

A New Pd Nanoparticle-Silica Nanotube (Pd@SNT) as an Efficient Catalyst for Suzuki-Miyaura Coupling and sp^2 C-H Arylation in Water

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1. General Information

Aluminum foil (99.99%, Alfa aesar), (3-aminopropyl)triethoxysilane (APTES, Sigma), 3-trimethoxysilylpropyl diethylenetriamine (DETA, Sigma), 2-[methoxy(polyethylenoxy)propyl]trimethoxysilane (PEG, Gelest), trimethoxyoctadecylsilane (C18, Sigma), fluorescein isothiocyanate (FITC, Fluka), tetrachlorosilicon (SiCl_4 , Acros), sodium tetrachloropalladate (Na_2PdCl_4 , Sigma-Aldrich), ninhydrin (Sigma-Aldrich), 4-(hydroxymethyl)phenoxyethyl polystyrene resin cross-linked with 1 % DVB (Wang resin, TCI, cat #: H0987, 1.7 mmol/g, 74-37 μm) were purchased from commercial sources.

TLC (Thin-layer chromatography) analysis was carried out on Merck silica gel 60 F254 TLC plate and was visualized with UV lamp and potassium permanganate solution. Flash column chromatography was performed on Kieselgel 60 (230-400 mesh). For analysis, the following instruments were used: ICP-MS (PERKIN-ELMER SCIEX, ELAN 6100, Seoul National University National Center for inter-university research facilities), HR-TEM (AP Tech Tecnai G2 F30 S-Twin, GachonUniversity Center for Advanced Functional Ceramics), UV-vis Spectroscopy (Scinco, S-3100), optical microscopy (Nikon, ECLIPSE 80i), contact angle measurement (Surface Electro Optics, Phoenix 300) and NMR spectroscopy (400 MHz, Mercury, Varian).

2. Preparation of Pd@SNTs

2.1 Anodization of aluminum film to form AAO¹

Annealed aluminum sheets (10 cm x 3 cm x 0.25 mm) were immersed in acetone for 1 h, then

1. a) G. L. Hornyak, C. J. Patrissi, C. R. Martin, *J. Phys. Chem. B.* **1997**, *101*, 1548. b) H. Masuda, Fukuda, K. Masuda, *Science.* **1995**, *268*, 1466. c) B. He, S. J. Son, S. B. Lee, *Anal. Chem.* **2007**, *79*, 5257.

electro-polished in a mixture of perchloric acid and ethanol (volume ratio, 1:5) at 0 °C and at 15 V.

A high purity aluminum foil was used as the cathode in the electrochemical cell. Anodization was conducted in a 0.3 M oxalic acid solution for 10 ~ 15 h at 10 °C and at 40 V, then the resultant aluminum oxide layer was subsequently removed using a solution of phosphoric acid (6 wt%) and chromic acid (1.5 wt%) at 60 °C. The etched aluminum foil was subject to the second anodization under conditions identical to the first anodization. The depth of the template can be controlled by the second anodization time with a growth rate of 78 nm (± 2)/min. The initially formed pores on the AAO template have random orientations and have broad diametric distributions, which forms regularly spaced- and uniformly sized pores upon the second anodization. Pores were further reamed in an aqueous 0.1 M phosphoric acid solution at 38 °C for 20 to 50 min. The diameter of the pores is proportional to etching time and could be precisely controlled in the range of 60 to 100 nm.

2.2 Deposition of silica layer and fabrication of SNTs²

The silica layer was deposited using the surface sol-gel (SSG) method according to literature.¹² The aluminum template was immersed neat SiCl₄ for 5 min, quickly rinsed several times with pure *n*-hexane to remove excess SiCl₄, and was kept in the pure hexane for 5 min. For a complete hydrolysis and removal of SiCl₄, the template were immersed in the following solutions for 5 min, with drying under N₂ for 5 min between each cycles: a mixture of methanol and hexane (volume ratio 2:1), ethanol, deionized (DI) water and methanol.

In this work, a different number of cycles of SSG processes were employed for the

2. a) H. Masuda, M. Satoh, *Jpn. J. Appl. Phys., Part 2: Lett.* **1996**, *35*, L126. b) D. T. Mitchell, S. B. Lee, L. Trofin, N. C. Li, T. K. Nevanen, H. Soderlund, C. R. Martin, *J. Am. Chem. Soc.* **2002**, *124*, 11864. c) E. D. Steinle, D. T. Mitchell, M. Wirtz, S. B. Lee, V. Y. Young, C. R. Martin, *Anal. Chem.* **2002**, *74*, 2416. d) R. Gasparac, P. Kohli, M. O. Mota, L. Trofin, C. R. Martin, *NanoLett.*, **2004**, *4*, 513.

preparation of different-lengthed SNTs. For example, for deposition of silica layer on 3 μm and 20 μm -depth AAO templates, five and eight cycles of SSG processes were employed, respectively (Section 11).

2.3 Surface functionalization on SNT to form Pd@SNT³

The inner surface of silica layer was modified using commercially available silane reagent. A SNTs-embedded template was soaked into a mixture of toluene, 3-trimethoxysilylpropyl diethylenetriamine (DETA) and diisopropylethylamine (DIEA) (volume ratio 100:30:1). The solution was heated to reflux for 2 h and then allowed to cool to RT. The template was washed with MeOH (10 mL x 3) and was dried with air. The templates were soaked into a 0.1 wt% Na₂PdCl₄ solution for 1 h and then subsequently heated to 120 °C for 2 h under vacuum. Then the template was dissolved by treating with phosphoric acid solution (25 wt%) to provide Pd@SNTs which were collected by filtration, rinsed with deionized (DI) water until neutral pH and were dispersed in DI water. For transmission electron microscopy (HR-TEM), the following apparatus was used: AP Tech Tecnai G2 F30 S-Twin; FE-SEM, JEOL JSM-6700F.

