Supplementary Information

Pd/Co_3O_4-Pd/PdO formed in situ on the surface of the self-assembly ferrocenylimine Pd(II)/Co(II) monolayer for catalyzing Suzuki cross coupling reaction ----Formation, synergistic effect, and catalytic mechanism

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Contents

1. Figure caption

Fig. S1 FT-IR spectra of **GO**, **GO@APTES**, **GO@APTES-Fcl**, and **GO@APTES-Fcl-Pd/Co**.

Fig. S2 XRD spectra of **GO**, **GO@APTES**, **GO@APTES-Fcl** and **GO@APTES-Fcl-Pd/Co**.

Fig. S3 Raman spectra of **GO**, **GO@APTES**, **GO@APTES-Fcl** and **GO@APTES-Fcl-Pd/Co**.

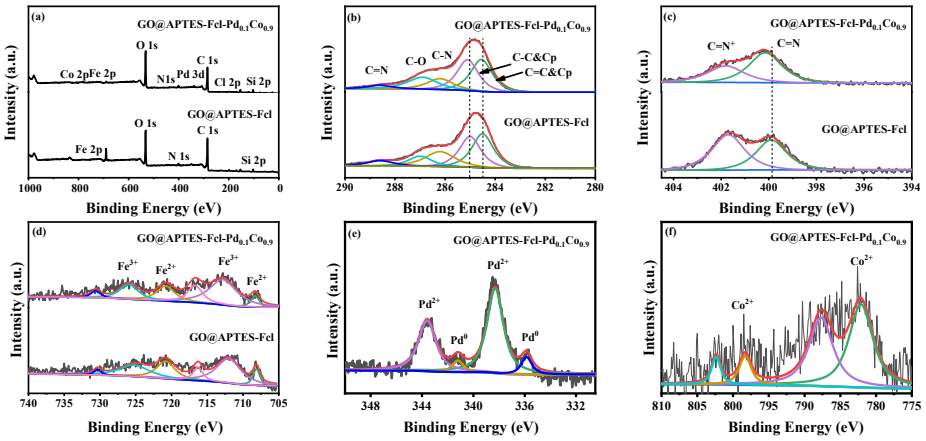

Fig. S4 (a) Survey XPS spectra of **GO@APTES-Fcl** and **GO@APTES-Fcl-Pd/Co**, HR-XPS of (b) C 1s, (c) N 1s , (d)Fe 2p , (e) Pd 3d, and (f) Co 2p.

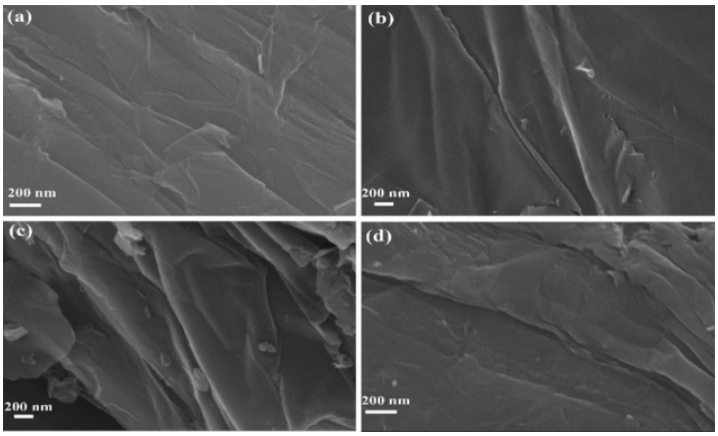

Fig. S5 SEM images of (a) **GO**, (b) **GO@APTES**, (c) **GO@APTES-Fcl**, (d) **GO@APTES-Fcl-Pd/Co**.

