Editor's Choice

Toward step-by-step nuclear growth of surface two-dimensional porphyrin nanonetworks

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ABSTRACT

We report the development of a solution-based step-by-step technique, which utilizes the coordination bond between metalloporphyrin molecular units and metal linkages and results in the nuclear growth of nano-networks on solid substrates. The growth of the surface structures is strongly influenced by the choice of substrate materials and solvents: the molecule–substrate interaction and the solubility of the molecular units are important parameters in tuning the size and growth of the domains.

1. Introduction

Development of rational and facile methods for creating ordered structures with nanometer scale precision is one of the central issues in the fields of nanoscience and nanotechnology. Bottom-up approaches utilizing self-assembly processes of molecular systems allow the simple and quick formation of supramolecular structures on surfaces [1–8]. Using suitable designs and choices of molecular building blocks, a variety of surface nanoarchitectures can be prepared – these can be tuned and specific structural motifs can be stabilized by either covalent [9], coordination [10–20], and hydrogen bonds [21,22], or by π−π [23,24] and van der Waals interactions [24–26]. Metal–organic coordination architectures provide further diverse types of ordered structures with one-dimensional (1D, chain), two-dimensional (2D, monolayers) or three-dimensional (3D, multilayers) arrangement as well as attractive chemical–physical properties, such as redox change, catalytic activity and magnetism derived from the metal ion components.

A number of 2D networks of molecular building blocks connected by coordination bonds have been constructed on solid surfaces by both ultra-high vacuum (UHV) techniques and solution-based methods and they have been well-authenticated by scanning microscopy [9–14,21–31]. Surface assemblies fabricated by solution-based processes are more attractive from the point of view of developing realistic candidates for device application because they maintain their ordered arrangement under ambient working conditions [15–20,29–31]. In addition, the preparative protocols can be usually performed with simple inexpensive glass tools and facile reproducible chemical laboratory processes – that is, the primary molecular components and secondary building units (metal ion linkers) are prepared in solution and typically the solution is dropped on the substrate surfaces or the substrate itself is immersed into the solution. A successive step-by-step immersion procedure – alternate dipping of substrates into molecular building block and metal ion solutions accompanied by in-between rinsing and drying processes – provides well-ordered multilayers including extended porous assemblies (so called metal–organic frameworks, MOFs or porous coordination polymers, PCPs) on surfaces [15–20,32–34].

Recently, we have developed a new solution-based methodology in our quest to construct surface MOF (or PCP) nanoarchitectures with high crystalline order in both the in-plane and out-of-plane directions to the substrate [15–20]. The technique involves the combined sequential use of the Langmuir–Blodgett (LB) method [35–40] (this allows us to exercise superb control of the nanofilm crystallinity in the horizontal direction and to

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fabricate well-ordered monolayers on liquid surfaces that can be deposited onto solid substrates) and the layer-by-layer (LbL) growth method (this provides excellent control of the film orientation and the number of layers in the vertical direction to the substrate). The power of the integrated LB–LbL methodology was demonstrated by employing metalloporphyrin building units and metal ion joints to fabricate for the first time a perfectly crystalline surface MOF nanofilm. Porphyrins including metalloporphyrins are excellent candidates as molecular building blocks for the construction of both 2D and 3D architectures as they are characterized by an approximate two-dimensional (2D) square planar geometry [41–44]. The existence of a rich variety of (metallo)porphyrin derivatives, incorporating different center-coordinated metals (or void) and functional group substituents in the periphery of the molecules, such as pyridine or carboxylate ions, allows a fine control of the potential linkage motifs in coordination-bond-driven array fabrication both in the bulk crystalline state and at the nanoscale level, as demonstrated by the LB–LbL method [15–18].

As the dimensions of nanosized objects strongly influence their chemical and physical properties [45–50], fine control of the domain size of the surface nanostructures both laterally and vertically is an important target to address. The layer-by-layer (LbL) film growth strategy used above is an invaluable tool towards achieving the goal of generating surface crystalline multilayer assemblies of any desired thickness at the nanometer scale (*i.e.* with controlled domain size in the vertical direction). However, although the LB fabrication component of our earlier methodology obviously ensures the construction of well-crystalline monolayers, the assembly of surface 2D nanoarchitectures with completely controlled domain size at the sub-monolayer level in the film orientation parallel to the substrate surface has not been developed as yet.

In this paper, we demonstrate how a successive step-by-step immersion procedure can be applied to allow fabrication of metal-directed surface nanostructures consisting of metalloporphyrin molecular units. The developed experimental process is based on the idea of nuclear growth, which has been applied to the controlled synthesis of oligomeric suprastructures. Optimization of the fabrication conditions together with appropriate selection of the molecular building units and substrates employed have allowed us to guide the growth of nanostructured films in the direction parallel to the substrate.

