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Highly Functionalized SWCNTs with a Dopamine Derivative as a Support for Pd Nanoparticles: A Recyclable Catalyst for the Reduction of Nitro Compounds and the Heck Reaction

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Single-walled carbon nanotubes (SWCNTs) were functionalized with a dopamine derivative in which the amine group was converted to azide (dopamine azide). The direct reaction of SWCNTs and dopamine azide in *o*-dichlorobenzene at high temperature (160 °C) led to very highly functionalized CNTs (≈ 60 wt.%). Surprisingly, despite this high degree of functionalization, Raman spectroscopy detected a low disruption of the π -network of the carbonaceous support. This finding was justified by the rehybridization from sp^3 to sp^2 of the sidewall carbon atoms of CNTs involved in the functionalization process. Further characterization by means of different techniques such as X-ray photoelectron spectroscopy (XPS) analysis and transmission

electron microscopy (TEM) allowed to shed some light on the chemical composition and morphology of the obtained material. Moreover, the estimation of the total content of phenolic units and their reducing potential after CNTs functionalization was also assessed using Folin and Ciocalteu and 2,2-diphenyl-1-picryl hydrazide (DPPH) assays. The functionalization of CNTs was exploited to immobilize palladium(II) species that were subsequently reduced with NaBH_4 leading to the formation of Pd nanoparticles (NPs). The so obtained hybrid material was used as a recyclable heterogeneous catalyst for the reduction of nitro compounds and the Heck reaction.

Introduction

Carbon nanoforms (CNFs) and especially carbon nanotubes (CNTs) benefit from great popularity due to their widespread use for a plethora of applications in different research areas such as electronics, photonics, nanomedicine or their use for the production of high-performance composite materials.

All of these applications are due to their peculiar electronic properties, high thermal stability, and mechanical resistance, which can hardly be found in other materials. However, the full exploitation of such unique properties is hampered by a lack of compatibility and poor processability of the pristine CNFs in commonly used solvents due to their hydrophobicity and tendency to agglomerate because of the strong Van der Waals interactions.

The covalent functionalization of CNTs with specific moieties represents a valuable solution to this issue to improve their affinity with different solvents^[1] and impart peculiar properties, which are fundamental in many fields, such as catalysis.^[2] Certainly, the most widely used functionalization technique consists in the oxidative acid treatment of CNTs with the generation of defects onto their surface with the introduction of different oxygenated functions such as carbonyl, carboxyl, and hydroxyl^[3] or even, under the most harsh conditions, with formation of severe damage to the nanotube structure that can cause their shortening.^[4]

The alternative is to proceed with the direct covalent functionalization of pristine CNTs by means of different routes, avoiding any oxidative pre-treatment.^[5] However, any kind of nanotube modification, except for supramolecular modification, leads to the more or less severe disruption of the π -network with the rehybridization from sp^2 to sp^3 of the sidewall carbon atoms involved in the functionalization process. The partial loss of the π -conjugation constitutes a detrimental event that can affect the mechanical, electronic and thermal properties of CNTs.

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Attempts to retain the native properties of CNTs have been pursued, for example, by using mild oxidation conditions with the purpose of introducing carboxyl groups only at initial defects that already exist in the CNTs sidewall.^[3a] Furthermore, some theoretical studies have identified [2 + 1] cycloadditions onto CNTs sidewall as a potential route to preserve the π -conjugated electronic structure of CNTs by cleaving bond between adjacent sidewall carbons, recovering the sp^2 hybridization and the properties of the pristine CNTs.^[6] The experimental proof of such hypothesis was provided by Adeli, Haag, Reich et al.,^[7] and very recently by Donskyi and co-workers,^[8] who covalently functionalized SWCNTs by means of nitrene [2 + 1] cycloaddition reaction using the electron-poor monoazido-dichloro-triazine that allows the introduction of stable functionalities onto single-walled carbon nanotubes (SWCNTs) sidewall while preserving the aromaticity.

Here we have chosen dopamine as a precursor for the corresponding dopamine azide,^[9] which in turn was used for the functionalization of SWCNTs. The conversion of amine to the azide group in dopamine has considerable consequences on the course of oxidative polymerization of this catechol derivative as the cyclization routes leading to indole units are clearly suppressed and consequently the possibility to generate melanin like pigments commonly referred to as polydopamine.^[10] Mrówczyński et al.^[11] investigated the polymerization process of dopamine azide, which requires stronger oxidation conditions (NaIO_4) compared to native dopamine. Furthermore, the obtained polymers result soluble in organic solvents due to the lack of cross-linkage between building blocks consisting of dopamine azide monomers.

Several reports have described the properties of CNTs coated with polydopamine as obtained by exposure of the CNTs to dopamine solution under oxidative conditions. Though, under these conditions, the structure of the CNTs is not affected at all, deposition of the pigmented material cannot be controlled and excess can be formed assembling together the CNTs.^[12]

On this basis, the functionalization of SWCNTs with dopamine azide could represent a valuable route to get a selective controlled modification of SWCNTs avoiding the pigment formation that takes place when amino groups are present. It is also expected that this functionalization can both modify surface properties of the CNF and reduce to a minimum the disruption of π -network responsible for the unique properties of carbon nanotubes.

The presence of catechol moieties onto SWCNTs allowed their surface properties to be tailored, resulting in a material with high compatibility towards polar solvents and with the possibility to exploit the *o*-diphenol functionalities as binding sites for different metal species.

A high degree of functionalization of SWCNTs (≈ 60 wt.%) with catechol moieties was obtained with a relatively low increase in the D band intensity (I_D) with respect to the G band (I_G) as detected by Raman spectroscopy, indicating that there was only a partial loss of the original π -network of pristine SWCNTs. This result could have interesting implications in certain application fields of CNFs that require both high

electrical conductivity and specific surface properties such as in the case of SWCNTs-based sensors.^[13]

The catechol functionalized SWCNTs were used as support and stabilizer for palladium nanoparticles (Pd NPs) and the resulting hybrid material was tested for two catalytic applications, namely the reduction of nitro compounds and the Heck reaction.

Results and Discussion

The diazotransfer reaction allowed to convert dopamine **1** into the corresponding dopamine azide **2**,^[9] which was reacted in refluxing *o*-dichlorobenzene (*o*DCB) and under an argon atmosphere in the presence of pristine SWCNTs. Under these conditions, the direct functionalization of SWCNTs was achieved resulting in material **5** (Scheme 1). The use of dopamine azide was initially selected with the aim of exploiting the well-established functionalization route of CNTs via *in situ* generated reactive nitrenes.^[14]

Surprisingly, thermogravimetric analysis (TGA) under air flow (Figure 1), showed an unusually high functionalization degree of material **5**. A 59.5 wt.% loading was estimated taking into account the weight loss at 530 °C, at which temperature pristine SWCNTs are still stable with only 1 wt.% loss. We therefore questioned the reasons for this result.

Recently, Mrówczyński et al.^[11] have shown that the polymerization of dopamine azide can only be achieved under highly oxidizing conditions (NaIO_4), producing polymers soluble in organic solvents.

Herein no oxidant was used and the reaction of functionalization of SWCNTs was carried out under inert atmosphere in refluxing *o*DCB. Therefore, it can be assumed that oxidation and polymerization process of dopamine azide (**2**) under the reaction conditions herein adopted play a marginal role in the functionalization process of SWCNTs, although some oxidation due to the presence of adventitious oxygen and the high temperature adopted cannot be ruled out at all.

