Pd nanoparticles immobilized on carbon nanotubes with a polyaniline coaxial coating for the Heck reaction: coating thickness as the key factor influencing the efficiency and stability of the catalyst

Rui Yu[a,b†], Rui Liu[a,b†], Jie Deng[c], Maofei Ran[d], Ning Wang[e], Wei Chu[a], Zhiwei He[b], Zheng Du[f], Chengfa Jiang[a,*], Wenjing Sun[b,*]

[a.] China-America Cancer Research Institute, Key Laboratory for Medical Molecular Diagnostics of Guangdong Province, Guangdong Medical University, Dongguan, Guangdong 523808, China;

[b] Department of Chemical Engineering, Sichuan University, Chengdu 610065, China;

[c.] College of pharmacy and biological engineering, Chengdu University, Chengdu 610106, China;

[d] College of Chemistry & Environment Protection Engineering, Southwest University for Nationalities, Chengdu 610041, China

[e.] Physical Sciences and Engineering Division, Advanced Membranes and Porous Materials Center, King Abdullah University of Science and Technology, Thuwal, 23955-6900, Saudi Arabia;

[f.] National Supercomputing Center in Shenzhen (Shenzhen Cloud Computing Center), Guangdong, Shenzhen, 518055, China

[†] These authors contributed equally to this work.

*Corresponding author: jiangcf@scu.edu.cn (C. Jiang); swj_gdmc@163.com (W. Sun)

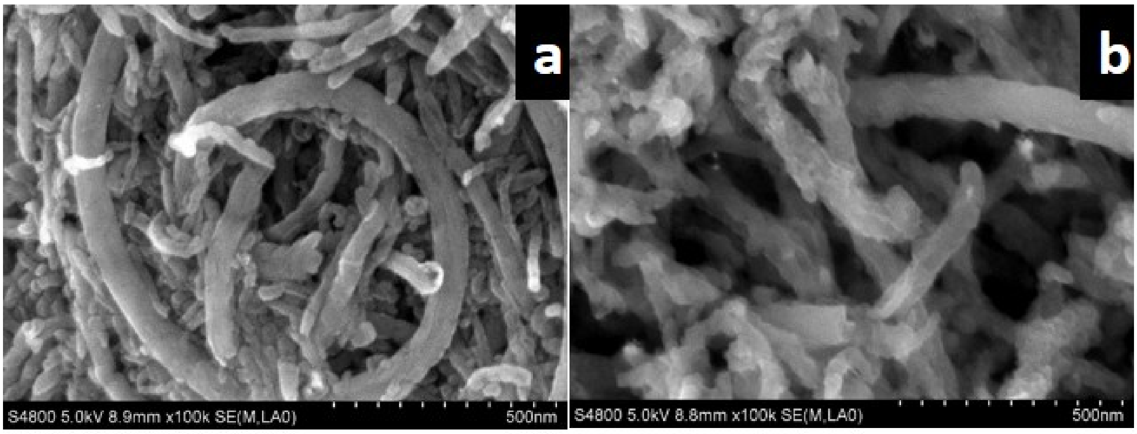


Fig. S1 SEM results of (a) CNT and CNT@PANI-0.5(b).

