Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Supplementary information of

Three Dimensional Composites of Graphene as Supports in Pd-Catalyzed Synthetic Applications

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S1 SEM image

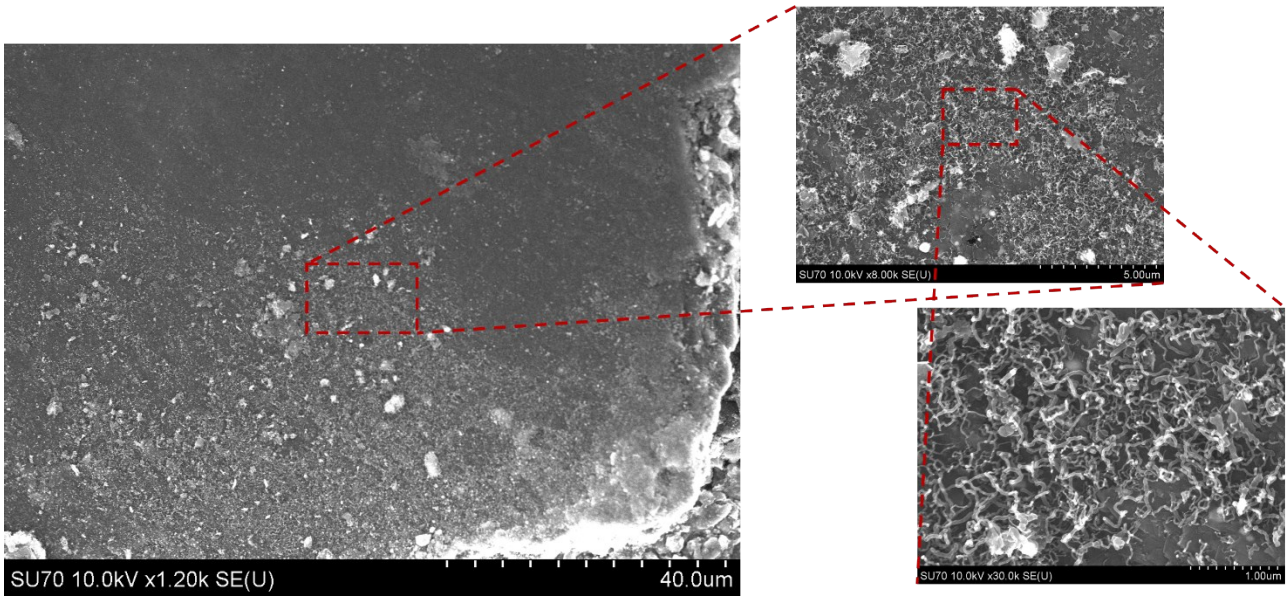


Figure S1 SEM images of NiGCNNT 3 mins

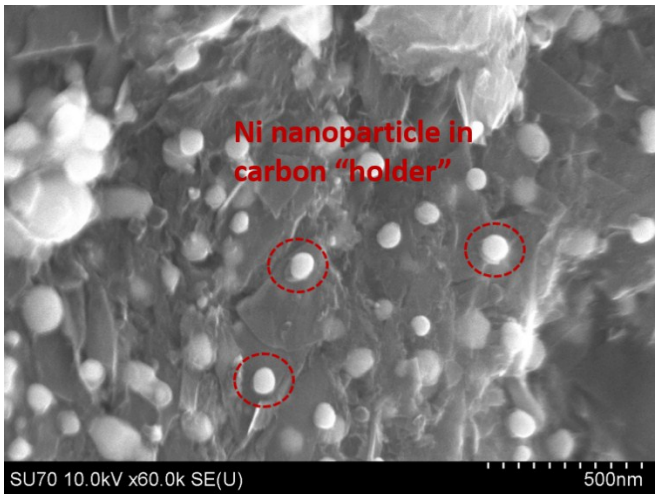


Figure S2 Bare Ni nanoparticles sit in carbon "holder". SEM images of NiGCNT 3 mins is shown. Some Ni nanoparticles are not successfully induced the growth of carbon nanotube. However, some bare Ni nanoparticle were partially coated with carbon which demonstrates the initial state of the growth process.

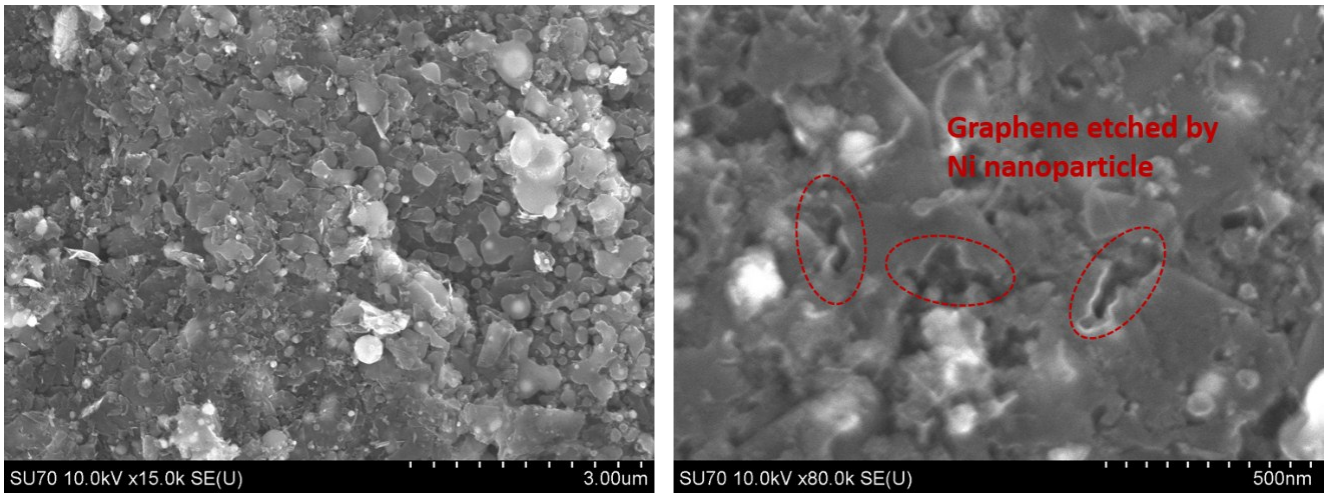


Figure S3 Graphene etched by Ni nanoparticles during the microwave process. The consumed carbon in the graphene is thought to be the source of carbon to grow carbon nanotube.

