Supporting Information

Nanocontact-Induced Catalytic Activation in Palladium Nanoparticles

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General. Unless otherwise noted, all chemicals were obtained from commercial sources and used as received. The Pd/C catalyst (10%) was purchased from Alfa Aesar.

Preparation of Pd nanowires. In a typical experiment, palladium acetate (122 mg; 0.538 mmol) and poly(*N*-vinylpyrrolidone) (Mw = 40,000; 400 mg; 0.01 mmol) were dissolved in methanol (15 mL), followed by addition of trace copper powder (25 mg; 0.39 mmol). The resulted mixture was heated without stirring at 50 ^{o}C for 24 h to give a black precipitate, which was collected, washed with ethanol and distilled water several times, and dried in air for further characterization and organic reactions.

Characterization. The sample morphology and crystal structure were investigated by field-emission scanning electron microcopy (SEM, JEOL 6701) and transmission electron microscopy (TEM, JEOL 3010). Samples for TEM studies were prepared by depositing small amounts of a sample solution in ethanol onto holey carbon-coated Cu grids. X-ray photoelectron spectroscopy (XPS) spectra were performed with a Phobios 100 electron analyzer (SPECS GmbH) equipped 5 channeltrons, using an unmonochromated Mg Kα X-ray source (1253.6 eV). The pass energy of the hemisphere analyzer was maintained at 50 eV for wide scan and 20 eV for narrow scan, while the takeoff angle was fixed at normal to the sample. Binding energies of XPS spectra were corrected by referencing the C1s signal of adventitious hydrocarbon to 284.8 eV. The crystallographic phase of the sample was determined by powder XRD on a Siemens D5005 X-ray diffractometer (XRD) with Cu Kα radiation (λ = 1.5406 Å) at a scan rate of 0.01 ^{o}/s.

Catalytic Reactions. Catalytic testing was performed in a glass vial (20 mL) equipped with a stir bar. In a typical Suzuki cross-coupling reaction, a mixture of phenylboronic acid (1.2 mmol), aryl halide (1 mmol), Pd nanowire catalyst (6.5 mol%), and $NaO^{t}Bu$ (2 mmol) was stirred in water (10 mL) or water/ethanol (3:2; v:v) at room temperature for 4 to 24 h. The resulting reaction mixture was then centrifuged to remove the Pd catalyst, followed by the removal of the solvent in a rotary evaporator. The residue was dissolved in dichloromethane and washed with water three times. The organic layers were dried with anhydrous sodium sulfate and concentrated under vacuum. The product was analyzed by ^{1}H NMR (300 MHz Bruke) and GC-MS (Hewlett-Parkard). The recycling catalyst that is collected by centrifugation was washed with ethanol several times and air dried for repeated use. For a Heck cross-coupling reaction, aryl halide (1 mmol), alkene (1.2 mmol), triethylamine (2 mmol) and Pd nanowire catalyst (6.5 mol %) were combined in dimethylformide (10 mL) or water/ethanol (1:1; v:v). The kinetic profiles were studied in ethanol by taking aliquot samples (6 μL) from the reaction solution at different time intervals. The samples were then diluted with ethanol (total volume: 5 mL), centrifuged to remove the catalyst, and analyzed by absorption spectroscopy. UV—vis absorbance spectra were obtained at 23 ^{o}C using quartz cells and a SHIMADZU UV-2450 spectrophotometer.

