Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Electronic Supplementary Information (ESI)

Biofilm-Enhanced Continuous Synthesis and Stabilization of Palladium Nanoparticles (PdNPs)

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H_2 delivery fluxes calculation

We calculated maximum H_2 delivery fluxes ($J_{H_2,\,max}$) using the modified equation established by Tang et al. [1]:

$$J_{H_2,\,max} = 0.8 D_m \frac{K_m}{z_m} K_L P_0 \left(\frac{d_m - z_m}{d_m} \right) \quad (1)$$

where D_m is H_2-diffusion coefficient in the membrane (1.4×10^{-7} m^2/d for polypropylene fibers), k_m is H_2 solubility coefficient in membrane (1.29 m^3 H_2 @ standard temperature and pressure/m^3 membrane bar), K_L is coefficient that converts H_2 from volume to mass (1g/0.0112m^3 @ standard temperature and pressure), P_0 is H_2 pressure in the hollow-fiber lumen (bar), d_m is hollow-fiber outer diameter (200μm for polypropylene fibers) and z_m is membrane thickness (55μm for polypropylene fibers).

Chemical fixation of fiber samples for SEM/STEM analysis

The fiber samples were directly incubated in the fixative, 2% glutaraldehyde in Dulbecco's phosphate-buffered saline (D-PBS), at pH 7.2 for 30 minutes. Then, the fibers were washed in D-PBS three times (15 minute each) and incubated in 1% osmium tetroxide in D-PBS for 1 hour. After this, the fibers were washed with deionized water four times (10 min each) and dehydrated in graded acetone series with 20% increments (10 min per step). The fully dehydrated fibers were infiltrated with a graded series of epoxy resin[2] in 25% increments for a total of 54 hours. All the previous steps were carried out at room temperature, ~23°C. Following dehydration, SEM samples are critical-point dried and sputter-coated. TEM samples were infused with epoxy resin and polymerized in molds at 60^{o}C for 24 hours. The polymerized blocks were then trimmed and thin-sectioned in a Leica Ultracut-R ultramicrotome at 70-nm thickness.

