

Electronic Supporting Information:

Role of boric acid in nickel nanotube electrodeposition: a surface-directed growth mechanism

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Experimental:

Prior to deposition, a homemade working electrode was fabricated. First, a Denton Desk III Sputter machine was used to sputter a ~200nm layer of gold on the branched side of a Whatman AAO membrane. Copper tape was attached to the gold layer to allow for good electrical contact. The membrane was sandwiched between two pieces of teflon with a 1.92 cm² window in which the non-branched side was exposed.

All electrodeposition experiments were performed using a VSP Modular Potentiostat/Galvanostat by Bio-Logic Science Instruments. First, the working electrode was placed in a gold plating solution (OROTEMP 24) along with a Pt counter electrode and an Ag/AgCl reference electrode. Au nanowires, which acted as the base electrode for Ni deposition, were formed by applying a constant current of -0.3 mA for 30 min. All three electrodes were rinsed and placed in Ni plating solution (0.5 M NiSO₄, 0.4 M H₃BO₃, pH 4.3; unless otherwise specified). NaOH and HCl were added to the plating solution for experiments performed at higher and lower pH, respectively. Ni was deposited at a constant potential of -1V for 30 min, unless otherwise specified. The AAO membrane was dissolved by soaking in 3 M NaOH for 30 min, resulting in free standing nanotubes. Imaging of the nanomaterials was performed on a Hitachi SU-70 FEG-SEM and a JEM 2100 FE-TEM. Energy-dispersive X-ray spectroscopy (EDS) was performed using an Oxford INCA 250 system attached to the FE-TEM.

Calculations:

Ni²⁺ concentration at the pore wall in the presence of boric acid

For this calculation a small volume of solution around the inner nanotube wall was chosen to act as our area of interest. Based on a literature search, the AAO was estimated to contain 15 hydroxyl groups per nm² on the alumina surface¹, and boric acid was assumed to adsorb to the alumina via a bidentate interaction. As a result, 7 nickel molecules per nm² were assumed to be bound to the template surface.

Inner nanotube radius= 90nm

$$\begin{aligned}\text{Volume} &= [2\pi(90\text{nm}) \times 1\text{nm} \times 0.4\text{nm}] \times (1\text{ cm} / 10^7\text{nm})^3 \times (1\text{ L} / 1000\text{cm}^3) \\ &= 2.26 \times 10^{-22}\text{L}\end{aligned}$$

$$\begin{aligned}\text{Nanotube surface area} &= 2\pi(90\text{nm})(1\text{nm}) \\ &= 565\text{nm}^2\end{aligned}$$

$$\begin{aligned}\text{Nickel concentration} &= 565\text{nm}^2 \times (7\text{ Ni}^{2+}\text{ molecule} / 1\text{nm}^2) \times (1\text{ mol} / 6.022 \times 10^{23}\text{ molecules}) / \\ &\quad (2.26 \times 10^{-22}\text{L}) \\ &= 29\text{ M}\end{aligned}$$

The concentration of nickel in the standard electrolyte is 0.5 M, which means the concentration at the alumina surface in the presence of boric acid is 58 times greater than the bulk solution.

Images:

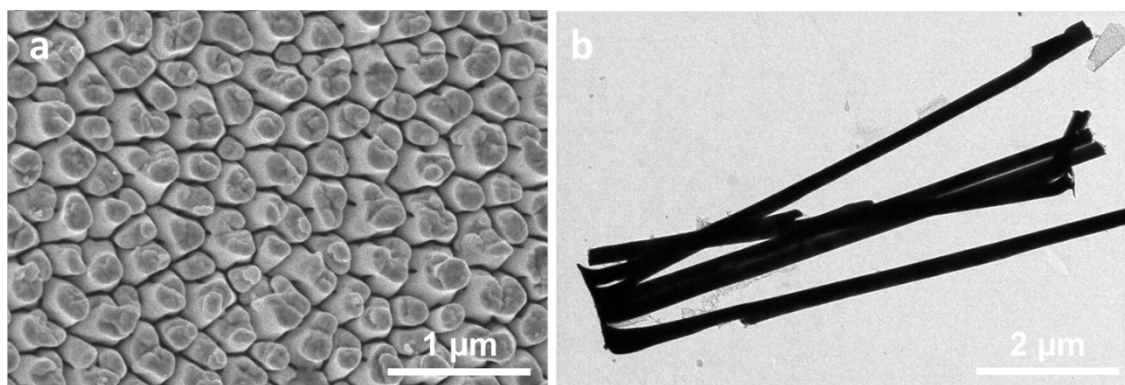


Fig. S1 (a) SEM and (b) TEM images of Au nanowires employed as the base electrode

¹ 1 A. Phan, D. R. Cole, and A. Striolo, *The Journal of Physical Chemistry B*, 2013, 117, 3829.

