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Room temperature spontaneous surface condensation of boronic acids observed by scanning tunneling microscopy

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ABSTRACT

Herein, we discovered that the surface-confined condensation of boronic acid can happen spontaneously at room temperature, by comparing the kinetics of condensation of boronic acids with and without the negative sample bias, we found that the negative sample bias indeed accelerates the self-condensation reaction of boronic acid. Combining with *in-situ* STM images and ultraviolet photoemission spectrum (UPS) analysis, a reversible adsorption mechanism model was proposed and reasonably explains the reversible electric-field-induced phase transformation.

Surface-confined polymerization of organic molecules is a promising route to create exceptionally robust two-dimensional (2D) materials, including single layer covalent organic frameworks (COFs), or also termed as 2D polymers, which, with their well-defined chemical structure, represent a kind of fascinating 2D materials [1–6]. Taking advantage of the reversible nature of bond formation, dynamic covalent reactions such as boronic acid condensation and Schiff base condensation were widely used in producing COFs [7–11]. Understanding the mechanism of the dynamic covalent chemistry (DCC) is the basis for rationally controlling the formation of these materials [12,13].

In 2005, the first COF material, COF-1, was synthesized by Yaghi [14]. Subsequently, constructing bulk COFs and single-layer COFs based on the reversible condensation of boronic acids were reported by Louis Porte and other groups [15–19], in both cases, the polymerization required temperature of around 100 °C. Therefore, annealing is traditionally considered a necessity for the formation of boroxine rings (B3O3). Recently, De Feyter *et al.* have reported an inconceivable room-temperature condensation of boronic acids under electric field between the STM tip and the surface [20]. Remarkably, the polymerization or depolymerization can be selectively driven by an electric field at room temperature, which is unprecedented in COF-forming reactions. In order to comprehend the reaction mechanism, the solvent dependence of the reaction was studied, in which the local concentration of water at the 1-octanoic acid/highly oriented pyrolytic graphite (HOPG) interface was proved to be important [21]. However, further understanding the mechanism is challenging due to the reaction system at liquid-solid interfaces is highly complex, in which many crucial factors could affect the surface reactions, including solvents, adsorption and desorption of monomers and even dissolved impurities. So, devising experiments to get insight into the role of local electric field and provide further clues about the mechanism in the surface-confined condensation of boronic acids are meaningful.

Herein, a surface-confined synthesis protocol of self-condensation of 4,4′-biphenyldiyldiboronic acid (BPDA) has been studied as a model system at the solid-liquid interface using *in-situ* scanning tunnelling microscopy (STM) under ambient conditions. Intriguingly, we found that the condensation of boronic acid cannot only be realized by an electric-field inducing (Path 1), but also react spontaneously at the solid-liquid interface (Path 2) at room temperature (Fig. 1a). Through kinetic analysis, we verified the acceleration effect of negative bias on the condensation of boronic acid, and the mechanism was studied based on *in-situ* STM images and ultraviolet photoemission spectrum (UPS) analysis.

Typical STM images of self-assembly of BPDA (2.07×10^{-4} mol/L) and the hexagonal polymer networks obtained from the

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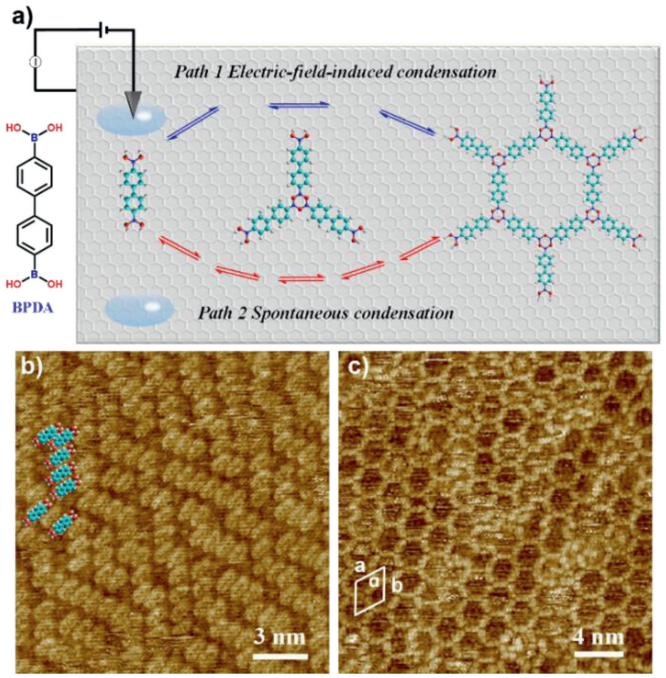

