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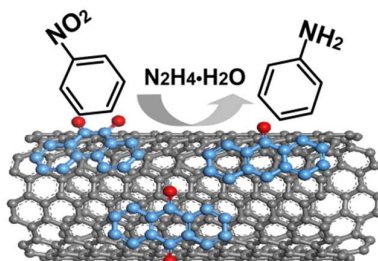
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Noncovalent functionalization of multi-walled carbon nanotubes as metal-free catalysts for the reduction of nitrobenzene

Xianmo Gu,^{a,b} Wei Qi,^b Shuchang Wu,^b Zhenhua Sun,^b Xianzhu Xu,^{*a} and Dangsheng Su^{*b}



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COMMUNICATION

Noncovalent functionalization of multi-walled carbon nanotubes as metal-free catalysts for the reduction of nitrobenzene

Xianmo Gu,^{a,b} Wei Qi,^b Shuchang Wu,^b Zhenhua Sun,^b Xianzhu Xu,^{*a} and Dangsheng Su^{*b}

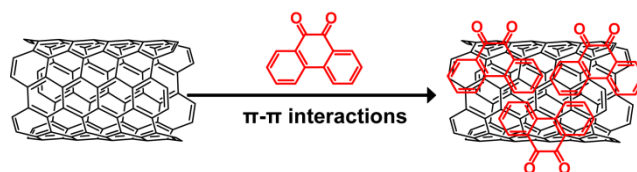
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Multi-walled carbon nanotubes are functionalized with small organic molecules containing specific ketonic carbonyl groups through noncovalent van der Waals and π - π interactions. The comparison of intrinsic activities for series of catalysts indicates that carbonyl groups are active sites in the reduction of nitrobenzene, and the catalysts functionalized with phenanthraquinone exhibits relatively high activity and selectivity.

Recent years, the applications of nano-carbon materials, such as carbon nanotubes (CNTs), carbon nanofibers and nanodiamond, as metal-free catalysts have attracted considerable attention due to their excellent catalytic activity. For example, CNTs have shown their unique advantages as heterogeneous catalysts for direct or oxidative dehydrogenation of aromatic or low alkanes, such as ethane, propane, butane, and ethylbenzene.¹ Nano-carbon materials exhibit high selectivity, long term stability, and environmental friendliness comparing with traditional noble metal or metal oxides catalysts. Furthermore, the acid-base property and electronic density of nano-carbon materials can be regulated through chemical functionalization to meet various requirements. It is generally accepted that the oxygen functional groups and defects on nano-carbon materials are active sites for specific catalytic reactions.² However, it is difficult to control the identity and quantity of oxygen functionalities by traditional chemical modification method such as HNO₃ oxidation or O₃ treatment. Moreover, these treatments are aggressive and have obvious influences on the surface structure of CNTs. Therefore, a controllable and universal modification method to obtain CNTs with identified oxygen functionalities and integrated surface is needed, especially for profound understanding and delicate study of catalytic mechanism and kinetics. Noncovalent functionalization of CNTs through van der Waals and π - π interactions provides a promising way to meet above requirements. Dai *et al* have reported a controllable and specific method for immobilizing proteins onto unmodified SWCNTs.³ Stoddart *et al* have successfully prepared pyrenecyclodextrin-SWCNT hybrid materials served as a chemical sensor to detect organic molecules by means of noncovalent functionalization.⁴ However, there are only few works about preparing catalysts through noncovalent functionalization.

