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Cite this: DOI: 10.1039/c0cp00000x

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COMMUNICATION

Nitrogen-doped carbon nanotube by a facile two-step approach as an efficient catalyst for ethylbenzene direct dehydrogenation†

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

A novel and efficient nitrogen-doped carbon nanotube (A-M-CNT) catalyst has been prepared by a facile two-step method including prior air activation and subsequent pyrolysis of carbon nanotube with melamine. The as-synthesized A-M-CNT affords superior catalytic activity to the nitrogen-doped CNT without air activation (M-CNT) and pristine CNT, ascribed to its unique microstructure and surface chemical properties.

Nanocarbons catalyzed direct dehydrogenation (DDH) of ethylbenzene has been considered as a promising route for clean and energy saving the production of the styrene, one of the most industrially important organic chemicals.¹⁻⁶ Carbon nanotube, as one of the typical and commercially available nanocarbon materials, has been generally used as support to fabricate supported metal and its derivatives catalysts for diverse reactions.⁷⁻¹² The relatively few reports on the usage of carbon nanotubes as catalyst are found. Once its catalysis was significantly improved, the carbon nanotube could have become a huge potential carbocatalyst for diverse organic transformation reactions. As a rolled graphenes, the carbon nanotubes have been demonstrated to be catalytically active for oxidative dehydrogenation of hydrocarbons to produce their corresponding olefins.¹³⁻²¹ However, rare report on direct dehydrogenation can be found. On the basis of the commercial availability of carbon nanotubes in a large scale and their relative low-cost, the development of highly efficient carbon nanotube-based carbocatalysts for styrene production through DDH reaction is highly desirable.

Nitrogen doping has been established as an efficient strategy to improve the catalytic performance of carbon nanotube, graphene, activated carbon, carbon nanosphere, and the other carbon materials in many reactions.²²⁻³² It was previously demonstrated that the nitrogen-doped nanocarbons including CNT could be a promising candidate for styrene production through DDH reaction of ethylbenzene under oxidant- and steam-free conditions.^{3-5,33-35} The nitrogen-doped carbon materials can be prepared by two different methods: direct synthesis and post treatment. The former may have potential to synthesize homogeneous heteroatoms doped materials, but the synthesis of nitrogen-doped carbon nanostructures with diverse morphologies via direct synthesis approach still remains a challenge. However, the post treatment may be considered as a facile approach for fabricating many N-doped nanostructured carbon materials.²²⁻³²

Post treatment includes thermal treatment, plasma treatment, and N₂H₄ treatment.²⁶ Thermal treatment refers to the method of heating carbon nanostructures in ammonia atmosphere or pyrolysis of carbon materials with nitrogen-containing precursors to produce nitrogen-doped nanostructured carbon materials,^{26,36,37} which has been considered to be a facile and scalable method to prepare nitrogen-doped carbon materials. The incorporation of nitrogen atom into carbon matrix entirely takes place on the surface of carbon nanostructures by the post thermal treatment, where the reactions take place. Therefore, the post treatment by heating is a facile and robust strategy to prepare metal-free nitrogen-doped carbocatalysts.²²⁻³⁴

Due to high toxicity and strong corrosiveness of ammonia gas, the pyrolysis of diverse nitrogen-containing precursors such as melamine, pyridine, urea, etc. could be considered as an attractive approach for synthesizing nitrogen-doped carbon materials.³⁶⁻⁴¹ Furthermore, the pyrolysis of carbon materials with such solid N sources like melamine can lead to more structural defects,^{3,41} which benefits for the absorbing and activating reactants, and therefore improves the catalytic performance of carbocatalysts in diverse reactions including dehydrogenation.⁴²⁻⁴⁶ Moreover, the introduction of nitrogen can improve the basic properties of carbon materials resulting in promotion in dehydrogenation activity but inhibition in cracking side reaction of ethylbenzene by decreasing the amount of phenolic hydroxyl group, as well as can improve the nucleophilicity of ketonic C=O groups and therefore can improve the activity of C=O for C-H activation.^{3-5,33-35} Just like a coin has its two sides, this kind of pyrolysis method has its inherent disadvantage: high temperature resulting in low doping level due to the splitting of C-N bonds at such as high temperature; but low pyrolysis temperature would lead to thicker CN_x layer coating on carbon nanostructures, which may deteriorate their catalysis by inhibiting surface active sites from reactants.^{33,35} In order to achieve highly active carbocatalysts, it's highly desirable to create surface CN_x layer-free nitrogen-doped carbonaceous nanostructures with higher nitrogen-doping level at a lower pyrolysis temperature.