Figures

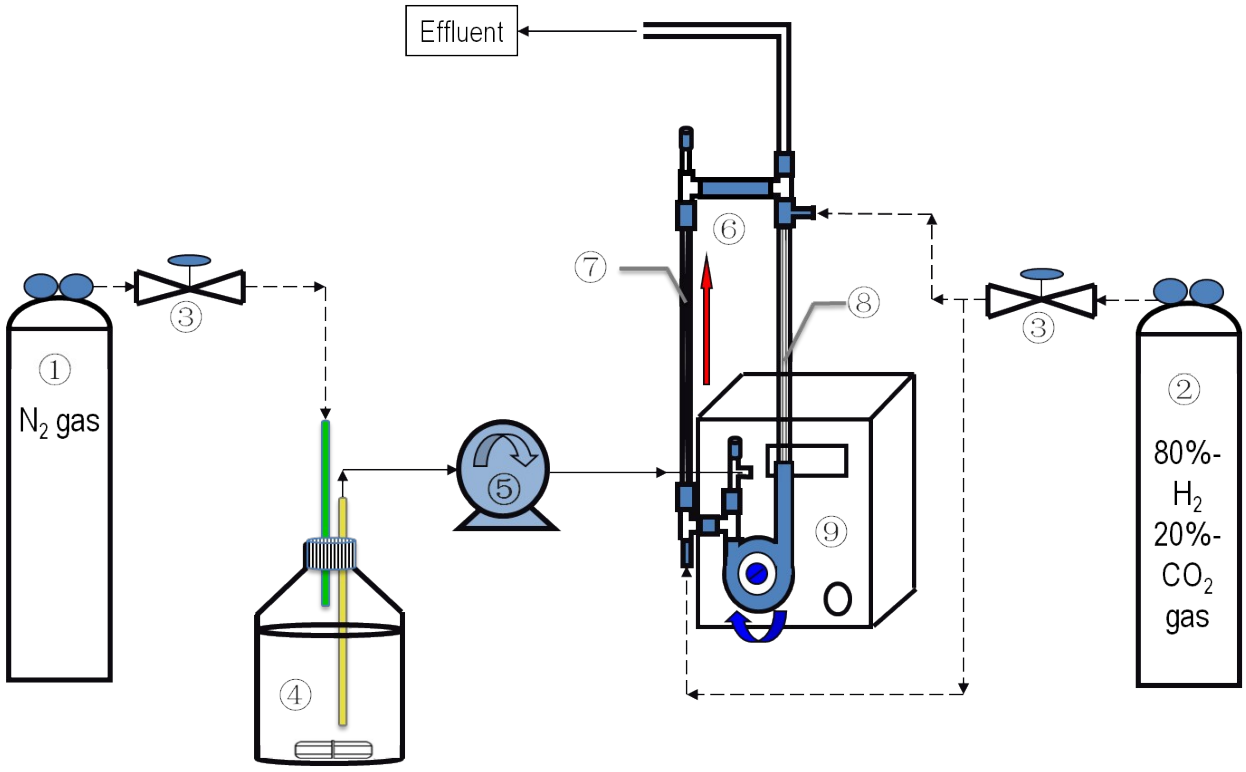

Figure S1. Schematic of the bench-scale MBfR system used to investigate Pd reduction and recovery. The major components include: ① pure N_2 gas to feed the headspace of the medium bottle; ② mixed gas tank with 80% H_2 and 20% CO_2 gas tank to feed the fiber bundles of the MBfR; ③ gas pressure regulators; ④ Pd medium bottle with a stir bar; ⑤ feeding pump; ⑥ MBfR configuration (the red arrow indicates the flow direction; ⑦ main bundle with 50 fibers; ⑧ biofilm sampling bundle with 10 coupon fibers; ⑨ recirculation pump. The black solid arrows indicate the liquid flow, and the black dashed arrows indicate the gas flow.

