Fabrication and Photocatalytic Activity of Fullerodendron/$CaCO_3$ Composites

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Novel composite materials consisting of fullerodendrons and $CaCO_3$ particles were fabricated to have better efficiency as photosensitizers in singlet photooxygenation reactions compared to pristine fullerodendrons. Moreover, fullerodendrons in composites demonstrate the ability to control $CaCO_3$ polymorphism through formation of thermodynamically least stable form of $CaCO_3$: vaterite.

Organic–inorganic hybrid materials have been drawing great attention in research for acquisition of better insights into natural processes like biomineralization and to create new and more-advanced materials for better and novel applications.[1] Among various kinds of hybrid materials studied so far, composites of $CaCO_3$ with different organic motifs have been studied extensively.[2] Particularly, the controlled formation of crystal polymorphs of $CaCO_3$, i.e., vaterite, aragonite, and calcite, in the presence of different organic moieties has been the focus of intense research.[2–4] In this context, dendrimers, which are monodispersed macromolecules with a regular and highly branched three-dimensional architecture, are better candidates for studying crystal nucleation and growth of $CaCO_3$ than are other synthetic linear polymers.[3] Recently, Naka and co-workers demonstrated the controlled formation of vaterite using the poly(amidoamine) (PAMAM) dendrimer with carboxylate groups at the external surface.[4] Although many studies have been devoted so far to the control of crystal polymorphs of $CaCO_3$,[2,3] there are only a limited number of reports concerning the chemistry of a photoreactive dendrimer within organic–inorganic hybrid materials. In this regard, recently, we fabricated a new composite material consisting of anthryl dendron and vaterite particles of $CaCO_3$.[5] Furthermore, we observed photodimerization of the anthracene unit, showing that the photoreactivity of the anthryl dendron is preserved within the composite, despite effects of light-scattering and low concentration.[5] Meanwhile, the development of fullerene-based photosensitizers have been drawing much attention because of their widespread application in the field of synthetic organic chemistry[6] and photodynamic therapy.[7] Nakamura reported that C_{60}, C_{70}, and their derivatives are synthetically useful photosensitizers for the photooxygenation of olefins with singlet oxygen.[6m] Recently, we developed a method for facile synthesis of fullerodendron,[8] which can act as a homogeneous photocatalyst.[9] Although homogeneous photosensitizers for reactions with singlet oxygen based on fullerene derivatives have been widely reported, there have been only a few reports of heterogeneous photocatalysts containing fullerenes.[10–13] Herein, we report the synthesis of a new composite material consisting of the least thermodynamically stable form of $CaCO_3$, i.e., vaterite, stabilized by carboxylate salts of a fullerodendron, and the investigation of photosensitizing ability of a fullerodendron within an organic–inorganic hybrid. During our investigation, we found that this new composite material serves as an efficient heterogeneous photocatalyst through incorporation of spherical vaterite crystals of $CaCO_3$ to the fullerodendrons. This photocatalyst is demonstrably more efficient than pristine fullerodendron.

Results and Discussion

The composite material (Fig. 1) was prepared by carrying out $CaCO_3$ crystallization in the presence of fullerodendron (**I**)[8] (Fig. 2) under the same conditions as those of our previous work (see Experimental Section).[5] The dendrimer content in the crystalline $CaCO_3$ was found to be approximately 34 wt %, which was determined from the UV–vis spectra according to the same method (see Experimental Section) as applied in our previous report.[5] After preparation of the composite material, the crystal phases of $CaCO_3$ were characterized using FT-IR analysis, XRD, and SEM. The FT-IR spectrum of the composite showed bands at 877 and 746 cm^{-1} (Fig. 3), indicating the formation of vaterite, whereas characteristic bands

Fig. 1. Photograph of fullerodendron/$CaCO_3$ composite.

