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Novel synthesis of organic nanowires and their optical properties†

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Aligned nanowires of organic luminescent material were prepared by introducing the organic luminants into nanochannels of variable size in an anodic aluminum oxide (AAO) membrane, and the emission spectra from these nanowire arrays exhibited novel size-dependent luminescent properties.

The preparation of nanoparticles for metals, metal oxides, and semiconductors has been extensively studied, and their novel characteristic properties have been investigated for prospective applications.[1–3] For example, unique electronic and optical properties, the so-called quantum size effect, were found in several semiconductor nanoparticles with sizes in the range of 1 to 10 nm.[3,4] A quantum size effect for organic compounds could also be expected, but the weak van der Waals intermolecular interaction[5] might result in different phenomena contrasting with those of strongly bound nanoparticles of metals, metal oxides, and semiconductors. Although there are a handful of known preparation methods for organic nanoparticles such as reprecipitation,[6] evaporation,[7] and microemulsion,[8] general fabrication methods of organic nanoparticles and nanowires have so far hardly been investigated probably due to their thermal instability and weak mechanical properties. Recently, anodic aluminum oxide (AAO) membranes[9] with a regular porous structure have been prepared by electrochemical methods and have widely been used to produce various nanostructured materials.[10] This method involves the introduction of various materials within highly ordered channels in the AAO membrane, in which the diameters and lengths of the inserted nanowires can be well controlled.[10–12] In this study, for the first time, we present the novel synthesis of organic nanowires and their optical properties. Organic luminescent nanowires ranging from tens to hundreds of nanometers in diameter showed unusual size-dependent photoluminescence (PL) phenomena, which seem to be related to the different intermolecular interactions of surface molecules depending on the diameter of organic nanowires.

The AAO membranes were prepared in a two-step anodizing process.[13] Aluminum foil (99.999%) was annealed at 500 °C in vacuum for 5 h, and then electropolished in a mixture of perchloric acid and ethanol. The foil was then anodized in various conditions at a constant voltage, and the first generated membrane was subsequently removed by an aqueous mixture of phosphoric acid (6%) and chromic acid (1.8%) at 60 °C. The second anodization was performed under the same conditions as the first one. The resulting porous membrane was detached by the voltage reduction method[14] and was washed with deionized water for purification. The average diameters of the nanochannels were controlled to 20, 70, and 130 nm by the changing electrolytes and voltages applied,† and the diameters of the nanochannels were confirmed by FE-SEM. Pyrene and 1,4-bis[2-(5-phenyloxazolyl)]benzene (POPOP) were deliberately chosen as organic luminants for investigating molecular-size dependent optical properties in nanowires of various sizes. The pyrene has a relatively shorter circular plate (9.8 Å × 6.3 Å) shape, and the POPOP has a larger linear rod (19.0 Å × 6.2 Å) shape than pyrene.[15] They were inserted into the AAO membranes by sublimation and the excess organic molecules on the membrane surface were removed by washing with acetone and chloroform. SEM images in Fig. 1 show the shape of POPOP nanowires generated within 70 nm and 130 nm AAO membranes as a representative sample. After the AAO membrane was partially dissolved with 0.1 M NaOH, 130 nm POPOP nanowires aligned perpendicular to the membrane surface are observable (Fig. 1a). When the alumina template is completely dissolved out, mutually entangled POPOP nanowires with an average diameter of 70 nm were observed looking like cooked spaghetti; this is probably due to the weak mechanical strength of organic solids (Fig. 1b).

The POPOP nanowires with various diameters in AAO membranes showed very interesting size-dependent emission sprectra (λ_{ex} = 330 nm), compared to the emission of POPOP molecules in solution and bulk POPOP solid (Fig. 2). The emission of nanowires with a diameter of 20 nm appears in a similar position as that due to the monomeric POPOP molecule in dilute solution, although the vibronic structure of the emission spectrum is broader and featureless due to the extended vibronic coupling in the condensed solid phase of POPOP nanowires.

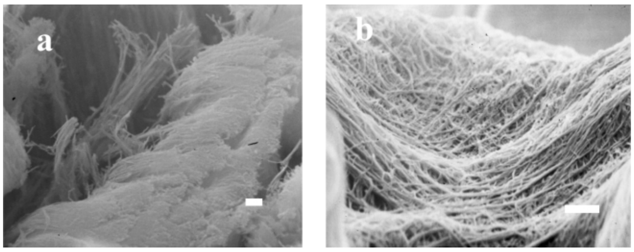

Fig. 1 SEM images of POPOP nanowires (a) with 130 nm diameter after partial etching and (b) with 70 nm diameter after complete etching of AAO membrane with 0.1 M NaOH (scale bars = 1 μm).

