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Two-Dimensional Nanostructured Growth of Nanoclusters and Molecules on Insulating Surfaces

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Organic thin films are believed to be a versatile competitor to silicon-based materials because they can be produced at low temperatures also on flexible substrates and tailored by low-cost methods like molding and printing.[1–3] In many cases, the organic structures must be two-dimensional and well-ordered (crystalline) for optimal electronic transport.[1] The advantage of two-dimensional cluster arrangements on the other hand is a very high cluster density and, at the same time, a narrow distribution of the cluster sizes[4] - ideal conditions for data storage solutions[5,6] or catalysis.[7]

In order to obtain two-dimensional structures of such nano-objects, a promising technique is to make use of self-assembly or self-organized growth,[8] which is often assisted by a template or surface regions structured at the nanometer scale as in the case of anisotropic surfaces.[9,10] Most of such surfaces are conductors since they can be imaged with atomic resolution with a scanning tunneling microscope.[11,12] On the contrary, insulating surfaces have been largely neglected although they are essential in microelectronics[1,2] and in catalysis.[7] Insulator surfaces have the advantage of electronically decoupling nano-objects from the support, unlike metal surfaces.[13] It is therefore of importance to study two-dimensional molecular and cluster systems also on these surfaces, and to investigate the interaction of nano-objects with the substrate and amongst the nano-objects, which all leads to phenomena like ordering, assembly and self-organized growth.

Amongst other surfaces,[14,15] the (001) surfaces of alkali halides are widely used standard substrates, which can be seen by the large amount of publications in the recent years. This is because they exhibit large atomically flat terraces and mono-atomic steps, providing easy access for high resolution techniques such as noncontact atomic force microscopy (nc-AFM) and Kelvin probe force microscopy (KPFM).[16] Organic molecules mostly decorate the steps of the alkali halide surface leading to molecular nanowires[17–19] whereas only rarely a molecular system can be found that crystallizes into large two-dimensional films.[20–22] With respect to metal on alkali halide surfaces it has been known for a long time that deposited metal grows into clusters, decorating the steps of clean surfaces.[7] In order to guide and control the growth of nano-objects, alkali halide surfaces can be nanostructured by controlling the steps on the surface (density, structure and shape), as shown by vicinal surfaces[23] or steps of regular pits.[13,24] However, despite one case[13] almost no work exists to date that deals with two-dimensional films of molecules or two-dimensional cluster arrangements on a nanostructured insulating surface.

Here, we show that the nanostructured surfaces of doped alkali halides[25,26] can be used to confine the growth of metal into two-dimensional cluster arrangements or molecular films into well-ordered surface regions. We demonstrate this by depositing palladium clusters and racemic functionalized brominated pentahelicene molecules (7-bromo-[5]helicene)[27–29] onto the Suzuki surface of sodium chloride ($NaCl:Cd^{2+}$ (001)) in ultra-high vacuum (UHV). Palladium is a very common material choice for studies of the catalytic properties of metallic nanoparticles,[7] and as such provides a clear link to many real applications. The choice of the helicene molecules is due to a fundamental interest in distorted polyaromatic π-systems, which generate helicity and chirality.[30] They have become very important in fields like asymmetric catalysis, molecular opto-electronics and nanosciences.[31] Apart from a single example,[15] chiral helicenes have been studied exclusively on metal surfaces.[32,29]

Despite its discovery 50 years ago,[33] the Suzuki phase is not well-known today. Here we briefly summarize the key details, but the reader is referred to a recent review for a full discussion.[26] The unit cell of the Suzuki phase (**Figure 1**a) is cubic and almost twice as large as the one of the corresponding alkali halide.[33,34] It is composed of alternating layers of pure NaCl (layer 1) and layers, which include the positive divalent impurities, but also vacancies for compensating the additional valences of the impurities (layer 2). Inside the crystals, the Suzuki structure exists in large three-dimensional cubes, which are almost perfectly incorporated in the pure NaCl matrix. Cleavage of a crystal in UHV and additional annealing leads to a nanostructured (001) surface, the *Suzuki surface*, which exhibits two types of atomically flat surface regions:[26] one from pure NaCl and one from a regular Suzuki structure (Figure 1d and 1e). The