2. Experimental

2.1. Materials and measurements

5,10,15,20-Tetra(4-pyridyl)-porphine zinc (II) (ZnTPyP) (purity 90%) was purchased from Porphyrin Systems. *Trans*-bis(benzonitrile)dichloropalladium (II) (PdCl$_2$(NCPh)$_2$) (99.99%) was purchased from Alfa Aesar. Pure grades of chloroform and methanol were purchased from Wako Pure Chemical Industries Ltd. or Junsei Chemical Co. Ltd. All chemicals were used as received without further treatment.

Three different solid substrates were employed for deposition and growth of the 2D submonolayer molecular arrays: (i) Au substrate (Au/Cr/ITO/glass): indium tin oxide (ITO) (3000 Å ± 10%), chromium (50–100 Å) and gold (99.99%, 100 Å ± 10%) were deposited successively under high vacuum onto glass plates at GEOMATEC Corporation. (ii) Quartz substrates: these were purchased (20 × 25 mm^2, 0.5 mm thickness) from SEIKO Co. Ltd. (iii) Sapphire (α-Al$_2$O$_3$ single crystal) substrates: the sapphire (0 0 0 1) surface was annealed with a hydrogen flame which created a uniform step structure with a terrace width of about 100 nm and a step height of 0.2 nm, attributed to the monolayer height of α-Al$_2$O$_3$. The off-angle was 0.15°. All substrates were immersed into an ultrasonic bath of chloroform and methanol, and then dried before the film fabrication.

UV–vis absorption spectra of the solutions and the films fabricated on Au/Cr/ITO/glass, quartz and sapphire substrates (*vide infra*) were measured in transmission mode with a Jasco V-570 spectrophotometer at room temperature. In the solution UV–vis spectroscopy measurements, 15 μL of a 10 μM PdCl$_2$(NCPh)$_2$ solution in chloroform was titrated into a quartz cell containing 3 mL of a 0.5 μM ZnTPyP chloroform/methanol (3:1, v/v) solution (1.5 nmol) and stirred for 10 min at room temperature. The titration was repeated eight times and the total amount of added PdCl$_2$(NCPh)$_2$ was 12 nmol.

2.2. Fabrication of nanoarrays on solid substrates

The 2D ZnTPyP–Pd arrays were deposited on the solid substrates and control of their domain size was attempted by repeated step-by-step growth protocols that included sequential reagent deposition, intermediate rinsing/solvent immersion and drying steps. The experimental procedures for the two growth protocols employed in this work are collected in Table 1.

2.2.1. Protocol I

Each substrate was first immersed into a 10 μM ZnTPyP chloroform/methanol (3:1, v/v) solution for 5 s (process #1). This was followed by immersion into chloroform for 5 s, and drying by nitrogen blowing (process #2). Then the substrate was immersed into a 10 μM PdCl$_2$(NCPh)$_2$ chloroform solution for 1 min (process #3). This was again followed by immersion into chloroform for 5 s, and finally drying by nitrogen blowing (process #4). The growth of the resulting Pd-mediated ZnTPyP arrays (ZnTPyP–Pd) is controlled by the number of deposition cycles (processes #1 ∼ #4). For comparison, for each substrate treated with the procedures described by protocol I above, an additional substrate was also prepared using the same number of cycles as before but omitting processes #3 and #4 (*i.e.* omitting the PdCl$_2$(NCPh)$_2$ deposition steps).

2.2.2. Protocol II

This involved a modified procedure to the experimental processes adopted in protocol I above. While the two reactant solution (ZnTPyP and PdCl$_2$(NCPh)$_2$) immersion steps (#1 and #3) were kept the same, the solvent rinsing procedures (#2 and #4) were

Table 1
Summary of the experimental procedures employed in the two protocols of 2D ZnTPyP–Pd array fabrication on solid substrates.

	Protocol I	Protocol II
Process #1		
ZnTPyP deposition	10 μM ZnTPyP in CHCl$_3$/CH$_3$OH, 5 s	10 μM ZnTPyP in CHCl$_3$/CH$_3$OH, 5 s
Process #2		
Rinsing	CHCl$_3$, 5 s	CHCl$_3$/CH$_3$OH, 10 s
Process #3		
PdCl$_2$(NCPh)$_2$ deposition	10 μM PdCl$_2$(NCPh)$_2$ in CHCl$_3$, 1 min	10 μM PdCl$_2$(NCPh)$_2$ in CHCl$_3$, 1 min
Process #4		
Rinsing	CHCl$_3$, 5 s	CH$_3$OH, 10 s, followed by CHCl$_3$/CH$_3$OH, 10 s