3. Characterization of Pd@SNT

3.1. TEM analysis

The morphology of Pd nanoparticles embedded at the inner surface of SNT's was characterized by a transmission electron microscopy (Figure S1). The size of Pd nanoparticles had average diameter of 3.59 nm \pm 0.93 (dimensions of SNT, length: 3 μm , diameter: 70 nm).

3.2. Quantitation of Pd amount in the Pd@SNT

Pretreatment: An aliquot of 0.1728 g of a solution of Pd@SNT in DI water (see 2.1-2.3) was treated with 2 mL of HF and 5 mL of HCl-HNO₃ mixture (3:1) and the resulting solution was heated at 180 °C for 3 h. The resulting solution was analyzed by ICP-MS. The concentration of the Pd@SNT solution in DI water was measured to be 1004 ppm.

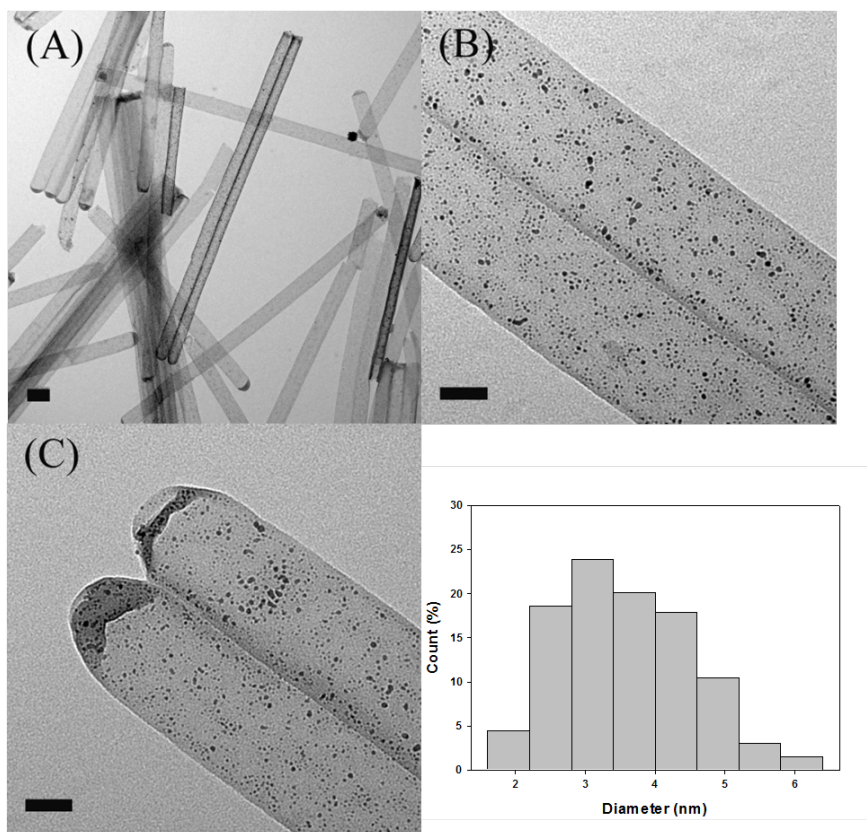


Figure S1. TEM images of the Pd@SNTs at different magnifications; Scale bars are (A) 200 nm (B), (C) 50 nm (dimensions of SNT, length: 3.0 μ m, diameter: 70 nm).

4. Suzuki-Miyaura Reactions

4.1. Synthesis of substrates

Arylboronic acids (**1a-e**, Table 2)⁴ and thiazole derivatives (**4a-c**, Table 3)⁵ used were prepared following literature procedure. For catalytic applications, a stock solution of

4. V. Percec, B. C. Won, M. Peterca, P. A. Heiney, *J. Am. Chem. Soc.*, **2009**, *131*, 17500.

5. S. A. Ohnmacht, P. Mamone, A. J. Culshaw, M. F. Greany, *Chem. Comm.* **2008**, 1241.

Pd@SNT in DI water at a concentration of 1.0×10^3 ppm (See 3.2) was used.

4.2. Suzuki-Miyaura coupling

The reaction of phenyl boronic acid (**1a**) with 4-iodophenol (**2a**) is representative:

A mixture of phenylboronic acid (0.24mmol, 1.2 equiv), sodium bicarbonate (0.60 mmol, 3.0 equiv), 4-iodophenol (0.2 mmol, 1.0 equiv) and Pd@SNT (0.1 mol % Pd, 20 μ L of 1,004 ppm dispersion in H₂O) in H₂O (2 mL) was stirred in oil bath (80 °C) (Note: For reactions using less than 0.1 mol % Pd, an appropriately diluted Pd@SNT stock solution was used.) After the reaction is finished by TLC, the reaction mixture was acidified (pH 2) with 2 N HCl and the aqueous phase was extracted with ether (2 mL x 3). The combined ethereal extracts were dried (MgSO₄), concentrated and the residue was purified by column chromatography or by recrystallization from CH₂Cl₂.