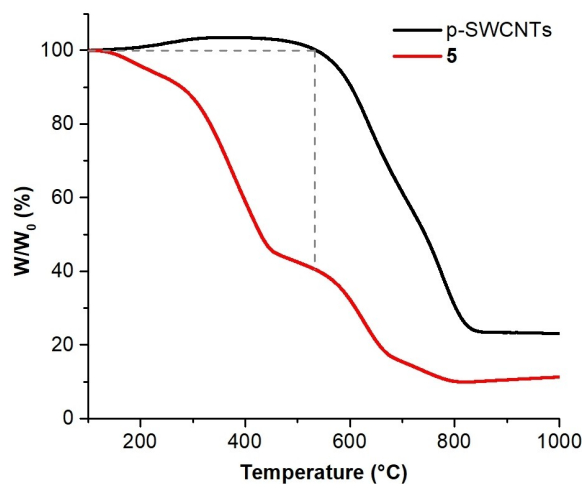
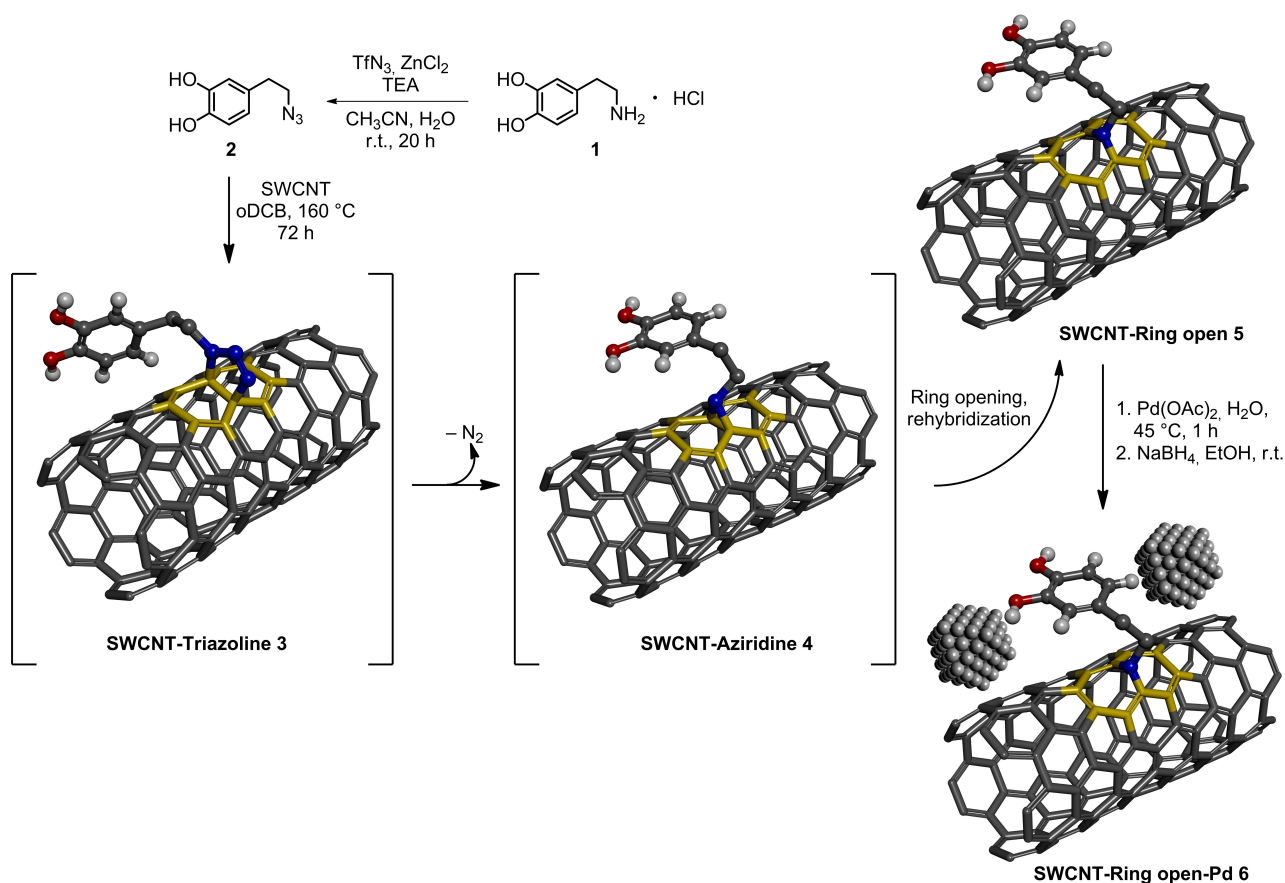


Figure 1. Thermogravimetric analysis under air flow of p-SWCNTs and **5**.



Scheme 1. Preparation of the functionalized SWCNTs material 5 by means of the formation of the proposed 1,2,3-triazoline adduct 3 and immobilization of Pd NPs to obtain hybrid 6.

To obtain further evidence and shed some light on why such a high functionalization degree of SWCNTs was obtained, in an additional blank test the dopamine azide was refluxed in oDCB under inert atmosphere for 72 h without the presence of SWCNTs. If thermal decomposition of the organic azide takes place, initial extrusion of nitrogen occurs with the formation of the nitrene species, which can undergo stabilization through different reactions leading to consumption of the starting azide, such as isomerization to imines, dimerization to azo compounds, hydrogen abstraction followed by ring closure to heterocyclic compounds, among others.^[15] The result of this experiment was quite interesting, indeed, it was possible to recover the starting dopamine azide (2) along with traces of a residue, probably generated as a result of oxidation and polymerization of catechol moieties, slightly soluble in dimethyl sulfoxide (see blank test in the Experimental Section). FTIR analysis of this residue (Figure 2) was in accordance with that shown by Mrówczyński and co-workers still confirming the presence of both azido group (2100 cm^{-1}) and a network of H-bonded hydroxyl groups ($3500\text{--}3200\text{ cm}^{-1}$). These results allowed us to draw some preliminary conclusions: 1) dopamine azide 2 has a very high thermal stability that can probably undergo classical azide decomposition with the formation of nitrene moiety only under very harsh conditions; 2) the oxidation/polymerization process of the catechol moiety is a

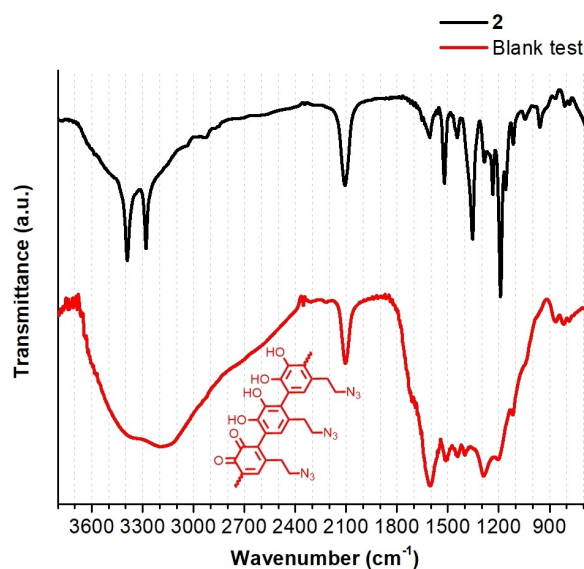


Figure 2. FTIR spectra of dopamine azide 2 and the residue recovered from the blank test.

