Supplementary Information

Periodic Nanowire Arrays with Alternating Compositions and Structures Fabricated using a Simultaneous Nanowire Formation Step

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Discussion of process optimization

The sequence of the assembly/fabrication steps involved in preparation of NP-decorated NW arrays, namely, DIB treatment, Au NP deposition, metal impregnation, and plasma treatment, strongly influences the end results. Obviously, the DIB treatment must always precede the NP deposition step, and the plasma treatment that affords the NWs must conclude the process. This leaves three possible sequences that differ in the location of the metal impregnation step. Experiments to determine the step order were performed on monolayer films, though their conclusions are applicable to bilayer films as well. The sequence that was found to be optimal for obtaining NWs that are selectively decorated with a high density of NPs involves metal impregnation as the last step (**Figure S1**a).

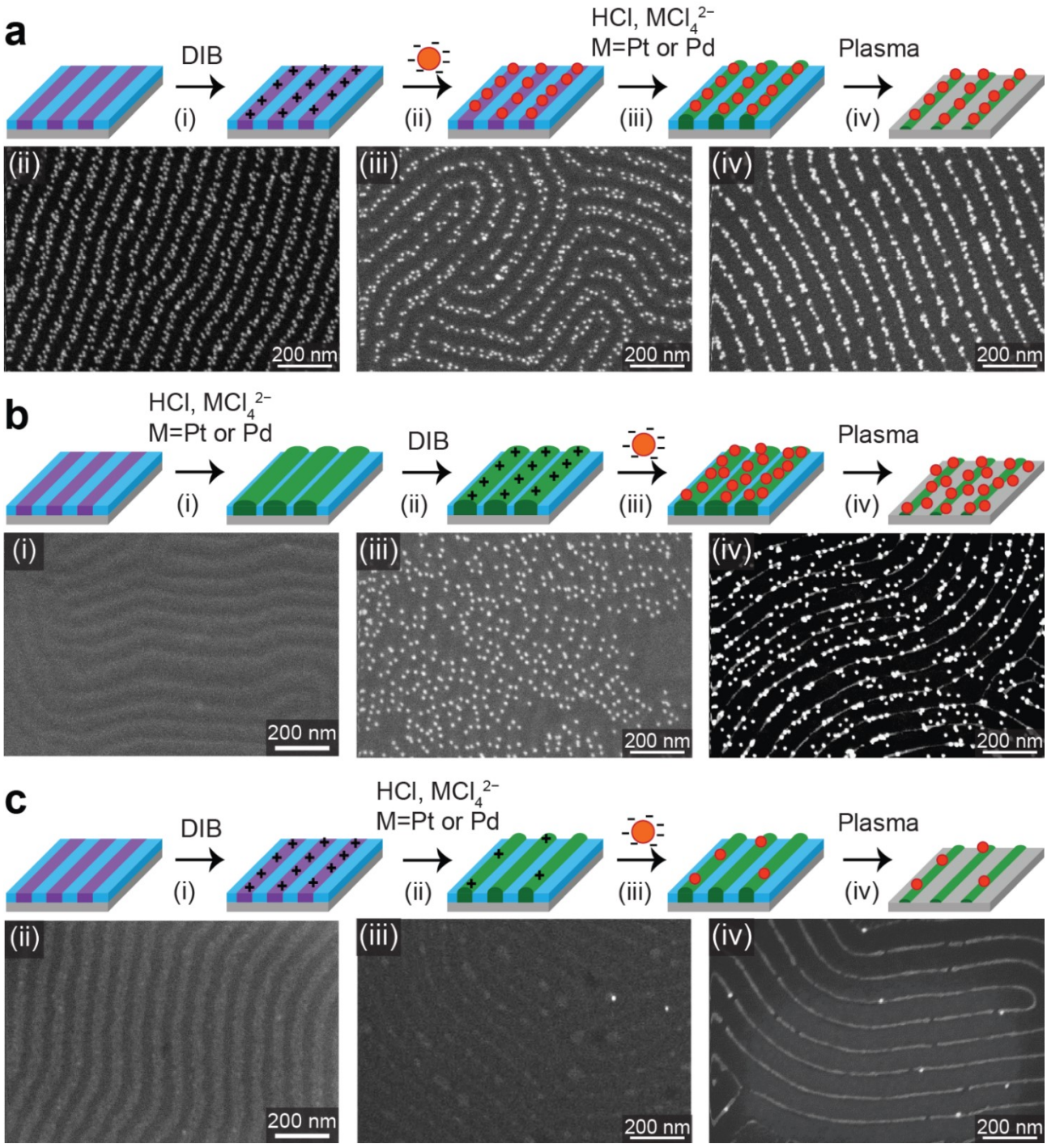

Figure S1. The influence of the sequence of the assembly/fabrication steps on the final result. (a) The optimized process; (b) a modified process, in which metal impregnation is the first step; (c) a modified process, in which metal impregnation is the second step.

