Electronic Supporting Information (ESI)

Rapid Synthesis of Pt(0) Motors-Microscrolls on Nickel Surface via H_2PtCl_6-Induced Galvanic Replacement Reaction

Valeri Tolstoy,*[a] Kirill Nikitin,[a] Aleksei Kuzin,[b, c] Fenyang Zhu[c], Xing Li[c], Gregory Goltsman[d], Dmitry Gorin,[b] Gaoshan Huang*[c], Alexander A. Solovev,[c] and Yongfeng Mei*[c]

Affiliation:

a. Saint Petersburg State University, Institute of Chemistry, 26 Universitetskii Prospect, Petergof, St. Petersburg, 198504, Russia

b. Center for Photonic Science and Engineering, Skolkovo Institute of Science and Technology, 3 Nobel Str, Moscow, 121205, Russia

c. Department of Materials Science & State Key Laboratory of Molecular Engineering of Polymers, Fudan University, Shanghai, 200433, P. R. China

d. Department of Physics, Moscow State Pedagogical University, 119992, Russia

* *Corresponding authors*

Author Contributions

V.T. conceptualized the study, and drafted the manuscript. **A.K.** and **X.L.** provided the laser lithography process, **G.N.** and **D.A.** curated the data and conducted formal analysis. **F.Z.** and **G.H.** supervised the research and provided critical feedback. **A.A.S.** and **K.N.** contributed to experiments and results validation. **Y.M.** provided resources, and revised the manuscript. Large language model GPT 4.0 was instrumental in refining the early versions of the manuscript. All authors reviewed and approved the final manuscript version.

1. Experiment Section

1.1. Materials

Dihydrogen hexachloroplatinate (IV) hydrate ($H_2PtCl_6 \cdot 6H_2O$, JSC "Aurat") and Ni foil with a size of 0.5_7.0_20.0 mm were used as precursor and a substrate, respectively, to synthesize the platinum layer by Galvanic Replacement Reaction (GRR). Ni plates were degreased with acetone by ultrasonic treatment for 30 min and treated in hydrochloric acid (HCl, 3 M). Then the samples were chemically polished according to the method [1] in a solution of a mixture of acetic, nitric, sulfuric, orthophosphoric acids taken in the ratio of 5:3:1:1 (by volume). Processing time was 40 seconds, temperature was 90 °C, correspondingly. Next the substrates were washed in deinosized water.

1.2. Preparation of Pt(0) microscrolls

Pt(0) microscrolls were prepared on the Ni surface by immersing in solutions of H_2PtCl_6 (C = 0.005 – 0.2 M) or applying drops of such the solutions to its surface. The processing time ranged from 10 seconds to 60 minutes. As a

result, a platinum nanolayer was formed on the surface, which is rolled up during the GRR reaction. Analysis of the results of a large array of experimental data showed that the best conditions for the formation of microscrolls are concentrations of H_2PtCl_6 solutions in the range of 0.005 - 0.02M and processing time from 4 to 10 minutes. It is under these conditions that microscrolls were obtained and the model of the GRR process, which is described in the main text of the article, was built on the example of these microscrolls.

For forming patterns on Ni surface, a solid-state laser Matrix 355 was used. A maximum pulse repetition rate was 100 kHz. Pulse duration was 25 ns. Average power for 60 kHz was 1 W. Using this laser, an array of parallel tracks approximately 20 microns by 350 microns in size and spaced about 50 microns apart was deposited on the surface of nickel.

For forming array with the fixed geometry of holes in a photoresist (AZ-5214) layer on the Ni surface, the photoresist layer with about 1 μm thickness was spin-coated (4000 RPM, 30 s, KW-4A) at a speed of 4000 r/min and the pattern was defined by photolithography (HEIDELBERG, UPG501). During the photolithography steps, the experimental method of a laser lithography technique for direct design writing was used. Using 390 nm light and a micro-mirror array instead of 355/365 nm UV, the system reproduced GDSII format CAD patterns directly on positive photoresist with the maximum resolution equal to 1 micron. A photolithography process was used to create an array of holes, approximately 100 microns by 200 microns in the photoresist layer on the nickel surface, which were spaced approximately 200 microns apart.

1.3. Characterization

FESEM, HRTEM, EDX and Optical microscopy methods were used to characterize the samples. FESEM micrographs and EDX spectra were obtained using a Zeiss Merlin electron microscope and a EDX Oxford Instruments SDD detector with an area of 10 mm^2. HRTEM micrograph were received with a Zeiss Libra 200 microscope. Optical micrographs were obtained using a Biolam-I microscope (LOMO JSC). The speed of Pt(0) micromotors was measured in a solution mixture of 4% H_2O_2 and 0.01% Sodium Dodecyl Sulfate (SDS).