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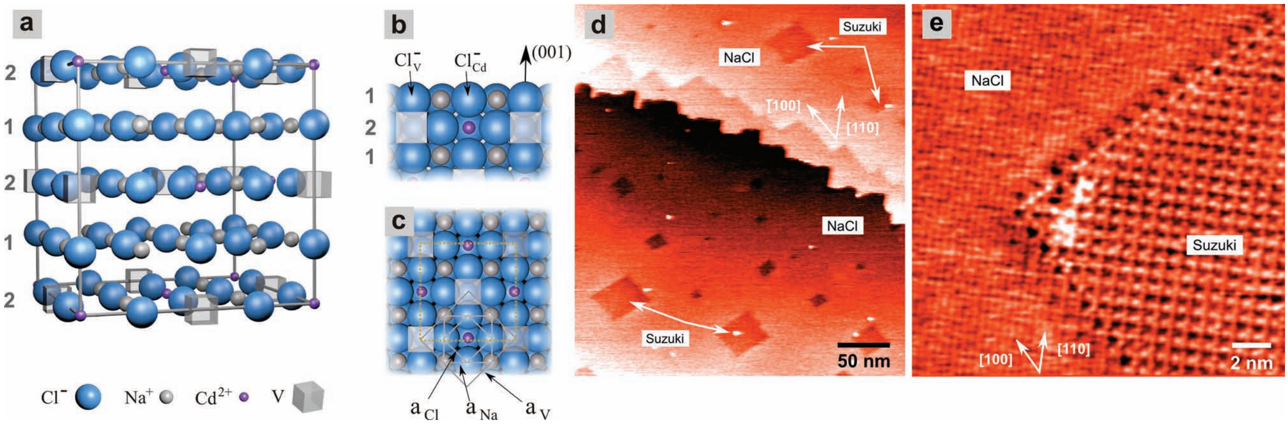

Figure 1. The unit cell of the Suzuki phase and the nanopatterned Suzuki (001) surface of a NaCl:Cd^{2+} crystal. a) The Suzuki unit cell (a_S = 11.24 Å) is almost two times larger ($a_S = 2\,a_{NaCl}$) than the one of NaCl (a_{NaCl} = 5.64 Å).[33] b) Side view of the NaCl terminated (001) surface with chloride ions above the vacancies and Cd^{2+} ions. c) Top view with a projection of the Suzuki unit cell (yellow dotted square) on the Suzuki terminated (001) surface. The Cd^{2+} ions and the vacancies form each a sub-lattice with a size of $a_V = a_{Cd^{2+}} = a_S/\sqrt{2}$, which is larger than the sub-lattices of the Na$^+$ ($a_{Na^+} = a_S/2$) and Cl$^-$ ions ($a_{Cl^-} = a_S/(2\sqrt{2})$). d) The Suzuki surface is composed of pure NaCl and Suzuki regions (topography image). e) Atomic resolution shows that the interface formed by the two regions is well-defined at the atomic scale (constant height image). Either the sub-lattice of the vacancies or the Cd^{2+} ions is imaged in Suzuki regions. In regions of NaCl either the sub-lattice of the Na$^+$ or Cl$^-$ ions are imaged.[35]

Suzuki regions can be terminated either by a pure NaCl layer (*NaCl termination*, layer 1) or a layer that includes the impurities and the vacancies (*Suzuki termination*, layer 2), as shown in Figure 1b and Figure 1c. The two regions can be easily imaged with true atomic resolution,[25] with the benefit of identifying each ionic species in the Suzuki lattice thanks to the specific geometry of the Suzuki structure.[35]

If palladium atoms are deposited on the (001) surfaces of pure NaCl (sample at room temperature) they diffuse on the terraces. Because of the specific kinetics at room temperature the nucleation at steps is faster than on terraces[7] so that palladium preferentially forms nanometer sized clusters decorating the steps.[23,24] Almost no stable clusters can be found on the terraces. On the contrary, depositing palladium on a Suzuki surface results into a completely different surface, which is characterized by three different types of clusters (**Figure 2**a and e). The first type of cluster (I) can be found occasionally on the flat terraces of pure NaCl. Due to the low defect density in these regions, the clusters, once formed, collect a large part of the palladium atoms diffusing on the pure NaCl terraces, so that the clusters become quite large (height h_I = 2.4 nm, diameter D_I = 3–4 nm).[7] The second type of cluster (II) is located at the NaCl-Suzuki boundary where the clusters collect obviously less palladium - this can be seen by the smaller size of the clusters (h_{II} = 1.5 nm, D_{II} = 2.5 nm).