Moving the metal impregnation step to be the first step of the process led to a final structure, in which a large number of NPs are not attached to NWs (**Figure S1**b, rightmost image). Inspecting the sample before plasma treatment (**Figure S1**b, middle image)

reveals a rather uniform distribution of NPs compared to that observed in the optimized process after NP deposition (**Figure S1**a, middle image). This suggests that the surface of the film is enriched with P2VP. Indeed, right after the impregnation step, the P2VP domains (bright tone in **Figure S1**b, leftmost image) appear swollen. As the impregnation process involves protonation, the P2VP domain swelling is explained by the mutual repulsion between charged pyridine groups.[1] A control experiment, in which NPs were assembled on a BCP film that was treated only with 1% HCl solution, supports this conclusion: **Figure S2**a clearly shows that the NPs are deposited on swollen P2VP domains. In metal impregnated films, this situation leads to domain separation that is considerably smaller than interparticle distances, which is further translated into NPs that are located at a large distance from the center line of the domain (where the NW would eventually form), and thus end up detached from the NWs after plasma treatment.

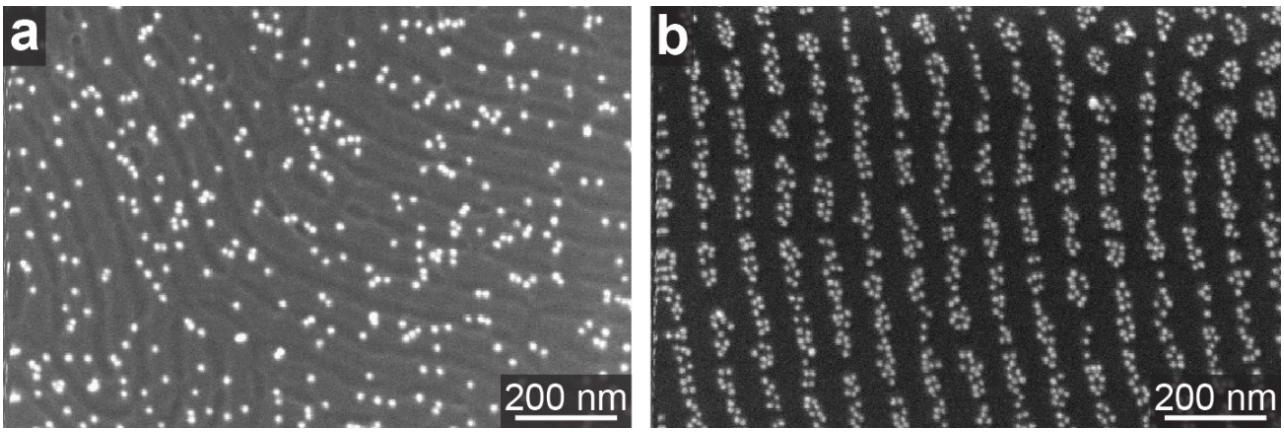

Figure S2. SEM images of: (a) a sample that underwent protonation with 1% HCl solution for 24 h, followed by NP deposition; (b) a sample that was treated with DIB as the first step, then dipped into 1% HCl solution for 24 h, followed by NP deposition.