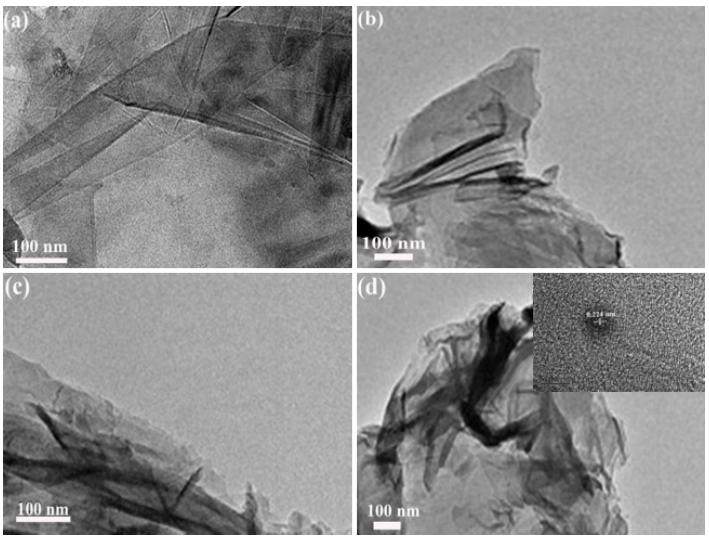

Fig. S6 TEM images of (a) **GO**, (b) **GO@APTES**, (c) **GO@APTES-Fcl**, (d) **GO@APTES-Fcl-Pd/Co**.

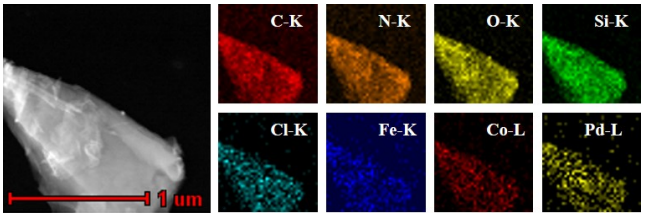

Fig. S7 TEM image and the corresponding elemental mapping analysis of **GO@APTES-Fcl-Pd/Co**.

Fig. S8 EIS of the catalyst on the ITO glass for GO, **GO@APTES**, **GO@APTES-Fcl**, **GO@APTES-Fcl-Pd/Co**.

Fig. S9 (a) N2 adsorption-desorption isotherms and (b) the corresponding pore size distribution for GO, **GO@APTES**, **GO@APTES-Fcl**, **GO@APTES-Fcl-Pd/Co**.

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Fig. S 10 XRD spectra of **Si-OH**, **Si@APTES**, **Si@APTES-Fcl**, **Si@APTES-Fcl-Pd/Co**.

Fig. S11 Water contact angle images of **Si-OH**, **Si@APTES**, **Si@APTES-Fcl**, **Si@APTES-Fcl-Pd/Co**.

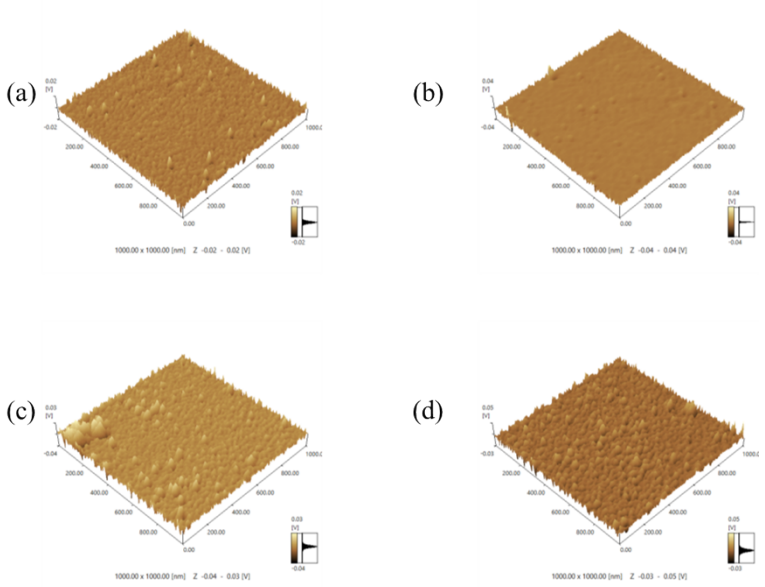


Fig. S12 AFM images of the surface topography of the modified silicon wafer (a) Si-OH,

(b) **Si@APTES**, (c) **Si@APTES-Fcl**, (d) **Si@APTES-Fcl-Pd/Co**

Fig. S13 Hot filtration and kinetic experiment of **GO@APTES-Fcl-Pd$_{0.1}$Co$_{0.9}$**.