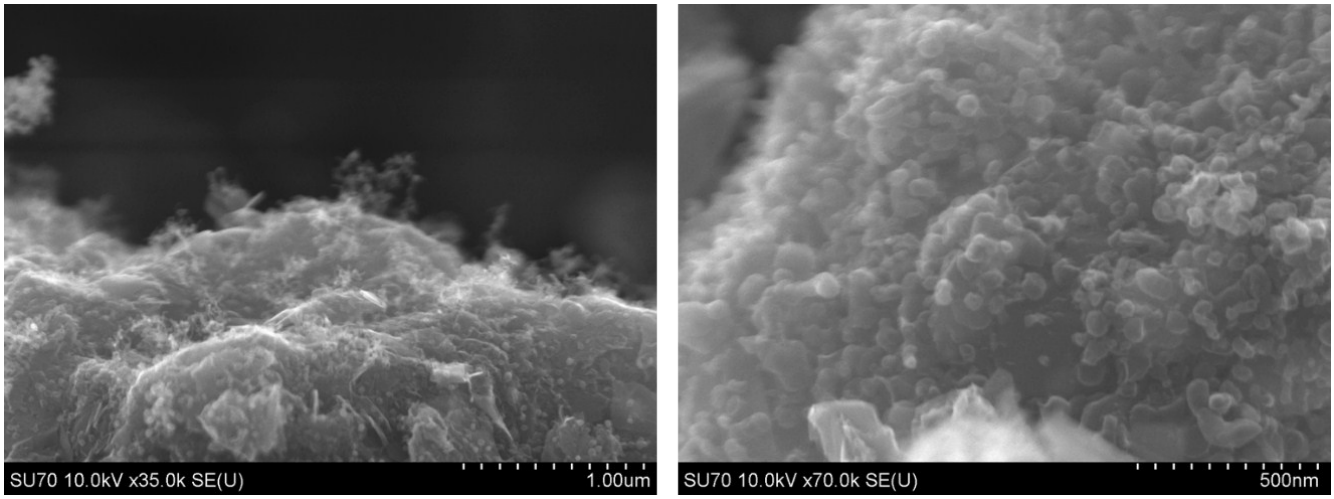


Figure S4 Graphene is coated by small fragments of carbon nanotube/GNP. The exact cause of the coating process is still unknown.

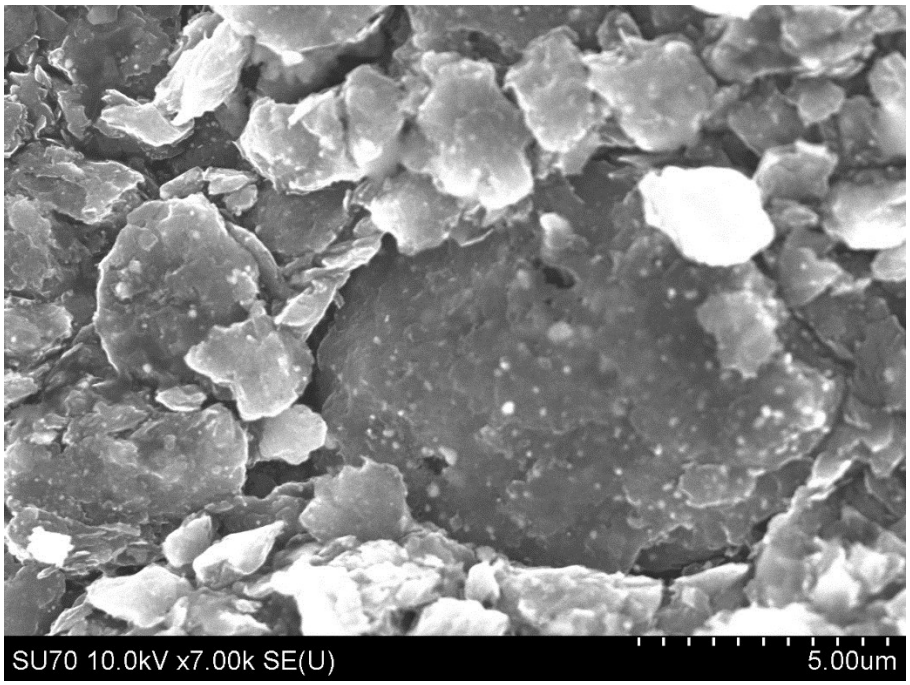


Figure S5 Ni/AC produced by ball milling and 1100 W fix power microwave irradiation. No carbon nanotube was generated.

