[Supplementary Information]

Title: Tyrosine-rich peptide induced flower-like palladium nanostructure and its catalytic activity

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1. Experiments

Chemicals: 2-Chlorotrityl chloride (CTC) (100-200 mesh, 1.26 mmol/g) resin, fritted polypropylene reactors (Libra tube RT-20M, 20 ml), Fmoc-protected amino acids, 2-(1*H*-benzotriazole-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate (HBTU), and hydroxybenzotriazole (HOBt) were purchased from BeadTech (Seoul, Korea). *N,N*-Diisopropylethylamine (DIPEA) was purchased from Alfa Aesar (Ward Hill, MA). Triisopropylsilane (TIPS), 3,6-dioxa-1,8-octanedithiol (DODT), anisole, sodium tetrachloropalladate (Na_2PdCl_4), ascorbic acid, iodobenzene, ethynyl pyridine, 1-ethynyl-1-cyclohexanol, 4-iodoanisole and phenylacetylene were purchased from Sigma-Aldrich (St. Louis, MO, USA). 1-Iodo-4-nitrobenzene was purchased from TCI (Tsukuba, Japan). Triethylamine was purchased from Junsei (Japan).

Peptide synthesis: The peptides were synthesized on a 2-chlorotrityl chloride (CTC) resin (1.26 mmol/g) with Fmoc chemistry in the fritted reactor. After loading the first amino acid (0.3~0.5 mmol/g), each coupling step was performed with 2 eq. of Fmoc-amino acid, 2 eq. of HBTU, 2 eq. of HOBt and 4 eq. of DIPEA for 2 hours until the Kaiser-test was turned out negative. The mixture of DCM and DMF in a ratio of 1:1 was used as the solvent. The deprotection step of Fmoc group proceeded for 20 min by 20% piperidine/DMF. Cleavage of the final peptides from the CTC resin was conducted in 93% TFA, 2% TIPS, 2% DODT and 3% anisole for 90 min. The cleavage mixture was filtered and washed with DCM and methanol, and the filtrate was concentrated in vacuum. The resulting peptide residue was precipitated with cold diethyl ether, centrifuged, and dried in vacuum. The peptides were purified with reverse phase HPLC, when necessary, and identified by ESI mass spectrometer. The purity of the peptide was above 95%.

Nanoparticle synthesis: Pd nanoflowers were synthesized by following the method. A peptide stock solution (0.41 mg/ml) and a Na_2PdCl_4 stock solution (10 mM) were freshly prepared in every synthesis. For total of 10 ml volume synthesis, 1 ml of the peptide stock solution was diluted with 6 ml of water. The Na_2PdCl_4 stock solution was injected into the diluted solution as per Pd:peptide ratio of 20. And additional water was injected to adjust total volume equally. This mixture was vigorously stirred for 30 min at room temperature and then 1 ml of a freshly pre-prepared 50 mM reductant (ascorbic acid) was added. The reaction was carried out for 1 hr to make assembly of peptide and reduction of Pd^{2+} sufficient. Formed particles were centrifuged at 9000 rpm to wash out unreacted residues. This was repeated two more times. After supernatant was removed at final centrifugation, 5 ml of water was added into the precipitant.

Copper-free Sonogashira reaction: The following procedure was chosen as a modified copper-free Sonogashira reaction[1]. The most effective base was chosen based on the preliminary experimental results. For each reaction, 0.5 mmol of iodobenzene, 0.6 mmol of phenylacetylene and 2.5 mmol of triethylamine (TEA) were added into the well-dispersed Pd nanoflower solution (containing loading Pd) in 10 ml of total reaction volume. The mixture was stirred vigorously for 18 hr at 65-75 ℃. After the reaction mixture was extracted with diethyl ether, small portion of the extracts were taken to be monitored by GC-MS (equipped with a DB-5 capillary column).

Characterization

1) **UV/Vis spectroscopy:** Samples before/after reduction were characterized by Optizen 2120UV spectrometer (Mecasys) in sample cell (Hellma Analytics, 10 mm pathlength). [Condition; room temperature, 0.5 nm intervals, 190 to 600 nm]

2) **Circular dichroism (CD) spectroscopy:** The CD spectra of each solution samples were recorded using a Chirascan™-plus CD detector (Applied Photophysics) in sample cell (Hellma Analytics, 0.05mm pathlength). The data from 5 scans were averaged for each spectrum. [Condition; room temperature, 1 nm intervals, 190 to 260 nm].

3) **Fourier Transform Infrared (FT-IR) spectroscopy**: Samples were analyzed with a Agilent Cary660 FT-IR spectrometer equipped with an attenuated total reflection (ATR) accessory. Solution samples (80 ul) were deposited to a clean silicon wafer and dried under vacuum. The deposited samples on a silicon wafer were placed on a ZnSe/diamond for analysis. The scanned wave numbers ranged from 650 cm^{-1} to 4,000 cm^{-1} at a resolution of 2 cm^{-1}. The spectra were scanned 32 times.