4.3 TEM image of Pd@SNT after Suzuki coupling (Table 1)

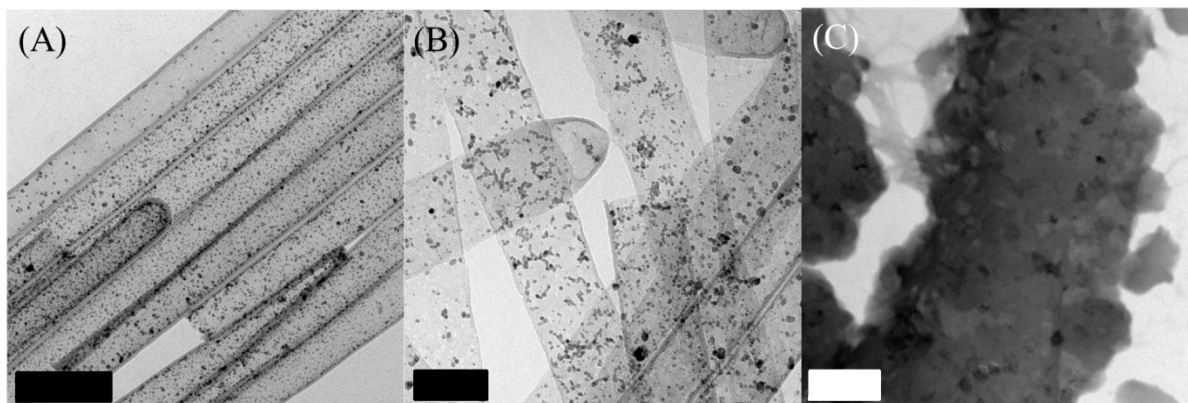


Figure S2. TEM image of the Pd@SNT (A) before Suzuki coupling, (B) Intact Pd@SNTs after the run in entry 6, Table 1, (C) Disrupted Pd@SNTs after the run in entry 2, Table 1. Scale bars are (A), (C) 200 nm, (B) 100 nm.

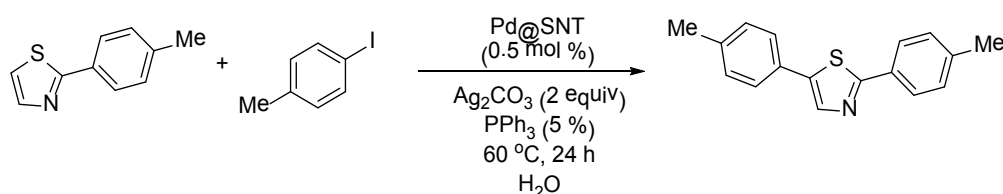
5. C-H arylation of thiazoles

The reaction of 2-tolylthiazole (**4c**) with 4-iodotoluene (**2k**) is representative:

A mixture of 2-tolylthiazole (0.1 mmol, 1.0 equiv), 4-iodotoluene (0.12 mmol, 1.2 equiv), silver(II) carbonate (0.2 mmol, 2.0 equiv), triphenylphosphine (0.01 mmol, 10 mol%) and Pd@SNT (0.5 mol%, 50 μ L of 1,004 ppm dispersion in H₂O) in water (1 mL) was stirred in oil bath (60 °C) for 24 h. After the reaction is finished (by TLC), the mixture was filtered through a Celite pad and was rinsed with acetone (1 mL x 3) and CH₂Cl₂ (1 mL x 3). The organic solvents were concentrated under reduced pressure and the aqueous phase was extracted with CH₂Cl₂ (1 mL x 3). The combined organic layers were dried (MgSO₄), concentrated and the residue was purified by column chromatography.

5.1 Optimization of C-H arylation of thiazoles⁶

Table S1. Optimization of C-H arylation



Deviation from optimized condition	Yield (%)
none	99 %
Ag ₂ O instead of Ag ₂ CO ₃	53 %
AgOAc instead of Ag ₂ CO ₃	NR
CsCO ₃ instead of Ag ₂ CO ₃	NR
K ₂ CO ₃ instead of Ag ₂ CO ₃	NR
K ₃ PO ₄ instead of Ag ₂ CO ₃	NR
No PPh ₃	NR
PPh ₃ (1 mol %)	43 %
PPh ₃ (2 mol %)	61 %
No Pd@SNT	NR
PdCl ₂ (dppf) (5 %) instead of Pd@SNT	80 %

S7

6. G. L. Turner, J. A. Morris, M. F. Greaney, *Angew. Chem., Int. Ed.* **2007**, *46*, 7996.

6. Tests for Heterogeneity and Absence of Catalyst Leaching

6.1 Three-phase test⁷

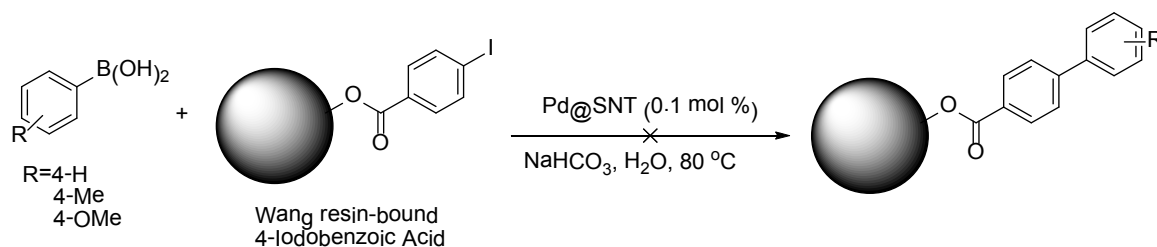
Preparation of Wang resin-bound iodonzoic acid: Wang resin (1 g, 200-400 mesh, 37~74 μm) was washed with dichloromethane and EtOH (10 mL each, three times) and dried for 24 h *in vacuo* before use. The washed resin (500 mg, 0.85 mmol), 4-iodobenzoic acid (1.05 g, 4.25 mmol), and 4-(dimethylamino)pyridine (520 mg, 0.425 mmol) were combined in dry DMF (17 mL). To this mixture, 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI; 814.7 mg, 4.25 mmol) was added at 20 °C and the mixture was then stirred at 60 °C for 12 h. The resin was filtered and washed successively with CH_2Cl_2 , MeOH, water, MeOH and CH_2Cl_2 (10 mL each) successively. A portion of this resin (100 mg) was treated with TFA/ CH_2Cl_2 (1.2 mL/0.4 mL) at room temperature for 1 h, and resin was removed by filtration. The filtrate was evaporated *in vacuo* to afford iodobenzoic acid (28.2 mg). Thus the loading of iodobenzoic acid on Wang resin was determined to be 1.14 mmol/g of resin).

