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# Wiring-up Catalytically Active Metals in Solution with Sulfonated Carbon Nanotubes

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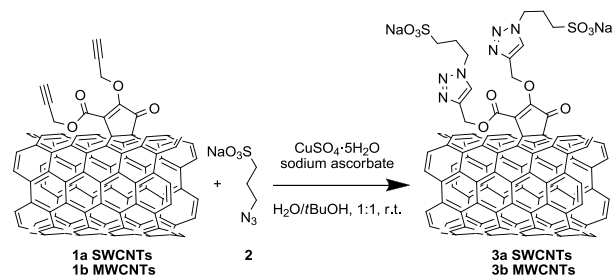
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Highly water soluble sulfonate MWCNTs were synthesized and could be used to facilitate the electron transfer between Pd and Cu in a Wacker-type oxidation in solution.

Carbon nanotubes (CNTs) are of increasing interest in recent years as a result of their outstanding mechanical and electrical properties.<sup>1, 2</sup> Despite intense investigations the limited stability of CNT dispersions in water remains a ongoing challenge, which complicates processing, manipulation and ultimately the scope of their applications.<sup>3</sup> Approaches that improve CNT water solubility include the noncovalent attachment of solubilizing molecules,<sup>4-8</sup> functionalization by oxidation of defect sites to carboxylates<sup>9, 10</sup> (with concomitant amide or ester formation<sup>11-14</sup>), as well as sidewall functionalization by reaction with azomethine ylides<sup>15</sup> or diazonium chemistry.<sup>16</sup> Noncovalent approaches often require mixing and sonication of the solubilizing agent and the CNTs only and thus have the advantage of being easy to execute. Covalent functionalization on the other hand has the advantage of potentially yielding very high solubilities especially when ionic groups are attached to the CNTs.<sup>15</sup> Water solubilities afforded by the described methods typically range from below 1.0 mg/mL up to 20 mg/mL. ‡ A further increase in solubility will not only simplify manipulation and handling of CNTs, but will also lead to new applications. One such application enabled by soluble CNTs is their use as electronic interconnects in an aqueous system. Such a system can accelerate electron transfer processes between metal centers in small molecule catalysis as well as between proteins in biocatalysis leading to more efficient processes. Herein we present a method for the covalent functionalization to give multi-walled CNTs (MWCNTs) containing a high density of sulfonate groups with solubilities up to 31 mg/mL in water. We further show that these sulfonate MWCNTs (sulfMWCNTs) can be used to facilitate electron transfer between metal ions in solution and we demonstrate this effect using the Wacker oxidation reaction.

In order to achieve a sufficient density of solubilizing ionic groups on the CNT surface, we chose to follow a two-step protocol. We first utilize a synthetic method developed in our laboratory<sup>17</sup> to install acetylene moieties on the CNT surface (1, Scheme 1). Compared to other functionalization approaches, this route leads to high functional group densities and exhibits a good functional group tolerance compatible with terminal acetylenes.<sup>18, 19</sup> The obtained materials are then reacted with sodium 3-azidopropane-1-sulfonate in a copper catalyzed 1,3-dipolar cycloaddition reaction yielding



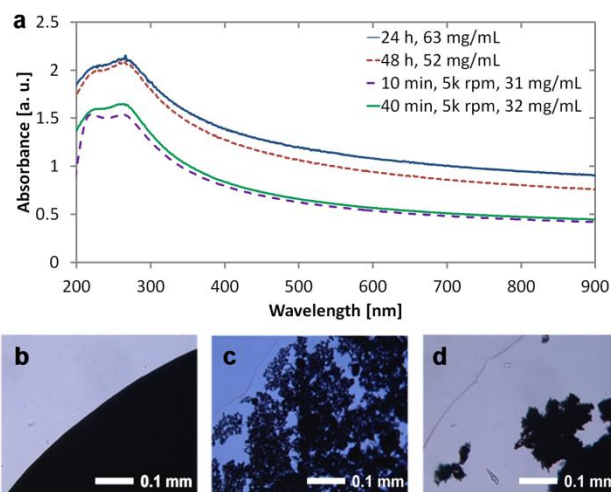
Scheme 1 Synthesis of sulfonate CNTs

sulfMWCNTs (3, Scheme 1). Although azides such as 3-azidopropane-1-sulfonate are known to react directly with CNTs under thermal conditions,<sup>20</sup> the utilized two-step approach allowed us to install two sulfonate moieties per functional group on the CNT offering higher sulfonate densities.

To best confirm the functionalization process and the role of the electronic properties of MWCNTs, we functionalized single-walled CNTs (SWCNTs). Fourier-transform infrared (FT-IR) spectroscopic analysis indicated the presence of acetylene units in 1a and subsequent formation of 1,2,3-triazole groups as well as the introduction of sulfonates in 3a. The functional group density was determined by X-ray photoelectron spectroscopy (XPS) to be one triazole sulfonate group per 17 SWCNT-carbon. Thermogravimetric analysis (TGA) provided a slightly lower estimate of one triazole sulfonate per 20 SWCNT-carbons. After confirming high degrees of SWCNT functionalization, we extended this method for the synthesis of sulfMWCNTs 3b.

