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Introduction

Transition metal carbides and nitrides (TMCs and TMNs) have shown unique properties for strongly binding reaction intermediates and d-block transition metals and have been used as heterogeneous catalysts. Due to the predicted strong binding with metals, TMCs and TMNs are also very promising support for single atom catalysts (SACs), which possess high atomic efficiency and high catalytic performance compared to traditional catalysts yet face a common challenge of thermal instability. Elucidating the structures of TMCs and TMNs at an atomic level and the interactions between the surface and adsorbate is a crucial fundamental question to address. Herein, well-defined transition metal carbide and nitride films are prepared on Cu(111) and Ni(111) surfaces as model catalyst supports for SACs (Figure 2). The insights gained from the model catalyst surfaces will be used to promote the development of catalytic reactions, such as aqueous phase methanol reforming (APRM).

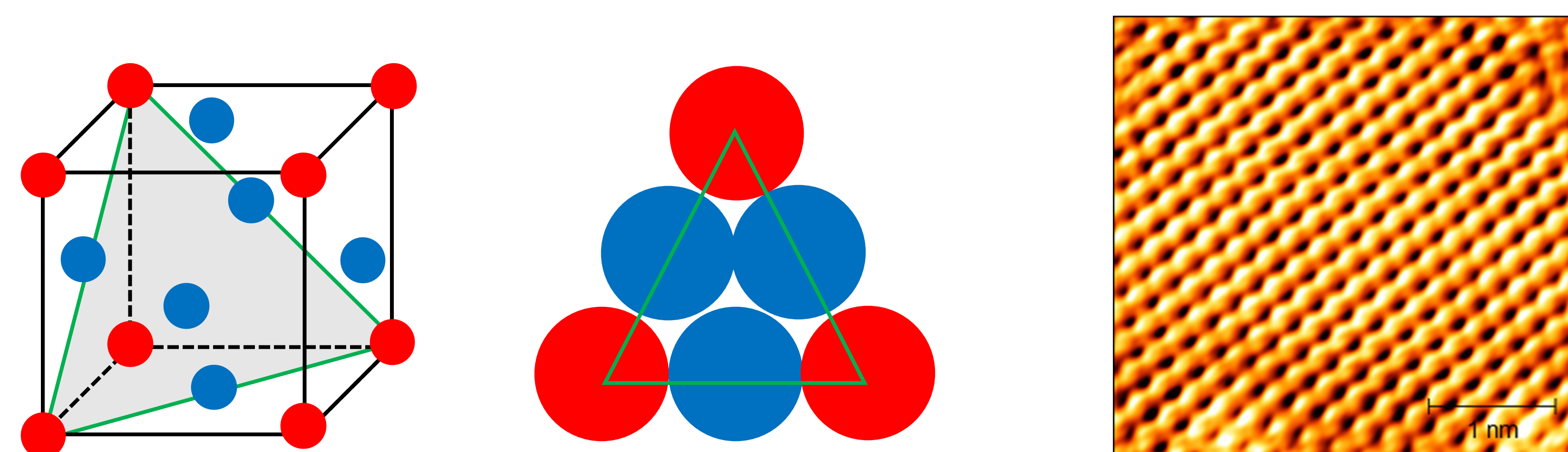
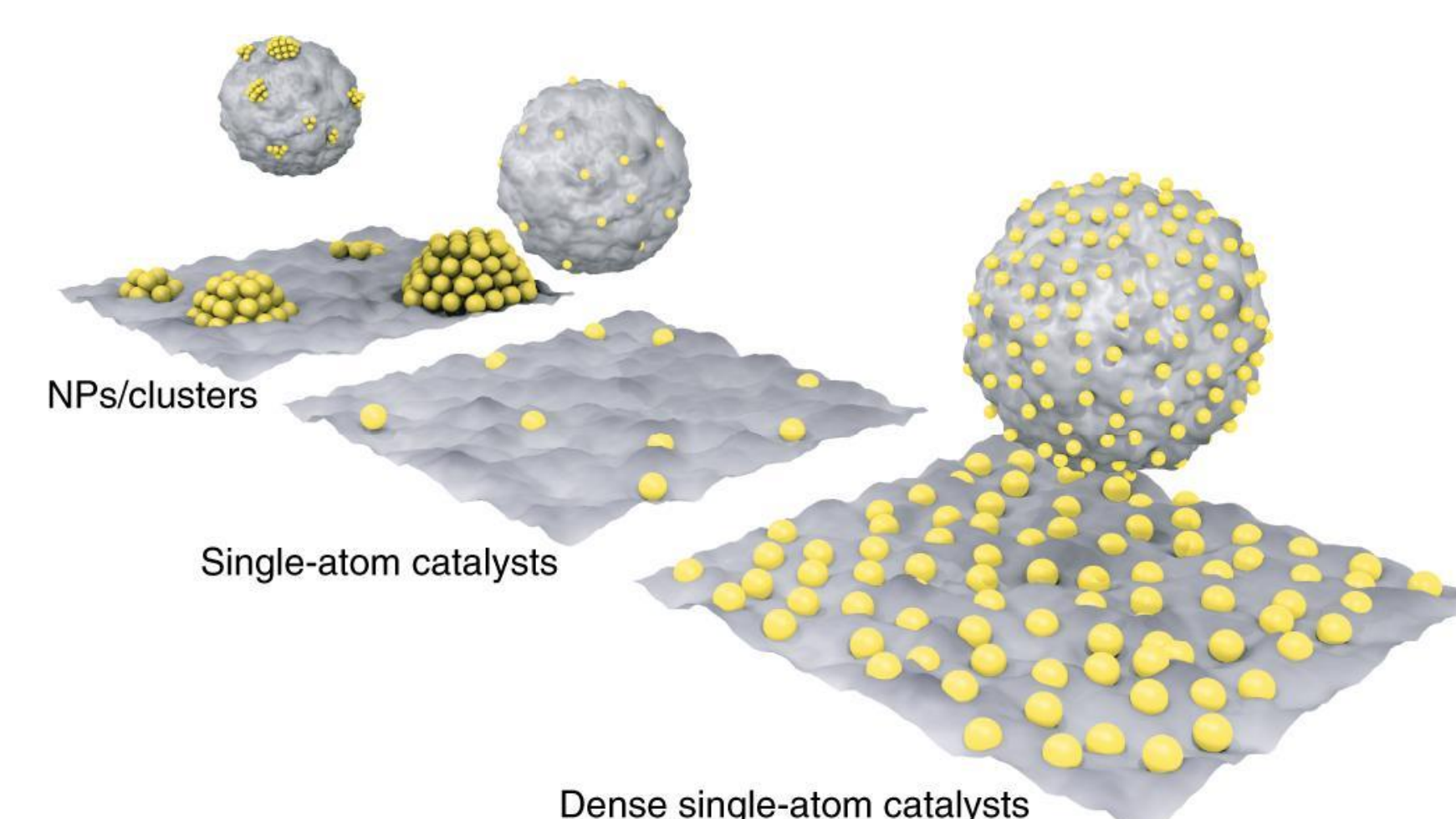


