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PAPER

Knitting an oxygenated network-coat on carbon nanotubes from biomass and their applications in catalysis†

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In this work, we presented a new way for the functionalization of carbon nanotubes (CNTs) with the use of biomass as starting materials and introduced a novel concept of knitting process in the chemistry of CNTs for the first time. A mixture of aromatic compounds obtained from the hydrothermal treatment of biomass, rather than the traditional polymer monomers, was used as the nanoscale building blocks to knit an oxygenated network-coat on the CNTs layer-by-layer. It is an effective, mild, green and easily-controlled method for the functionalization of CNTs. The obtained f-CNTs were proved to be a promising catalyst support for metal catalysts, such as Ru/f-CNTs, showed high activity and selectivity for the hydrogenation of citral to unsaturated alcohol. More importantly, we opened a pioneering way for the conversion of low-cost, abundant and renewable biomass into a hydrophilic/chemical reactive network-coat on the inert surface of a wide range of sp² carbon materials, such as prevalent fullerene, carbon nanotubes, carbon nanohorns and hot graphene *etc.*

Introduction

The hydrophobic sidewalls of carbon nanotubes (CNTs) that consist of sp² hybridized carbon atoms often limit their solubility and dispersibility in solvents, which seriously restricts their manipulations and applications. Therefore, surface functionalization has been always demanded in most nanotechnologies, such as in the fabrication of multifunctional CNTs based composites,¹ template synthesis of tube materials,² preparation of an effective catalyst support³ or a series of biocompatible vehicles,⁴ and so forth.

However, to date, most functionalizations are started on the harsh oxidation (usually using acid or other strong oxidant) of CNTs with the aim of forming functional groups (*e.g.*, carboxylic groups) on the CNTs surfaces, and then followed by suitable reactions with desired functionalities through the covalent linkage of the formed groups.⁵ Inevitably, the sp² nanotube structure and their electronic characteristics of CNTs were

damaged at least in the process of oxidation. Although non-covalent functionalizations such as polymer wrapping and adsorption could do much for preserving the intact microstructures, organic functionalities were always adopted and most modification procedures were performed in harmful organic solvents, which could burden the post-treatment and bring some unexpected biological toxicity to the final nanotube composites.⁶ Biomacromolecule-based functionalizations give researchers the edification that environmental friendly functionalities, such as simple saccharides, polysaccharides, proteins, enzymes, *etc.*, could be adopted widely.⁷ However, directional adsorption or wrapping of tangled biomacromolecules on the CNTs surface just through π - π interactions, Van der Waals forces and characteristic surface adsorption seems difficult to control and sometimes gives rise to an unstable form of the composite, especially when they redispersed in solvent which has a strong dissolving ability for the biomacromolecules. Therefore, an effective, mild and green strategy that endows CNTs with requisite functional groups without harsh treatment is pursued vigorously, not only for the easy functionalization of CNTs but also for preserving the intact micro-/macro-structure of the CNTs and the stability of composite.

Furthermore, the functionalities (*e.g.*, polymers) that linked with branched carboxylic or hydroxyl groups could not fully coat the CNTs surface in theory because they seemed more likely to form a branched structure like that of a millipede or a brush.⁸ Moreover, CNTs-composites bundles were often formed in traditional functionalization methods because the neighbouring CNTs were easily assembled into bundles by the linear/tangled functionalities, such as polymers and biomacromolecules.⁹ Thus, designing a conformal coat compactly surrounded on the CNTs

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surface is necessary for preserving their macroscopic cylindrical structure and individual dispersity, both of which are important for the applications of CNTs in a wide field.¹⁰ Therefore, herein, we used a mixture of small molecules of cyclic/heterocyclic aromatic compounds as nanoscale building blocks for the first time to knit an oxygenated network-coat conformally surrounded on CNTs layer-by-layer. This method not only successfully functionalizes the CNTs effectively without any harsh treatment, but also perfectly preserves an intact micro-/macro-structure and the individual dispersity of CNTs.

Experimental

Materials

The chemical reagent of glucose was purchased from Sinopharm Chemical Reagent Beijing Co. Ltd, and cellulose was purchased from Alfa Aesar. The multiwalled carbon nanotubes (MWCNTs) with a length of 5~15 μm (purity > 95%, outer diameter 40~60 nm) were purchased from Shenzhen Nanotech Port Co., Ltd.

