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Short Communication

Studies on the functionalization of MWNTs and their application as a recyclable catalyst for C – C bond coupling reactions

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ABSTRACT

Functionalization of multi-walled carbon nanotubes (MWNTs) was studied using various anchoring methods. Among them, nitrene chemistry was employed as the method of choice to preserve desirable physical properties of MWNTs. Using this method, synthesis of carboxyl-functionalized carbon nanotubes (CNTs) was achieved, and then transition metals were incorporated on the linker-MWNT via reductive methods using hydrazine monohydrate. Among various reducing reagents, the use of hydrazine hydrate allowed us to load palladium uniformly. After immobilization of palladium on CNT, its role as a catalyst for C – C bond coupling reaction (Suzuki reaction) was examined. The catalysts could be retrieved upon completion of the reaction by filtration and drying; the recycled catalysts could then be used in further reactions up to seven times before any loss in catalytic activity was observed. Further studies revealed that the Pd leached out of the MWNT may be responsible for the reactivity.

1. Introduction

Carbon nanotubes (CNTs) have attracted much attention due to their high specific surface areas, chemical stability and electrical conductivity. Modified CNTs are utilized in many applications in molecular electronics, biological sensors, catalyst support, sorbent materials and polymer composites [1–3]. In this regard, the unique properties make CNTs very useful for supporting metal nanoparticles. Consequently, since the first discovery of multi-walled carbon nanotubes (MWNTs) by Iijima in 1991, method for chemical modifications of CNTs have been actively studied [4,5]. Common methods include both covalent or non-covalent interactions, including wrapping of the nanotubes with surfactants, oxidation with strong acids and direct addition of functional groups with highly reactive intermediates [6,7]. Covalent functionalization of CNTs may allow the materials to better disperse in solvents, however, covalent interactions with CNT surfaces may cause undesired defects because of chemical functionalization. Common methodologies of direct covalent modification include radical chemistry, Prato and Bingel reactions, as well as dichlorocarbene and nitrene chemistry [8]. We chose to further explore the reactive nitrene chemistry as a functionalization method, since only desired functional groups of the reactive species can be anchored to the CNT wall without significantly damaging CNTs. Generation of nitrene is performed in situ from an azide moiety to minimize unwanted additions such as insertions or rearrangement reactions. Aziridine rings can be formed as reported in studies examining nitrene chemistry [9–13].

Among various functional groups, carboxylates are the most commonly employed for the immobilization of enzymes, ligands and sensors on CNT [14–21]. Since carboxylated CNT's can stabilize metal nanoparticles, these materials have also been used for the incorporation of transition-metals on CNT (Pd, Pt, Ru, Rh, Au, Ni, Cu) [22–27].

The Suzuki reaction is a very useful Pd-catalyzed coupling reaction for the synthesis of unsymmetrical biaryl compounds and has witnessed wide use in organic synthesis [28]. Though examples on the use of Pd-CNT catalyst systems abound in the literature, reports on the use of the heterogeneous Pd-CNT systems for recyclable and highly reactive catalyst systems are rare [29–35]. In this work, a novel Pd-CNT catalyst was prepared through the incorporation of a new ligand system and its performance as a recyclable catalyst in the Suzuki reaction was investigated.

To prepare functionalized CNTs, we have used several functionalization methods to modify the sidewalls of MWNTs. We utilized previously reported nitrene chemistry using an amino alkyl azide for CNT functionalization. Various functional groups were attached to the azido linker and transition metals were loaded on MWNTs for use in catalytic systems.

