Formation of Unconventional Stoichiometric Na–Cl Magic-Number Nanoclusters and 2D Assembly on Ir(111)

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Sodium chlorides in non-1:1 stoichiometry are counterintuitive but recently their existence has been found under the high pressure condition or in the confined space between graphene sheets. Here the direct observation of the formation of Na$_3$Cl nanoclusters, a stable magic-number structure, is reported on an Ir(111) surface using scanning tunneling microscopy and non-contact atomic force microscopy. The stability of Na$_2$Cl nanoclusters in the free and adsorbed state is corroborated by density functional theory calculations. It is also found that a density of nanoclusters together with Cl adatoms may further aggregate and self-assemble into a Na$_2$Cl$_4$ monolayer, forming a novel metastable phase of NaCl(111) with a honeycomb lattice. Further calculations suggest that charge transfer between the polar nanoclusters and the metal substrate stabilizes NaCl of non-1:1 stoichiometry. The work exhibits the possibility of exploring unconventional ionic crystals on the surface with atomically precise control of structure and composition.

1. Introduction

Sodium chloride (NaCl) is an archetypal ionic compound, which has a stable 1:1 stoichiometry and face-centered cubic (FCC) structure at ambient conditions due to the significant electronegativity difference between Na and Cl atoms. Unintuitively, recent works have shown that various unconventional phases or stoichiometries in the Na–Cl system exist in extreme conditions.[1–6] For instance, non-1:1 Na–Cl species, Na$_3$Cl and NaCl$_3$, which are predicted to host unusual electronic properties, have been achieved in high-pressure diamond anvil cells.[6] Much intriguing as the new phases are, the harsh synthesis environment hinders further exploration in this field.

Crystal surfaces could be viewed as another type of extreme conditions, which usually possess different physical and chemical properties from its bulk. Pioneering works have demonstrated that unexpected atomic structures of crystals with extra stability could be realized on various surfaces, resulting in fascinating identical (magic-number) nanoclusters[7–13] or even 2D crystals with unusual stoichiometry.[14,15] 2D Na–Cl and Ca–Cl crystals with unconventional stoichiometry (Na$_2$Cl, Na$_3$Cl, CaCl, etc.) have been demonstrated to be stable on graphene surface, inspiring the further exploration of more exotic phases or unconventional structures with the assist of crystal surfaces. Here we report the formation of magic-number Na$_2$Cl nanoclusters and 2D self-assembled Na$_2$Cl$_4$ monolayer on the Ir(111) surface. By scanning tunneling microscopy (STM) and noncontact atomic force microscopy (nc-AFM), we unambiguously identify the atomic structure of Na$_2$Cl nanoclusters. It is also found that a density of nanoclusters together with Cl adatoms may further aggregate and self-assemble into Na$_2$Cl$_4$ monolayer. Defects of the assembled monolayer indicate a metastable phase of NaCl(111) in a honeycomb lattice. Theoretical calculation suggests that the existence of unusual structures is attributed to the strong charge transfer between adsorbates and metal substrates.

2. Results

2.1. NaCl Nanoclusters Grown on Ir(111) Surface

≈0.3 ML of NaCl was deposited on the surface of Ir(111) at ≈373 K. Bilayer and multilayer NaCl films in 1:1 stoichiometry are formed on the Ir(111) surface (Figure S1, Supporting Information). The coverage described here is estimated based on the total amount of NaCl deposited on surface. X-ray photoelectron spectroscopy (XPS) confirms the on-surface species (Figure S2, Supporting Information). It is found that a bunch of nanoscale protruded features are observed on the surface, as shown in Figure 1a (for experimental details see the Experimental...
Section), which is different from the typical NaCl(001) films on other substrates such as Cu, Ag, and Au.[16–24] Figure 1b presents the zoom-in STM image, which appears to have two characteristic species denoted as type I and II (height profile in Figure 1c). As shown in Figure 1d, the statistics show the two features have different heights (34 pm on average for type I and 205 pm for type II), and full width at half maxima (FWHM) (0.47 nm for type I and 0.76 nm for type II), respectively. But their atomic structures cannot be identified from the STM image. Moreover, it is noticed that the distribution of type I and type II is not equal, which is close to 2:1 in statistics (Figure 1e). Taking the supposition that the total 1:1 stoichiometry of Na and Cl atoms is maintained on the surface from evaporation source (solid NaCl crystal), two possible explanations are listed below: one is that the two species correspond to adsorbed NaCl monomer or dimer molecules.[25–27] Another intriguing answer is that new Na–Cl species with unconventional non-1:1 stoichiometry are formed on the surface, similar to those on a graphene surface.[15]