Functionalization of MWCNTs with the use of carbohydrates (e.g., glucose)

0.3 g pristine MWCNTs (p-CNTs) were well dispersed in 30 L deionized water under stirring and ultra-sonic treatment for 30 min respectively, and then 3.75 g glucose was dissolved in the solution under vigorous stirring. After 2 h, the mixed solution was transferred to a 50 mL Teflon-sealed autoclave and then maintained at 180 $^{\circ}\text{C}$ for 4~12 h. After the reaction, the mixed solution was filtered and washed completely with deionized water and ethanol, and dried at 50 $^{\circ}\text{C}$ overnight, giving rise to functional carbon nanotubes (f-CNTs).

Functionalization of MWCNTs with the use of crude plant materials (e.g., grass) and cellulose

2.0 g grass or cellulose were treated hydrothermally with 35 mL H_2O in a 50 mL Teflon-sealed vessel at 220 $^{\circ}\text{C}$ for 5 h, and then filtration of the mixture after cooling down, giving rise to a clear yellow solution of aromatic compounds. Subsequently, 75 mg pristine MWCNTs were dispersed in such solution (30 mL) and were processed by the same procedures as with the glucose used.

Preparation of catalyst

The catalysts of Ru/f-CNTs and Ru/p-CNTs were prepared by a wet impregnation method. The supports (0.27 g) were added to the aqueous solution of $\text{RuCl}_3 \cdot 1.8\text{H}_2\text{O}$ (33.2 mg/100 mL H_2O) and the resulting slurry was stirred vigorously for 24 h at room temperature. The solid materials were separated by filtration and then washed thoroughly with deionized water and ethanol. Then, the obtained solid materials were dried in a vacuum oven at 80 $^{\circ}\text{C}$ overnight. The as-prepared samples were reduced in a H_2 (99.999%) stream at 150 $^{\circ}\text{C}$ for 3 h before being used for reaction.

Selective hydrogenation of citral

The catalysis reaction was performed in a 50 mL stainless steel autoclave reactor with a magnetic stirrer. Citral (2 mmol), solvent

(5 mL) and catalysts (20 mg) were put into the reactor under nitrogen atmosphere and the reaction was carried out with continuous stirring at 80 $^{\circ}\text{C}$ and a hydrogen pressure of 4 MPa. After the reaction, the reaction mixtures were centrifuged and analyzed by gas chromatography with an FID detector (GC-Shimadzu-14C, FID, Capillary column Rtx-Wax 30 m-0.53 mm-0.25 mm) and gas chromatography/mass spectrometry (GC-MS, Agilent 5890). The catalyst after reaction was washed with deionized water and ethanol repeatedly, and then dried in a vacuum oven at room temperature before the next recycling test.

Results and discussion

Knitting an oxygenated network-coat on CNTs and the mechanism analysis

To date, many results have demonstrated that a mixture solution of aromatic heterocyclic/cyclic compounds, such as 5-hydroxymethyl-2-furaldehyde, furfural, 5-methylfurfural, and 1,2,4-benzenetriol, *etc.*¹¹ could be formed during the hydrothermal carbonization (HTC) of biomass, like carbohydrates, crude plant materials and cellulose (see the Supporting Information, Fig. S1†). These intermediates with a high density of reactive groups (C–OH, C=O, COOH, *etc.*) have a strong tendency to intra-/inter-molecular dehydration, aromatization and subsequently act as a surfactant for self-assembling to form a specific structure if the concentration of intermediates achieved a critical value.^{12a} The self-assembly polymers could undergo further intermolecular dehydration to form a series of carbonaceous materials with different morphologies.^{11,12} While in the presence of CNTs, these intermediates could preferentially adsorb on the CNTs surface through π - π interactions because of the π - π conjugated surface of CNTs (Fig. 1a–c),¹³ and then followed by dehydration and aromatization to knit

