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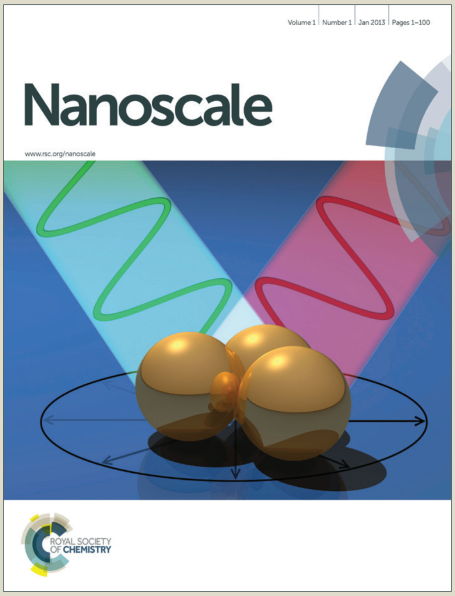

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Construction of carbon-based two-dimensional crystalline nanostructure by chemical vapor deposition of benzene on Cu(111)

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Abstract

A new carbon-based two-dimensional (2D) crystalline nanostructure is discovered. The nanostructure is facilely constructed by chemical vapor deposition (CVD) of benzene on Cu(111) in an ultrahigh vacuum (UHV) chamber. Low temperature scanning tunneling microscopy and spectroscopy (STM/STS) study of the nanostructure indicates an orthorhombic superstructure and a semiconductor character with an energy gap of 0.8 eV. X-ray photoelectron spectroscopy (XPS) study shows that C-C(sp^2) bonding is predominantly preserved, suggesting a framework consisting of π-conjugated building blocks. The periodic nanostructure is found to be a surprisingly excellent template for isolating and stabilizing magnetic atoms: Co atoms deposited on it can be well dispersed and form locally ordered atomic chains with their atomic magnetism preserved. The nanostructure may thus serve as a potential playground for organic spintronic applications. A most possible structural model of the nanostructure is proposed with the aid of density functional theory (DFT) calculation and simulation, suggesting that the 2D nanostructure may consist of polyphenylene chains interconnected by Cu adatoms.

1 Introduction

The carbon-based low-dimensional materials have attracted broad interest due to their unique physical and chemical properties. There are examples like graphene, graphene nanoribbon, carbon nanotube, fullerene, all kinds of organic chains[1,2] and films[3,4] etc. showing great potential in practical application for the next-generation transistors, optoelectronic devices and biological sensors.[5] Besides their intrinsic properties, new properties and functions can be generated when combining with metal atoms. Working as the template or doping matrix for transition metals and alkali metals can create new magnetically coupled nanostructures as spintronic devices[3,6,7] and generate superconductivity[8–10] respectively. As the generally existing π-electron conjugated state, low-dimensional carbon-based materials are thought to induce huge magnetic anisotropy energy when interacting with magnetic transition atoms.[11,12] This kind of system may also give rise to pronounced Kondo effect.[13,14] Considering all of the above points, it's of interest and importance to look for new carbon-based low-dimensional structures with potential applications in organic electronics and spintronics.

Aromatic molecules are important carbon sources for low-dimensional carbon-based nanostructures like graphene[15] and graphene nanoribbon.[16,17] As the simplest aromatic molecule, benzene has been used to fabricate graphene on copper foil at relatively low temperature using traditional CVD method.[15] In this work, we fed benzene onto Cu(111) single crystal surface using UHV CVD method and surprisingly discovered an unprecedented 2D periodic nanostructure. It was characterized in detail with low-temperature STM/STS. Ex-situ XPS was also measured to analyse the chemical constitution of the nanostructure. As Co atoms on benzene and graphene are proposed as high density magnetic storage units,[11] we further deposited cobalt atoms on this nanostructure. The cobalt atoms deposited at room temperature can disperse on the substrate in disorder. After annealing to 400 K, cobalt atoms diffuse to become locally ordered atomic chains. Both the individual cobalt atoms and atoms in the cobalt chain show Kondo effect[18] in dI/dV spectra measured at 5.5 K. This new carbon-based 2D nanostructure may have potential applications in organic electronics and spintronics.

