AFM Observation of Organogel Nanostructures on Graphite in the Gel-Assisted Transfer Technique

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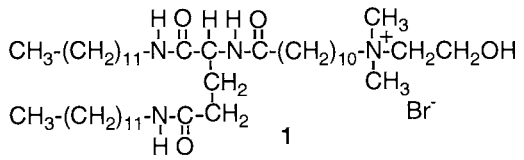
An ultrathin layer of organogel comprised of an L-glutamate-based ammonium amphiphile was transferred from the bulk gel surface onto a graphite plate. Atomic force microscopy showed the presence of fibrous and helical nanostructures on the graphite, reflecting their existence at the original gel surface.

Organogels are formed from fibrous aggregates of a variety of organic molecules[1] as exemplified by hydroxy group-substituted fatty acids,[2,3] steroid derivatives,[4,5] metal soaps,[6,7] lipids[8,9] and other hydrogen-bonding organic substances.[10-12] In these systems, extended network structures of aggregates are responsible for physical gelation of organic liquids, and these structures have been observed by transmission (TEM) and scanning (SEM) electron microscopies. TEM has been applied to diluted samples in order to avoid overlayering of aggregate structures,[9] and therefore TEM images may not be directly related to nanostructures present in the gel state. On the other hand, three dimensional structures can be observed by SEM for freeze-dried, metal-coated specimens under high vacuum.[5,10] It is probable that rigorous evaporation of the solvent under high vacuum and metal coating inherent in these electron-microscopy induce changes of the fragile 3D gel structure.

Atomic force microscopy (AFM) allows observation of surface nanostructures without staining or metal-coating. AFM observation of gel structures has been reported for air-dried hydrogels of polysaccharides in butanol[13] and poly N-isopropylacrylamide gel in water.[14] On the other hand, there have been no reports on the AFM observation of organogels comprised of low molecular weight organic molecules. This is because it requires ultrathin organogel structures to be formed on atomically flat surfaces without interference of the solvent evaporation process, and such preparative methodology has not been developed.

We recently demonstrated that hydrogel surfaces were utilized to two-dimensionally organize hydrophilic silica nanoparticles[15] and water-soluble proteins.[16] These materials were successively transferred onto solid substrates, together with network structures of the gel surface that acted as molecular glue (gel-assisted transfer, GAT).[15,16] The observed transfer of the molecular glue provides a convenient means to study the network structure of gels. Thus, we decided to investigate organogel surfaces transferred onto atomically flat highly oriented pyrolytic graphite (HOPG) surfaces, as schematically shown in Figure 1.

As an organogel-forming compound, L-glutamate-based



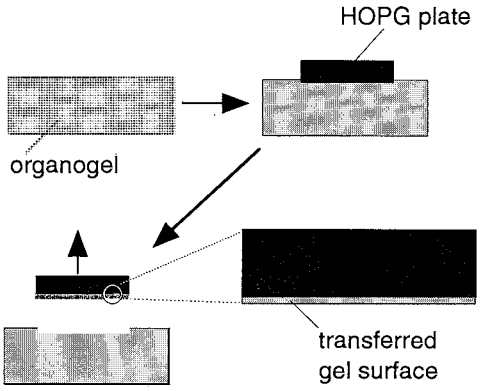


Figure 1. Schematic illustration of gel-transfer process.

ammonium amphiphile **1** was synthesized.[17] A family of glutamate-derivatives which contain three amide groups have been known as effective gelators.[18] When **1** was dissolved in chloroform at a concentration of 1 mM by heating, a transparent solution was obtained. In contrast, **1** gelatinized chloroform when a hot solution of **1** (50 mM) was rapidly cooled to 4 ℃. Formation of the organogel was thermo-reversible. HOPG was then pressed against the gel surface for 12 h. Figure 2 shows

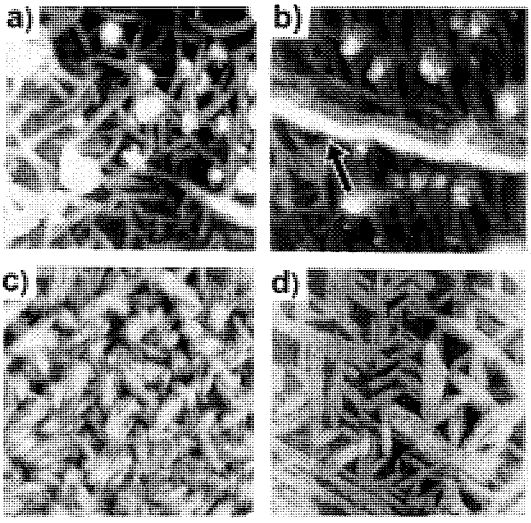


Figure 2. AFM images of **1** on HOPG surfaces.
(Scan area ; 2600 × 2600 nm²).
(a),(b) HOPG surface detached from organogel **1**.
(c) Cast sample prepared from 1mM solution.
(d) Cast sample prepared from 0.1mM solution.
The surfaces were observed in air.
(Topometrix, TMX-2100 Explorer, non-contact mode).