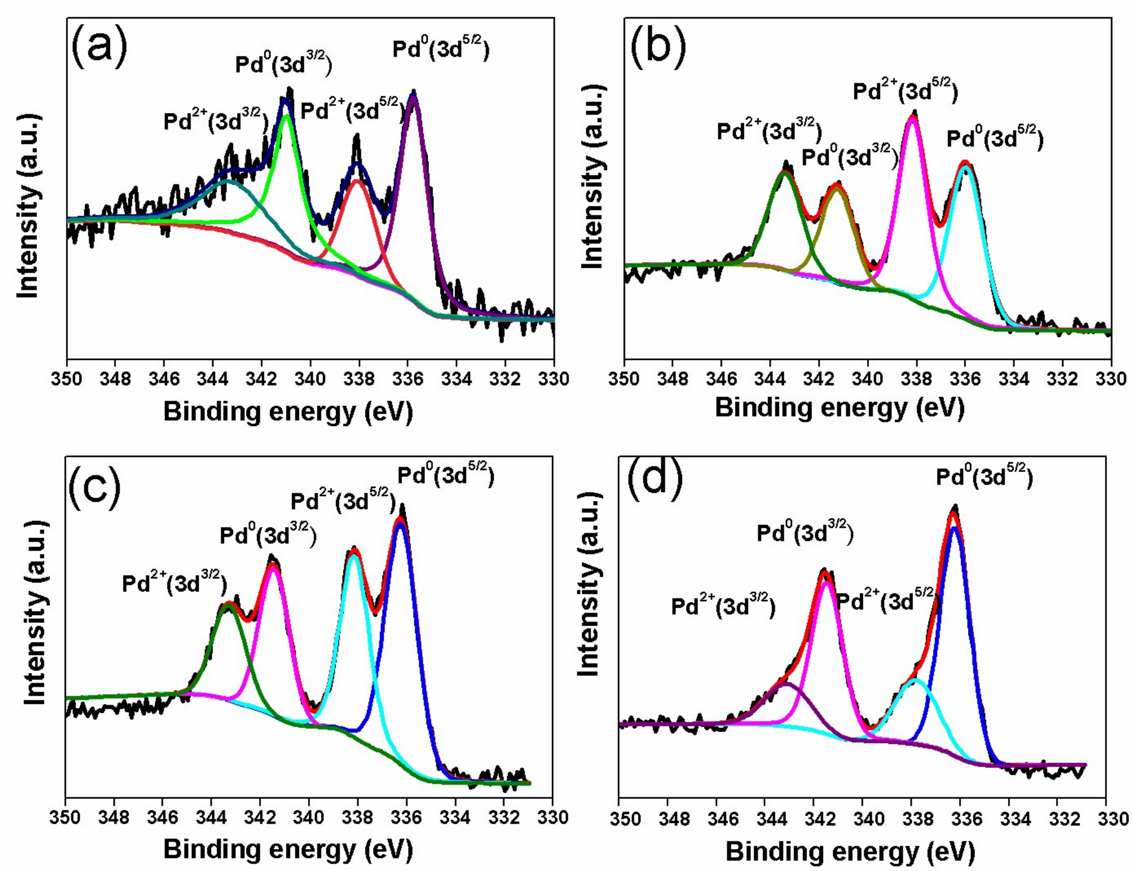


Fig. S2 Pd 3d core level of XPS spectra of the four catalysts. Pd/CNT(a); Pd/PANI@CNT-0.5(b); Pd/PANI@CNT-1(c); and Pd/PANI@CNT-4(d). The data point of the Pd 3d peaks are fitted by four profiles. The fitting results are shown in Table S1.

Table S1 Assignment and atomic% of the four catalysts

Catalysts	Pd $3d^{5/2}$				Pd $3d^{3/2}$			
	Pd^0		Pd^{2+}		Pd^0		Pd^{2+}	
	BE/eV	at%	BE/eV	at%	BE/eV	at%	BE/eV	at%
Pd/CNT	335.8	68%	338.08	32%	341	58 %	343.2	42%
Pd/PANI@CNT-0.5	336	48%	338.2	52%	341.3	48%	343.4	52%
Pd/PANI@CNT-1	336.2	58%	338.2	42%	341.4	58%	343.3	42%
Pd/PANI@CNT-4	336.2	71%	337.8	29%	341.5	72%	343.1	28%

