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Received 5th December 2013, Accepted 25th December 2013 Ni-induced supramolecular structural transformation of cytosine on Au(111): from one-dimensional chains to zero-dimensional clusters<sup>†</sup>

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Interplay between high-resolution STM imaging and DFT calculations demonstrates that through introduction of Ni atoms the self-assembled structures of cytosine could undergo a structural transformation from 1-D chains to 0-D clusters on Au(111). Interestingly, the 0-D clusters formed are separately distributed on the surface.

The fabrication of desired nanostructures on solid surfaces in a controllable manner has gained tremendous attention due to potential applications in the field of nanotechnology such as molecular electronic devices,<sup>1</sup> organic photovoltaic devices,<sup>2</sup> and nanosensors.3 To facilitate the construction of more and more complicated structural motifs, artificial regulation of the on-surface nanostructures to generate multiple dimensions and patterns through simple routes has become an appealing and challenging strategy. To pave the way for exploring the formation and transformation mechanisms of surface nanostructures, ultrahigh vacuum scanning tunnelling microscopy (UHV-STM) has been employed since it allows a direct, realspace characterization of the formed nanostructures at the atomic scale.<sup>4</sup> Recently, supramolecular structural transformations triggered by external stimuli, such as heating,<sup>5</sup> irradiation,<sup>6</sup> changing the deposition coverage,<sup>7</sup> STM manipulation,<sup>8</sup> and introduction of metal atoms,<sup>9</sup> have been extensively studied. Among these attempts, attention has been mainly focused on changing the structural motifs, bonding types, structural chiralities, etc. within 2D surface nanostructures,<sup>5,9-11</sup> or changing the surface structures from lower to higher dimensions.<sup>12</sup> However, in situ regulation of the surface nanostructures from higher to lower dimensions has been scarcely reported to date.<sup>8,13</sup> Therefore, it is of general interest to explore dimension-related structural transformations especially from higher to lower dimensions and to unravel the underlying

a A: electron acceptor D: electron donor C gray N blue C rudio C rudio C gray N blue C rudio C

**Fig. 1** (a) The chemical structure of the cytosine molecule, A and D represent the binding sites of the molecule: hydrogen donor (electron acceptor) and hydrogen acceptor (electron donor) for hydrogen bonding and metal–organic coordination bonding. (b) STM image of 1-D zigzag chains formed by cytosine molecules on Au(111). (c) STM image of 0-D clusters formed by codeposition of cytosine molecules and Ni atoms on Au(111). (scanning conditions: (b)  $I_t = 0.22$  nA,  $V_t = -1.25$  V; (c)  $I_t = 1.63$  nA,  $V_t = -1.27$  V)

mechanism, which may shed light on artificially fabricating nanostructures with controllable dimensions on surfaces.

The cytosine molecule is known to be capable of forming intermolecular hydrogen bonds,14,15 and its binding sites (see Fig. 1a) could also be employed for metal-ligand coordination bonds. Introduction of metal atoms such as Co, Fe, Cu, K, and Cs, has been proven to be effective for versatile in situ regulation of structural characteristics.<sup>16-19</sup> In this communication we demonstrate, from the interplay between highresolution STM imaging and density functional theory (DFT) calculations, that cytosine molecules initially form hydrogenbonded glassy zigzag chains after direct deposition on a surface held at room temperature (RT), whereas, surprisingly, when Ni atoms are introduced one-dimensional (1-D) chains can transform into zero-dimensional (0-D) triangular clusters stabilized by three cytosine molecules coordinating with three Ni atoms, and the clusters are found to discretely distribute on the surface. The DFT calculations indicate that such a structural transformation from 1-D to 0-D results from competition between hydrogen bonding and coordination bonding. Due to the heterogeneous distribution of the binding sites on the cytosine molecule (see Fig. 1a), the coordination between

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cytosine molecules and Ni atoms completely screens the available binding sites within the formed triangular clusters, which inhibits the formation of any potential hydrogen bonds or coordination bonds between the clusters, and moreover, the repulsive intermolecular forces between clusters finally leads to the discrete distribution of clusters. Such findings may provide some theoretical basis for regulating structural dimensions with simple routes which could be extended to more general cases.

After deposition of cytosine molecules on Au(111) held at RT, characteristic 1-D molecular chains randomly linked together are observed as shown in Fig. 1b. As reported previously,<sup>14,15</sup> in this structure, each cytosine molecule links with two neighbouring molecules by hydrogen bonding to form 1-D zigzag chains, and the chains growing along arbitrary directions are then hydrogen bonded to each other by end-to-end or end-to-side connections to form the so-called glassy structure. The 1-D chains are found to be highly mobile at RT and are easily broken during scanning indicating that the interconnections between cytosine molecules are not stable at RT.

To explore the possibility of metal-induced structural transformations on the self-assembled structure of cytosine, we sequentially codeposited cytosine molecules and Ni atoms onto the Au(111) surface at RT. Surprisingly, when Ni atoms were introduced 1-D chains could transform into 0-D clusters, discretely distributed on the surface as shown in Fig. 1c. A smaller dosage of Ni atoms led to the coexistence of 1-D chains and 0-D clusters (see Fig. S1a and b, ESI†), which verifies that the structural transformation is induced by the addition of Ni atoms. The predominant species among these clusters have an equilateral triangular shape which is speculated to be composed of cytosine molecules coordinating with Ni atoms. Note that some triangular clusters show irregularity (*i.e.* compressed or elongated triangular clusters) which is attributed to movement of the whole cluster as demonstrated in Fig. S2 (ESI†).