In our previous report, the introduction of guanidine nitrate into pyrolysis process to remove the CN_x layers on carbon nanotubes has been established. At the same time, the enlarged structural defectiveness caused by the explosive decomposition of guanidine nitrate enhanced the DDH reactions,³⁴ which is consistent with the reported results that the surface structural defects can activate the C-H to enhance the DDH reaction.^{34,45}

However, by adopting the above developed method, the excessive chemical reagents were used, and this is not clean and economical approach. Therefore, it's highly desirable to develop a facile, low-cost and clean approach for fabricating CNx layer-free nitrogen-doped CNT catalyst.

In this communication, we have developed a facile, low-cost and clean two-step method including prior air activation and subsequent pyrolysis of CNT with melamine (PAA-PM) to prepare novel nitrogen-doped CNT (A-M-CNT) catalyst for DDH reaction of ethylbenzene. In comparison with the nitrogen-doped CNT (M-CNT) prepared by pyrolysis of CNT with melamine but without the prior air activation process, the thick CNx layers were removed, and the surface ketonic C=O groups were enriched. As a result, the as-synthesized A-M-CNT catalyst demonstrates remarkably higher catalytic activity for DDH reaction of ethylbenzene, compared with that of the classical M-CNT and the pristine CNT. The directed PAA-PM approach opens a new and facile horizon for fabricating novel and efficient nitrogen-doped carbon catalysts.

Scheme 1 shows the schematic illustration of the fabrication of the A-M-CNT catalyst. The detailed preparation process is given in the ESI.† The preparation route includes two major steps: firstly, air activation of the mixture containing pristine CNT and melamine, followed by the pyrolysis of the air activated mixture at 750 °C in N₂ atmosphere to produce A-M-CNT. For comparison, the classical M-CNT was also prepared by the pyrolysis of the CNT and melamine but without PAA process.

Figure 1 depicts the HRTEM images of A-M-CNT, M-CNT and the pristine CNT samples including the magnified images of typical regions. From Fig. 1a-c, the thick CNx layers coated on CNT wall of M-CNT sample can be formed by the pyrolysis of melamine. However, no visible CNx layer on A-M-CNT (Fig. 1d-f) can be observed. In comparison of M-CNT, the disappearance of CNx layers may be ascribed to enriched surface oxygen caused by the PAA process (30:1 of melamine to CNT and no visible weight loss after PAA process rules out the possible reason of the decrease in melamine by the PAA process). In comparison of the perfect CNT wall on pristine CNT (Fig. 1g-i), the increased structural defect on the M-CNT can be clearly seen on the CNT wall of A-M-CNT sample (Fig. 1d-f). From references, besides surface ketonic C=O, the structural defects also perform as active sites for activating C-H bonds. The elimination of CNx layers on A-M-CNT can enhance the accessibility of catalytically active sites to reactants.^{33,34} Therefore, the A-M-CNT may exhibit superior catalytic performance to the other two samples.

The structural feature of the as-prepared A-M-CNT, M-CNT



Scheme 1 Schematic illustration for the fabrication of novel nitrogen-doped carbon nanotube (A-M-CNT) through a facile PAA-PM approach.

