



# Copper underpotential deposition on boron nitride nanomesh



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## ABSTRACT

The boron nitride nanomesh is a corrugated monolayer of hexagonal boron nitride (h-BN) on Rh(111), which so far has been studied mostly under ultrahigh vacuum conditions. Here, we investigate how copper underpotential deposition (upd) can be used to quantify defects in the boron nitride monolayer and to assess the potential window of the nanomesh, which is important to explore its functionality under ambient and electrochemical conditions. In dilute sulfuric acid, the potential window of h-BN/Rh(111) is close to 1 volt, i.e. larger than that of the Rh substrate, and is limited by molecular hydrogen evolution on the negative and by oxidative removal on the positive side. From copper upd on pristine h-BN/Rh(111) wafer samples, we estimate a collective defect fraction on the order of 0.08–0.7% of the geometric area, which may arise from line and point defects in the h-BN layer that are created during its chemical vapour deposition. Overpotential deposition (opd) is demonstrated to have significant consequences on the defect area. We hypothesise that this non-innocent Cu electrodeposition involves intercalation originating at initial defects, causing irreversible delamination of the h-BN layer; this effect may be used for 2D material nanoengineering. On the relevant timescale, upd itself does not alter the defect area on repeated cycling; therefore, metal upd may find use as a general tool to determine the collective defect area in hybrids between 2D materials and various substrate metals.

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## 1. Introduction

Two-dimensional materials, including graphene [1] and metal-organic frameworks [2], are enjoying exceptional electrochemical research activity for a number of reasons to which non-scalability and economy of resources belong. Wide-band-gap insulators, such as hexagonal boron nitride (h-BN), are less obvious material candidates, as—with few exceptions [3]—high electrical conductance appears paramount for electrochemistry to be possible. For a single- or few-layer dielectric on a free-electron metal, however, the electronic wave function extends sufficiently for tunnelling across this barrier to occur [4]. In addition, the question whether an ultrathin layer of a dielectric on a conductor remains dielectric in nature is not trivial, and requires the interaction between the substrate and overlayer to be considered in detail [5]. As a recent example of such counterintuitive behaviour, electrocatalytic properties of BN nanosheets on Au have been demonstrated [6,7].

A particularly intriguing dielectric-metal hybrid is the boron nitride nanomesh [8,9], an atomically thin layer of h-BN on Rh(111). Due to a 10% mismatch in lattice constants between the Rh(111) substrate and the h-BN overlayer, and suitably strong binding between the two materials [10], a pronounced corrugation with a coincidence lattice constant of 3.2 nm emerges, the details of which have been studied in considerable detail over the past decade. The superstructure is characterised by areas with registry between the N and Rh atoms where strong binding occurs (“pores” of the nanomesh) and areas with weaker binding (in part even repulsive interactions), where the h-BN monolayer buckles up (so-called “wires”). A major consequence of the h-BN monolayer corrugation is the existence of in-plane dipole rings [11], which are responsible for trapping of polarisable atoms and molecules where the gradient of the electric field is largest, that is, at the edge of each pore. To date, all published work regarding molecular trapping on the nanomesh has been in vacuum [11–13], even though solution-based studies are underway that demonstrate the usefulness of the nanomesh as a substrate for intact immobilisation of reactive species such as monodisperse tungsten oxide clusters [14].

Recently, we demonstrated that electrochemical intercalation of hydrogen renders the boron nitride nanomesh flat [15], and that

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the effect of this nanoscale transformation can be seen in dynamic contact angles of an electrolyte drop, six orders of magnitude larger than the nanomesh corrugation. This observation makes the nanomesh a promising model system for the study of wetting, adhesion and stiction (static friction). Naturally, linking microscopic properties with their macroscopic expression implies that the density of defects should be kept to a minimum. Also other processes based on 2D materials, such as field-driven sieving of isotopes [16], electrochemical exfoliation to produce freestanding one-atom-thick crystals [17], and the prospect of osmotic pumps for power generation [18] require a detailed understanding of their electrochemical stability. For the boron nitride nanomesh, the stability of the nanomesh in water [9] and electrolytes [15,19] has been demonstrated in principle, but more detailed studies are essential to explore the full potential of this class of materials.

In the years following the discovery of the boron nitride nanomesh, substantial efforts have been invested in understanding the deposition conditions that lead to highly uniform monolayer h-BN growth [20–22]. A consensus has emerged that high-quality layers require step-flow growth conditions, as the formation of line defects where h-BN domains meet is unavoidable. Suitable growth conditions include promoting fast diffusion of adsorbed precursor molecules and limitation of the number of nuclei from where growth proceeds. However, reliable yet fast and simple experimental methods to quantify the defect density remain necessary, as direct observation with a scanning probe technique is not scalable to large areas.

Here, copper upd on the h-BN nanomesh is used to quantify the collective defect area, and we propose that metal upd can be applied in general as a sensitive probe for defects in 2D materials on suitable metal substrates. Classically, hydrogen upd has been used often to determine the microscopic, as opposed to the geometric, surface area [23–25], subject to assumptions such as commensurability between upd layer and metal surface (e.g., one H atom per metal atom). For the boron nitride nanomesh, the added complexities of hydrogen intercalation, and the apparent limit at 1/3 of a monolayer [15,26], make such presumed simple calibration impossible. Using copper electrodeposition, we explore how the upd signature changes as a function of the width of the electrochemical excursion to which we subject the nanomesh,

both in negative (towards copper opd) and positive direction (where the nanomesh and/or Rh(111) substrate are oxidised).