The reduction of nitrobenzene is an important reaction, because the main product, aniline, serves as valuable intermediate and key precursor in the synthesis of pharmaceuticals, dyes, agrochemicals, pigments, herbicides, and pharmaceuticals.⁵ At present, this reduction reaction is generally carried out with metal or metal oxide as catalysts, such as Pd, Ru, Ni, Fe, Fe₂O₃, and Fe₃O₄.⁶ However, these catalysts are either too expensive or highly toxic, which could not meet the requirements of sustainable chemistry. It has been demonstrated that nitric acid oxidized carbon-based materials exhibit a relatively high reactivity and aniline selectivity for reduction of nitrobenzene.⁷ However, the active sites and mechanism for this reaction is still unclear because of the complexity of the chemical composition and structure of oxidized CNTs. In this work, we firstly report on noncovalent functionalization of CNTs with small organic molecules containing ketonic carbonyl groups, and their applications for heterogeneous catalysts towards liquid phase reduction of nitrobenzene. The structure of the functionalized CNTs with only ketonic carbonyl groups on their surface are thoroughly characterized by X-ray photoelectron spectroscopy (XPS), thermogravimetric (TG) and Raman spectroscopy. The relatively high catalytic activity in the reduction of nitrobenzene indicates that ketonic carbonyl groups on CNTs are active sites, and the present research shows that functional CNTs with single oxygen functionality are proper candidates for detailed mechanism and kinetic study.



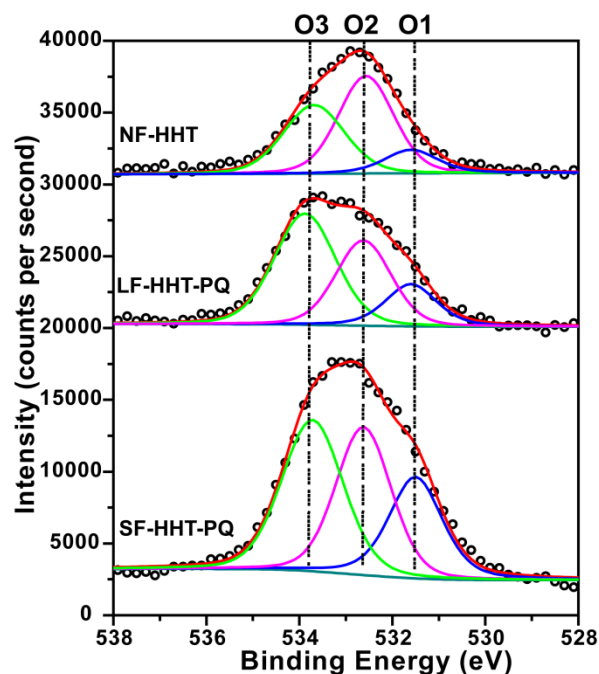
Scheme 1 The noncovalent functionalization of CNTs

Scheme 1 showed the strategy for fabrication of phenanthraquinone (PQ) functionalized CNTs. A kind of highly graphitized multi-walled CNTs, labeled as HHT, was selected in present research to increase the π - π interactions between two materials. Meanwhile, the samples were prepared by liquid phase and solid phase method, respectively. Detailed experimental process was described in supporting information.

Table 1 Summary of characterization data.

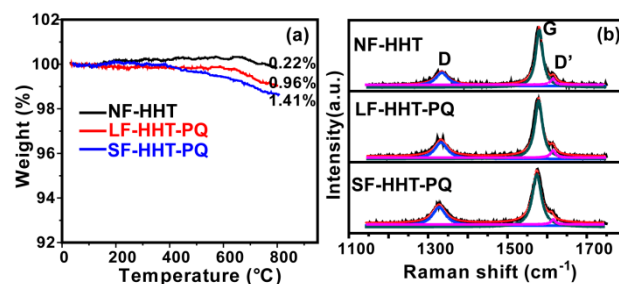
Sample	XPS (atomic percentage)			Δm (wt%) ^c	I_D/I_G
	C	N	O		
NF-HHT ^a	97.07	1.59	1.34 (0.17 ^b)	-	0.39
LF-HHT-PQ ^a	95.98	2.14	1.88 (0.33 ^b)	0.74	0.44
SF-HHT-PQ ^a	95.25	1.62	3.10 (0.78 ^b)	1.09	0.49

a. NF stands for nonfunctionalized, LF-HHT-PQ stands for liquid phase functionalized with PQ and SF-HHT-PQ stands for solid phase functionalized with PQ; b. the atomic percentage of C=O was calculated based on the deconvoluted of the XP O1s spectra; c. Δm is obtained by subtracting the weight loss of the non-functionalized CNT.

