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Facile Morphological Control of Cyclodextrin Nano- and Microstructures and Their Unique Organogelation Ability

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Much effort has been devoted to the fabrication of nano- and microstructures of various morphologies because of their unique and morphology-dependent optical, electronic, magnetic, and catalytic properties.[1−6] In particular, cubic nano- and microstructures have attracted considerable attention in the fields of optics, electronics, and organic synthesis.[7−12] For example, Xia et al. prepared interesting gold and silver nanocubes of various sizes, which are potentially useful as templates for photolithography, catalysts, and molecular computers.[7] Thus far, most cubic nano- and microstructures have been fabricated using inorganic compounds[7−18] such as metals[7−11,13−15] and metal oxides.[12,16,17] On the other hand, much less attention has been paid to the fabrication and function of organic nano- and microcubes,[19−21] although they are expected to work as unique molecular containers and drug carriers as well as novel semiconductor materials. Recently, we found that channel-type assemblies of γ-cyclodextrin (γ-CD$_{\text{channel}}$), in which γ-CD molecules are stacked in a head-to-head or head-to-tail orientation to form a column in the crystal,[22,23] formed unique cubic microstructures.[24] CDs can form inclusion complexes with various organic molecules and anions via the incorporation of these guests into their cavities (see Figure 1).[25,26] By utilizing the inclusion complex formation between CDs and their guests, we expected to achieve morphological control of the resulting CD microstructures. Herein, we report for the first time morphological control of γ-CD microstructures by manipulating the fabrication conditions. In particular, dramatic size and shape changes of the γ-CD microstructures were easily achieved by utilizing the inclusion of anionic guests into the γ-CD cavity. We also describe the unique morphology-dependent gelation ability of γ-CD microstructures toward oils and organic solvents.

γ-CD microcubes with an average edge length of 7 μm (Figure 2A)[24] can be fabricated by dropping a saturated aqueous γ-CD solution into acetone as a poor solvent at ambient temperature, based on the γ-CD$_{\text{channel}}$ preparation method reported by Tonelli et al.[23] In this study, we first examined the effects of varying the fabrication conditions, such as the γ-CD concentration in the aqueous solution and the type of poor solvent, on the morphology of the resulting γ-CD cubic structures. The overall size of the γ-CD cubes increased with decreasing γ-CD concentration in the aqueous solution (Figure 2A−D). For instance, the size of the γ-CD cubes became about four times as large as that of the original microcubes when we decreased the γ-CD concentration to one-hundredth of its original concentration (Figure 2D). This phenomenon can be explained by considering that a decrease in the γ-CD concentration in aqueous solution reduces the number of nuclei in the nucleation stage, and induces the formation of larger γ-CD microcubes, similar to the case of fullerene C_{60} nano- and microcrystals.[27] The X-ray diffraction (XRD) patterns of these microcubes, which all showed a strong peak at 7.5° characteristic of the channel structure of γ-CD,[23] clearly showed that they were composed of channel-type assemblies of γ-CD (see Figure S2 in the Supporting Information). The size of the γ-CD microcubes was also altered when we used 2-propanol or 2-butanol instead of acetone as the poor

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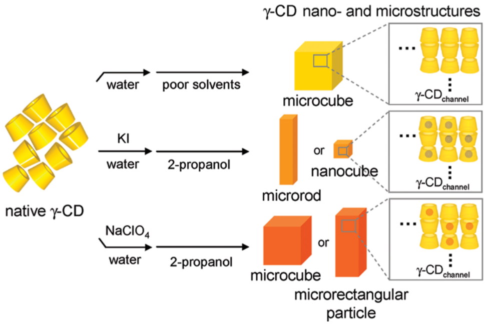

Figure 1. Schematic illustration of the formation of γ-CD nano- and microstructures of various sizes and shapes.

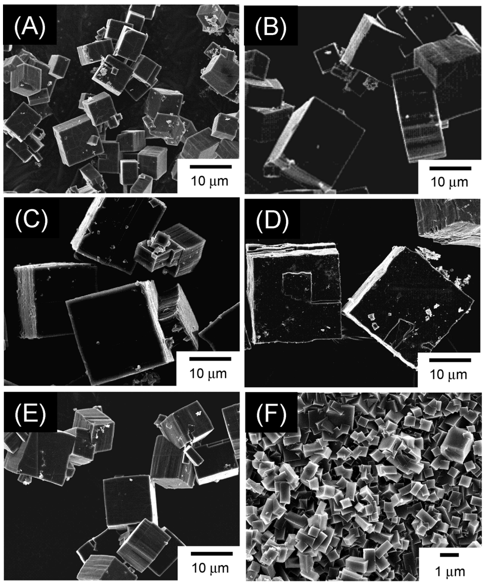

Figure 2. SEM images of γ-CD microcubes formed by dropping aqueous γ-CD solutions [(A) 0.17, (B) 1.7×10^{-2}, (C) 3.5×10^{-3}, and (D) 1.7×10^{-3} M] into acetone or aqueous γ-CD solution [0.17 M] into (E) 2-propanol or (F) 2-butanol.

