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Mixing of Molecular Crystals by Dry Cogrinding with Silica Nanoparticles

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The dry bead milling of a mixture of anthracene crystals and a tiny amount tetracene in the presence of surface-modified silica nanoparticles led to the fluorescence quenching of anthracene due to the doping of tetracene, supporting the occurrence of crystal mixing under dry conditions.

The dry grinding of solid matter provides cost-effective and ecologically clean processes in large scale to produce fine particles.[1] An alternative significance of dry grinding exists in the mechanochemical processes to activate solid materials to cause phase changes, nanosized mixing of components, and chemical reactions. This technique has been extensively applied to inorganic materials, which cannot be liquefied at ambient conditions. Meanwhile, organic syntheses in solid state have been exploited so far in relation to green chemistry,[2] and some of them have been accelerated by dry grinding. Our current efforts have been concentrated on the dry grinding of organic pigments[3] and molecular crystals[4] in the presence of silica nanopowder to provide organic–inorganic particulate nanocomposites composed of organic shell layers and core silica nanoparticles. We anticipated that the dry grinding causes the attrition of organic solid particles with silica nanoparticles to result in the cohesion of organic solid fragments to build up shell layers onto surfaces of silica nanoparticles.[3,4] In line with this idea, crystals of crystal violet lactone adsorb on surfaces of silica nanopowders under the dry bead grinding to form monolayers of blue-colored triphenylmethane dye through Langmuir isotherms at the solid/solid interface.[5] The results obtained so far motivated us to perform the mechanical mixing of organic crystals under dry conditions. A crystalline couple of anthracene (AN) and tetracene (TE) was employed here, because the solid-state excited singlet energy transfer between the couple arises from the doping of TE molecules in AN crystals and is monitored sensibly by fluorescence.[6] In fact, we carried out the wet milling of a mixture of both in an aqueous solution of poly(vinyl alcohol) (PVA) to prepare aqueous dispersion to perform the mechanochemical doping of TE molecules into AN crystals.[7] A major concern of this work is to verify crystal mixing under dry conditions in the presence of silica nanopowder by using a couple of AN and TE. Excited singlet energy transfer occurred for milled powder, revealing efficient solid-state mechanochemical doping.

The dry milling was achieved by means of a table-top planetary mill (Fritsch, P-7) because of the suitability for small scale experiments.[4] According to our work,[3,4] hydrophilic surface silanols of commercially available 14.0-nm primary particle diameter Stöber silica nanopowder[5] were protected with a polysiloxane in advance to make the surface hydrophobic for the core–shell hybridization.[3a] It was revealed that the surface-modified silica nanoparticles (m-SiO_2) were primarily composed of aggregates of primary particles of an average diameter of 14.2 nm.[3] According to our report,[4] a 0.1:1 (w/w) mixture of AN and m-SiO_2 was milled with the planetary mill using nylon beads (9.5 mm ϕ) at a rotation speed of 400 rpm to give powdery products,[8] TEM images of which are shown in Figure 1.[9] Primary particles were not well separated after the milling for 5 min, whereas better results were obtained after 30 min. TEM images after the 2 h-milling displayed the formation of nanoparticles with narrow size distribution of primary particles.

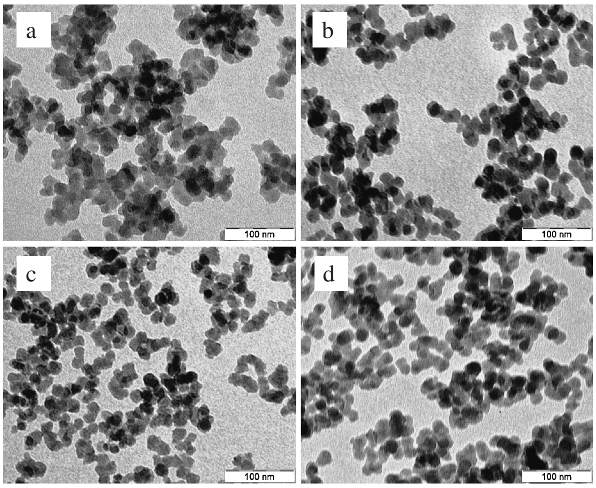

Figure 1. TEM images of a 0.1:1 (w/w) mixture of anthracene and m-SiO_2 after the dry grinding for (a) 5 min, (b) 35 min, and (c) 2 h at 400 rpm with aid of nylon beads and (d) after the grinding for 2 h at 400 rpm with aid of zirconia beads.

Figure 2 shows spectral changes of fluorescence of a ternary mixture of AN, TE, and m-SiO_2 during the dry milling. The milling with the nylon beads resulted in the increment of new peaks at 494 and 530 nm due to TE emission as a result of singlet energy transfer in AN crystals, whereas spectral changes leveled off after the milling for 2 h. The wavelengths of AN belonging to type A crystals emitting monomer fluorescence[10] is unchanged during and after the milling and thoroughly superimposed with AN crystals, suggesting that crystal structure is not deteriorated. Note that the milling with zirconia beads (3 mm ϕ) for 2 h at 400 rpm[8] leads to considerable fluorescence quenching whereas the appearance of particles is similar to that milled with nylon beads (Figure 1d). This behavior is not only interpreted in terms of enhanced mixing of shell layers but also is suggestive of the involvement of disaggregation of silica aggregates. Our previous reports on nanohybrids of organic pigments[3] and rubrene[4a] described that organic shell layers cover complicated surfaces of aggregated silica nanoparticles. It follows that organic solids are squashed locally into hollow sites formed among joined primary silica nanoparticles, leading to inhomogeneous shell thickness. Accordingly, there exist portions of