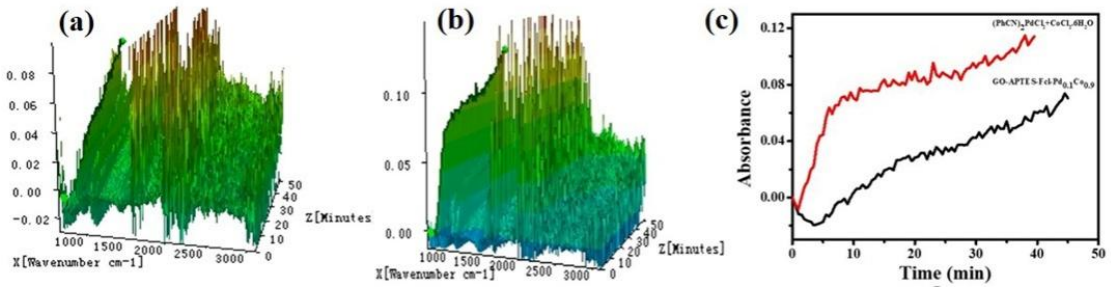


Fig. S14 React-IR plots over time for the formation of 4-Phenyltoluene by Suzuki reaction (a) 3D map catalyzed by **GO@APTES-Fcl-Pd$_{0.1}$Co$_{0.9}$**, (b) 3D map catalyzed by $(PhCN)_2PdCl_2/CoCl_2\cdot 6H_2O$, (c) Kinetic analysis of the reaction catalyzed by **GO@APTES-Fcl-Pd$_{0.1}$Co$_{0.9}$** (black line) and $(PhCN)_2PdCl_2/CoCl_2\cdot 6H_2O$.(red line)

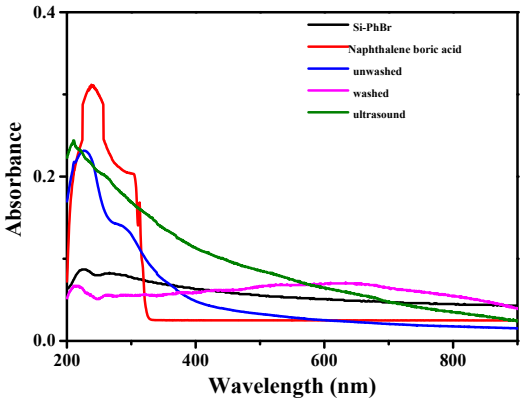


Fig. S15 UV spectra of **Si-PhBr** in the three-phase testing. Treatment: washed with solvents (DCM, EtOH, and MeOH) and ultrasonic.(naphthybronoic acid, red; **Si-PhBr**, black; **Si-PhBr**[add **Si@APTES-Fcl-Pd$_{0.1}$Co$_{0.9}$** without wash], blue: **Si-PhBr** [added **GO@APTES-Fcl-Pd$_{0.1}$Co$_{0.9}$**, washed], pink).

Fig. S16 The varied ratios of Co(III)/Co(II) on the surface of **GO@APTES-Fcl-Pd$_{0.1}$Co$_{0.9}$** during catalysis and recycling.