Three-phase test: Wang resin-bound 4-iodobenzoic acid (0.12 mmol, 1.2 equiv), sodium bicarbonate (0.3 mmol, 3.0 equiv), arylboronic acid (1.0 mmol, 1.0 equiv) and Pd@SNT(0.1 mol% Pd, 10 μL of stock solution of 1,004 ppm) were combined in H_2O (1 mL) and the mixture was stirred at 80 °C. After 24 h, the reaction mixture was filtered and washed with CH_2Cl_2 (5 mL). The filtrate was evaporated to dryness to afford aryl boronic acid which was analyzed by ^1H NMR spectroscopy. The filtrant resin was dried 24 h *in vacuo*, collected and was treated TFA/ CH_2Cl_2 (1.2 mL/0.4 mL) for 1 h at RT. The resin was

7. a) K. Okamoto, R. Akiyama, H. Yoshida, T. Yoshida, S. Kobayashi, *J. Am. Chem. Soc.* **2005**, *127*, 2125. b) J. P. Collman, K. M. Kosydar, M. Bressan, W. Lamanna, T. Gerrett, *J. Am. Chem. Soc.* **1984**, *106*, 2569.

removed by filtration and was washed with CH₂Cl₂ (5 mL). The filtrate was evaporated to dryness and the residue was analyzed by ¹H NMR spectroscopy. The amount of recovered arylboronic acid, 4-iodobenzoic acid and the cross-coupled product were tabulated in Table S2. It was concluded that the absence of reaction of Wang resin-bound substrates with Pd@SNT was due to the inability of Wang resin to diffuse into the inner surface of Pd@SNT where the reaction occurs. In contrast, a control experiment with homogeneous system (Pd₂(dba)₃ (1 mol %) and Na₂CO₃ (3 equiv) in DMF) gave 61 % of cross-coupling product.

Table S2. Cross-coupled product was not observed by GC-MS.



	Cataylst	R	Recovered ArB(OH) ₂ ^a	Recovered 4-iodobenzoic acid ^a	Cross-coupled Product ^a
1	Pd@SNT	4-H	62 %	66 %	0 %
2	Pd@SNT	4-Me	74 %	51 %	0 %
3	Pd@SNT	4-OMe	84 %	78 %	0 %
4	Pd ₂ (dba) ₃	4-H	- ^b	- ^b	61 %

^a Isolated yield; TLC and/or GC-MS was used for detection of the

products. ^b Not determined.

6.2 Hot filtration test⁸

A mixture of PhB(OH)₂ (0.12 mmol), 4-iodophenol (0.10 mmol) and Pd@SNT (0.005 mol %) in water (1 mL) was heated at 80 °C. After 20 min, the reaction mixture was filtered through a membrane (Millipore[®], pore size: 110 nm). The filtrate was further stirred for

2 h at 80 °C. However, no additional product of the Suzuki coupled product was observed while a control experiment without the filtration showed gradual increase in conversion (Figure 1b). Thus it is concluded that the filtrate solution do not contain a catalytically active Pd species.

6.3 Hg Poisoning⁹

Similar to 6.2, the reaction mixture was treated with Hg droplet (300 equiv) at the reaction time of 20 min. An immediate suppression of catalytic activity was observed (Figure 1c).

7. Leaching Test by ICP-MS measurement

An aqueous solution containing Pd@SNT (10 ppm) at RT was filtered through commercially available polymer filter (Millipore[®], pore size: 110 nm) and the filtrate was analyzed by ICP-MS for the amount of Pd.

Suzuki reaction was conducted as follows: A mixture of PhB(OH)₂ (0.12 mmol), 4-iodophenol (0.10 mmol) and Pd@SNT (0.1 mol % Pd) in water (1 mL) was heated at 80 °C for 2 h then was allowed to cool to RT. The mixture was filtered through a Millipore[®] filter before ICP-MS analysis. ICP measurements were conducted both before and after the Suzuki reaction. The error limit of the measurements in Table 4 was ± 0.02 ppb.

Pre-treatment: The filtrate was treatment with 2 mL of HF and 5 mL of HCl-HNO₃ (3:1) and the resulting solution was heated at 180 °C for 3 h before ICP-MS analysis. ICP-MS measurements were conducted both before and after this pre-treatment.

8. Dependence of the Lengths of SNTs on the Rates

The Pd@SNTs with different lengths of SNTs were prepared by change in the anodization time (see Section 2.1), followed by the typical deposition of a silica layer and the surface functionalization to form Pd@SNTs (Section 2.2 and 2.3). Three different lengths of SNTs were prepared: 0.5 μm , 3.0 μm and 20 μm . Among these, Pd@SNTs with 0.5 μm showed a significant leaching by TEM inspection. The catalytic activity for the Suzuki coupling between **1a** and **2a** was compared for the rest two samples of Pd@SNTs.

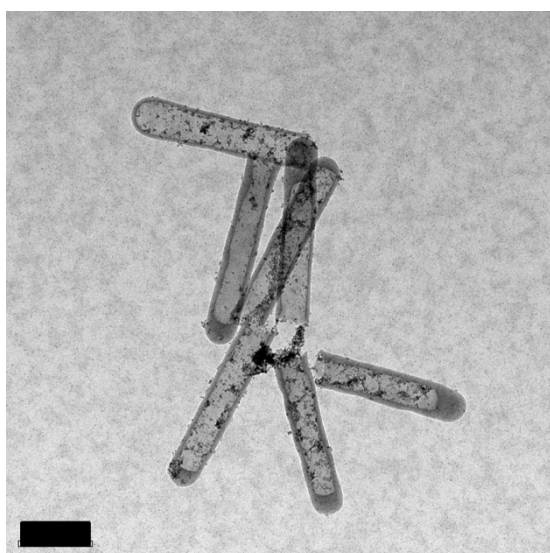


Figure S3. TEM image of the Pd@SNT with shorter (0.3 μm) SNT length (scale bar, 200 nm): A Pd-cluster is seen outside the SNTs at the center of the image