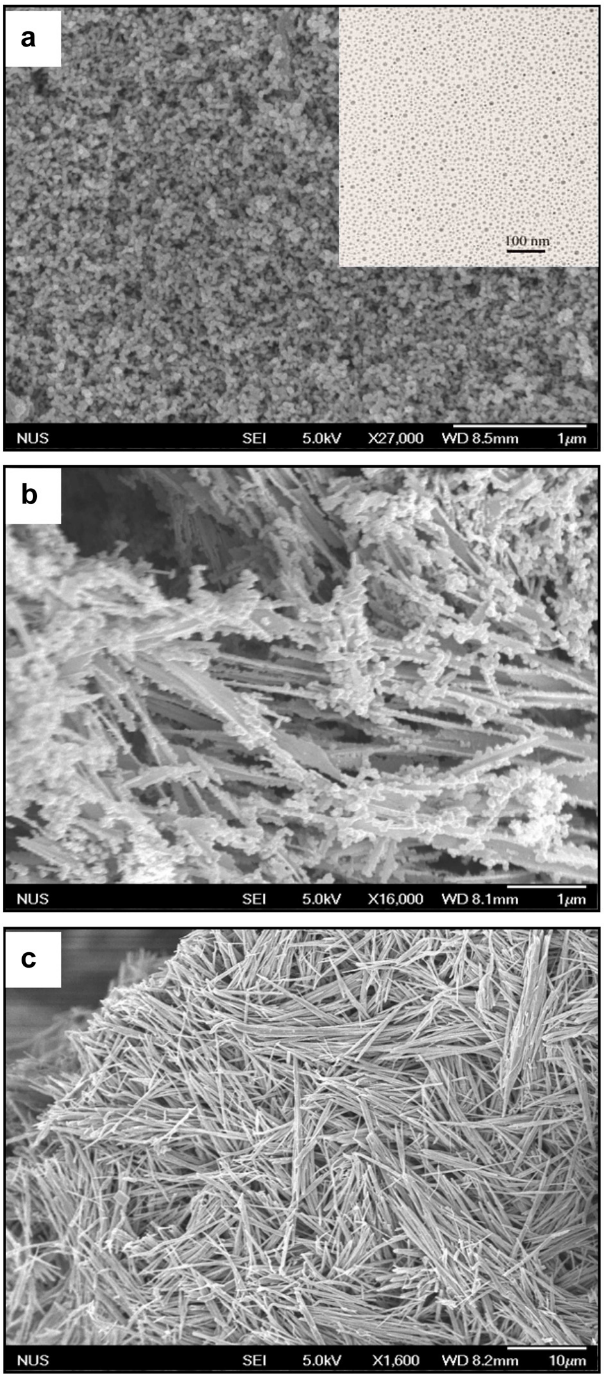


Figure S1. Control experiments for the synthesis of Pd nanowires as a function of PVP concentration. (a) SEM image of the Pd nanoparticles synthesized with 0.0025-mmol PVP. (Inset) TEM image of the as-synthesized nanoparticles. (b) SEM image of the reaction product obtained with 0.005-mmol PVP. (c) SEM image of the nanowires formed with optimum PVP concentration (0.01 mmol).

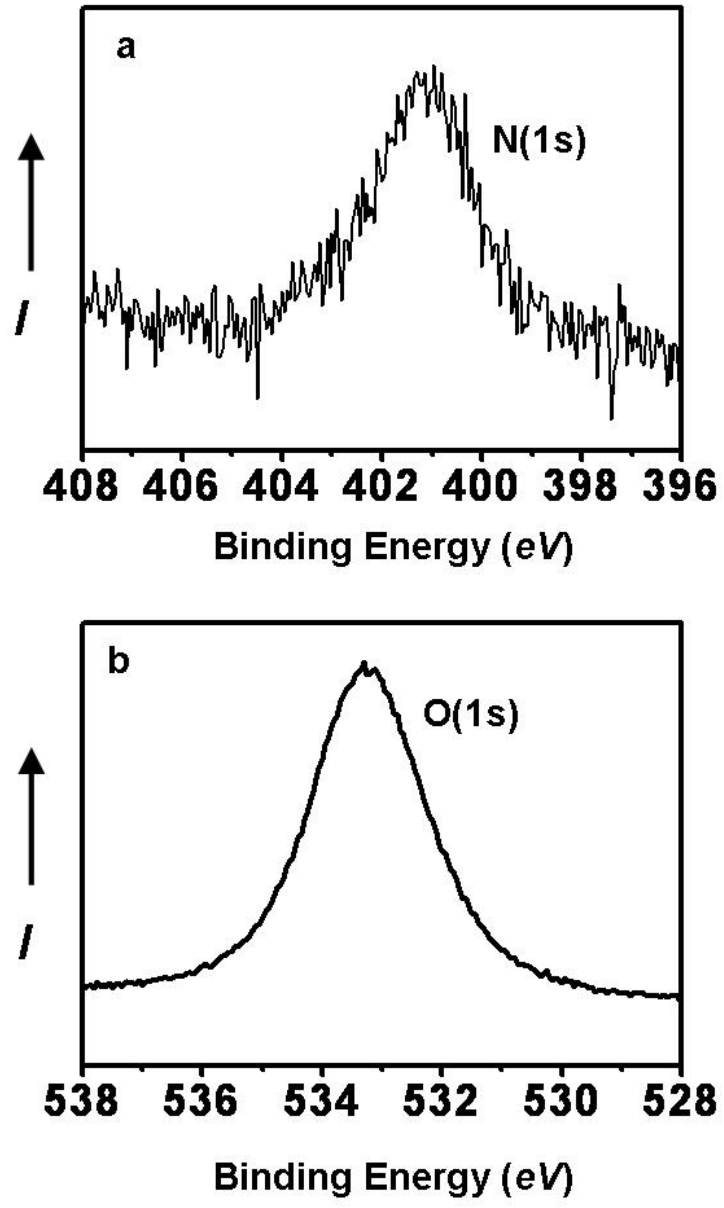


Figure S2. XPS N(1s) a) and O(1s) b) spectra of the PVP-coated nanowires. The peaks correspond to the PVP molecules absorbed on the surface of the nanowire.