solvent. When 2-propanol was used, the apparent size of the γ-CD microcubes became slightly larger than those prepared in acetone (Figure 2E). On the other hand, γ-CD microcubes of smaller size (an average edge length of 1 μm) were formed when 2-butanol was used as the poor solvent (Figure 2F). The increasing order of the size of the γ-CD microcubes formed was consistent with the increasing order of the solubilities of γ-CD in the poor solvents (the solubilities of γ-CD in 2-propanol, acetone, and 2-butanol at 20 °C are 0.21, 0.16, and 0.11 mM, respectively). This result indicates that the size changes of the γ-CD microcubes induced by changing the type of poor solvent was related to the different solubilities of γ-CD in these poor solvents. A higher solubility of γ-CD in the poor solvent would decrease the number of nuclei in the nucleation stage, and thus lead to an increase in the size of the γ-CD microcubes, similar to the case of the decrease in the γ-CD concentration mentioned above. The XRD patterns of these microcubes revealed that they were composed of γ-CD$_{channel}$ (see Figure S2 in the Supporting Information).

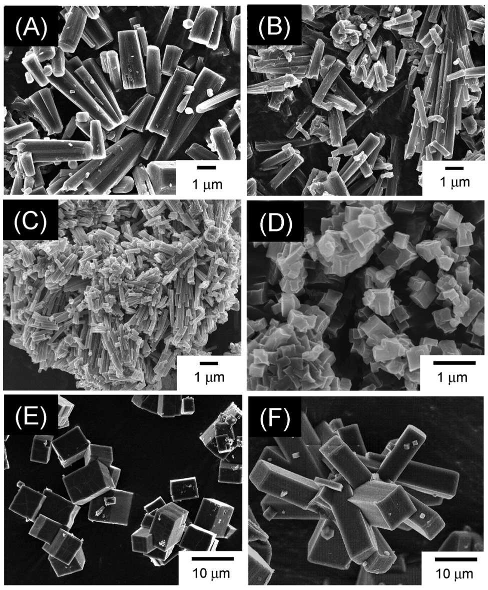

Figure 3. SEM images of γ-CD nano- and microstructures formed by dropping aqueous γ-CD solution [0.17 M], including potassium iodide [(A) 0.017, (B) 0.085, (C) 0.12, and (D) 0.17 M], or sodium perchlorate [(E) 0.017 M and (F) 0.17 M], into 2-propanol.

Next, we examined the effects of guest inclusion into the γ-CD cavity on the morphology of the resulting γ-CD microstructure. Potassium iodide (KI) and sodium perchlorate ($NaClO_4$) were chosen as guests because the I^- and $ClO_4{}^-$ anions can be incorporated into the γ-CD cavity in water,[28] and these salts show good solubility in 2-propanol, a poor solvent for the γ-CD microstructures. Thus, the guest anions not included into the γ-CD cavity would be easily removed from the mixtures with the resulting γ-CD microstructures by washing with 2-propanol. When an aqueous γ-CD solution (0.17 M) including 1 equiv. of KI (0.17 M) was dropped into 2-propanol, nanometer-sized cubes (an average edge length of 300 nm) were formed (Figure 3D). Interestingly, the morphology of the γ-CD structure was strongly affected by the added amount of KI. In the presence of 0.1 equiv. of KI, rodlike microstructures were produced (Figure 3A). These microrods became thinner with increasing amounts of KI between 0.1 and 0.8 equiv. (Figure 3A−C and see Figure S1 in the Supporting Information). When more than 0.9 equiv. KI was added, the morphology of the γ-CD structure changed from microrods to nanocubes. Elemental analyses of these nano- and microstructures indicated that the amount of KI included increased with an increase in the amount added. For instance, we estimated that when 0.1, 0.5, 0.7, and 0.9 equiv. of KI were added, KI to γ-CD molar ratios of about 0.045, 0.31, 0.57, and 0.74 were included into the γ-CD structures, respectively. On the other hand, in the presence of $NaClO_4$, we observed a different tendency for γ-CD microstructure formation. When less than 1 equiv. of $NaClO_4$ was added, there was no change in the morphology of the resulting γ-CD microcubes (Figure 3E). In contrast, microrectangular particles were formed when more