4) **Transmission electron microscope:** Each of the solution samples (20 ul) was deposited on a carbon-coated copper TEM grid (Ted Pella Inc., 300 mesh) and air-dried for 5 min. The remaining liquid was removed with a filter paper. The prepared TEM grids were kept in a desiccator before TEM and HR-TEM imaging to ensure the removal of moisture. Then, the microscopic images were observed at 80 kV using TEM (JEOL, JEM 1010), and at 300 kV using HR-TEM (JEOL, JEM 3010).

5) **Inductively coupled plasma-atomic emission spectroscopy (ICP-AES):** A Pd NFs solution was homogeneously dispersed using bath-type sonicator (Branson). The Pd NFs solution (100 ul) was injected into royal water (4 ml). After reaction for 8 hours at room temperature, the solution was diluted with DW. The concentration of palladium was quantified by ICP-AES (Shimadzu, ICPS-7500).

6) **X-ray diffraction (XRD) analysis:** A lyophilized Pd NFs sample was transferred to a sample holder. The XRD data were measured over the scattering angle ranging from 5˚

to 90˚ at 2θ step of 0.02˚ using CuK_{α} radiation with a diffracted beam monochromator in the reflection geometry at room temperature (Rigaku, Smart Lab).

2. Supplemental experiment results

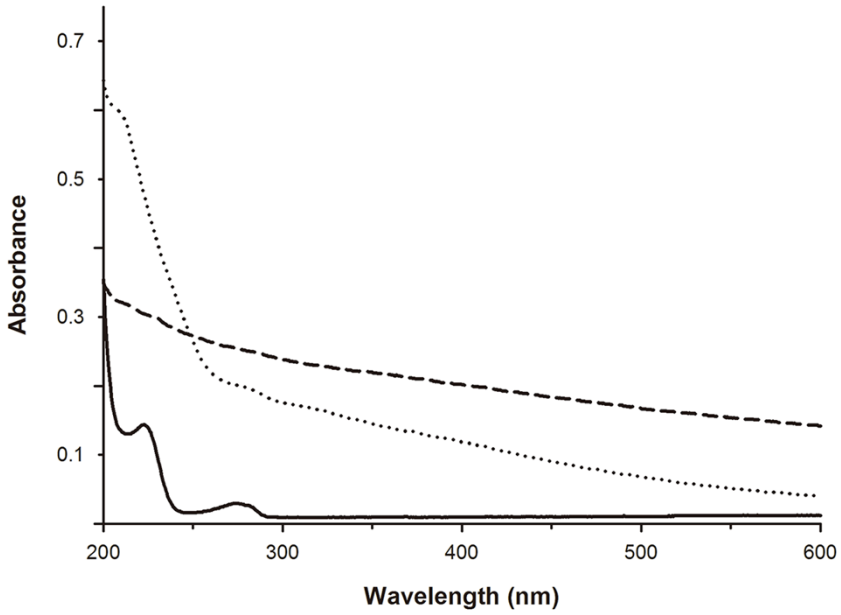

Fig. S1 UV-Vis spectra of peptide (line), Pd^{2+}/peptide complex (dotted), and reduced Pd flowers prepared by the peptide (dash).

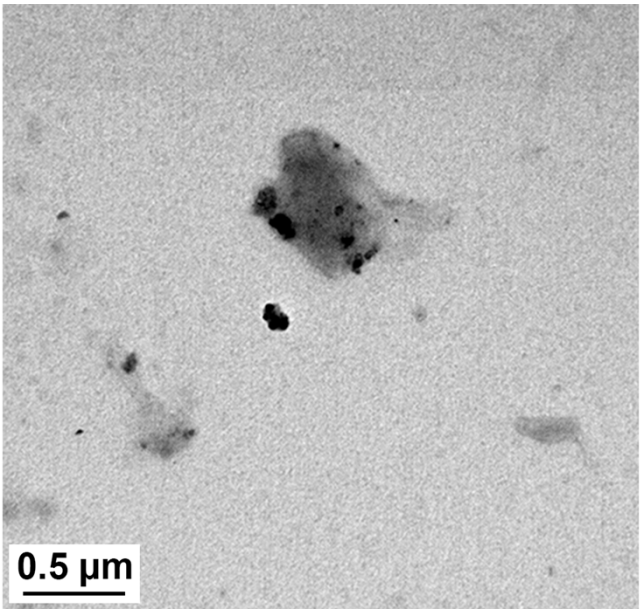

Fig. S2 TEM images of palladium nanoparticles prepared with YYAAAYY peptide.

