

Breath-Figures to Design Novel Functional Materials with Regular Features at Nanoscale

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ABSTRACT: *This article gives a brief account of how Breath-Figures (BF) are used as a dynamic templating method to prepare periodic nanostructures in sizes ranging from nanometers to micrometers. Although a defined, exact mechanism for BF formation is not yet known, literature surveys do conclude some important overviews. The formation of honeycomb structures, quasi-crystalline arrays, hexagonal arrays and highly ordered BFs of different shapes and pore sizes are summarized.*

KEYWORDS: Breath-Figures; dynamic templating; regular pattern design; nanoscale fabrication; microstructure surface; hexagonal arrays; honeycomb structures; quasi-crystalline arrays; polymers

REVIEW

Micro structured surfaces are used for adherent cell growth, as photonic-bandgap materials and as picoliter beaker [1-3]. Templating is the usual method used for their fabrication. Various types of templates are available some of which are, colloidal crystals obtained from polystyrene, ordered arrays of other colloidal particles [4-8], self-organizing emulsions or surfactants, microphase-separated block copolymers [9–15], certain bacteria [16] and filter membranes [17]. Two common features of these methods are that the size of the template is fixed, and the template often cannot be reused.

This is where Breath figures (BFs) come into play. It's a dynamic templating method for polymers, porous structured materials, nanoparticle-based micro- and nanostructures among others. It is a nontoxic and easily available templating medium which can create periodic structures of various sizes ranging from 50 nm to 20 μ m.

There is no single general mechanism for BF formation since the exact mechanism is not yet known. However, important generalizations had been concluded from literature surveys [18].

According to Srinivasarao, the hexagonally arranged arrays of air bubbles in thick (μ m) polymer films is due to "crystallization" of BFs [19-20]. Temperature of the surface of the polymer solution

is cooled to -6 to 0 °C due to the moist air blown over it. On the surface, water droplets nucleate and grow subsequently. Over time, rafts of non-coalescing droplets organize a hexagonal order on the surface. This leads to a quasi-crystalline array which is highly mobile. These arrays then sink into the solution of the polymer. This can be followed by deposition of the second layer of droplets on top of the first layer.

Once a monolayer of bubbles has formed, the remaining solvent and water will be evaporated if any solvent heavier than water is used. An imprint of the water droplets remains as a 2D or 3D material (air bubble array) in the polymeric matrix.

These bubble arrays are monodispersed for large areas ($4-50$ mm²) in most cases. They are interconnected which suggests that final stages of the bubble-array formation had coalescence phenomenon. The authors suggest that thermocapillary effect combined with Marangoni convection is the basis for to the observed stability of the droplet rafts.

BFs can form on solid surfaces as well as on liquids specially on paraffin oil in which it forms a hexagonal pattern [21]. The water droplets eventually get larger, more monodisperse and ordered over time. A disordered hexagonal array of very large water droplets can be attained in the last stages. Self-assembled honeycomb morphologies can be formed by exposing a drop of star polystyrene (SPS) and poly(para-phenylene)-block-PS (PPS) solution in carbon disulfide to a flow of moist air [22].

Highly ordered BFAs with bubble sizes ranging from $2-4$ μ m can be formed from polyquinoline–polystyrene block copolymer[23] using micelle formation for the gestation of the bubble arrays. Carboxylated and unmodified polystyrene can be casted from CS₂ and chloroform respectively to form highly ordered and well-developed bubble arrays [20,24]. Research shows that polymers with spherical shapes (block copolymers/star polymers) mostly form bubble arrays [25]. Yet, rigid-rod conjugated polymers too such as polythiophenes, poly-paraphenylene ethynylenes, nitrocellulose and polyfluorenes can yield monodisperse and highly ordered BFAs when correct conditions are used [26].

When solvents whose density is less than that of water are used for casting, multilayers of bubbles can be formed. Yet, certain research has observed multilayers when casting BFAs from CS₂[22,26]. This shows that obtaining multilayers is not only dependent on the solvent but also other effects like polymer structure.

Polymers such as star block polystyrenes (up to 18 arms) and grafted polystyrene [25,27–31] formed BFAs when cast from CS₂ in moist air and using low polymer concentrations. Pore size can be made smaller by increasing the number of arms attached to the specific core. E.g.: BFA pore size can be decreased from 750 to 450 nm by altering the end groups in a six-arm star PS (i.e. from an alkyl to an –OC₈H₂F₁₇ unit). Arrays with pore diameter of 250 nm can be produced using cyclodextrin based 18-arm star block polystyrenes.

Larger imprinted bubble arrays can be obtained by prolonging the time taken for the water droplets to grow [28]. This is because the bubbles can only grow for a short time since rafts of the droplets

sink into the water due to high polymer concentrations and constrains its growth.

When styrene and divinylbenzene are co-grafted into a microgel by an arm-first approach, crosslinked star polymers can be obtained [30]. The order and monodispersity of the bubbles depends upon the crosslinking time and the molecular weight of the stars.

The blue-fluorescent PPQ [(poly(5-phenyl-8-(4-vinylphenyl)quinoline)] of star block polymers can be used to form high quality BFAs whose bubble sizes range from 150 nm to 1 μ m when cast from CS₂. The bubble size depends on the velocity of the air flow [31]. Confocal fluorescence pictures of these arrays depict large bubbles where the BFA fluorescence depict the most intense fluorescence at 550 nm originating from the rims of the bubbles.

Well-shaped BFAs can be formed by casting organometallic PPE form CS₂[32]. This leads to an insoluble and highly crosslinked ceramic material when heated to even 600 °C due to high silicon, carbon, and cobalt content.

Honeycomb structures of 2- μ m size and 60 nm height which are flat with a 25 % ceramic yield can be obtained through pyrolysis of the cobalt/nickel containing bubble layers at 700 °C. This can be done by treating amyl acetate casted (carboxylated) nitrocellulose BFAs with with NiII acetate or CoII acetate in water. These permanent structures are reported to have exhibited interesting conducting properties too [33].

CONCLUSION

Although initially BFs were described by Rayleigh and Aitken in early 1910s[34,19], it was Knobler and coworkers [21] who explicated the fundamentals and mechanistic investigations of BFs around 1990s. BFs were imprinted in star and rod-coil polymers by Widawski and Francois et.al. in 1994[22a] which attracted the attention of material chemists. Srinivasarao's insight regarding Rayleigh's BFs to explain bubble array formation due to crystallization added further fame to this emerging field.

BF is in short, 'the fog' created when moist air is exhaled onto a cold surface which leads to formation of periodic structures. The larger bubbles produced are mainly used for micro lens arrays and cell growth while small-scale bubbles are utilized to study energy transfer. Marangoni convection and coalescence suppression are believed to contribute to high monodispersity and high ordering of the bubbles. In-depth mechanistic details of this seemingly simple process are yet to be understood.

This dynamic templating method has seen successful application in different polymers (star, rod-coil, linear, rigid-rod), metal nanoparticles, polyion complexes, and semiconductor nanoparticles [18]. Nitrocellulose graphitic structures, gold arrays and picoliter beakers are some of the examples which exhibit highly stable imprints. Photovoltaic applications, optics, cell-growth media, structural material encompassment and lotus-leaf surfaces are among the potential fields for BF methodology implementation.

Conflict of interest

The author declares no conflict of interest.

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