2. Experimental

2.1. Catalyst preparation

2.1.1. Preparation of amine-CNT using nitrene chemistry

All experiments on CNTs were carried out using MWNTs prepared by a chemical vapor deposition (CVD) method. Functionalized CNT (CNT-ED-OH) was confirmed by Fourier-transform infrared (FTIR) spectrometry, elemental analysis (EA) and Thermal Gravimetric

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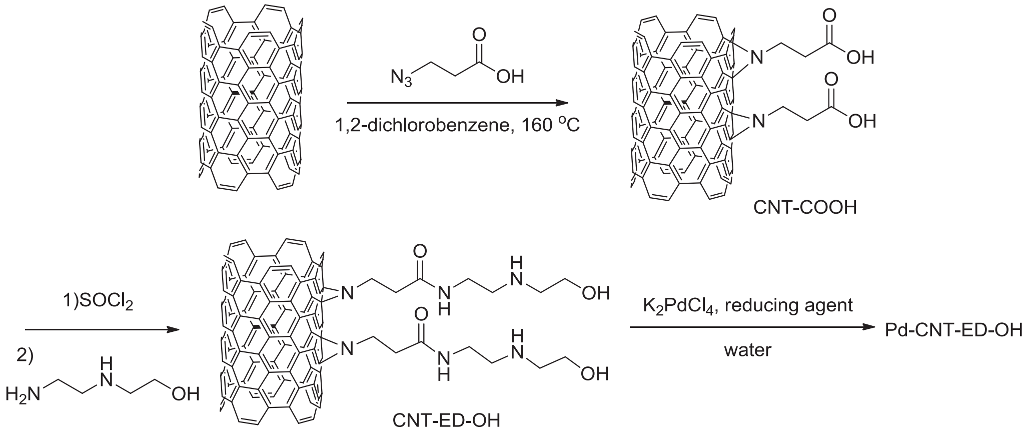


Scheme 1. Synthesis of Pd-CNT-ED-OH-.

Analysis (TGA, see Supporting Information Fig. S1). Pd-CNT-ED-OH catalyst (Scheme 1) was prepared using various reducing agents. Detailed procedure and data are included in the Supporting Information.

2.2. Characterization

The infrared spectrum of CNT-COCl (Fig. 1) exhibited a peak at 1711 cm^{-1}, indicative of the C=O stretching vibration of the COCl group. The C=O stretching frequency corresponding to the amide bond appeared at 1640 cm^{-1} (Fig. 1). The band at 1384 cm^{-1} was assigned to the C – N bond stretch.

The degree of functionalization on the MWNT could be calculated from the weight loss between 200 °C and 800 °C on TGA (Table 1). Comparison of the data from EA and TGA showed no significant differences, confirming successful installation of the linker. Palladium content in the synthesized catalyst was 0.98 wt.% as measured by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The shape and size of the palladium nanoparticles on Pd-CNT-ED-OH could be assessed from the TEM image (Fig. 2). Until now, a disadvantage of CNT catalysis has been the partial loading of palladium on MWNTs surfaces, with subsequent leaching of the metal after reaction. We examined various reducing agents such as hydrogen gas, sodium borohydride and hydrazine, in an effort to efficiently immobilize palladium on the CNTs surface. Palladium loading with hydrogen gas and sodium borohydride resulted in irregularly fixed metal on MWNTs, as shown in the TEM data. Fortunately, the use of the weaker reducing agent, hydrazine monohydrate for immobilization allowed loading of uniform-sized palladium (4–5 nm) as shown in Fig. 2. Further TEM images and XRD data are supplied in the Supporting Information (Fig. S2 and S3, respectively).

2.3. Activity tests on the Suzuki reaction

The Pd-CNT-ED-OH catalyst was chosen for the reactivity test on the Suzuki reaction due to its excellent dispersion properties. A 25 mL two-necked reaction flask was charged with Pd-CNT-ED-OH catalyst (20 mg, 0.3 mol%) in degassed DMF (5.0 mL). Bromobenzene (52 μL, 0.50 mmol), phenylboronic acid (91 mg, 0.75 mmol) and anhydrous sodium carbonate (106 mg, 1.0 mmol) were added and the mixture

