

Electrodeposition of palladium-dotted nickel nanowire networks as a robust self-supported methanol electrooxidation catalyst

Supporting information

Tim Boettcher^{a,*}, Sasho Stojkovikj^{b,c}, Prashant Khadke^d, Ulrike Kunz^a, Matthew T. Mayer^b, Christina Roth^d, Wolfgang Ensinger^a, Falk Muench^a

^aTechnische Universität Darmstadt, Department of Materials and Geoscience, Alarich-Weiss-Straße 2, 64287 Darmstadt, Germany

^bHelmholtz-Zentrum Berlin für Materialien und Energie GmbH, Chemical Energy Division, Hahn-Meitner-Platz 1, 14109 Berlin, Germany

^cInstitute of Chemistry and Biochemistry, Freie Universität Berlin, Arnimallee 22, 14195 Berlin, Germany

^dUniversität Bayreuth, Faculty of Engineering, Universitätsstraße 30, 95447 Bayreuth, Germany

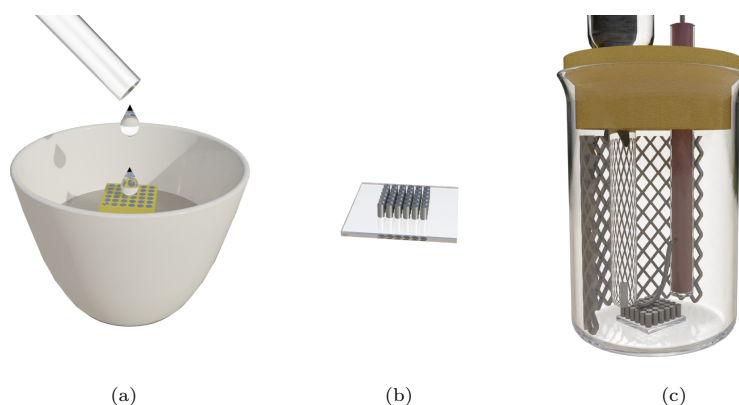


Figure S1: Preparation of dotted nanostructures for cyclic voltammetry. (a) The polymer template with the embedded nanostructures is dissolved in a crucible by using dichloromethane. (b) The free-standing network is then transferred to a glass slide and (c) placed in a beaker where it is fixed and contacted by a Ni wire coated with silicone.

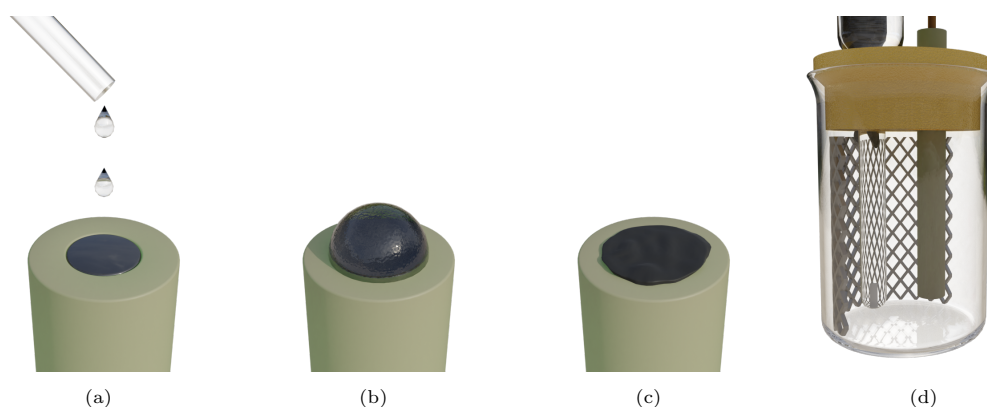


Figure S2: Preparation of the Pd@C reference catalyst for cyclic voltammetry. (a) The ultrasonicated dispersion of Pd@C and Nafion™ is applied to the glassy carbon electrode with a pipette. (b) Then, the assembly is dried at air for approximately 15 min so that (c) only the catalyst powder and the Nafion™ remain. (d) This electrode is then mounted in a beaker together with the reference and counter electrodes.