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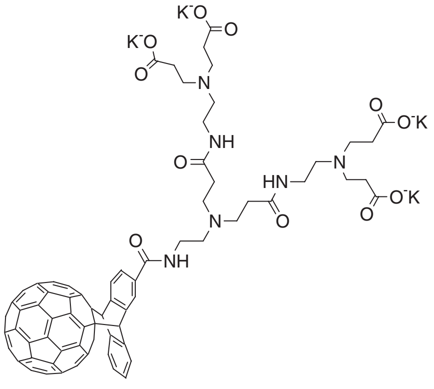


Fig. 2. Structure of fullerodendron (**I**).

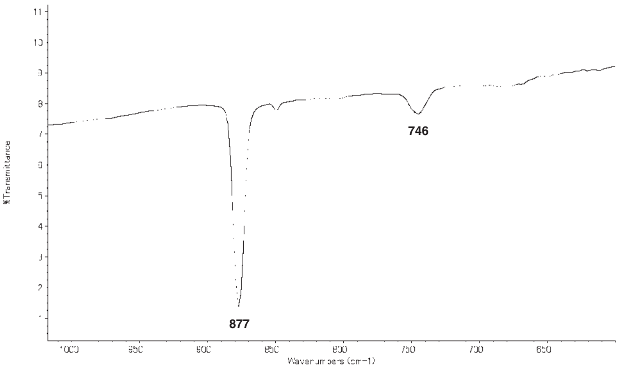


Fig. 3. FT-IR spectrum of CaCO$_3$ crystals in the fullerodendron/vaterite composite.

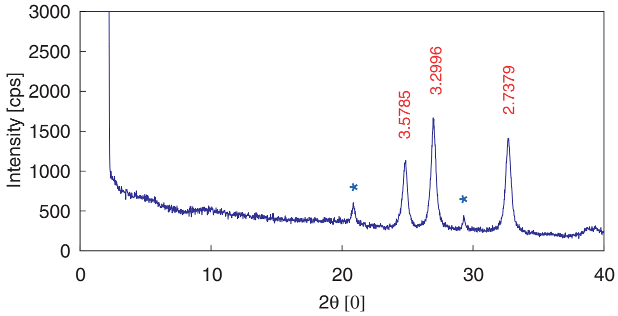


Fig. 4. XRD of the fullerodendron/vaterite composite. The asterisk (*) denotes the diffraction angle caused by calcite, indicating negligible contamination.

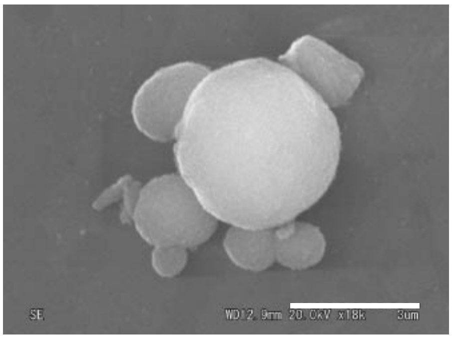
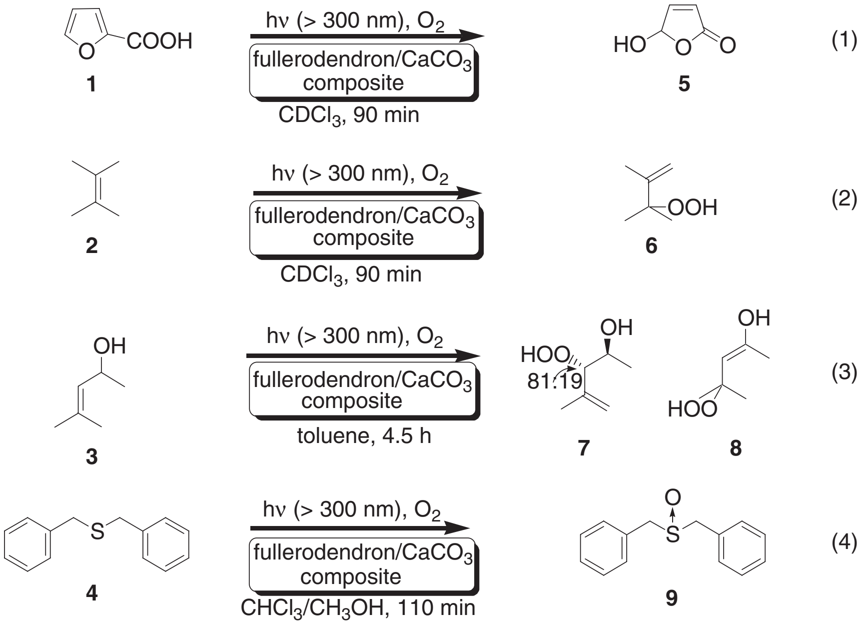