secondary path that can nevertheless contribute to the functionalization of SWCNTs by means of the reactive azide moieties 3) as a consequence of the first observation, it is

proposed that dopamine azide, in analogy to fullerene C_{60} reactivity with aryl azides,^[16] reacts with SWCNTs by means of an azide-alkene [3 + 2] cycloaddition to form 1,2,3-triazoline adduct **3**, which evolves to the formation of aziridine derivative **4** as a result of nitrogen extrusion at high temperature (Scheme 1). There are some aspects in favour of this hypothesis. First of all, the thermal stability of organic azides is strongly dependent on the nature of substituent and the temperature of decomposition with the generation of nitrene intermediate decreases in the order alkyl/aryl azides > azidoformates and sulfonyl azides > acyl azides.^[15,17] This means that if at high temperature the chosen azide does not decompose with the extrusion of nitrogen and the formation of nitrene derivative, then, the [3 + 2] cycloaddition of azide to the sidewall of CNTs will be favoured over [2 + 1] route. Thermogravimetric/differential scanning calorimetry analysis (TGA/DSC) under nitrogen atmosphere of the dopamine azide **2** (Figure S1) proved that it was stable up to 200 °C, quite above 160 °C adopted in the reaction conditions for the functionalization of SWCNTs. In particular, dopamine azide decomposes with an exothermic process between 190 and 265 °C. The onset temperature of exothermic decomposition ($T_{on, exo}$) is 200 °C and the maximum heat flow of 1.62 W/g was reached at 236 °C.

Further investigations about structural changes of SWCNTs in material **5** were carried out by means of Raman spectroscopy (Figure 3), which represents a powerful technique to assess the covalent functionalization of SWCNTs by the change in the intensity ratio of the D band to the G band (I_D/I_G) compared to I_{D0}/I_{G0} ratio in the pristine SWCNTs. Despite the very high functionalization degree of 59.5 wt.% (see above) a relatively low normalized I_D/I_G ratio from the I_{D0}/I_{G0} ratio of 1.85 was detected, leading one to wonder how such high functionalization degree was eventually reached.

A plausible explanation of such results could have been provided by Adeli, Haag, Reich et al.,^[7] and very recently by Donskyi and co-workers,^[8] who obtained high degree of functionalization up to one functional moiety per 25 carbon

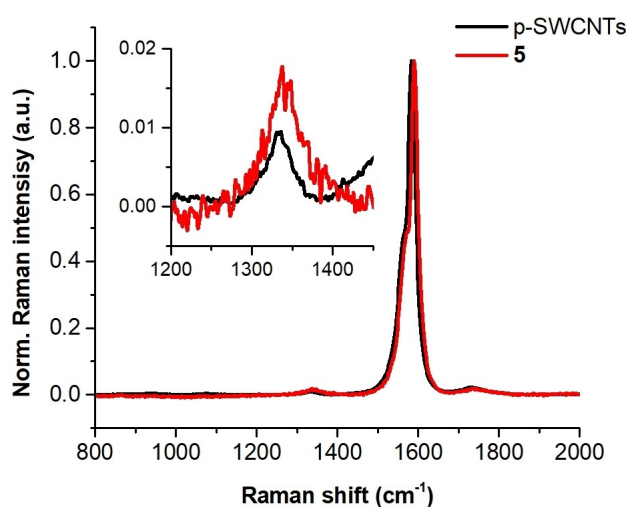


Figure 3. Raman spectra of p-SWCNTs and **5**. The inset shows the increase of the intensity of the D band of material **5**.

atoms and proved experimentally what until then had only been theorized,^[6] namely that the covalent functionalization of SWCNTs with an electron-poor aromatic azide led to a non-destructive covalent functionalization still maintaining the electronic and optoelectronic properties of SWCNTs preserving the π -network of the pristine carbon nanoform. An initial in situ generation of a nitrene that can undergo to [2 + 1] cycloaddition to form an aziridine derivative, whose strained ring opens to the final rehybridized structure with the recovering of the π -network of SWCNTs has been hypothesised. Quantum chemical calculations predict that the entire reaction proceeds without activation barrier at room temperature.^[7]

In the present work, if the thermal stability of dopamine azide (**2**) is taken into account, the same conclusions can be drawn when the initial stage is constituted by the [3 + 2] cycloaddition of the azide derivative onto SWCNTs sidewalls with the generation of the corresponding triazoline **3**, which after nitrogen extrusion can evolve in the formation of the aziridine derivative **4** and eventually in the open form **5** (Scheme 1) in analogy to the reaction of fullerene C_{60} with alkyl azides leading to the preferential formation of the [5,6]-open isomer.^[18] However, it should be emphasized that the distinction between the direct (formation of nitrene) and the indirect ([3 + 2] cycloaddition) method for the formation of aziridines from organic azides and alkenes remains a hard task. One way to discriminate between the two routes is to perform a blank experiment in the reaction conditions in absence of any olefin (see above) to assess the thermal stability of the chosen organic azide.

All the evidence gathered on the high functionalization degree of material **5** despite the small modification of the π -conjugate network leads to conclude that the modification of the nanotubes is mainly due to a [3 + 2] cycloaddition mechanism of dopamine azide **2** onto the nanotube sidewalls to obtain triazoline derivative **3** and the subsequent extrusion of nitrogen to form the aziridine derivative **4**, which subsequently undergoes partial rehybridization (the incomplete rearrangement could be due to the high functionalization degree reached: one functional moiety per ca. 10 carbon atoms) restoring the conjugate network of the nanotube in the material **5**.

The presence of intact phenolic units onto material **5** and their reducing potential was also assessed by use of chemical assays namely the Folin and Ciocalteu and the 2,2-diphenyl-1-picryl hydrazide (DPPH), measuring the presence of phenol groups and the hydrogen donor ability of a given material, respectively. Data in Table 1 confirm the presence of phenolic functionalities in material **5** that also exhibit a good hydrogen

Table 1. Results of the Folin-Ciocalteu assay and DPPH assay on the material **5** and its acetylated derivative **5Ac**.

Material	FOLIN-CIOCALTEU ASSAY (Gallic acid equivalents)	DPPH ASSAY (EC50 [mg/mL])
5	$4.17 \times 10^{-04} \pm 1.2 \times 10^{-05}$	$0.81 \pm 8.5 \times 10^{-03}$
5Ac	$5.07 \times 10^{-05} \pm 1 \times 10^{-05}$	$1.8 \pm 5 \times 10^{-02}$

donor ability as indicated by the EC_{50} value. For comparative purposes, and as a control that the observed activity was indeed due to the free catechol groups of the dopamine derivative linked to the SWCNT, a derivative of dopamine azide having the catechol groups protected as acetyl derivative was used for functionalization of the SWCNT. As expected, the resulting material **5Ac** gave a very low response to both assays.

Material **5** was used as support for palladium species by means of exposure to palladium acetate in distilled water at a SWCNT/Pd ratio of 9:1 over 1 h at 45 °C. After repeated washings, the material was subjected to a reduction treatment with sodium borohydride to obtain material **6** (Scheme 1). The palladium content of **6** was found to be of 1.27 wt.%, as determined by means of inductively coupled plasma optical emission spectroscopy (ICP-OES).