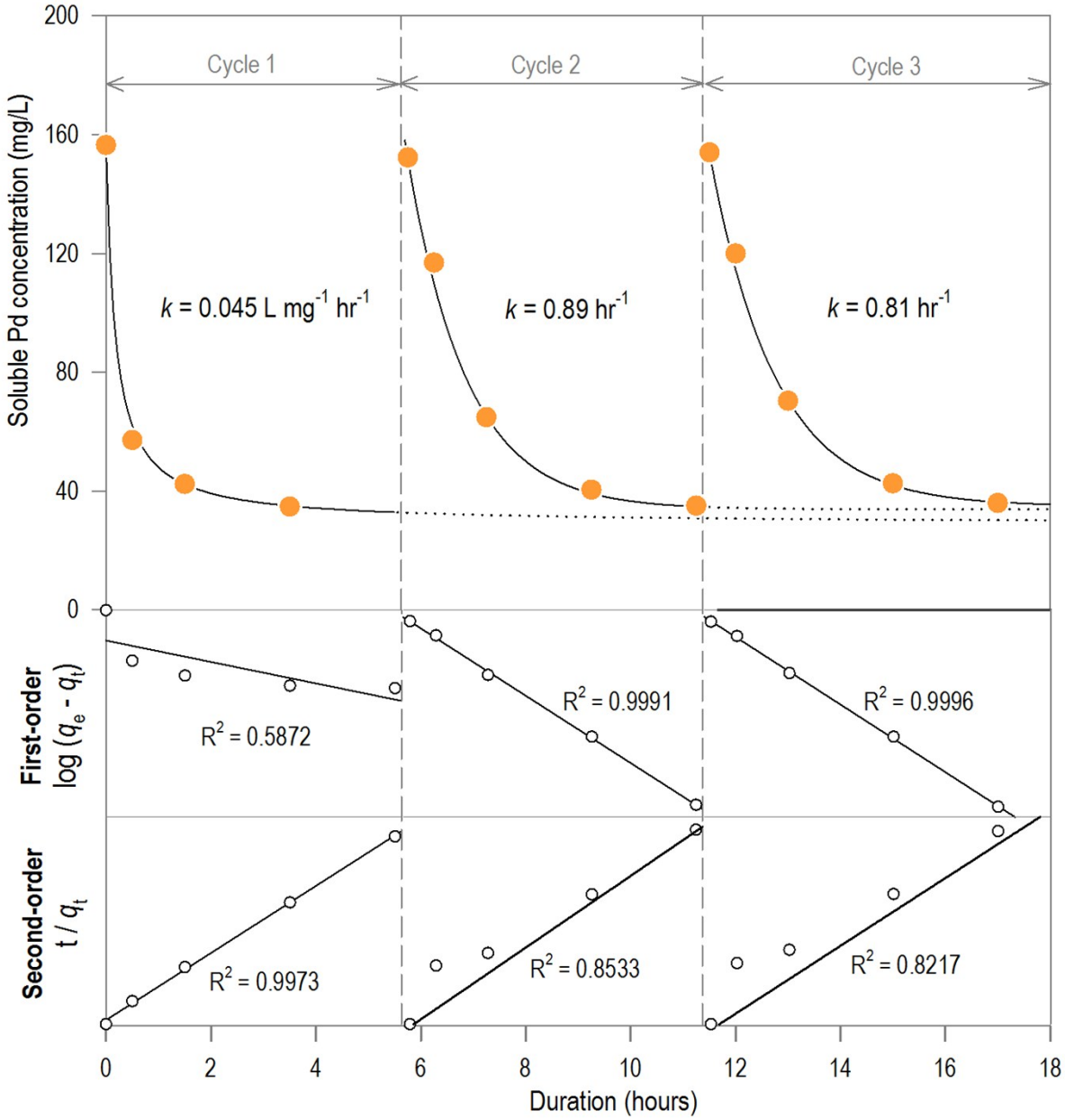

Figure S2. Fitting of experimental soluble Pd^{II} concentrations during the initial batch period in Pd-biofilm using the 1st-order and 2nd-order decay models for each cycle.

