination of uncoated templates was carried out in the same manner.

Miscellaneous. SEM images were taken using a JEOL JSM-670F equipped with an EDX analyzer.

Results and Discussion

Figure 1 show SEM images of structures of gills of *Ganoderma lucidum*, ash structures obtained after calcining native gills, and silica–ash hybrid structures obtained by calcining gills coated with silica. Figure 1b shows that ashes

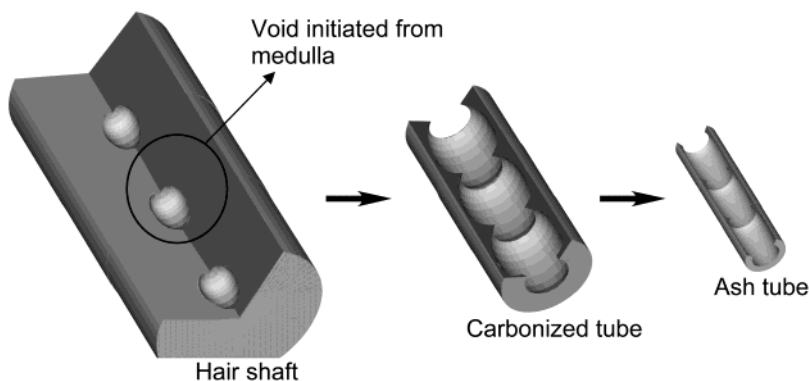


Figure 5. Process of tube formation in human hair.

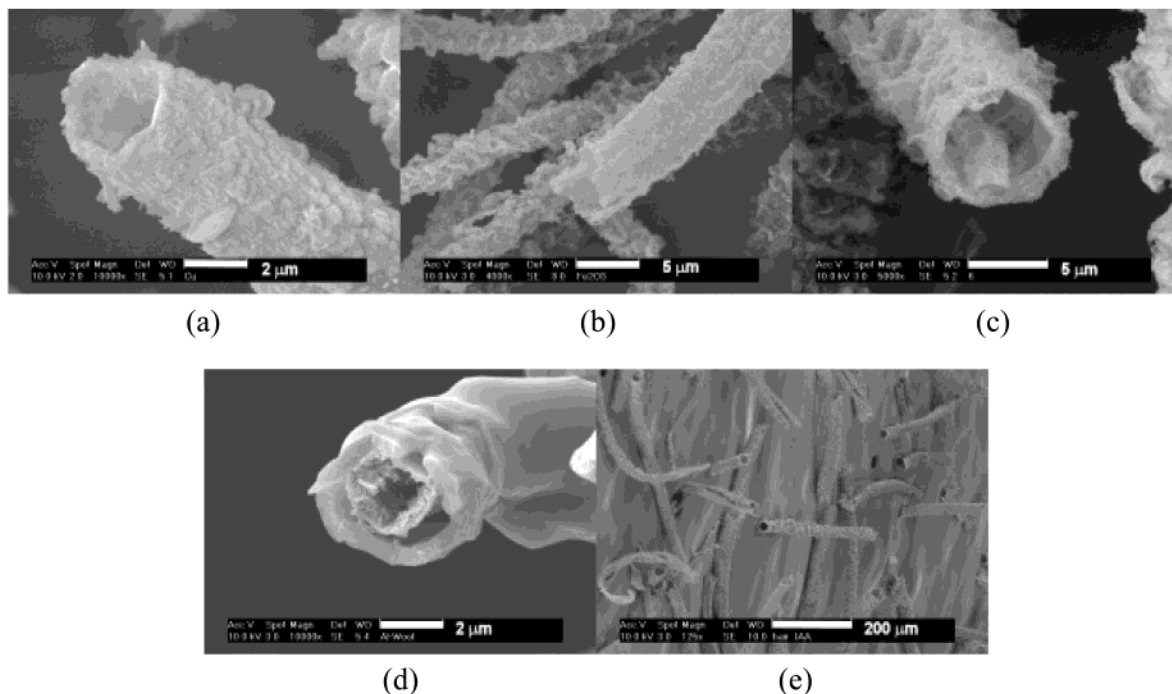


Figure 6. Tubes obtained by calcining (a) dog's hair coated with copper oxide, (b) dog's hair coated with iron oxide, (c) dog's hair coated with titania, (d) dog's hair coated with alumina, and (e) human hair coated with iron oxide.

were not randomly shaped but were miniaturized replica of original gills. EDX spectra shown in Figure 1, parts f and g, showed respectively that the main inorganic element found in the ash from gills of *G. lucidum* was Ca and Si was present in the calcined product of gills that were coated with silica.