A different situation can be found inside the Suzuki regions, where the clusters (III) are much smaller and the cluster density much higher (Figure 2b). The density ($\rho_{Suzuki} \approx 1.3 \times 10^{13}$ clusters per cm^{-2}) is more than forty times larger with respect to the density in the pure NaCl regions ($\rho_{NaCl} \approx 3 \times 10^{11}$ clusters per cm^{-2}). Each cluster occupies a circular surface area of radius $r_c = \sqrt{1/\pi\rho_{Suzuki}} \approx 1.6$ nm and has therefore a mean distance of $d_{CC} = 2r_c \approx 3.2$ nm to their neighboring clusters, which is four times larger than the size of the largest sub-lattice formed by either the Cd^{2+} impurity ions or the vacancies ($a_{V,Cd^{2+}} = 0.8$ nm). Due to the high density of nucleation sites, each cluster collects much less palladium during the metal deposition than the clusters in the pure NaCl regions, which explains their quite small size: the almost round clusters have a very small diameter of $D_{III} = 1.8 \pm 0.4$ nm (see histogram in Figure 2c), but also a very small height that corresponds to only a few atomic layers ($h_{III} = 0.6 \pm 0.2$ nm). Due to the different sizes of the three types of clusters, a cluster in the Suzuki region has roughly $n_{III} \approx 50$ atoms, whereas a much larger number of atoms can be found in a cluster at the NaCl-Suzuki boundary ($n_{II} \approx 400$ atoms) and especially in a cluster that is located somewhere on the flat NaCl terrace ($n_I \approx 1500$ atoms).

It is obvious that the specific ionic structure of the Suzuki phase plays a key role in the nucleation of the clusters. An interesting conclusion can be drawn when considering the ratio of height-to-diameter: The value is almost the same for the clusters in the NaCl regions and at the interface Suzuki-NaCl ($h_I/D_I = 0.68 \approx h_{II}/D_{II} = 0.6$), but two times larger than the value of the clusters inside the Suzuki regions ($h_{III}/D_{III} = 0.33$). This is directly related to the adhesion energy E_a: the flatter a cluster is, the larger is the substrate-cluster interaction.[7] Therefore, the cluster-surface interaction must be stronger inside the Suzuki regions than in the NaCl regions. Since metal especially likes electronegative surface sites,[36,37] potential candidates that can exhibit a strong interaction with the clusters are the negative vacancies on Suzuki terminated surfaces or, on NaCl terminated surfaces, the chlorine ions above the vacancies (Cl^-_V). Our first principles calculations predict indeed that atomic palladium prefers to adsorb in Suzuki regions by up to 0.4 eV over the ideal NaCl surface with the favoured sites of Cl^-_V for the NaCl surface termination, and the vacancies and Cl$^-$ ions for the Suzuki surface termination. Surprisingly, from the experiments it can be found that not all of these sites, which exhibit a high density of $\rho_{V,Cd^{2+}} \approx 1.6 \times 10^{14}$ sites per cm^{-2}, are occupied by clusters. Only every ~12th surface site is occupied (Figure 2b and 2d), which could be due to kinetics,[7] but also due to repulsive forces amongst the clusters. It has been shown that clusters may repel each other if elastic forces caused by strain fields in the cluster-substrate

