

Electronic Supplementary Information (ESI) for

Fabrication of silica nanotubes with anisotropic functionality as a smart catalyst supporter

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Supporting Figures

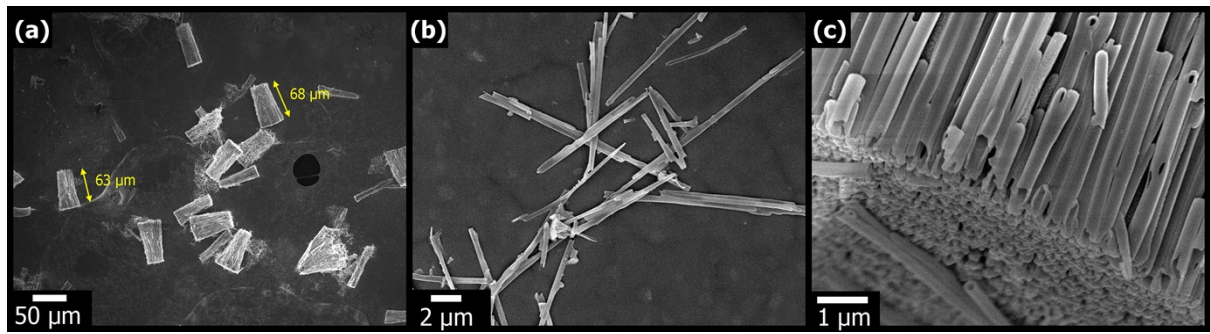


Fig S1. SEM images of pristine silica nanotube. a) $\times 200$ magnification, b) $\times 4500$ magnification, c) $\times 15000$ magnification.

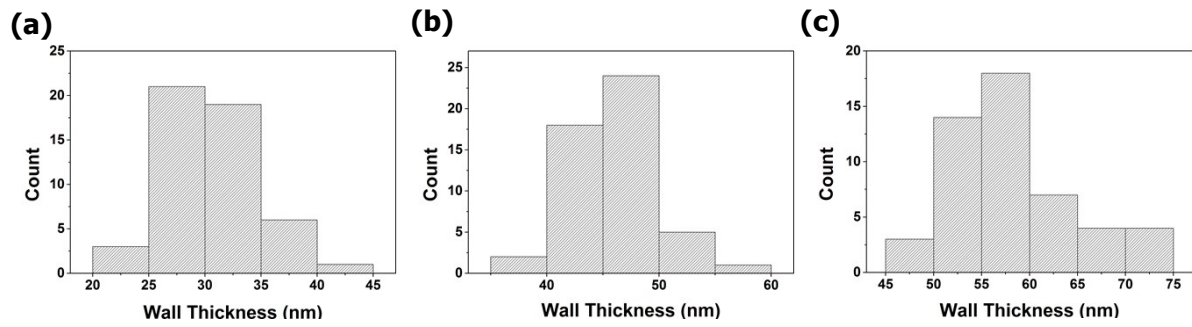
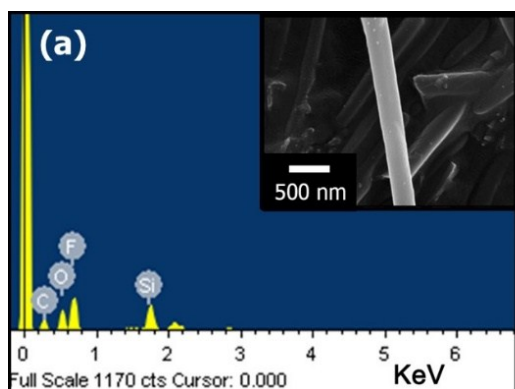


Fig S2. TEM histogram of wall thickness a) pristine silica nanotube, b) PAA-silica nanotube
c) F-PAA silica nanotube

The average wall thickness is 31.1 nm, 46.2 nm, 58.0 nm separately. The wall thickness became gradually thicker as introduction of poly acrylic acid an fluorosilane.