**Figure 1** Deconvoluted XP O1s spectra of NF-HHT, LF-HHT-PQ and SF-HHT-PQ

XPS is used to analyze the loading content and surface structure of functionalized CNTs. As shown in Table 1, the oxygen atom percentage of functionalized CNT is obviously higher than non-functionalized one. Moreover, the solid phase functionalization strategy is more efficient than liquid phase (oxygen atomic percentage is over 50 % higher, 3.10 % vs. 1.88 %). Figure 1 presents the deconvolution of XP O1s spectra of non-functionalized and functionalized CNTs. Deconvolution of the spectra gives three peaks corresponding to unsaturated C=O (O1) and saturated C-O (O2 and O3) components at 531.5 eV, 532.6 eV and 533.7 eV, in turn (Table S1).⁸ The O2 species were attributed to O=C-O in ester and anhydrides, and the O3 species were attributed to C-O in phenol and ether.^{8c} As shown in Table 1, the surface atomic concentration of carbonyl groups (C=O) also increases after functionalization (nearly five times increasing from 0.17 % to 0.78 %). Meanwhile, C1s high-resolution spectra could also provide some information about the chemical environments of oxygen atoms on nano-carbon materials. But the C1s spectra of CNTs before and after functionalization are similar, which may be attributed to the low content of oxygen (Figure S1).

TGA studies performed under inert atmosphere are used to estimate the loading content of functionalized group in terms of weight loss, and the results were shown in Table 1 and Figure 2a. Δm (%) represents the difference of weight loss comparing with NF-HHT (weight loss at 0.22 %), which reflects the functionalization degree through different strategy. The loading content of PQ on SF-HHT-PQ is higher than LF-HHT-PQ, which is in accordance with XPS measurement.

**Figure 2** TGA curves (a) and Raman spectra (b) of NF-HHT, LF-HHT-PQ and SF-HHT-PQ

Additional evidence of the CNT functionalization was provided by Raman spectroscopy. Raman bands of the samples and quantitative results are summarized in Figure 2b and Table S2. It is well-known that the D band centered at ca. 1330 cm^{-1} is usually related to defects and amorphous carbon impurities on CNTs, and the G band centered at ca. 1580 cm^{-1} is attributed to in-plane E_{2g} zone-center mode, that is, the graphitic structure of the sample.⁹⁻¹¹ The D' band around 1620 cm^{-1} is assigned to a lattice vibration of several graphene layers or small graphite domains on bulk graphite crystals, which usually appears in defective graphite.^{9, 12} The intensity ratio I_D/I_G of all samples follows such order: SF-HHT-PQ > LF-HHT-PQ > NF-HHT, indicating that the van der Waals and π - π interactions between PQ and CNT surface increase the disorder of graphene layers. However, the variation of I_D/I_G ratio is not significant comparing with that of the non-functionalized CNT because of the low loading of functionalized groups, which is consistent with TGA. In addition, as shown in Figure S2, SF-HHT-PQ exhibits highest dispersibility in ethanol, indicating the success of surface functionalization of CNTs.

It has been demonstrated that the oxygen functional groups on CNTs, including diketone, carboxyl, lactonic and phenolic groups, exhibit positive effects on reduction of nitrobenzene.⁷ However, it is still unclear which kind of oxygen functional groups are active sites in this reaction. CNTs functionalized through this non-covalent mode were used as model catalysts in this reaction, which helps us understanding the detailed mechanism (Figure 3a). The kinetics of the reduction reaction catalyzed by NF-HHT, LF-HHT-PQ and SF-HHT-PQ are summarized in Figure 3b. SF-HHT-PQ shows an obviously higher catalytic activity than NF-HHT and LF-HHT-PQ. Moreover, when reaction time was at 6h, SF-HHT-PQ also exhibited the highest selectivity of 100 % comparing to the selectivity of 95.9 and 93.9 % of LF-HHT-PQ and NF-HHT, respectively (Table S3 and Figure S3a). A linear relationship