MWCNTs are of interest because the outer CNT sidewalls can be covalently functionalized to provide the necessary high solubility while the inner CNTs remain in their electronically active sp<sup>2</sup> hybridized conductive state. FT-IR, TGA and XPS confirmed successful functionalization at densities of up to 1 sulfonate group per 43 carbon atoms of the MWCNT (by XPS).

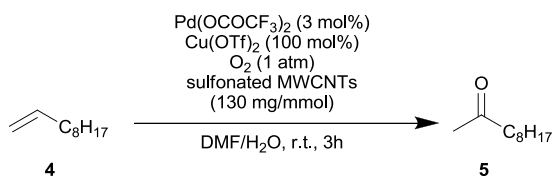
In order to quantify the water solubility of 3b for comparison to other methods, the compound was sonicated for 1 h in milliQ water at a concentration of 65 mg per mL. Aggregates were allowed to settle for 24 h after which a sample was taken from the supernatant. Its sulfMWCNT concentration was determined to be 63 mg/mL using UV-vis spectroscopy (see ESI†). Another sample was taken after an additional 24 h showing a decrease in concentration to 52 mg/mL. In order to complete the precipitation of aggregates, the mixture of dissolved and aggregated sulfMWCNTs was



**Fig. 1** (a) UV-vis spectroscopy was used to determine the concentration of sulfMWCNT in water 24 h and 48 h after sonication as well as after subsequent centrifugation for 10 and 40 minutes (all samples were diluted 5 1:1000 directly before the measurement). (b) Optical micrograph of sulfMWCNTs in a water droplet, (c) pristine MWCNTs, (d) propargyl MWCNTs.

then centrifuged for 10 minutes at 5,000 rpm resulting in a sulfMWCNT concentration of 31 mg/mL in the supernatant. 10 Centrifugation for an additional 30 min did not further reduce the concentration, suggesting that the precipitation of aggregates was complete and the measured concentration represents the amount of dissolved sulfMWCNTs (Fig. 1a). We attribute the obtained high CNT concentration to the large 15 dissociation constant of the sodium sulfonate groups as well as the high density of these moieties. Optical micrographs of droplets of **3b** (20 mg per mL) in water showed a homogeneous solution while aggregates were visible with pristine and propargyl MWCNTs (Fig. 1b-d).

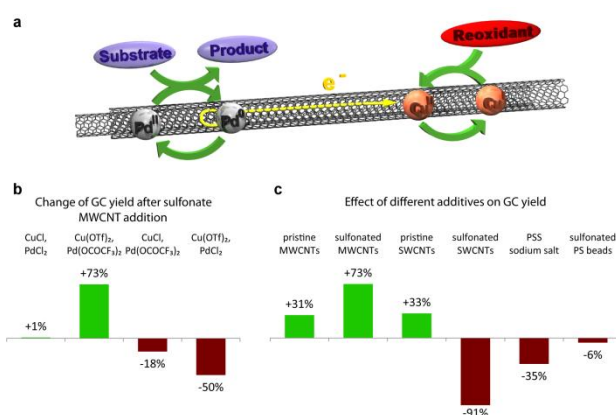
20 After confirming the high solubility of sulfMWCNTs in water, we investigated the possibility of using these CNTs to connect metal ions in solution. In this context, the sulfonate and 1,2,3-triazole groups that were introduced on the CNT surface could potentially act as metal binding sites in addition 25 to providing water solubility. As a model demonstration system we examined the Wacker oxidation of 1-decene to 2-decanone (Scheme 2).<sup>21</sup>



**Scheme 2** Wacker-type oxidation in the presence of sulfonated MWCNTs

30 Mechanistically, during the Wacker reaction, the palladium(II) catalyst is first reduced to palladium(0) and then regenerated by oxidative electron transfer to copper(II).<sup>22</sup> Provided that the sulfMWCNTs can provide an electrical connection between the two metals, the addition of 35 sulfMWCNTs should lead to an observable rate enhancement for metals with similar activities (Fig. 2a).

According to the literature,<sup>21</sup> as well as in our hands, the



**Fig. 2** (a) Schematic representation of the proposed mechanism of sulfMWCNT facilitated electron transfer. The CNT-bound Pd(II) is reduced during the catalytic cycle and is subsequently regenerated via an electron transfer to Cu(II) taking advantage of the conductivity of the sulfMWCNT. (b) The addition of sulfMWCNTs leads to an increase in yield compared to the control without MWCNTs if metal sources with 45 weakly coordinating counterions are used. (c) The addition of highly soluble sulfMWCNTs leads to an increase in yield which is more than twice as high as the yield-increasing effect of pristine SWCNTs and MWCNTs. Non-conductive sulfonated materials such as sulfSWCNTs lower the yield of **5**.