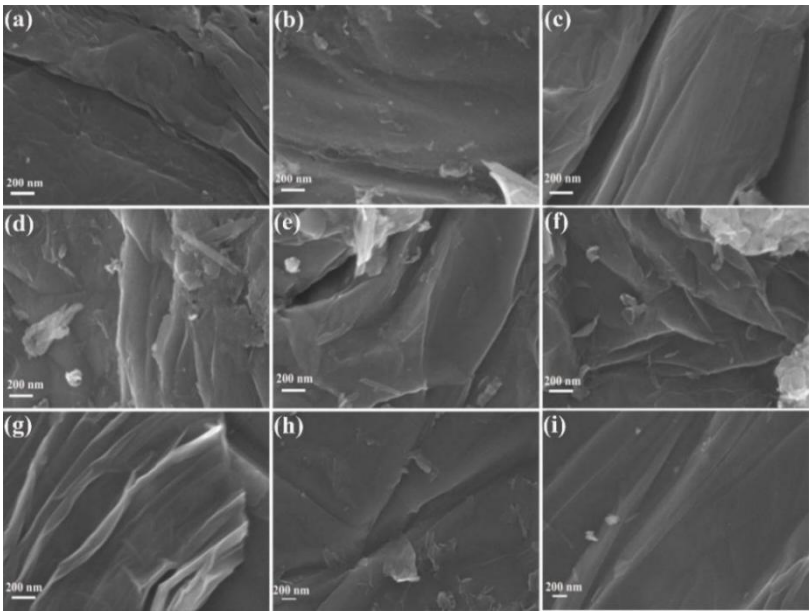


Fig. S17 SEM images of **GO@APTES-Fcl-Pd$_{0.1}$Co$_{0.9}$** (a) fresh, (b) 1st run, (c) 2nd run, (d) 3rd run, (e) 4th run, (f) 5th run, (g) 6th run, (h) 7th run, (i) 8th run

Fig. S18 XRD spectra of **GO@APTES-Fcl-$Pd_{0.1}Co_{0.9}$** in the process of recycles

Fig. S19 Raman spectra of **GO@APTES-Fcl-$Pd_{0.1}Co_{0.9}$** in the process of recycles

Fig. S20 FT-IR spectra of **GO@APTES-Fcl-$Pd_{0.1}Co_{0.9}$** in the process of recycles.

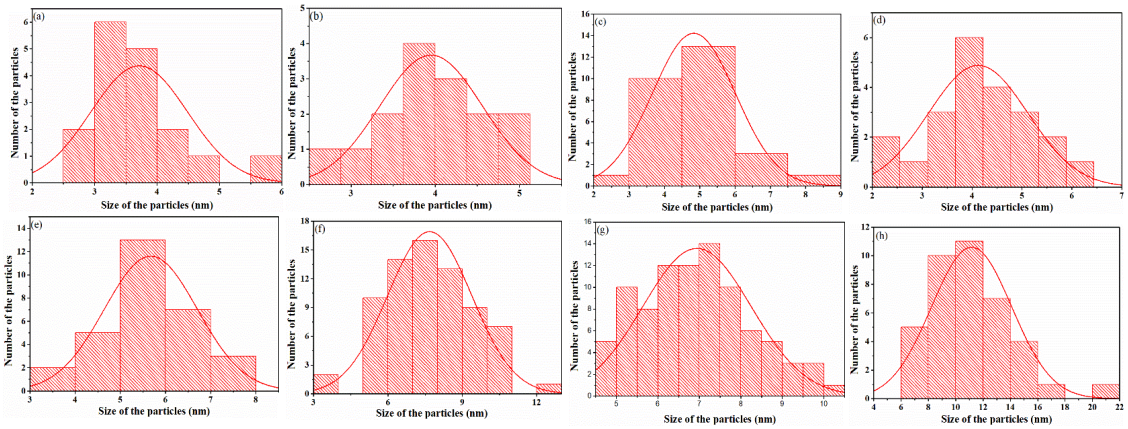
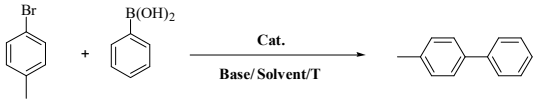


Fig. S21 histogram of the particles diameters in the process of recycling.: (a) 1st run, (b) 2nd run, (c) 3rd run, (d) 4th run, (e) 5th run, (f) 6th run, (g) 7th run, (h) 8th run

2. Table Lists

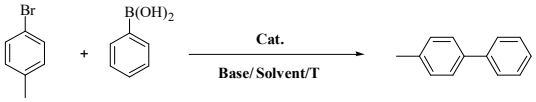
Table S1 Screening of Pd sources in the Suzuki coupling reaction using **GO-APTES-Fcl-Pd/Co**.[a]



