Self-assembled Nanocages of Anthracene by Liquid–Liquid Interface Recrystallization Technique

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Nanoparticulate films of anthracene were formed by liquid–liquid interface recrystallization technique at the water surface by spreading 0.2 mL of precursor solution (anthracene/benzene/CCl_4) containing 10^{-5} M anthracene solution in benzene. XRD confirmed the presence of monoclinic anthracene. TEM and AFM investigations revealed the formation of nanocages presumably by interlocking of anthracene chains in spontaneously self-assembled process. The optical spectrum for such nanoparticulate films displays 3 excitonic features that are signatures of anthracene molecule.

Anthracene is the most widely studied organic semiconductor owing to its vivid applications in molecular electronics.[1] Most of these applications rely upon thin films produced by variety of techniques. Since the electronic and optical properties of thin films inherently depend upon their local structure, it is vitally important to gain control over the assembly of molecules in these films. The realization of nanodevices for future electronic applications demands a greater control over such assemblies at nanoscale.[2] Herein, we offer a simple solution approach to fabricate nanostructured thin films of organic materials which was basically pursued to make nanostructured thin films of anthracene. Our methodology, liquid–liquid interface recrystallization technique (LLIRCT), closely resembles the conventional and well-established Langmuir–Blodgett technique.[3] But, the fundamental difference between the two is that Langmuir–Blodgett method is confined to monolayer forming materials, while LLIRCT can be advantageously exploited to fabricate free standing nanostructured thin films without the prior usage of any monolayer forming materials, surfactants, stabilizers, and templates. Quite interestingly, during the course of present work, we could observe nanocaged structures of anthracene formed presumably by interlocking of anthracene chains in a spontaneously self-driven process—a phenomenon analogous to formation of biological supramolecular nanoassemblies as exemplified by microtubules, flagella, chromatins, and viruses.[4] A preliminary account of this work is presented in this letter.

In a typical procedure, deionized water was taken in polypropylene tray ($15 \times 15 \times 2\,cm^3$) so that it forms a meniscus at the edges. The surface is divided in two compartments by a teflon thread barrier. Initially 10^{-5} M solution of anthracene in benzene was prepared. 0.05 mL of the same was mixed with 5 mL of CCl_4. Subsequently, 0.2 mL of this precursor (anthracene/benzene/CCl_4) solution was spread initially with the help of a syringe on a water surface in one compartment of polypropylene tray at room temperature in ambient atmosphere. After all the CCl_4 along with dissolved benzene had evaporated, a thin film is generated on the water surface which is then compressed by means of an oleic acid piston (pressure 30 dynes/cm). For this purpose, a drop of oleic acid is spread on the surface of water in other compartment (side) of the tray. The spreading of oleic acid leads to lateral compression of anthracene film via Teflon thread. The as-formed film on the water surface was transferred onto a glass substrate ($1 \times 1 \times 0.25\,cm^3$) by immersing the substrate vertically in the solution at a constant rate of 0.5 cm/min and lifting it vertically at the same rate (lifting-off technique) so that the film covers the dipped area (Blodgett technique). This operation was repeated many times to get the desired film thickness. We have processed films with 10 dips and 40 dips.

X-ray powder diffractometry analysis was performed using Philips PW 1729 X-ray diffractometer using Cu Kα radiation (1.5418 Å) and Ni filter. TEM images were taken on JEOL 1200 EX Electron microscope. SEM image was taken on JEOL (6360 LA) SEM instrument. AFM images were obtained by using WTIEC Alpha SNOM in AC mode. The optical spectra were recorded on Hitachi 330 Spectrophotometer.