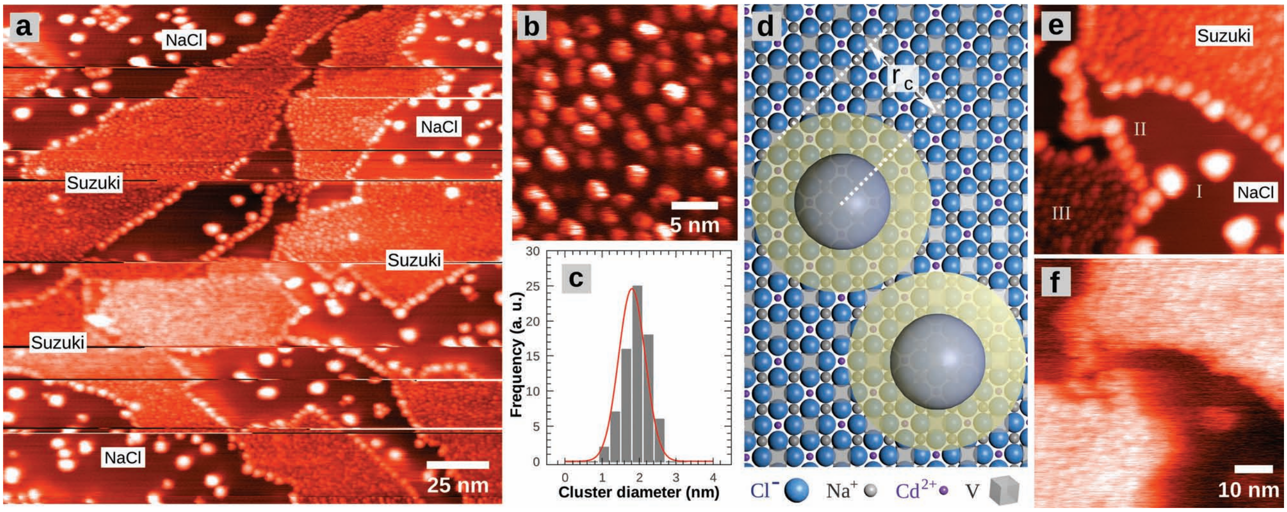

Figure 2. The confined growth of palladium clusters in Suzuki regions (quantity: 0.35 mono-layers, flux: 1.5×10^{13} atoms per cm^{-2} sec^{-1}, sample temperature: 300 K). a) Large-scale topography image after the deposition (each bright dot is a single cluster). Palladium forms clusters preferentially in the Suzuki regions. b) Constant height image obtained inside a Suzuki region and histogram (c) of the cluster sizes found from image b). d) The relation between the ionic Suzuki structure and the cluster dimension. For simplicity it is assumed that the surface is Suzuki-terminated and that the clusters are localized above the vacancies. The yellow disk with radius r_c shows the surface area kept by a cluster for its growth. Topography (e) and Kelvin image (f) obtained in one KPFM measurement. The Kelvin image exhibits large voltage differences between the stoichiometric NaCl terraces and the clusters inside the Suzuki regions ($\Delta U_{\mathrm{Kelvin}} \approx 3$ to 4 V).

interface[38] or repulsive electrostatic forces amongst 'charged' clusters occur.[39]

Although each layer of the Suzuki structure is neutral, the (001) surface exhibits a net negative surface charge in comparison to the neutral stoichiometric NaCl regions.[26,35] This can be best understood for the Suzuki terminated surface where the negative potential results from the vacancies, where four negative Cl^- ions on the surface and one Cl^- ion directly below the vacancy can be found in the vicinity. On the surfaces of pure alkali halides it has been shown by KPFM that similar, negative cation vacancies influence the electronic properties of metal clusters,[40] which is a result of a charge transfer or polarization effect.[41] Because a cluster can cover several of equivalent surface sites like vacancies on the Suzuki terminated surface (Figure 2d), large polarization or charge effects can be expected. Indeed, Kelvin images show a very bright contrast at the clusters inside the Suzuki regions with respect to the neutral and stoichiometric NaCl regions, which appear dark in the Kelvin images. The change of contrast from bright to dark corresponds to voltage differences ($\Delta U_{\mathrm{Kelvin}} = U_{\mathrm{Cluster}} - U_{\mathrm{NaCl}}$) of several volts, which can be sometimes as large as 4 V (Figure 2f). These values are much larger than the highest voltage difference measured between clean Suzuki and NaCl regions ($U_{\mathrm{Suzuki}} - U_{\mathrm{NaCl}} \approx$ 1.0 to 1.5 V).[26] In comparison to the small clusters in the Suzuki regions, the large clusters in the pure NaCl regions exhibit a less bright contrast ($\Delta U_{\mathrm{Kelvin}} \approx 1.5$ V), which is because such clusters probably cover only a single vacancy. The Kelvin images therefore confirm a charging or polarization of the clusters inside the Suzuki regions, which could explain in turn possible repulsive electrostatic forces amongst the clusters as discussed above.