Pd source	Base	Solvent	Time(min)	T(°C)	Isolated yield(%)
$(C_{17}H_{14}P)_2Fe \cdot PdCl_2$	K_2CO_3	H_2O:EtOH(1:1)	120	70	44
$(CF_3COO)_2Pd$	K_2CO_3	H_2O:EtOH(1:1)	120	70	35
$PdCl_2$	K_2CO_3	H_2O:EtOH(1:1)	120	70	92
$Pd(OAc)_2$	K_2CO_3	H_2O:EtOH(1:1)	120	70	88
$(C_6H_5CN)_2PdCl_2$	K_2CO_3	H_2O:EtOH(1:1)	120	70	99
Li_2PdCl_4	K_2CO_3	H_2O:EtOH(1:1)	120	70	93

[a]Reaction condition:$PhB(OH)_2$ (0.30 mmol), 4-bromotoluene (0.25 mmol), Base (0.5 mmol), **GO-APTES-Fcl-Pd/Co** (1mg), solvent (4 mL), temperature (70 °C), 120 min.

Table S2 Optimization of reaction conditions in Suzuki coupling using **GO@APTES-Fcl-$Pd_{0.1}Co_{0.9}$**.[a]



Entry	Base	Solvent	Time (min)	T (°C)	Isolated yield (%)
1	K_2CO_3	H_2O:EtOH(1:1)	120	80	99
2	K_2CO_3	H_2O:EtOH(1:1)	120	60	38
3	K_2CO_3	H_2O:EtOH(1:1)	120	70	99
4	K_2CO_3	H_2O	120	70	26
5	K_2CO_3	EtOH	120	70	14
6	K_2CO_3	CH_3OH	120	70	4
7	K_2CO_3	THF	120	70	96
8	K_2CO_3	Toluene	120	70	12
9	K_2CO_3	$CH_3COOC_2H_5$(EA)	120	70	trace
10	K_2CO_3	H_2O:EtOH(3:1)	120	70	78
11	K_2CO_3	H_2O:EtOH(2:1)	120	70	80
12	K_2CO_3	DMF	120	70	12
13	K_2CO_3	DMSO	120	70	14
14	K_2CO_3	1,4-Dioxane	120	70	11
15	K_2CO_3	H_2O:EtOH(1:1)	5	70	10
16	K_2CO_3	H_2O:EtOH(1:1)	10	70	13
17	K_2CO_3	H_2O:EtOH(1:1)	20	70	40
18	K_2CO_3	H_2O:EtOH(1:1)	40	70	42
19	K_2CO_3	H_2O:EtOH(1:1)	60	70	86
20	K_2CO_3	H_2O:EtOH(1:1)	90	70	91
21	K_2CO_3	H_2O:EtOH(1:1)	120	70	99
22	K_2CO_3	H_2O:EtOH(1:1)	120	70	99
23	Na_2CO_3	H_2O:EtOH(1:1)	120	70	89
24	$NaHCO_3$	H_2O:EtOH(1:1)	120	70	32
25	NaOH	H_2O:EtOH(1:1)	120	70	74
26	K_3PO_4	H_2O:EtOH(1:1)	120	70	50
27	K_2CO_3	H_2O:EtOH(1:1)	120	70	58[b]
28	K_2CO_3	H_2O:EtOH(1:1)	150	70	67[b]

[a]Reaction conditions: $PhB(OH)_2$ (0.30 mmol)，4-bromotoluene (0.25 mmol)，Base (0.5 mmol)，solvent (4 mL)

at 70 °C ; [b]$PhB(OH)_2$ (0.55 mmol)，4-bromotoluene (0.50 mmol)，Base (1.0 mmol)，catalyst: **GO@APTES-Fcl-$Pd_{0.1}Co_{0.9}$** (1 mg).

Table S3 Effect of metal types and proportions on the catalytic performance of **GO@APTES-Fcl-Pd/M**.