The above experiment attests to the importance of crosslinking the P2VP domains prior to metal impregnation to limit their swelling. **Figure S1**c shows the last sensible sequence, in which DIB treatment is performed first, followed by metal impregnation, and then NP deposition. Interestingly, this sequence led to structures with scant amount of NPs (albeit all are admittedly attached to NWs; **Figure S1**c, rightmost image). Thus, although this sequence led to retention of the P2VP domain sizes as expected (**Figure S1**c, leftmost image), it also confined the positively-charged sites at the film surface to smaller areas. Metal impregnation, which was performed before NP deposition, apparently saturated these sites, leaving almost no site available for NP adhesion. To prove this hypothesis, a control experiment performed with the same sequence from which the metal precursors were omitted (i.e., only HCl was used) indeed yielded the normal NP deposition pattern (**Figure S2**b).

The conclusion from this set of experiments is that the first step must be P2VP domain crosslinking, and it must be followed by the NP deposition. As the metal precursors penetrate throughout the entire film, the presence of the already adsorbed NPs has a negligible effect on the ability to saturate the P2VP domains with the metal precursors.

To demonstrate the effect of DIB treatment on NP deposition, two samples underwent NP deposition, one after DIB treatment and the other without any treatment prior to NP deposition (**Figure S3**a,b, respectively). The sample that underwent DIB treatment features NPs that are concentrated at smaller areas than the aggregates that resulted from the sample that was not crosslinked by DIB, indicating higher selectivity towards the P2VP domains due to the formation of positive charges on the surface.

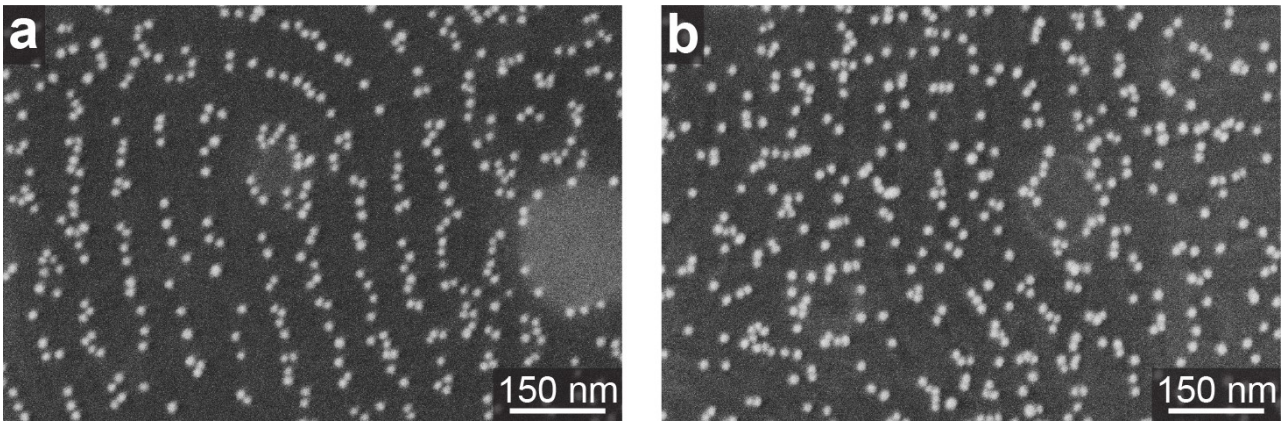

Figure S3. SEM images of Au NPs deposited on a PS-*b*-P2VP film: (a) with DIB crosslinking before NP deposition; (b) without DIB crosslinking.