The latter examples show that the growth of metal on the Suzuki surface is almost fully confined in the Suzuki regions such that a two-dimensional arrangement of nanometer sized clusters is created. A similar nanostructured growth can also be observed when functionalized, brominated pentahelicene molecules (**Figure 3**a) are deposited on Suzuki surfaces. In general, such molecules adsorb only at defects on the NaCl surface, which can be best observed on the surfaces of undoped, pure NaCl crystals: the molecules stick exclusively at the steps and form molecular wires (Figure 3b and Figure 3c). In comparison, a completely different adsorption behavior can be observed on the Suzuki surface (Figure 3d): The molecules cover all Suzuki regions by forming flat homogeneous islands. No molecule can be found in the NaCl regions (see supporting information). Due to the two-dimensional shape of the Suzuki regions and the well-defined NaCl-Suzuki interface the islands have the same shape and size as the Suzuki regions. The height of the islands is below one nanometer and measures $h_{\mathrm{helicene}} = 0.8 \pm 0.1$ nm. Since no molecules could be found in the stoichiometric NaCl regions, it is obvious that the specific Suzuki structure plays yet again an important role. First principles calculations, including van der Waals interactions self-consistently, show that a helicene molecule lies parallel on the surface for both surface terminations as shown in Figure 3e) and Figure 3f) for the Suzuki termination. The bromine substituent of the molecule sits either above a Cd^{2+} ion (Suzuki surface termination) or a $\mathrm{Na}^{+}_{\mathrm{Cl}}$ ion (NaCl surface termination). Similar in comparison to PTCDA,[42] an important part of the bonding stems from a van der Waals contribution whereas an electrostatic interaction between the bromine atom and the positive surface ions pins the molecule to some extent. In this flat configuration the top most atom of the helicene (hydrogen at C12) has a distance of $h_{\mathrm{C12-surface}} = 0.74$ nm to the surface, which is in very good agreement with the experimental observations.

