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# Pd-$Co_3[Co(CN)_6]_2$ hybrid nanoparticles: Preparation, Characterization, and Challenging for the Suzuki–Miyaura coupling of aryl chlorides under mild conditions

Ren Li*a, Ran Lia, Changlai Wanga, Lei Gaob, and Qianwang Chen*ab
[a]Hefei National Laboratory for Physical Sciences at Microscale and Department of Materials Science & Engineering, & Collaborative Innovation Center of Suzhou Nano Science and Technology, University of Science and Technology of China, Hefei 230026, China
[b]High Magnetic Field Laboratory, Hefei Institutes of Physical Science, Chinese Academy of Sciences, Hefei 230031, China

**Table S1** Catalytic performance of different Pd-Based catalysts in the coupling reaction of chlorobenzene and phenylbronic acid in recent two years.

| Entry | catalyst | solvent | time (h) | temp (℃) | yield (%) | ref |
|---|---|---|---|---|---|---|
| 1 | Poly-NHC-2–Pd2 | EtOH/H2O (3:2) | 3 | 80 | 100 | 1 |
| 2 | PdNPs）H2P-CMP | TBAB-H2O | 12 | 80 | 96 | 2 |
| 3 | Zwitterionic Palladium Complexes | 1,4-dixoxane/H2O (1:4). | 12 | r.t. | 33 | 3 |
| 4 | HT-Pd(0) | H2O | 4.5 | 100 | 95 | 4 |
| 5 | 2-(3-sulfonatomesityl)-5-sulfonatoindenyl) dicyclohexylphosphine hydrate-$Pd(OAc)_2$ sodium salt | H2O | 24 | 100 | 78 | 5 |
| 6 | Pd@[C12,C12−Im]Cl | H2O/p-dioxane (1:1) | 10min | r.t. | 94 | 6 |
| 7 | $PdCl_2$-L5 | DMF | 2 | 130 | 95 | 7 |
| 8 | Cyclometalated-2-Phenylimidazole Palladium Carbene Complexes | EtOH | 1 | 60 | 96a | 8 |
| 9 | Pd/PPhen solid composite | $H_2O$ | 3 | 80 | 82 | 9 |
| 10 | Pd(II) doped UiO-67 | EtOH | 20 | 100 | 90 | 10 |
| 11 | palladium complexes 5h | dioxane | 1 | 80 | 70 | 11 |
| 12 | GO–NHC–Pd | DMF-$H_2O$(1:1) | 1 | 80 | 65 | 12 |
| 13 | monoligated imine–Pd–NHC complexes | PrOH/$H_2O$ = 10:1 | 2 | 80 | 98 | 13 |
| 14 | Palladium(II)-N-heterocyclic carbene complexes | DMF/H2O (1:1) | 3 | 50 | 93 | 14 |
| 15 | [Pd(OAc)2]-Resorcinarenyl-Phosphines | DMF | 1 | 100 | 97 | 15 |
| 16 | Pd/Fe3O4@SiO2@KCC-1 | NMP | 12 | 140 | 83 | 16 |
| 17 | CoAl–LDH/Pd | EtOH | 2 | 80 | 66 | 17 |
| 18 | Pd-$Co_3[Co(CN)_6]_2$ | EtOH | 2 | 80 | 86 | This work |

Table 2. Catalytic Performance of Different Pd-Based Catalysts in the Coupling Reaction of chlorobenzene and Phenylbronic Acid

| Entry | catalyst | solvent | time (h) | temp (℃) | yield (%) |
|---|---|---|---|---|---|
| 1 | Pd-$Co_3[Co(CN)_6]_2$ | EtOH | 2 | 80 | 86 |
| 2 | $Co_3[Co(CN)_6]_2$@Pd | EtOH | 2 | 80 | 32 |
| 3 | $Pd_xCo_{3-x}[Co(CN)_6]_2$ | DMF | 4 | 90 | 76 |
| 4 | Pd-$Fe_3O_4$@C[18] | DMF | 4 | 100 | 82 |