Fig. 1. (a) Schematic illustration of condensation paths of BPDA. (b) High-resolution STM image of self-assembled structure of BPDA. (c) High-resolution STM image of boroxine-linked COFs obtained by spontaneous condensation of BPDA at the octanoic acid/HOPG interface. Imaging conditions: $I_{set} = 300.0$ pA, $V_{bias} = 0.60$ V.

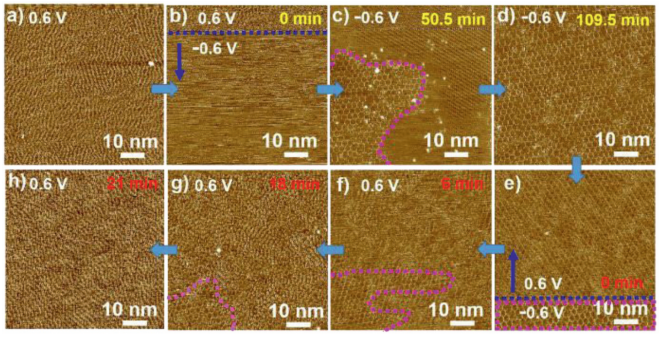

Fig. 2. (a–h) Sequential STM images showing the phase transition between boroxine-linked COFs and SAMs by change the polarity of bias at the octanoic acid/HOPG interface. Images are recorded at the same location. Imaging conditions: $I_{set} = 300.0$ pA, (a) $V_{bias} = 0.60$ V, (b-d) $V_{bias} = -0.60$ V. (e-h) $V_{bias} = 0.60$ V.

self-condensation of BPDA were shown in Figs. 1b and c. Fig. 1b shows a typical STM image of the assembly of boronic acid. The shape and size of each rounded rectangle in the high-resolution STM image match those of a BPDA molecule. The majority of the self-assembled molecular networks (SAMs) of BPDA is disordered, these assemblies are stabilized by the π-π stacking interactions with the HOPG substrate and O-H···O hydrogen bonds between neighboring boronic acid groups. The lattice parameters of the hexagonal COFs in Fig. 1c are $a = b = 2.3 \pm 0.2$ nm, $\alpha = 61 \pm 2°$, well in line with the theoretical value of boroxine-linked COFs by the polymerization of BPDA reported [16,17].

As a breakthrough, De Feyter *et al.* reported the polymerization of boronic acids induced by application of negative bias at the solid-liquid interface at room temperature. In our work the reversible local electric field induced polymerization of BPDA at the solid liquid interface was also verified. As shown in Figs. 2a–d, under negative sample bias, the self-assembly of BPDA can gradually transform to hexagonal polymer networks, indicating occurrence of field induced condensation. After about 110 min continuous scanning under negative sample bias, the supramolecular network of BPDA completely transform into hexagonal COFs (Fig. 2d). Once the 2D covalent network structures were obtained, we reversed the sample bias to positive and scanned the same area continuously. It was revealed that SAMs gradually appeared with the disappearance of COFs, the surface coverage of SAMs reached around 98% after *ca.* 21 min (Figs. 2e–h). Therefore, we draw the conclusion that negative sample bias induces condensation of boronic acids, while positive sample bias induces the decomposition of hexagonal COFs.