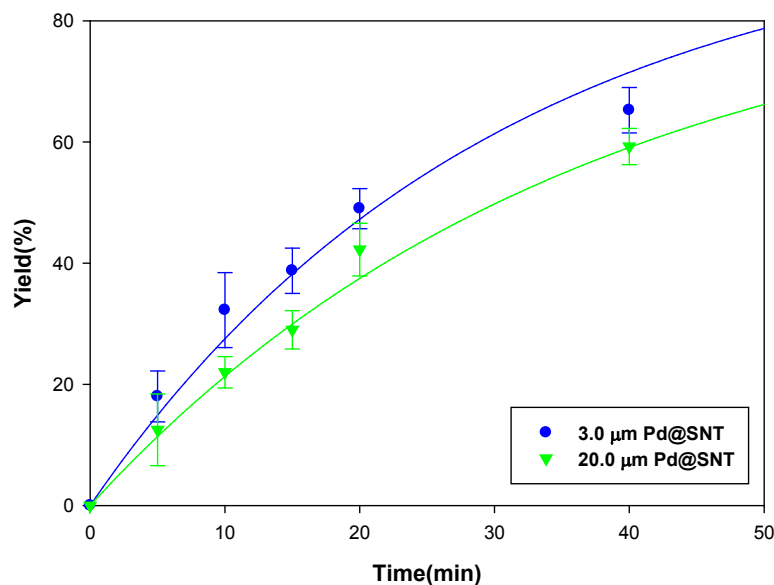


Figure S4. Comparison of the rates of Suzuki coupling between longer (20 μm) Pd@SNTs and typical (3 μm) Pd@SNT at a loading of 0.005 mol % Pd.

9. Surface Modification of Pd@SNT

Three different Pd@SNTs having distinct surface characteristics were prepared using APTES, PEG and C18-derived orthosilicates. The AAO-bound Pd@SNTs were treated with these modifying agents while still imbedded in the template and thus the outer surface is not affected in this process.

A similar procedure as in 2.1-2.3 was followed for the preparation of Pd@SNT imbedded in the AAO template. Before the template-imbedded Pd@SNT was dissolved out of AAO template by phosphoric acid, the Pd@SNTs-incorporated template (4.8×10^{11} count of SNTs per $3 \times 8 \text{ cm}^2$ plate) was soaked into a mixture of toluene (25 mL) / modifying reagent (Table S3, 7.5 mL) / DIEA (100 : 30 : 1, total of 0.25 mL). Then the solution was heated to reflux for 2 h before it was allowed to cool to RT. The template was washed with MeOH (10 mL x 3) and was dried under air. After the surface modification is complete, the

modified Pd@SNT imbedded on AAO was removed from the template by dissolution in phosphoric acid as in 2.3. Thus prepared modified Pd@SNTs were collected by filtration and were dispersed in DI water (1 mL).

Table S3. Abbreviations for Modified Pd@SNT

Abbreviations	Modifying Reagents
APTES-Pd@SNT	(3-aminopropyl)triethoxysilane
PEG-Pd@SNT	2-[methoxy(polyethylenoxy)propyl]trimethoxysilane
C18-Pd@SNT	trimethoxy(octadecyl)silane

10. Characterization of Surface-Modified Pd@SNT

10.1 Quantitation of amino residue (Kaiser Test) in Pd@SNTs

Trace amount of amino residue (from DETA or DIEA) during the preparation of Pd@SNTs could interfere with the subsequent modification or could work additively with the subsequent surface modifying agents. These could also interfere with subsequent characterization and activity of the modified Pd@SNTs, such as contact angle measurement, fluorescence imaging and catalytic performances. Thus, to completely eliminate the effect of the residual amino group from DETA treatment (Section 2.3) from the subsequent surface modifications (APTES-, PEG- and C18-modification), a Kaiser test was conducted to check the absence of the amino group from DETA.

The sampling was conducted just before the Pd@SNTs were dissolved out of the AAO template with phosphoric acid (while the SNTs were still imbedded in the AAO template) because acid treatment could result in a possible loss of amino residue. The reaction of the residual amino groups on Pd@SNT-template with ninhydrin was measured by UV-vis spectroscopy.

10.1.1. Standard curve

Solution A: Ninhydrin (600 μ l of 6 % ethanolic solution, 0.207 mmol) was dissolved in 27 mL of absolute ethanol (7.7 mM solution).

Solution B: DETA (22 μ l, 0.064 mmol) was added to 9.0 mL of absolute ethanol (7.1 mM).

Table S4. Standard Solutions for Figure S3(A)

Standard	Solution A	Solution B	EtOH	[DETA] (M)	Abs. (595 nm)
1	4.50 mL	0.90 mL	3.60 mL	0.000712	0.2051
2	4.50 mL	1.80 mL	2.70 mL	0.001423	0.4055
3	4.50 mL	2.70 mL	1.80 mL	0.002135	0.5389
4	4.50 mL	3.60 mL	0.90 mL	0.002847	0.7136

Each standard solutions were heated for 1 h in a 80 °C oven for ninhydrin reaction before UV-vis measurement. See Figure S5(A) for results.

10.1.2. Quantitation of the amino residues by Kaiser test

Solution A (2.0 mL, see 10.1.1) was diluted with absolute EtOH (2.0 mL). DETA-SNT-template and Pd@SNT-template (see below) was dipped in this solution and was heated for 1 h in an 80 °C oven before UV-vis measurement. See Figure S5B for results.

- Preparation of DETA-SNT-template:

An SNTs-imbedded in a AAO template (Section 2.3, before dissolution out of the template) was soaked into a mixture of toluene, 3-trimethoxysilylpropyl diethylenetriamine (DETA) and diisopropylethylamine (DIEA) (volume ratio, 100:30:1). The solution was heated to reflux for 2 h and then allowed to cool to RT. The template was washed with MeOH (10 mL

x 3) and was dried with air. (template dimension : $3 \times 8 \text{ cm}^2$, 4.8×10^{11} count of SNT)

- Preparation of Pd@SNT-template:

The above templates were then soaked into a 0.1 wt% Na_2PdCl_4 solution for 1 h and then subsequently was heated to $120 \text{ }^\circ\text{C}$ for 2 h under vacuum.