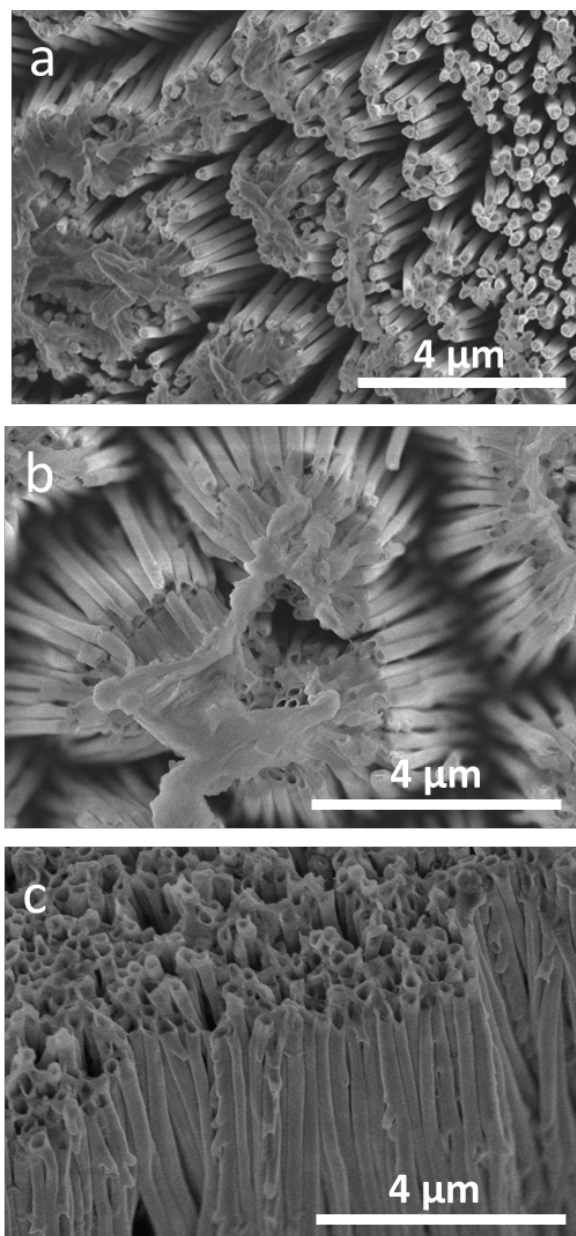


Fig. S2 SEM images of nickel nanostructures electrodeposited at -1V from a 0.5 M NiSO₄ solution containing (a) 0.4 M, (b) 0.1 M, and (c) 0 M H₃BO₃. As the concentration of boric acid was decreased, the nanostructures became more rigid. When boric acid was absent in the electrolyte nanowires, capable of standing upright, formed with shallow nanotube tips. It is important to note that the change in structure was not a result of a change in ionic conductivity, as Ni NWs were still formed when boric acid was replaced by NaSO₄.