50 Wacker oxidation of 1-decene to 2-decanone, in the absence of MWCNTs as additives, goes to completion within 24 h. To successfully observe meaningful rate enhancements in this transformation both the catalyst loading as well as the reaction time was reduced compared to the literature procedure (3 55 mol% vs. 10 mol% Pd, 3 h instead of 24 h). The yield after 3 h *versus* biphenyl as an internal standard was determined by gas chromatography (GC) and used as an indicator for the influence of the sulfMWCNTs on the reaction rates.

In initial studies using PdCl<sub>2</sub> and *in situ* oxidized CuCl as 60 the metal sources, the addition of sulfMWCNTs did not have an appreciable effect on the yield after 3 h, suggesting negligible metal-CNT interactions. This prompted us to investigate metal sources with less coordinating counterions to favor metal-CNT association. Repeating the reaction with 65 palladium bistrifluoroacetate and copper triflate reduced the yield of the CNT-free control reaction. However, under these conditions, the addition of sulfMWCNTs resulted in a 73% increase in yield after 3 h compared to a CNT free control reaction. When only one of the metal chlorides 70 was replaced by the more soluble metal source, a decrease in yield was observed which suggests that only one metal bound to the CNT. As a result, the CNT-facilitated electron transfer could not take place and sequestration of one of the metals caused the negative effect on the yield (Fig. 2b).

75 To further explore which role the conductivity, solubility, and surface functionalization of the sulfMWCNTs played for the observed effect on the Wacker-type oxidation, we investigated pristine MWCNTs and SWCNTs as conductive, but less soluble alternatives to sulfMWCNTs. Both additives 80 resulted in an improved yield (+31% for MWCNTs and +31% for SWCNTs) compared to CNT-free controls (see Fig. 2c). Nevertheless, this improvement was significantly lower than the effect of sulfMWCNTs even though both types of pristine CNTs showed a higher conductivity (3.9 S cm<sup>-1</sup> for

MWCNTs, 21.8 S cm<sup>-1</sup> for SWCNTs compared to 2.8 cm<sup>-1</sup> for sulfMWCNTs in thin film measurements, see ESI†).

When on the other hand equally soluble but significantly less conductive sulfSWCNTs (0.6 S cm<sup>-1</sup> in thin film) were used instead of sulfMWCNTs, the yield was decreased by 91%. This finding further supports the idea that binding of the catalytically active metal ions to a conductive CNT is needed to facilitate electron transfer. If the inner conductive CNTs are not present as in the case of sulfSWCNTs, sequestration of the metal ions has a negative effect on the yield. In further control experiments we examined the effect of sodium poly(styrene sulfonate) as well as sulfonated polystyrene spheres. Similar to sulfSWCNTs the addition of these non-conductive sulfonated materials resulted in a reduction in the reaction yield confirming that the positive effect of the sulfMWCNTs is based primarily on their conductivity and not on the type or density of surface functionalization (Fig. 2c).

In summary, we have functionalized SWCNTs and MWCNTs with a high density of sulfonate groups. The obtained sulfMWCNTs exhibited a water solubility of 31 mg per mL, which is considerably higher than solubilities obtained with current methods. Furthermore, the addition of sulfMWCNTs to a Wacker type oxidation reaction led to an increase in yield compared to controls without CNTs. SulfMWCNTs performed significantly better than conductive but less soluble pristine CNTs as well as soluble but less conductive sulfonated materials such as sulfSWCNTs which suggests that modified CNTs that combine solubility and conductivity can be used to provide an electrical connection between catalytically active metals in solution.

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## Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental procedures, TGA, FT-IR, XPS, Raman data of **1** and **3**, GC yields of **5**. See DOI: 10.1039/b000000x/

‡ Different methods to determine the solubility of CNTs have been reported. In some cases, the CNT/water mixture is centrifuged to remove aggregates before determining the concentration by UV-vis spectroscopy. In other cases, the reported solubility refers to a concentration at which the CNT solution is stable for a certain amount of time. Herein, we utilize the first method, because it gives more conservative estimates, and because it is being widely used making it easier to compare results of different solubilizing methods. It has to be noted in this context that reported CNT solubilities usually do not represent the formation of a solution with a negative free energy change of mixing but rather maximum concentrations that form stable dispersions for an extended amount of time and/or under centrifugation conditions.<sup>23</sup>

§ In the CNT free reactions, 41 % yield were obtained using PdCl<sub>2</sub> and CuCl while the yield using Pd(OCOFCF<sub>3</sub>)<sub>2</sub> and Cu(OTf)<sub>2</sub> was 16 %. In the second case, the addition of sulfMWCNTs led to an increase in yield from 16 % to 29 % (see ESI†)

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