	Abs. (595 nm)	[DETA] (M)	DETA (mmol/cm^2) ^a
DETA-SNT-template	0.496	0.001965	7.37×10^{-4}
Pd@SNT-template	0.05 (below detection limit)	less than 0.000198	less than 7.4×10^{-5}

^a The amount of DETA (mmol) per area (cm^2) of the DETA-SNT-template and Pd@SNT-template.

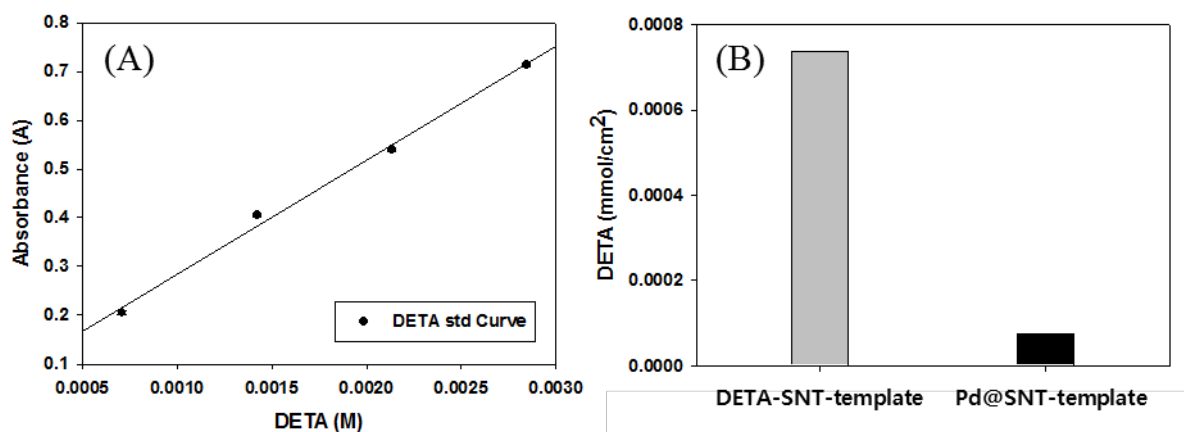


Figure S5. Kaiser test; (A) standard curve, (B) the amount of DETA per unit area of DETA-SNT-template and Pd@SNT-template.

Results: The results described above (Figure S5) showed that most of the amino residue from DETA treatment disappeared in the process of Pd nanoparticle formation (baking at $120 \text{ }^\circ\text{C}$, Section 2.3) and therefore there is no amino group left in the Pd@SNT-template, within the error limit, interfering with or working additively with the subsequent surface modifying agents.

10.2 Fluorescence imaging of APTES-Pd@SNT

To check if APTES modification (see section 8) was conducted successfully, a change of surface amino functional groups was imaged by a fluorescent and optical microscopy with the aid of fluorescence probe. For example, when Pd@SNT modified with APTES was treated with fluorescein isothiocyanate (FITC), the amino group from APTES at the surface would form a covalent conjugate with FITC through a thiourea bond. Thus observation of fluorescence is an indication that the desired modification of Pd@SNT had occurred to bear a primary amino functions.

As a control, an SNT modified with APTES (APTES-SNT), but not loaded with Pd nanoparticles was prepared as follows.

- Preparation of APTES-SNT:

At the end of SNTs fabrication (see 2.2), the template-bound SNTs (4.8×10^{11} count per template of $3 \times 8 \text{ cm}^2$) were soaked into a mixture of toluene (25 mL) / APTES (see Table 1, 7.5 mL) / DIEA (100 : 30 : 1, 0.25 mL) as described in Section 8. Then the solution was heated to reflux for 2 h before it was allowed to cool to RT. The template was washed with MeOH, dried under air, and dissolved by phosphoric acid to yield APTES-SNTs.

Figure S6(A) and (B) shows the dark field and fluorescence images of APTES-SNTs (control), respectively. Figure S4(C) and (D) shows those of APTES-modified Pd@SNT (APTES-Pd@SNT). The observation of the expected dark field and fluorescence images in (C) and (D) as well as in controls (A) and (B) shows the desired presence of amino residues in the APTES-modified Pd@SNTs.

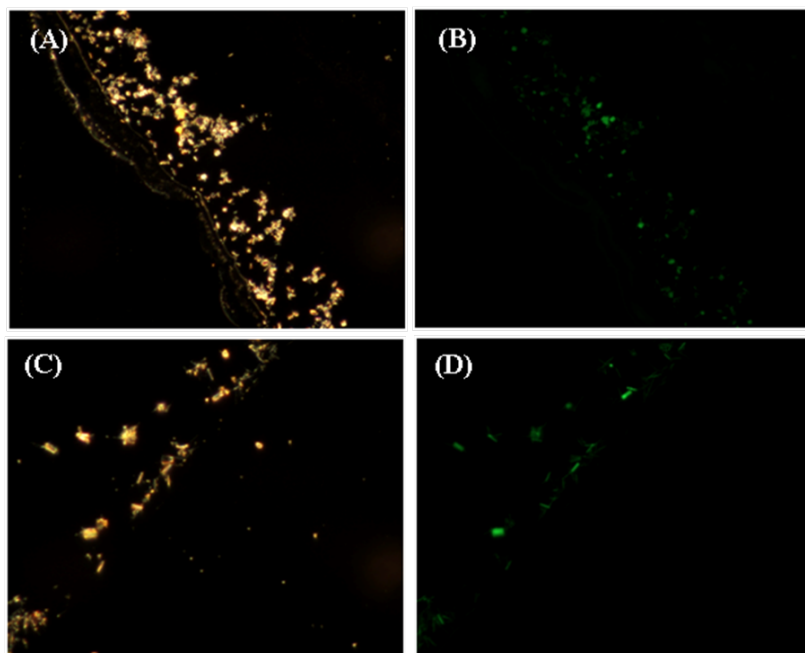


Figure S6. Microscopy images of the modified FITC
(A) Dark field image of the APTES-SNTs (control)
(B) Fluorescence image of the APTES-SNTs (control)
(C) Dark field image of the APTES-Pd@SNTs
(D) Fluorescence image of the APTES-Pd@SNTs