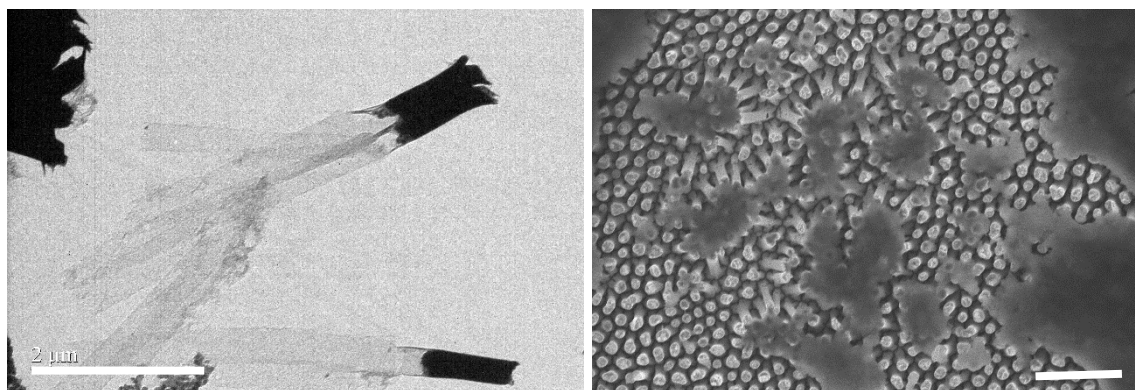


Fig. S3 a) TEM and b) SEM images of nickel NTs synthesized after rinsing the AAO template with acetonitrile and depositing from 1 M NaSO₄. Scale bars represent 2 μm.

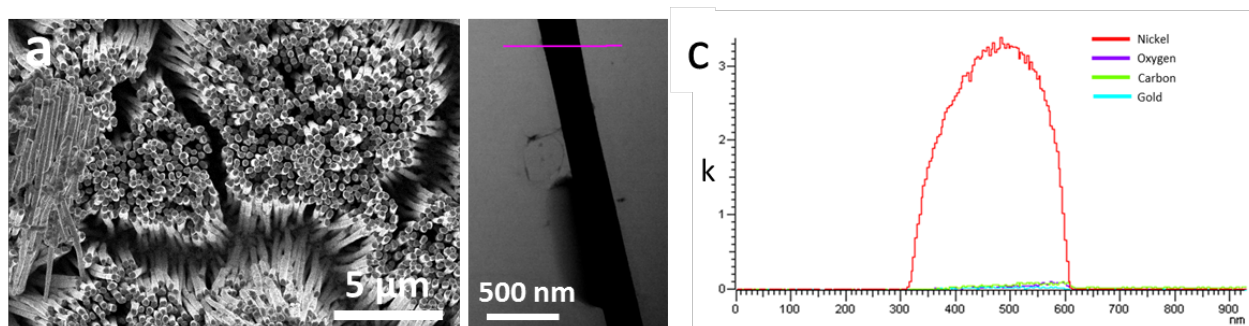


Fig. S4 (a) SEM image of nickel nanowires synthesized at -1V in 0.5 M NiSO₄ and 0.4 M acetic acid. (c) TEM image with corresponding (d) EDS line scan of a nickel nanowire synthesized in acetic acid.

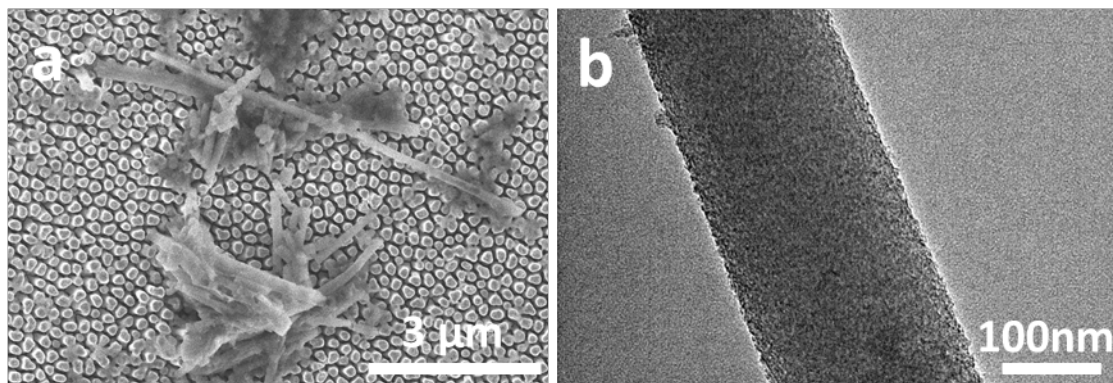


Fig. S5 (a) SEM and (b) TEM image of nickel nanowires synthesized at -1V in 0.5 M NiSO₄ and 0.2 M citric acid.