The X-ray diffractograms corresponding to 10 dips and 40 dips films are shown in the Figures 1a and 1b, respectively. The strongest diffraction peak at $2\theta = 9.455$ i.e. $d = 9.3427$ Å and the second (in order) intense peak at $2\theta = 19.254$ i.e. $d = 4.6043$ Å is in close agreement (in both the cases) with the literature values for the monoclinic anthracene [JCPDS Card N0:39-1848]. No other peaks are observed, indicating that the films are oriented in (100) direction. Although the diffraction peak due to (111) is close to (200) peak, the intensity ratios of I(100)/I(200) is in agreement with literature, while expected higher intensity ratio of I(100)/I(111) is totally absent.

The TEM micrograph [Figure 2a] reveals the formation of cage like morphological features at nanometer scale. The individual crystallites of anthracene can be identified at nanoscale and their spontaneous self-assembly forming cage like features is clearly noticed. No exact estimates of the smallest entity constituting these structures can be drawn at this juncture. Furthermore, considering the width of the interface (typically 30 Å), it is understandable that the nucleation takes place favouring 2-dimensional

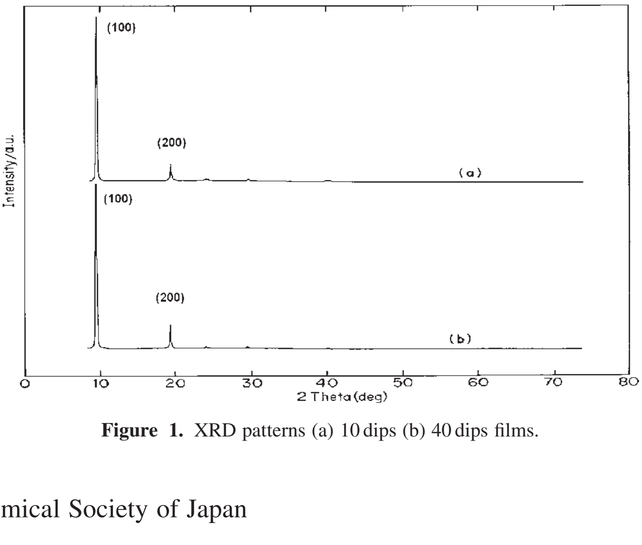

Figure 1. XRD patterns (a) 10 dips (b) 40 dips films.

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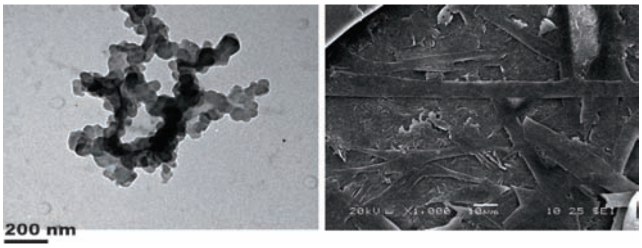

(a) (b)

Figure 2. (A) TEM of single dip anthracene film (B) SEM of 40 dips anthracene film.

growth of crystallites rather than 3-dimensional growth from nucleus confined to few molecules. It is postulated that restrictive 2-dimensional growth might impose the interlocking alignment of anthracene chains that spontaneously self-assemble to form cage like structure. Self-assembly in this case might be simply entropy driven, or there might be some Coulomb/double layer repulsion as applicable to aqueous systems. When a single drop of precursor solution (anthracene/benzene/CCl_4) is evaporated from the surface, the coverage is relatively non-uniform. It is postulated that multiple dipping under constant compressional force exerted by the oleic acid piston leads to formation of microtapes (occasionally piling over each other) as seen in SEM image corresponding to 40 dips film [Figure 2b] from cage like structures observed in TEM corresponding to a single dip film [Figure 2a]. Curiously, it is worth while to note that the formation of microribbons from nanospheres due to supramolecular assembly of protein molecules is a well studied phenomenon.[5] It may not be too contrived to state that the anthracene system could be a biomimic of such protein systems and further investigations in this direction are underway. In order to get decisive evidence for the formation of cage like features, we have carried out AFM investigations.