10.3 Contact angle measurements

Preparation of Pd@SNT on slide glass: A similar procedure to Section 2.2-2.3 (and Section 8) was followed for the preparation of modified Pd@glass. The slide glass was soaked into a mixture of toluene/DETA/DIEA (volume ratio 100:30:1). The solution was heated to reflux for 2 h and then allowed to cool to RT. The slide glass was washed with MeOH (10 mL x 3) and was dried with air. The slide glass was soaked into a 0.1 wt% Na₂PdCl₄ solution for 1 h and then subsequently was heated to 120 °C for 2 h under vacuum. For a further modification process, the slide glass was soaked into a mixture of toluene (25 mL)/modification reagent (7.5 mL)/DIEA (100:30:1, 0.25 mL) (see Table S5). Then the solution was heated to reflux for 2 h before it is allowed to cool to RT. The template was washed with MeOH (10 mL x 3) and was dried under air.

To quantitatively analyze the hydrophobicity or hydrophilicity of the inner surfaces of modified Pd@SNT, a Pd@glass was similarly modified with these reagents to emulate the inner surface of modified Pd@SNTs and their contact angles were measured (Table S5 and Figure S7).

Table S5. Abbreviations of Pd@glass

Abbreviation	Description	Counterpart
Pd@glass	Pd-NP formed on a glass slide	Pd@SNT
APTES-Pd@glass	Pd-NP on a glass slide was surface-modified by APTES	APTES-Pd@SNT
PEG-Pd@glass	Pd-NP on a glass slide was surface-modified by PEG	PEG-Pd@SNT
C18-Pd@glass	Pd-NP on a glass slide was surface-modified by C18	C18-Pd@SNT

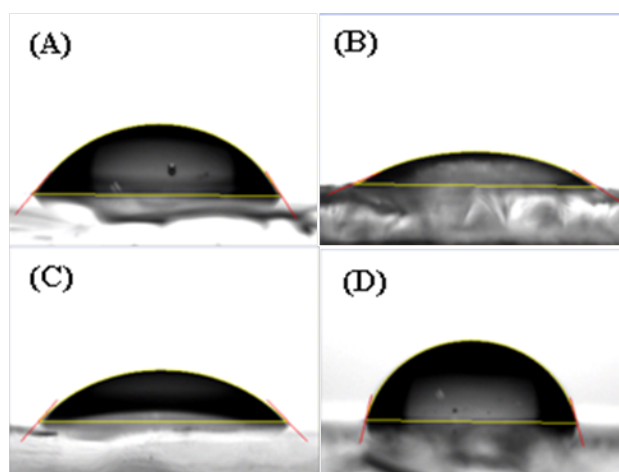


Figure S7. The shape of a water drop on the modified silica surface (A) Pd@glass, $\theta = 55.20^\circ$, (B) APTES-Pd@glass, $\theta = 27.76^\circ$, (C) PEG-Pd@glass, $\theta = 45.06^\circ$, (D) C18-Pd@glass, $\theta = 75.40^\circ$.

The APTES-Pd@glass simulates the inner surface characteristics of APTES-Pd@SNT. Similar correlation could be made with other samples as in Table S5. The contact angles of

Pd@glass, APTES-Pd@glass, PEG-Pd@glass and C18-Pd@glass were measured to be 55.20°, 27.76°, 45.06° and 75.40°, respectively (See Figure 3A, manuscript).

10.4 Kinetic study on Suzuki coupling with modified Pd@SNTs

The following stock solutions (Table S6) of Pd@SNT was prepared in water and was used in catalysis described in this section. The concentration of Pd was measured by ICP-MS as described in Section 3.2.

Table S6. Pd concentrations of Pd@SNTs stock solutions (ICP-MS)

	Pd concentration (ppm) ^a
Pd@SNT	1,004
APTES-Pd@SNT	348
PEG-Pd@SNT	397
C18-Pd@SNT	410

The catalytic activities of the variously modified Pd@SNTs samples above (Table S6) were compared for Suzuki coupling as in Table S7.

Table S7. Initial Rates of Modified Pd@SNTs in Suzuki-Miyaura Coupling (at 5 min)

	Rate
Pd@SNT	$3.2 \times 10^{-4} \text{ M min}^{-1}$
APTES- Pd@SNT	$5.8 \times 10^{-4} \text{ M min}^{-1}$
PEG- Pd@SNT	$5.0 \times 10^{-4} \text{ M min}^{-1}$
C18- Pd@SNT	$3.8 \times 10^{-4} \text{ M min}^{-1}$

Surprisingly, all modification led to an increase in the catalytic performance (Table S7 and Figure 3B in manuscript) and among them, APTES-modified SNTs were found to be the most reactive catalyst, followed by PEG- and C18-modified SNTs in the Suzuki-Miyaura coupling of **1a** and **2a**.

We have further tested surface dependent catalytic activities for direct C-H arylation of

2-*p*-tolylthiazole with 4-iodotoluene. Although the detailed kinetic study was not conducted, APTES-modified Pd@SNTs showed much enhanced rate in C-H arylation reaction during 24 h period (72 % for APTES-Pd@SNT vs. 54 % for unmodified Pd@SNT). For detailed discussions on the factors affecting these catalytic performances, see text.