Supporting videos

SI Video 1. Formation, cracking and roll-up of Pt(0) layer on Ni surface in a drop of aqueous H_2PtCl_6 solution ($C_{H2PtCl6}$ = 0.2M, V_{drop} = 5 μL, the video was recorded between 2:11 - 2:41 after applying a drop of solution to the nickel surface).

SI Video 2. Movement of Pt(0) microscrolls in an aqueous solution of a mixture of H_2O_2 and SDS (Variant 1).

SI Video 3. Movement of Pt(0) microscrolls in an aqueous solution of a mixture of H_2O_2 and SDS (Variant 2).

Supporting figures

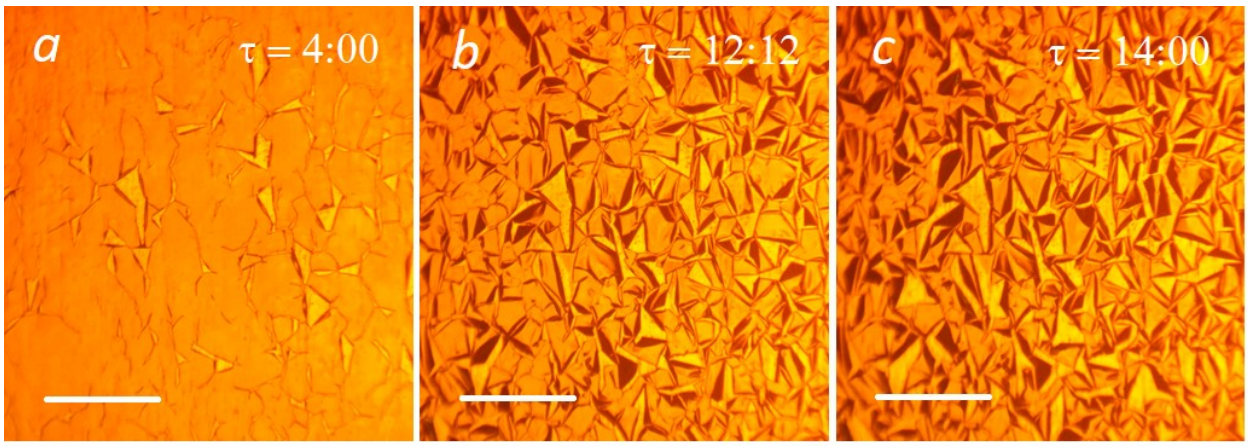

Fig. S1. Optical micrographs of the Ni surface during its treatment in a 5 µl drop of 0.005M H_2PtCl_6 solution (τ - treatment time, the scale corresponds to 200 µm).

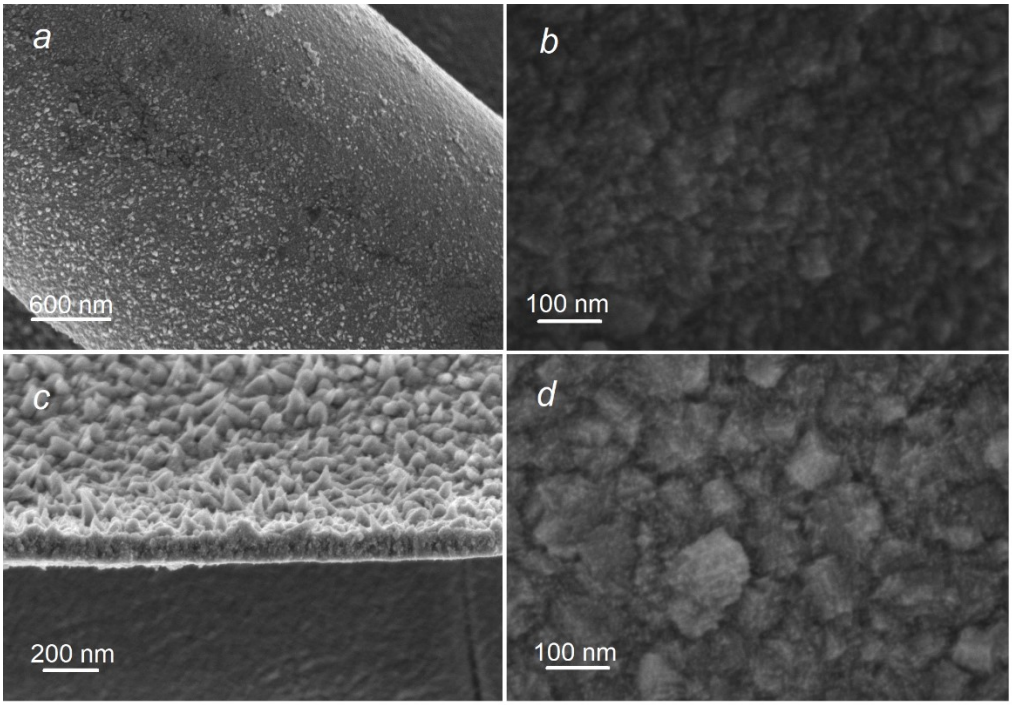

Fig. S2. SEM micrographs taken at different magnifications of the outer (a, b) and inner (c, d) walls of the microscroll obtained by treating Ni for 10 min. in 0.005M H_2PtCl_6 solution.