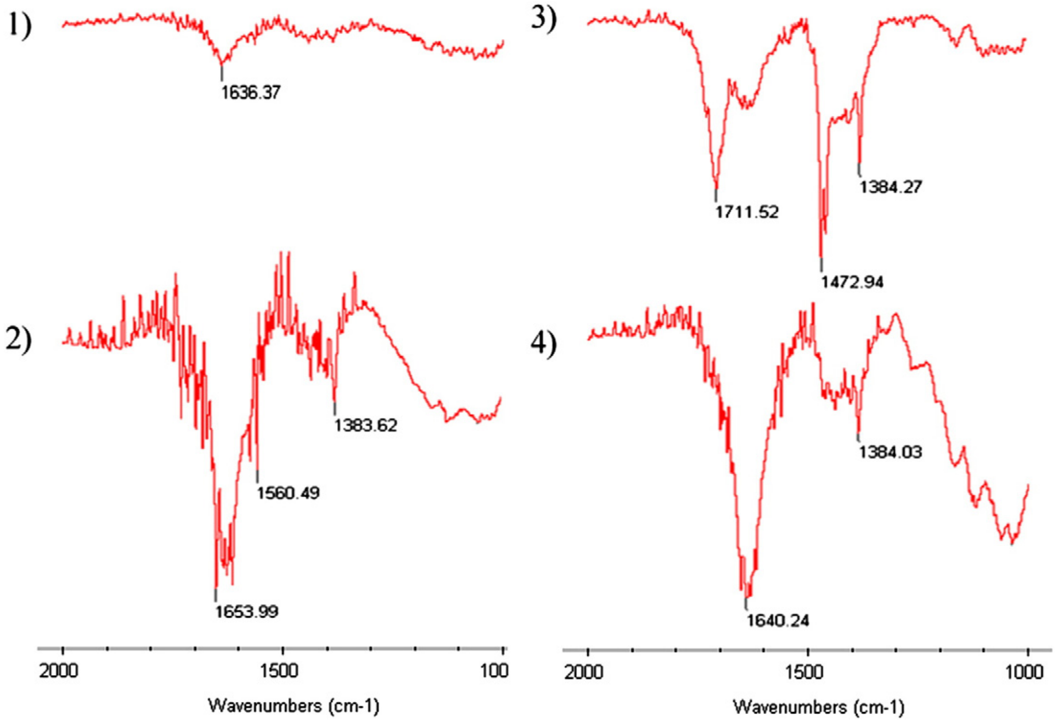


Fig. 1. FT-IR of functionalized CNT: 1) CNT-pristine, 2) CNT-COOH, 3) CNT-COCl, and 4) CNT-ED-OH.

Table 1
Comparsion of TGA and elemental analysis data.

Sample	Weight loss between 200–480 °C (%)	The amount of functional groups per gram of MWNT (mmol)	Elemental (C,N,S) analysis result (mmol)
CNT-COOH	34.78	6.20	4.00
CNT-ED-OH	30.96	1.66	1.80

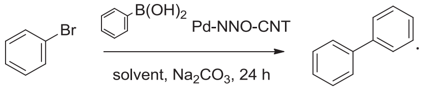
was heated to 120 °C. After 24 h, the reaction mixture was cooled to room temperature; solids formed during the reaction were collected by filtration. Pd-CNT-ED-OH was sequentially washed with DCM, water and ethanol, and dried under vacuum for 2 h. Dried Pd-CNT-ED-OH was transferred to a 25-mL two-necked reaction flask, which was subsequently used for the next reaction cycle.

3. Results and discussion

First, the catalytic activity of Pd-CNT-ED-OH in various solvents was tested for the Suzuki-coupling reaction of bromobenzene and phenylboronic acid. As shown in Table 2, the reaction in DME gave 47% yield based on GC measurement; in 1,4-dioxane, however, much lower yields were obtained (entries 1 and 2). Then a higher-boiling solvent, DMF, was investigated. As a result, the coupling reaction proceeded smoothly at 120 °C in DMF, yielding biphenyl in 60% yield upon the use of 10 mg (0.15 mol%) of Pd-CNT-ED-OH (entry 3). When a higher catalyst loading (20 mg, 0.3 mol%) of Pd-CNT-ED-OH was employed, excellent yield was observed (entry 4).

With the optimized reaction conditions in hand, we then carried out recycling tests on the Pd-CNT-ED-OH catalyst. After completion of the reaction, the catalyst was filtered off and the reaction products were directly analyzed with GC. The remaining catalyst was then washed with ethanol and water, dried under vacuum, and reused for the next reaction; the yields obtained for eight reaction cycles using the recycled catalyst are summarized in Table 3.