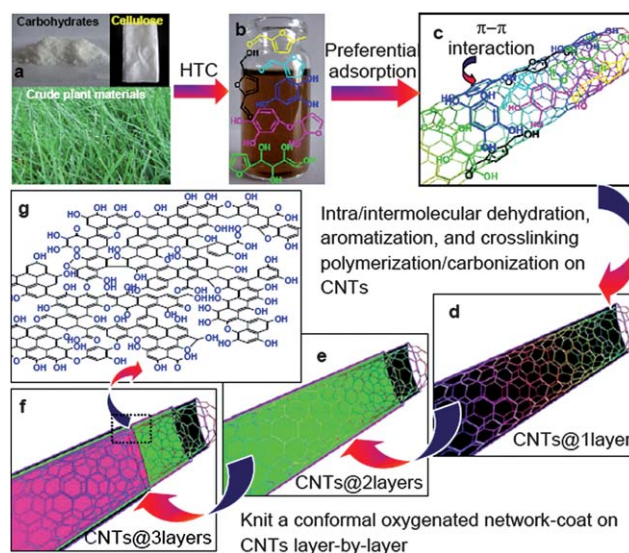


Fig. 1 (a,b) Hydrothermal treatment of a series of biomass gives rise to a mixture solution of heterocyclic/cyclic aromatic compounds (a small typical part of chemicals was listed on bottle); (c–f) the schematic behaviours and knitting mechanism of the aromatic compounds on surface of the CNTs; (g) the schematic structure and compositions of the knitted layer.

a conformal layer surrounded on the CNTs surface compactly (Fig. 1d).^{11d-f} These intermediates acting as nanoscale building blocks could be continuously knitted layer-by-layer on the CNTs because of the presence of carbon nanotubes, which act as nuclei. The formed layers could be knitted compactly because the dehydration could occur between adjacent layers; in addition, the π - π interactions, Van der Waals forces and H-bond were also responsible for the stacking of them (Fig. 1e,f). The mixed cyclic/heterocyclic compounds that experienced a series of intra-/inter-dehydration, aromatization and subsequent cross-linking polymerization/carbonization are more preferential to form a network structure like that of graphene (Fig. 1g),^{11d-f} rather than a linear one that is polymerized from traditional polymeric monomers.⁶ Therefore, a novel concept of knitting process is suitable for interpreting the complex behaviors of the aromatic compounds coating on the CNTs surface and showing their perfect combination with CNTs sidewalls.

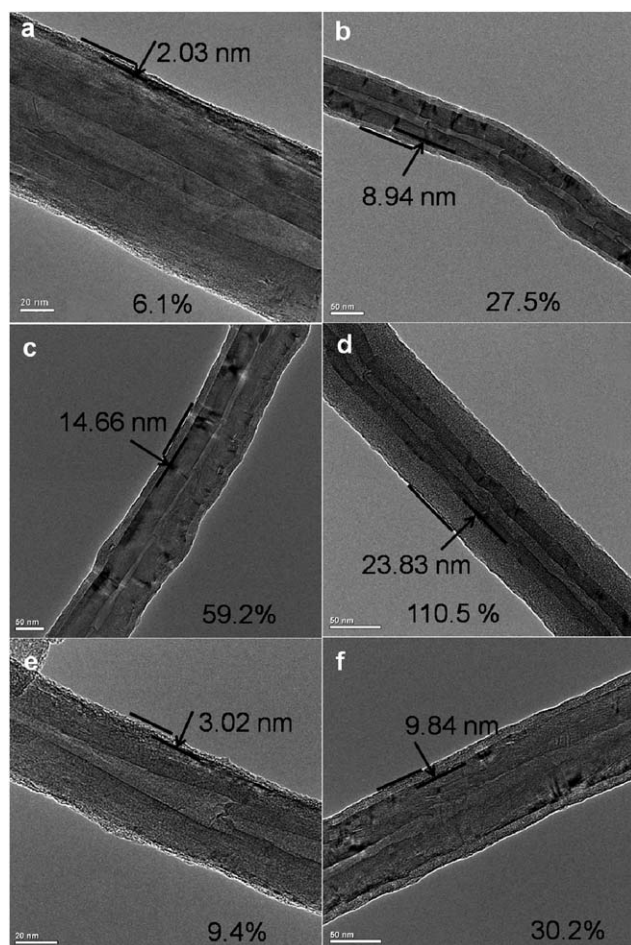


Fig. 2 HRTEM images of f-CNTs functionalized at 180 °C (a–d) for 4 h, 6 h, 8 h, 11 h with the use of glucose; (e,f) with the use of grass and cellulose, respectively. Inset is the thickness and percentage loading of the knitted layer. The percentage loading = $(m_{f-CNTs} - m_{p-CNTs})/m_{p-CNTs}$; m_{f-CNTs} = the weight of f-CNTs, m_{p-CNTs} = the weight of CNTs before functionalization.