between the yield of aniline and the atomic percentage of O1 (C=O) (Figure 3c) was observed, but similar results are not found for O2 and O3 (as shown in Figure S3b and S3c), which may indicate that O1 specie is the one that closely related to the catalytic activity in present reaction. In addition, catalysts containing other type of ketonic groups, such as anthraquinone (AQ) or anthrone (AR), were also prepared using the same solid method (Table S1). Similarly, there is also a linear dependence of the yield of aniline on the atomic percentage of C=O (Figure S3d) for HHT-AQs (HHT functionalized with AQ). The intrinsic activity of single ketonic carbonyl group represented by turnover frequency (TOF) was also provided, which was the basis information for detailed kinetic study. As shown in Figure S4a, the TOF of HHT functionalized with di-ketone groups was higher than that with only one carbonyl group, furthermore, the TOF of HHT-PQ (HHT functionalized with PQ) was also higher than HHT-AQ's, due to the difference of their structure. PQ is a more powerful electron acceptor than AQ, because PQ itself can be fully conjugated with a backbone π -electron system, however, the two aromatic rings in AQ are not fully conjugated each other.¹³ In addition, the polarity of PQ with two carbonyl groups lying on the same side of the molecule is much stronger than that of AQ, which may benefit the adsorption and promote the decomposition of hydrazine (it is also a strong polar agent), thus accelerating the reaction rate. Meanwhile, we have tested the recycling performance of SF-HHT-PQ in order to study the stability of catalyst. As shown in Figure S4b, the yield of aniline decreased from 97.5 to 86.5% after recycling four times, which probably was owing to the loss of catalyst in the transfer process. Comparing with literature,¹⁴ our catalysts showed relatively low activity, which may be ascribed to the difference of the reaction conditions and active sites. However, our main purposes in this work were the functionalization of CNTs via noncovalent interactions and study of the active sites in the nitrobenzene reduction.

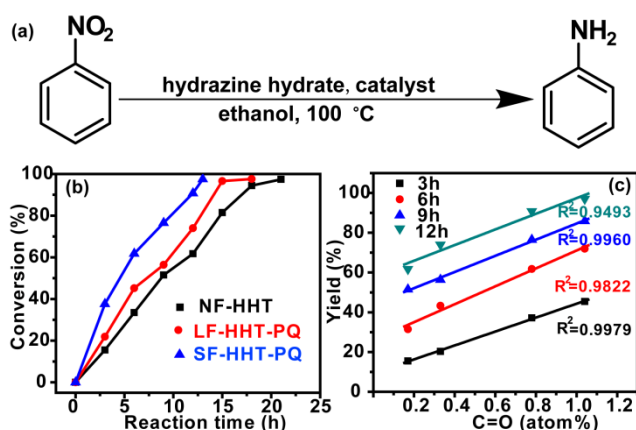


Figure 3 (a) Reaction pathway of the reduction of nitrobenzene to aniline. (b) The conversion of nitrobenzene as a function of time; (c) The yield of aniline as a function of atomic percent of C=O in different reaction times

Conclusions

In conclusion, the small organic molecules containing

ketonic carbonyl groups, such as phenanthraquinone, anthraquinone and anthrone can be facily supported on multi-walled carbon nanotubes through noncovalent van der Waals and π - π interactions, and the resulted CNTs with carbonyl groups on their surface, especially quinone groups, showed high catalytic activity in the reduction of nitrobenzene. The catalytic activity exhibits a linear dependence on the surface concentration of carbonyl groups, confirming the identity of the active sites. We found that the TOF of HHT functionalized with di-ketone groups was higher than that with only one carbonyl group, furthermore, the TOF of HHT-PQ was also nearly twice as high as that of HHT-AQ, because the fully conjugated structure and high polarity of PQ molecules. The present research provides a promising way to fabricate model catalysts for detailed mechanism or kinetic study of carbon catalysts.

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