

# Nanodiamond Supported Ultra-Small Palladium Nanoparticles as an Efficient Catalyst for Suzuki Cross-Coupling Reactions

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## Experimental section

**General information.** All commercial reagents were applied as received unless otherwise mentioned. For analytical and preparative thin-layer chromatography, Merck 0.2 mm and 0.5 mm Kieselgel GF 254 pre-coated gels were used. Spots were visualized with iodine and UV light.

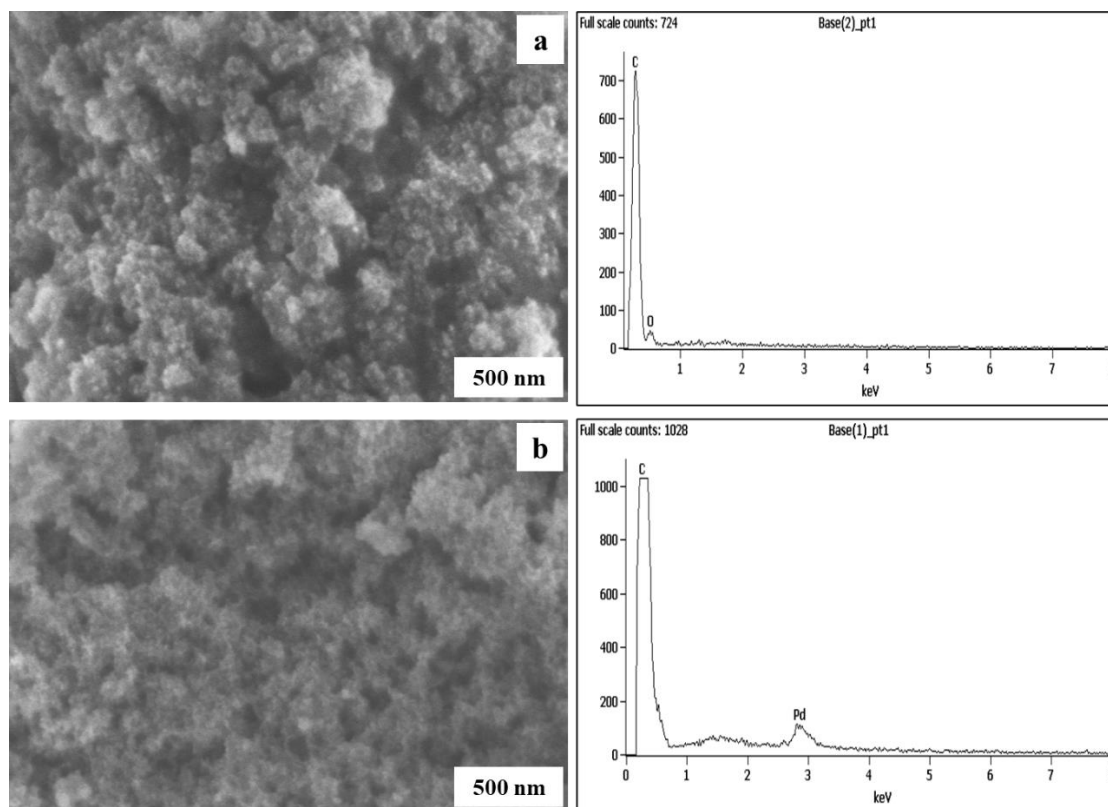
## Characterization techniques

A Hitachi SU6600 scanning electron microscope (SEM) with accelerating 15 kV voltage was used; energy dispersive spectrometry (EDS) was acquired via the SEM using a Thermo Noran System 7 Si(Li) Detector. The accelerating voltage was 15 kV and the acquisition time was 300 s. Each sample in a small Eppendorf tube was added to purified water and ultra-sonicated for 5 minutes. Suspensions were dropped on a copper grid with holey carbon film and dried in air. Transmission electron microscopy (TEM) analysis was performed on a JEOL JEM 2010F at 160kV of accelerating voltage. Microscopic images were obtained via a HRTEM TITAN 60-300 with an X-FEG type emission gun operating at 80 kV. This microscope was equipped with Cs image corrector and a STEM high-angle annular dark-field detector (HAADF). The point resolution was 0.06 nm in TEM mode. The elemental mappings were obtained via STEM-Energy Dispersive X-ray Spectroscopy (EDS) with an acquisition time of 20 min. For HRTEM analyses, the powder samples were dispersed in ethanol and ultrasonicated for 5 min. One drop of this solution was placed on a copper grid with holey carbon film. The sample was dried at room temperature.