The unique features of f-CNTs

HRTEM images of the f-CNTs (Fig. 2a–f) demonstrate that a conformal coat was compactly knitted on the surface of the CNTs when a wide variety of low-cost biomass, including the carbohydrate of glucose, grass and cellulose, was used as green precursors. The thickness of the layers was controlled precisely over a wide range within an extra-small change of Angstrom meter (\AA) (2.03–24.83 nm) through varying the reaction time or the concentration of the precursors. Clearly, the conformal coat compactly surrounded on the CNTs surface was incomparably continuous, uniform and smooth, perfect like graphitic layers, therefore allowing the f-CNTs to preserve a good individual dispersity and a perfect macroscopic cylindrical structure, as confirmed by FESEM (Fig. 3, a1). Furthermore, the outer layer of the f-CNTs has a large amount of chemically reactive groups originated from the knitted aromatic compounds, as demonstrated by FTIR and XPS. For example, the absorption bands around 1000–1460 cm^{-1} (Fig. 3a, yellow area) belonged to the C–O stretching vibrations and/or O–H bending vibrations confirming the presence of the hydroxyl (C–OH, 1079 cm^{-1}), ester, or ether groups (C–O–C, 1258 cm^{-1}). Moreover, the absorption band near 1563 cm^{-1} is attributed to the C=C stretching vibrations of condensed aromatic skeleton, which proved that the layer indeed resulted from the intra-/inter-dehydration, aromatization and subsequent cross-linking polymerization/carbonization of the heterocyclic/cyclic aromatic compounds. Meanwhile, the bands around 1717 cm^{-1} , attributed to the C=O vibrations corresponding to carbonyl, quinone, ester or carboxy groups (Fig. 3a, tangerine area), also show that a series of reactions occurred between aromatic compounds on the CNTs surface. Additionally, the outer layer seems also to possess aliphatic structures, which were confirmed by the band at 2855 cm^{-1} and 2925 cm^{-1} (Fig. 3a, gray area).^{11,14,15} Except the proof in FTIR spectra, the peak intensity and area of the C1s spectrum of the f-CNTs, which is much lower than that of p-CNTs, further demonstrate that the chemical compositions of layers are carbonaceous materials and rich in oxygenated groups.¹⁴ As shown in Fig. 3, b1, the C1s peak of f-CNTs contains five signals which are attributed respectively to the aromatic carbon groups (C=C/C–C) (284.6/285.0 eV), hydroxyl groups (C–OH/C–O–C) (285.7 eV), carbonyl groups (C=O) (287.3 eV) and carboxylic groups, esters or lactones (O–C=O) (289.2 eV).^{11,14} Simultaneously, the higher peak intensity and area of the O1s spectrum of f-CNTs than that of p-CNTs also prove that the layers contain a large amount of oxygen atoms (Fig. 3, b2). Moreover, the kind of oxygenated groups could be confirmed by the O1s spectrum, in which two signals were identified at 531.7 and 533.0 eV. The first signal corresponds to C=O groups, whereas the peak at 533.0 eV is mainly attributed to C–OH/C–O–C groups.¹¹ The above results strongly prove that there was an abundance of oxygenated groups on the outer layer of hte f-CNTs (Fig. 1g), and hence the hydrophobic/inert CNTs were successfully coated with a hydrophilic/chemically reactive coat. Therefore, the solubility and dispersity of the f-CNTs could achieve a high concentration, to 2.0 mg mL^{-1} in deionized water and 2.5 mg mL^{-1} in ethanol, which were drastically improved when compared to the pristine CNTs (<0.2 mg mL^{-1}) (Fig. 3, a2, inset). Moreover, to prove that the coating layer is a new carbonaceous