Table 2
Optimization of the Suzuki coupling reaction of phenyl boronic acid with bromobenzene.[a]



Entry	Pd-CNT-ED-OH amount (mg)	Solvent	Temperature (°C)	GC conversion (%)[b]
1	20	DME	80	47
2	20	1,4-Dioxane	80	4
3	10	DMF	120	60
4	20	DMF	120	90

[a] All reactions were carried out with 0.5 mmol bromobenzene in 5.0 mL of solvent with 0.3 mol% catalyst.
[b] Conversions were determined through GC analyses.

To examine the extent of Pd leaching from the CNT catalyst, the concentration of the CNT-bound palladium was measured through ICP-MS analysis. The palladium in the catalyst after seven reaction cycles was 0.70 wt.%, corresponding to slight reduction from the initial concentration of 0.98 wt.%. To study the leaching of Pd into the reaction solution, we investigated the amount of Pd after the first reaction and also carried out a test reaction using 2-mercaptoethylamine resin for Pd capture. After the first run, 0.65 ppm of palladium was detected in the solution. It was also found that the coupling reaction of bromobenzene and phenylboronic acid was considerably slower than the original rate when 1 mol% 2-mercaptoethylamine resin was added at 5 h. When the reaction was run in the presence of the resin at the beginning, there was almost no reaction. This indicates that the leached Pd species from the Pd-CNT-ED-OH catalyst is at least partially responsible for the Suzuki reaction. Detailed data are included in the Supporting Information (Fig. S4). Fig. 3 shows the TEM images of the Pd-CNT-ED-OH catalyst after the seventh run. Although a slight aggregation of nanoparticles was observed, the structure did not change significantly in size and shape.

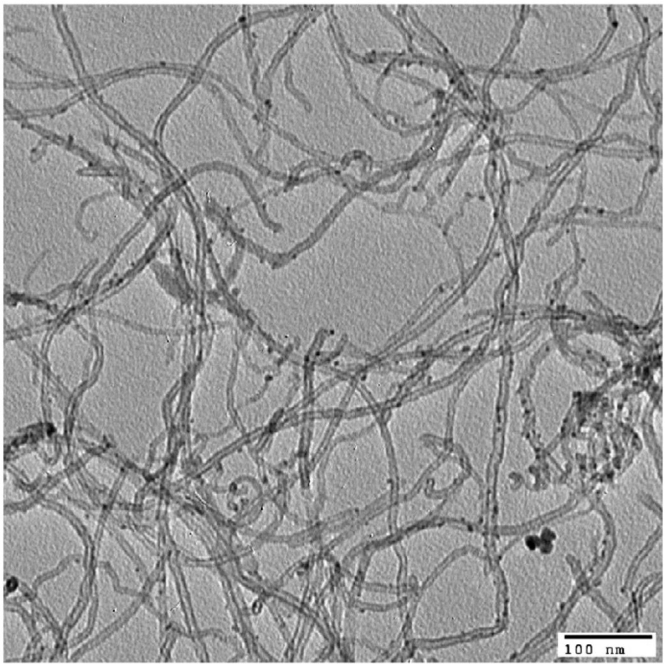


Fig. 2. TEM image of Pd-CNT-ED-OH catalyst.

We then carried out a series of Suzuki coupling reactions to test the scope of the substrates on the Pd-CNT-ED-OH catalyzed reaction (Table 4). The Pd-CNT-ED-OH catalyst showed a broad substrate scope for the reactions of various arylboronic acids with iodobenzene (entries 1–6). Under the optimized reaction conditions, a maximum yield of 94% could be obtained (entries 1 and 2). Although the reactions of aryl bromides proceeded smoothly (entries 10–12), low yield was observed for the reaction of sterically hindered substrate (entry 12). Reaction of chlorobenzene (entry 13) gave a poor yield of the coupling product. The Pd-CNT-ED-OH catalyst also showed compatibility with various substituted aryl iodides in CNT-catalyzed reactions with phenylboronic acid, with moderate yields (entries 7–9).