Figure 3a shows the overview image of tape like structures and the presence of topographic spherical features. The small scan area ($3 \times 3\,\mu m^2$) displays the presence of interlinked polygonal structures (20–25 nm in height) in the topography image. These polygonal structures are highlighted in the simultaneously recorded phase image in Figure 3b. The prima facie investigations by TEM and AFM suggest that the cavity in the cages extends to micrometer scale (2-dimensional growth) while its height is confined to nanometer scale.

The optical spectra for the (a) 10 dips [black curve] and (b) 40 dips [red curve] anthracene thin films are displayed in Figure 4. The absorption spectra are nearly similar except the absence of a peak at 350 nm in the 10 dip film. The absorption spectra recorded for the higher dip films are similar to that of anthracene in chloroform.[6] A red shift observed in these spectra is characteristic of quantum confinement in organic nanocrystals.[7,8] The similarity between the spectra implies that the absorption of the anthracene nucleus prevails in all cases, which, is more or less perturbed by matrix environment in the individual case that differs due to disparity in number of dips. In summary, with the example of anthracene, we offer a simple solution approach to produce surfactant-free, self-stabilized, and thermodynamically stable nanoparticulate thin films of organic semiconductors. Formation of nanocages with microcavities is an interesting aspect of our work which needs to be further exploited for the potential formation of nanocontainers and/or nanoreaction vessels commonly encountered with biomolecules.

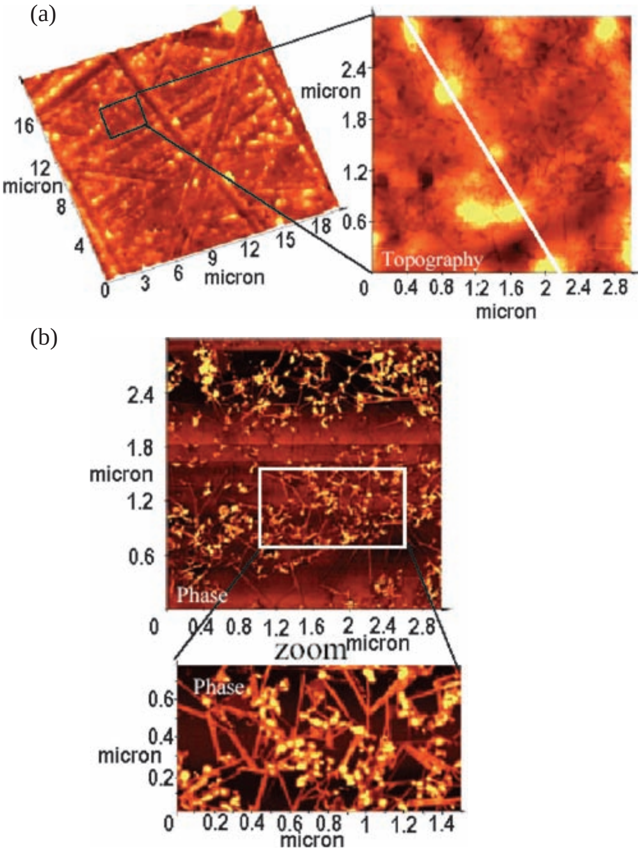

Figure 3. (A) AFM topographic image(s) of 40 dips film. (B) Simultaneously recorded phase image(s) of 40 dips film.

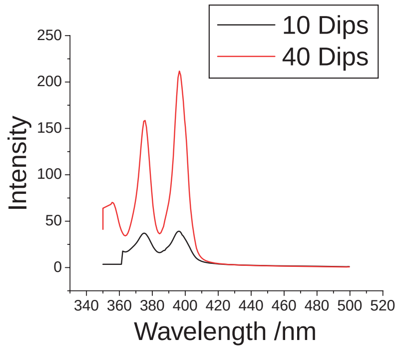

Figure 4. UV–visible spectra corresponding to 10 dips (black curve) and 40 dip (red Curve) films.

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