Table S8. Comparison of reaction yields with modified-Pd@SNTs

	APTES- Pd@SNT	C18- Pd @SNT	PEG- Pd @SNT	Pd@SNT
Suzuki rxn ^a	98%	86%	90%	53%
C-H arylation ^b	72%	69%	61%	54%

^aFor the formation of **3aa**. ^bFor the formation of **5ck**.

11. Catalyst Recovery and Reuse

Recovery procedure: We tested three different methods for catalyst recovery and reuse, employing APTES-Pd@SNTs (0.1 mol % Pd; SNT dimension (i.d.: 70 nm, length: 3 μm); average Pd-nanoparticle size: 2.2 nm ± 0.86) as a catalyst.

Method A: filtration of Pd@SNT through commercial available polymer filter (Millipore[®], pore size: 110 nm) with the help of ultra-centrifugation (5000 rpm, 10 min) and re-suspension of the filtrant Pd@SNT in water for the next run.

Method B: Precipitation of Pd@SNT by ultracentrifugation (5000 rpm, 10 min) and decantation of the reaction mixture, followed by re-suspension of Pd@SNT precipitate in water.

Method C: Extraction of aqueous layer with ether (three times) and the reuse of aqueous layer for the next run.

Among the three methods, extraction with ether (*Method C*) gave the most efficient

catalyst recovery. Intermittently (before 3th, 5th, 7th and 9th cycle), NaHCO₃ was added to compensate for the loss of base and more than ten recycling of APTES-Pd@SNT was possible (Table S9).

Table S9. Catalyst recovery and reuse.^{a,b}

cycle	time	yield(%)	cycle	time	yield(%)
1	0.5 h	93	6	1 h	98
2	0.5 h	99	7 ^c	1 h	94
3 ^c	0.5 h	99	8	1 h	88
4	0.6 h	98	9 ^c	2 h	92
5 ^c	0.6 h	92	10	2 h	89

^a **1a** (0.12 mmol) and **2a** (0.1 mmol) in water (0.5 mL) in the presence of APTES-Pd@SNT (0.1 mol % Pd). ^b Method C was followed; after each cycle, the products were extracted with ether (0.5 mL x 3) and the aqueous layer was reused for the next cycle. ^c 2 equiv of NaHCO₃ was added before the reaction.

12. Characterizations of All New Products

The following products in Table 2 were known compounds.¹⁰

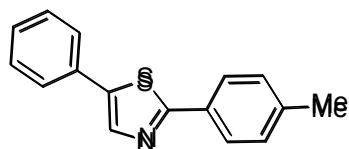
Products	Reference	Products	Reference	Products	Reference	Products	Reference
3ba	10b	3cc	10a	3ea	10g	3ah	10c
3ca	10a	3ad	10a	3ae	10h	3ai	10a
3ab	10c	3bd	10e	3ee	10i	3df	10d
3ac	10a	3cd	10a	3af	10a	3cg	10a
3da	10d	3dc	10f	3ag	10a	3dg	10f
3aa	10a						

The following products in Table 3 were known compounds.¹¹

Products	Reference	Products	Reference	Products	Reference
5aj	11a	5ao	11a	5bj	11b
5ak	11a	5ap	11a	5bl	11a
5al	11a	5ar	11a	5ck	11a
5am	11a	5an	11a	5cl	11a

Compounds **5cj**, **5aq** and **5as** are new compounds.

5-phenyl-2-p-tolylthiazole (**5cj**)

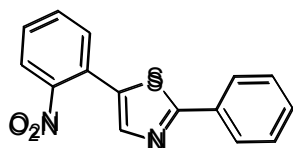


¹H NMR (400MHz, CDCl₃) : δ 7.99 (s, 1H), 8.76 (d, *J* = 8.2Hz, 2H), 7.65 (d, *J* = 7.8Hz, 2H), 7.41 (t, *J* = 7.6Hz, 2H), 7.33 (t, *J* = 7.2Hz, 1H), 7.25-7.27 (m, 2H), 2.40 (s, 3H); ¹³C NMR (100Mhz, CDCl₃) : δ 167.4, 140.3, 139.0, 138.8, 131.5, 131.0, 129.7, 129.1, 128.2, 126.6, 126.2, 21.5; HRMS(EI+) Calcd for C₁₆H₁₃NS [M+1] 252.0847, found 252.0845.

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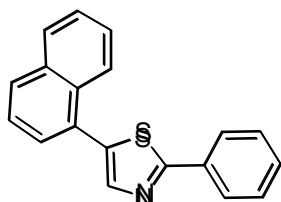
5-(2-nitrophenyl)-2-phenylthiazole (**5aq**)



^1H NMR (400MHz, CDCl_3) : δ 7.95-7.98 (m, 2H),
7.91-7.89 (d, $J = 7.8\text{Hz}$, 1H), 7.67-7.58 (m, 3H) 7.47-
7.45 (m, 3H); ^{13}C NMR (100Mhz, CDCl_3) : δ 169.8,
149.2, 142.7, 132.2, 132.7, 132.5, 132.2,

130.5, 129.6, 129.0, 126.6, 124.4; HRMS(EI+) Calcd for $\text{C}_{15}\text{H}_{10}\text{N}_2\text{O}_2\text{S}$
[M+1] 283.0541, found 283.0542.

5-(naphthalen-1-yl)-2-phenylthiazole (**5as**)



^1H NMR (400MHz, CDCl_3): δ 8.19-8.21 (m, 1H),
8.02 (dd, $J = 1.5, 7.8\text{ Hz}$, 2H), 7.90-7.95 (m, 3H),
7.60-7.62 (m, 1H), 7.45-7.55(m, 6H); ^{13}C NMR
(100Mhz, CDCl_3): δ 168.4, 142.7, 136.3, 133.8, 133.7,

131.9, 130.1, 129.3, 129.0, 128.7, 128.6, 128.5, 126.9, 126.4, 126.3, 125.3,
125.3; HRMS(EI+) Calcd for $\text{C}_{19}\text{H}_{14}\text{NS}$ [M+1] 288.0847, found 288.0845.