2.2. Imaging and Model of Na₃Cl Nanoclusters

Nc-AFM was further utilized to identify the atomic structures. As shown in Figure S3 (Supporting Information), the nc-AFM images of type I recorded by the bare metal tip and Cl-functionalized tip show reversed contrasts, appearing as depression and protrusion, respectively. Considering the fact that type I has attractive force with a metal tip and repulsive force with Cl-functionalized tip, type I is likely to be negatively charged. We tentatively assign the type I to a Cl adatom adsorbed on Ir(111) surface. Meanwhile, a control experiment with only Cl atoms deposited onto Ir(111) shows similar STM morphologies as to type I feature with an apparent height of ≈40 pm (Figure S4, Supporting Information). Density functional theory (DFT) calculation indicates the adsorption of Cl atom prefers to the top site of Ir(111) surface (seen in Figure S3 in the Supporting Information). We follow the same protocol to identify the atomic structure of type II. Figure 2a shows a typical constant-height nc-AFM image of type II structures using a metal tip. Depression is also observed at the center of the feature with a similar size as type I structure (Cl atom). Differently, three protrusions are observed around the center with trigonal symmetry. With a Cl-functionalized tip, the contrast of the nc-AFM image (Figure 2b) is inversed compared to that of the metal tip, suggesting that the three spots were positively charged. Thus, we can attribute the type II feature to a Na₃Cl nanocluster (more height-dependent nc-AFM images acquired by different tips shown in Figure S5 of the Supporting Information).

The result of the 2:1 quantity ratio of Cl atoms and Na₃Cl nanoclusters fit well with the 1:1 stoichiometry of NaCl sources. Large-area image in Figure 2c shows that all the Na₃Cl clusters are not only identical in trigonal symmetry but also in the same 30° twisted orientation with Ir(111) surface. Based on the above experimental observation, DFT calculation revealed that the adsorbed Na₃Cl nanocluster is in C₃V symmetry, with Cl atom on the top site of the Ir(111) surface and Na atoms on the bridge sites (Figure 2d). The theoretical height of Na₃Cl nanocluster is ≈4.2 Å. We further conduct force spectra to measure the height of Na₃Cl nanocluster (Figure 2e).
difference between the feature and Ir(111) substrate, as shown in Figure 2e. Heights of 2.7 and 4.7 Å for Cl atom and Na3Cl nanocluster are measured with the CO-terminated tip, which are consistent with the theoretical values.

Electron localization function (ELF) (Figure 2f) shows a local maximum (ELF = 0.8, red) only around the Cl atom, confirming the ionic nature. It is also noted that weak localization of electrons (ELF = 0.3, yellow) is observed between Na atoms and underlying Ir atoms, indicating significant charge transfer processes between the NaCl nanoclusters and Ir surface. Further Bader analysis[30] (Figure 2g) shows that the atomic charges of Na and Cl atoms in the adsorbed Na3Cl nanoclusters are equal to +0.81e and −0.84e, respectively, confirming the charged nature of Na3Cl nanoclusters. It is noted that the Na3Cl nanocluster is unexpectedly stable in free state, in which the atomic charges of Na and Cl atoms are equal to +0.33e and −1e. Therefore, −1.60e net charges are transferred to the Ir(111) surface, with −2.39e for the first layer and +0.76e for the second layer (top view of charge distribution based on Bader analysis seen in Figure S6 of the Supporting Information). The strong charge transfer process may explain why such charged Na–Cl nanoclusters with non-1:1 stoichiometry could be stable on the surface.[31,32] Surprisingly, the unconventional stoichiometry of Na3Cl species have been found both in high-pressure diamond anvil cells and graphene surface, suggesting that the 3:1 may be the metastable coordination number other than the conventional 1:1 stoichiometry in the phase diagram of Na–Cl system. It is noted that the charge transfer process is not universal between the nanoclusters of other alkali metal chlorides (M3Cl, M = Li, K, Rb, Cs) and the Ir(111) substrate. DFT calculations indicate Li3Cl nanocluster may be stabilized on the Ir(111) substrate (Figure S7, Supporting Information).