## 2. Experimental

Boron nitride nanomesh was grown in a dedicated apparatus [27] on four-inch Si(111) wafers protected with a 40-nm yttria stabilised zirconia (YSZ) diffusion barrier and covered by a 150-nm thick single-crystalline rhodium film. Briefly, the Rh(111)-coated film was cleaned by oxygen and argon plasmas, and high-temperature degassing and annealing. The growth of h-BN itself occurred by exposing the substrate at 820 °C to 675 Langmuir ( $1 \text{ L} = 10^{-6} \text{ torr}\cdot\text{s}$ ) borazine [(HBNH)<sub>3</sub>] as a precursor, which leads to self-limiting monolayer growth [8,27].  $1 \times 1 \text{ cm}^2$  samples were cut from these wafers in a clean room and protected by a UV-cured polymer film until seconds before use. Reference measurements on Rh(111) were carried out on a Clavilier-type rhodium single crystal (Mateck GmbH, Germany), oriented (miscut  $\sim 0.1^\circ$ ) and polished to mirror finish. Prior to measurements, the bead crystal was flame-annealed and cooled in a 2:1 Ar:H<sub>2</sub> atmosphere, which is known to yield good-quality (111) terraces [28].

Cyclic voltammetry was performed using a Metrohm–Autolab PGSTAT32 potentiostat. Measurements on wafer samples were carried out in a single-compartment PTFE cell pressed onto the sample by means of a 4-mm diameter Kalrez O-ring, holding a Pt wire counter and Ag/AgCl/3 M NaCl reference electrode. Rh(111) single-crystal measurements were performed in hanging-meniscus configuration in a standard two-compartment glass cell carrying a reversible hydrogen reference and Pt wire counter electrode. All measurements in this paper are reported with reference to the reversible hydrogen electrode (RHE). The electrolytes were prepared from ultrapure H<sub>2</sub>SO<sub>4</sub> (Merck suprapur), copper sulfate (99.999% metals basis, Alfa Aesar) and water (Milli-Q, Millipore, 18.2 MΩ cm,  $\leq 3$  ppb total organic carbon). All glassware and the PTFE cell were cleaned by boiling in 20% nitric acid and rinsing with ultrapure water; the Kalrez O-ring was treated with carboxylic acid (3:1 conc. H<sub>2</sub>SO<sub>4</sub>:30% H<sub>2</sub>O<sub>2</sub>; *Caution! This mixture is very aggressive and should be handled with extreme care*) and rinsed with ultrapure water. Electrolytes were degassed by

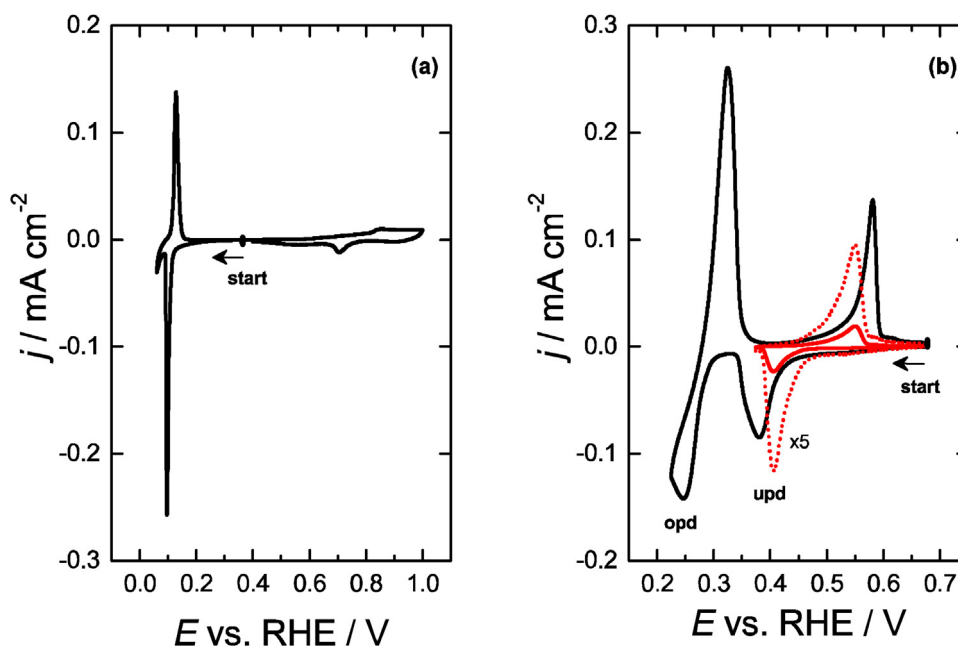


Fig. 1. Cyclic voltammogram of Rh(111) (single crystal) in (a) 0.1 M H<sub>2</sub>SO<sub>4</sub> and (b) 1 mM Cu<sup>2+</sup> + 0.1 M H<sub>2</sub>SO<sub>4</sub>. Scan rate, 10 mV s<sup>-1</sup>; (b) upd only, 2 mV s<sup>-1</sup>.

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