

Supplementary Material

for

Enhanced electrocatalytic hydrogen evolution from nitrogen plasma-tailored MoS₂ nanostructures

You Li,^{1,†} Yi Wan,^{1,†,*} Jiamin Yao,¹ Hongqian Zheng,¹ Xi Wang,¹ Xuan Liu,¹ Bo Ouyang,^{1,*} Chengxi Huang,¹ Kaiming Deng,¹ and Erjun Kan^{1,*}

*¹MIIT Key Laboratory of Semiconductor Microstructure and Quantum Sensing, and
Department of Applied Physics, Nanjing University of Science and Technology,
Nanjing 210094, China*

† These authors contributed equally to this work.

* Correspondence and requests for materials should be addressed to

E.K. (email: ekan@njust.edu.cn)

Y.W. (email: wany@njust.edu.cn)

B.O. (email: ouyangboyi@njust.edu.cn)

This file includes:

- Section 1 Materials preparation and synthesis of nitrogen plasma-tailored MoS₂
- Section 2 TEM images of nanostructured MoS₂ powder before plasma treatment
- Section 3 Comparison of morphology for MoS₂ before and after plasma treatment
- Section 4 Elemental analysis for MoS₂ prepared by N₂ plasma treatment
- Section 5 Effect of treatment power on MoS₂-based catalytic performance
- Section 6 *C_{dl}* normalization analysis
- Section 7 HER catalytic performance comparison

S1 Materials preparation and synthesis of nitrogen plasma-tailored MoS₂

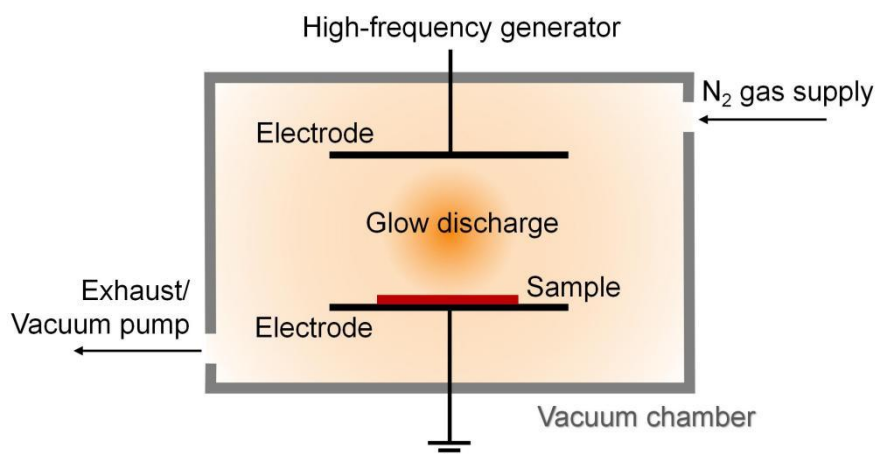


Figure S1. Schematic diagram of home-made plasma processing equipment for preparing N₂ plasma-engineered MoS₂ catalysts for hydrogen evolution reactions.

Commercial MoS₂ (99.99%, mean grain size ~ 80 nm) was purchased from Zhejiang Yuante New Materials Co., Ltd. All chemicals are analytical grade and used without further purification. The purchased MoS₂ powder was placed in the reaction tube of the plasma-enhanced chemical vapor deposition (PECVD) system for N₂ radio-frequency (RF) plasma treatment (Fig. S1). The chamber pressure was pumped down to 0.3 mbar at a nitrogen flow rate of 50 sccm. The N-doped MoS₂ products were obtained by N₂ RF plasma discharge at 300 W and 13.56 MHz for 0.5, 1.0, 3.0, and 5.0 min at room temperature (called N_{0.5}-MoS₂, N_{1.0}-MoS₂, N_{3.0}-MoS₂, and N_{5.0}-MoS₂). The MoS₂ powder without plasma treatment is called pristine MoS₂.