2 Materials and Methods

The growth of the nanostructure was performed in a UHV chamber with a base pressure of 1×10^{-10} mbar. A Cu(111) single crystal (12×5 mm^2, MaTeck GmbH, Purity 99.999%) was used as the substrate and cleaned by cycles of Ar$^+$ sputtering and annealing. Before growth the substrate was heated to about 710 K by an electron beam heater with the background pressure of 5×10^{-10} mbar. Benzene molecules were then dosed through a leak valve and a tube (diameter ∼8 mm) to about 5×10^{-7} mbar. The distance between the tube nozzle and sample was fixed to 2 cm. Before dosing, benzene molecules were purified by cycles of freeze-pump-thaw method in which molecules were firstly frozen by liquid nitrogen cooling, secondly pumped through a rotary pump, thirdly thawed with the valve to vacuum pump closed. The growth time was 50 minutes and then we closed the leak valve and the heater to let the temperature of sample drop freely. An in-situ low-temperature scanning tunneling microscope (Omicron GmbH) was used to characterize the sample at 77 K and 5.5 K with a base pressure of 2×10^{-11} mbar. The tunneling conductance spectra (dI/dV) were measured with lock-in technique (V_{mod} = 4 mV, f_{mod} = 733 Hz). As for the x-ray photoelectron spectroscopy, the x-ray source gun type is Al-K$_\alpha$ and the spot size of the light is 500 μm. DFT calculation was performed using the Vienna ab initio simulation package (VASP) within the Perdew-Burke-Ernzerhof (PBE) parameterized generalized gradient approximation[19] and the electron-ion interaction was described with the projector-augmented wave (PAW) method. One layer of copper atoms were used as substrate and were fixed during the optimization. The surface Brillouin zone was sampled using Monkhorst scattering method with 4×4×1 mesh. The STM image was routinely simulated using the Tersoff-Hamann approximation.

3 Results and discussion

The STM topographic image of the obtained nanostructure is presented in Fig. 1a. It shows a high-ordered periodic corrugation with few defects. The structure is found uniformly all over the Cu(111) substrate. Hexagonal rings are very clear at the bias of -1 V, but that's obviously not the carbon hexagonal ring of graphene. By simply averaging the distances between adjacent height peaks in the two orthogonal directions (Fig. 1b,c), we roughly estimate the diameter of the hexagonal ring to be 0.52 nm which is about twice larger than that of graphene(about 0.25 nm). The nanostructure has a rectangular unit cell (Fig. 1d) with the period of 0.88 nm in the blue line marked direction and 1.76 nm in the red line marked direction (Fig. 1a,b,c). The two directions coincide with the crystal direction $[11\bar{2}]$ and $[1\bar{1}0]$ of Cu(111) surface respectively which have been calibrated by atomic resolution STM imaging of the bare Cu(111) surface prior to the growth. This gives approximately the surface Wood's notation c(2×7) considering Cu nearest neighbor distance of 2.55 Å which is shown in Fig. 1d. A possible arrangement of substrate Cu atoms is also shown for a suggestive picture.

We also performed STS experiment on the nanostructure. A representative dI/dV tunneling spectrum of the nanostructure is shown in Fig. 1e. The spectrum shows a typical gap feature near the Fermi level. A weak resonance lies at 0.2 eV below the Fermi level is attributed to the edge of valence band. There is a strong resonance peaked at 1.2 eV above the Fermi level. The resonance is so broad that we attribute the edge of conduction band to the onset of the resonance at 0.6 eV above the Fermi level. We thus conclude that the nanostructure takes on the characters of semiconductors with a gap of 0.8 eV. We notice that the nanostructure's dI/dV tunneling spectrum is very much like that of armchair graphene nanoribbon (AGNR).[17] As we know, graphene nanoribbon's band gap stems from its broken period. Specifically, both quantum confinement effect and effect of bonding at edge contribute to band gap of AGNR.[20] As benzene molecule who works as the building unit is aromatic, the nanostructure here is very likely π-conjugated. The energy gap here may also result from these effects. This indicates there exist edges or, in another word, confinement in this nanostructure. The confinement can be one dimensional or two dimensional in the surface plane. If the confinement is one dimensional, it is something like GNR or polymerized phenylene. If the confinement is two dimensional, it could be the arrays of carbon clusters like that in Wang et al.'s work[21] or a two-dimensionally polymerized phenylene.