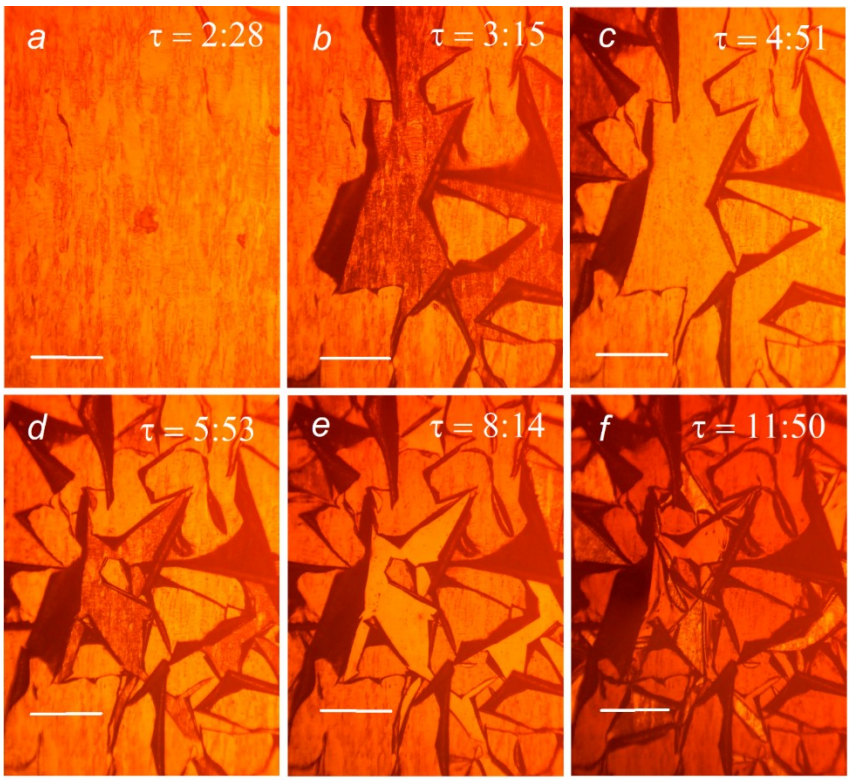

Fig. S3. Optical microphotographs of the nickel surface during its treatment in a 10 μl drop of 0.2M H_2PtCl_6 solution (τ - treatment time, the scale corresponds to 200 μm).

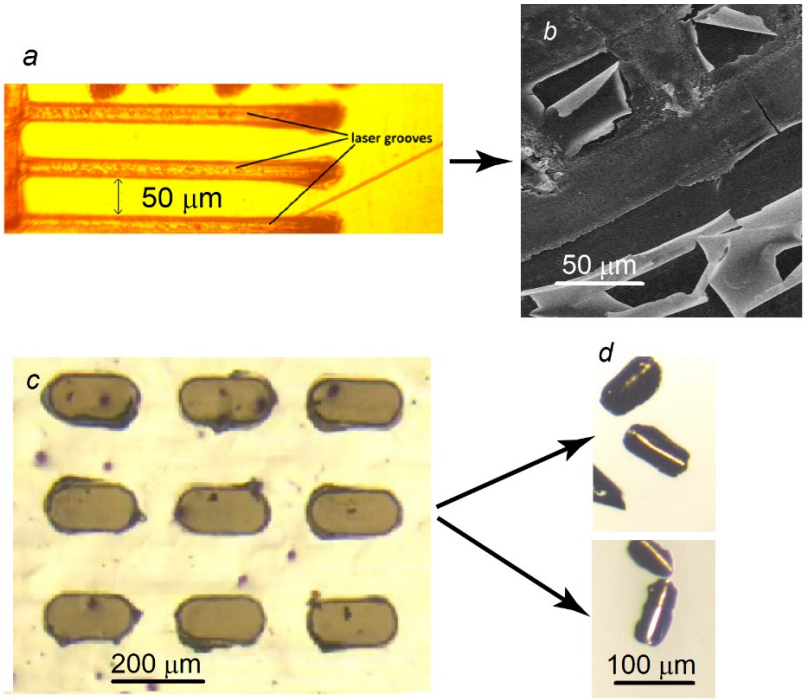

Fig. S4. An example of forming tracks of a specified size on the nickel surface using a laser (a) and the subsequent formation of Pt(0) microscroll fragments after treatment in an H2PtCl6 solution (b), as well as an example of the formation on the nickel surface after photolithography and treatment with an H2PtCl6 solution of an array of localized Pt(0) areas of specified size (c)

and the formation of microscrolls of a specified size from them after treatment in an HCl solution (d).