S2 TEM images of nanostructured MoS₂ powder before plasma treatment

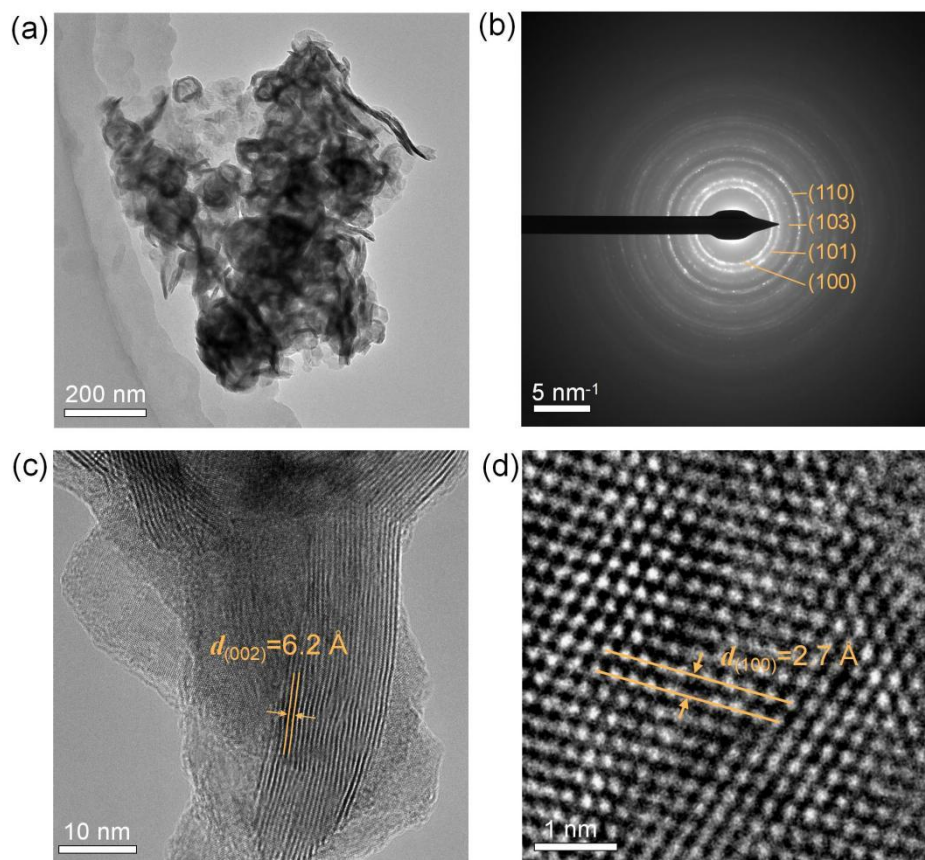


Figure S2. (a) TEM image of nanostructured MoS₂ powder before plasma treatment. (b) The corresponding SAED patterns. (c, d) High-resolution TEM images of nanostructured MoS₂ powder before plasma treatment. The crystal constants along 2H-MoS₂ (002) and (100) are measured to be 0.62 and 0.27 nm, respectively.

The crystalline structures of nanostructured MoS₂ powder before plasma activation were investigated by TEM, as shown in Fig. S2 (a). The selected area electron diffraction (SAED) patterns (Figure S2, b) further confirmed that MoS₂ powder had very poor crystallinity, in which all the reflection circles were indexed. High-resolution TEM images provide further insight into the structure of MoS₂, as shown in panels (c) and (d) of Fig. S2. The lattice fringes were about 0.62 and 0.27 nm, respectively, corresponding to the spacing between the MoS₂ (002) and (100) basal planes.