The ash structure shown in Figure 1b was too fragile to be attached to the carbon tape without being broken for SEM analysis. The silica-ash structures were smaller than ash structures as diameters of channels in the silica-ash structure were approximately 1/5 of those of original channels whereas those in the ash structure were 1/3 of those of original channels. Figure 1, parts c and e, also shows that walls of channels in silica-ash structures were thicker and distorted. The walls distorted more severely when the amount of TMEES used to coat the gills was higher. Formation of smaller structures and distorted walls from silica-coated gills indicated that silica continued to shrink beyond the extent of shrinkage caused purely by calcination as secondary condensation reaction between silanols proceeded.

Replicas of smaller materials in gills were also found in the silica-ash structure as shown in Figure 2. Figure 2 shows

that silica did not fill the interstitial spaces between small materials in gills but coated each of them. These results showed that the interface-selective sol-gel polymerization method was efficient in coating biological materials and that ashes from biological materials did not disturb formation of replicas of them.

Structures of ashes should be determined by how inorganic ingredients are distributed in the original materials. Formation of ash replicas will take place when inorganic materials are evenly distributed and inorganic ingredients can somehow aggregate without losing their relative positions. Spider silk and silk fiber formed fibrous ashes that were replicas of their original shapes. However, cotton wool, dog's hair and human hair formed tubular ashes as shown in Figure 3. Ashes from cotton wool and dog's hair were extremely fragile and it was not possible to attach them to carbon tape for SEM analysis without losing most of their original shapes. On the other hand, ash tubes from human hair were much more rigid and could be handled easily. Our further investigation was concentrated on using hairs as templates in this study.