2.3. Self-Assembled Na3Cl4 Monolayers

With the prolonged time of NaCl deposition (~0.5 ML), the Na3Cl nanoclusters begun to aggregate, and a new phase of
Na–Cl crystal was occasionally formed on the surface of Ir(111) (Figure 3a). The apparent height profile (Figure 3b) shows two typical heights of ≈215 and ≈142 pm, respectively, suggesting the new phase is bilayer-like or buckled monolayer. Zoom-in STM image (Figure 3c) shows that the monolayer structure is composed of a triangle-like unit, in which four atomic features are arranged in a triangular pyramid shape. Based on previous data (Figures 1 and 2), we conclude that the atomic features here are attributed to Cl atoms. Fourier transform analysis (Figure 3d) reveal that the Cl atoms in this 2D structure form two sets of hexagonal patterns, which are in an apparent $R \times 30\times 30$ relationship. Combined with FFT-filtered images (Figure S8, Supporting Information), we can directly see that the higher Cl atoms (Cla) correspond to the inner patterns with a lattice constant of 0.92 nm (marked by red circles), while the lower Cl atoms (Clb) corresponds to the outer patterns with a lattice constant of 0.56 nm (blue circles). Taking the lattice constant (≈0.28 nm) and direction of Ir(111) surface into consideration, we find that the Cla atoms are perfectly commensurate with Ir(111) surface in a $R \times 30\times 30$ way, while the Clb atoms are slightly distorted but averagely coincident with a $(2 \times 2)$ Ir(111) surface. Thus, we propose an atomic model of Na3Cl4 monolayer on Ir(111) surface, which is verified by DFT calculation (Figure 3e). The structure resembles a result of the supramolecular assembly of Na3Cl4 nanoclusters, which are composed of Na3Cl nanoclusters and three extra Cl adatoms. But it should be noted that individual Na3Cl4 nanoclusters were not observed in our experiment. The weak nonuniformity as seen in Figure 3a (indicated by white arrows) may be attributed to the defects from underlying substrates. DFT calculation and Bader analysis show that neglect charge transfer (+0.03e) happens between proposed Na3Cl4 nanoclusters and Ir substrate (Figure S9, Supporting Information). It is guessed that the electrostatic attraction between Clb sites and Na atoms in neighbor nanoclusters stabilizes the self-assembled structure. Simulation of the STM image based on this model is provided in Figure 3f, showing excellent agreement with the atomic resolution STM image.

2.4. Metastable NaCl(111) Monolayer

A single defect of the assembled Na3Cl4 monolayer was demonstrated in Figure 4a. It is reasonably deduced that a Clb atom is missing in one Na3Cl4 nanocluster, leaving a Na3–Cl3 ring. DFT calculation shows that the absence of Clb atom in one Na3Cl4 nanocluster would lead to a transformation from a pyramid triangle to a typical hexagonal ring (Figure 4b). The simulated STM image (Figure 4c) based on this model is well fit with the experiment data, where the Cl–Cl distance is slightly decreased after the removal of the top Cl atom. It is worth noting that in specific nanoscale regions, the Cl-vacancy defects are multiple and form a hexagonal pattern. Thus, we propose an existence of a Cla-absent phase bridging between the Na-rich Na3Cl nanoclusters and Cl-rich Na3Cl4 assembled monolayer, demonstrated in Figure 4d. DFT calculation reveals that the Cla-absent structure of Na3Cl4 assembled monolayer is stable and strictly commensurate with the $(2 \times 2)$ Ir(111) surface, which is exactly the honeycomb-like NaCl(111) monolayer. The STM simulation is shown in Figure 4e, which is alike to the FFT-filtered image (Figure S8b, Supporting Information). It is known that the polar NaCl(111) surface is unstable, and the monolayer has not been observed yet. Here we establish that the polar surface is metastable on the Ir(111) substrate, though the special structure may be sensitive to the local chemical potential of Na and Cl atoms. This explains why the structure is rarely observed in our experiment.
3. Conclusion