Entry	Cat.	Solvent	Time (min)	T (°C)	Isolated yield (%)	TOF (h^{-1})
1	GO@APTES-Fcl-$Pd_{0.5}Co_{0.5}$	H_2O:EtOH(1:1)	120	70	96	2280
2	GO@APTES-Fcl-$Pd_{0.1}Co_{0.9}$	H_2O:EtOH(1:1)	120	70	99	11353
3	GO@APTES-Fcl-$Pd_{0.07}Co_{0.93}$	H_2O:EtOH(1:1)	120	70	82	2613
4	GO@APTES-Fcl-$Pd_{0.05}Co_{0.95}$	H_2O:EtOH(1:1)	120	70	16	9878
5	GO@APTES-Fcl-$Pd_{0.02}Co_{0.98}$	H_2O:EtOH(1:1)	120	70	3	1413
6	GO@APTES-Fcl-$Pd_{0.1}Cu_{0.9}$	H_2O:EtOH(1:1)	120	70	99	2750
7	GO@APTES-Fcl-$Pd_{0.1}Ru_{0.9}$	H_2O:EtOH(1:1)	120	70	93	870
8	GO@APTES-Fcl-$Pd_{0.07}Ru_{0.93}$	H_2O EtOH(1:1)	120	70	99	1767
9	GO@APTES-Fcl-$Pd_{0.05}Fe_{0.95}$	H_2O:EtOH(1:1)	120	70	19	164
10	GO@APTES-Fcl-$Pd_{0.1}Fe_{0.9}$	H_2O:EtOH(1:1)	120	70	40	3940
11	GO@APTES-Fcl-$Pd_{0.5}Fe_{0.5}$	H_2O:EtOH(1:1)	120	70	94	422
12	GO@APTES-Fcl-$Pd_{0.05}Ni_{0.95}$	H_2O:EtOH(1:1)	120	70	23	2521
13	GO@APTES-Fcl-$Pd_{0.1}Ni_{0.9}$	H_2O:EtOH(1:1)	120	70	66	43552
14	GO@APTES-Fcl-$Pd_{0.5}Ni_{0.5}$	H_2O:EtOH(1:1)	120	70	90	499
15	GO@APTES-Fcl-$Pd_{0.1}Co_{0.45}Ni_{0.45}$	H_2O:EtOH(1:1)	120	70	88	1337

[a]Reaction conditions: $PhB(OH)_2$ (0.30 mmol)，4-bromotoluene (0.25 mmol)，Base (0.5 mmol)，**GO@APTES-Fcl-Pd/M** (1 mg)，solvent (4 mL)，temperature (70 °C).

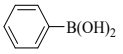
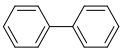
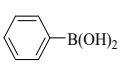
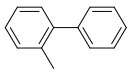
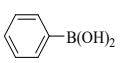
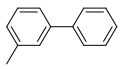
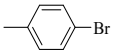
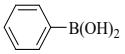
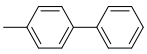
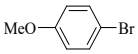
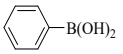
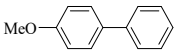
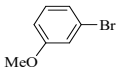
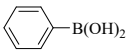
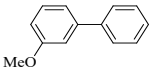
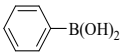
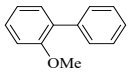
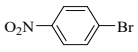
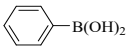
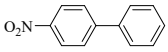
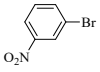
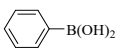
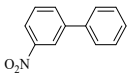
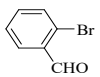
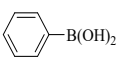
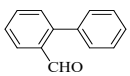
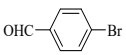
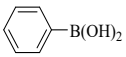
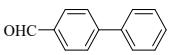
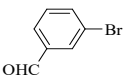
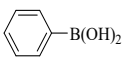
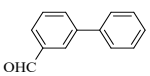
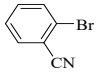
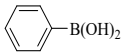
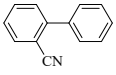
Table S4 Catalytic activity of different catalytic system in the Suzuki cross coupling reaction [a]