To investigate the chemical constitution of the nanostructure, an ex-situ x-ray photoelectron spectroscopy analysis of the nanostructure was carried out as shown in Fig. 2. From the overall energy scan we can see signals of Cu, O and C. The corresponding excitation electron states of each peaks are signed (Fig. 2a). The O 1s peak at 530.49 eV mainly arises from adsorbed molecular oxygen. The narrow scan of C 1s peak is shown in Fig. 2b. The strong peak at 284.4 eV indicates most carbon atoms in the sample have a chemical environment of C-C(sp^2) bonding.[22] It confirms that the nanostructure is a π-electron system, as we expected. It's known that metal carbides such as VC, NbC, TaC have a binding energy range from about 281 eV to 283 eV.[23,24] The peak at 283.2 eV implies the possibility of copper involved in the binding of the structure which have been seen in some reported structures.[1,25] The Cu atoms may act as bridging atoms between carbon clusters which hinder the units to form into graphene, or act as bonding atoms between the nanostructure and the substrate. There is a weak peak at 288 eV corresponding to C=O bonds. This implies there exist carbon dangling bonds in the nanostructure, which were oxidized by oxygen in air when the sample was taken out from the vacuum chamber. The dangling bonds can be from the edges we inferred in the above paragraph. We can further predict that the edges are not or at least not fully passivated by hydrogen. We attribute the peak at 285.7 eV to C-C (sp^3) bond which may result from torque of carbon bonds at edges.[22]

To further understand formation of the nanostructure, evolution of the structures with ascending pressures was investigated, the results are shown in Fig. 3. At lower pressure, we can see clearly isolated dots and amorphous aggregations (Fig. 3a). These dots are identical and stable at 77 K. We speculate that they are phenyl radicals or other partially dehydrogenated benzene molecules which bond to the Cu(111) substrate. A kind of ordered structure forms partially (Fig. 3b) at 1×10^{-7} mbar. The single phase crystalline nanostructure in Fig. 1a covering all over the Cu(111) single crystal can be obtained with a growth pressure of 5×10^{-7} mbar (Fig. 3c). A slightly higher growth pressure of 8×10^{-7} mbar results in appearance of two kinds linear defects (Fig. 3d). At much higher pressure of 6×10^{-5} mbar, the ordered nanostructure transforms into nonhomogeneous and more complex structure (Fig. 3e) with multiple phases. We performed the same experiments on Au(111) and got nothing but a surface remaining clean. We suggest that the formation of the nanostructure we obtained on Cu(111) is initialized by the catalyzed dehydrogenation of benzene molecules into chemically active species, which cannot occur on a catalytically inert substrate like Au(111). These species get polymerized or interconnected on the hot surface to form the ordered two-dimensional nanostructure. Attempts of growth at higher temperatures are also performed. Higher temperatures up to 960 K will lead to more complex locally-ordered structure which is speculated to be multi-layered 3D carbon nanostructure or highly dehydrogenated polyphenylene network differed from present 2D nanostructure. However, we didn't obtain graphene at all temperatures we tested from 600 K to 960 K with benzene pressure up to 1×10^{-4} mbar. The fact that we did not get graphene from benzene source in UHV implies a distinct chemical mechanism of the UHV CVD method differed from that of traditional CVD method whose typical pressure is much higher than 1×10^{-3} mbar.

CVD process in UHV for copper should differ quite from that of traditional CVD. Copper has relatively lower catalytic activity than Ru, Ir, Ni which can be used to fabricate graphene in UHV simply by exposing them to hydrocarbon source.[26–28] This may be the result of low adsorption probability of carbon-hydrogen molecules on copper. Gao et al.[29] have fabricated graphene on Cu(111) with ethylene in UHV by repeated fast annealing the substrate. During this process they think ethylene which they have used increase its sticking probability at low temperature while at high temperature the probability is rather low. Robinson et al.[30] have fabricated graphene on Cu(111) in a UHV system with argon assisted ethylene at an extremely high pressure of 50 mTorr. They think Cu sublimation at high temperature reduces the sticking efficiency of ethylene while presence of high-pressure argon prevents the sublimation and increases Cu vapor pressure above the surface. Although benzene is thought to have larger adsorption energy than smaller molecules because of the existence of London dispersion force,[31] the low amount of benzene involved in the surface catalysis due to reduced adsorption probability at low pressure and high temperature can still greatly affect the surface dynamic process. Low concentration of benzene molecules on Cu surface reduces the probability of dehydrogenation and the rate of dehydrogenated benzene's colliding with each other. In our experiments, the evolution of the morphology of the surface aggregates with different growth pressures indicates that the single phase crystalline nanostructure in Fig. 3c relies on the elaborate balance among benzene adsorption, dehydrogenation, on-surface polymerization/coordination, and residual desorption.