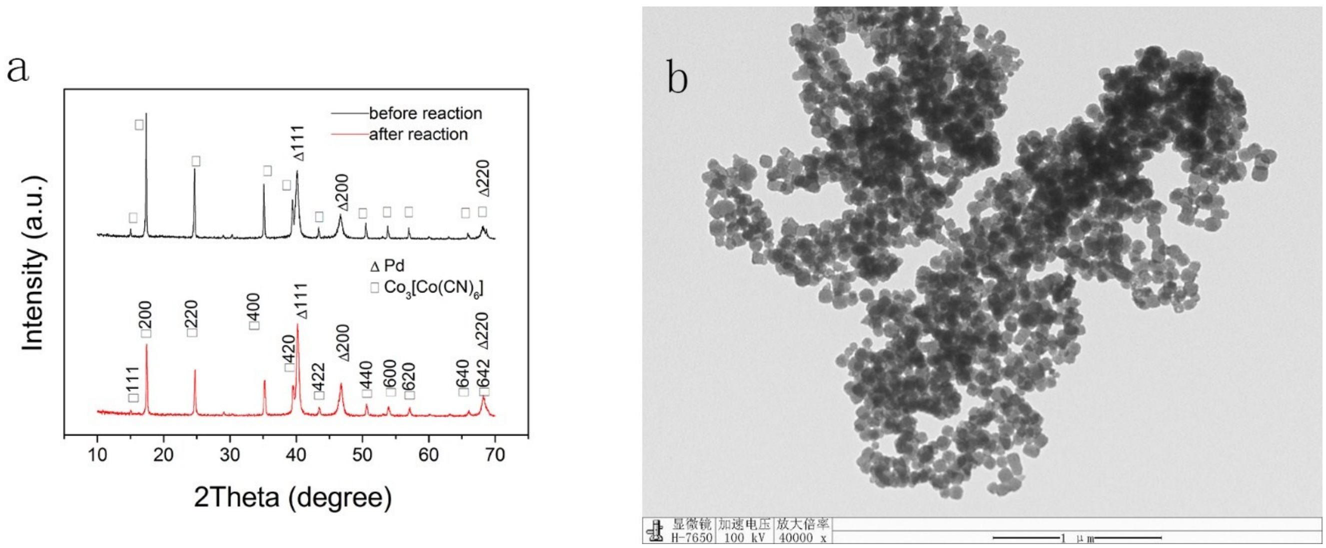


Figure 1. a) XRD pattern of $Co_3[Co(CN)_6]_2$@Pd after reaction, b) TEM image of large scale Pd-$Co_3[Co(CN)_6]_2$ NPs after reaction.

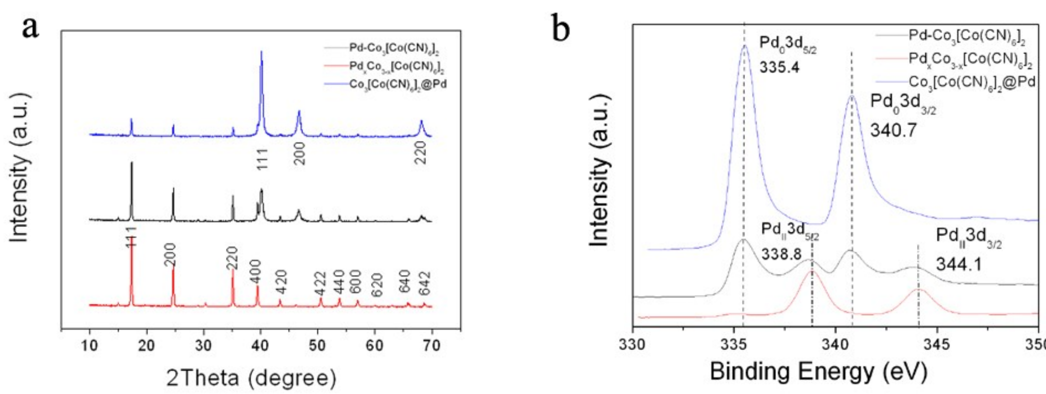


Figure 2. a) XRD pattern of $Co_3[Co(CN)_6]_2$@Pd, b) XPS spectrum of Pd 3d spectrum in $Co_3[Co(CN)_6]_2$@Pd

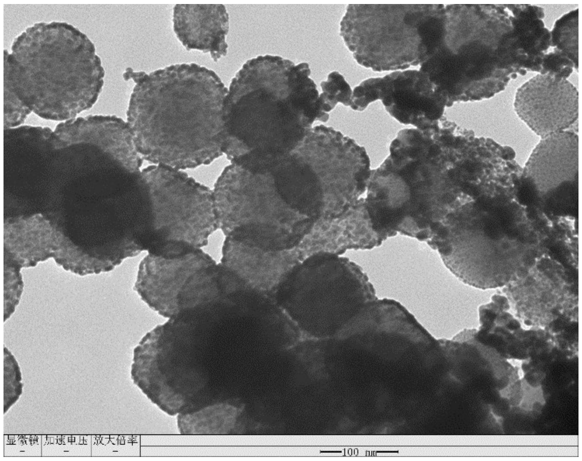

Figure 3. TEM image of $Co_3[Co(CN)_6]_2$@Pd NPs.

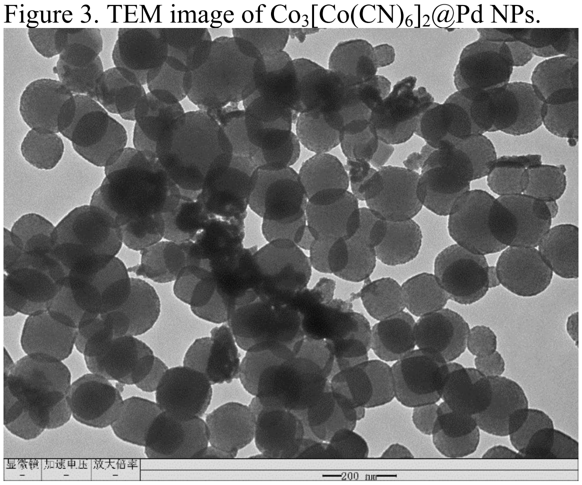

Figure 4. TEM image of large scale Pd-$Co_3[Co(CN)_6]_2$ NPs.

Synthesis of $Co_3[Co(CN)_6]_2$@ Pd NPs

0.01 g of $Co_3[Co(CN)_6]_2$was dissolved in 20 ml water solution. 0.3 g lysine was added to solution with stirring 30mins, then 10ml palladium chloride water solution (1g/L) was slowly added into the above mixture solution followed by 1 ml 0.1M NaBH4 solution was added to the solution quickly. About half hour later, the solid products were collected by centrifuging and were washed with water several times. The products were dried in vacuum.

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