S3 Comparison of morphology for MoS₂ before and after plasma treatment

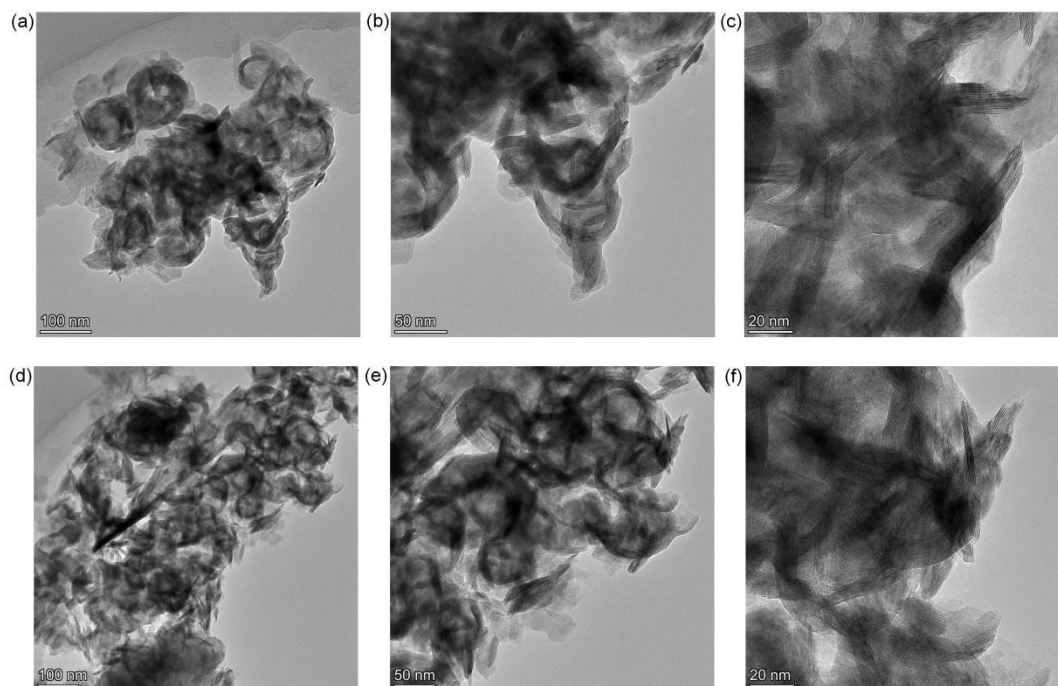


Figure S3. TEM images of nanostructured MoS₂ powder before plasma treatment (a-c) and after 500 W, 5 min N₂ plasma activation (d-f) at different magnifications.

The size and microscopic morphology of all MoS₂ samples were determined by TEM (JEM-2010F, JEOL., Ltd.) using an accelerating voltage of 200 kV. TEM specimens were prepared via the following procedure: the samples were dispersed in alcohol with the assistance of 10-minute ultrasonic vibration. Then a drop of the solution was transferred onto a standard holey carbon-covered copper TEM microgrid.

The TEM images (Fig. S3) captured from MoS₂ specimens before (a-c) and after (d-f) plasma treatment showed that the micro-morphology of MoS₂ powder was not significantly affected by N₂ plasma treatment. No clear changes were observed.

S4 Elemental analysis for MoS₂ prepared by N₂ plasma treatment

Table S1. Elemental analysis for MoS₂ prepared by N₂ plasma of 500 W and 5 min

| Z | Element | Family | Atomic Fraction (%) | Atomic Error (%) |
|----|---------|--------|---------------------|------------------|
| 7 | N | K | 1.12 | 0.13 |
| 16 | S | K | 67.66 | 4.23 |
| 42 | Mo | K | 31.22 | 4.14 |

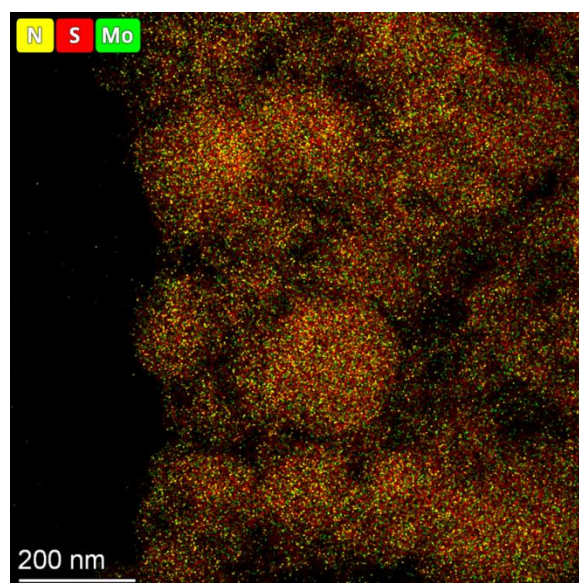


Figure S4. Elemental mapping image (N, S, and Mo) of MoS₂ prepared by N₂ plasma treatment of 500 W and 5 min.

The elemental mapping and EDS analysis of the N₂-plasma-engineered MoS₂ are displayed in Table S1 and Fig. S4. The mapping image indicates that the nanostructured MoS₂ powder comprises a uniform and homogeneous elemental distribution of N, S, and Mo elements. Moreover, the yellow region of N, the red region of S, and the green region of Mo are typically overlapped. The plasma processing power is 500 W, and the treatment duration is 5 min. The EDS analysis shows that the N-doped MoS₂ contains about 1.12 atomic% of N, 67.66 atomic% of S, and 31.22 atomic% of Mo.