Wetting of PS and P2VP on SiOx

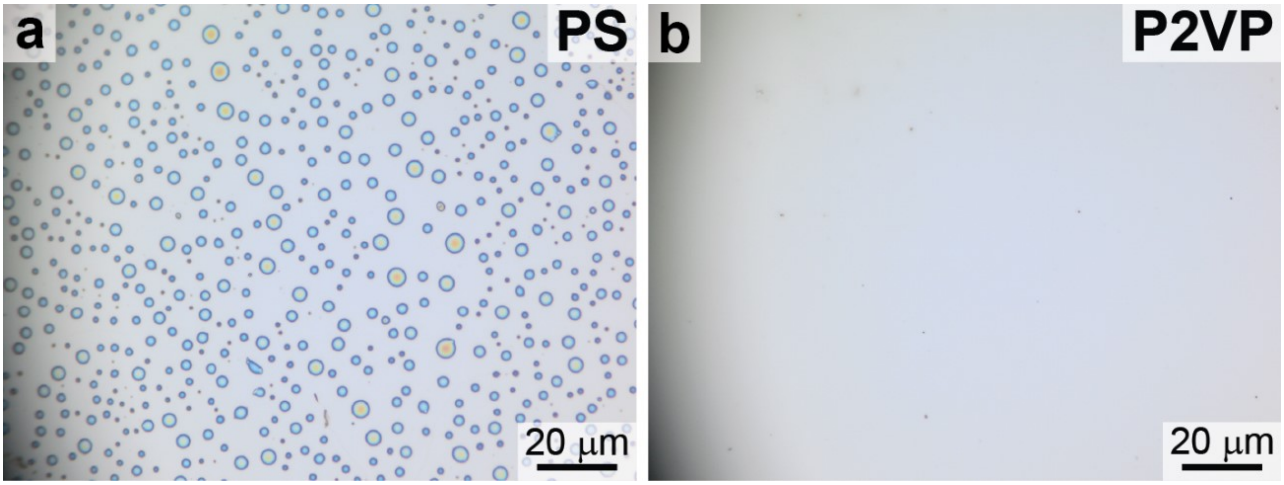

Figure S4. Optical microscopy images of 23-24 nm-thick films cast on hydrophilic SiOx substrates and annealed in chloroform vapour for 20 min, showing significant difference in wetting properties: (a) PS (M_n 50 kDa) and (b) P2VP films (M_n 50 kDa).

AFM Images of Monolayer and Bilayer Films

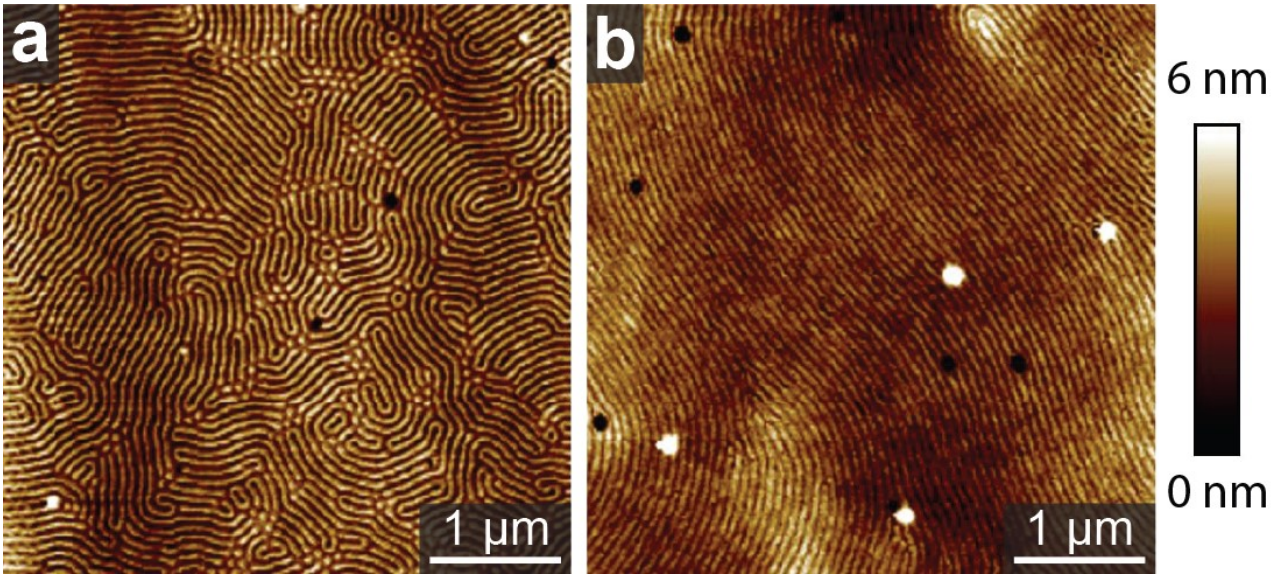

Figure S5. AFM images of cylindrical PS-*b*-P2VP films featuring: (a) a monolayer of P2VP cylinders (local film thickness 30 nm); (b) a bilayer of P2VP cylinders (local thickness 58 nm).