Both materials **5** and **6** were subjected to X-ray photoelectron spectroscopy (XPS) analysis (Figure 4 and Table S1). In Figure 4 high resolution XPS spectra of C1s, N1s regions for materials **5** and **6**, and Pd3d region for material **6** are shown. The C1s peak of both **5** and **6** shows the presence of five components at 284.6, 285.6, 286.4, and 287.4 eV characteristic of sp^2 and sp^3 carbon atoms, C–O and C–N, and C=O bonds, respectively. Furthermore, the peak centred at 290.6 eV is attributed to the shake-up satellite ($\pi \rightarrow \pi^*$) process,^[19] clearly visible in the C1s peak of pristine SWCNTs (Figure S7 and Table S2). N1s peak of both materials **5** and **6** show two contributions associated with aziridine at 399.0 eV (close structure)^[20] and open structure nitrogen atoms at higher binding energies.^[21] The atomic ratio between the two types of nitrogen atoms in material **5**, open and closed form, respectively, of about 78:22 (Table S1) confirms the preliminary results obtained by Raman spectroscopy, which showed a relatively low perturbation of the conjugated network of SWCNTs despite

of the high functionalization degree. Since, as mentioned above, the oxidation/polymerization process of the catechol moieties does not affect the azido groups, the absence of any azide-attributable peaks in the N1s region shows how all these functional groups totally reacted with the SWCNTs. The Pd3d spectrum of material **6** shows the presence of two doublets due to the typical spin-orbit splitting ($Pd3d_{5/2}$ and $Pd3d_{3/2}$ components) and the concomitant presence of two species of palladium, namely Pd(0) and Pd(II). The relative amount of the components due to Pd(0) and Pd(II) species allowed to estimate a degree of reduction of 56% after treatment with $NaBH_4$.

Transmission electron microscopy (TEM) was used to investigate the morphology of materials **5** and **6** (Figure 5). Pristine SWCNTs are arranged to form a highly entangled network of long carbonaceous structures (Figure 5a). Their functionalization with dopamine azide to obtain material **5** did not result in the dispersion of individual nanotubes, but rather in the presence of a dense network of rough filaments, probably due to both the establishment of numerous hydrogen bonds between the functionalized CNTs and the presence of a polymeric matrix arising from the partial oxidation of catechol moieties as stated above (Figure 5b). TEM micrograph of material **6** (Figure 5c) showed how the network of functionalized CNTs served as support for the stabilization of palladium nanoparticles, which are all clearly visible and uniformly dispersed throughout the material.

The catalytic activity of **6** was investigated in the reduction of nitrobenzene derivatives to the corresponding anilines. The catalytic performances were evaluated in terms of conversion, yield, selectivity, turnover number (TON, calculated as moles of nitrobenzene converted/moles of Pd), turnover frequency (TOF) and recyclability. Firstly, *p*-nitroaniline was picked out as the model substrate in the screening studies to improve reaction

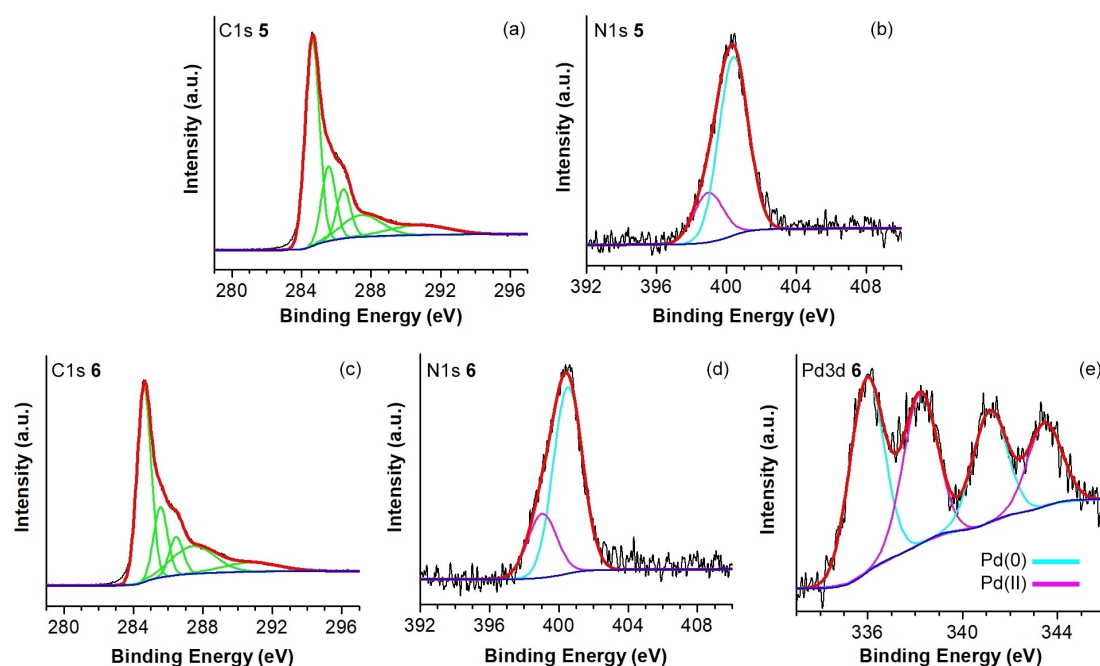


Figure 4. High resolution XPS spectra of C1s, N1s regions for materials a-b) **5** and c-d) **6** and Pd3d region for material e) **6**.

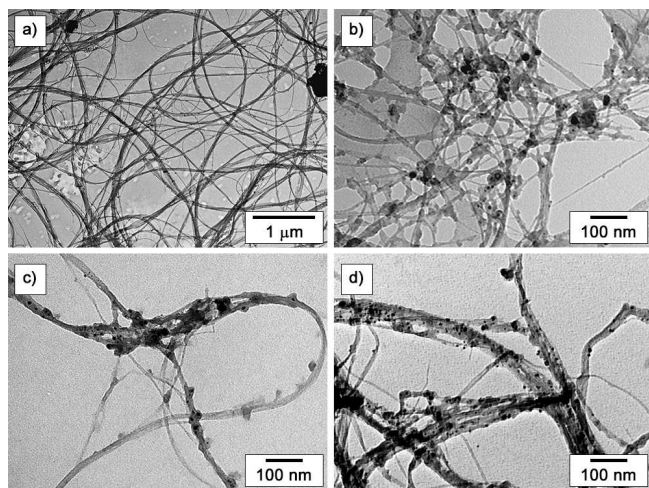


Figure 5. TEM images of a) pristine SWCNTs, b) materials 5, c) 6, and d) 6 after recycling tests in the Heck reaction.

conditions. Preliminary tests were performed in water by employing sodium borohydride as the hydrogen source. In one hour, with a catalytic loading of 0.02 mol% and using a molar ratio of 1:4 (substrate/hydrogen source), 72% conversion to the corresponding aniline was achieved (Table 2, entry 1). When the reaction was run in 2 h the conversion into the desired product was almost complete (entry 2). By increasing the amount of NaBH_4 a full conversion was recorded in only one hour (entry 3). An identical result was also obtained by doubling the amount of catalyst with a lower substrate/ NaBH_4 ratio of 1:2.5 (entry 4).