AFM images of the HOPG surface. In these images, bright domains correspond to aggregate structures of **1**, and those with higher brightness are layered on top of less bright aggregates. Fibrous structures with widths of 70 – 150 nm and heights of 19 – 23 nm are abundantly observed (Figure 2a). A helical superstructure (width ; ca. 180 nm, height ; ca. 80 nm) is also observed (Figure 2b, indicated by arrow).[19] Similar nanostructures were also observed when an acetonitrile-based gel of **1** was transferred to a HOPG surface. Formation of helical superstructures has been reported for L-glutamate derived ammonium bilayer membranes in water.[20]

The observed superstructure may be directly transferred from the gel surface or it may develop due to solvent evaporation during detachment of a HOPG plate from the gel surface. In order to distinguish these two possibilities, one drops of chloroform solutions (50 mM, 1 mM and 0.1 mM) of **1** were cast on HOPG and dried in air. The 50 mM- and 1 mM-cast samples gave analogous aggregate structures (Figure 2c). Individual aggregate structures in these cast samples are not clearly discernable, due to their high population on the surface. The average size of these cast-aggregates is 250 - 670 nm in length, and these structures are not developed to fibrous aggregates as found for the transferred sample (Figure 2a, 2b).

In the casting procedure, the solvent is removed only by evaporation, and aggregates originally dispersed in chloroform must be accumulated as multilayers on the surface. Fibrous and helical aggregates might have been buried in the cast-aggregates, since they were not observable by AFM.

On the other hand, a cast sample from 0.1 mM solution displayed rectangular islands with uniform heights of 6-8 nm (Figure 2d). The islands intersect each other at an angle of 120°. This unique morphology is characteristics of epitaxial crystallization on the graphite hexagonal lattice.[21] Therefore, **1** must be molecularly dispersed in chloroform at the concentration of 0.1 mM, and its crystallization on surface is induced by the topology of the HOPG surface.

Apparently, cast specimens are devoid of developed fibrous and helical nanostructures such as found for the transferred samples, and therefore, the latter structures are not produced in a casting-like process of solvent evaporation during detaching the substrate. We conclude from these observations that the developed nanostructures existing on the HOPG surface (Figure 2a, 2b) have been part of the surface portion of the organogel.

These AFM images were further compared with that obtained by transmission electron microscopy. Following a standard procedure,[9,20] we placed one drops of the 1 mM- and 0.1 mM- solutions in chloroform on a carbon-coated TEM grid on a filter paper. The drops immediately penetrated into the filter paper, and the grids were allowed to dry in air. The samples were then post-stained by dropping aqueous uranyl acetate. In a TEM picture of Figure 3, networks of fibrous structures with widths of 50 – 200 nm and lengths of more than 8 x 10^3 nm were abundantly observed (1 mM-sample). A similar morphology has been reported as TEM pictures of organogels.[9,10] The observed fibrous structures are considerably longer than those observed for the transferred (Figure 2a, 2b) and cast samples (Figure 2c). On the other hand, such an aggregate structure was not observed for the 0.1 mM-sample. This is consistent with the AFM observation that **1** is molecularly dispersed in the 0.1 mM-solution, and crystallization of **1** on the carbon-coated TEM grid is not likely.

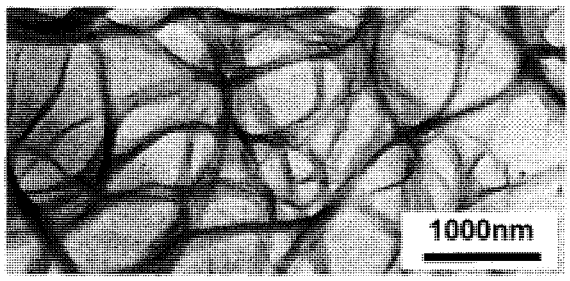


Figure 3. Transmission electron micrograph of **1** in chloroform. Sample is post stained by uranyl acetate.

It is noteworthy that AFM images of **1** transferred on HOPG surface provided more minute structures compared to those observed in TEM. In addition, they are transferred from the gel surface as nanostructures devoid of huge, bulk masses. Similar observations have been made for the hydrogel nano-networks in the GAT process,[15] and it is likely that the gel surface consists of two-dimensional networks rather than three dimensional cross-linked structures in the interior. Formation of these surface nanonetworks would be useful in a wide variety of contexts. Together with gel-assisted transfer of nanoparticles we previously reported,[15,16] a new research area related to gel surfaces will become versatile.

References and Notes

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