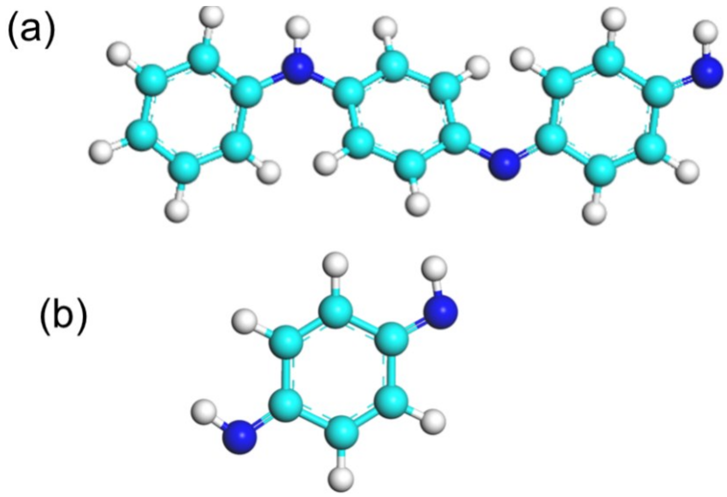


Fig. S3 Molecular structure of PANI unit(a); selected fragment of PANI in this work(b).

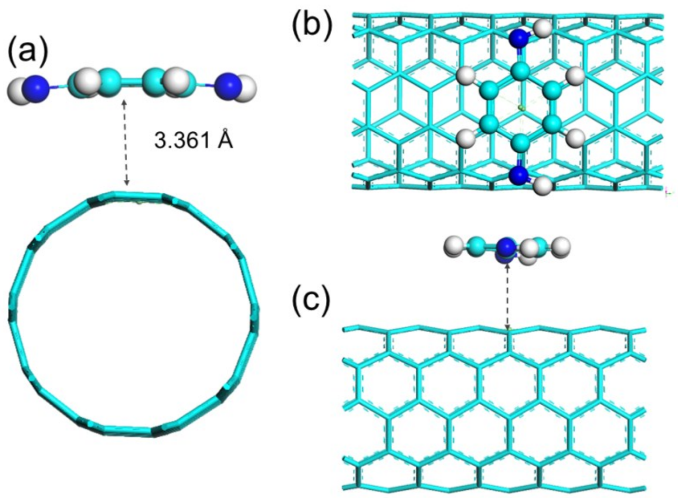


Fig. S4 Optimized structure of PANI@CNT: (a)side view (along the tube); (b)front view; (c)side view