Figure 1. Miller index characterizations for (111) face center cubic (FCC) unit cells (Cu and Ni).



Beniya, A.; et al.; Nat. Catal 2019, 2 (7), 590-602.

Figure 2. Schematic indicating the purpose of the TMC and TMN as supports for SACs.

CuN_x Characterization

First, in order to define these model surfaces, the miller index of (111) is described above (Figure 1), indicating the scanning tunneling microscopy (STM) image of the surface of Cu(111), who has a face centered cubic (fcc) unit cell, and subsequently shown in Figure 3 dosed with varying coverages of nitride. These STM images captures the Cu(111) surface at atomic resolution, revealing the distinct hexagonal pattern of the (111) miller index (Figure 1). The observed spacing between adjacent atoms corresponds to the expected lattice constant of the Cu(111) crystal plane (0.254 nm), exhibiting a close-packed arrangement. The hexagonal pattern formed by the copper atoms signifies the crystallographic symmetry of the Cu(111) surface, showcasing its ordered atomic structure. The different coverages (Figure 3) were made by first sputtering nitrogen on the surface and subsequently annealing the sample to only remove the distinct peaks shown in the mass spectrometry data below. The structures indicated on the surface display a square pattern for the copper nitride film, which is due to the lattice mismatch strain, which can be partially relieved by forming a quasi-square pattern. This pattern allows for a better matching of atomic positions between the nitride and the substrate. reducing the strain energy.