Detailed analysis reveals that the triangular clusters mainly distribute in four distinct directions with respect to the substrate as denoted by A, B, C and D in Fig. 2a. From the highresolution magnified STM images of the triangular clusters (cf. Fig. 2b) we can identify that the clusters are formed by three bright protrusions, attributed to cytosine molecules. When we scanned with a special tip state a bright spot could also be resolved in the centre of each triangular cluster (indicated by green arrows) as shown in Fig. S3 (ESI<sup>+</sup>). As mentioned above, the triangular clusters are formed by codeposition of cytosine molecules and Ni atoms, thus, the central bright spot is naturally attributed to the electronic states related to Ni atoms. Based on the STM analysis above, detailed DFT calculations including the substrate are performed. After an extensive structural search and comparison with high-resolution closeup STM images, we have identified the four most energetically favourable configurations with the same energy. Both the optimized configurations and the simulated STM images are found to correspond well to the observed configurations A, B, C and D in both topographies and directions (see Fig. 2b). From the optimized model we can identify that the triangular cluster



**Fig. 2** (a) STM image of triangular metal–organic clusters showing four distinct directions as denoted by A, B, C and D. (b) High-resolution close-up STM images, DFT optimized models and simulated STM images of A, B, C and D, respectively. A (C) and B (D) are enantiomers of each other with respect to the [112] direction. A and C could be obtained from each other by 60 degree rotation, likewise for B and D. (scanning conditions:  $I_t = 1.63$  nA,  $V_t = -1.27$  V, STM image simulation was carried out at the bias voltage of -1.2 V).

is built up by three cytosine molecules coordinating with three Ni atoms, and there is also a single NH···O hydrogen bond in between the cytosine molecules. Combining STM images and DFT calculations, we find that configurations A and C are formed by homochiral cytosine molecules, while B and D are the enantiomers of A and C with respect to the  $[11\overline{2}]$  direction. Configurations A and C could be obtained from one to the other by 60 degree rotation of the whole cluster, and the same applies for B and D. It is noticeable that if we increase the amount of



**Fig. 3** (a) Electrostatic potential map qualitatively shows the positively charged hydrogen atoms at the periphery of the triangular cluster (red and blue colours represent negative and positive potential regions, respectively). (b) Bader charge analysis quantitatively shows the positively charged hydrogen atoms at the periphery of the cluster.

clusters to increase surface coverage, the clusters are still highly separated from each other as shown in Fig. S1c (ESI $\dagger$ ).

To reveal the origin of the discreteness of the clusters on the surface we have performed further analysis on the optimized models of the triangular cluster. From the models we can identify that within the triangular clusters all of the potential binding sites (O and N) of cytosine molecules are occupied when coordinating with three Ni atoms, which inhibits the formation of any potential hydrogen bonds or coordination bonds between clusters. In such cases only hydrogen atoms are available in the periphery of the clusters. We therefore speculate that there should be repulsive interactions between the clusters, dominating the discrete distribution of the clusters.<sup>20</sup> The electrostatic potential and Bader charge analysis based on DFT calculations including the gold surface were performed to qualitatively and quantitatively elaborate on the repulsive interactions between the triangular clusters as shown in Fig. 3. From the electrostatic potential map we can recognize that all of the hydrogen atoms are positively charged, and from the Bader charge analysis we can further quantify the charges on each hydrogen atom. Thus, the discreteness of the clusters is attributed to the electrostatic repulsion induced by the positively charged hydrogen atoms.

Hence, the scenario for the structural transformation from 1-D chains to 0-D clusters could be proposed as follows: (1) after deposition of cytosine molecules 1-D chains are formed by hydrogen bonding on the surface; (2) after introduction of Ni atoms, because cytosine molecules are more prone to bind to Ni atoms due to the competition between coordination bonds and hydrogen bonds, moreover, due to the heterogeneous distribution of the binding sites on the cytosine molecule, the N and O atoms preferentially coordinate with Ni atoms leading to the formation of 0-D metal-organic triangular clusters; (3) the formation of such triangular clusters leads to the complete occupation of all the available binding sites on the cytosine molecules after coordinating with Ni atoms, subsequently, the formation of any potential hydrogen bonds or coordination bonds between the clusters is inhibited. The electrostatic repulsion induced by positively charged hydrogen atoms in

the periphery of the formed clusters results in the discrete distribution of the clusters on the surface.

In conclusion, from the interplay of high-resolution STM imaging and DFT calculations, we have demonstrated that by introduction of Ni atoms the self-assembled structures of cytosine could undergo a structural transformation from 1-D chains to 0-D clusters on Au(111). Interestingly, the formed 0-D metal–organic triangular clusters discretely distribute on the surface and the heterogeneous distribution of potential bind-ing sites on cytosine molecule is revealed to be the key. These findings may inspire further investigations into fabrication of low dimensional surface nanostructures by carefully choosing appropriate molecules and metallic atoms.

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