(b)

Element	Atomic%	Weight%
Carbon	33.43	23.94
Oxygen	21.53	20.54
Fluorine	36.75	41.64
Silicon	8.28	13.87

Fig S3. a) EDX analysis results and b) elemental composition table of F-PAA silica nanotube (inset: SEM image).

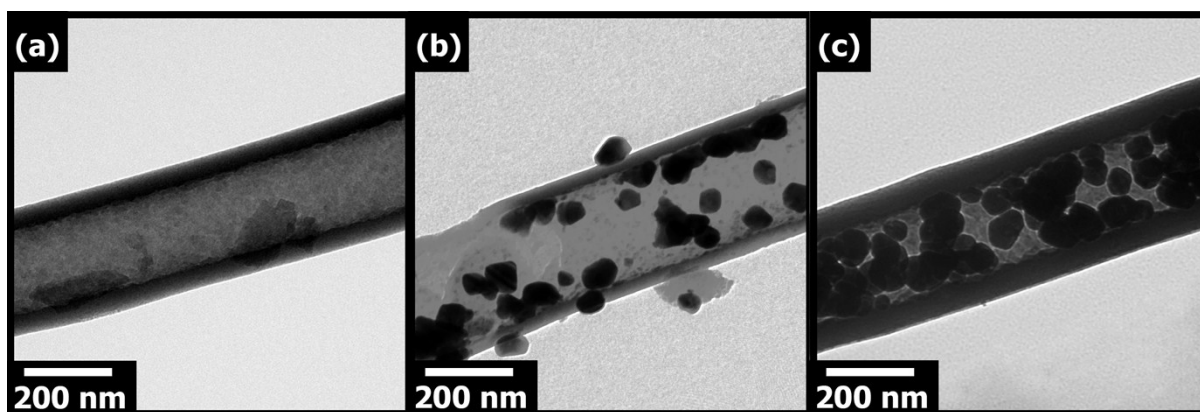


Fig S4. TEM images of Pd-F-PAA silica nanotubes with different palladium chloride concentrations. a) 1.0×10^{-3} M, b) 2.5×10^{-3} M and c) 5.0×10^{-3} M.

The introduction of Pd nanoparticle was optimized by adding 2.5×10^{-3} M PdCl_2 solution, where Pd nanoparticles with *ca.* 50nm diameter do not block the inner pathway of nano-channel.

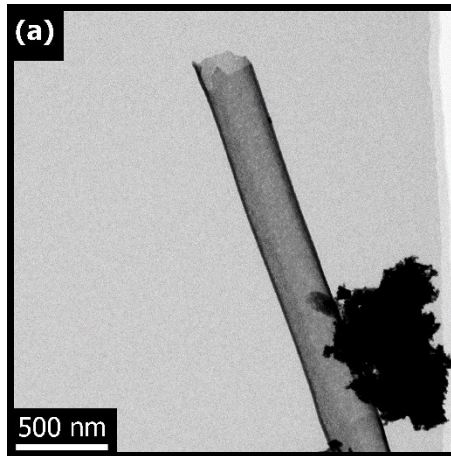


Fig S5. TEM images of bare silica nanotubes with introduction of palladium nanoparticle

We newly observed the pristine silica nanoparticle by TEM and palladium particle was not coordinated inside the pristine silica nanotube because there is no coordination site like carboxylic group.