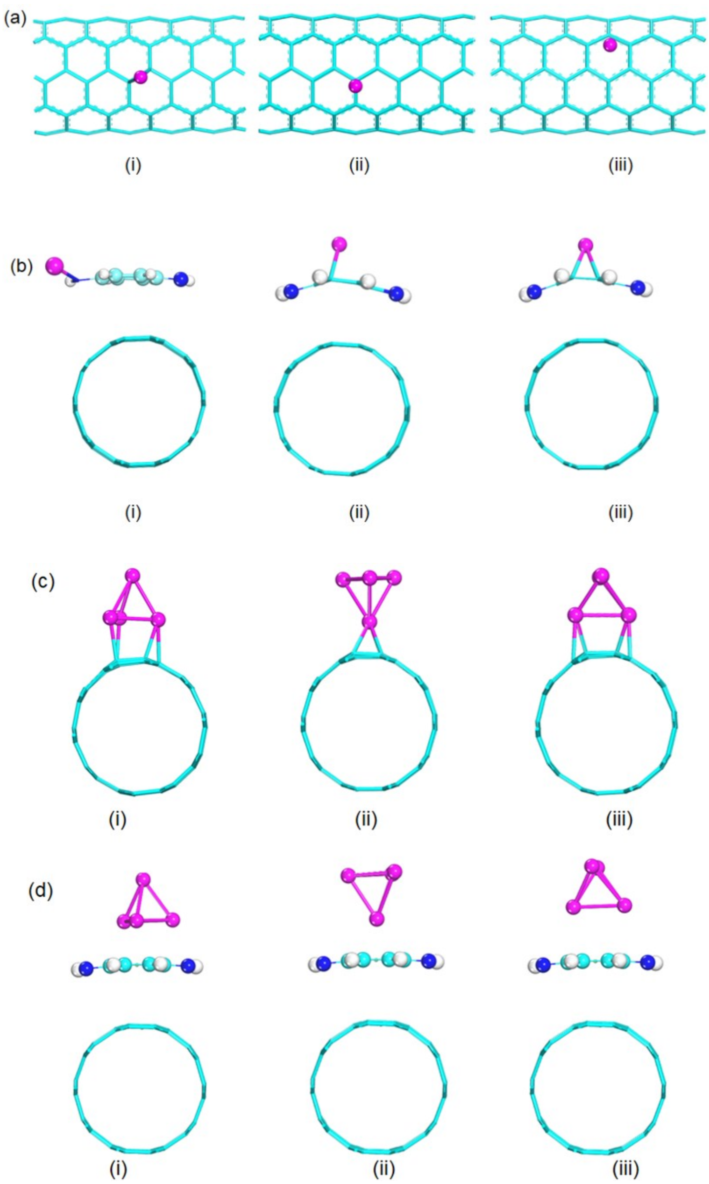


Fig. S5 Adsorption sites of Pd on CNT(a); Adsorption sites of Pd on PANI@CNT(b); adsorption sites of Pd4 on CNT(c); adsorption sites of Pd4 on PANI@CNT(d).

Table S2 Catalytic performance of catalytic performance of different Pd based catalysts in the coupling reaction

Entry	Catalyst[1]	Temp (°C)	Time (h)	Amount (mol% Pd)	Yield[2] (%)	Reuse	Final Yield (%)
1	Pd/HCN[3] [1]	120	1	0.255	100[4]	6th	100
2	Pd/MFC[5] [2]	120	4	0.308	100[4]	5th	95
3	Pd/graphene oxide [3]	Reflux	5	0.54	62[6]	/	/
4	Pd/MCPPy[7] [4]	120	3	0.01 g, 21 wt%	97[6]	5th	/
5	PdNs-PAMAM-g-MWCNTs [5]	100	2.5	0.3	95[8]	7th[9]	95
6	Fe_3O_4-NH_2-Pd [6]	130	10	5	>99[4,10]	4th	94
7	[Pd]-APTS-Y[11] [7]	120	2	0.075 g, 4.5 wt%	95[4,10]	3rd[9]	94
8	PVP-Pd/SiO_2 [8]	120	1	0.5	93[8]	7th[12]	100
9	Pd/N-MCNPs[13] [9]	120	3	0.01g, 40 wt%	97[8,10]	3rd	97
10	PANI-Pd [10]	120	40	2.25	98[8]	3rd	90
11	Pd/PANI@CNT-0.5[14]	110	1.5	0.15	98[4]	10th	94
12	Pd/PANI@CNT-0.5[14]	100	2.5	0.2	95[4]	/	/

[1]References; [2]Coupling reaction of iodobenzene and styrene; [3]HCN=hollow carbon nanonets; [4]Yields were calculated against the consumption of the aryl halides; [5]Pd/MFC=Pd nanoparticles supported on magnetic Fe_3O_4@C nanocomposites; [6]GC Yield; [7]MCPPy= magnetic carboxylated polypyrrole nanotubes; [8]Isolated yields; [9]Reaction of 4-methyl-iodobenzene and methyl acrylate; [10]N_2 atmosphere; [11]APTS-Y=Amine-Functionalized Zeolite; [12]Reaction of iodobenzene and n-butyl acrylate; [13]N-MCNPs=Nitrogen-doped magnetic carbon nanoparticles; [14]Reaction conditions: iodobenzene (1 mmol), styrene (1.5 mmol), NEt_3 (1.5 mmol) and 2 mL of DMF.