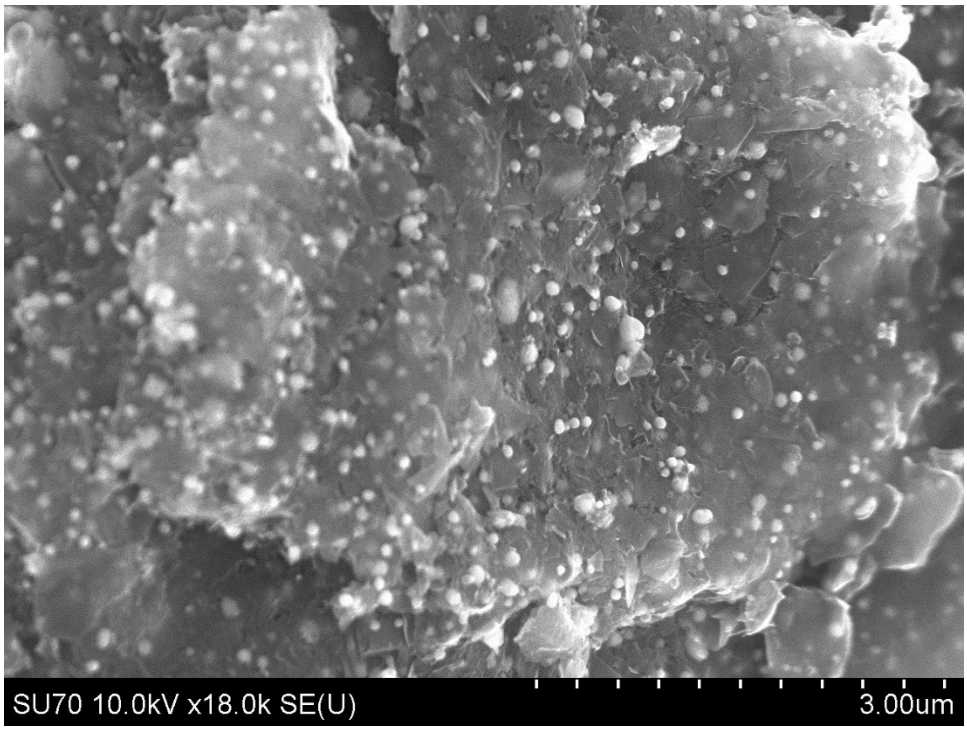


Figure S6 Ni/GNP produced by ball milling and microwave irradiation in a water bath. Large Ni nanoparticles on graphene were generated. No carbon nanotube was synthesized.

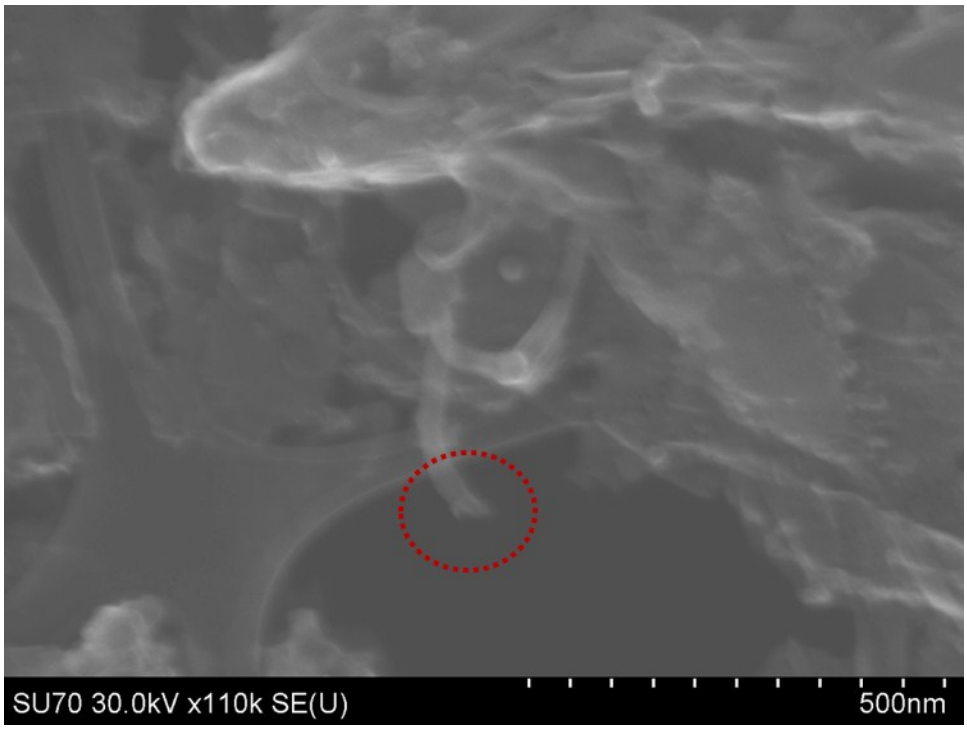
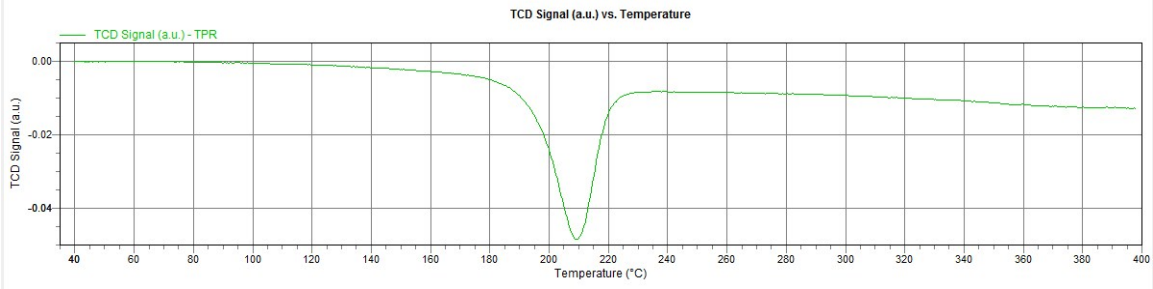