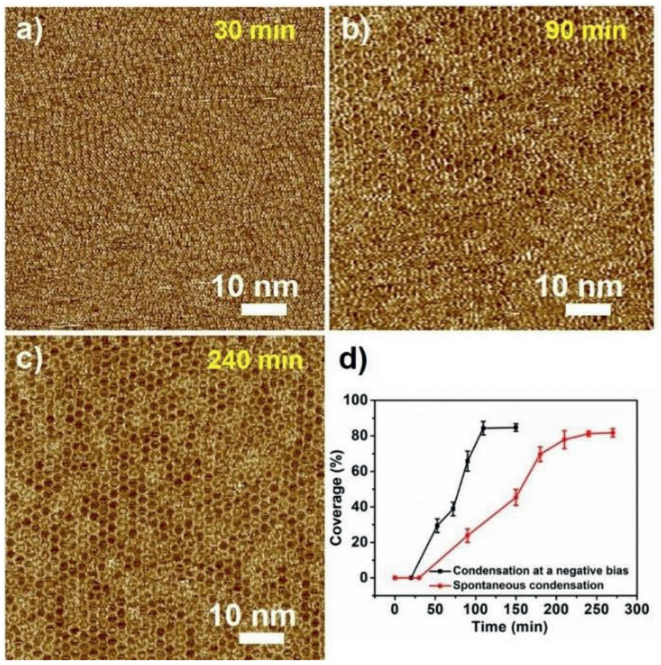

Fig. 3. (a–c) Representative STM images of spontaneous condensation of BPDA, STM images were obtained under a transient positive sample bias after BPDA was deposited onto the HOPG surface and laid aside for 30 min, 90 min and 240 min, respectively. Imaging conditions: $I_{set} = 300.0$ pA, $V_{bias} = 0.60$ V. (d) Plot of the coverage of boroxine-linked COFs against time under spontaneous condensation and condensation reaction induced by a negative bias.

To our surprise, STM observation verified that spontaneous condensation could happen without the induction of external electric field at room temperature. The sample was prepared by depositing BPDA solution onto the HOPG surface and then laying it aside for a period of time, after which the STM characterization was performed with a transient positive sample bias. It is worth noting that the purpose of STM characterization with a positive sample bias was to avoid the electric field induced condensation of boronic acids by negative sample bias. Intriguing, the honeycomb network was also observed after the sample was laid for a period of time (Fig. 3). Since the positive sample bias was unable to induce the condensation of boronic acids, it means that boronic acid condensation happens spontaneously at room temperature. Sequential characterization at different standing time provides insight into the kinetics of the spontaneous condensation (Fig. 3 and Fig. S1 in Supporting information). The spontaneous condensation appears to need some induction time. When BPDA solution was deposited onto the HOPG surface and laid aside for 30 min, BPDA was exclusively in the form of self-assembly, no domains of COFs were observed (Fig. 3a). The domains of boroxine-linked COFs network of BPDA keeps growing with standing time, 25% of the surface was covered by COFs at 90 min, while the surface coverage of COFs reached around 83% *ca.* 240 min after BPDA solution was deposited onto the HOPG surface (Fig. 3c). A more detailed sequential STM images of the spontaneous reaction process obtained by spontaneous condensation of BPDA was shown in Fig. S1. In addi-

tion, the spontaneous condensation of BPDA was also verified by comparative X-ray photoelectron spectra (XPS) that acquired from both COFs film prepared on HOPG surface at room temperature and BPDA monomers. Since hydrogen is slightly more electronegative than boron, the O 1s of COFs film shifts slightly toward lower binding energy (Fig. S2 in Supporting information), provides further evidence for the spontaneous condensation of BPDA [18].

In contrast to the surface confined polymerization of boronic acid, the ^{1}H NMR spectra (Fig. S3 in Supporting information) indicate that the extent of the boronic condensation in solution at room temperature is very small, and the reaction does not proceed as time of reaction extended to one, three and five days. What is more, after BPDA solution (2.07×10^{-4} mol/L) standing in microcentrifuge tube for about 4 h/24 h at room temperature, we took 5 μL of the solution phase product dropped onto the HOPG surface, followed by an immediate STM characterization, a single layer of assembly of BPDA was obtained with nearly full surface coverage (Fig. S4 in Supporting information) and no detectable domain of COFs. The above results further proved that the surface confinement has a significant effect on promoting boronic acid self-condensation [22,23], while in solution the degree of reaction of BPDA is low.