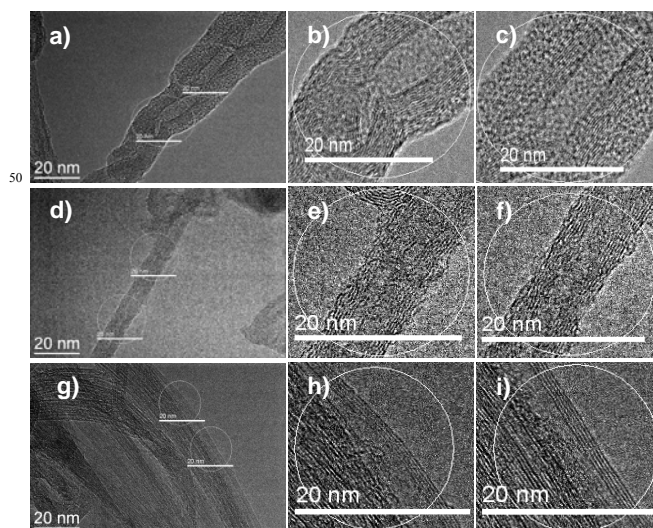


Fig. 1 HRTEM images of the as-synthesized M-CNT (a-c) and A-M-CNT (d-f) as well as the pristine CNT (g-i) samples.

and the pristine CNT was further investigated by XRD and Raman. From Fig. 2a, we could observe that there are two main first-order Raman modes at around 1334-1337 and 1596 cm⁻¹, corresponding to A1g mode in disorder carbon or structural defect and to E 2g mode ideal graphitic carbon, respectively.^{46,47} Correlated to the HRTEM results illustrated in Fig. 1, the higher I_D/I_G for A-M-CNT in comparison with that for pristine CNT shows more structural defects and lattice edge of the as-prepared hybrid composite,^{34,41,48} but the higher I_D/I_G for M-CNT in comparison with that for pristine CNT suggests the surface

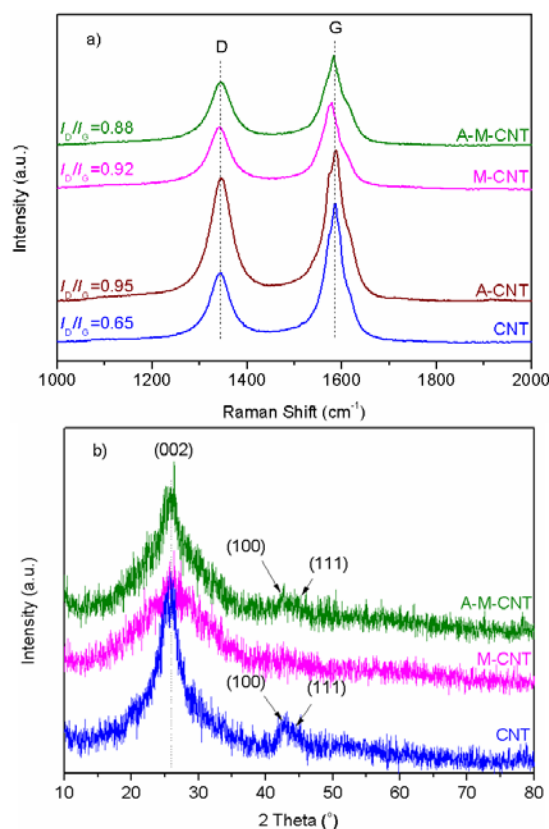


Fig. 2 Raman spectra (a) and XRD patterns (b) of A-M-CNT, M-CNT, and pristine CNT samples.

disordered CN_x layers. The PAA process possibly produces more surface oxygen, and therefore the surface oxygen can remove the CN_x that would be formed by the pyrolysis of melamine, besides can increase the structural defects. The much higher I_D/I_G for A-CNT in comparison with that for CNT may be indicator for the defects production roles of increased surface oxygen by the PAA process. In comparison with A-CNT, A-M-CNT has a little lower I_D/I_G , which may be caused by the protection role of the melamine. As shown in Fig. 2b, for A-M-CNT and the pristine CNT, the diffraction peaks corresponding to (002), (100) and (111) can be identified,^{33,34} indicating the well-formed graphitic structure. However, no peaks corresponding to (100) and (111) planes for M-CNT can be well resolved. Correlated to HRTEM images, the disappearance of diffraction peaks may be resulted from the surface CN_x layers formed by the pyrolysis of melamine. The increased structural defects and the disappeared CN_x layers confirmed by HRTEM and Raman characterization render A-M-CNT to be a superior catalyst to M-CNT and pristine CNT for DDH reaction.