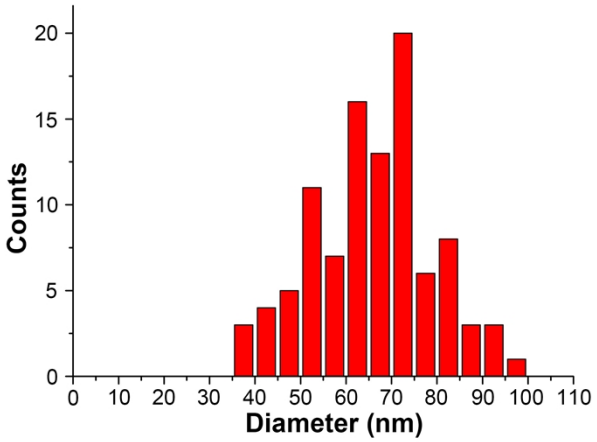

Fig. S3 Size distribution histogram of Pd NFs.

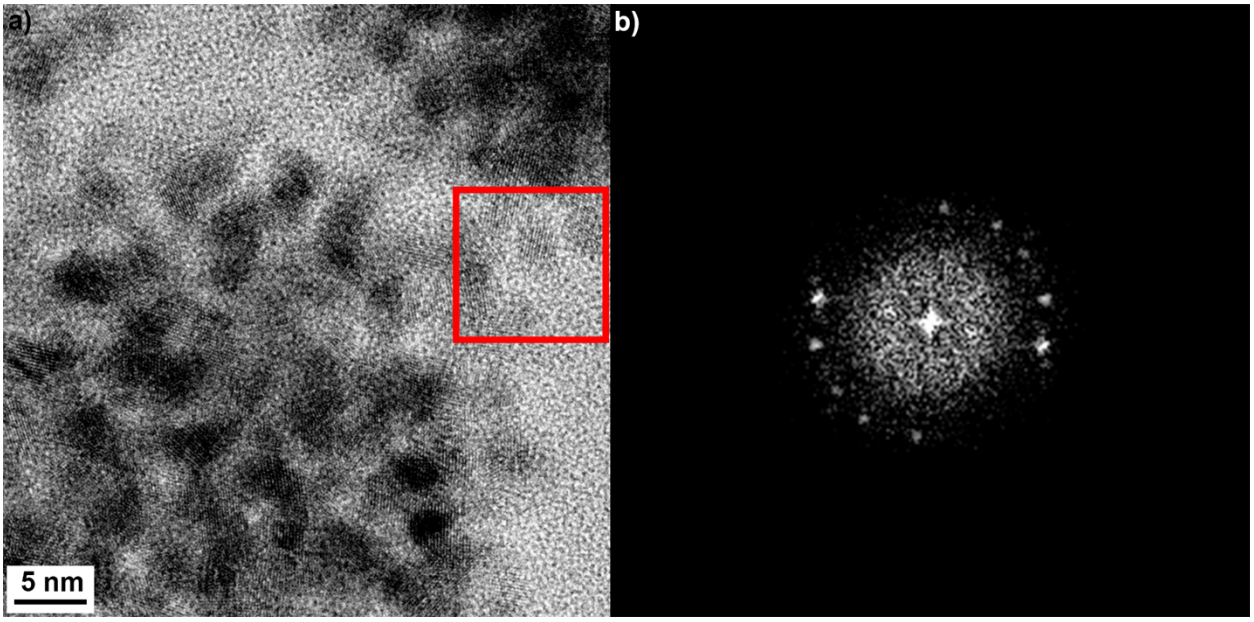

Fig. S4 (a) HR-TEM image and (b) electron diffraction pattern of the red square region in (a).

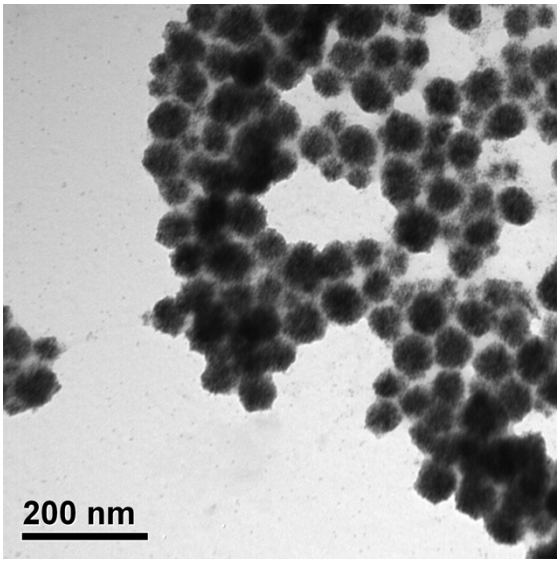

Fig. S5 TEM image of Pd NFs after copper free Sonogashira cross-coupling reaction.

3. Reference

1. S. Sawoo, D. Srimani, P. Dutta, R. Lahiri and A. Sarkar, *Tetrahedron*, 2009, **65**, 4367-4374.