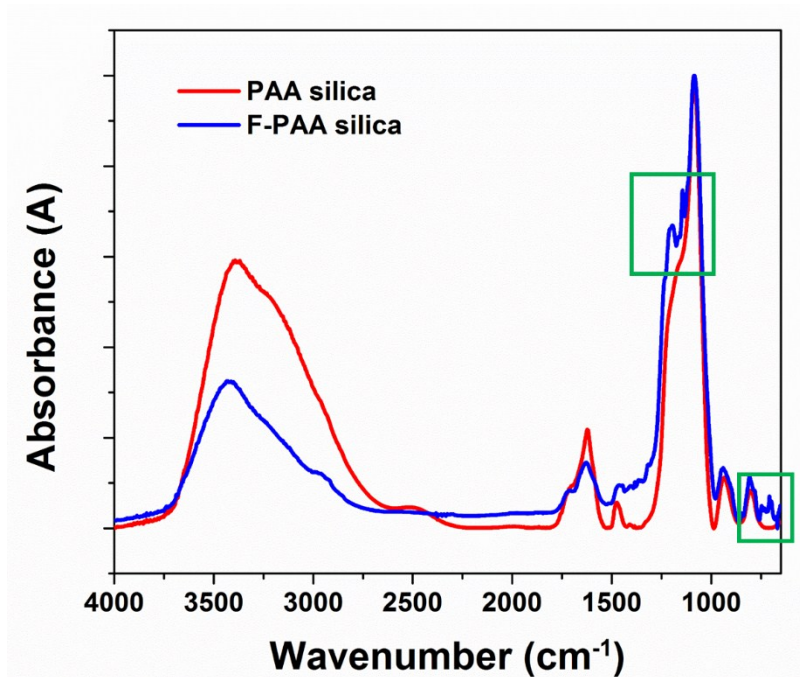


Fig S6. IR spectra comparing PAA silica with F-PAA silica

By directly comparing IR spectra of PAA silica and F-PAA silica, 1360-1000 cm⁻¹ C–F stretching peak and 830-520 cm⁻¹ C–F deformation peak of spectrum of F-PAA silica was distinguished from the spectrum of PAA silica in the green box.

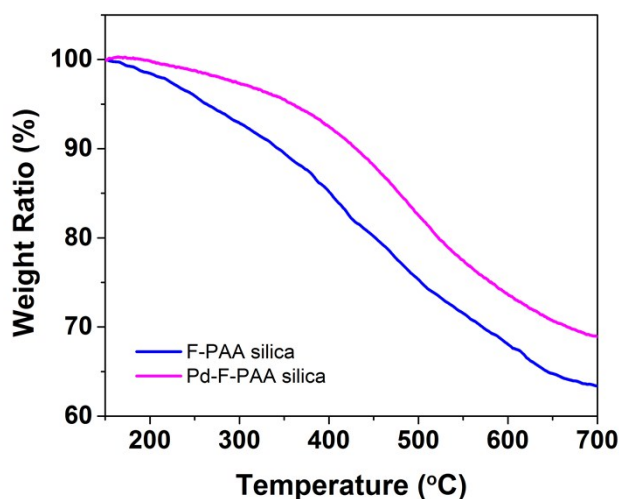


Figure S7. TGA analysis of F-PAA silica nanotube and Pd-F-PAA silica nanotube

As a result of TGA analysis, we can calculate the real loading of Pd in nanotube comparing between Pd loading F-PAA silica nanotube and F-PAA silica nanotube. At the end of thermal decomposition, the residue of Pd-F-PAA silica and F-PAA silica is 69.0 %, 63.4 % separately. So, we assumed that the real loading of palladium is 5.6 %.

In 0.01 g of nanotube, the weight of palladium is $0.01 \text{ g} \times 0.056 = 0.56 \text{ mg}$. Since the atomic mass of palladium is 106.42 amu, the amount of palladium is $\frac{5.6 \times 10^{-4}}{106.42} = 5.3 \times 10^{-6} \text{ mol}$. To assess the activity of Pd catalyst, we calculate the turnover number(TON) and turnover number

$$\text{is } \frac{2.0 \times 10^{-3} \text{ M} \times \frac{20}{1000} \text{ L}}{5.3 \times 10^{-6} \text{ mol}} = 7.5$$