Given the highly ordered nanostructure with a period of only 0.88 nm in one direction, one would expect it can act as a template for accommodating isolated cobalt atoms and potassium atoms, which is related to electron doping, high density magnetic storage and spintronic devices. Our experiments show that K atoms deposited on the nanostructure at 77 K can directly form atomic chains (Fig. 4a). Cobalt atoms deposited on the nanostructure at 77 K cannot form atom chains but randomly adsorb on the structure, as shown in Fig. 4b. From the uniformity and small size (about 8 Å, little less than the short period of 8.8 Å of the structure) of bright spots, it's believed that single cobalt atom lies in each position. After further annealing the sample to 400 K for 30 minutes, we get locally ordered arrangement of cobalt atoms as shown in Fig. 4c.Cobalt atoms are still isolated from each other, but they can rank into atomic chains now. This is unique because cobalt atoms always form islands above liquid nitrogen temperature.[32,33] Forming cobalt islands is not welcomed for pursuing high magnetic anisotropy because clustering atoms can dramatically reduce atomic magnetic anisotropy.[34] It is surprising that Co atoms can still be well isolated even when annealed to such a high temperature of 400 K.

To verify the presence of magnetism, the dI/dV tunneling spectra on the Co atoms were taken at 5.5 K. All the cobalt atoms, no matter with or without adjacent atoms, show the same characters. One typical spectrum is given in Fig. 4d. A tunneling spectrum near the Fermi level of the bare nanostructure is also presented for comparison. A pronounced asymmetric resonance can be seen in the spectrum taken on cobalt atoms. Although it looks very much like a Fano-associated Kondo resonance,[35] the curve can't be fitted well using a single Fano lineshape. Instead of simply regarding the spectrum as a Kondo resonance, we interpret it as superposition of the d-orbital resonance of cobalt atom and Kondo resonance. And when the d-orbital resonance intersects with Fermi level, the impurity enters into the so called mixed valence regime with high Kondo temperature as in systems of Ni, Ti on Au(111)[36] and Ti on Ag(100).[37] In this scenario, two Fano lineshapes are used to fit the dI/dV spectrum. We also facilitate this method to fit our data in Fig. 4d. The fitted line (red line) is the sum of the green line representing d resonance and the blue line representing the Fano-associated Kondo resonance at +22 meV with a width of 40 meV. The corresponding Kondo temperature is 232 K. This large Kondo temperature is consistent with the expectation from d resonance's approaching Fermi level. The dI/dV spectrum indicates that the atomic magnetism is preserved for individual isolated Co atoms on the 2D nanostructure, emphasizing the potential application in carbon-based organic spintronics.

Although STM can give topographic and local density of states information and XPS can provide chemical information of such a complex 2D surface structure, unambiguous determination of a precise structural model is not accessible. However, one would otherwise expect a plausible structural model deduced from the currently available experimental observation. DFT calculation and simulation are hereby employed for this purpose. The model was rationally proposed on the basis of the following considerations and speculations: i) Benzene rings are unlike to be broken at the growth temperature according to the literature.[38] The sp^2 signal in XPS data also support that the nanostructure is predominantly constituted by polymerization of dehydrogenated benzene molecules, i.e. phenylene units, with their carbon rings remaining unbroken. ii) The nanostructure forms at a relatively high temperature of 710 K indicated that it must be stabilized by strong bonding of these phenylene units, mostly via polymerization. iii) the signal of C-Cu bonding in XPS data indicates that part of carbon atoms in the nanostructure are bonded to the underneath Cu surface and/or coordinated by Cu adatoms. iv) The nanostructure is terminated with a sharp and straight edge on the Cu $[11\bar{2}]$ step (Fig 4b), suggesting a weaker bonding along $[1\bar{1}0]$ direction than along $[11\bar{2}]$ direction. Combining the above arguments we speculate that the 2D nanostructure most probably consists of parallel polyphenylene chains along $[11\bar{2}]$ direction interconnected by Cu atoms. A most possible structural model is presented in Fig 5a and 5b to maximally fit the STM images of the observed nanostructure. The proposed structural model has a unit cell of $c(2 \times 7)$ with parameters of 0.883 nm and 1.785 nm along $[11\bar{2}]$ and $[1\bar{1}0]$ directions respectively. There are seven benzene rings in one unit cell. Six of them form a branched hexaphenylbenzene group, mimicking the observed large hexagonal ring with diameter of about 0.5 nm. The polyphenylene chains are interconnected with each other by coordinating with single Cu adatoms. To evaluate the rationality of the proposed model, a STM image is simulated in Fig. 5d, which reproduces fairly well the experimental STM image (Fig. 5c). The calculated LDOS on the polyphenylene chain in Fig. 5e also agrees very well with the experimental dI/dV curve in Fig. 1e , further stressing the rationality of the proposed structural model. In the proposed scenario, since surface Cu atoms are very reactive to oxygen, it is possible that exposing to oxygen atmosphere may break the C-Cu bonds and oxidize simultaneously both the C atoms and Cu atoms that may be evidenced by XPS experiment as shown in Fig. 2b.