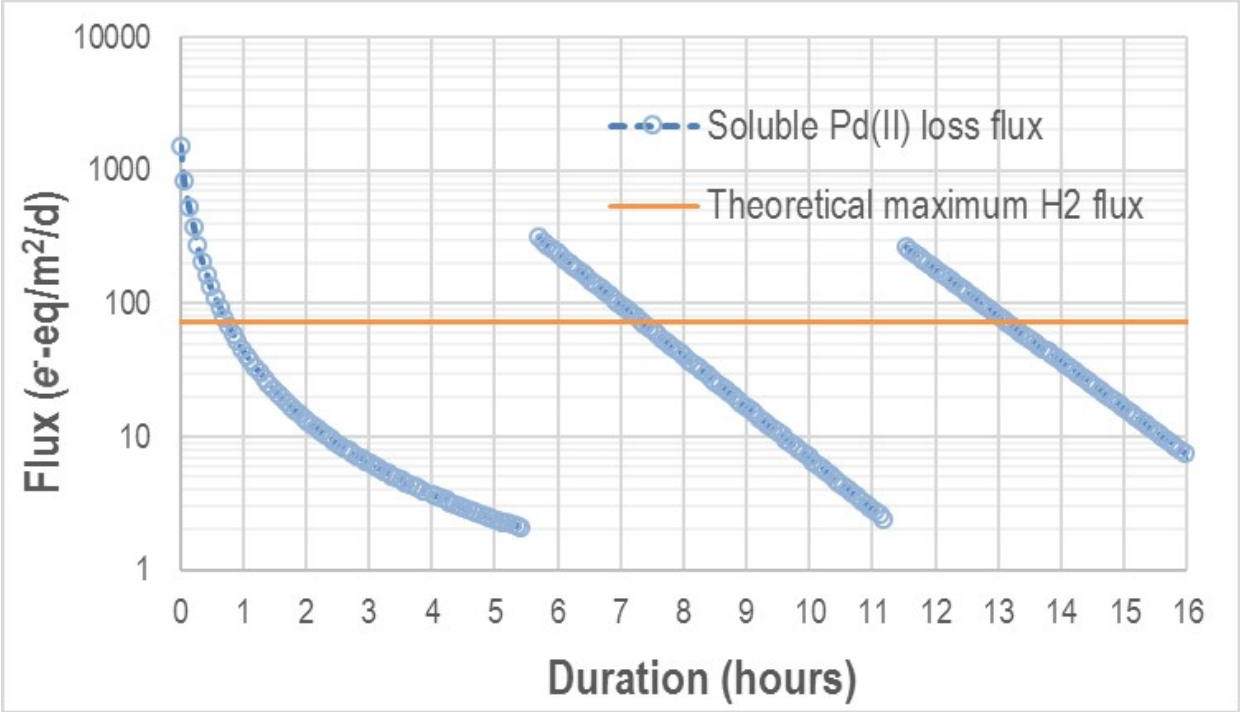

Figure S3. Calculated fluxes of soluble Pd^{II} loss and maximum H_2 diffusion in Pd-biofilm during the initial batch period.