In order to verify the universality of surface-confined spontaneous boronic acid condensation at room temperature, 1,3,5-tris (4-phenylboronic acid) benzene (TPBA) and 1,3,5-tris(4-biphenyl boronic acid)benzene (TBPBA) were also tested. After TPBA (2.28×10^{-4} mol/L)/TBPBA (2.14×10^{-4} mol/L) was deposited onto the HOPG surface and laid aside for 4 h, we performed the STM characterization at a transient positive sample bias. Some hexagonal network structures were observed in both systems (Fig. S5 in Supporting information). Combined with the corresponding high resolution STM images in Fig. S6 (Supporting information), we draw a conclusion that the spontaneous polymerization reaction has taken place successfully in both TPBA and TBPBA systems. The surface coverage of boroxine-linked COFs for BPDA, TPBA and TBPBA after 4 h of spontaneous condensation were estimated to be 83%, 26% and 8%, respectively. From BPDA to TBPBA, the degree of polymerization decreases with the increase of the molecular size, which can be explained by the reduced surface mobility of the larger molecule. Although the polymeric domains for TPBA and TBPBA are small and discrete compared to those of BPDA, we have attested the universality of surface-confined spontaneous condensation reaction of boronic acid at room temperature.

In order to further understand the effect of negative sample bias on boronic acid self-condensation, a comparative statistical analysis on the time dependence of coverage of COFs both under negative electric field and without electric field (spontaneous condensation) are shown in Fig. 3d. It takes about 110 min for the surface to be fully covered by COFs at a negative sample bias, while it needs 240 min for the spontaneous condensation. Obviously, the negative sample bias accelerated the self-condensation reaction of BPDA, and the internal mechanism can be understood by *in-situ* STM observations and UPS analysis.

As shown in Fig. 4a, on the STM image of COFs obtained by spontaneous boronic acid condensation at room temperature, the white dotted lines highlighted some fuzzy disordered regions that may be caused by the adsorption of monomers or oligomers on the HOPG surface. When the sample bias was changed from positive to negative (Fig. 4b), the fuzzy regions become clear and the molecules are desorbed from the surface. Subsequently, some newly formed condensation products of boric acid were clearly observed in these areas. As shown in the continuous STM images of Figs. 4b and c, the arrows with different colors highlighted the sites where the growth and nucleation of COFs. On this basis, we speculate that the negative sample bias could facilitate the desorption of monomers from the surface, and further promoted the

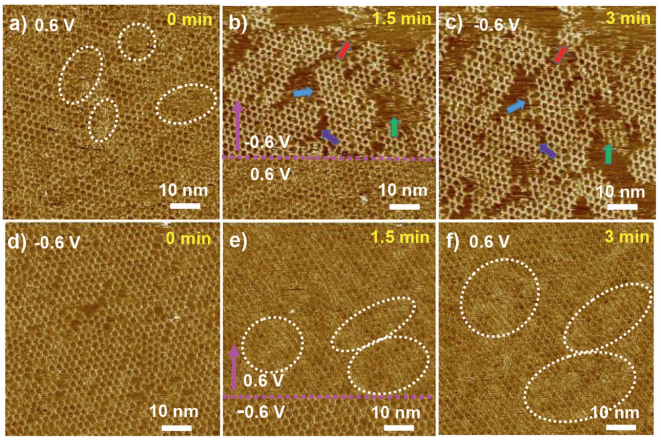

Fig. 4. *In-situ* STM images with a time interval of 1.5 min, showing the reversible adsorption and desorption of molecules on the surface. (a) STM images of spontaneous condensation boroxine-linked COFs obtained under positive sample bias. (b, c) The sample bias is changed from positive to negative, and the arrows with different colors highlight the sites where the growth and nucleation of COFs. (d) STM images of boroxine-linked COFs obtained under the induction of negative bias at the octanoic acid/HOPG interface. (e, f) The sample bias is changed from negative to positive, some blurry areas appeared. Imaging conditions: $I_{set} = 300.0$ pA, (a, e, f) $V_{bias} = 0.60$ V, (b-d) $V_{bias} = -0.60$ V.

polymerization of boronic acid on the surface. As a complementary proof, for boroxine-linked COFs obtained by electric-field induced condensation, the empty pore structure of COFs can be clearly observed under negative sample bias, while when the sample bias was changed from negative to positive, some of the pore structures became blurred, which may be attributed to the adsorptions of monomers in the pores of the COFs (Figs. 4d–f). After continuous scanning under positive sample bias, high density of SAMs gradually appeared with the disappearance of COFs (Figs. 2e–h, which have been discussed above). Obviously, positive sample bias promotes the adsorption of molecules on the surface.