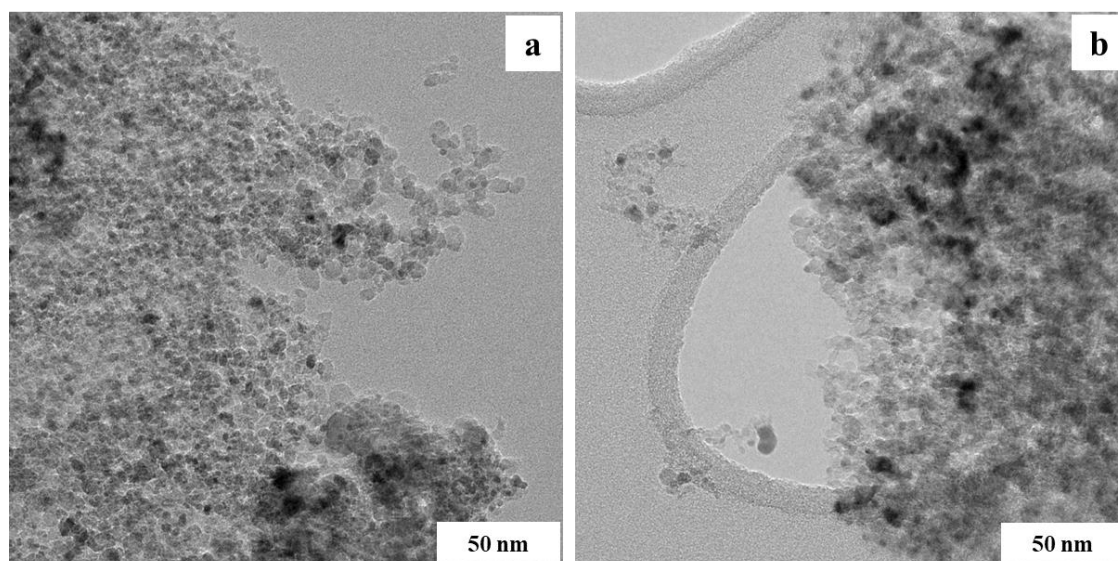
Powder samples of nanocomposite were mounted to the sample holder via double-sided tape (SCOTCH). The XPS measurement was carried out with a PHI 5000 VersaProbe II XPS system (Physical Electronics) using a monochromatic Al-K $\alpha$  source (15 kV, 50 W) with a photon energy of 1486.7 eV. Dual beam charge compensation was used for all measurements. All the spectra were measured in a vacuum of  $1.4 \times 10^{-7}$  Pa and at a room temperature of 22 °C. For high-resolution spectra, the pass energy was set up to 23.500 eV and a step size of 0.200 eV. The spectra were evaluated with MultiPak (Ulvac - PHI, Inc.) software. All binding energy (BE) values were referenced to the C1s peak at 284.80 eV.

X-ray diffraction patterns were recorded with a PANalytical X'Pert PRO MPD (PANalytical, The Netherlands) diffractometer in the Bragg–Brentano geometry, Co-K $\alpha$  radiation (40 kV, 30 mA,  $\lambda = 0.1789$  nm) equipped with an X'Celerator detector and programmable divergence and diffracted beam anti-scatter slits. The measurement range was 2 $\theta$ : 5° - 105°, with a step size of 0.017°. The identification of crystalline phases was performed using High Score Plus software (PANalytical) that included the PDF-4+ database.

The amount of palladium Pd/rNDs and the quantity of palladium released from nanocomposites were determined using an atomic absorption spectrophotometer (AAS) ContrAA 300 (Analytik Jena, Germany) using a flame atomization method. For measurements on AAS, all samples were added into a solution of aqua regia (6,5 wt %) and shaken for two hours in order to quantitatively dissolve the palladium. For confirmation of AAS data, ICP-MS analysis was applied; samples were dissolved in a mixture of concentrated HNO<sub>3</sub> and HCl (both Analpure, Analytika Ltd., Czech Republic) and filled-up to a defined volume with ultra-pure water. All elements were quantified via ICP-MS (Agilent 7700x, Agilent, Japan) using external calibration and appropriate isotopes. The conversion and selectivity of the reactions were analyzed via gas chromatograph Agilent 6820 (Agilent, United States) with a flame ionization detector (FID) and column DB5 (30x0.250x0.25). The following experimental parameters were used: an initial temperature of 100 °C, increased to 250 °C at a rate of 10 °C/min.



**Figure S1.** SEM images with EDS mapping of (a) oxidized nanodiamond and (b) catalyst Pd/rNDs.



**Figure S2.** TEM analysis of (a) fresh prepared Pd/rNDs catalyst and (b) Pd/rNDs catalyst after five cycles of Suzuki reaction.