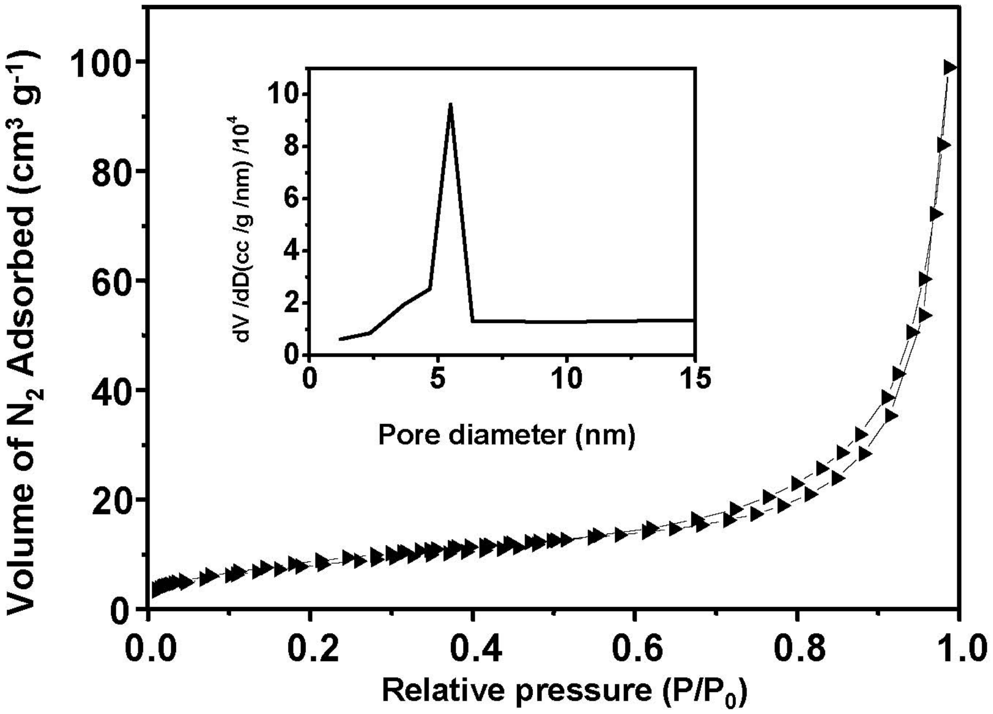
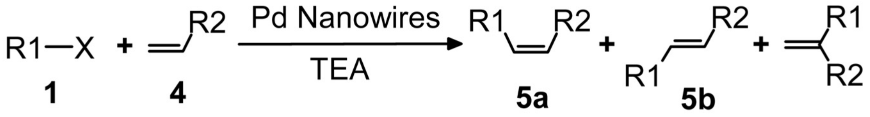
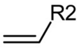
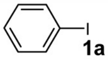
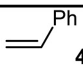
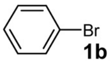
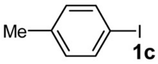
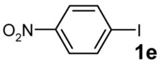
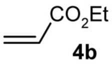


Figure S3. N_2 adsorption-desorption isotherms and Pore-size distribution (insert) of the Pd nanowires measuremed by Barrett-Joyner-Halenda analysis.

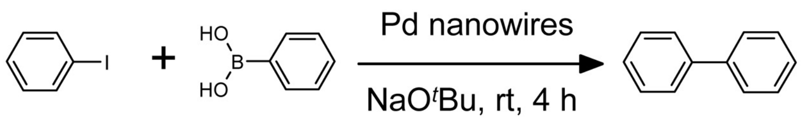
Table S1. Palladium nanowire-catalyzed Heck coupling of aryl halides and alkenes[a]



Entry	R1—X		Solvent	Temp[b]	*t* [h]	5a % Conv[b]	5b % Conv[b]
1	 1a	 4a	DMF	rt	48	2	85
2	**1a**	**4a**	DMF	120	8	18	81
3	**1a**	**4a**	H_2O	80	8	2	97
4[c]	**1a**	**4a**	H_2O	80	10	1	7
5	**1a**	**4a**	E/W[d]	80	8	2	94
6	 1b	**4a**	DMF	120	11	9	87
7	**1b**	**4a**	E/W[d]	80	8	2	98
8	 1c	**4a**	E/W[d]	80	36	16	76
9	 1e	**4a**	DMF	80	36	8	91
10	**1a**	 4b	E/W[d]	80	24	7	91
11	**1c**	**4b**	E/W[d]	80	24	6	81
12	**1e**	**4b**	DMF	80	48	1	98

[a] Reaction conditions: aryl halide (1 mmol), alkene (1.2 mmol), triethylamine (TEA) (2 mmol), Pd nanowire catalyst (6.5 mol %), total solvent volume (10 mL). [b] GC/MS yields. [c] The entry relates to an analogous reaction using Pd nanoparticles as catalysts. [d] E/W refers to a solvent mixture of ethanol and water (1:1; v:v).