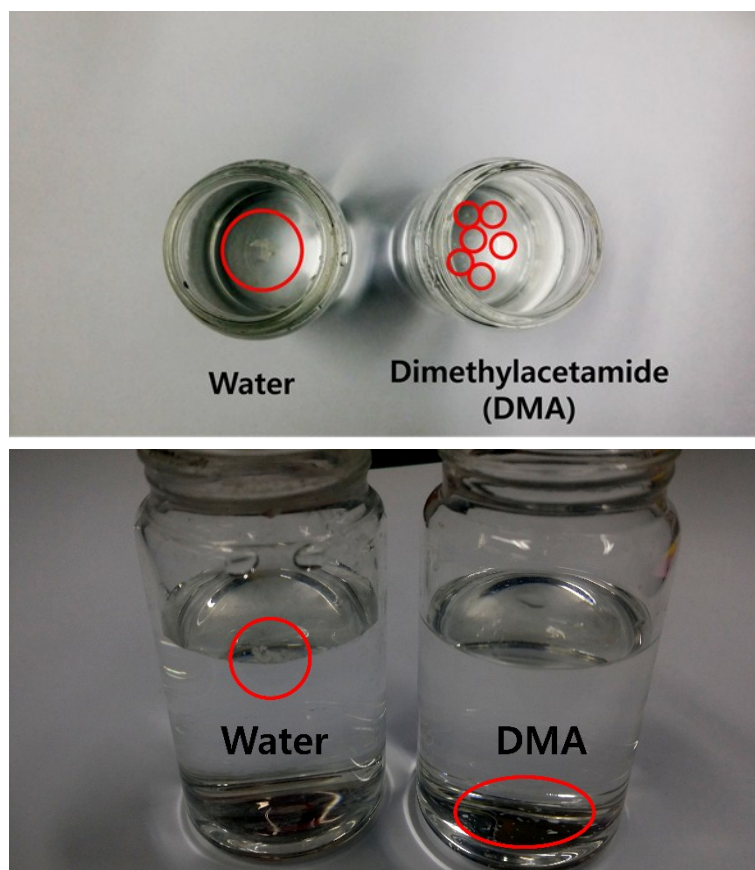


Fig S8. DC images comparing the F-PAA silica in water and *N,N*-dimethylacetamide

Comparing between F-PAA silica nanotube in water and *N,N*-dimethylacetamide, the dispersity in solvent is quite different. Cause of hydrophobic modification, almost of the F-PAA silica nanotubes are gathered together at the surface of water while F-PAA silica nanotubes are scattered in the *n*-butyl acrylate. Also, the catalytic performance was not descending after the chemical modification.

Table S1. Zeta potential values of variously functionalized nanotubes (Dispersed in water, all solutions adjusted to pH 7).

Entry	Material	Treatment	ζ -potential
Inner surface functionalization			
1	Pristine silica		-48.30 mV
2	Vinyl silica	VTMS(Vinyltrimethoxysilane)	-48.91 mV
3	PAA silica	Poly (acrylic acid)	-44.27 mV
Outer surface functionalization			
4	Carboxy silica	CEST (Carboxyethylsilanetriol di-sodium salt)	-63.23 mV
5	Amino silica	APTES ((3-aminopropyl) triethoxysilane)	-38.52 mV

The zeta potential value of pristine silica nanotube was -48.30 mV by $-OH$ groups of the surface of silica. After the introduction of amine group by APTES treatment, zeta potential value became more positive due to NH_4^+ in neutral condition. Meanwhile, zeta potential became more negative due to carboxylic acid after CEST treatment because of dissociated protons in neutral pH. On the other hand, there is no notable change in zeta potential after treatment of VTMS and PAA inside the silica nanotube. The zeta potential value is obtained from outer layer in electrical double layer on outer surface, inner functionalization may have no influence on zeta potential. So, It is possible that we easily fabricate nanocarrier having different zeta potential by surface modification. furthermore, this means that fabrication of nanocarrier is possible increasing dispersibility in certain solvents.

Experimental Section

Materials: Circular anodic aluminum oxide (AAO) film with 25 mm diameter and pore size of 0.2 micrometer was obtained from Whatman, UK. Absolute ethanol (HPLC grade) was purchased from Fisher Scientific, UK. Acrylic acid was supplied from Junsei Chemical Co., Japan. Hydrochloric acid (HCl, 35.0 %~37.0 %), anhydrous toluene, potassium persulfate (KPS, 98 %) and anthracene (99%) were purchased from Samchun Chemical. Co., Korea. Tetraethyl orthosilicate (TEOS, Reagent grade), vinyltrimethoxysilane (VTMS, 98 %), palladium chloride (PdCl₂, 99 %), N,N-dimethylacetamide (DMA), tributyl amine (TBA, 98.5%, Reagent grade), iodobenzene (98%), 2-iodotoluene(98%), 3-Aminopropyltriethoxysilane (APTES, 99%), 4-iodoacetophenone(98%), styrene (≥99%, inhibited by 4-tert butyl catechol) and pyrene (99%) were purchased from Sigma-Aldrich Co., USA with no further purification. n-butyl acrylate (98%, inhibited by monomethyl ether hydroquinone) was acquired from Kishida tech, Japan. Carboxyethylsilanetriol (CEST) and Tridecafluoro-1,1,2,2-tetrahydrooctyl triethoxysilane (TTS) were purchased from Gelest. Inc., USA.