The most significant difference between tube-forming

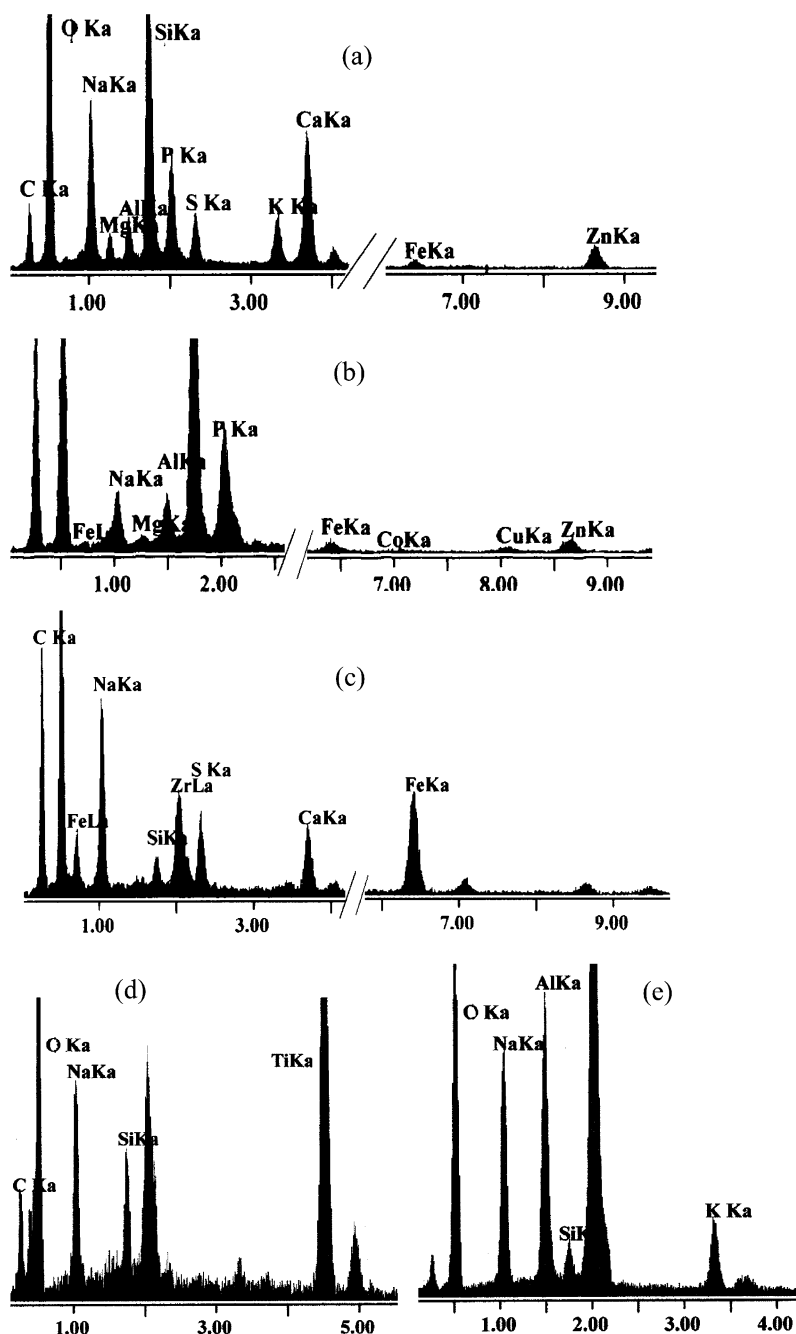


Figure 7. EDX spectra of tubes shown in (a) ash of dog's hair, (b) Figure 6a, (c) Figure 6b, (d) Figure 6c, and (e) Figure 6d. The intensities for Si and C changed depending on the mount used, glass or carbon tape. The X axis is in electronvolts (eV).

fibrous materials (cotton wool, dog's hair, and human hair) and rod forming fibrous materials (silks) is that tube-forming materials are known to have tubular structures in the middle of their stems, linen or medulla, whereas silks do not. It is also to be noted that medulla in human hair is often discontinuous or absent.⁷

Inside morphologies of tubes obtained by incompletely calcining human hair provided a clue to explain the process how tubes are formed in human hair during calcination. Figure 4, parts a and b, shows tubes prepared by incompletely calcining human hairs and dog's hair coated with titania, respectively. The incompletely calcined tube from human hair had diameters of approximately 40 μm that were much larger than those of fully calcined ash tubes, typically 10–20 μm . Figure 4, parts c and d, shows the inside of

incompletely calcined human hair tubes. These figures show acorn-shaped voids formed along the hair and these voids got larger, eventually to be interconnected to form continuous tube. The nodal structures were observed in some images of fully calcined ash tubes. The anisotropic shape of voids suggested that formation of these voids might be related to anisotropic phenomenon, probably the growth of hair. However, the length of the node estimated after roughly compensating the shrinkage, 40–50 μm , was much shorter than the daily growth length of human hair, 300 μm . The magnified image of ash tube from human hair in Figure 3d showed ash tubes from human hairs had two layers; the inner one should have formed from the inorganic ingredient in the cortex layer and the outer one from those in the cuticle layer.

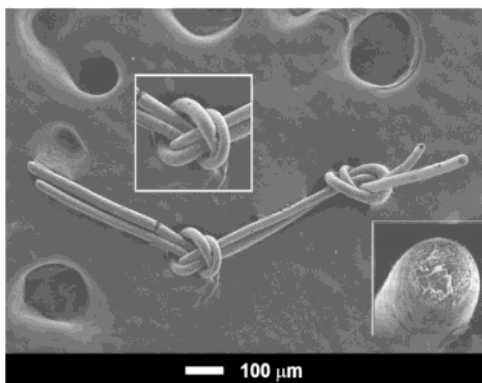


Figure 8. Complex tubular structure obtained by incompletely calcining tied human hair.

The process of tube formation in human hair is illustrated in Figure 5.

Figure 6 shows tubular products obtained after calcining dog's hair and human hair coated with different inorganic materials. EDX analysis results shown in Figure 7 and the fact that surface textures of tubes varied depending on the coated inorganic materials proved that hairs were successfully coated.

Figure 6, parts c and d, show that two tubes formed when dog's hair coated with titania and alumina were calcined. Because diameters of ash tubes from dog's hair were smaller than $5\ \mu\text{m}$, the inner tubes should have formed from dog's hair and the outer tubes should have formed from coated inorganic materials. No such double tubes were found in calcined products from coated human hairs.

The most interesting feature of fabricating tubes using human hairs is demonstrated by the tubular structure shown in Figure 8. The tubular structure in Figure 8 was fabricated by incompletely calcining two tied hairs. The hairs did not

break during calcination even though they were bent so severely. The closed end in this structure shown in the inset of Figure 8 was formed by cutting the hair with a blunt knife so that the cuticle and cortex deformed inward to close the end after calcination.

Results in this study have revealed interesting facts that biological materials form ashes that are replicas of their original shapes. It is very interesting that hairs formed tubular ashes. Also, results in this study show biological materials are useful as templates to fabricate small structures regardless of ash formation. Therefore, one can prepare very complicated small structures if only biological materials with appropriate structures and sizes are available. The fact that replicas prepared in this method were smaller than the small original materials is also advantageous to obtain small complicated structures. The resulting inorganic small materials might be used as building blocks in fabricating more complicated larger structures or as templates to prepare structures made of different materials.

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