This work demonstrates that magic-number Na₃Cl and 2D assembly of Na₃Cl₄ exist on Ir(111) surface at room temperature. It is noticed that these nanoclusters and assembled monolayer are not observed on Au, Ag, and Cu substrates. The result suggests that the Ir substrate may have a stronger interaction with the Na–Cl crystals, which provides extra stability to these unconventional species compared with the above ones.

Another interesting point is that the same stoichiometry of Na₃Cl has been reported on graphene surface, in high-pressure bulk forms, and on Ir substrate in this work. It indicates that the 3:1 stoichiometry is a stable platform in the phase diagram of Na–Cl system, and also Na₃Cl may have multiple phases, considering that the structure verified in this work is different with the proposed structures in previous works. Nevertheless, the observation of magic-number Na₃Cl nanoclusters and its 2D assembly may shed light on the formation process of bulk NaCl on surfaces and other unconventional ionic crystals. Additionally, the 2D magic cluster assembly provides an opportunity to tailor the surface state electron gases via atomic-scale local gating and periodic templating, enabling a further exploration of exotic quantum states on metallic surfaces.[33–37]

4. Experimental Section

STM/nc-AFM Experiments: The experiments were carried out in an Omicron UHV LT-STM/nc-AFM system with a base pressure below 1 × 10⁻¹⁰ mbar. The Ir(111) single-crystal surface was cleaned by repeated cycles of Ar⁺ sputtering and annealing to 870 K. A NaCl bulk crystal with a purity of 99.9% was then evaporated thermally at ≈720 K from a homemade evaporator onto the Ir(111) surface held at ≈373 K. STM and nc-AFM images were recorded at 5 K using a qPlus force sensor.[38]

XPS Experiments: The measurements were performed using a Thermo Scientific ESCALAB 250 Xi system with monochromatized AlKα X-rays (1486.8 eV, 500 µm spot size) as the excitation source. All spectra were charge referenced independently to graphitic carbon (C 1s = 284.8 eV).

Calculations: The Vienna ab Initio Simulation Package (VASP) was used with the projector augmented wave (PAW) potentials for the exchange-correlation functional.[39,40] The energy convergence criterion and the cut-off energy were set to be 0.02 eV Å⁻¹. At least 15 Å vacuum slab was used to avoid spurious interaction between neighboring slabs due to the periodic condition. The periodic slab models of Na₃Cl/Ir(111) included five layers of (4 × 4) Ir(111) substrate and one Na₃Cl nanocluster. The periodic slab models of Na₃Cl₄/Ir(111) included three layers of (4 × 3 × 3) Ir(111) and (2 × 2) Na₃Cl₄ nanoclusters. For all of the calculations, the 3 × 3 × 1 k-points of Monkhorst–Pack meshes at Γ center were used. And the bottom two layers of substrate atoms were fixed, while all the other atoms were fully relaxed. The STM simulations were performed using the Tersoff–Hamann approach.[41]

Supporting Information

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

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Figure 4. a) A zoom-in STM image of a Cl defect in Figure 3a marked by white hexagonal frame. Clₐ and Cl₋ are indicated by red circles. b) Top view of the Na₃Cl₃ ring atom model. c) STM simulation image of the hexagonal ring at bias voltages of 0.5 V. d) Top view of NaCl monolayer on Ir(111) atomic model. e) STM simulation image of NaCl monolayer on Ir(111) at bias voltages of 0.5 V.
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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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