

Electronic Supplementary Information

Microfluidic System Incorporated with Peptide/Pd Nanowires for Heterogeneous Catalytic Reactions

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Materials: The peptide nanowires were built up with diphenylalanine (Phe-Phe, FF) in a lyophilized form, bought from Bachem AG (Bubendorf, Switzerland). 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), aniline, dopamine hydrochloride, PdCl₂ were purchased from Sigma-Aldrich (St. Louis, MO). For microchemical catalytic reactions, polyvinylsilazane (-[HSi(R)NH]_x-, R=CH₃ or Vinyl, HTT1800, Clariant, USA) was used by diluting in anhydrous toluene (99.8%, Aldrich) for fabricating the microchannel. The microchemical reagents such as 1-phenyl-1-cyclohexene, trans-cinnamaldehyde, triethylsilane, phenylboronic acid, 4-bromobenzene, 4-bromobenzaldehyde were purchased from Sigma-Aldrich (St. Louis, MO). Potassium carbonate was purchased from Samchun chem.(Korea).

Fabrication of microfluidic system incorporated with peptide/Pd hybrid NWs: Solvent resistant and optically transparent polyvinylsilane derived microreactor was fabricated as reported by our own group. In typical, a piece of microchannel was firstly constructed by

imprinting molding technique. A mold with relief structure (height: 50 μm and width: 500 μm , length: 3 cm) made of polydimethylsiloxane (PDMS) (DowCorning, Midland, MI) was stamped onto the pre-coated polyvinylsilazane layer on a cleaned glass slide under nitrogen atmosphere. And the stamped polymer layer was consecutively consolidated by photo-curing step under a UV exposure (ELC-4100 UV light system) for 20 min, and finally removed the stamp from the patterned polyvinylsilazane. After post-treatment at 150 $^{\circ}\text{C}$ for 3 h, the both shoulders of the microchannel were completely covered with aluminum tape to avoid the unwanted dopamine deposit. This selectively exposed surface of polyvinylsilazane microchannel was immersed into an aqueous dopamine solution (2 mg/ml in 10 mM Tris buffer, pH 8.5) for 16 h to coat with polydopamine, washed with water, and then post-cured at 65 $^{\circ}\text{C}$ for 1 h. Fresh peptide solution was prepared by dissolving FF in HFIP (50 mg/ml) and allowed to dry on the internal surface of microchannel under anhydrous condition at room temperature to obtain an amorphous FF peptide thin film with 3~4 μm thickness. The solid phase amorphous film was then treated with vaporized aniline at 100 $^{\circ}\text{C}$ for 12 h to induce the growth of vertically aligned FF peptide NWs. After incubation, the FF peptide NW film was cooled to room temperature and then immersed in an alkaline dopamine solution for 16 h to form polydopamine ad-layer outside the FF peptide nanowires. The adhesion of FF peptide NWs to the substrates was tested by applying sonication in a ultrasonic cleaner (Sonicor SC-100T 100W, Sonicor Instrument, Copaique, NY, USA) for 30 sec. The water contact angle before and after the PDA coating on the FF peptide NWs film was comparatively measured with a Phoenix 300 contact-angle meter (Surface Electro Optics Co., Korea) at five different locations on each film using 6 mg of water droplet.

Finally, the nanowire built-in microchannel was cleaned using ethanol after taking off the aluminum tape, then securely sealed by bonding with UV-cured polyvinylsilazane coated PDMS slab after plasma treatment for 5 min. The additional thermal post-curing at 150 $^{\circ}\text{C}$ for

3 h was conducted at a heating and cooling rate of 2.5 °C/min, equally. In order to deposit Pd metal nanoparticles on the nanowires in the microchannel, the optimal condition of nanoparticle formation and deposition was adjusted by preliminary test with varying pH. Briefly, the 5 mM water and ethanol (4:1) solution of PdCl₂ was infiltrated into the sealed microreactor and kept for 3 h at room temperature for deposition of black Pd nanoparticles on the FF peptide nanowires. Then the microchannel was flushed with excess amount of ethanol several times at the flow rate of 1 µl/min to removed residual Pd ion and freely dispersed Pd nanoparticles. For the comparison, plain microreactor with no nanowires in the channel surface was prepared by immobilizing the Pd nanoparticles on flat polydopamine surface after the polysilazane surface was coated using aqueous dopamine solution under the same conditions as aforementioned (Scheme S1). The morphology of FF peptide/Pd metal hybrid nanowires was investigated using an S-4800 SEM and a HD-2300A STEM (Hitachi High-technologies Co., Tokyo, Japan).