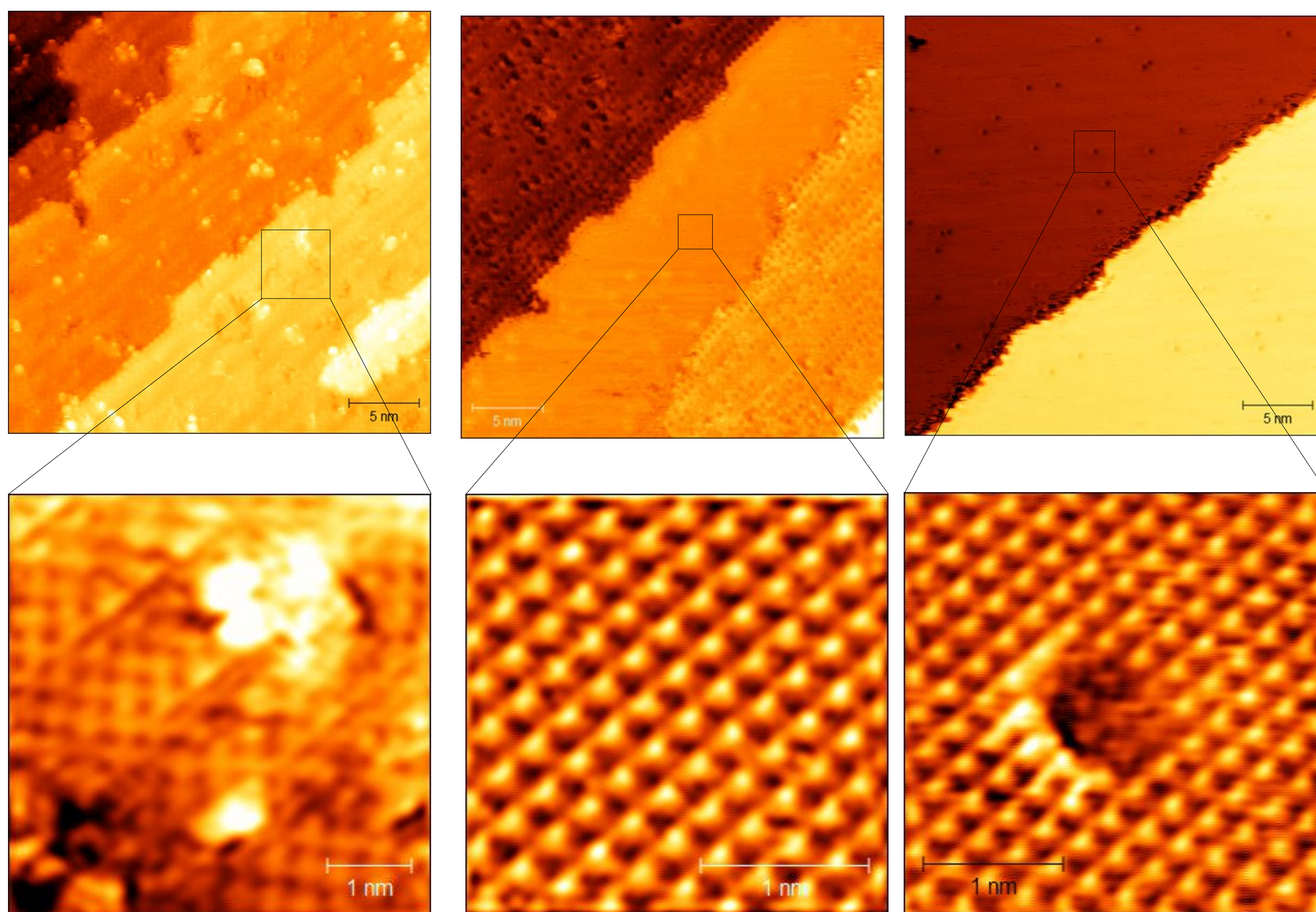


Figure 3. High, low, and single adsorbate coverages of CuN_x (top) and atomically