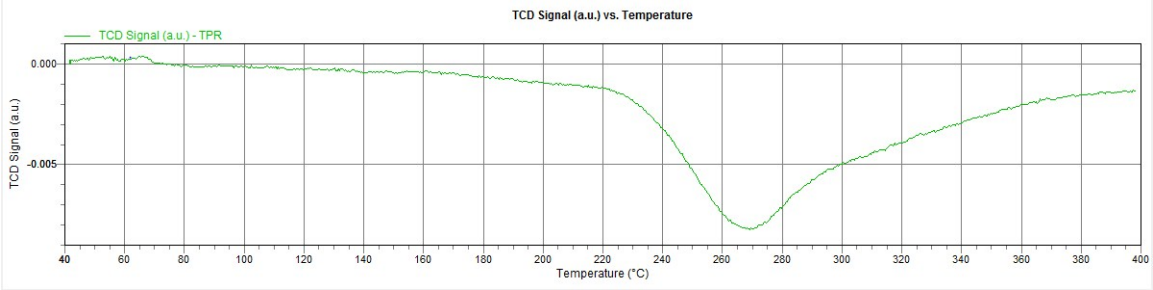
Figure S7 SEM image shows CNT has been broken by the second ball milling process

S2 Chemisorption test of the GCNT supported catalysts

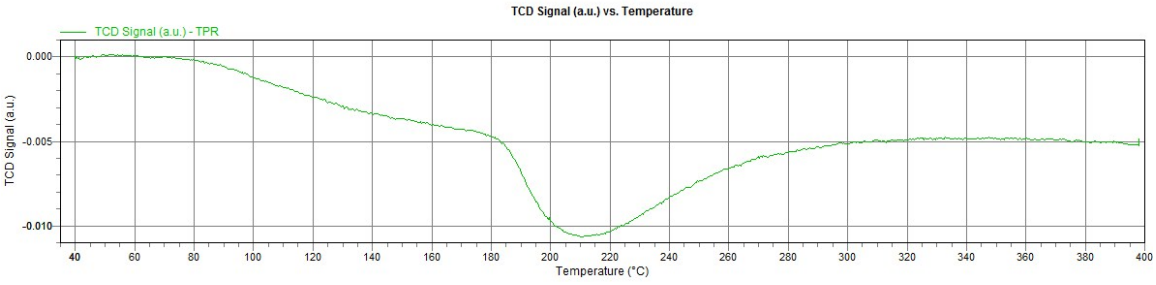
Method: Temperature programmed reduction (TPR) and pulse chemisorption experiments with H_2 titration were conducted with the Micromeritics AutoChem II 2920 chemisorption analyzer to determine the number of active sites, metal dispersion, metallic surface area, and active particle size. For a pulse chemisorption experiment the sample was first pretreated, to reduce all Pd sites, with flowing 10%H2/ Ar balance for 1 h at 200 °C followed by a purge step using Ar flow for 30 min at 200 °C. The sample was allowed to cool to 40 °C under Ar flow. Next, oxygen was adsorbed on surface metal sites with flowing 10% O2/He balance for 30 min and then purged for 30 min with flowing Ar. After purging, the loop was filled with a calibrated amount of 10%H2/Ar and dosed every 4 min over the sample, titrating the adsorbed oxygen with the hydrogen producing water and chemisorbed hydrogen. Hydrogen consumption was determined using TCD measurements recorded every 0.1 s. Oxygen adsorption stoichiometry was assumed to be one atom of oxygen per surface Pd site. Furthermore, assuming one H2 is consumed for each adsorbed oxygen atom and there is one adsorbed hydrogen atom per surface Pd site, the overall stoichiometry of Pd surface sites to H2 consumed is 0.667 Pd:1 H2.