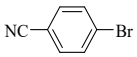
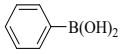
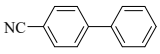
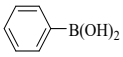
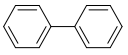
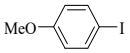
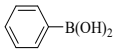
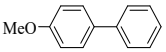
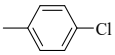
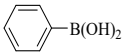
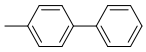
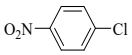
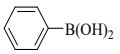
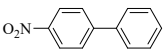
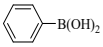
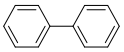
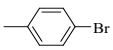
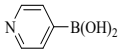
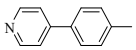
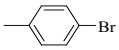
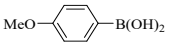
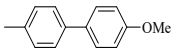
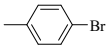
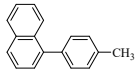
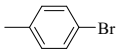
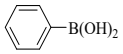
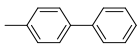
Entry	Catalyst	Pd loading($mmol \cdot mg^{-1}$)	Yield (%)	TON/TOF
1	GO	-	0[b]	-
2	GO@APTES	-	0[c]	-
3	GO@APTES-Fcl	-	0[d]	-
4	$(C_6H_5CN)_2PdCl_2/CoCl_2 \cdot 6H_2O$	1.09×10^{-5}	69[e]	15825/7918
5	GO+$(C_6H_5CN)_2PdCl_2/CoCl_2 \cdot 6H_2O$	1.09×10^{-5}	53	12155/6078

Entry	Catalyst	Pd loading(mmol·mg^{-1})	Yield (%)	TON/TOF
6	GO@APTES-Fcl +$(C_6H_5CN)_2PdCl_2/CoCl_2{\cdot}6H_2O$	1.09×10^{-5}	62	142201/7110
7	Si@APTES-Fcl-$Pd_{0.1}Co_{0.9}$	4.16×10^{-7}	45[f]	130216/10851
8	GO@APTES-Fcl-$Pd_{0.1}Co_{0.9}$	1.09×10^{-5}	99[g]	22706/11353
9	Si/APTES-Fcl-$Pd_{0.1}Co_{0.9}$	1.09×10^{-5}	33[h]	7568/3784

[a]Reaction conditions: $PhB(OH)_2$ (0.30 mmol), 4-bromotoluene (0.25 mmol), K_2CO_3 (0.5 mmol), catalyst 1 mg, solvent (50% aqueous alcohol 4 mL) at 70 °C for 2 h. [b]GO 1 mg. [c]**GO@APTES** 1 mg. [d]**GO@APTES-Fcl** (1mg). [e]$(C_6H_5CN)_2PdCl_2/CoCl_2{\cdot}6H_2O$ (1.09×10^{-5} mmol). [f]**Si@APTES-Fcl-$Pd_{0.1}Co_{0.9}$** (1×1 cm^2) for 12 h. [g]**GO@APTES-Fcl-$Pd_{0.1}Co_{0.9}$** (1 mg). [h]Si/APTES-Fcl-$Pd_{0.1}Co_{0.9}$ (spin- coated film on silicon wafer).

Table S5 Screening of different aryl halides with arylboronic acid in the Suzuki cross coupling reaction [a]

Entry	Ar-X	Ar-$B(OH)_2$	Product	Yield(%)
1				85
2				99
3				89
4				99
5				98
6				99
7				58
8				99
9				97
10				55
11				71
12				62
13				67

Entry	Ar-X	Ar-B(OH)$_2$	Product	Yield(%)
14				99
15				99
16				99
17				trace
18				trace
19				trace
20				trace
21				96
22				81
23				58[b]

[a]Reaction conditions: Ar-B(OH)$_2$ (0.30 mmol)，Ar-X (0.25 mmol)，Base (0.5 mmol)，**GO@APTES-Fcl-Pd$_{0.1}$Co$_{0.9}$** (1 mg)，solvent (4 mL) at 70 ℃。[b]PhB(OH)$_2$ (0.55 mmol)，4-bromotoluene (0.50 mmol)，Base (1.0 mmol)，**GO@APTES-Fcl-Pd$_{0.1}$Co$_{0.9}$** (1 mg).