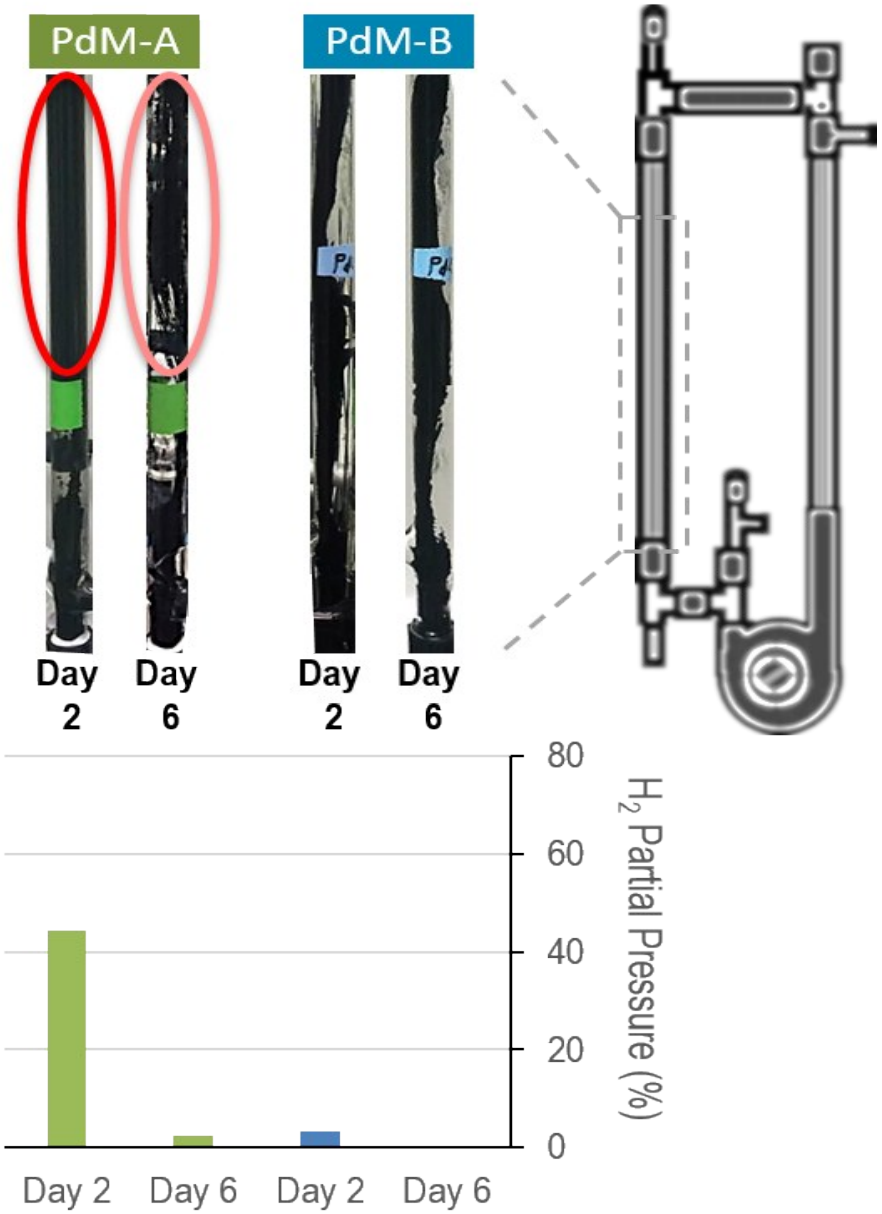

Figure S4. (Top) Photos of the main fiber bundles in both reactors, taken on the 2nd and 6th days. The black from Pd^0 is evident, since the membrane fibers originally were white. The red circle highlights an area in PdM-A where suspended Pd clusters caused the medium to become so opaque on Day 2 that the fibers were not visible. The pink circle highlights the same area when fibers could be seen on day 6 due to the agglomeration of Pd clusters on the fibers. The fibers always were visible in PdM-B. (Bottom) Measured H_2 partial pressure of the effluent on Days 2 and 6 in both reactors.