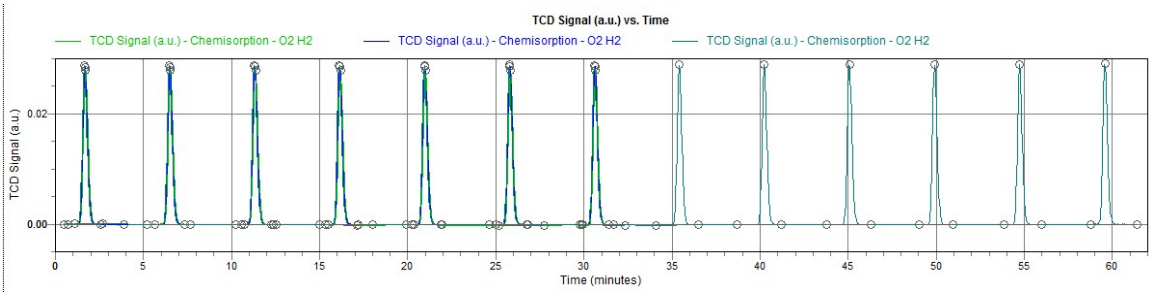
TPR of NiGCNT support



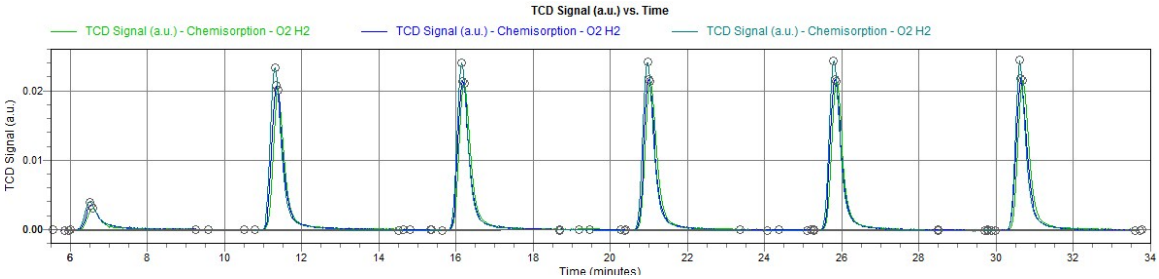
TPR of Pd/ NiGCNT BM



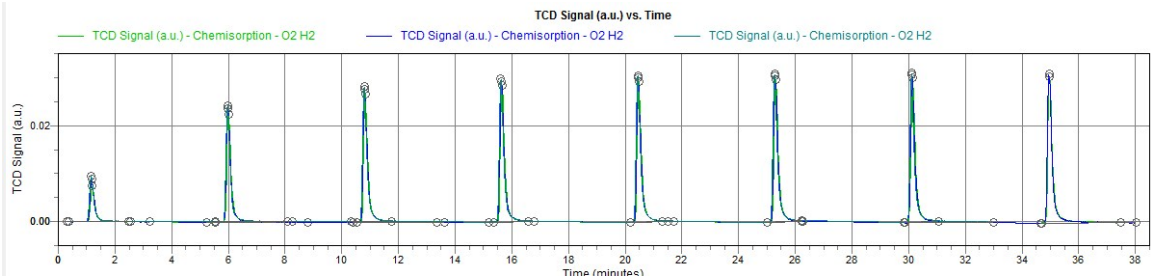
TPR of Pd/ NiGCNT CO



Chemisorption of the NIGCNT which shows no H_2 uptake for Ni NPs under the test condition.



Chemisorption result of Pd/ NiGCNT CO sample, the surface area of Pd is, the estimated Pd nanoparticle size is around 18 nm. The surface area of the metal is 21 m^2/g.



Chemisorption result of Pd/ NiGCNT BM sample, the surface area of Pd is, the estimated Pd nanoparticle size is around 11 nm. The surface area of the metal is 36 m^2/g.

Catalysts	Pd surface area (m^2/g)	Size of Pd NPs (nm)	Active Pd site (mmol/g)
Pd/ NiGCNT CO	36	11	0.017
Pd/ NiGCNT BM	21	18	0.050

S3 XPS

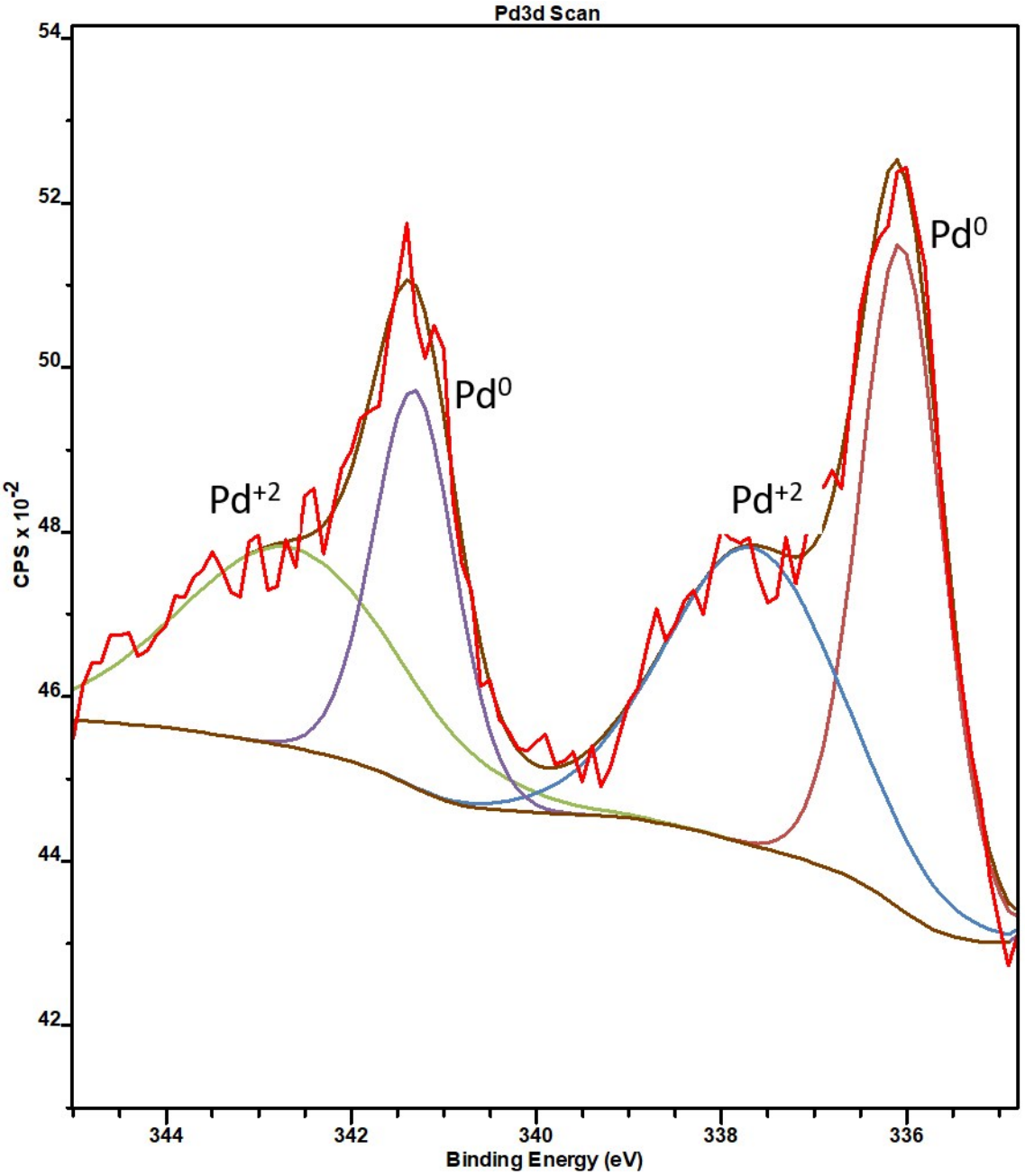


Figure S8 Pd 3d XPS spectrum of Pd/NiGCNT BM. Pd^{+2} content in Pd/NiGCNT BM is higher than that in Pd/NiGCNT CO sample presented in Figure 2 (E).