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than 1 equiv. of $NaClO_4$ was added (Figures 3F). Elemental analyses of these microstructures showed that the amount of $NaClO_4$ included increased with an increase in the amount added, similar to the case of KI. When 1 equiv. of $NaClO_4$ was added, we estimated that a molar ratio of about 0.43 of $NaClO_4$ to γ-CD was included in the γ-CD structures. These results show that the morphology of the γ-CD structures can be controlled by the type and amount of anions incorporated into the γ-CD cavities. In the XRD patterns of these anion-incorporated nano- and microstructures, we observed a shift of the peak at $2\theta = 7.5°$[23] to a low angle (see Figures S3 and S4 in the Supporting Information), indicating that the lattice spacing of [200] planes in the γ-$CD_{channel}$ crystal increased. These results may suggest that anions such as I^- and ClO_4^- are incorporated into the γ-CD cavities; on the other hand, cations such as Na^+ and K^+ are located between the neighboring γ-CD molecules in the γ-CD channel or among the γ-CD channels in the γ-CD structures. Here, the water molecules in the original γ-CD microcubes, which are present between neighboring γ-CD molecules in the γ-CD channels or among the γ-CD channels, would have been replaced by these cations, leading to an increase in the distance between the γ-CD channels corresponding to [200] planes in the microstructures.[22,29] Thus, the counter cations as well as guest anions may affect the morphology of γ-CD structures. However, the mechanism responsible for the morphological change of the γ-CD structures triggered by guest inclusion is unclear at present.

In a previous report, we demonstrated that γ-CD microcubes induced organogel formation in various oils and organic solvents via the construction of three-dimensional networks of γ-CD microcubes.[24] However, the organogelation ability of the γ-CD microcubes was lower compared to the conventional organogelators.[30−32] This result prompted us to explore the relationship between the morphology of γ-CD structures and the organogelation ability, and to find out an effective morphology of γ-CD structures for the organogel formation. Thus, we examined the gelation ability of various γ-CD nano- and microstructures toward tetradecane, benzene, 1,4-dioxne, and soybean oil by adding an increasing amount of the γ-CD structures into the solvents with shaking. Figure 4 shows the minimum gelation concentration of γ-CD nano- and microcubes, with average edge lengths of 300 nm (including KI), 7 μm, and 20 μm, required to induce organogelation at 20 °C. Interestingly, this gelation ability tended to increase with a decrease in the size of the γ-CD cubes, indicating that γ-CD cubes of smaller sizes could construct three-dimensional networks more efficiently. Furthermore, the gelation ability of the γ-CD microcubes was higher than that of the γ-CD microrectangular particles with a similar edge length in the base (see Figure S7 in the Supporting Information). Here, the effect of guest inclusion into the γ-CD cavity on the organogelation ability was almost negligible. Comparison of organogelation ability of the γ-CD microcubes with that of $NaClO_4$-incorporated γ-CD microcubes of the same size showed that the $NaClO_4$ incorporation little affected the organogelation ability (Figure 4 and Figure S7 in the Supporting Information). These results suggest that organogel formation with γ-CD structures was greatly affected by their sizes and shapes. Further tuning of the morphologies of the γ-CD nanostructures could produce a high-performance organogelator.

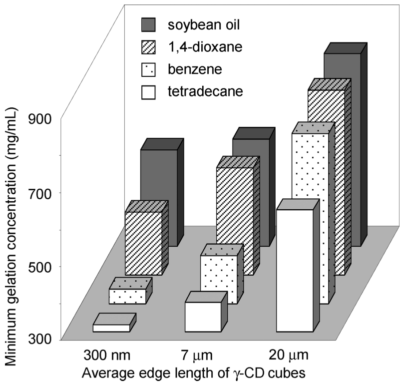

Figure 4. Minimum gelation concentration of γ-CD nano- and microcubes of different sizes in tetradecane, benzene, 1,4-dioxne, and soybean oil at 20 °C.

In conclusion, we demonstrated that the morphologies of γ-CD microstructures were easily controlled by manipulating the fabrication conditions, including the γ-CD concentration in the aqueous solution, the type of poor solvent used for reprecipitation, and the addition of anionic guests such as I^- and ClO_4^- into the aqueous γ-CD solution. The resulting γ-CD nano- and microstructures formed organogels in oils and organic solvents. Their organogelation ability depended on their sizes and shapes, and the smallest cubic nanoparticles showed the greatest gelation ability. By utilizing the inclusion of various molecules into the CD cavities, these γ-CD nano- and microcubes can be expected to be useful not only as organogelators but also as molecular containers and drug carriers.

Supporting Information Available: Experimental details, SEM images, XRD patterns, and organogelation ability of γ-CD nano- and microstructures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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