resolved zoomed-in images (bottom).

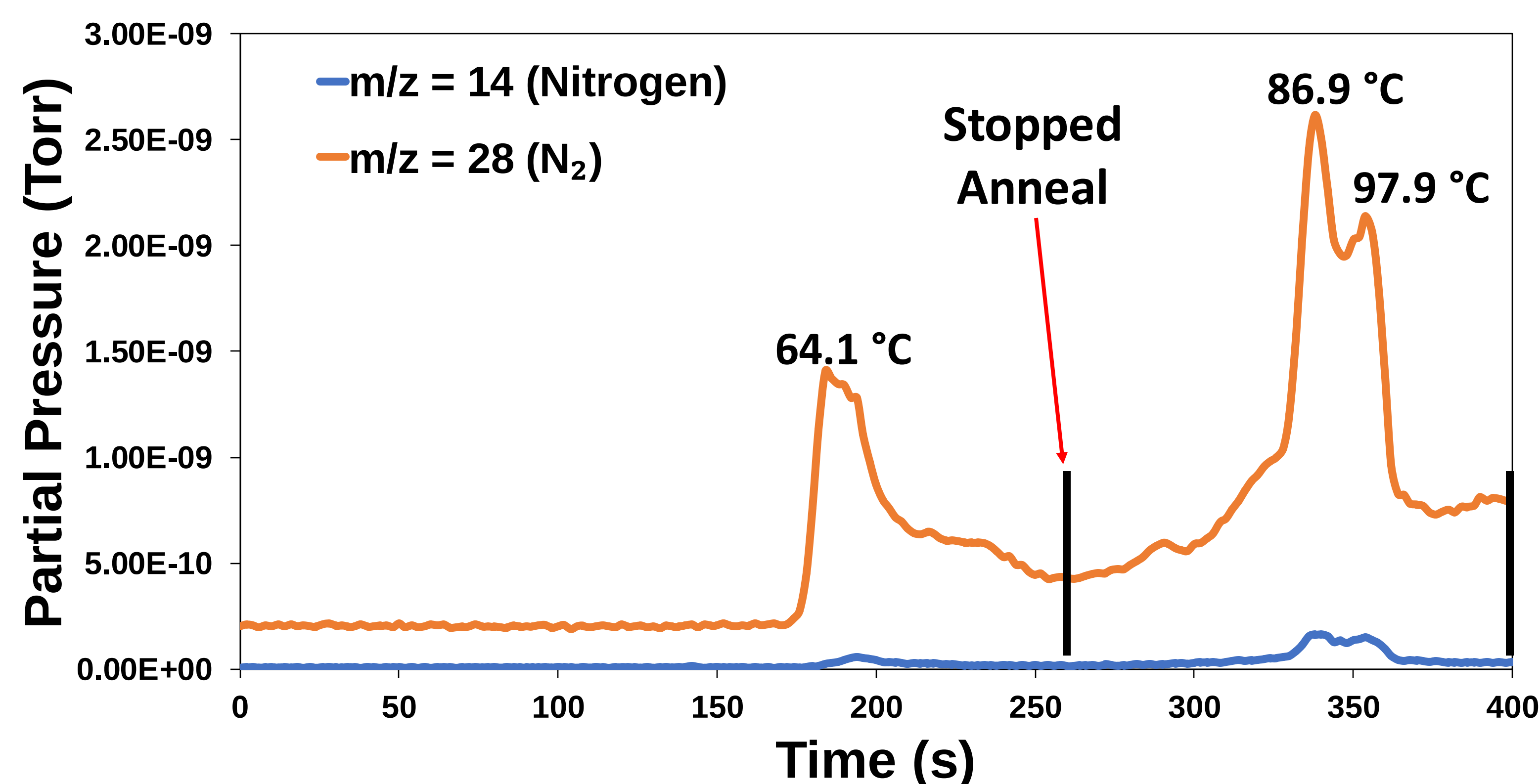
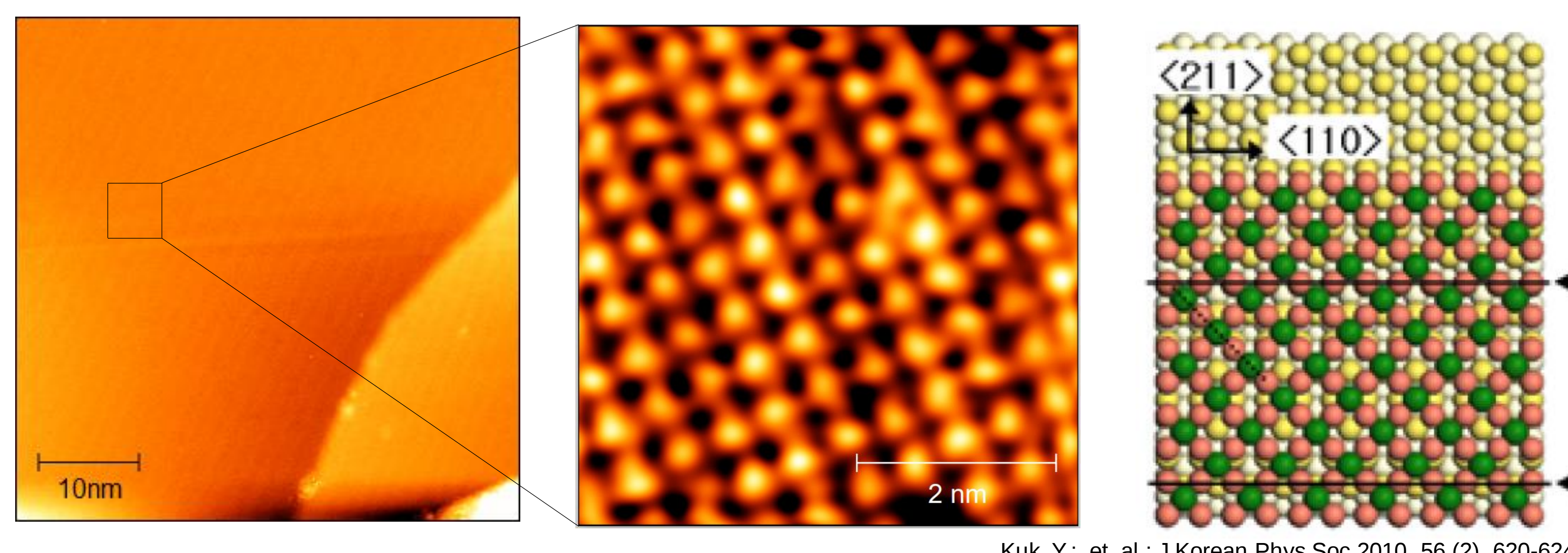