Fig. 5. SEM image of fullerodendron/vaterite composite material (scale bar = 3 μm).

of calcite at 874 and 712 cm^{-1} were barely detectable.[14] The diffraction pattern, which was observed through XRD of the composite materials, indicates the presence of vaterite crystals in the composite with negligible calcite contamination (Fig. 4). Finally, SEM observation (Fig. 5) showed spherical vaterite crystals, which might be attributable to aggregation of numerous small vaterite nanoparticles.[15] Although the complete phase transformation of vaterite into the thermodynamically stable calcite occurs within 80 h in aqueous solution, the obtained vaterite crystals did not change the crystal morphology even after incubation in water for 20 days. According to similar results using PAMAM dendrimer reported by Naka and co-workers,[16] we speculated that the vaterite surface was stabilized by the carboxylate-terminated fullerodendron, i.e., the surface of vaterite might be covered with fullerodendrons. The color of the composite (Fig. 1), brown-orange surface, is consistent with this speculation.

To examine the scope of the composite material as a photosensitizer and to investigate the nature of the generated reactive species, we carried out a photooxygenation reaction with various olefins sensitized using fullerodendron/CaCO$_3$ composites. The Diels–Alder reaction and the ene reaction are two widely used applications of singlet oxygen with olefins.[17] Therefore, we examined the Diels–Alder conversion of furan-2-carboxylic acid (**1**) to it's corresponding lactone as well as the ene reaction of 2,3-dimethyl-2-butene (**2**) and 4-methylpent-3-en-2-ol (**3**). Oxidation of benzyl sulfide (**4**) was also examined. All of these reactions were catalyzed by the composite materials under heterogeneous conditions (Scheme 1).

In a typical photooxygenation reaction, a solution of furan-2-carboxylic acid (**1**) (115 mg, 1 mmol) in CDCl$_3$ (7 mL) in presence of the composites (5 mg) was irradiated using a 500 W high-pressure mercury lamp through a Pyrex filter at room temperature. During irradiation, oxygen was bubbled through the reaction mixture. After irradiating for 90 min, the corresponding lactone (**5**) was obtained in 95% yield (see Scheme 1, Eq. 1). The photooxygenation reaction of 2,3-dimethyl-2-butene (**2**) gave the corresponding photooxygenated product 3-hydroperoxy-2,3-dimethyl-2-butene (**6**) in 61% yield using the composite material (5 mg) as a photocatalyst (Eq. 2). The ene reaction of 4-methylpent-3-ene-2-ol (**3**) with singlet oxygen generated by photosensitization with the composite gave compounds **7** and **8** in 98 and 1.6% yields, respectively (Eq. 3). The observed regioselectivity and stereoselectivity of the products conform to the known selectivity of singlet oxygen reactions,[6m] indicating that the composite material-sensitized reaction generates free singlet oxygen. Moreover, photooxygenation of dibenzyl sulfide (**4**) gave the corresponding sulfoxide in 96% yield (Eq. 4). In this case, a mixture of chloroform and methanol was used as the solvent, according to the observation of Foote and Peters that protic solvents minimize the physical quenching of singlet oxygen to afford better yields of sulfoxides than aprotic ones.[18] When we used pure chloroform as the solvent for the photooxygenation reaction, sulfoxide (**5**) was obtained in 30% yield. The crystal phase of CaCO$_3$ did not change after the photoreactions, which was confirmed by using FT-IR spectroscopy after the photoreactions.