Examples of Periodicity Calculations

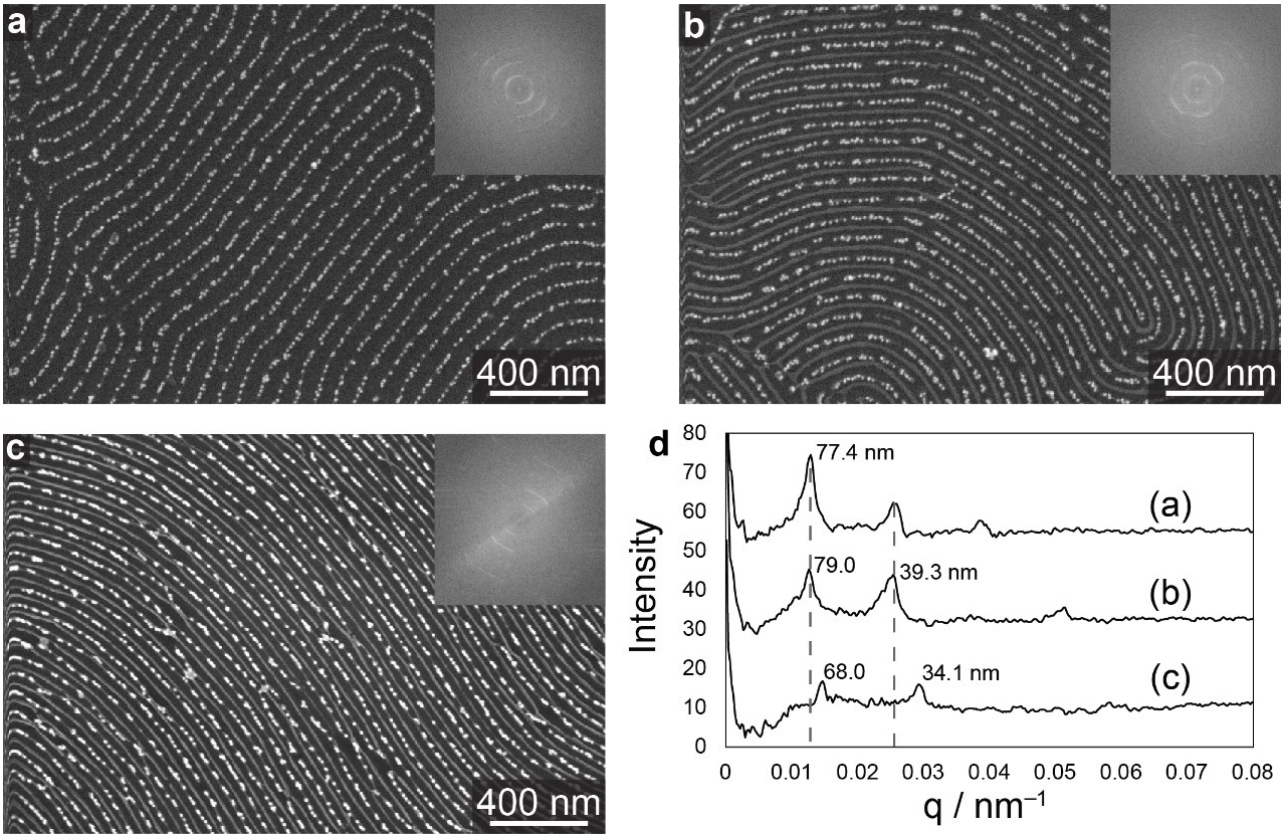

Figure S6. (a-c) SEM images of: (a) a periodic Au NP-decorated Pd NW array, and arrays of alternating bare and NP-decorated wires obtained in (b) 37 nm-thick film and (c) 60 nm-thick film. Insets represent FT analyses. (d) Radially integrated plots of the FT images after background subtraction. The lamellar periodicities are denoted next to the principal peaks. Dashed lines mark the principal periodicities in the thin films.