Table 2. Screening of reaction conditions for the reduction of 4-nitroaniline.^[a]

Entry	Catalyst [mol %]	NaBH_4 [mmol]	Time (h)	Conv. (%) ^[b] / TON ^[c] / TOF [h^{-1}] ^[c]	Selectivity [%]
1	0.02	4	1	72/3600/ 3600	> 99
2	0.02 ^l	4	2	98/4900/ 2450	> 99
3	0.02	8	1	> 99/5000/ 5000	> 99
4	0.04	2.5	0.5	> 99/2500/ 5000	> 99
5 ^[d]	0.005	4	2	73/14600/ 7300	> 99
6 ^[e]	–	8	1	< 5/–/–	> 99
7 ^[f]	SWCNT	8	1	8/–/–	> 99

[a] Reaction conditions: 4-nitroaniline (1 mmol), sodium borohydride (2.5 or 4 or 8 mmol), catalyst (0.005 or 0.02 or 0.04 mol%; 0.42 or 1.68 or 3.36 mg), water (5 mL), 30 °C, 1600 rpm. [b] Determined by ^1H NMR; isolated yield: $\geq 95\%$ of conversion. [c] TON and TOF values calculated based on the Pd content obtained from ICP. [d] Water (2 mL). [e] Without catalyst, water (5 mL). [f] In the presence of pristine SWCNT (0.8 mg).

Still a good conversion value (73%) and a very high TON value was reached when **6** was decreased to 0.005 mol% (entry 5). Notably, by conducting the reaction in the absence of the catalyst, using only sodium borohydride as the reducing agent, less than 5% conversion to the corresponding aniline occurred (entry 6) whereas in the presence of pristine SWCNTs a ca. 8% conversion was obtained (entry 7).

Considering the high catalytic activity of **6**, reaction conditions reported in Table 2, entry 3, were selected to explore the versatility of the hybrid material in the reduction of different aromatic nitro compounds, including aryl halides, phenols, and nitroarenes with aliphatic chain. Some of the catalytic tests were repeated, thus confirming the good reproducibility of the experiments. As mentioned in Table 3, in all the catalytic tests, a full selectivity toward the corresponding aniline was reached together with excellent TON and TOF values, without the noticeable influence of functional groups on the reaction.

In particular, the reduction of nitroarenes with strong electron-donating substituents in both ortho, meta and, para occurred quite rapidly, though reaction times were not optimized (entry 1–4). Less electro-donating alkyl chains gave the corresponding anilines in two hours (entry 5 and 6). The reduction of halogen-substituted nitroarene was effective within 1–4 h and selectively produced the corresponding anilines without any observable dehalogenation except for iodo as a substituent (entry 7–11). and 12, H_2 was used.

Indeed, in this case, dehalogenation occurred, which can be explained as a function of the less strong C–I bond (entry 11).

To thoroughly investigate the catalytic behavior and robustness of the solid, recycling experiments were conducted. The recyclability of the heterogeneous hybrid material **6** in the *p*-nitroaniline reduction was studied. As illustrated in Figure 6, **6** was reused for six consecutive runs without any considerable decrease of the catalytic performance. Overall, TON of 30,000 is achieved.

More in-depth studies on the recyclability of **6** have been carried out by changing substrates (Figure 7). In the first cycle

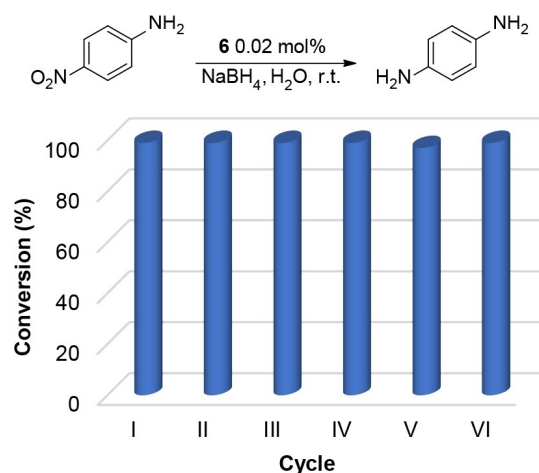
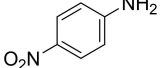
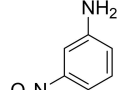
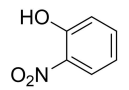
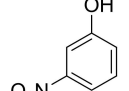
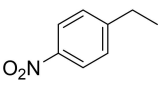
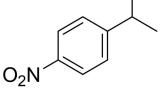
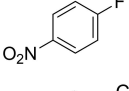
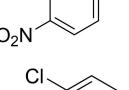
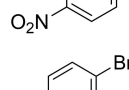
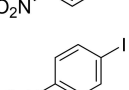
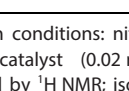


Figure 6. Recycling test of **6**. Reaction conditions: 4-nitroaniline (1 mmol), sodium borohydride (8 mmol), catalyst (0.02 mol%), water (5 mL), 30 °C, 1 h, 1600 rpm.

Table 3. Nitro-reduction reactions catalyzed by **6**.^[a]

Entry	Substrate	Time [h]	Conv. (%) ^[b] / TON ^[c] / TOF [h ⁻¹] ^[c]	Selectivity [%]
1		1	> 99/5000/ 5000	> 99
2		1	> 99/5000/ 5000	> 99
3		0.5	> 99/5000/ 10000	> 99
4		0.5	> 99/5000/ 10000	> 99
5		2	> 99/5000/ 2500	> 99
6		2	95/4750/2375	97
7 ^[d]		3	90/4500/1500	> 99
8		1	> 99/5000/ 5000	> 99
9		2	> 99/5000/ 2500	> 99
10		1	> 99/5000/ 5000	> 99
11 ^[e]		4	80/4000/1000	> 99

[a] Reaction conditions: nitro compounds (1 mmol), sodium borohydride (8 mmol), catalyst (0.02 mol%), water (5 mL), 30 °C, 1600 rpm. [b] Determined by ¹H NMR; isolated yield: ≥ 95% of conversion. [c] TON and TOF values calculated on the basis of the Pd content obtained from ICP. [d] Isolated yield 60%. [e] Dehalogenation occurred with the formation of aniline; selectivity, TON, and TOF values refer to the obtained aniline.

1-isopropyl-4-nitrobenzene was used (green), changing from the second cycle to 1-ethyl-4-nitrobenzene (orange). A decrease in catalytic activity in the second cycle was evident. The decrease in conversion at the second cycle is due to the poor dispersion of the catalyst. This was attributed to the fact that, in this case, the nitro derivative was added first and then the solvent. The catalyst, being hydrophilic, aggregates strongly on

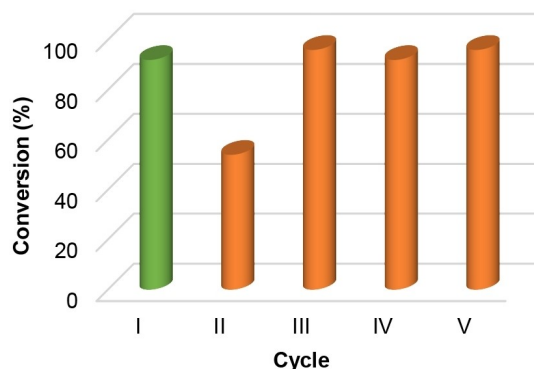
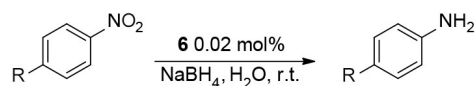


Figure 7. Recycling test of **6**. Reaction conditions: 1-isopropyl-4-nitrobenzene (green) or 1-ethyl-4-nitrobenzene (orange) (1 mmol), sodium borohydride (8 mmol), catalyst (0.02 mol%), water (5 mL), 30 °C, 1 h, 1600 rpm.

contact with the liquid hydrophobic reactant and remains in that aggregated form even after the addition of water. But the situation turned out to be reversible. After recovering the used catalyst and changing the order of addition, conversion returns quantitatively without further treatment. Once again, the catalyst was shown to be versatile, robust and reusable for multiple runs.