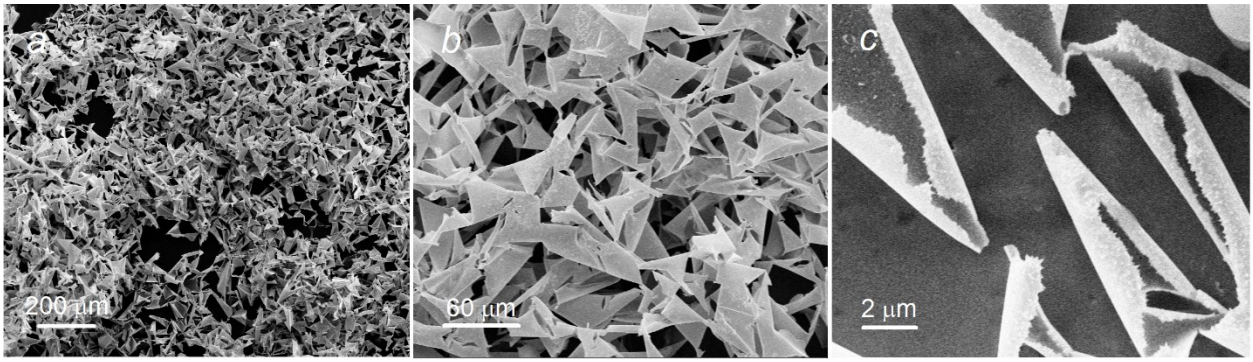

Fig. S5. SEM microphotographs, taken at different magnifications, of the precipitate formed after treating nickel with a layer of Pt(0) microscrolls in H_2PtCl_6 solution as a result of GRR for 10 minutes and subsequent treatment in HCl solution.

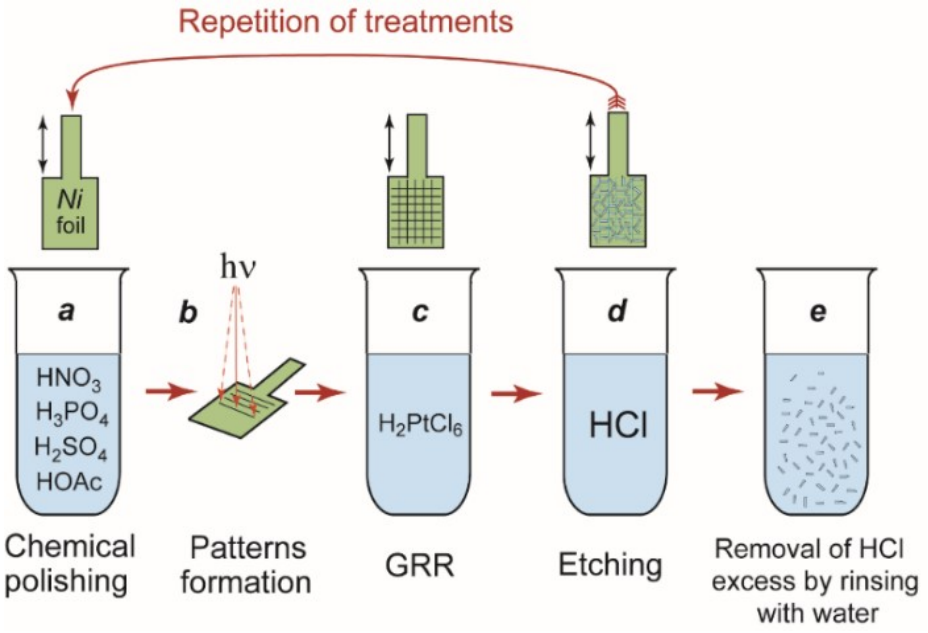

Fig. S6. Fabrication steps of the overall strategy by which catalytic micromotors based on Pt(0) microscrolls are formed using GRR. a) Ni is chemically polished, b) Specific patterns are applied to the nickel surface, c) Ni is treated with an H_2PtCl_6 solution, d) Samples are processed in an HCl solution, and a suspension of microscrolls is obtained, e) microscrolls are separated by size during their sedimentation in the solvent.

Reference

1. W.J. McG. Tegard, *The electrolytic and chemical polishing of metals*, 1956, London, Pergamon Press Ltd.