S5 Effect of treatment power on MoS₂-based catalytic performance

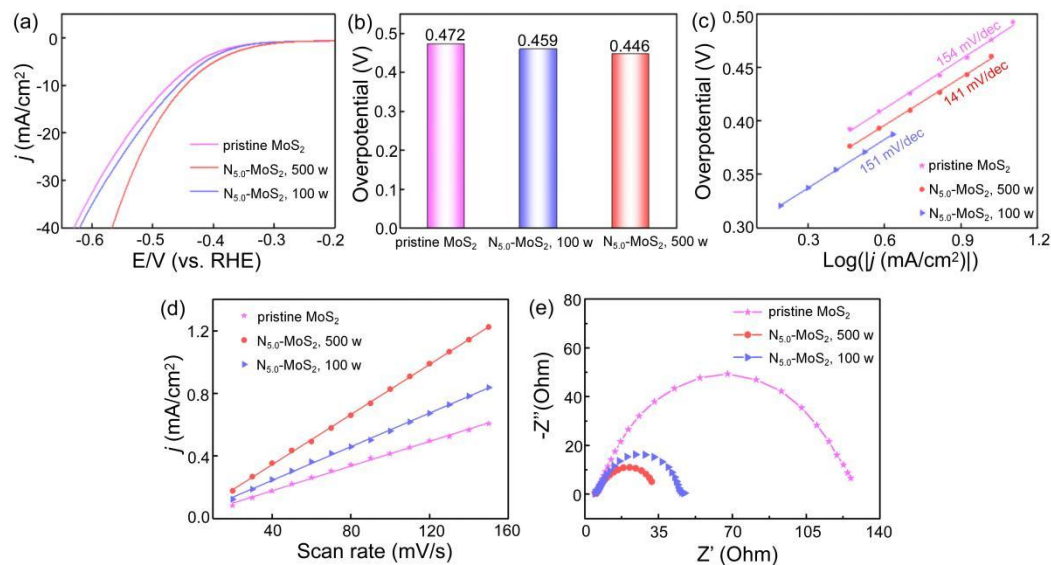


Figure S5. (a) LSV curves of pristine MoS₂, and N_{5.0}-MoS₂ with different plasma treatment power, 500 W and 100 W. (b) The corresponding overpotentials when the current density is -10 mA/cm^2 . (c) Tafel curves of pristine MoS₂, and N_{5.0}-MoS₂, 500 W, and N_{5.0}-MoS₂, 100 W. (d) C_{dl} curves. (e) EIS spectra.

For nitrogen doping of MoS₂, the sample processing steps involve the plasma bombardment with 100 W or 500 W power lasting 5 min. The MoS₂ samples without plasma treatment and the MoS₂ samples with plasma treatment lasting for 5 min are labeled as pristine MoS₂ and N_{5.0}-MoS₂. To prepare a well-mixed catalyst solution, 5 mg of MoS₂ (both before and after N₂ plasma treatment) and 1 mg of acetylene black were mixed. Next, 2 ml of naphthol with a mass fraction of 0.2% and 4 ml of alcohol were added. The mixture was then sonicated for an hour. Then, transfer the catalyst solutions onto the glassy carbon electrode using a 10 μl sample injector. After the catalyst solutions have dried naturally, drop another 10 μl solution twice, and a comparatively thickness-uniform film will form.

In the HER tests, a 0.5 M H₂SO₄ solution was used as the electrolyte. At the very beginning, we performed CV tests on all samples to activate the catalytic sites and stabilize the catalytic performance. The CV curves were obtained with 20 cycles at a speed of 10 mV/s and a voltage range of 0.04-1.08 V. The LSV curves were measured

at a speed of 5 mV/s (panels a-c, Fig. S5), with the same voltage range as the CV test. The AC impedance curves were collected in the range of 10 mHz-100 kHz at an open circuit voltage of 0.3 V (panel d, Fig. S5). The ECSA was measured at a non-operating zone voltage of 0.004 V to 0.04 V (panel e, Fig. S5).