*Corresponding author

Email address: boettcher@ma.tu-darmstadt.de (Tim Boettcher)

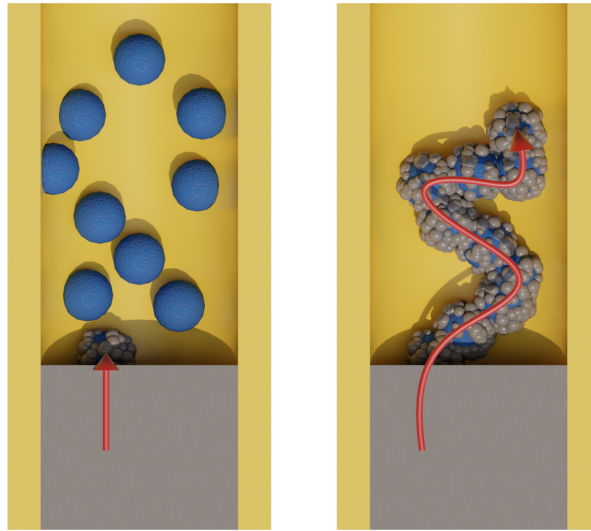


Figure S3: Illustration of conductive paths with non-intersecting (left) and intersecting (right) Pd seeds. In the left case, the foremost point of the back electrode is still near the nanowire end. Thus, the electrode surface is only slightly deformed and regular growth occurs. In the right case, the foremost point of the back electrode extends a comparably long distance along the template pore. For diffusion reasons, most of the electrodeposition will occur on the foremost electrode point and thus, the possibility for void formation inside the pores is given.

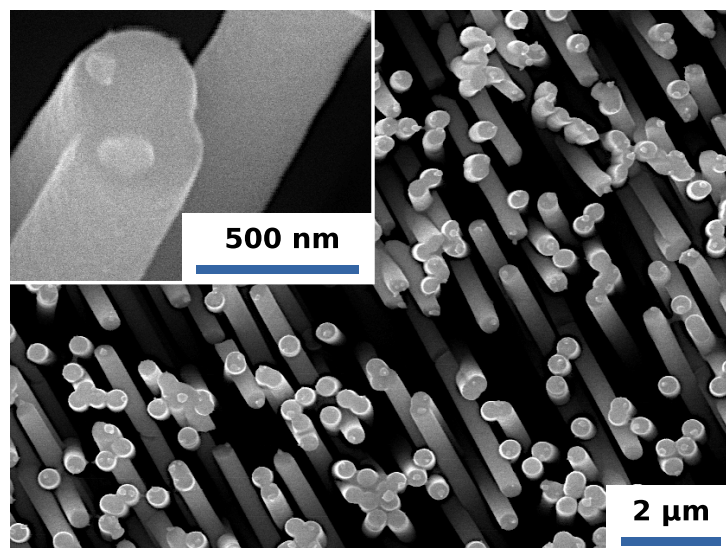


Figure S4: SEM images of the Ag-dotted Ni nanowire networks, in this case a four times activated sample. The wire surfaces are smooth and do not indicate any obvious presence of nanoparticles.