It was previously demonstrated that the surface chemistry of carbon materials significantly affects their catalysis in DDH reaction.^{3-5,33,34} Therefore, the XPS analysis was carried out to investigate the surface chemical properties of the as-prepared A-M-CNT, M-CNT and the pristine CNT. From Fig. 3 and Table 1, the nitrogen incorporation into carbon matrix of the A-M-CNT and M-CNT can be confirmed. Furthermore, the as-prepared A-M-CNT in comparison with M-CNT has lower N content, which

ascribed to the enhancing effect of increased surface oxygen by the PAA process before pyrolysis. As is shown in our previous reports, the main side-products for the DDH are benzene and toluene resulted from the cracking of ethylbenzene, which is consistent with the results reported in the literatures.¹⁻⁶ The surface phenolic hydroxyl group and/or possible COOH may promote the cracking of ethylbenzene due to its acidity, since acid sites are active for cracking reaction of hydrocarbon. The incorporated N atom into carbon structure increases the electron density of carbon materials, and therefore strengthens the basic properties but weakens the acidity of the catalyst, and therefore results in an improvement in catalytic activity for styrene production and simultaneously compressing the benzene and toluene formation.³⁻⁵ Moreover, the increased electron density can strengthen the nucleophilicity of surface ketonic C=O groups, and therefore can increase the activity of C=O on the C-H bond activation.³¹⁻³⁵ From Fig. 3d, the O 1s XPS spectra can be deconvoluted into three peaks corresponding to C=O, O=C-O and C-O-C/C-OH containing groups with the binding energies at around 531.6, 532.7 and 534.0-535.1 eV. From Table 1, the contents of surface ketonic C=O, main active sites for DDH reaction, on the A-M-CNT, M-CNT, and pristine CNT are 0.66, 0.50, and 0.65, respectively. Although the pyrolysis process at high temperature leads to the decreased surface oxygen amount on the A-M-CNT and M-CNT, the increased surface C=O group amount on the two samples than that on pristine CNT is seen. Furthermore, a little more surface oxygen on A-M-CNT than that on M-CNT can be observed, ascribed to the PAA process. The more the surface C=O groups are, the higher the catalytic activity may be.^{1-6,33-35} The more surface ketonic C=O groups and the higher accessibility of active sites by removing CN_x layers on the A-M-CNT may allow it to be a superior catalyst to M-CNT for DDH reaction of ethylbenzene.

Figure 3 shows the steady-state styrene rate of the as-prepared A-M-CNT, M-CNT, and pristine CNT. The commercially available K-Fe catalyst is included for comparison. The A-M-CNT catalyst demonstrates 4.0 mmol g⁻¹ h⁻¹ of steady-state styrene rate, which shows a 17.6% of styrene rate climbing in comparison with M-CNT. Correlated to characterization results, the higher catalytic activity of A-M-CNT than that of M-CNT can be ascribed to the increased surface C=O groups and the

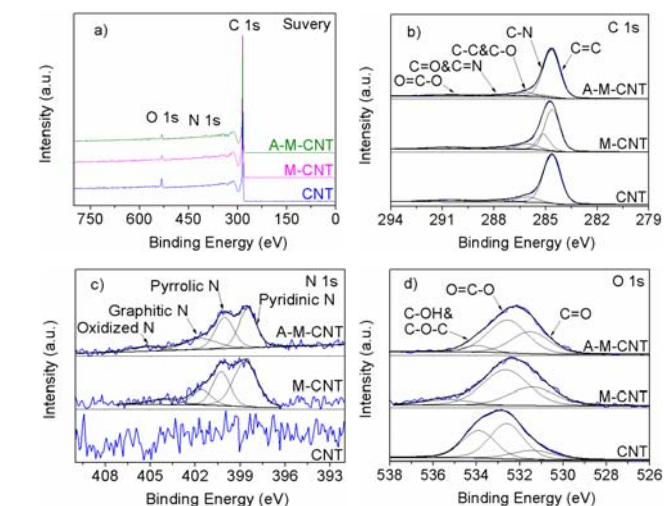


Fig. 3 XPS spectra of A-M-CNT, M-CNT, and the pristine CNT samples: (a)-(d) are the Survey, C 1s, N 1s, and O 1s spectra, respectively.