As the current density reaches a negative 10 mA/cm², the overpotential measured for pristine MoS₂ is 472 mV. N_{5.0}-MoS₂ treated with 100 W and 500 W exhibits the corresponding overpotentials of 459 mV and 446 mV, respectively. It is clear that nitrogen plasma treatment reduces the overpotential of MoS₂. The Tafel slope of N-doped MoS₂ is 10 mV/dec lower than that of pristine MoS₂. To verify whether the ECSA increases, we measured and calculated the C_{dl} : 3.95 mF/cm² for pristine MoS₂, 5.38 mF/cm² for N_{5.0}-MoS₂, 100 W, and 8.01 mF/cm² for N_{5.0}-MoS₂, 500 W. It indicates that after the incorporation of nitrogen, the number of electrochemically active sites increases. The electrochemical hydrogen evolution performance was further improved. By comparing the measured EIS, it can be seen that the Nyquist impedance of N_{5.0}-MoS₂ is much lower than that of pristine MoS₂, demonstrating that the kinetics of the hydrogen evolution reaction at the catalytic interfaces have been improved after nitrogen doping. We discovered that the catalytic performance of MoS₂ after nitrogen plasma treatment was enhanced compared to the original sample according to the tests of electrochemical hydrogen evolution performance, and the processing impact of high power is better than that of low power.

S6 C_{dl} normalization analysis

The overall relative activity is inversely associated with the total relative number of active sites, and is determined by both the total relative surface area and the relative density of active sites per surface area. By comparing the exchange current density and the double-layer capacitance for both doped catalysts and the pristine sample, one may ascertain how many active sites there are per surface area in comparison to a pristine one, as indicated in Table S2. In our strategy, two significant factors were responsible for the increase in HER activity. On the one hand, the nitrogen plasma treatment roughens the sample surface and increases the electrochemical effective surface area. On the other hand, the doping of nitrogen atoms substantially decreases Gibbs free energy by modifying the density of electronic states of S atoms in N-MoS₂.

Table S2. Electrochemical analysis of the N-doped MoS₂ and pristine MoS₂ based on the exchange current density, j_0 , and the double-layer capacitance, C_{dl} .

| Materials | pristine MoS ₂ | N _{0.5} -MoS ₂ | N _{1.0} -MoS ₂ | N _{3.0} -MoS ₂ | N _{5.0} -MoS ₂ |
|---|---------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|
| $\log(j \text{ (mA}\cdot\text{cm}^{-2}))$ at $\eta=0$ V | -1.646 | -1.352 | -1.236 | -1.169 | -1.064 |
| Exchange current density (j_0)/ $\mu\text{A}\cdot\text{cm}^{-2}$ | 22.59 | 44.46 | 58.08 | 67.76 | 86.30 |
| Enhancement relative to pristine MoS ₂ | 1 | 1.97 | 2.57 | 3.00 | 3.82 |
| Double-layer capacitance (C_{dl})/ $\text{mF}\cdot\text{cm}^{-2}$ | 4.54 | 7.04 | 7.95 | 13.33 | 15.55 |
| Surface area relative to pristine MoS ₂ | 1 | 1.55 | 1.75 | 2.94 | 3.43 |
| Number of active sites per surface area relative to pristine MoS ₂ | 1 | 1.27 | 1.47 | 1.02 | 1.11 |

S7 HER catalytic performance comparison

A catalytic table for comparing the reported catalysts with previous ones is summarized in Table S3. We provided a novel, convenient synthesis method for preparing N-doped MoS₂-based catalysts. Compared with previous ones, the proposed N-MoS₂ catalysts exhibit considerable double-layer capacitance (C_{dl}), excellent catalytic stability, and a relatively high Tafel slope.