Table S6 Catalytic performance of the **GO@APTES-Fcl-Pd$_{0.1}$Co$_{0.9}$** in Suzuki coupling reaction compared with other Pd-based catalysts reported

No.	Catalyst	Reaction conditions	X	Yield (%)	TOF (h^{-1})	Ref.
7	GO-Diimine-Ni/Pd1 (2.2×10^{-6}mol%Pd)	H_2O:EtOH, 70 ℃, Na_2CO_3, 1h	Br	99	21277	[64]
8	GO@Fcl-Pd$_{0.1}$Cu$_{0.9}$ (0.032 mol%Pd)	Na_2CO_3, H_2O:EtOH, at 80 ℃, 2h	Br	99	1484375	[74]
9	GO@T-Pd$_{0.01}$/Cu$_{0.99}$ (0.0033 mol%Pd)	Na_2CO_3, EtOH:H_2O, 1h, 70 ℃	Br	99	118588	[76]
10	GO@PPD-Pd (0.017 mol%Pd)	K_2CO_3, H_2O:EtOH (1:1), 20 min, 60 ℃	Br	97	17118	[77]
11	GO@Apimp-Pd1/C u$_{6.5}$ (0.000145 mol%Pd)	K_2CO_3, H_2O:EtOH=1:1, 70 ℃, 2h	Br	89	307320	[79]
12	Fe_3O_4@SiO_2-APBA-Pd (1.2 mol%Pd)	K_2CO_3, H_2O:EtOH, 60 ℃	Br	97	6230	[89]

13	GO@NHC-Pd (0.01 mol%Pd)	K_2CO_3, C_2H_5OH, 50 ℃, 1h	Br	92	1823	[90]
14	Pd/Fe_3O_4/s-G (0.3 mol%Pd)	K_2CO_3, EtOH:H_2O, 30 min, 80 ℃	Br	97	1293	[91]
15	$Pd_{0.5}Ru_{0.5}$-PVP NPs (0.16 mol%Pd)	K_2CO_3, DMA:H_2O, 100 ℃, 0.08h	Br	96	15000	[92]
16	GO-Fe_3O_4/Pd (0.5 mol%Pd)	K_2CO_3, H_2O:EtOH, 80 ℃, 0.15h	I	95	1140	[93]
17	Pd/CoO−C (1.2 mol%Pd)	K_2CO_3, H_2O, at 80 °C, 4h	Br	96	28	[108]

Table S7 Poisoning experiments of **GO@APTES-Fcl-$Pd_{0.1}Co_{0.9}$**[a]

Entry	Poisoning additive	Isolated yield (%)
1	---	99[a]
2	2, 2'-Dipyridyl	trace[b]
3	Thiophene	40[c]

[a]Reaction conditions: 4-bromotoluene (0.25 mmol), Phenylboric acid (0.3 mmol), K_2CO_3 (1 mmol), **GO@APTES-Fcl-$Pd_{0.1}Co_{0.9}$** 1 mg，solvent (4 mL) at 70 °C for 120 min. [b] 0.5 equiv of 2,2'-Dipyridyl (per metal atom). [c] 0.5 equiv of Thiophene (per metal atom).

Table S8 The BE changes of Pd, Co, and Fe on the surface of **GO@APTES-Fcl-$Pd_{0.1}Co_{0.9}$** during catalysis

Time(min)	0	5	10	20	40	60	90	120
Pd^0	335.85	335.95	335.55	335.20	335.00	335.10	335.45	335.41
Pd2+	338.35	338.65	338.66	338.72	338.50	338.49	338.46	338.59
Co3+	780.56	780.60	779.55	780.66	780.73	780.40	779.64	780.15
Co2+	782.04	782.29	782.15	782.52	782.84	782.59	781.81	782.59
Fe2+	708.16	707.89	708.32	708.21	709.27	708.41	708.10	708.26
Fe3+	712.19	712.33	712.22	712.18	712.13	713.93	712.78	712.07

Table S9 The BE changes of Pd, Co, and Fe on the surface of **GO@APTES-Fcl-$Pd_{0.1}Co_{0.9}$** in

recycling

Recycle(Times)	0	1	2	4	6	8
Pd0	335.85	335.41	335.43	335.74	335.51	335.71
Pd^{2+}	338.38	338.59	337.99	338.02	337.92	337.89
Co^{3+}	780.56	780.15	781.49	781.42	780.53	781.61
Co^{2+}	782.04	782.59	783.29	782.92	782.18	783.34
Fe^{2+}	708.16	708.26	709.01	708.58	710.02	711.12
Fe^{3+}	712.19	712.07	712.58	712.90	712.92	713.44