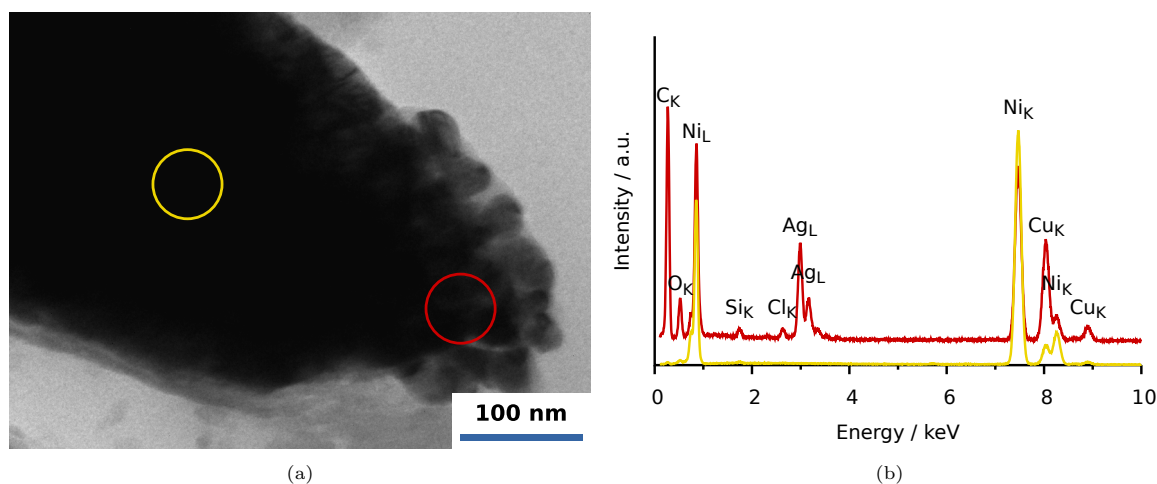


Figure S5: a) TEM image of a cross-section of a single wire of the Ag-dotted Ni nanowire networks, in this case a five times activated sample. EDX measurements were performed at the two marked spots. b) TEM EDX of the Ag-dotted Ni nanowire networks. The line colours correspond to the colours of the two marked spots in the TEM image. Note that the chlorine signal is caused by the formation of a layer of AgCl due to the employment of a NiCl_2 -based electrolyte in the electrodeposition step.

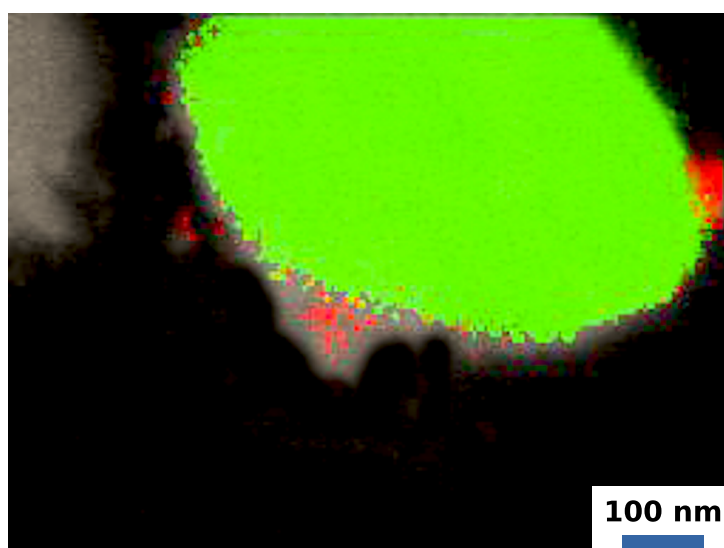


Figure S6: TEM mapping of a cross-section of a six times activated Pd-dotted Ni nanowire network. The core of the wire only consists of Ni (green), while Pd (red) is only found in the outer wire region.

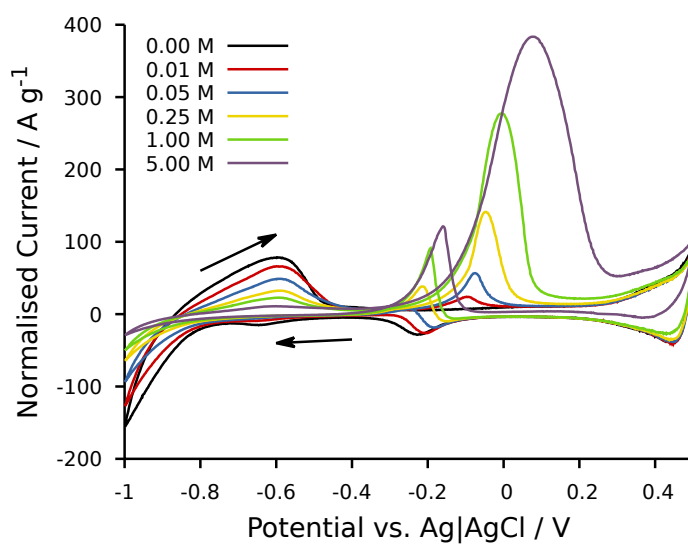


Figure S7: iR drop-corrected CV curves of a four times activated Pd-dotted Ni nanowire network in 0.1 M NaOH solution with various amounts of methanol at a scan rate of 50 mV s^{-1} . The arrows indicate the scan direction.