Then, in order to understand the internal mechanism of electric field driven adsorption and desorption of monomers on the surface, the clean HOPG and HOPG covered with BPDA (HOPG + BPDA) were characterized by UPS. As shown in Fig. 5a, the binding energy of the secondary cutoff edge (E_{cutoff}) of clean HOPG and HOPG + BPDA is 16.96 eV and 17.30 eV, respectively, and the work function (Φ) are determined by

$$\Phi = h\upsilon - (E_{cutoff} - E_{Fermi}) \quad (1)$$

Here, $h\upsilon = 21.2$ eV and $E_{Fermi} = 0$ eV. So, Φ of clean HOPG and HOPG+BPDA were calculated to be 4.24 eV and 3.90 eV, respectively. The work function decreased after adsorption of BPDA onto HOPG surface, which indicates that electrons were transferred from the boronic acid molecules to HOPG (Fig. 5b). Combining with STM observation, a reversible adsorption mechanism model was proposed in Figs. 5c–e. When applying a positive bias on the HOPG, the electric field favors the electron transfer from the BPDA to HOPG, and then enhances the adsorption of BPDA, thus more molecules are attached to the HOPG surface to form a condensed self-assembling network (SAMs) of BPDA (Fig. 5d). On the contrary, under a negative sample bias, the electron transfer is impeded, thus boronic acid molecules desorb into the solution, which provides more space and favors the growth of open COFs (Fig. 5e).

Thus, based on the reversible adsorption mechanism model, the reversible electric-field-induced SAM-COF transformation can be explained in terms of concentration-dependent phase transformation. The positive sample bias could enhance the adsorption of BPDA. Once a sufficient quantity of monomers are supplied, the formation of close-packed assemblies with high density is energetically favored over the open porous COFs. On the contrary, when

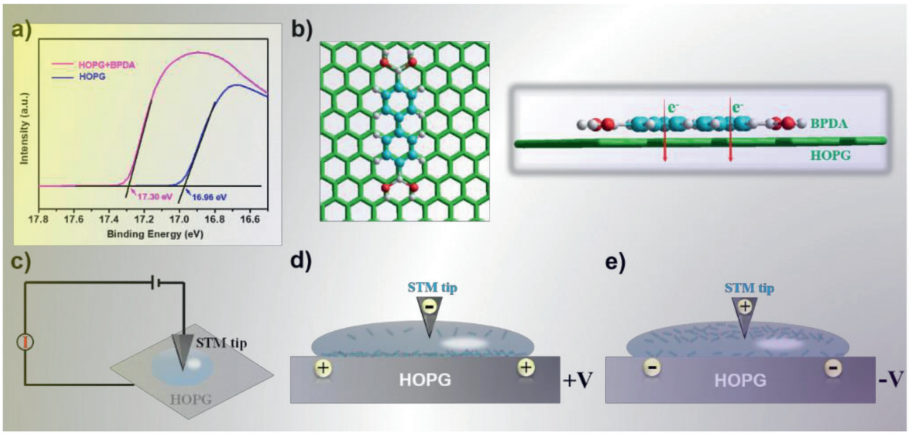

Fig. 5. (a) The binding energy of the secondary cutoff edge (E_{cutoff}) of pure HOPG and HOPG+BPDA. (b) The schematic illustration of electron transfer from the boronic acid molecules to HOPG. (c-e) The reversible adsorption mechanism model.

the sample bias is negative, the monomer desorbs into the solution and lower surface concentration facilitates the on-surface condensation reaction to form open COFs.

In conclusion, herein we verified the spontaneous condensation of boronic acid at room temperature in the surface confined synthesis of COFs. By comparing the kinetics of condensation of boronic acids with and without the negative sample bias, we found that the negative sample bias indeed accelerates the self-condensation reaction of BPDA. The reversible electric-field-induced SAM-COF transformation could be explained in terms of concentration-dependent phase transformation. We envision that these results will give more insights into the boronic acid condensation reaction at the solid-liquid interface.

Declaration of competing interest

The authors declare no confliction of interest.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2022.108006.

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