Supporting Information

Nitrogen Plasma Enhanced Growth of Carbon Nanotubes

Man-Chen Zhang[1,2], Gen-Cai Guo[1,2], Ru-Zhi Wang[1,2*], Yan-Lei Cui[1,2], Xiao-Yu Feng[1,2], Bing-Rong Wang[1,2]

[1]*College of Materials Science and Engineering, Beijing University of Technology, Beijing 100124, China*

[2]*Key Laboratory of Advanced Functional Materials, Education Ministry of China, Beijing University of Technology, Beijing 100124, China*

In the manuscript, we only gave two examples to introduce the low ΔH and ΔG which were required for the CH_4 conversion. Both of them were far less than that of +18.31 eV. However, many possible reactions could occur in the chamber with the introduction of N*, more calculations were performed to confirm this phenomenon based on different reaction approaches. Interestingly, the results showed that the energies were even lower than 2.87eV. It turned out that no matter what the reactions were, the total energies were obviously lower than +18.31eV, indicating that the introduction of N* could significantly facilitate the CH_4 conversion and CNTs growth.

Table 1 Reaction mechanism and energy change during growth of CNTs

	Energy (eV)	**Reaction Energy（eV）**		
H	-1.11721755	without N_2 and H_2	$CH_4 \rightarrow CH_3+H$	ΔH=+4.72
H_2	- 6.77109571		$CH_3 \rightarrow CH_2+H$	ΔH=+4.97
NH_3	-19.53880829		$CH_2 \rightarrow CH+H$	ΔH=+4.93
			$CH \rightarrow C+H$	ΔH=+3.69
				ΔG=+18.31
NH_2	-13.53511480	N*	$N_2 \rightarrow 2N^*$（with the effect of e^- and thermal）	
NH	-8.10230197		$N^*+CH_4 \rightarrow NH+ CH_3$	ΔH=+0.86
N	-3.12396706		$N^* + CH_3 \rightarrow NH+ CH_2$	ΔH=+1.11
CH_4	-24.03942856		$N^*+ CH_2 \rightarrow NH+ CH$	ΔH=+1.07
			$N^* + CH \rightarrow NH+ C$	ΔH=-0.17
				ΔG=+2.87

CH_3	-18.19661694	H*	H_2→2H*（with the effect of e^- and thermal）	
CH_2	-12.10793087		H*+CH_4→H_2+ CH_3	△H=+0.18
CH	-6.05554338		H* + CH_3→H_2+ CH_2	△H=+0.44
C	-1.25067543		H*+ CH_2→H_2+ CH	△H=+0.4
			H* + CH →H_2+ C	△H=-0.84
				△G=+0.18

Table 2 Possible reactions and the corresponding energy.

	Possible reaction	**Reaction Energy（eV）**
1	NH+CH_4→NH_2+ CH_3	△H=+0.4
	NH + CH_3→NH_2+ CH_2	△H=+0.65
	NH_2+ CH_2→NH_3+ CH	△H=+0.05
	NH_2+ CH →NH_3+ C	△H=-1.19
		△G=-0.09
2	NH_2+CH_4→NH_3+ CH_3	△H=-0.16
	NH_2 + CH_3→NH_3+ CH_2	△H=-0.07
	NH_2+ CH_2→NH_3+ CH	△H=+0.05
	NH_2+ CH →NH_3+ C	△H=-1.19
		△G=-1.37
3	N*+CH_4→NH+ CH_3	△H=+0.86
	NH + CH_3→NH_2+ CH_2	△H=+0.65
	NH+ CH_2→NH_2+ CH	△H=+0.61
	NH + CH →NH_2+ C	△H=-0.63
		△G=+1.49
4	N*+CH_4→NH+ CH_3	△H=+0.86
	NH + CH_3→NH_2+ CH_2	△H=+0.65
	NH_2+ CH_2→NH_3+ CH	△H=+0.05
	NH_2+ CH →NH_3+ C	△H=-1.19
		△G=+0.37
5	NH+CH_4→NH_2+ CH_3	△H=+0.4
	NH_2 + CH_3→NH_3+ CH_2	△H=-0.07
	NH_2+ CH_2→NH_3+ CH	△H=+0.05
	NH_2+ CH →NH_3+ C	△H=-1.19
		△G=-0.81
6	N*+CH_4→NH+ CH_3	△H=+0.86
	N* + CH_3→NH+ CH_2	△H=+1.11
	NH+ CH_2→NH_2+ CH	△H=+0.61
	NH + CH →NH_2+ C	△H=-0.63
		△G=+1.95

*To whom correspondence should be addressed: wrz@bjut.edu.cn.