Scheme 1. Photooxygenation reactions carried out with the composite material in heterogeneous condition.

The heterogeneous photosensitizer fullerodendron/$CaCO_3$ composite was recovered easily at the end of the reaction by centrifugation. It was recycled by washing ($CHCl_3$, MeOH, and H_2O) and drying. When reused in subsequent runs, the composite materials afforded the corresponding products, but in noticeably lower yields, showing that the effectiveness of the sensitizer gradually decreases. For example, photooxygenation of dibenzyl sulfide (**4**) gave the corresponding sulfoxide (**9**) in 96% yield in the first run, and after recycling of the fullerodendron/$CaCO_3$ composite, 61 and 47%, in a second and third run, respectively. This might be attributed to a slight decomposition of the fullerodendron during the photooxygenation reaction. A similar result was observed when pristine fullerodendron (**I**) was used as a catalyst.[9]

Comparison of the photocatalytic ability of the composite material with that of the fullerodendron showed that the heterogeneous photocatalyst fullerodendron/$CaCO_3$ composite is more efficient than our previous homogeneous catalyst fullerodendron.[9] For example, the photooxygenation of dibenzyl sulfide (**4**) with the composite (containing 1.7 mg of fullerodendrimer) gave 96% of the desired product (**9**) when irradiated with high-pressure mercury lamp for 110 min, whereas the homogeneous photooxygenation reaction using the same amount of fullerodendron (**I**) (1.7 mg) for the same duration gave a 70% yield of **9**. The catalytic turnover of the heterogeneous photocatalyst was estimated for the photooxygenation reaction of dibenzyl sulfide (**4**) to be >450, which was calculated based on the fullerodendron content in the composite. However, that number is expected to be even greater because only the fullerodendrons on the surface of the composite were expected to exhibit photoreactivity. The photoreactivity of fullerodendrons within the composite might be inhibited because of the light-scattering effects. The turnover number of the composite (>450) is apparently more than 1.5 times higher than that of fullerodendron (300). The reason for this enhanced photoreactivity of fullerodendron/$CaCO_3$ composite can be attributed to better isolation of the individual photoactive C_{60} moieties in the composites as compared to that of pristine fullerodendron, which prevents self-quenching of excited state of C_{60}.

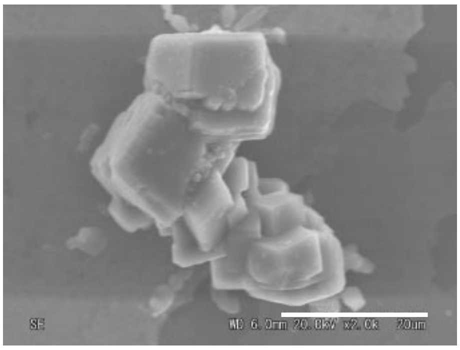


Fig. 6. SEM image of the fullerodendron/calcite composite (scale bar = 20 μm).

Finally, in order to clarify the unique reactivity of our fullerodendron/vaterite composite, we fabricated a fullerodendron/calcite composite and investigated it's photocatalytic activity. The calcite composite of fullerodendron was prepared by delaying the addition time of fullerodendron. After the formation of calcite of $CaCO_3$, fullerodendron (**I**) was added to a dispersion of calcite crystals. The dispersion was then stirred for 3 days with the expectation of surface modification of calcite crystal of $CaCO_3$ and separated by filtration. It is notable that this new composite seems to be less stable than our previous composite of vaterite since most of the fullerodendrons in the calcite composite gets washed away with water. This is evident from the comparison of the fullerodendron contents of both of the composites, which is 9 and 34 wt % for calcite and vaterite composite, respectively. Figure 6 shows a SEM image of the fullerodendron/calcite composite, in which rhombohedral calcite crystals were observed. The FT-IR spectrum of the composite had bands around 874 and 712 cm^{-1}, indicating the formation of calcite. In order to compare the photocatalytic activity of the fullerodendron/calcite composite with the fullerodendron/vaterite composite, we investigated the photooxygenation reaction of dibenzyl sulfide (**4**) using these two composites. For example, the photooxygenation of dibenzyl sulfide (**4**) with the calcite composite containing 1.7 mg of fullerodendrimer gave 87% of the desired product **9** when irradiated with a 500 W high-pressure mercury lamp for 110 min, whereas, for the same duration, the vaterite composite containing the same amount of fullerodendron (1.7 mg) gave 96% of **9**. On comparision of the photocatalytic activity of both composite materials, we found that the photoreactivity of fullerodendron/calcite composite is lower than fullerodendron/vaterite composite as evident from the yields of their photooxygenated products.