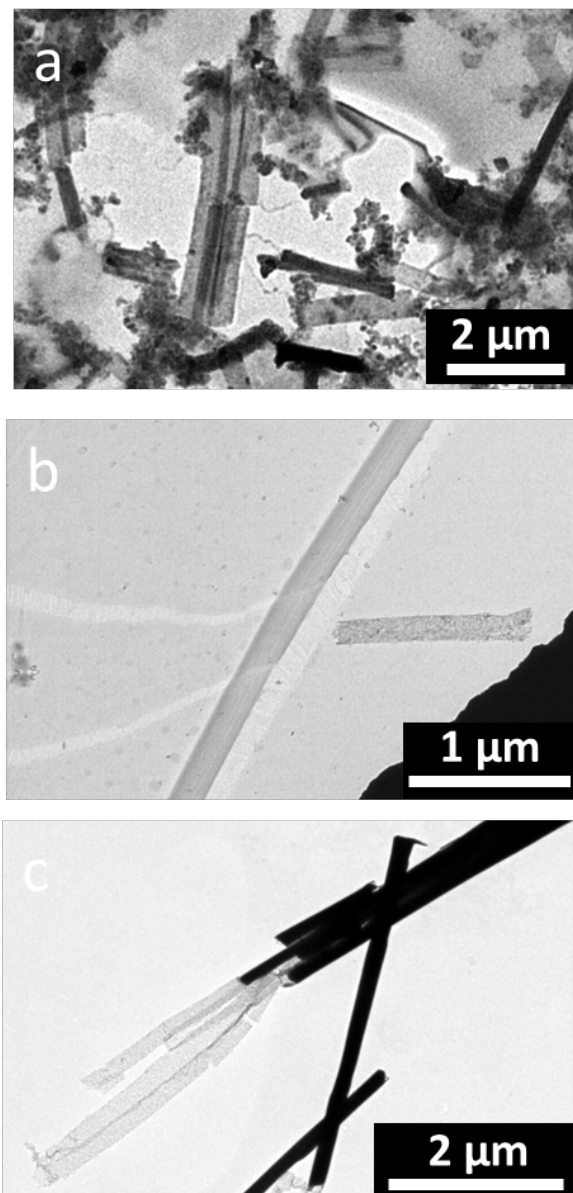


Fig. S6 TEM images of nickel nanotubes synthesized at -1V in 0.5 M NiSO₄, 0.4 M H₃BO₃ at pH (a) 1.8, (b) 3.1, and (c) 5.2.