Preparation of silica nanotube: Mixture of distilled water (9 g), absolute ethanol (1.15 g), and hydrochloric acid (0.3 g) was prepared as an initiator solution. A piece of AAO film was dipped in the initiator solution for 15 min for complete wetting of inside wall of the AAO pore. After removal of excessive solution on the surface, a piece of AAO membrane was put in the reaction vessel. Then 0.1 ml of TEOS, silica precursor, was put into the reaction vessel separately and the reaction vessel was stored in 80 °C dry oven for 3 h to initiate vapor phase synthesis. After reaction, a piece of AAO was carefully taken from the vessel and was treated with 3M HCl aqueous solution (50 mL) and the solution was put in 100 °C dry oven for

complete etching of AAO substrate during 3 days. The silica nanotubes were obtained after washing with ethanol for 3 times.

Preparation of inner-wall-silane-treated silica nanotube: After vapor phase synthesis of silica nanotube inside the AAO wall, a piece of AAO was carefully withdrawn from the vessel and washed with distilled water and ethanol for several times. After complete drying, A piece of AAO membrane containing silica nanotube was put into another reaction vessel, and additional VPS was carried out by introducing 0.1 ml of silane liquid (CEST, APTES). After 6 h treatment in 100 °C dry oven, a piece of AAO membrane was collected from the device and was put into 3M HCl solution (50 mL) for complete etching of AAO substrate during 3 days.

Preparation of inner-wall-PAA-silica nanotube (PAA-silica): After vapor phase synthesis of silica nanotube inside the AAO wall, a piece of AAO was carefully withdrawn from the vial and was washed with distilled water and ethanol for several time. After complete drying, a piece of AAO with bundles of silica hollow nanotube was put into 30 ml of 5 % VTMS/toluene solution in RB flask. After 12 h treatment in 80 °C reflux system, a piece of AAO was collected from the flask and was washed thoroughly. After washing process, the vinyl group-treated AAO piece was put into the reaction vessel and the vessel was evacuated for 30 min. Then 0.15 ml of acrylic acid monomer was separately injected into the system and initiator solution (KPS 0.05 g in 1 ml of water) was injected to completely soak the AAO piece. Then the device was put into 80 °C dry oven. After 12 h treatment, the piece of AAO was put into 3M HCl solution (50 mL) for complete etching of AAO substrate during 3 days. The PAA-polymerized silica nanotube, PAA-silica, was collected and dried in powder form.

Preparation of bifunctional silica nanotube (F-PAA-silica): After complete etching of AAO after polymerization of PAA in silica nanotube, the white powder of PAA-silica were collected. After introducing the PAA silica powder (0.01g) into the reaction vessel, additional VPS was performed for 6 h at 140 °C by adding 0.1 ml of tridecafluoro-1,1,2,2-tetrahydrooctyl triethoxysilane (TTS). The as-prepared F-PAA-silica was collected and dried in powder form.

Preparation of palladium inserted bifunctional silica nanotube (Pd-F-PAA-silica): After the white powder of F-PAA-silica nanotube was collected, 0.01g of nanotube was added to 30 ml of PdCl₂ solution with different concentration ranged from 1.0×10⁻³ M ~ 5.0×10⁻³ M and vigorously stirred for 2 h under nitrogen atmosphere at room temperature. Then, Pd salt were conjugated with carboxylates inside the silica nanotube. After that, palladium ion was reduced by bubbling hydrogen gas into the solution for 2 min. During the reduction, the colour of solution was changed and residual PdCl₂ was precipitated. Then, residual PdCl₂ was washed by distilled water and product was dried in a vacuum oven at room temperature.