**Table S1.** Comparison of selected heterogenous Pd catalysts used for Suzuki reactions.

Entry	Catalysts	Conditions	Conversion/Yield (%)	Ref.
1	Pd/rGO(org.mod.)	K <sub>2</sub> CO <sub>3</sub> , r.t., H <sub>2</sub> O:EtOH (1:1), 2 min (MWI)	8.4-100 <sup>a</sup>	1
2	Pd/AAPTm@GO	K <sub>3</sub> PO <sub>4</sub> , 90 °C, H <sub>2</sub> O, 25 min	32-98 <sup>b</sup>	2
3	Pd/CNTs	K <sub>3</sub> PO <sub>4</sub> , 90 °C, EtOH, 40 min.	90-100 <sup>b</sup>	3
4	Pd@MC	Na <sub>2</sub> CO <sub>3</sub> , 80 °C, H <sub>2</sub> O:EtOH (1:1), 60 min.	97-100 <sup>c</sup>	4
5	Pd NPs	K <sub>2</sub> CO <sub>3</sub> , r.t., H <sub>2</sub> O:EtOH (1:1), 35-240 min	82-95 <sup>b</sup>	5
6	Pd-ECN	K <sub>2</sub> CO <sub>3</sub> , 120 °C, H <sub>2</sub> O:DME (4.5:1.5), 10 min	24-73 <sup>b</sup>	6
7	PdNP@PPh <sub>2</sub> -SiO <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub> , 60 °C, H <sub>2</sub> O:PrOH (1:1), 5-6 h	58-98 <sup>b</sup>	7
8	Pd@MO <sub>x</sub>	K <sub>2</sub> CO <sub>3</sub> , 75 °C, H <sub>2</sub> O:EtOH (1:1), 15-120 min	>99 <sup>c</sup>	8
9	Pd@TMC-BpyCOP	K <sub>2</sub> CO <sub>3</sub> , 90 °C, Ethyl lactate, 1.5-8 h	59-95 <sup>b</sup>	9
10	Pd NPs	KF, r.t., DMF:H <sub>2</sub> O, 24 h	94 <sup>b</sup>	10
11	Pd <sub>np</sub> -2	K <sub>2</sub> CO <sub>3</sub> , 110°C, DMF, 4h	94 <sup>b</sup>	11
12	Pd/rNDs	K <sub>2</sub> CO <sub>3</sub> , Water: EtOH (1:1.5 mL), Temp 100 °C), 1-2.5 h	75-98 <sup>c</sup>	Present work

<sup>a</sup>Conversion, <sup>b</sup>Isolated yield, <sup>c</sup>GC/LC yield.

## References

1. Ibrahim, A. A.; Lin, A.; Adly, M. S.; El-Shall, M. S., Enhancement of the catalytic activity of Pd nanoparticles in Suzuki coupling by partial functionalization of the reduced graphene oxide support with p-phenylenediamine and benzidine. *J. Catal.* **2020**, 385, 194-203.
2. Rana, S.; Maddila, S.; Yalagala, K.; Jonnalagadda, S. B., Organo functionalized graphene with Pd nanoparticles and its excellent catalytic activity for Suzuki coupling reaction. *Appl. Catal. A: Gen.* **2015**, 505, 539-547.
3. Chen, X.; Hou, Y.; Wang, H.; Cao, Y.; He, J., Facile deposition of Pd nanoparticles on carbon nanotube microparticles and their catalytic activity for suzuki coupling reactions. *J. Phys. Chem. C* **2008**, 112 (22), 8172-8176.
4. Zhong, L.; Chokkalingam, A.; Cha, W. S.; Lakhi, K. S.; Su, X.; Lawrence, G.; Vinu, A., Pd nanoparticles embedded in mesoporous carbon: A highly efficient catalyst for Suzuki-Miyaura reaction. *Catal. Today*, **2015**, 243, 195-198.
5. Phukan, S.; Mahanta, A.; Kakati, D.; Rashid, M. H., Green chemical synthesis of Pd nanoparticles for use as efficient catalyst in Suzuki-Miyaura cross-coupling reaction. *Appl. Organomet. Chem.* **2019**, 33 (3), e4758.

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6. Chen, Z.; Vorobyeva, E.; Mitchell, S.; Fako, E.; Ortuño, M. A.; López, N.; Collins, S. M.; Midgley, P. A.; Richard, S.; Vilé, G.; Pérez-Ramírez, J., A heterogeneous single-atom palladium catalyst surpassing homogeneous systems for Suzuki coupling. *Nat. Nanotechnol.* **2018**, *13* (8), 702-707.
  7. Sahu, D.; Das, P., Phosphine-stabilized Pd nanoparticles supported on silica as a highly active catalyst for the Suzuki–Miyaura cross-coupling reaction. *RSC Adv.* **2015**, *5* (5), 3512-3520.
  8. Lichtenegger, G. J.; Maier, M.; Hackl, M.; Khinast, J. G.; Gössler, W.; Griesser, T.; Kumar, V. S. P.; Gruber-Woelfler, H.; Deshpande, P. A., Suzuki-Miyaura coupling reactions using novel metal oxide supported ionic palladium catalysts. *J. Mol. Catal. A Chem.* **2017**, *426*, 39-51.
  9. Han, Y.; Di, J.-Q.; Zhao, A.-D.; Zhang, Z.-H., Synthesis, characterization and catalytic performance of palladium supported on pyridine-based covalent organic polymer for Suzuki-Miyaura reaction. *Appl. Organomet. Chem.* **2019**, *33* (10), e5172.
  10. Ganapathy, D.; Sekar, G., Palladium nanoparticles stabilized by metal–carbon covalent bond: An efficient and reusable nanocatalyst in cross-coupling reactions. *Catal. Commun.* **2013**, *39*, 50-54.
  11. Dutta, P.; Sarkar, A., Palladium Nanoparticles Immobilized on Chemically Modified Silica Gel: Efficient Heterogeneous Catalyst for Suzuki, Stille and Sonogashira Cross-Coupling Reactions. *Adv. Synth. Catal.* **2011**, *353* (14-15), 2814-2822.