Finally, the remarkable catalytic activity of **6** was compared with several reported catalytic systems. Table 4 shows that **6** is highly competitive with other systems used in the nitro reduction reaction. Even if some of these systems require lower amount of reducing agent or shorter reaction times, usually a larger amount of catalyst was used, up to 50–60 mg per mmol. Among these examples, a similar material was prepared by polymerization of catechol with terephthalaldehyde under basic condition (Pd@MOPOH).^[32]

Palladium was immobilized from a Pd(NO₃)₂ solution followed by reduction with NaBH₄. Pd@MOPOH was used for the reduction of 4-nitrophenol at r.t. by using a 100-fold excess of NaBH₄ and a very high catalytic loading following the reaction spectroscopically (UV). Recycling tests were carried out on 6 mmol scale with 10 mg of catalyst. The reaction was complete in a short time (6 min), but no other substrates were investigated.

Material **6** was also tested as catalyst for the Heck reaction. As first approach, recyclability was investigated. The probe reaction was the C–C coupling between 4-iodoanisole and methyl acrylate (Table 5). The reaction was carried out in the presence of triethylamine (TEA) and DMF as solvent at 105 °C. A blank test with pristine SWCNTs gave no product. In the first two runs, catalyst was used in 0.125 mol% for 3 h giving complete conversion and almost quantitative isolated yield. Then, we halved the amount of catalyst (0.062 mol%) maintaining the reaction time. Conversion was complete (entry 3). In the following runs we continued decreasing the amount of catalyst down to 0.025 mol%. After 6 runs, complete conversions were observed after 3 h of reaction (entries 4–6). Decreasing the

Table 4. Comparison of catalytic performance of different heterogeneous catalysts based on palladium nanoparticles in the nitro reduction of p-nitroaniline.

Entry	Catalyst	Conv. [%]/TON/TOF [h ⁻¹]	mol %	Reaction conditions ^[a]	Ref.
1	6	99/5000/5000	0.02	1:8; 1 h; 30 °C; H ₂ O	This work
2	6	98/4900/2450	0.02	1:4; 2 h; 30 °C; H ₂ O	This work
3	Pd@NC	95/95/3166	1	1:2; 2 m; r.t.; H ₂ O/EtOH	[22]
4	PdNi–G2-Fe ₃ O ₄ –GO	93/465/1409	0.21	1:2; 20 m; r.t.; H ₂ O	[23]
5	Fe ₃ O ₄ @Guanidine-Pd	96/738/1119	0.13	1:2; 40 m; r.t.; H ₂ O	[24]
6	PdCl ₂ (Bbtb-H) ₂	80/80/40	1	1:4; 2 h; r.t.; EtOH	[25]
7	Ti _{0.97} Pd _{0.03} O _{1.97}	91/541/2164	0.17	1:4; 15 m; r.t.; MeOH	[26]
8	Pd@CQD@Fe ₃ O ₄	90/11250/2812	0.008	1:2; 4 h; r.t.; H ₂ O/EtOH	[27]
9	Pd@PANI	90/3300/5000	0.026	1:2.5; 0.66 h; r.t.; H ₂ O	[28]
10	Pd@CNx	94/82/628	1.15	1:3 (H ₃ B-NH ₃); 8 m; r.t.; H ₂ O	[29]
11	Pd _{1.4} /TB-COF	69/386/162	0.2	H ₂ ; 3 h; 40 °C; EtOH	[30]
12	Pd/COF-BASU2	99/58/72	1.71	H ₂ ; 50 m; 75 °C; H ₂ O/EtOH	[31]

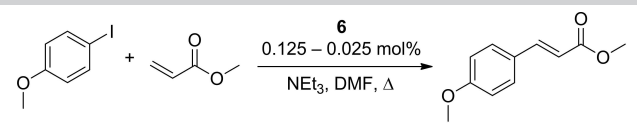
[a] Substrate/NaBH₄ or substrate/H₃B-NH₃ ratio; time; temperature; solvent. In entries 11.

reaction time to 1 h (entries 7–10) still high conversions were observed, albeit in two runs the reaction was not complete. A final run, the 11th, was carried out under the same condition but at lower temperature, also in this case conversion was still good. This investigation clearly showed two important aspects i.e. recyclability and optimization. The material appears to be recoverable and reusable, at least for 11 cycles with a total TON of 33,000.

In addition, TEM micrographs of catalyst **6** after recycling showed no remarkable differences with respect to fresh catalyst (Figure 5d).

Furthermore, we have found that the reaction can be carried out under mild conditions being the catalyst used only at 0.025 mol% in a short reaction time. These reaction conditions (catalyst: 0.025 mol%; 105 °C; 1 h) were used in the reaction between methyl acrylate and a small set of iodobenzene compounds (Table 6). Products were obtained in excellent conversions and yields. In the case of reaction between 4-iodoanisole and styrene, a lower conversion was obtained (77%, entry 7).

Table 5. Recycling test of **6** in the reaction between 4-iodoanisole and methyl acrylate.^[a]



Cycle	Catalyst [mol %]	4-iodoanisole [mmol]	t [h]	T [°C]	Conv. (%) ^[b] /TON ^[c] /TOF [h ⁻¹] ^[c]
1	0.125	0.5	3	105	>99/800/267
2	0.125	0.5	3	105	>99/800/267
3	0.062	0.5	3	105	>99/1613/538
4	0.031	1	3	105	>99/3226/1075
5	0.025	1	3	105	>99/4000/1333
6	0.025	1	3	105	>99/4000/1333
7	0.025	1	1.5	105	97/3880/2587
8	0.025	1	1.5	105	97/3880/2587
9	0.025	1	1	105	>99/4000/4000
10	0.025	1	1	105	>99/4000/4000
11	0.025	1	1	80	70/2800/2800

[a] Reaction conditions: 4-iodoanisole (1 equiv.), methyl acrylate (1.1 equiv.), triethylamine (1.2 equiv.), DMF (1 mL). [b] Determined by ¹H NMR with a yield of 98% of the conversion. [c] TON and TOF values calculated based on the Pd content obtained from ICP.

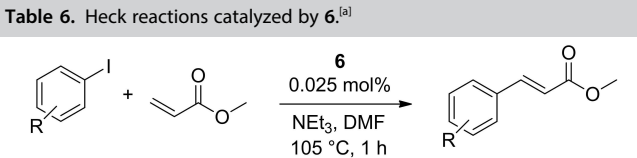
Conclusions

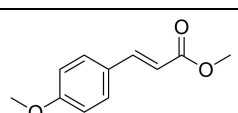
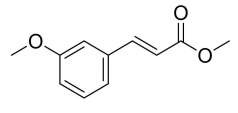
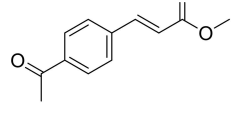
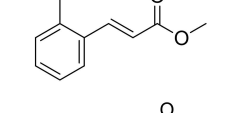
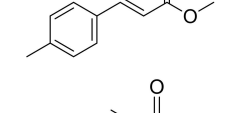
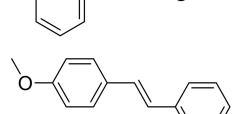
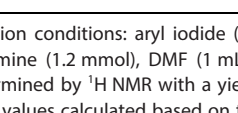
Single-walled carbon nanotubes were efficiently functionalized with a dopamine derivative, namely dopamine azide in which the amine group was converted to azide. Despite the high degree of functionalization of CNTs, Raman spectroscopy showed only a minor disruption of the π -network of the carbonaceous support. This finding was justified by taking into account the rehybridization process from sp^3 to sp^2 of the sidewall carbon atoms of CNTs after functionalization. The obtained material was thoroughly characterized, and the presence of the catechol units was exploited to immobilize palladium nanoparticles. The hybrid material was then used as active and recyclable catalyst for the reduction of nitro compounds and the Heck reaction.