In terms of accommodation of K and Co atoms, one would expect two energetically favorable adsorption sites surrounded by three standing phenylene rings that are in accordance with the experimental observation in the insets of Fig. 4a and 4c.

4 Conclusions

In summary, a new 2D carbon-based crystalline nanostructure on Cu(111) was constructed and investigated with LT-STM. The nanostructure is facilely constructed by chemical vapor deposition of benzene on Cu(111) in an ultrahigh vacuum chamber. STM/STS study indicates that the nanostructure has rectangular unit cells with c(2×7) reconstruction and a semiconductor character with an energy gap of 0.8 eV. Ex-situ XPS study of the sample shows that C-C(sp^2) bonding is predominantly preserved, suggesting a superstructure consisting of π-conjugated building blocks involving Cu bridging atoms. Surprisingly, the nanostructure is found to be an excellent template for isolating and stabilizing metal atoms from clustering. K and Co atoms deposited on the periodic nanostructure can be well dispersed and form locally ordered atomic chains. By checking the dI/dV spectra we found that the dispersed Co atoms exhibit clear Kondo effect indicating the presence of atomic magnetism. A detailed structural model is proposed and agrees fairly well with the experimental observation, suggesting that the 2D nanostructure may consist of polyphenylene chains interconnected by Cu adatoms. This newly discovered 2D nanostructure makes a supplement to the large family of carbon-based low-dimensional nanostructures, which may have potential applications in organic electronics and spintronics. We look forward to further studies such as in-situ synchrotron X-ray techniques to resolve the crystal structure and the chemical constitution. We also expect this UHV-based CVD method can be employed to discover more 2D organic nanostructures by other organic molecules.

Acknowledgments

We are grateful to Prof. Qunxiang Li for the helpful discussion on theoretical modeling. This work was partially supported by the National Basic Research Program of China (No. 2011CB921400), the Natural Science Foundation of China (Nos. 11074236, 90921013, 51132007, 21121003), the Chinese Academy of Sciences (Nos. KJCX2-EWJ02, XDB01020100) and the Fundamental Research Funds for the Central Universities (No. WK2060190027).

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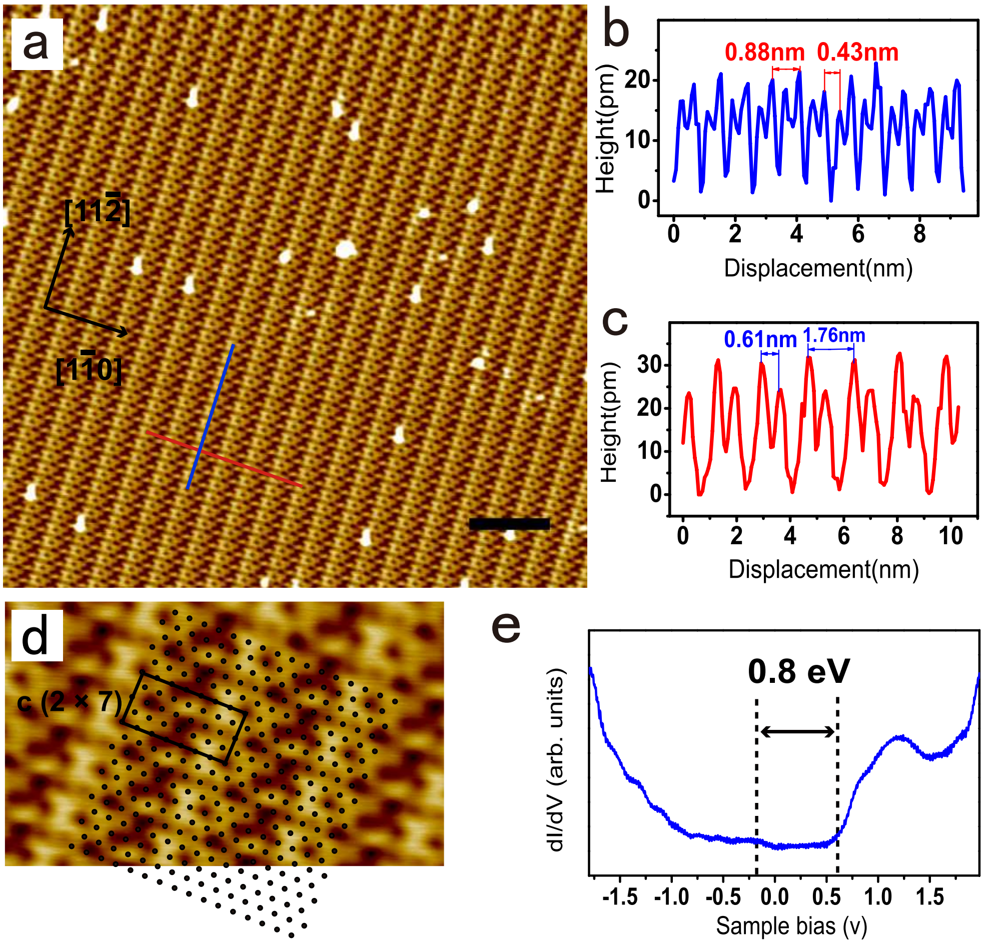