S4 ICP test of the NiGCNT supported catalysts

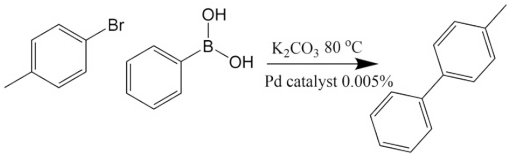
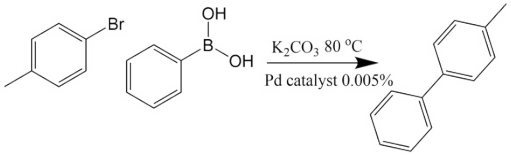
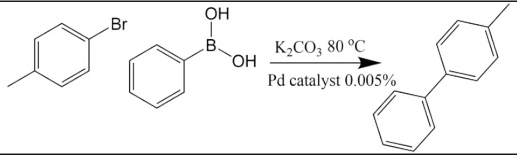
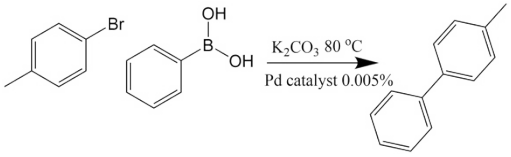
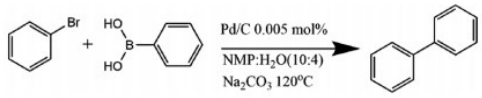
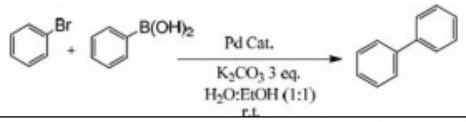
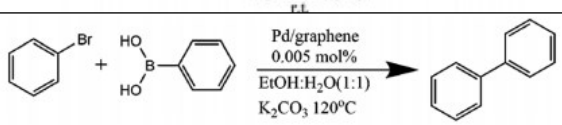
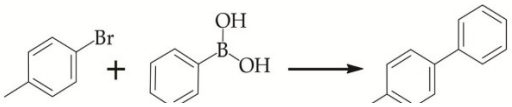
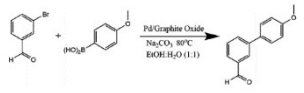
Catalyst	Ni Content (wt. %)		Pd Content (wt. %)	
	Nominal	ICP	Nominal	ICP
Pd/GCNT BM	10	6.3	10	8.6
Pd/GCNT CO	10	6.4	10	8.3

Ni and Pd content determined by ICP

Catalyst	leached Ni		leached Pd	
	ppm	% of overall Ni	ppm	% of overall Pd
Pd/GCNT BM	1.4	4.7	0.9	2.6
Pd/GCNT CO	1.5	4.8	0.98	2.7

The amount of leached Ni and Pd in the model Suzuki reaction were determined by ICP.

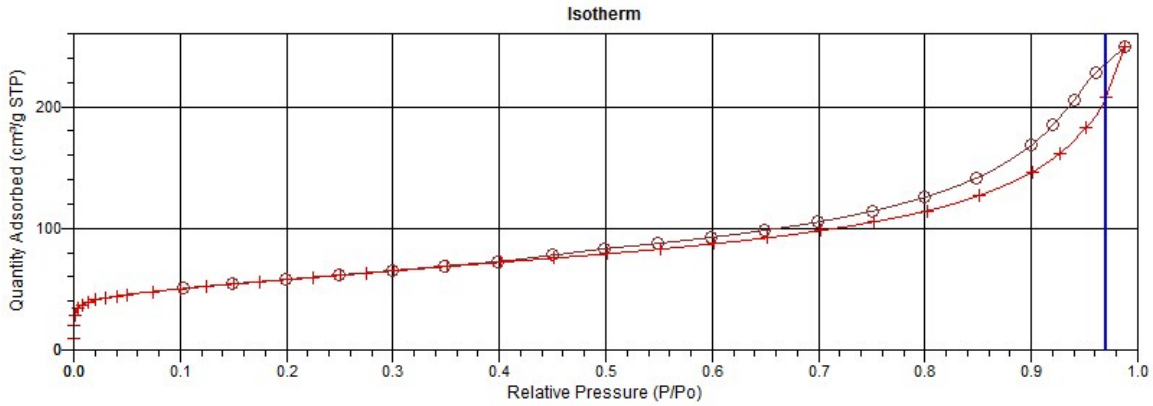
S5 TOF for Suzuki reactions catalyzed by graphene and carbon nanotube supported Pd NPs.