7	$N^*+CH_4 \rightarrow NH+CH_3$	ΔH=+0.86
	$N^*+CH_3 \rightarrow NH+CH_2$	ΔH=+1.11
	$NH+CH_2 \rightarrow NH_2+CH$	ΔH=+0.61
	$NH_2+CH \rightarrow NH_3+C$	ΔH=-1.19
		ΔG=+1.39
8	$N^*+CH_4 \rightarrow NH+CH_3$	ΔH=+0.86
	$N^*+CH_3 \rightarrow NH+CH_2$	ΔH=+1.11
	$NH+CH_2 \rightarrow NH_2+CH$	ΔH=+0.61
	$N^*+CH \rightarrow NH+C$	ΔH=-0.17
		ΔG=+2.41
9	$NH+CH_4 \rightarrow NH_2+CH_3$	ΔH=+0.4
	$NH_2+CH_3 \rightarrow NH_3+CH_2$	ΔH=-0.07
	$N^*+CH_2 \rightarrow NH+CH$	ΔH=+1.07
	$N^*+CH \rightarrow NH+C$	ΔH=-0.17
		ΔG=+1.23

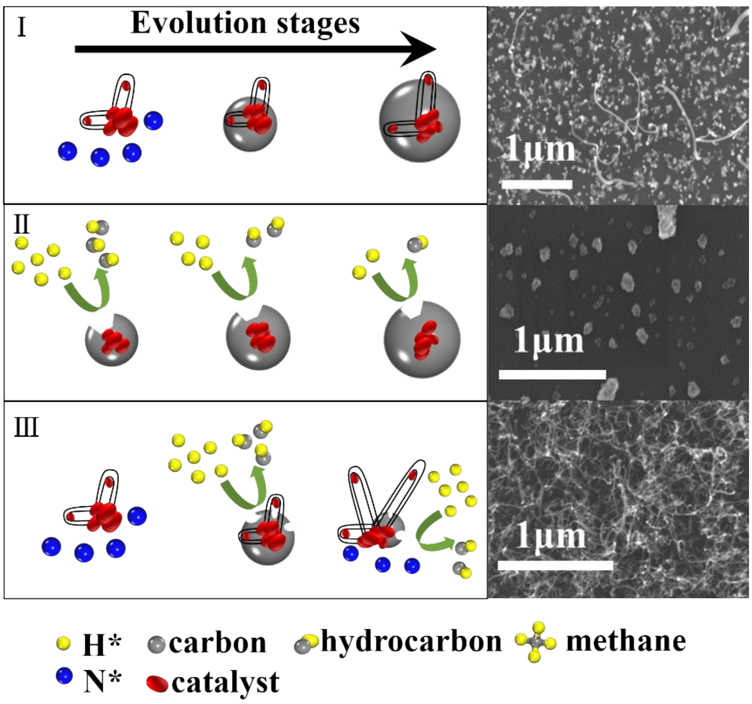

Fig. S1 Catalyst change kinetics by the introduction of N* and/or H*, and the corresponding SEM images.

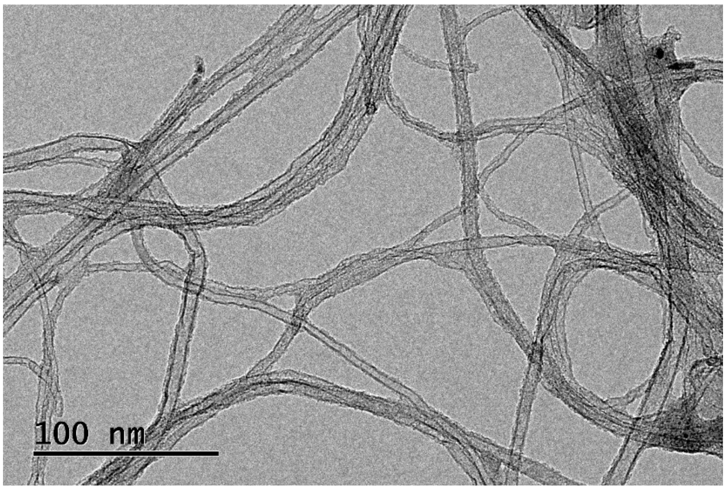

Fig. S2 TEM images of MWCNTs coated by disengaged carbon