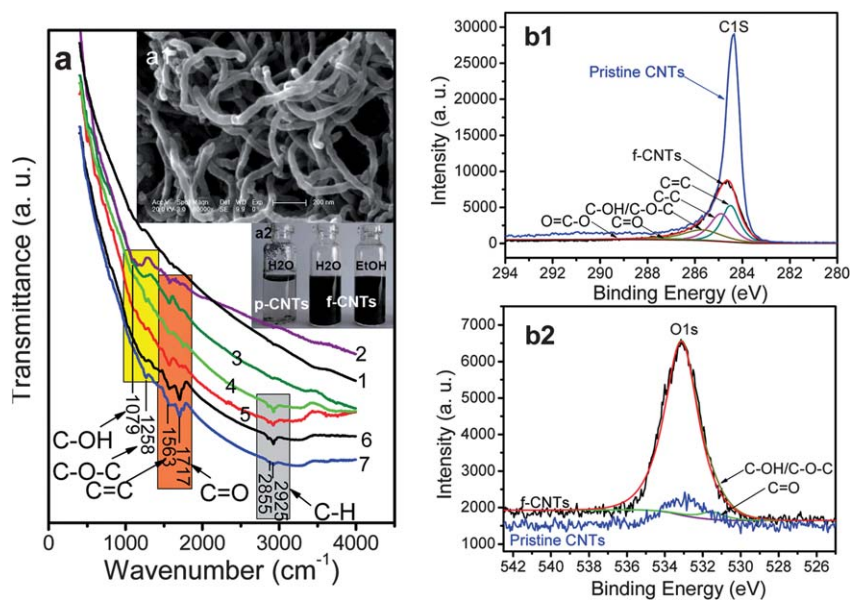


Fig. 3 (a) FTIR spectra of p-CNTs (1) and f-CNTs with different thickness of layers (2–7: 2.03, 3.02, 8.94, 9.84, 14.66, 23.83 nm, respectively) or functionalized with different precursors (2,3,6,7: glucose; 4: grass; 5: cellulose). Inset is the FESEM images of f-CNTs (6), and the picture of dispersion ability of p-CNTs and f-CNTs in solvent. (b1, b2) Comparing the XPS (C1s, O1s) of p-CNTs and f-CNTs (6).

material but not the biomass or the decompositions of biomass, we further checked the FTIR spectra for the mixture of biomass and CNTs, as well as the decompositions of biomass and CNTs. Clearly, the spectra of them (see the Supporting Information, Fig. S2†) are totally different from those of the CNTs@layers (Fig. 3a), which strongly confirm the results that the knitted network-coat on CNTs was really a new-formed carbonaceous material, rather than being the original biomass or the decompositions of the biomass.

Compared to the previous methods of the functionalization of CNTs,^{5–7,16} our present strategy has several distinctive advantages: (i) it is a green process because the used functionality precursors and solvent are environmentally-friendly; (ii) the functionalization conditions are mild and can be tuned over a wide range, making the functionalizations more specific and easy; (iii) the formed aromatic compounds adsorbed on the CNTs through π - π interactions could undergo further intra-/inter-molecular dehydration, aromatization, and subsequent cross-linking polymerization/carbonization, thereby allowing them to knit a network like a bag-coat, which strongly bonded on the CNTs surface conformally as a graphitic layer. The strong interactions including π - π interactions, Van der Waals forces, H-bonds, as well as the unique physical structure of the bag-like coat could greatly improve the stability of the CNTs@layers composite, even in the solvent during the process of further preparing CNT-based materials; (iv) the whole knitting process was a self-catalyzed polymerization/carbonization without any initiators or catalysts, and the degree of the process could be finely controlled *via* varying the reaction conditions; and (v) the knitted layers could coat the CNTs conformally, continuously and compactly as a graphitic-like layer, therefore preserving the cylindrical structure and individual dispersity of the CNTs very well. Based on the knowledge of the source and the knitting mechanism of the intermediates, an efficient and simple way was

developed for the conversion of low-cost, abundant and renewable biomass into a hydrophilic/chemical reactive network-coat on the inert surface of a wide variety of sp^2 carbon materials, such as fullerene, carbon nanohorns/nanotubes and graphene because they consist of the same sp^2 hybridized carbon atoms and have the same π - π conjugated surface. It is well known that the functionalization of these typical sp^2 carbon materials is necessary for constructing carbon-based materials and expanding their applications.¹⁷ Therefore, with our presented method, these inert carbon materials could be effectively endowed with the requisite functional groups for further preparation of new carbon-based materials while still preserving their intact micro-/macro-structures perfectly.