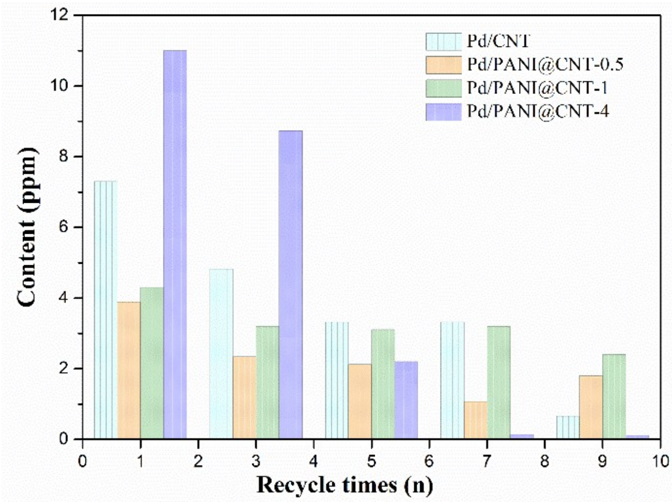


Fig. S6. Leached amounts of the Pd species in solvent in selected runs. Reaction conditions: The reaction was carried out with 5 mmol of IB, 7.5 mmol of styrene, 7.5 mmol of NEt_3, 0.15 mol% Pd with respect to the IB and 10 mL of DMF at 110 ^oC. The tested details are presented in experimental section.

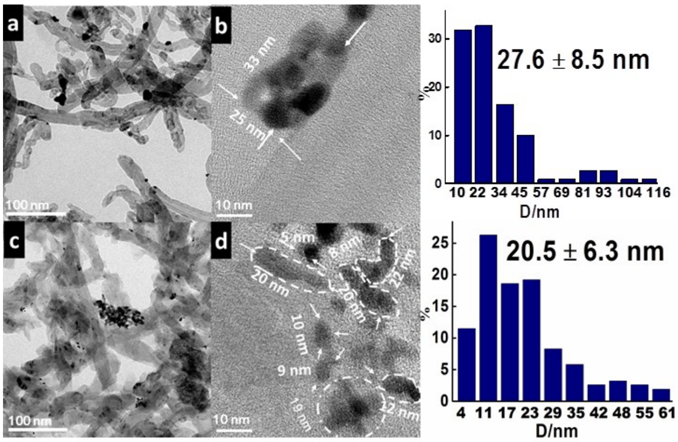


Fig. S7. TEM of catalyst after recycling ten times: Pd/CNT(a,b); Pd/PANI@CNT-0.5(c,d). The used catalyst was washed with DMF, ethyl alcohol and water to remove organic compounds like stilbene.

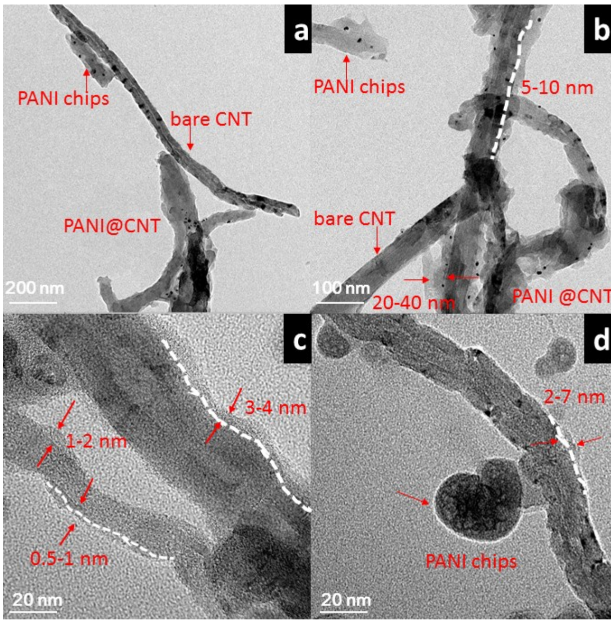
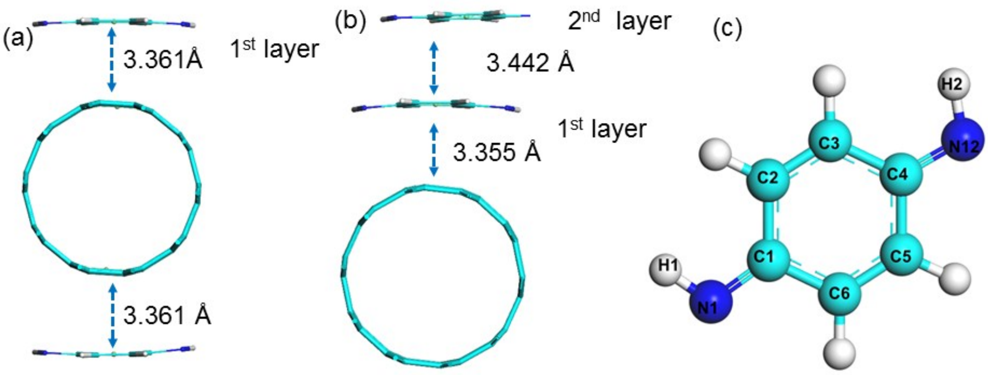