Table S2. Recycling test of the Pd nanowires for room-temperature Suzuki coupling.[a]



Run[b]	1	2	3	4	5	6	7
% Conv[c]	99	99	99	99	99	99	99

[a] Reaction conditions: phenyl halide (1mmol), phenylboronic acid (1.2mmol), NaO^{t}Bu (2mmol), Pd catalyst (6.5 mol %), ethanol/water (2:3; v:v; total volume 10 mL). [b] After each run the catalyst was isolated by centrifugation, washed with EtOH three times and air-dried at room temperature for seven consecutive reactions. [c] GC yields.

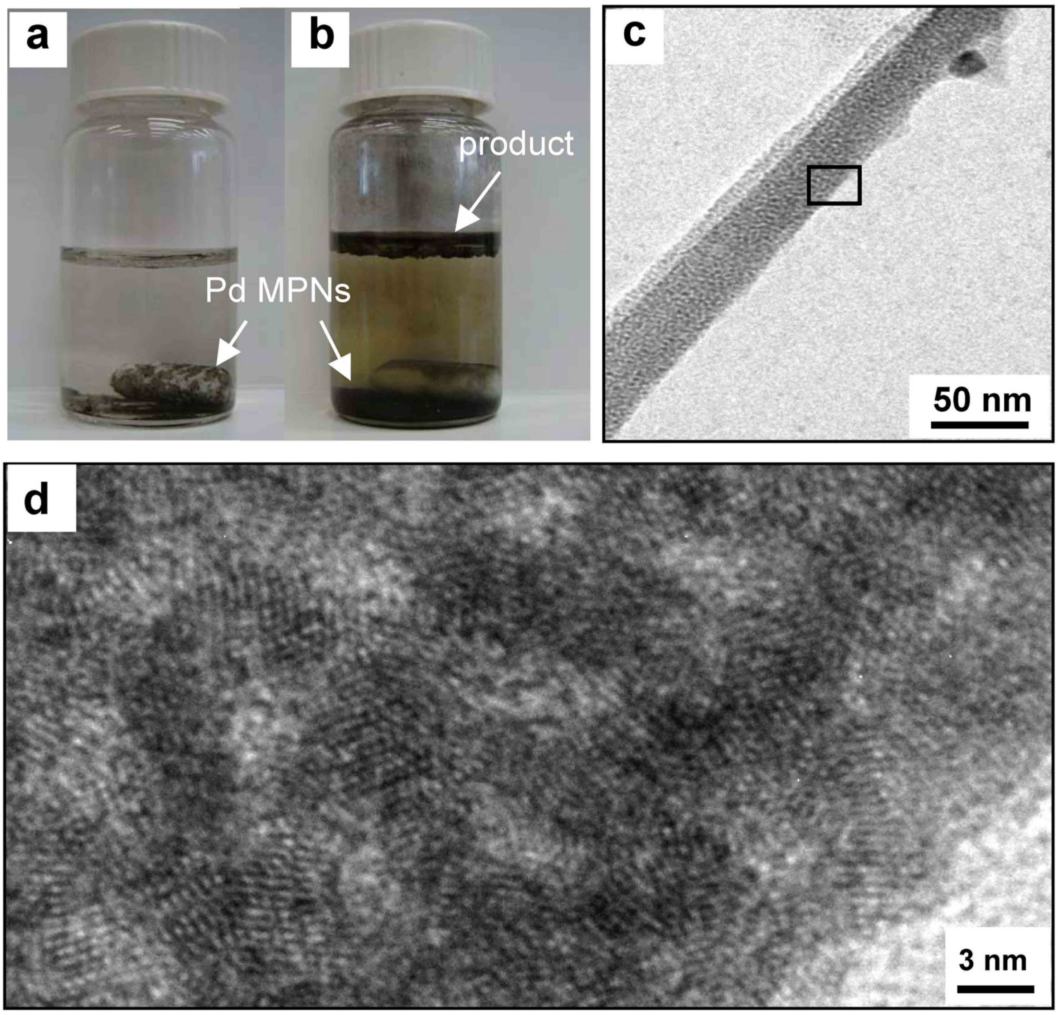


Figure S4. (a) Optical image of the reaction set-up for the room-temperature nanowire-catalyzed Suzuki coupling between iodobenzene and phenylboronic acid in water. (b) Optical image of the reaction set-up after 24 h. Note that the insoluble biphenyl product formed at water-air interface can be easily separated from the catalyst precipitated to the bottom of the solution. (c) TEM image of a recovered catalytic nanowire from the Suzuki reaction. (d) High-magnification TEM image of the nanowire shown in c. Note that the high density nanocontacts within the nanowire framework are essentially unaltered.