Conclusion

In conclusion, this work demonstrates that the photoreactivity of the fullerodendron does not diminish on fabrication of a hybrid material; in fact, its photoreactivity is further enhanced. When pristine C$_{60}$ was used as a photosensitizer as shown by Nakamura,[6m] the reactivity was much less as compared to the fullerodendron due to self-quenching effect of the C$_{60}$ moieties. Furthermore, on fabrication of the composite material, the isolation of the photoactive C$_{60}$ core is further enhanced as compared to fullerodendrons in solution due to the incorporation of organic fullerodendron moieties into inorganic, spherical CaCO$_3$ particles of vaterite. Moreover, this work demonstrates the ability to control the polymorphism of CaCO$_3$ based on the formation of the more active spherical vaterite, which is important for better catalytic performance. Further work is in progress to explore applications and advantages of organic–inorganic hybrid based on the fullerodendron.

Experimental

NMR spectra were recorded on a JEOL JNM-AL300 spectrometer. FT-IR spectra were recorded on a Thermo Nicolet Avatar 360T2 infrared spectrophotometer. X-ray diffraction (XRD) patterns were measured with Cu Kα radiation using a Rigaku RAD. Scanning electron microscopy (SEM) was recorded on a Hitachi S-3500N. Photoirradiation was carried out in a Pyrex reactor at room temperature. A 500 W high-pressure mercury lamp was used as the light source. The reagents were obtained from Kanto Kagaku Co., Ltd., Aldrich Chemical Co., and Tokyo Kasei Co., Ltd. All chemicals were used as received without further purification.

Crystallization of CaCO$_3$ in Presence of Fullerodendron (I) for Obtaining Vaterite Composite. To a solution of fullerodendron (**I**) (7.5 mM, pH 8.5) in water (13.2 mL), aqueous solutions of CaCl$_2$ (4.6 mL, 0.5 M, pH 8.5), and (NH$_4$)$_2$CO$_3$ (4.6 mL, 0.5 M, pH 10.2) were added simultaneously at 30 °C using a syringe. After gentle stirring for 4 days, the obtained crystalline CaCO$_3$ was washed with water to remove the excess fullerodendron that was not involved in the crystals. It was subsequently separated by filtration.

Crystallization of CaCO$_3$ in Presence of Fullerodendron (I) for Obtaining Calcite Composite. After injection of aqueous solutions of CaCl$_2$ (4.6 mL, 0.5 M, pH 8.5) and (NH$_4$)$_2$CO$_3$ (4.6 mL, 0.5 M, pH 10.2) simultaneously using a syringe, a solution of fullerodendron (**I**) (7.5 mM, pH 8.5) in water (13.2 mL) was added to the reaction mixture after incubation for 6 h. The dispersion was then kept at 30 °C for 3 days under gentle stirring. The crystalline CaCO$_3$ was collected after 3 days and washed several times with water.

Estimation of the Content of Fullerodendron (I) in the Composite Material. 5 mg of the composite material was dissolved in 30 mL of 1 M HCl. Absorbance of the solution at 400 nm was 0.454. According to the molecular extinction coefficient (ε) that was calculated by measurement of pristine fullerodendron (**I**), content of the fullerodendron (**I**) in the composite material of vaterite was estimated to be 34 wt %. Similarly, the wt % of the calcite composite was estimated to be 9%.

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