Microchemical heterogeneous catalytic reactions: The microchemical catalytic performances of both Pd nanoparticles immobilized microreactors were evaluated by carrying out two types of reactions (i.e., hydrogenation and Suzuki coupling) in a continuous flow manner as shown Scheme S2. Each reaction was carried out at both reactors with the same feedstocks. (a) For the hydrogenation, the stock solutions were prepared by mixing of olefins (0.1 mol/l) (i.e., 1-phenyl-1-cyclohexene and cinnamaldehyde) and a reducing agent, triethylsilane (0.4 mol/l), in ethanol. The catalytic activity was evaluated by the continuous feeding of these above stock solutions using a syringe pump at flow rates of 0.5 to 5.0 µl/min at room temperature. The obtained products at the respective rate were analyzed by gas chromatograph (GC, HP5890, Hewlett-Packard Co., Palo Alto, CA) using n-dodecane as an internal standard. (b) The Suzuki coupling reactions between phenylboronic acid and bromobenzenes were also

carried out in both microreactors. According to the conventional Suzuki coupling route, bromobenzene (50 mmol) was reacted with phenylboronic acid (75 mmol) with potassium carbonate (150 mmol) in ethanol-water 1:1 (v/v) mixture, and THF-water 1:1 (v/v) at room temperature at several flow rates. The reaction yields were also quantified by GC. The inductively coupled plasma-mass spectrometry (ICP-MS) analysis of the effluent collected during Suzuki reaction was determined to confirm the leach-out of Pd metal nanoparticles.

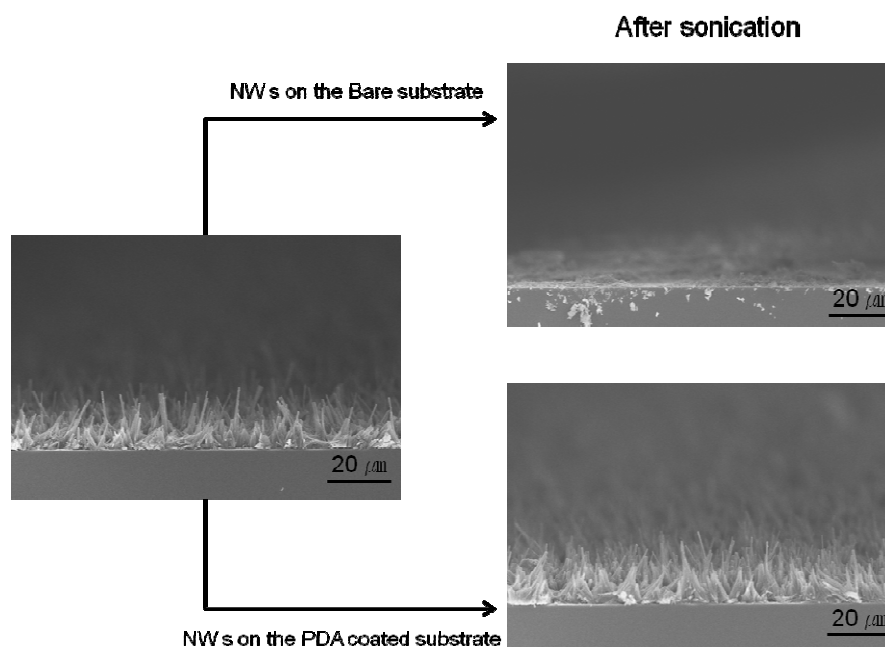
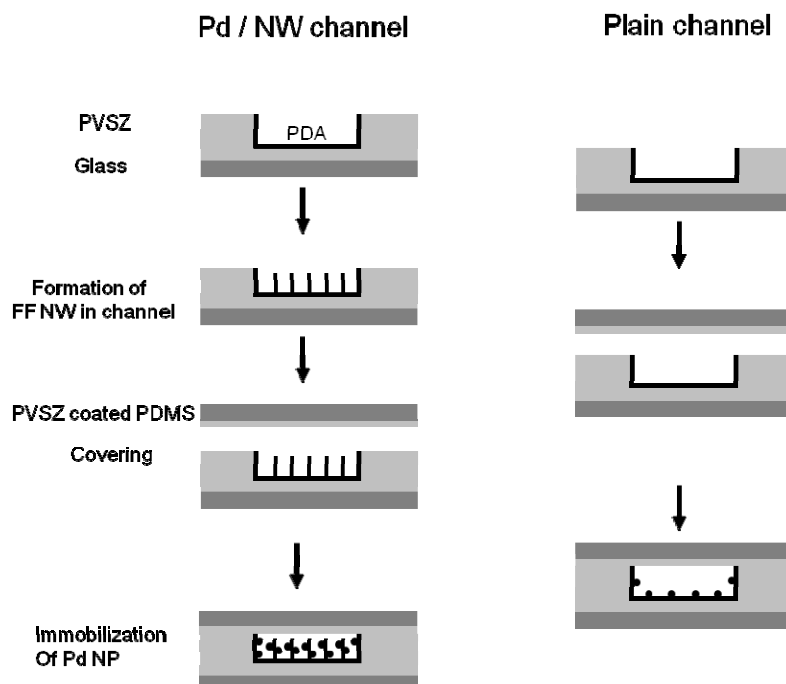


Fig. S1 Effect of the polydopamine (PDA) layer on the adhesion stability of FF peptide nanowires to the underlying substrate.



Scheme S1. Fabrication process of FF/Pd nanowire built-in microchannel and plain microchannel. The FF/Pd nanowire was constructed inside of polyvinylsilazane (PVSZ) microchannel according to the similar protocol as described in Figure 1. The plain microreactor without nanowires in the channel surface was prepared by immobilizing Pd nanowires on flat polydopamine surface after the PVSZ surface was coated using aqueous dopamine.