Heck reaction condition using Pd-F-PAA-silica: All Heck coupling reactions were done at 130 °C by bifunctional silica nanotube with palladium inserted. The heating mantle was preheated to 130 °C for reducing temperature gradient during heating the reaction vessel. The reaction was conducted with 20 ml of DMA, 3.0 mmol of tributylamine and 2.6 mmol of olefin (n-butyl acrylate or styrene) 2.0 mmol of aryl iodide (4-iodoanisole, 2-iodotoluene or iodobenzene), 2.0 mmol of pyrene, anthracene in presence of 0.01 g of Pd-F-PAA-silica nanotube in nitrogen atmosphere. At the end of the reaction, the reaction vessel was cooled down at room temperature. The yields of the reaction were 99%, 99%, 98% separately and their turnover numbers(TON) were 7.5. They are obtained by quantitative analysis for amount of

disappearing reagent peak of gas chromatography/mass spectrometry (GC/MS) comparing that of unreacted substance (pyrene, anthracene).

Heck reaction condition using Pd-PAA-silica: The Heck coupling reactions of entry 3(styrene, iodobenzene) were done at 130 °C by Pd-PAA silica nanotube. The heating mantle was preheated to 130 °C for reducing temperature gradient during heating the reaction vessel. The reaction was conducted with 20 ml of DMA, 3.0 mmol of tributylamine and 2.6 mmol of styrene, 2.0 mmol of iodobenzene, 2.0 mmol of pyrene, anthracene in presence of 0.01 g of Pd-PAA-silica nanotube in nitrogen atmosphere. At the end of the reaction, the reaction vessel was cooled down at room temperature. The yields of the reaction were 96%. They are obtained by quantitative analysis for amount of disappearing reagent peak of gas chromatography/mass spectrometry (GC/MS) comparing that of unreacted substance (pyrene, anthracene).

Recyclability test using Pd-F-PAA-silica: After the Heck coupling reactions, Pd-F-PAA silica was recollected by PTFE membrane filtration(Advantec). Then the PTFE membrane was put into 80 °C dry oven. After 12 h treatment, membrane was weighed and recovery rate was approximately 70%. The Heck coupling reaction of entry 3(styrene, iodobenzene) was conducted by recycled Pd-F-PAA silica nanotube. The reaction was conducted with 20 ml of DMA, 3.0 mmol of tributylamine and 2.6 mmol of styrene, 2.0 mmol of iodobenzene, 2.0 mmol of pyrene, anthracene in presence of 0.007 g of Pd-F-PAA-silica nanotube in nitrogen atmosphere and the yields of the reaction were 90%. They are obtained by quantitative analysis for amount of disappearing reagent peak of gas chromatography/mass spectrometry (GC/MS) comparing that of unreacted substance (pyrene, anthracene).

Characterization: Scanning electron microscope (SEM) images were obtained with a JSM-6701F (JEOL, Japan). EDX measurement was taken with an INCA energy dispersive X-ray spectrophotometer (Oxford Instruments Analytical Ltd. UK) linked with JSM-6701F SEM. Transmission electron microscope (TEM) images were acquired with a JEM-2100 (JEOL, Japan). Fourier-Transform Infrared (FT-IR) spectra measurement was conducted with a Perkin-Elmer Frontier FT-NIR/MIR Spectrometer, utilizing universal-ATR mode (US). Thermogravimetric analysis (TGA) spectra were also obtained with a Perkin-Elmer Pyris TGA 6 thermogravimetric analyzer (US). All TGA analyses were conducted in inert nitrogen atmosphere. Zeta potential measurement was taken with an ELS-8000 electrophoretic light scattering spectrophotometer (Otsuka electronics, Japan). All samples for zeta potential measurement were in powder form, which were then dispersed in aqueous solution with pH control. Gas chromatography-mass spectroscopy results were obtained with GMI HP-6890 (GC) and HP-5973 (MS).