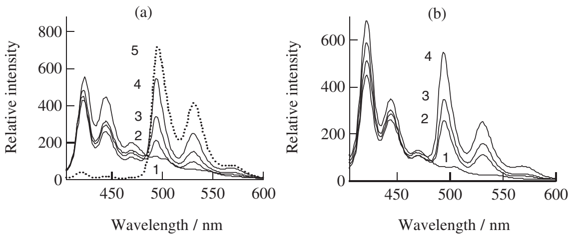

Figure 2. (a) Changes in fluorescence spectra of a mixture of AN, TE, and m-SiO_2 (AN/TE-2 in Table S1)[8] milled with nylon beads for (1) 5 min, (2) 30 min, (3) 1 h, and (4) 2 h at 400 rpm and (5) for 2 h with the aid of zirconia beads at 400 rpm. $[TE] = 1.22 \times 10^{-2}$ mol/mol. (b) Changes of fluorescence spectra of powdery hybrids milled with nylon beads for 2 h as a function of [TE] in AN (AN/TE-1, AN/TE-3, and AN/TE-4 in Table S1).[8] [TE] (mol/mol): (1); 0, (2): 7.01×10^{-4}, (3) 2.57×10^{-3}, and (4) 1.22×10^{-2}.

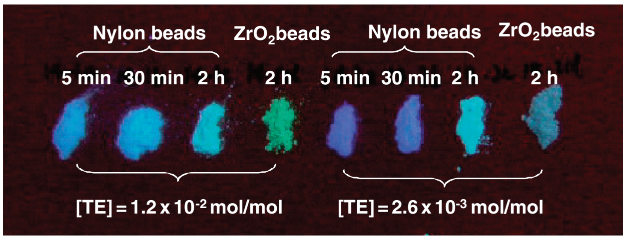

Figure 3. Changes in colors of fluorescence of powders during the dry bead milling. Loading amounts of TE ([TE]) relative to AN were 1.2×10^{-2} (the left part) and 2.6×10^{-3} mol/mol (the right part), respectively. The milling conditions are shown in the picture.

inoperative AN, which does not participate in mechanical crystal mixing with aid of nylon beads. On the contrary, zirconia beads may bring about the disaggregation of bound primary silica nanoparticles more or less to make idle AN active for the mechanical mixing. The effect of milling beads on the disaggregation of silica nanoparticles will be described elsewhere. At any rate, the progress of the dry milling was conveniently followed visually by color change of powder under UV irradiation, as shown in Figure 3.

Fluorescence quantum yield ratios of TE to AN depend linearly on concentrations of the former doped in the latter in double logarithmic representation.[6b] A similar situation was observed when AN was milled in an aqueous PVA solution in the presence of TE.[7] In this context, ratios of intensity at 530 nm due to TE to that at 444 nm ascribable to AN (I_{530}/I_{444}) of dry-milled hybrid powder were plotted against TE concentrations. As shown in Figure 4 as open circles, there is a good linearity. But TE concentrations are much higher than those obtained by the wet milling, as presented in Figure 4 as open squares.[5] When the hybrid powder was subjected to the wet milling in an aqueous PVA solution with the aid of finer zirconia beads (0.3 mm ϕ) at 650 rpm, fluorescence quenching efficiency became closer to that of the wet milling of crystals without the silica, as displayed in Figure 4 (closed circles). This behavior is in accordance with the disaggregation of silica core particles as a result of mechanical action of the finer zirconia beads. It should be mentioned that an I_{530}/I_{444} value for powder milled with the aid of zirconia beads shown in Figure 2a (dotted line 4) reaches 7.0 and is almost equivalent to that observed for the wet milling of the corresponding hybrid in a PVA solution.

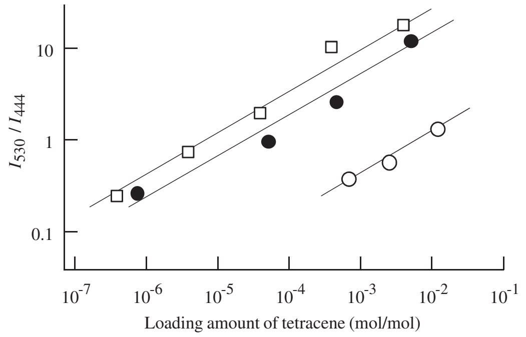

Figure 4. I_{530}/I_{444} ratios as a function of loading amounts of TE to AN (mol/mol) in various conditions for crystal mixing. Open circles: the dry milling to give core–shell nanohybrids, closed circles: the wet milling of the core–shell hybrids, and open squares: the wet milling of mixed crystals cited from Ref. 7.

In summary, the dry beads milling of AN and m-SiO_2 in the presence of tiny amounts of TE leads to mechanochemical doping of the latter to result in the quenching of fluorescence of the former. The fluorescence quenching efficiency is markedly influenced by the nature of milling beads. The milling with zirconia beads resulted in higher efficiency for fluorescence quenching probably because aggregated silica nanoparticles come apart mechanically to improve crystal mixing. The present technique is of potential significance to achieve solid-state complexation as well as reactions of molecular crystals in large scale without any solvent because conventional milling tools and procedures are usable.

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8 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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