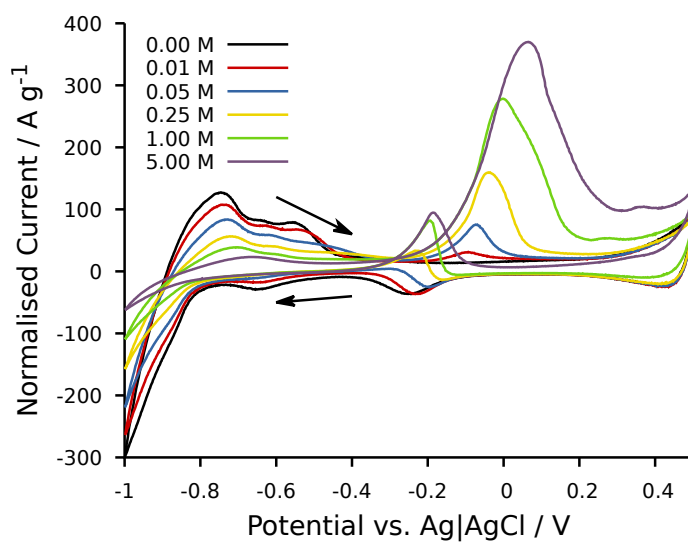


Figure S8: iR drop-corrected CV curves of a six times activated Pd-dotted Ni nanowire network in 0.1 M NaOH solution with various amounts of methanol at a scan rate of 50 mV s^{-1} . The arrows indicate the scan direction.

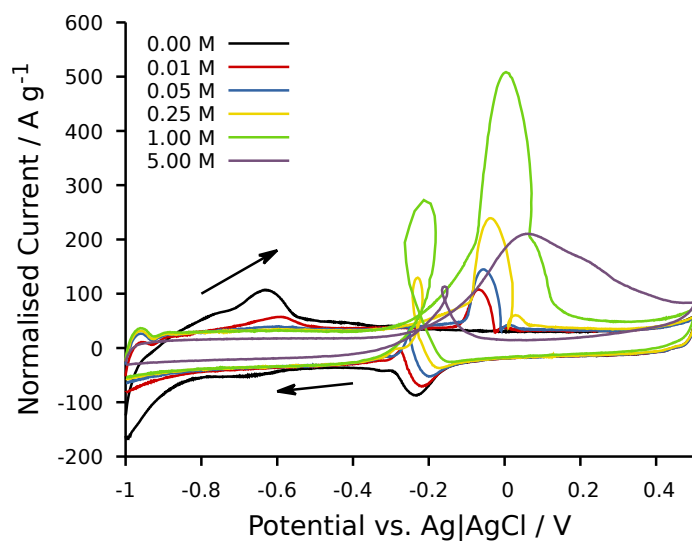


Figure S9: iR drop-corrected CV curves of a Pd@C reference catalyst in 0.1 M NaOH solution with various amounts of methanol at a scan rate of 50 mV s^{-1} . The arrows indicate the scan direction. Loops are caused by the applied iR drop-correction technique (current interrupt) which dynamically rescales the x-axis.

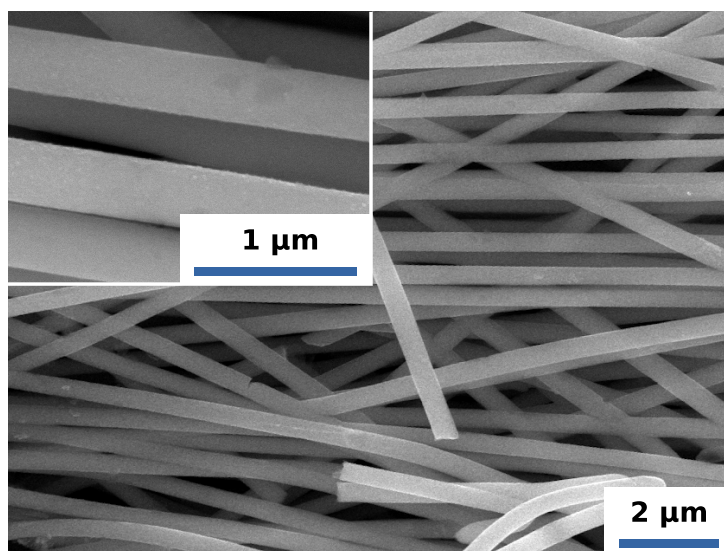


Figure S10: SEM images of the Pd-dotted Ni nanowire networks after electrochemical testing, in this case a two times activated sample. The wire surfaces are still smooth and do not indicate any degradation.