Experimental Section

Materials and methods: Chemicals and solvents were purchased from commercial suppliers (TCI chemicals, Sigma Aldrich) and used as received without further purification. SWCNTs were provided by TUBALLTM. UV-vis spectra were recorded on a Jasco V-730 Spectrophotometer. Transmission electron microscopy (TEM) images were recorded using a Philips Tecnai 10 microscope operating at 80–100 kV. Thermogravimetric analyses (TGA) were performed under air flow from 100 to 1000 °C with a heating rate of 10 °C min⁻¹.

Table 6. Heck reactions catalyzed by **6**.^[a]



Entry	Product	Conv. [%] ^[b]	TON ^[c]	TOF [h ⁻¹] ^[d]
1		> 99	4000	4000
2		> 99	4000	4000
3		> 99	4000	4000
4		> 99	4000	4000
5		> 99	4000	4000
6		> 99	4000	4000
7 ^[d]		77	3080	1026

[a] Reaction conditions: aryl iodide (1 mmol), methyl acrylate (1.1 mmol), triethylamine (1.2 mmol), DMF (1 mL), catalyst (0.025 mol%), 105 °C, 1 h. [b] Determined by ¹H NMR with a yield of 98% of the conversion. [c] TON and TOF values calculated based on the Pd content obtained from ICP. [d] Styrene (1.1 mmol), 3 h.

with a Mettler Toledo TGA/DSC STAR System. All samples were maintained at 100 °C for 30 min to remove the adsorbed water. The X-ray photoelectron spectroscopy (XPS) analyses were carried out with a VG Microtech ESCA 3000 Multilab, equipped with a dual Mg/Al anode. As excitation source was used the Al K α radiation (1486.6 eV). The sample powders were mounted on a double-sided adhesive tape. The pressure in the analysis chamber was in the range of 10⁻⁸ Torr during data collection. The constant charging of the samples was removed by referencing all the energies to the C 1s binding energy set at 285 eV. Raman spectra were acquired using Horiba LabRam HR Evolution equipment with a 532 nm laser line, using a spectral resolution of about 7 cm and a laser intensity that does not interfere with the signal. IR spectra (film for compound **2** and KBr pellet for blank test) were recorded on an Agilent Technologies Cary 630 FTIR spectrometer. ¹H NMR spectra were recorded on a Bruker 300, 400 or 600 MHz spectrometers using CDCl₃, CD₃OD or (CD₃)₂SO as solvent. Mass spectra were obtained using a GC-MS apparatus (Agilent technologies 7000 C GC/MS Triple Quad – 7890B GC System) at 70 eV ionization voltage.

Inductively coupled plasma optical emission spectroscopy (ICP-OES) was carried out with an Optima 8000 Spectrometer.

Synthesis of dopamine azide **2:** Dopamine azide **2** was prepared following a procedure previously reported in literature.^[9] In a 50 mL two-necked round bottom flask, TfN₃ was freshly prepared by means of the slow addition of Tf₂O (1.6 mL, 9.54 mmol, 1.2 equiv.) to an ice-cooled suspension of NaN₃ (1.879 g, 28.62 mmol, 3.0 equiv.) in CH₃CN (10 mL). The mixture was stirred at 0 °C for 2 h under an argon atmosphere. In another 100 mL two-necked round bottom flask, a solution of dopamine hydrochloride salt **1** (1.538 g, 7.95 mmol, 1.0 equiv.) and ZnCl₂ (112 mg, 0.80 mmol, 0.1 equiv.) in 37.5 mL H₂O:CH₃CN (3:7) were taken. Then Et₃N (4.1 mL, 28.62 mmol, 3.0 equiv.) and freshly prepared TfN₃ were added. The reaction was stirred at rt overnight under an argon atmosphere. The reaction mixture was filtered and washed with CH₃CN. The filtrate was concentrated under vacuum and then extracted with EtOAc (3 x 20 mL). The organic layers were collected, dried over Na₂SO₄ and concentrated. The crude product was purified by flash column chromatography (hexane/ethyl acetate 2:1 v/v) to give desired azide **2** in quantitative yield (1.424 g). ¹H NMR (400 MHz, CDCl₃) δ = 6.81 (d, *J* = 8.1 Hz, 1H), 6.74 (d, *J* = 2.0 Hz, 1H), 6.66 (dd, *J* = 8.1, 2.0 Hz, 1H), 5.28 (sbr, 2H), 3.45 (t, *J* = 7.2 Hz, 2H), 2.78 (t, *J* = 7.2 Hz, 2H) ppm; ¹³C NMR (150 MHz, CDCl₃) δ = 143.6, 142.2, 131.1 (quat.), 121.3, 115.9, 115.6 (aromatic CH), 52.6 (CH₂N₃), 34.6 (ArCH₂) ppm.

Preparation of material **5:** In a two-necked round bottom flask, 125 mg of SWCNTs were dispersed in 120 mL of oDCB by means of sonication (4 x 20') followed by vigorous stirring (3 x 20'). The dispersion was then stirred under argon atmosphere at 40 °C overnight. After that a solution of dopamine azide **2** (344 mg, 1.92 mmol) in 5 mL of oDCB was added and argon was bubbled in the reaction mixture for 30 min before increasing the temperature up to 160 °C and allowing it to react at this temperature and under argon atmosphere for 72 h. Afterwards, the reaction mixture was filtered under reduced pressure through a PTFE membrane filter (pore size 0.45 μ m) and washed with dimethylformamide. The black residue was then collected from the filter, suspended in dimethylformamide, sonicated and filtered again. The washings with DMF were repeated several times until a light-yellow filtrate was obtained. The washings were continued with diethyl ether and the residue was finally dried at 60 °C under reduced pressure to give 320 mg of a black solid.

Preparation of material **6 from **5** by Pd loading:** The SWCNT/Pd catalyst was prepared as previously described with slight modifications.^[33] Briefly, **5** (200 mg) was dispersed in a solution of Pd(OAc)₂ (22 mg, 98 μ mol) in distilled water (7 mL) and stirred vigorously for 1 h at 45 °C. The material was then collected by centrifugation at 7000 rpm at 4 °C, washed times with acetone (3x10 mL) and distilled water (3x10 mL) and lyophilized to give a black powder (yield 95% w/w).

The material was then suspended in 20 mL of absolute ethanol and put under vigorous stirring before a solution of NaBH₄ (30 mg, 0.75 mmol) in 3 mL of absolute ethanol was added dropwise. The resulting mixture was stirred at room temperature for 15 h and then filtered under reduced pressure through a PTFE membrane filter (pore size 0.45 μ m). The material was washed with water, methanol and Et₂O, and finally dried at 40 °C under reduced pressure (180 mg of a black solid). 1.27 wt.% Pd was measured by ICP-OES analysis.