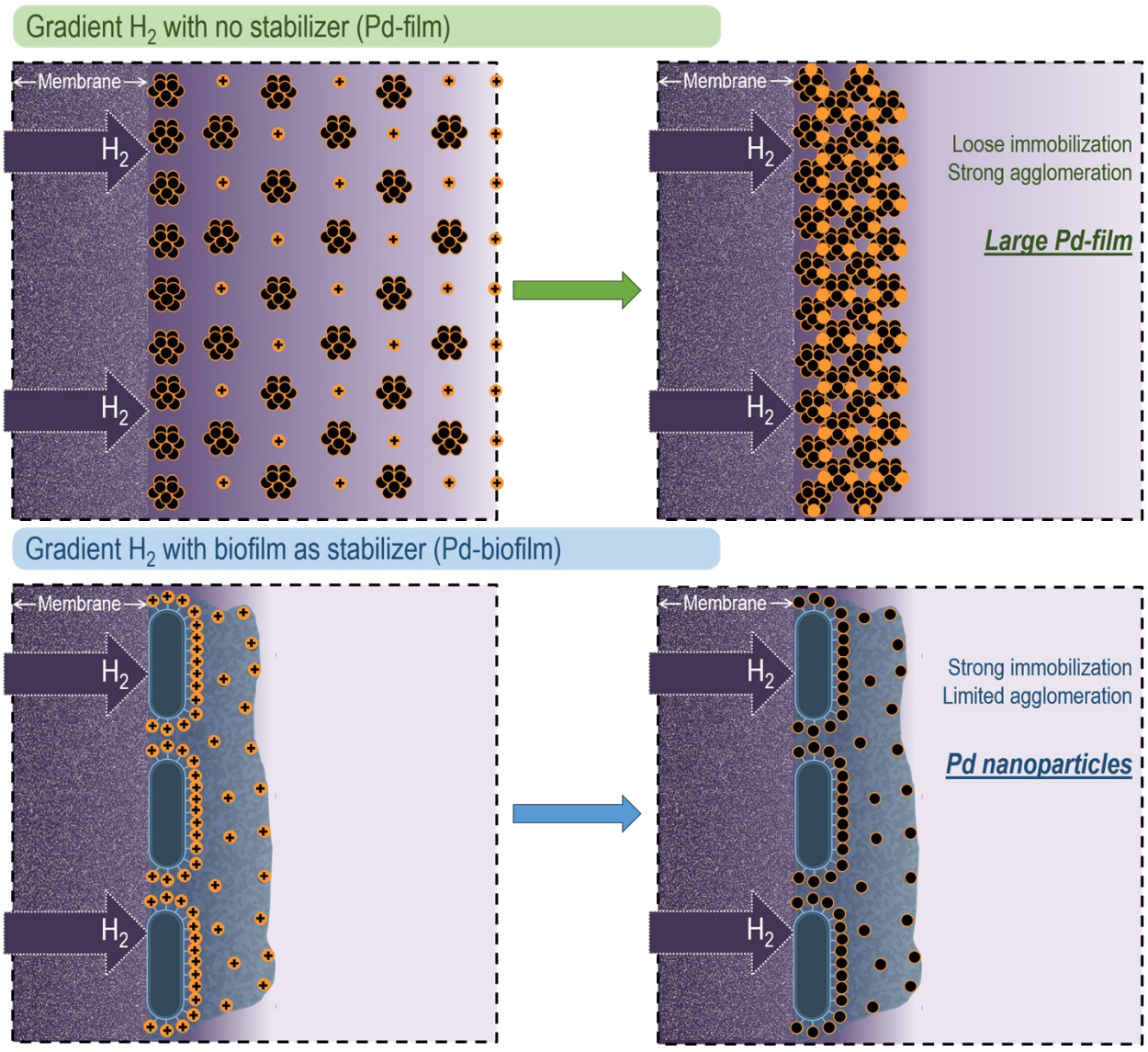

Figure S5. Schematic of Pd immobilization and agglomeration on H_2-diffusing membrane surfaces without (top) and with (bottom) biofilm as the Pd^0 stabilizer.