Catalysts	Reaction	TOF (h^{-1})
Pd/NiGCNT CO (This work)		115,000
Pd/NiGCNT BM (This work)		105,000
Pd/AC (This work)		12,000
Pd/CNT (This work)		110,000
Pd/AC[1]		16,600
Pd/CNT[2]		217,500
Pd/defective graphene[3]		230,000
Pd/GNP[4]		220,000
Pd/GO[5]		39,000

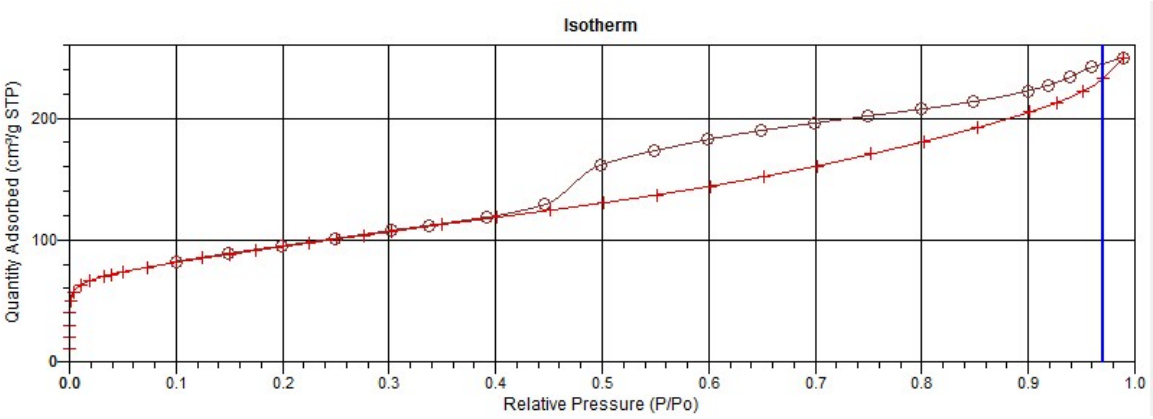
The TOFs calculated for different reagents and reaction conditions are not directly comparable. However, the graphene and carbon nanotube supported Pd catalysts show higher reactivities than Pd on activated carbon catalysts.

S6 BET and micropore area

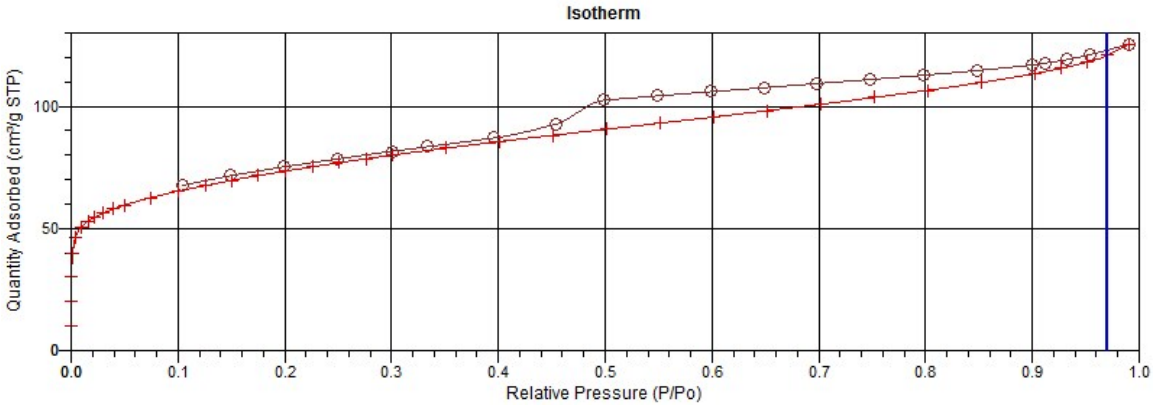
Sample	BET surface (m^2/g)	Micropore (m^2/g)
GNP 500	408	180
GNP 500 BM	258	185
GNP 500 BM-KMW	266	199
Ni/GNP BM	144	50
Ni/GNP CO	196	78
Pd/GNP BM	158	68
Pd/GNP CO	187	90
Ni/GNP BM-KMW1MIN	319	92
Ni/GNP BM-KMW2MIN	325	125
Ni/GNP BM-KMW3MIN	303	106
Pd/NiGCNT BM	282	172
Pd/NiGCNT CO	330	166



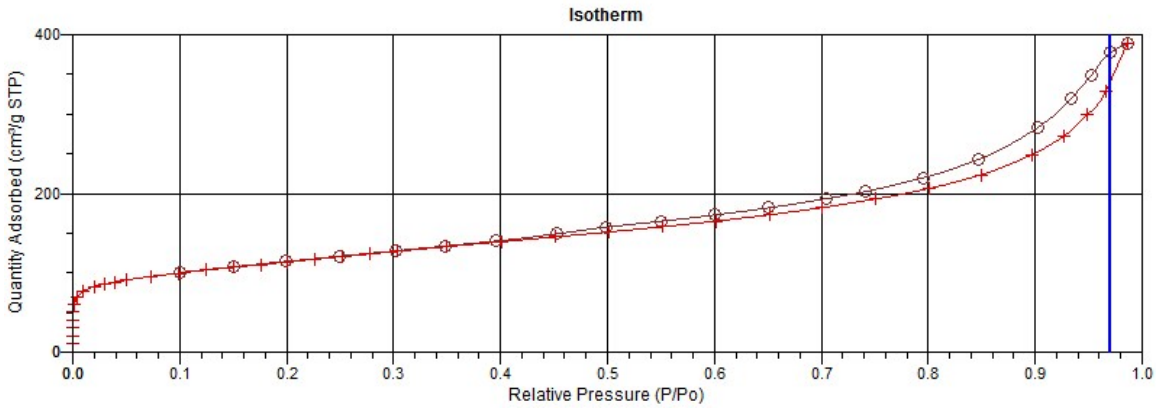
The adsorption-desorption isotherm of Ni/GNP BM