Figure 4. Desorption of high coverage copper nitride.

NiC_y Characterization

Due to nickel's strong affinity of carbon, it was selected as the transition metal carbide surface. It was first cleaned using sputtering in 1.0e-5 torr of Ar at 500 eV for 10 minutes, aiming to remove any contaminants. Subsequently, the sample was annealed at 1000.0K for 1 hour to promote surface restructuring. However, the carbide phase remained evident in the images and a clean nickel (111) surface was never obtained. This was shown by taking atomic resolution images that show the same square pattern features with the same spacing (0.504 nm) as previously observed in the literature (Tanaka, K., Materials 2010, 3 (9), 4518-4549). However, as we are investigating carbides, this characterization provides an easy method for obtaining a TMC surface to later deposit SACs and perform the methanol reforming reaction.



Kuk, Y.; et. al.; J Korean Phys Soc 2010, 56 (2), 620-624.

Figure 5. Nickel carbide large scale and atomic resolution images (left and middle, respectively). Atomic overlay of square pattern features on a hexagonal single crystal (right).

Physical vapor deposition was subsequently used to deposit Pd onto the clean nickel carbide surface. Single atoms of Pd adsorb on the four-fold site of the carbide terrace. Multi-layers of Pd islands also form on the surface. The top layer of the islands tend to adopt hexagonal packing, which is different from the carbide substrate, resulting in a rough island termination.

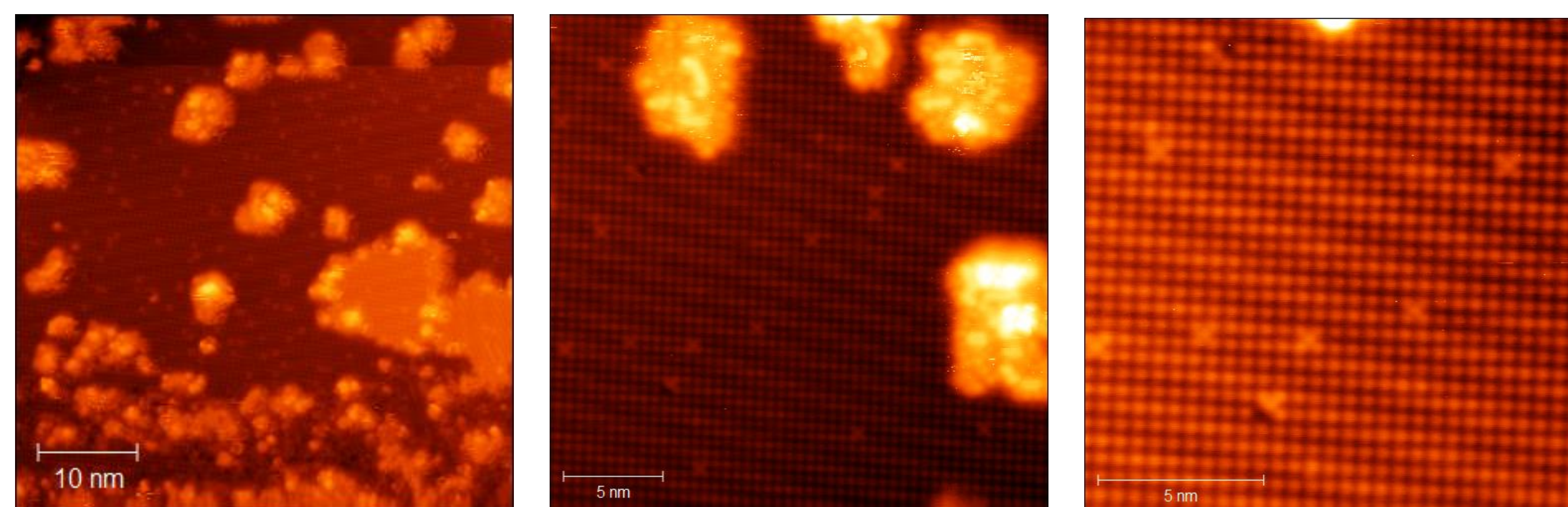


Figure 6. Pd deposited onto the nickel carbide surface at room temperature.

Conclusions

- Copper nitride and nickel carbide can be feasibly prepared in vacuum conditions by ionization of molecular nitrogen and CO disproportionation (Boudouard reaction). The formation of CuN_x prefers under-coordinated sites, such as step edges.
- Both CuN_x and NiC_y present a square pattern, which is different from the hexagonal patterned substrate, indicating strong bindings within the film.
- The four-fold site on NiC_y stabilizes a single atom of Pd. The single atoms and Pd islands form simultaneously on the carbide surface.

Acknowledgements

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