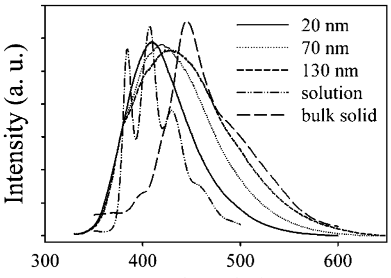

Fig. 2 Emission spectra of various POPOP samples: in solution (dash-double dotted), in bulk solid (long-dashed), in 20 nm AAO membrane (solid), in 70 nm AAO membrane (dotted), and in 130 nm AAO membrane (short-dashed).

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† Electronic supplementary information (ESI) available: experimental section and Figs. S1 and S2. See http://www.rsc.org/suppdata/cc/b1/b109881k/

In the case of POPOP nanowires having larger diameters, the maximum peak position of the emission spectra is gradually shifted to longer wavelength as the diameter increases to 70 and 130 nm. Furthermore, the emission spectra from 130 nm POPOP nanowires could be regarded as the mixed spectra of the emission of POPOP molecules in solution and bulk POPOP solid. Similar size-dependent emission characteristics belonging to organic luminants were recently observed from nanoparticles prepared by the reprecipitation method, and the unusual molecular arrangement on the surface was suggested as being responsible for these phemomena.[6]

In order to check the existence of any possible energetic coupling at the interface between the organic molecules and the AAO membrane, the AAO membrane was completely dissolved by 0.1 M NaOH solution, and the emission spectra of POPOP nanowires dispersed in aqueous solution were measured. As shown in Fig. 3, the maximum wavelength shift of PL spectra from the respective POPOP nanowires dispersed in NaOH solution shows a similar tendency, as the diameter of nanowire increases, to those from the POPOP nanowires inserted in the AAO membrane (Fig. 2). From the results of these emission characteristics of the dispersed organic nanowires, we have corroborated that the novel optical properties of POPOP nanowires result mainly from the size-dependant effects of the organic nanowire itself, rather than from the energetic coupling at the interface of the organic–inorganic composite.

These results can also be considered in light of the nanosize effect in the molecular solids of organic compounds. The fraction of molecules existing on the surface of nanostructures significantly increases as the size of nanostructures decreases. The energy states and the energetic coupling of such molecules on the surface predominantly determine the entire range of the optical properties of nanostructures. In molecular solids, dimer formation would not be efficient for the molecules, especially for larger size molecules, on the surface of nanostructures due to lattice softening,[6] which would result in short wavelength emission resembling the emission from the monomeric molecule in a dilute solution. On the other hand, the molecules in the core of the nanostructures experiences intermolecular interactions similar to those in the bulk molecular solid due to high crystallinity, which renders the formation of dimers easy. In a previous report for the emission properties of POPOP molecules, the emission bands around 410 nm and 450 nm were assigned to the emission from the ^1L_b state of the monomer and the dimer, respectively.[16] From the emission spectra in Fig. 2 and 3, the nanowires of 20 nm diameter show the emission from the monomer-like state, and the nanowires with larger diameter show the gradual shift of the emission to dimer-like emission characteristics in addition to the monomer-like emission. Consequently, as the diameter of nanowires decreases, the fraction of POPOP molecules on the surface of nanowires with respect to those in the core is relatively increased, which possibly results in monomeric emission in the nanowires of smaller diameter.

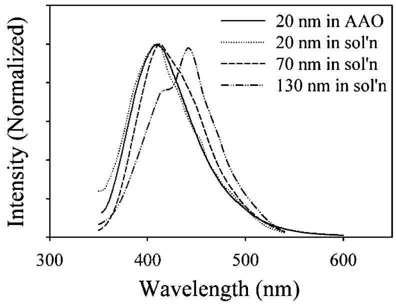

Fig. 3 Emission spectra of the POPOP nanowires: 20 nm diameter in the AAO membrane (solid), 20 nm diameter dispersed in solution (dotted), 70 nm diameter dispersed in solution (short-dashed), and 130 nm diameter dispersed in solution (dash-double dotted).

In order to check the molecular size effect of organic luminants, a smaller organic luminescent molecule, pyrene, was introduced into the AAO membrane channels. The emission characteristics of pyrene nanowires within the AAO membrane channels of different diameters showed no significant differences, however, and they were always the same as those of the bulk solid pyrene emission. (in ESI, see Fig. S2†). Therefore, no nanosize effect of relatively small pyrene molecules was observed in the range of the AAO template used in this study. It is probably because either the fraction of molecules existing on the surface of nanostructures would be not significant enough, for the smaller size circular plate molecule such as pyrene, to change the position of the entire emission spectrum or dimer formation would be efficient for the smaller size molecules on the surface of nanostructures not to give rise to lattice softening. More detailed investigation of the close relationship between molecular size and the nanosize effect is in progress.

In conclusion, various organic luminescent molecules were successfully assembled into the AAO nanochannels to generate novel organic nanowires. A size-dependent shift of emission maxima was observed from the POPOP nanowires of different diameters. The smaller organic luminant molecule, pyrene, did not show the size-dependent emission properties observed in the POPOP nanowires in the size range of the AAO template used in this study, which led us to conceive of a possible relationship for the nanosize effect between the size of organic molecules and the size of their nanostructures.

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