4. Conclusion

The synthesis and characterization of MWNTs modified by surface functionalization using nitrene chemistry and the utility of the resulting material as a new support for Pd catalysts were reported. Various reduction methods were scanned to immobilize Pd on the MWNT surfaces and use of hydrazine hydrate was found to be the most optimal. These new catalytic systems exhibited good distribution of the metal on

Table 3
Recycling test of Pd-CNT-ED-OH catalyst of Suzuki reaction.[a]

Run	Time (h)	GC yield (%)[b]
1	24 h	71
2		70
3		76
4		77
5		85
6		77
7		70
8		16

[a] All reactions were carried out with 0.5 mmol bromobenzene in 5.0 mL of solvent with 0.3 mol% of Pd-CNT-ED-OH catalyst.
[b] Dodecane was used as an internal standard.

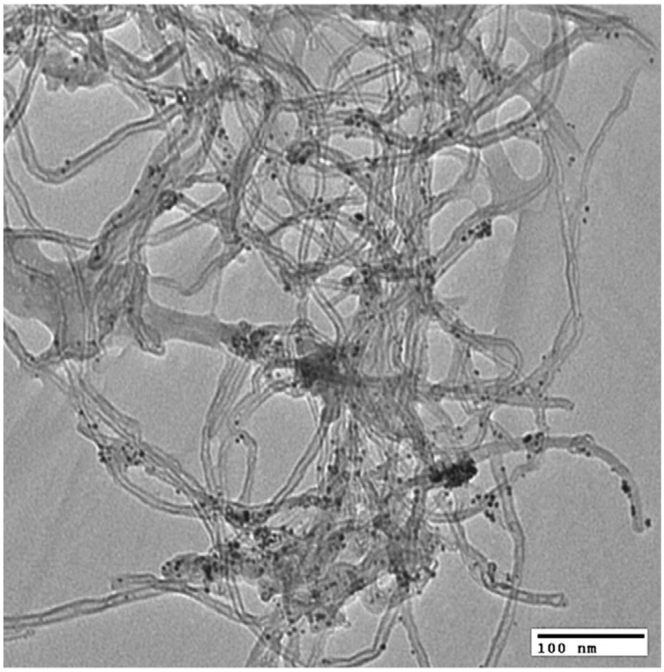
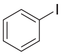
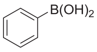
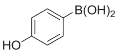
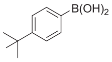
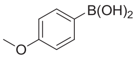
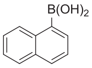
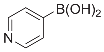
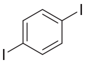
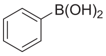
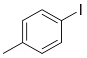
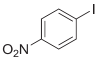
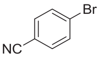
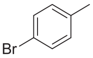
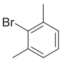
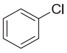


Fig. 3. TEM image of Pd-CNT-ED-OH catalyst after seven reaction cycles.

Table 4
Substrate scope of Pd-CNT-ED-OH catalyzed Suzuki reaction.[a]

$$\text{R-X} \xrightarrow[\text{DMF,110 °C, 24 h}]{\text{R'-B(OH)}_2\text{, Na}_2\text{CO}_3\text{, Pd-CNT}} \text{R-R'.}$$

Entry	Aryl halide	Arylboronic acids	Yield(%)[b]
1			94[c]
2			94
3			86
4			78
5			72
6			47
7			30
8			65
9			50
10			88
11			60
12			20
13			7[c]

[a] All reactions were carried out with 0.5 mmol aryl halide in 5.0 mL of solvent with 0.3 mol% of Pd-CNT-ED-OH catalyst.

[b] Isolated yield.

[c] Yields were determined through GC analyses.

the functionalized MWNT. The new Pd-MWNT catalyst showed good reactivity in Suzuki coupling reactions and the new linker incorporating *N*-(2-hydroxyethyl)ethylenediamine was effective in holding the metal more effectively than simple amine linkers. As a result, the catalyst was recycled over seven reactions before any loss of catalytic activity was observed, with only minimal catalyst loading (0.3 mol%). To develop more effective CNT-based transition metal catalysts, we are examining additional organic reactions in which these catalytic systems can be applied.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2013.11.028.

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