The application of f-CNTs in catalysis

The obtained f-CNTs were an effective support for the deposition and dispersion of metal catalyst because the high density of oxygenated groups could act as anchoring centres and specific nucleation sites for the deposition of precursors. As illustrated in Fig. 4a, the Ru nanoparticles on the f-CNTs surface were highly dispersed with a narrow size distribution of ~ 0.9 nm, which is smaller and more uniform than those on the p-CNTs (~ 1.8 nm) (Fig. 4b). Moreover, the coated layer with the riched oxygenated groups on the surface of f-CNTs make the resulted Ru/f-CNTs to be a hydrophilic catalyst and have a well dispersion in water, a clean medium in the chemical reactions. While for the p-CNTs, the formed Ru/p-CNTs could not disperse in water due to their rather inert surface (Fig. 4b, inset). The good dispersity, ultra-small size and incomparable uniformity of Ru nanoparticles of Ru/f-CNTs, together with their good dispersion in water, make them a promising candidate for catalytic reactions. Herein, the catalytic performance of Ru/f-CNTs was tested and compared with the Ru/p-CNTs and a commercial Ru/C catalyst in a selective

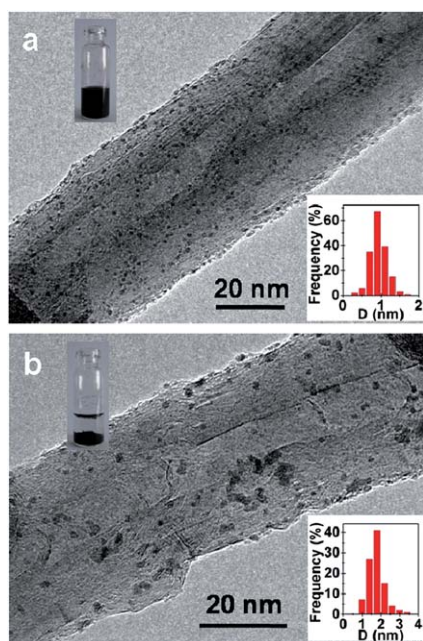
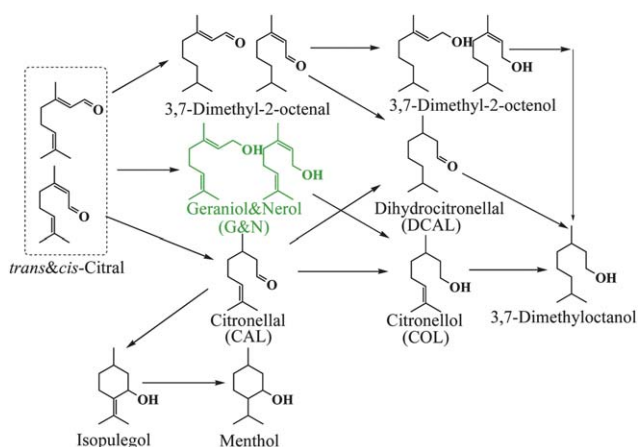


Fig. 4 TEM images of 1.5 wt% Ru/f-CNTs (a) and 1.2 wt% Ru/p-CNTs (b), the size distribution of Ru nanoparticles and the dispersion ability of catalyst in water (inset).

hydrogenation of citral, an unsaturated aldehyde, which is an important reaction in the flavour, fragrance and pharmaceutical industries.¹⁸ The hydrogenation of citral usually produces citronellal (CAL), citronellol (COL), menthol, geraniol and nerol (G&N), and other products due to it involving two C=C and one C=O unsaturated bonds (Scheme 1).^{19,20} It is therefore important to control the product selectivity as well as the overall conversion in this reaction, and thus it was selected as a model reaction to evaluate the catalytic performance of Ru/f-CNTs.

The unsaturated alcohols of G&N were produced as the main products over the Ru/f-CNTs catalyst, and it presented a high level of around 90% at the conversion of ~55%, and reduced slightly to 75% at complete consumption of citral because of its further hydrogenation to COL (Fig. 5a). By contrast, the selectivity of G&N was lower (~55%), and decreased quickly over the



Scheme 1 Reaction pathway of hydrogenation of citral.