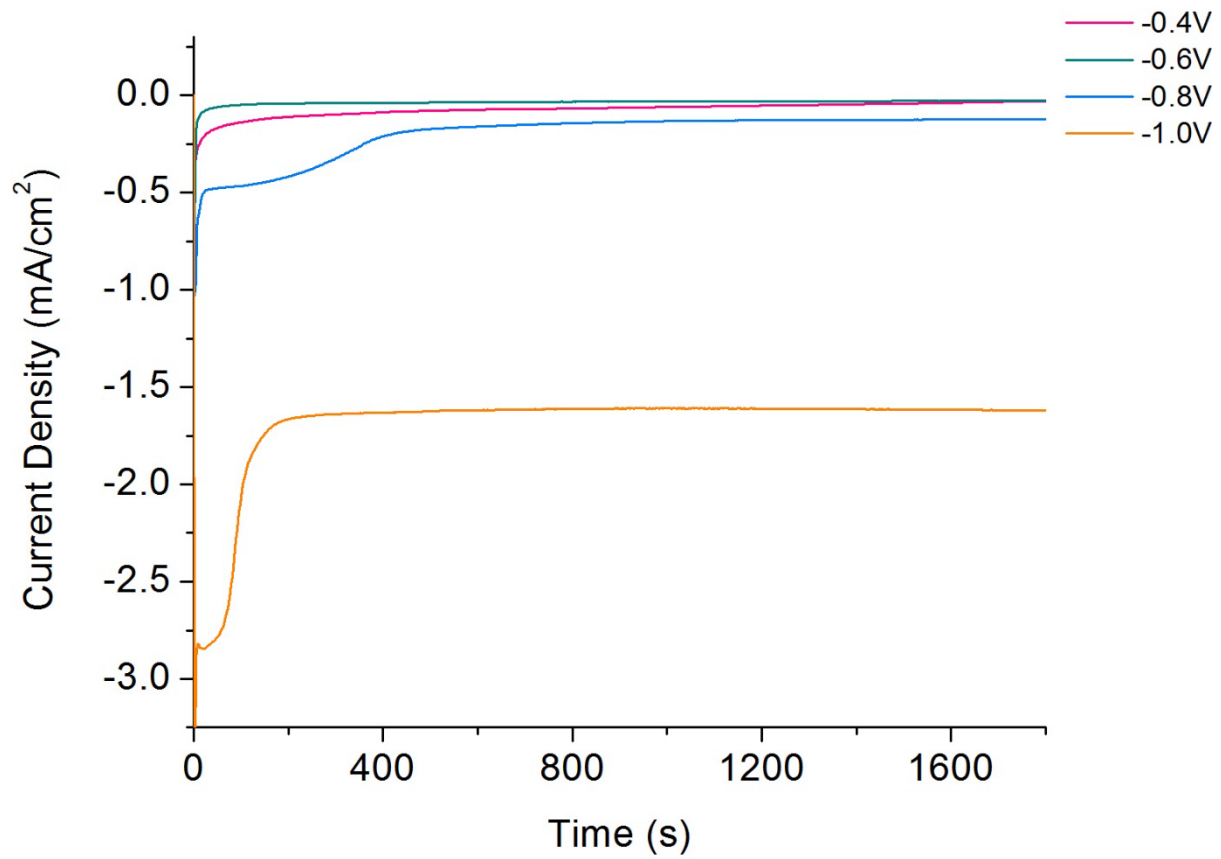


Fig. S7 Current density profile for the deposition of nickel.

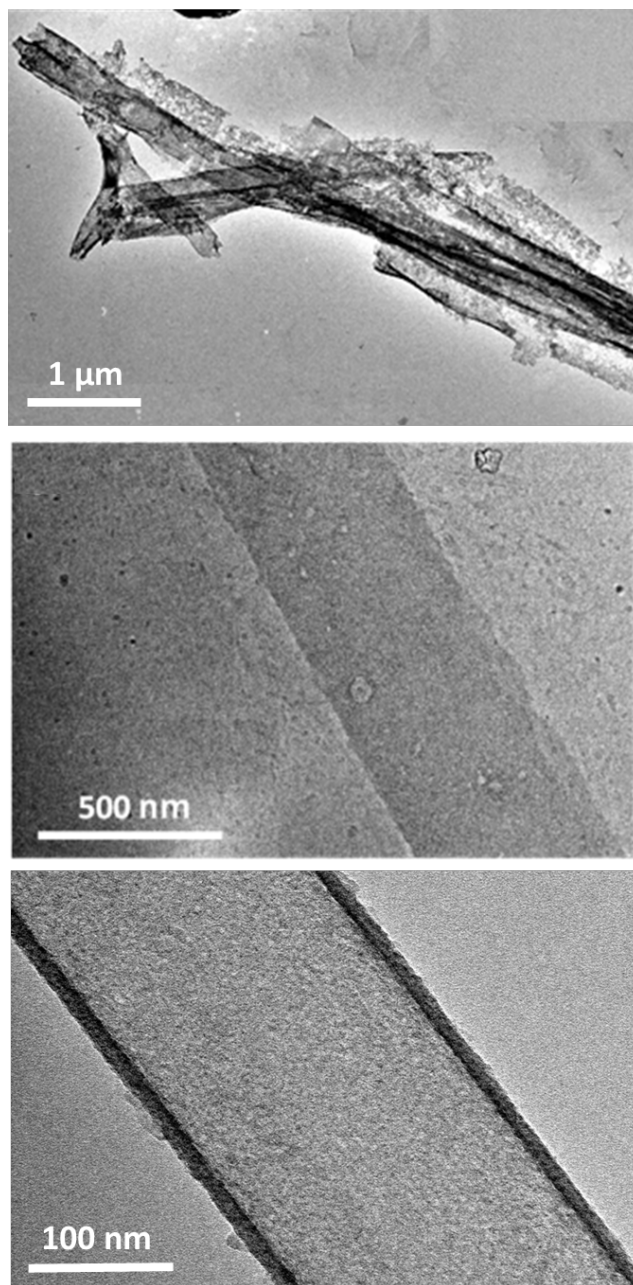


Fig. S8 TEM images of nickel nanotubes electrodeposited from a solution of 0.5 M NiSO₄ and 0.4 M H₃BO₃ at (a) -0.4V, (b) -0.6V, and (c) -1V.