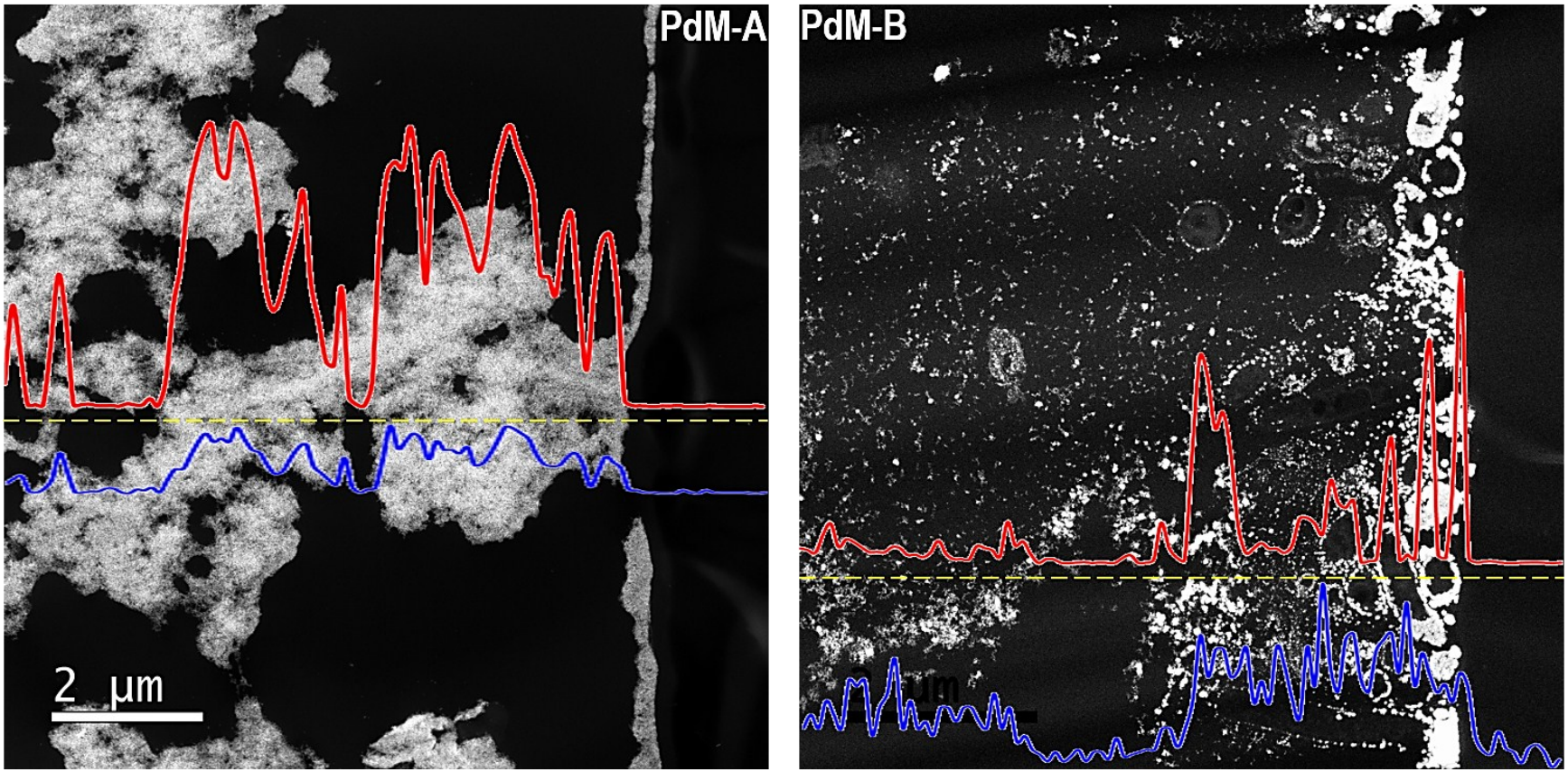

Figure S6. Representative STEM-EDX line profiles of Pd (red lines) and O (blue lines) along the yellow dash lines drawn across STEM-HAADF images of the same fiber sections from both reactors in Figures 3 and 4.

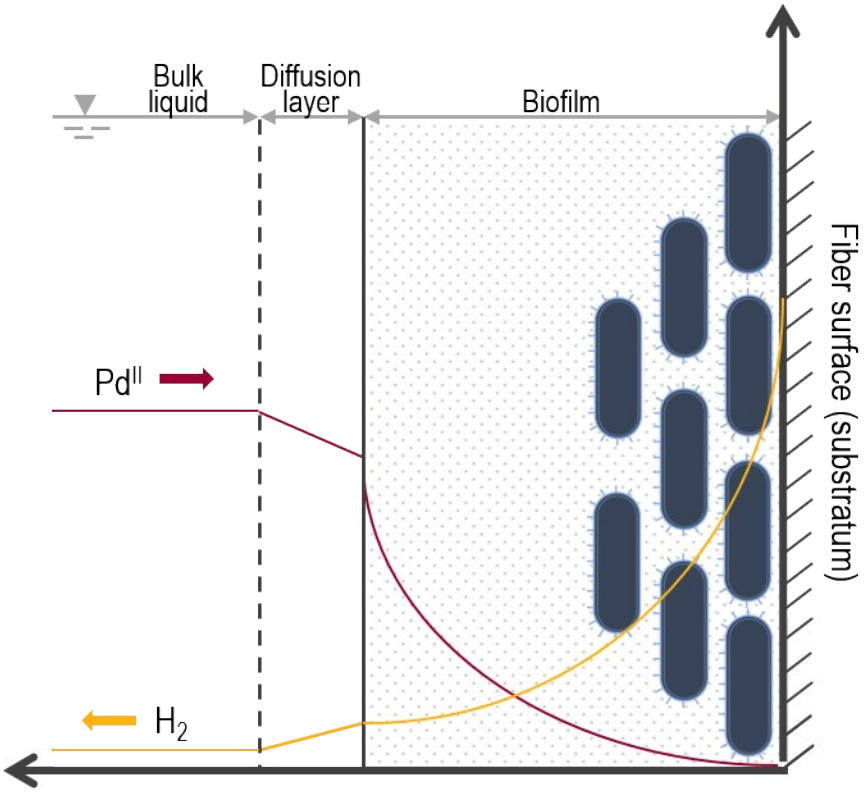

Figure S7. Schematic of the counter-diffusion model with substrate gradients in an MBfR biofilm, modified from Zhou, et al. [3].

References

1. Tang, Y.; Zhou, C.; Van Ginkel, S. W.; Ontiveros-Valencia, A.; Shin, J.; Rittmann, B. E. Hydrogen permeability of the hollow fibers used in H_2-based membrane biofilm reactors. *J Membrane Sci* 2012, 407, 176-183.
2. Spurr, A. R. A Low-Viscosity Epoxy Resin Embedding Medium for Electron Microscopy. *J Ultra Mol Struct R* 1969, 26, 31-43.
3. Zhou, C.; Ontiveros-Valencia, A.; Wang, Z.; Maldonado, J.; Zhao, H.-P.; Krajmalnik-Brown, R.; Rittmann, B. E. Palladium Recovery in a H_2-Based Membrane Biofilm Reactor: Formation of Pd(0) Nanoparticles through Enzymatic and Autocatalytic Reductions. *Environ Sci Technol* 2016, 50, 2546-2555.