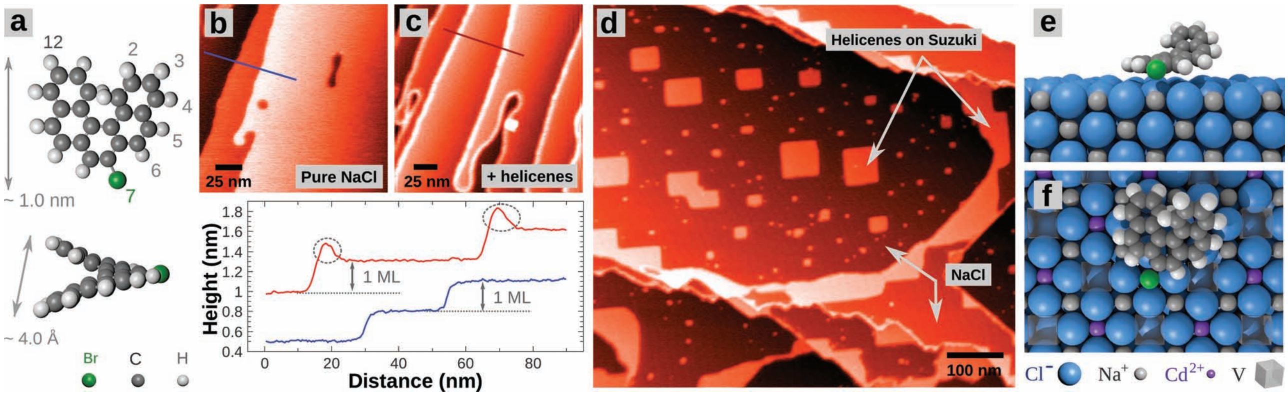

Figure 3. a) The structure and size of a 7-bromo-[5]helicene molecule. b), c) The adsorption of 7-bromo-[5]helicene on the (001) surfaces of pure NaCl takes place exclusively at the steps (topography images). The profiles obtained at the lines in the images show that the step-like shape of the clean steps (a, blue profile) changes to a shape which exhibits an elevation of 2 to 3 Å due to the adsorbed molecules (b, red profile). d) Large-scale topography image after the deposition of the molecules on the Suzuki surface. All Suzuki regions are completely covered by the molecules. e), f) The adsorption of a helicene on a Suzuki terminated Suzuki region in side (e) and top view (f) (see also supporting information).

In conclusion, we demonstrate the capability of a nanostructured, insulating Suzuki surface to confine both metal nanoclusters and molecular films to specific regions. Specifically, we exemplify this by depositing palladium and brominated pentahelicenes, and characterize them by nc-AFM and KPFM measurements. In comparison, such phenomena do not occur at all on the surfaces of undoped NaCl. The nanostructured growth on the Suzuki surface is due to the specific ionic structure of the Suzuki phase, in particular due to the high density of impurities and vacancies as verified by first principles calculations.

The small nanometer size and narrow size distribution of the palladium clusters is ideal for reactivity measurements, in which e.g. the CO oxidation and NO reduction can be studied. Specific properties from reactivity measurements can then be addressed to one type of cluster. With respect to the helicene molecules, phenomena like self-assembly in dependence on the functional group of the helicene molecules can be investigated. And indeed, recently we could observe differences in the adsorption for helicene molecules that carried one or two cyano groups. Chiral films composed of helicenes are in general useful model structures for opto-electronic or asymmetric catalysis applications.[31]

We believe that the insulating Suzuki surface can be used for confining the growth of also other clusters or molecules into two-dimensional structures and that fundamental aspects like the binding, nucleation, growth and other mechanisms like self-assembly or self-organized growth can be precisely studied. A benefit of Suzuki surfaces is the ease in imaging the surface by nc-AFM and KPFM with the option to obtain even atomic resolution in the best cases. Furthermore, by a choice of the chemical nature of the impurity, the chemistry of the surface can be tailored, which is very promising from the perspective of this system's future. The Suzuki phase can be produced in almost all alkali halides, but also in some oxides like MgO and NiO,[26] which enlarges even more the possible combinations of insulating surfaces and nano-objects. We believe that the Suzuki surface is a suitable *model surface* in general, which can be used for many possible applications in the field of nanotechnology and materials science.

Experiments and Theory

The molecules and clusters have been studied in ultra-high vacuum (10^{-10} mbar base pressure) by frequency-modulated nc-AFM and KPFM experiments with a room temperature Omicron AFM/STM. nc-AFM yields images of the surface topography whereas in a KPFM measurement an image of the charge/dipole distribution of the surface is obtained.[16] All (001) surfaces were prepared by UHV cleavage of the NaCl:Cd^{2+} crystals (4% $CdCl_2$ in NaCl) at room temperature and following annealing in an UHV oven. Palladium clusters were epitaxially grown by condensing a calibrated beam of neutral palladium atoms from a Knudsen cell onto the surface (flux: 1.5×10^{13} atoms per cm^{-2} s^{-1}). The racemic functionalized brominated pentahelicene molecules were evaporated from a second Knudsen cell at an estimated temperature of ~130 °C. During any deposition (Pd, helicene) the sample was at room temperature.

For understanding the experimental results, first principles calculations were performed using the periodic plane-wave basis VASP code,[43,44] implementing the spin-polarized density functional theory (DFT) and the generalized gradient approximation. Non-covalent interactions are described by means of the most recent version of the Langreth-Lundqvist density functional vdW-DF2.[45] The non-local term in it was evaluated using the adaptive real-space approach.[46] More details of the experimental techniques and theory can be found in the supporting information.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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