NW Arrays after Partial Removal of NPs

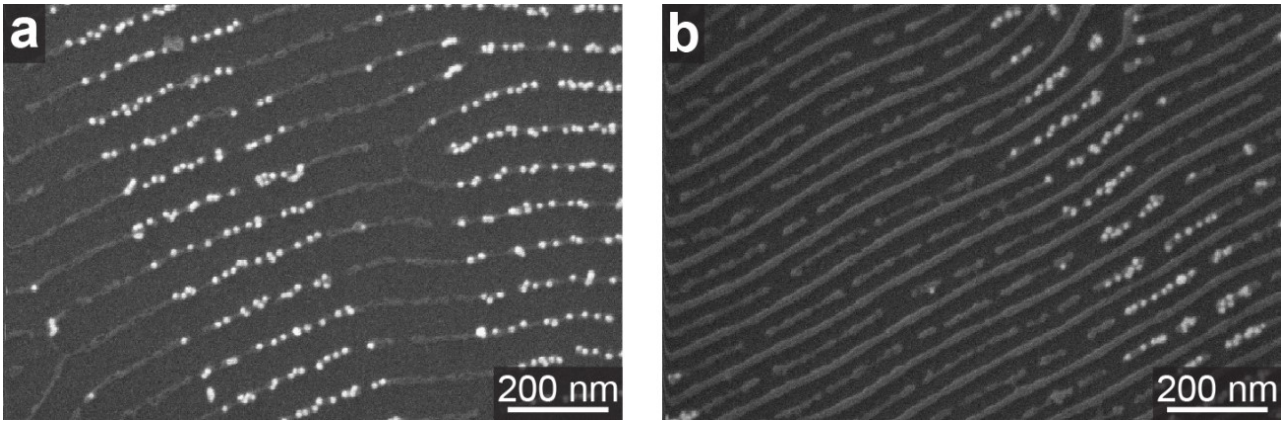

Figure S7. SEM images of a NW array with co-existing patterns originating from a 38 nm-thick film where some NPs were removed by a gentle scratch and exposed the underlying Pd NWs: (a) NP-decorated NW array originating from a region featuring a locally thin film; (b) alternating striped structure resulting from an area featuring a locally thick film.

Pd NW Arrays from Impregnation without acid.

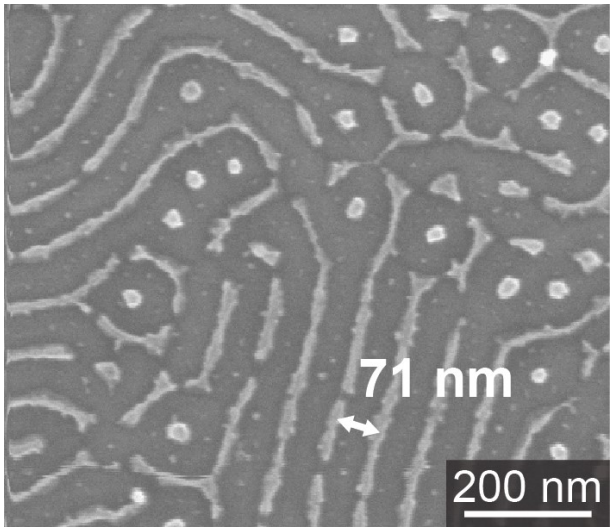

Figure S8. Top view SEM images of a Pd NW array resulting from impregnation under non-acidic conditions. The calculated periodicity of the array is denoted on the image.

References

1 J. Chai and J. M. Buriak, *ACS Nano*, 2008, **2**, 489-501.