Fig. S8 TEM results of Pd/CNT@PANI-4 after five times of reuse.



Parameter	M-model	D-model	
	PANI of 1st layer	PANI of 1st layer	PANI of 2nd layer
N1-C1	1.312 Å	1.313 Å	1.306 Å
C1-N1-H1	110.3^{O}	110.3^{O}	110.1^{O}

Fig. S9 Structural parameters of PANI2@CNT with M-model(a); D-model(b) and atom name of PANI fragment(c).

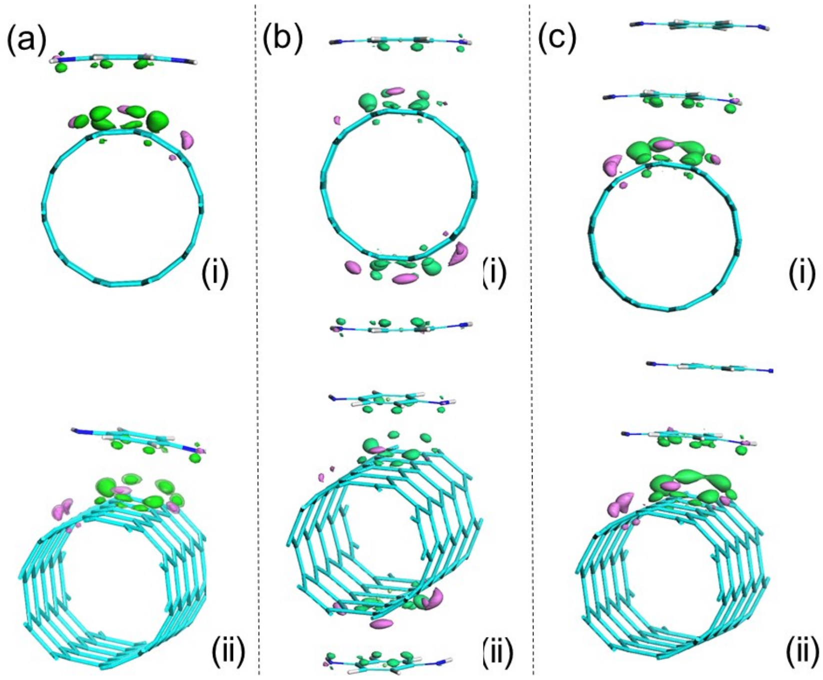


Fig. S10 Calculated charge density difference Δρ for PANI@CNT complex(a); PANI2@CNT with M-model(b); PANI2@CNT with D-model(c); front view(i); side view(ii). Iso-density surfaces for electron accumulation/depletion of 0.002 e/$Å^3$ are displayed in green (-)/pink (+).

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