Table 1 The relative integrated intensity of deconvoluted N 1s and O 1s XPS spectra for MCSA-CNT, M-C-CNT, M-CNT, C-CNT, and CNT samples.

Samples	N ^a (%)	N-1 ^b (%)	N-2 ^b (%)	N-3 ^b (%)	N-4 ^b (%)	O ^a (%)	C=O (%)	C-OH/ CO-C (%)	O=C-O (%)
A-M-CNT	0.9	38.4	32.9	20.5	8.1	1.8	36.4	7.8	55.8
M-CNT	1.8	50.1	27.9	14.2	7.8	1.6	31.2	10.0	58.8
CNT	0	-	-	-	-	4.1	15.8	36.4	47.8

^aThe N and O atom content measured by XPS analysis. ^bPercentage of various nitrogen species occupying in the total N content; N-1, N-2, N-3, and N-4 are denoted as pyridinic N, pyrrolic N, graphitic N, and oxidized N, respectively.

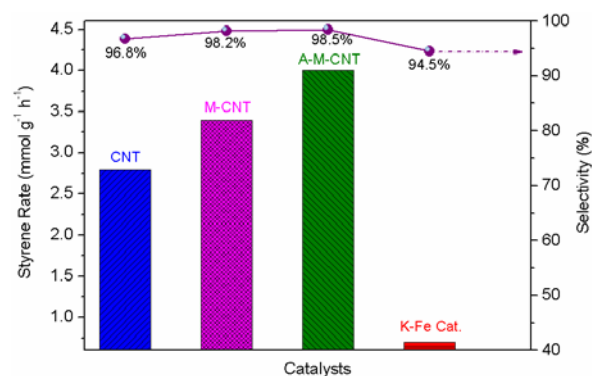


Fig. 4 Catalytic performance of the as-synthesized A-M-CNT, M-CNT, and the pristine CNT as well as K-Fe catalysts for DDH reaction of ethylbenzene under oxidant- and steam-free conditions (steady-state styrene rate at 20 h of time on stream). Reaction conditions: 0.025 g catalyst, 550 °C, 2.8% of ethylbenzene in argon, 10 mL min⁻¹.

enhanced accessibility of active sites owing to elimination of CN_x layers. However, from Table 1, the A-M-CNT has a lower N content than M-CNT. The results further show that the nitrogen doping can affect but not decide the catalytic performance. Moreover, it can be found that the A-M-CNT demonstrates 1.43 times of the steady-state styrene rate of the pristine CNT, ascribed to the increased structural defects and nitrogen-doping. Furthermore, the developed A-M-CNT shows 5.7 times the steady-state styrene rate of commercially available K-Fe catalyst. The superior catalytic performance of the developed A-M-CNT renders it to be a promising candidate for clean and highly efficient styrene production through carbon catalyzed DDH reaction of ethylbenzene under oxidant- and steam-free conditions.

In summary, this work presents a facile and low-cost two-step method (PAA-PM) to prepare the A-M-CNT catalyst. In comparison with classical pyrolysis of melamine, this approach efficiently increases the structural defects, enriches surface C=O groups, and also removes the formed CN_x from melamine pyrolysis. The A-MCNT catalyst demonstrates higher catalytic performance in DDH reaction in comparison with M-CNT, ascribed to increased active sites and their accessibility to reactants. This work may pay a new way for developing efficient carboxyl catalysts for diverse organic transformation reactions.

Acknowledgements

This work is financially supported by the National Natural Science Foundation of China (grant no. 21276041), the Joint Fund of Coal, set up by National Natural Science Foundation of China and Shenhua Co., Ltd. (grant no. U1261104), and also sponsored by the Chinese Ministry of Education via the Program for New Century Excellent Talents in University (grant no. NCET-12-0079), and by the Fundamental Research Funds for the Central Universities (grant no. DUT15LK41).

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- † Electronic Supplementary Information (ESI) available: Experimental details for materials synthesis, characterization, and catalytic performance measurement. See DOI: 10.1039/c0cp00000x/
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