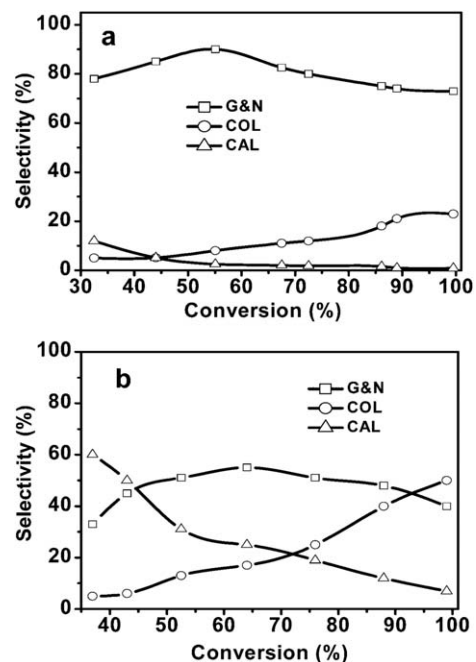


Fig. 5 Plots of selectivity vs. conversion for the selective hydrogenation of citral over 1.5 wt% Ru/f-CNTs (a) and 1.2 wt% Ru/p-CNTs (b).

Ru/p-CNTs catalyst (Fig. 5b). The higher selectivity to G&N obtained on the Ru/f-CNTs catalyst should be ascribed to the adsorption mode of the reactant molecule. The outer surface of the f-CNTs has a large amount of hydrophilic oxygenated groups, including C–OH, COOH, C=O and C–O–C, etc. The uniformity and continuity of the knitted oxygenated coat not only makes the catalyst well dispersed in solution, but also facilitates the directional adsorption of the polar part of the citral molecule (C=O bond) on the surface of the catalyst through H-bonding and then preferential hydrogenation of the C=O bond to produce an unsaturated alcohol (Fig. 6).²¹ While the part of C=C bond keeps away from the hydrophilic surface of the catalyst, due to the C=C bonds existing in the hydrophobic alkyl chain and near the branched methyl groups which have a certain degree of steric hindrance for the surface adsorption, therefore it successfully

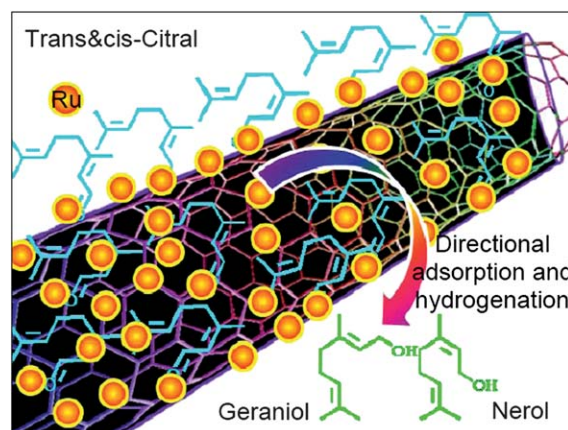


Fig. 6 The probable directional adsorption and hydrogenation of *trans*- & *cis*-citral on 1.5 wt% Ru/f-CNTs catalyst in water.

suppresses the hydrogenation of the C=C bond. Moreover, by comparison to the commercial 5 wt% Ru/C catalyst, the 1.5 wt% Ru/f-CNTs still show a higher selectivity to G&N with a high TOF of 400 h⁻¹, which is about 4 times higher than that (TOF, 83 h⁻¹) obtained on the 5 wt% Ru/C catalyst under the same reaction conditions. Obviously, using the support of CNTs or f-CNTs could largely enhance the activity and selectivity of the hydrogenation of citral, but even they themselves did not show any catalytic activity in the reaction. It is noteworthy that the catalyst of 1.5 wt% Ru/f-CNTs showed a good activity and relative stability in the recycling test (see the Supporting Information, Table S1†). Therefore, the f-CNTs with such an oxygenated coat were an effective support for the metal catalyst and presented outstanding catalytic activity and selectivity in a typical selective hydrogenation of unsaturated aldehydes.

Conclusions

In summary, a network-coat of carbonaceous materials with a high density of oxygenated groups was successfully knitted on CNTs layer-by-layer from the hydrothermal treatment of biomass, which was absolutely different to the linear polymers polymerized from the monomers. The thickness, compositions, and surface properties of the conformal coat could be easily controlled *via* varying the reaction conditions. The functionalized CNTs could still keep the micro-/macro-structure of the pristine CNTs and were proved to be a promising catalyst support for the hydrogenation of citral to unsaturated alcohol. With this strategy, carbon materials like fullerene, graphene and the carbon horns could also be homogeneously endowed with the requisite effective functional groups both more easily and precisely whilst still preserving their intact micro-/macro-structures, and thus constructing new carbon-based materials and exploring their applications.

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