Figure 1: a) Topographic image of the nanostructure fabricated from benzene on Cu(111) ($V_t = -1$ V, $I_t = 200$ pA). The scale bar is 5 nm. The two perpendicular crystal directions on Cu(111) surface are marked with black arrows. b,c) Height profiles of the two vertical directions. The period is 0.88 nm in the blue line marked direction and 1.76 nm in the red line marked direction. The hexagonal ring's diameter is about 0.52 nm in average. d) Enlarged image of the nanostructure. The black rectangle shows the primitive cell of the nanostructure with c(2×7) reconstruction while the black dots represent a possible arrangement of substrate Cu atoms. e) dI/dV tunneling spectrum of the nanostructure, showing a gap of 0.8 eV. ($V_t = -1$ V, $I_t =$ 200 pA).

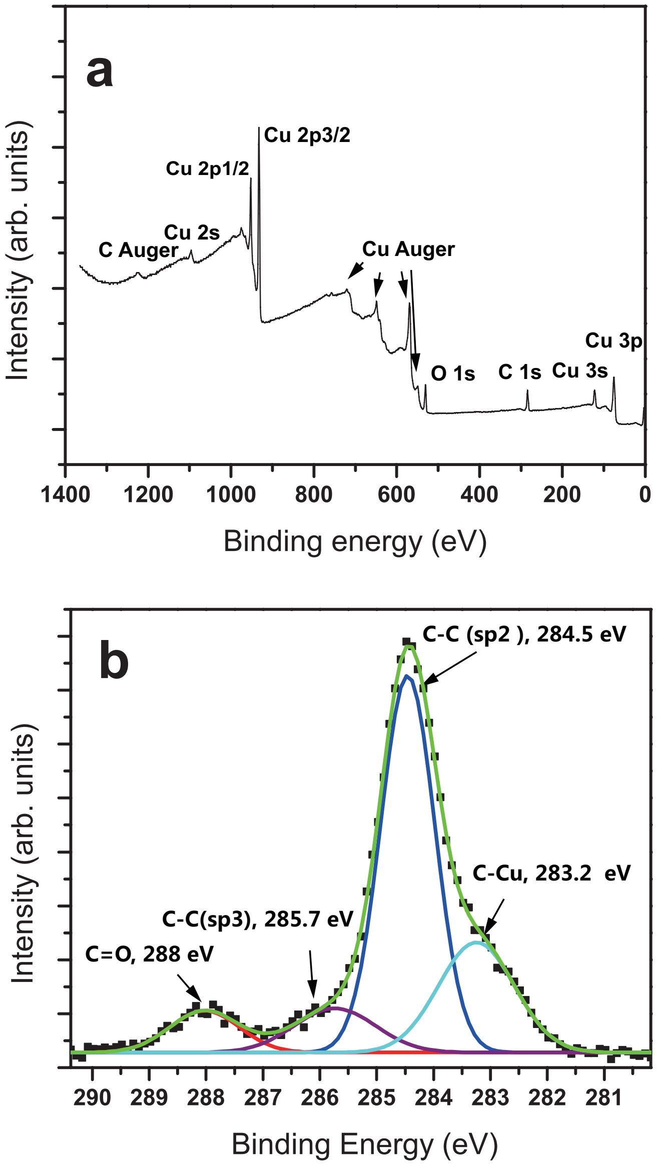

Figure 2: Ex-situ XPS spectra of the nanostructure: a) survey scan b) narrow scan around element C.