Table S3. Electrochemical performances of various MoS₂-based catalysts

| Electrocatalyst | Synthesis method | Tafel slope, b (mV/dec) | Double-layer capacitance, C_{dl} (mF·cm ²) | Stability | Reference |
|---|--|---------------------------|--|--|--|
| N-MoS ₂ | plasma nitriding | 120-170 | 4.54-15.55 | chronoamperometry (<i>i</i> - <i>t</i>), 20 h | This work |
| O-incorporated MoS ₂ | hydrothermal | 55 | 37.7 | negligible degradation after 3000 cycles | <i>J. Am. Chem. Soc.</i> 2013, 135, 17881-17888 |
| MoS ₂ thin films | chemical vapor deposition | 140 | 0.005-0.011 | - | <i>Nano Lett.</i> 2014, 14, 553-558 |
| Atomically-thin MoN | liquid exfoliation | 90 | 1.56 | negligible degradation after 3000 cycles | <i>Chem. Sci.</i> 2014, 5, 4615-4620 |
| 3D MoS ₂ /rGO hydrogels | hydrothermal | 41-81 | 0.72-29.60 | negligible degradation after 1000 cycles | <i>Electrochim. Acta</i> 2015, 182, 652-658 |
| Defect-rich MoS ₂ nanowall | hydrothermal | 78 | 426.3 | negligible degradation after 3000 cycles | <i>Nano Res.</i> 2017, 10, 1178-1188 |
| MoS ₂ /Vulcan carbon | hydrothermal | 40-48 | 0.71-2.53 | - | <i>Phys. Chem. Chem. Phys.</i> 2017, 19, 1988-1998 |
| Mo _{1-x} W _x S ₂ | hydrothermal | 67.0-117.8 | 4.24-9.42 | chronoamperometry (<i>i</i> - <i>t</i>), 25 h | <i>Nano Res.</i> 2018, 11(3): 1687-1698 |
| Hollow rGO@MoS ₂ | GO coating, hydrothermal reduction, SiO ₂ etching | 105 | 1.6 | negligible degradation after 2000 cycles | <i>Nano-Micro Lett.</i> 2018, 10, 62 |
| MoSe ₂ /MoS ₂ heterojunction | hydrothermal | 61 | 27.0 | negligible degradation after 2000 cycles; chronoamperometry (<i>i</i> - <i>t</i>), 20 h | <i>Chem. Eng. J.</i> 2019, 359, 1419-1426 |
| Hierarchical N-MoS ₂ /CN | high-temperature pyrolysis | 46.8 | 26.93 | negligible degradation after 1000 cycles | <i>J. Am. Chem. Soc.</i> 2019, 141, 18578-18584 |
| Rosette-like MoS ₂ nanoflowers | hydrothermal | 71.2 | 137 | chronoamperometry (<i>i</i> - <i>t</i>), 20 h | <i>RSC Adv.</i> 2019, 9, 13820-13828 |
| Pd, Ru-MoS ₂ -OH ₂ di-anionic surface | solvothermal | 45 | 0.0149 | chronoamperometry (<i>i</i> - <i>t</i>), 100 h | <i>Nat. Commun.</i> 2020, 11, 1116 |
| Pure MoS ₂ | hydrothermal | 125 | 2.24 | - | <i>J. Fuel Chem. Technol.</i> 2021, 49, 986-997 |
| C ₂ N ₄ -TiO ₂ -MoS ₂ | hydrothermal | 54 | 16.24 | negligible degradation after 10000 cycles; chronoamperometry (<i>i</i> - <i>t</i>), 35 h | <i>J. Fuel Chem. Technol.</i> 2021, 49, 986-997 |
| Mo ₂ C/MoS ₂ heterojunction | wet impregnation | 102.4-187.9 | 3.1-43.9 | negligible degradation after 2000 cycles | <i>J. Phys.: Conf. Ser.</i> 2022, 2267, 012118 |
| N-MoP core-shell nanorods | gas-solid phosphorization | 68-71 | 12-26 | negligible degradation after 1000 cycles; chronoamperometry (<i>i</i> - <i>t</i>), 20 h | <i>J. Fuel Chem. Technol.</i> 2022, 50, 1437-1448 |
| MoS ₂ /NiF | pulsed laser ablation | 85.5-139.8 | 0.46-3.19 | chronoamperometry (<i>i</i> - <i>t</i>), 24 h | <i>iScience</i> 2023, 26, 106797 |
| N-MoS ₂ /AOCFC | hydrothermal | 48.83 | 84.19 | negligible degradation after 1000 cycles; chronoamperometry (<i>i</i> - <i>t</i>), 16 h | <i>ChemistrySelect</i> 2023, 8, e20220469 |
| 1T phase MoS ₂ | colloidal chemistry, acid etching | 40 | 65.8 | negligible degradation after 10000 cycles; chronoamperometry (<i>i</i> - <i>t</i>), 36 h | <i>Adv. Mater.</i> 2023, 2303285 |