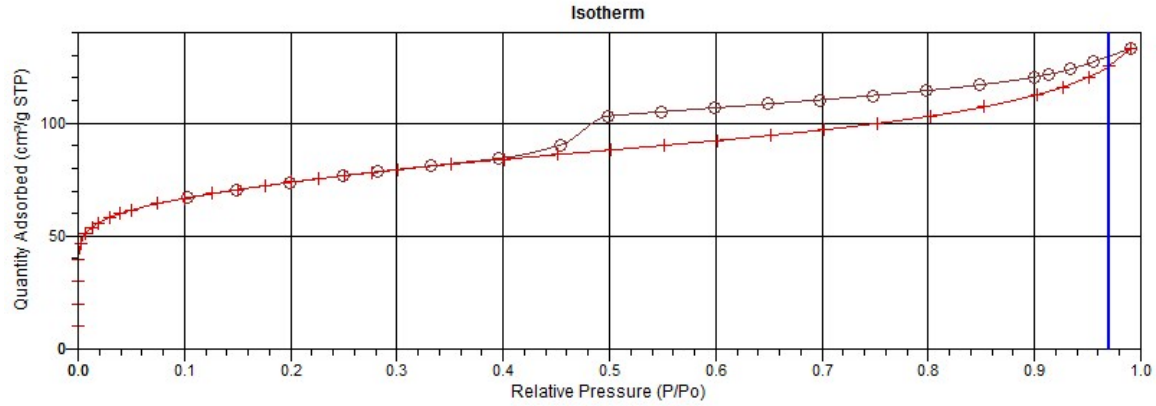
The adsorption-desorption isotherm of GNP BM



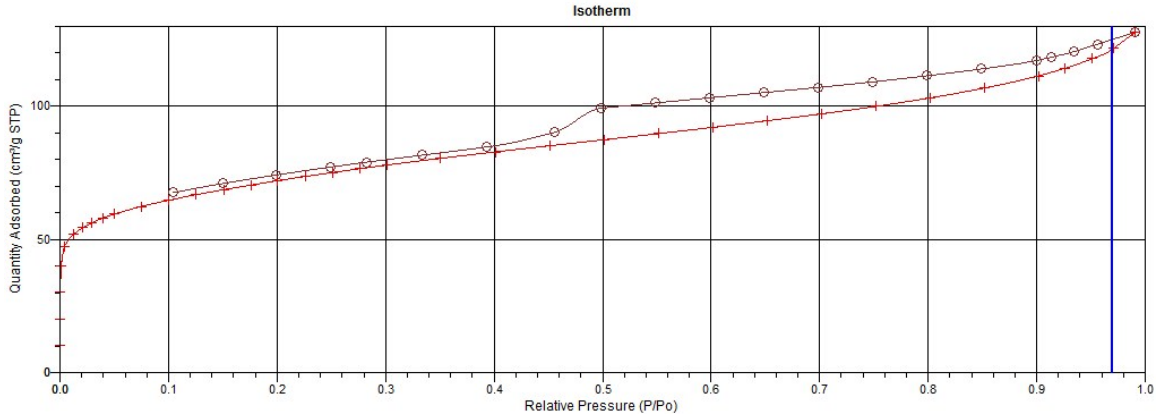
The adsorption-desorption isotherm of GNP BM KMW 2 MIN



The adsorption-desorption isotherm of Pd/NiGCNT BM

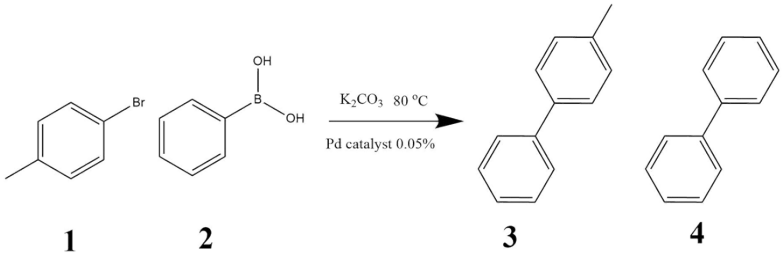


The adsorption-desorption isotherm of Pd/NiGCNT CO



The adsorption-desorption isotherm of Pd/GNP CO

S7 Recyclability test in Suzuki reaction



1 **2** **3** **4**

Cycle of reaction	**Pd/NiGCNT BM**		**Pd/NiGCNT CO**	
	Conversion* of 1	Conversion to 3**	Conversion of 1	Conversion to 3
1	100	86	100	89
2	100	89	100	93
3	100	90	100	93
4	100	88	100	98
5	100	92	100	98
6	100	90	100	98
7	95	90	100	97
8	98	89	94	94

* All conversions were determined by GC/MS as fractional conversion.

** The competing reaction is the homo-coupling of the phenylboronic reagent resulting in byproduct 4 and reduction of the Pd^{+2} to Pd^{0}.

Table S2 Recyclability test in model Suzuki reaction

Reference:

(1) Köhler, K.; Heidenreich, R. G.; Soomro, S. S.; Pröckl, S. S. *Advanced Synthesis & Catalysis* **2008**, *350*, 2930.

(2) Siamaki, A. R.; Lin, Y.; Woodberry, K.; Connell, J. W.; Gupton, B. F. *Journal of Materials Chemistry A* **2013**, *1*, 12909.

(3) Moussa, S.; Siamaki, A. R.; Gupton, B. F.; El-Shall, M. S. *ACS Catalysis* **2012**, *2*, 145.

(4) Gilliland, S. E.; Tengco, J. M. M.; Yang, Y.; Regalbuto, J. R.; Castano, C. E.; Gupton, B. F. *Applied Catalysis A: General* **2018**, *550*, 168.

(5) Scheuermann, G. M.; Rumi, L.; Steurer, P.; Bannwarth, W.; Mülhaupt, R. *Journal of the American Chemical Society* **2009**, *131*, 8262.