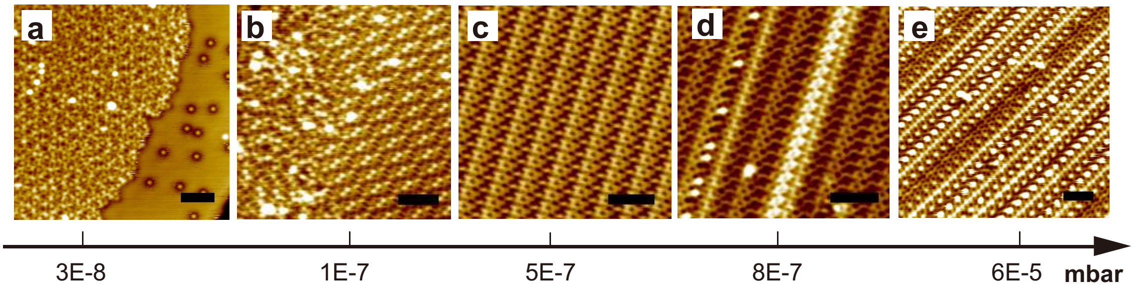

Figure 3: Morphologies with ascending growth pressures: a) identical dots and disordered aggregations form on the clean Cu(111) surface. b) A kind of ordered structure forms partially. c) The highly ordered nanostructure forms. d) Two kinds of line defects appear. e) More complex nonhomogeneous structure forms. All the images were taken at the same scanning condition of $V_t = -1$ V and $I_t = 200$ pA. The scale bars are all 3 nm.

