Supporting Information

Pt Nanoclusters Sandwiched between Hexagonal Boron Nitride and Nanographene as van der Waals Heterostructures for Optoelectronics

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The steps of the preparation process of the Pt nanocapsules are depicted in Figure S1 by XP spectra of the Pt 4f\(_{7/2}\), B 1s, Rh 3d, and N 1s core levels. At first, an ordered layer of hexagonal boron nitride was grown on the clean Rh(111) single crystal (purple spectrum) by chemical vapor deposition of \(2 \times 10^{-8}\) mbar borazine (B\(_3\)N\(_3\)H\(_6\)) at 1050 K (blue spectra).\(^1\) It shows the typical two-peak structures in the B 1s and N 1s with peaks that are assigned to the pores (B 1s: 190.72 eV, N 1s: 398.81 eV) and the wires (B 1s: 190.36 eV, N 1s: 398.16 eV) of the nanomesh.\(^2\,^3\) At the same time, the signal of the Rh surface core level shift at 306.89 eV decreases. After cooling to 150 K, 0.81 ML of Pt was deposited on the \(h\)-BN/Rh(111) nanomesh to grow Pt nanoclusters arrays in the pores of the nanomesh. The deposition of Pt results in damping of the substrate and the known shift of the \(h\)-BN B 1s and N 1s signals towards lower binding energies caused by interaction with Pt (green spectra). To stabilize the shape of the nanoclusters, they were saturated with CO and subsequently heated to 550 K.\(^4\) By this procedure, the nanoparticles become more three-dimensional-shaped and more robust towards ripening in follow up experiments (orange spectra). This causes a decrease of the Pt signal by increased damping, while the signals of the \(h\)-BN/Rh(111) nanomesh get less damped.
**Figure S1:** XP-spectra of the single steps of the preparation process of G/Pt/h-BN/Rh(111) measured in the Pt 4f_7/2 (a), B 1s (b), Rh 3d (c), and N 1s (d) core levels: Preparation of h-BN, Pt evaporation, nanocluster stabilization, annealing to 920 K, and graphene growth. All spectra were recorded at 150 K.

**Figure S2:** Test for impermeability of the graphene by exposing it to a supersonic molecular beam of CO with a pressure on the sample of 7.4 x 10^{-7} mbar at 150 K: a) C 1s XP-spectra measured during the experiment; b) Pt 4f_7/2 XP-spectra measured before and after the experiment.
A series of annealing and follow-up CO-adsorptions was conducted on 0.76 ML Pt/h-BN/Rh(111) to investigate the changes of the nanoparticle surface. Figure S3 shows the two measurements conducted after annealing to 500 and 900 K, reflecting the temperature-induced changes that occur for growing graphene at 920 K. Thereby, the total amount of adsorbed CO decreases by 20%. This means that also the sum of all nanocluster surfaces decreases by 20%. If one assumes a semi-spherical shape of the clusters and a constant amount of Pt, this results in a reduction of the number of clusters by 49%, while their average diameter increases by 25% and their average number of atoms increases by 95%. Thus, only half of the pores remain filled, while the other half is now empty.

![Figure S3: C 1s spectra of CO-saturated 0.76 ML Pt/h-BN/Rh(111) after annealing to 500 (black) and 900 K (red). CO-adsorption and measuring were conducted at 150 K.](image)

**References**