Synthesis of acetylated dopamine azide **2Ac:** The compound **2Ac** was synthesized by adapting a procedure reported elsewhere.^[34] In a two-necked round bottom flask, and under an argon atmosphere, a solution of **2** (1.002 g, 5.59 mmol) in acetic anhydride (5.4 mL)

and dry pyridine (270 μ L) was transferred. The reaction mixture was kept in an ultrasound bath at 200 W for 40 min, then evaporated under reduced pressure and the crude was purified by flash column chromatography (hexane/ethyl acetate 3:1 v/v) to afford **2Ac** as a yellow oil (855 mg, 58%). Spectroscopic data are in accordance with those reported in literature.^[35] $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.15–7.05 (m, 3H), 3.53 (t, $J=7.3$ Hz, 2H), 2.9 (t, $J=7.3$ Hz, 2H), 2.29 (s, 3H), 2.28 (s, 3H) ppm; $^{13}\text{C NMR}$ (150 MHz, CDCl_3) $\delta=168.3$, 168.2 (C=O), 142.0, 140.8, 136.9 (quat.), 126.9, 123.7, 123.5 (aromatic CH), 52.0 (CH_2N_3), 34.6 (ArCH_2), 20.6 (CH_3CO) ppm. GC-MS (EI, 70 eV) m/z (%) = 263 ([M]⁺, 1), 179(22), 151(51), 123(100), 136(11), 43(88).

Preparation of material 5Ac: In a two-necked round bottom flask, 100 mg of SWCNTs were dispersed in 95 mL of oDCB by means sonication (4x20') followed by vigorous stirring (3 x 20'). The dispersion was then stirred under argon atmosphere at 40°C overnight. After that a solution of **2Ac** in 5 mL of oDCB was added and argon was bubbled in the reaction mixture for 30 min before increasing the temperature up to 160°C and allowing it to react at this temperature and under argon atmosphere for 72 h. Afterwards, the reaction mixture was filtered under reduced pressure through a PTFE membrane filter (pore size 0.45 μ m) and washed with dimethylformamide. The black residue was then collected from the filter, suspended in dimethylformamide, sonicated and filtered again. The washings with DMF were repeated several times until a light-yellow filtrate was obtained. The washings were continued with diethyl ether and the residue was finally dried at 60°C under reduced pressure to give 153 mg of a black solid.

Blank test: In a 100 mL two-necked round bottom flask, dopamine azide **2** (225 mg; 1.26 mmol) and 50 mL of oDCB were charged. The flask was connected to a reflux condenser under the protection of an argon atmosphere. Argon was bubbled in the solution for 20 min before raising the temperature up to 160°C. The reaction was maintained under stirring at this temperature for 72 h. The solvent was removed under vacuum and the residue was taken with diethyl ether and transferred in a centrifuge tube. After centrifugation at 4000 rpm, the supernatant was recovered and the residue was subjected to a further treatment with diethyl ether and subsequent centrifugation. The brown/black residue was collected and dried under vacuum (29 mg; partially soluble in DMSO), whereas the combined organic washings gave rise to unreacted dopamine azide **2** after solvent removal under vacuum.

Total phenolic content assay: The Folin and Ciocalteu assay was performed by adapting a procedure currently used to quantify the total phenolic content.^[36] Briefly, **5** and **5Ac** were added at a final dose of 1–10 mg/mL to a solution consisting of Folin-Ciocalteu reagent, 75 g/L Na_2CO_3 , and distilled water in a 1:3:16 v/v/v ratio. After 2 h incubation at room temperature, the absorbance at 760 nm was measured. Results were expressed as gallic acid equivalents (GAE). Experiments were run in triplicate.

DPPH assay: DPPH assay was performed as previously described with slight modifications.^[37] To a 100 μ M ethanolic solution of DPPH (2 mL) **5** and **5Ac** were added (final dose 0.5–2 mg/mL) and after 10 min under stirring at room temperature the absorbance of the solution at 515 nm was measured. Data are expressed as EC50, that is the concentration of the sample at which a 50% DPPH reduction is observed. Experiments were run in triplicate.

General procedure for the reduction of nitroarenes: In a glass vial 1 mmol of nitroarene, 1.68 mg of **6** (0.02 mol%), and 5 mL of water were added. Before the addition of 8 mmol of sodium borohydride, the suspension was sonicated for a short time. The mixture was then stirred at 30°C for the specified time. After that it was filtered to remove the catalyst and extracted with ethyl acetate. The organic layer was dried with magnesium sulphate, filtered, and

evaporated under vacuum. The conversion into the corresponding aniline derivative was estimated by $^1\text{H NMR}$ spectroscopy in CDCl_3 , CD_3OD or $(\text{CD}_3)_2\text{SO}$.

General recycling procedure for reduction of nitroarenes: Catalyst reusability was verified in the reduction of *p*-nitroaniline to *p*-phenylenediamine in one hour at 30°C. After each catalytic test, the catalyst was recovered by filtration under vacuum using a membrane (0.2 μ m PTFE Membrane) and washed several times with water, ethyl acetate, ethanol and diethyl ether. Once recovered, the solid was reused for the next catalytic cycle. The conversions into the products were estimated by $^1\text{H NMR}$ analysis.

General procedure for the Heck reactions: The catalytic tests were performed in a 3 mL glass vial with screw cap, in which 2 mg of **6** (0.025 mol%), 1 mmol of aryl iodide, 1.1 mmol of alkene, 1.2 mmol of triethylamine and 1 mL of DMF were added. The reaction mixture was heated at 105°C under stirring for the required time. Then, it was allowed to cool down to room temperature and extracted with diethyl ether. The combined organic layers were dried over MgSO_4 , filtered and evaporated under reduced pressure. The conversions of the products were estimated by $^1\text{H NMR}$ analysis.

General recycling procedure for the Heck reaction: Recycling tests were carried out in a 3 mL glass vial with screw cap, using 4-iodoanisole as aryl iodide and methyl acrylate as alkene source. After each catalytic cycle the reaction mixture was centrifuged in order to remove the supernatant and recover the catalyst. The solid was washed by sonication and centrifugation with methanol (3x3 mL) and diethyl ether. The recovered catalyst was dried at 50°C under vacuum before being used in the next cycle. All the combined supernatants were extracted with diethyl ether and then dried over MgSO_4 . Once evaporated under reduced pressure the products of the recycling tests were analysed by $^1\text{H NMR}$ analysis.

Acknowledgements

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

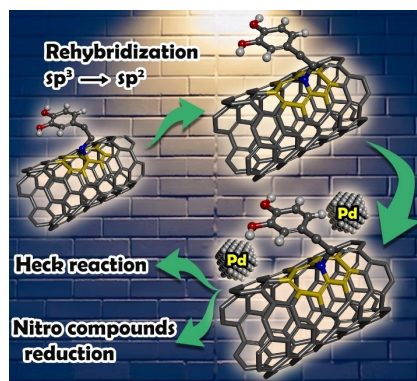
Keywords: carbon nanotubes · dopamine · Heck reaction · nitro compounds reduction · palladium nanoparticles

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RESEARCH ARTICLE

The [3 + 2] cycloaddition reaction of dopamine azide on SWCNTs in *o*-DCB at 160 °C gave a material with high degree of functionalization still maintaining π -network of SWCNTs. The presence of the catechol units was exploited to immobilize palladium nanoparticles. The hybrid material was used as a recyclable catalyst for the reduction of nitro compounds and the Heck reaction.



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Highly Functionalized SWCNTs with a Dopamine Derivative as a Support for Pd Nanoparticles: A Recyclable Catalyst for the Reduction of Nitro Compounds and the Heck Reaction