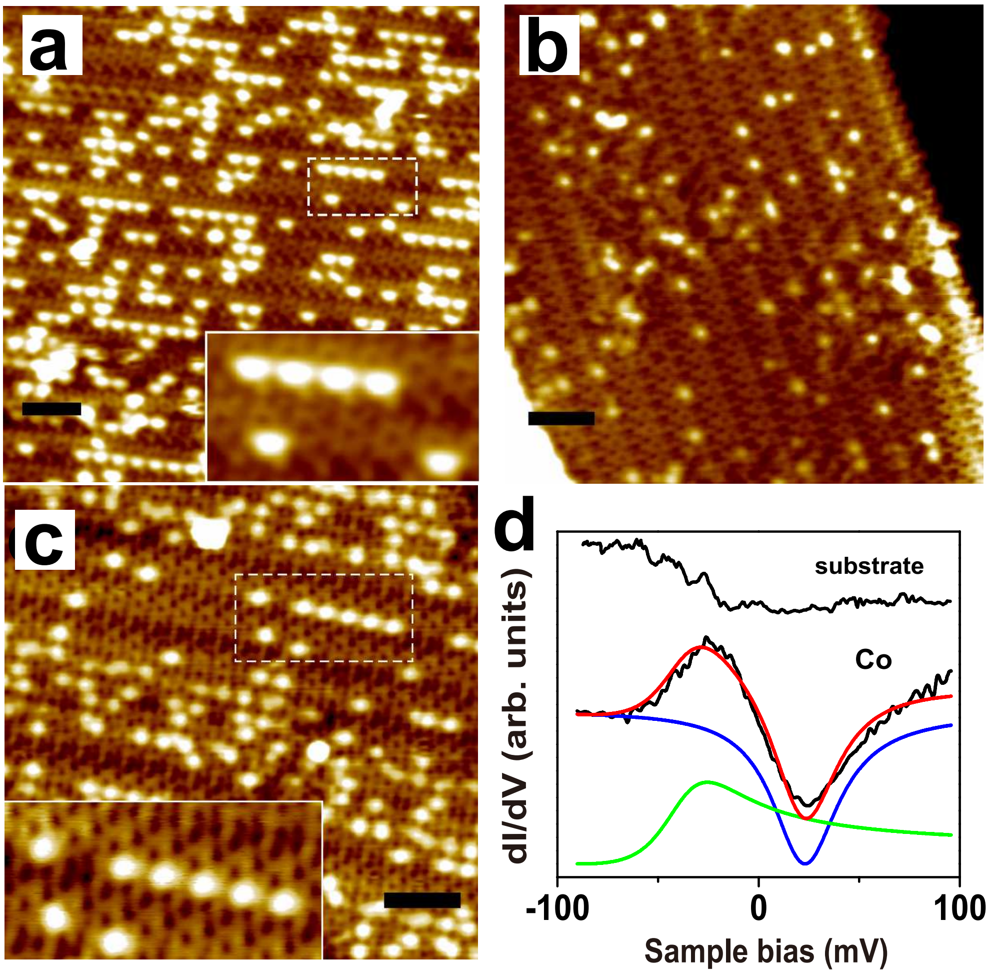

Figure 4: a) STM image of K atoms deposited on the nanostructure. b) STM image of Co atoms deposited on the nanostructure. c) STM image of Co atoms on the nanostructure after annealing at 400 K for 30 minutes with higher coverage. All the images were taken at the same scanning condition of $V_t = -1$ V, $I_t = 200$ pA. The scale bars are all 3 nm. d) dI/dV tunneling spectra of the bare nanostructure and Co atoms on it ($V_t = -0.1$ V, $I_t = 400$ pA). The black lines are measured spectra, the red line is the total fitted line, the blue line is the fitted Kondo resonance, the green line is the fitted d-orbital resonance.

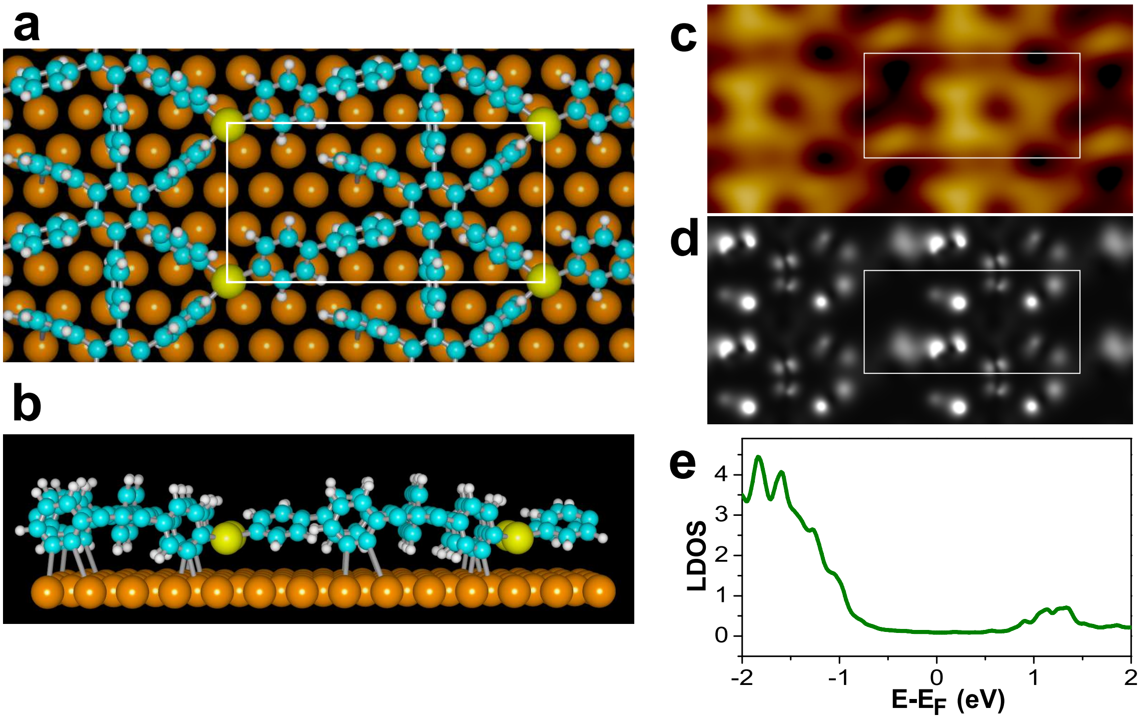

Figure 5: a) Top view of the relaxed structural model. (Orange, substrate Cu; Yellow, bridging Cu; Blue, C; White, H) The solid white rectangle shows the unit cell. b) Side view of the model. c) The topographic image of the nanostructure for comparison with (d) ($V_t = -1$ V, $I_t = 200$ pA). d) Simulated STM image of the model with bias voltage of -1 V. e) Calculated local density of states of the polyphenylene chain.