

Dalton Transactions

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



Journal Name

ARTICLE

Pd-Co₃[Co(CN)₆]₂ hybrid nanoparticles: Preparation, Characterization, and Challenging for the Suzuki–Miyaura coupling of aryl chlorides under mild conditions

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Ren Li^{*a}, Ran Li^a, Changlai Wang^a, Lei Gao^b, and Qianwang Chen^{*ab}

Because of their abundance and cheap price, organo chlorides are the most desirable substrates from the industrial point of view in Suzuki–Miyaura cross-coupling reactions. However, Catalytic application of Pd nanoparticles (NPs) for Suzuki coupling of aryl chlorides is still a challenge. Here, we design a novel catalyst by combining Pd NPs onto Co₃[Co(CN)₆]₂ nanocrystals for Suzuki–Miyaura coupling of aryl chlorides. This nanocatalyst demonstrated good activity (yield 86.2% @80 °C), high TOF, great stability, easy separation, excellent reusability (initial rates were not reduced after five cycles) and low cost in Suzuki reactions.

Introduction

Suzuki–Miyaura cross-coupling reactions, among the most widely used protocols for the formation of carbon–carbon bonds, have become one of the most efficient synthetic methods for the synthesis of biaryl compounds, which include a wide range of natural products and pharmaceuticals.¹ These reactions are generally catalyzed by soluble palladium (Pd) complexes or Pd NPs with various ligands in organic solvents and, more recently, in aqueous media as well.² Activation of the Pd pre-catalyst is followed by oxidative addition of the halogenated (X = Cl, Br, I) substrates. Coupling reactions of these substrates typically decrease in difficulty in the order of R–Cl > R–Br > R–I. This can be explained in terms of the R–X bond dissociation enthalpies (BDE). For example, the X–Ph BDE range from X–Cl=95.5±1.5 kcal mol⁻¹; X–Br=80.4±1.5 kcal mol⁻¹ to X–I=65.0±1 kcal mol⁻¹.³ Due to their abundance and cheap price, organo chlorides are the most desirable substrates from the industrial point of view.⁴ In traditional protocols, the Pd chelates catalyst with organo phosphine ligands, such as triphenylphosphine (PPh₃),⁵ N-heterocyclic carbenes (NHC)⁶ and palladacycle complexes⁷ have been established for the Suzuki coupling of aryl chlorides. However, these chelates sometimes require multistep syntheses and/or rigorously anhydrous and inert conditions even if the intermediate carbene ligand is not isolated.⁸ Additionally, the high air-

sensitivity of the complex makes the catalyst recovery/recycling difficult, and thus an excess amount of chelates is usually required to achieve a reasonable catalytic activity.⁹ Especially, these homogeneous catalysts are difficult to be separated, recovered and reused. Pd NPs, which enjoy several advantages such as excellent activity, greater selectivity, and high stability over conventional catalyst systems, partially due to their large surface-to-volume ratio, is widely used for C–C cross coupling reactions.¹⁰ But, Pd NPs were not used as appropriate catalysts for aryl chlorides transformation due to the low yield and high temperature condition (mostly up to 100 °C) and long reaction times. Therefore, developing a new type nanocatalyst owning both the advantages of homogeneous (e.g., high selectivity, high turn-over numbers, and effortless optimization of reaction activity) and heterogeneous catalysis (e.g., easily to separation and recovering and low cost) is still an aim for nanocatalyst design.

The porous materials with high surface area have attracted significant scientific attention because of their diverse potential applications in separation,¹¹ gass storage¹², and especially heterogeneous catalysis.¹³ During the last few decades, the surge to develop such useful materials has led scientists to prepare a number of novel porous materials such as metal organic frameworks (MOFs),¹⁴ porous organic cages,¹⁵ and microporous organicpolymers (MOPs)¹⁶ in addition to traditional porous materials such as zeolites and activated carbon. Among these porous materials, MOFs have attracted particular attention due to their unique properties such as large surface area, low skeletal density, and high chemical stability.¹⁷ The use of MOFs as solid catalysts is significantly interesting due to their large pore sizes are favorable for the diffusion of large substrates and products.¹⁸ Furthermore, it is often possible to tailor the pore structure and functionality to yield the chemo-, regio-, stereo- and/or enantioselectivity by

^a Hefei National Laboratory for Physical Science at Microscales, & Department of Materials Science & Engineering, & Collaborative Innovation Center of Suzhou Nano Science and Technology, University of Science and Technology of China, Hefei, China E-mail: liren@ustc.edu.cn cqw@ustc.edu.cn

^b High Magnetic Field Laboratory, Chinese Academy of Sciences, Hefei, China Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

creating an appropriate environment around the catalytic center in the restricted space available.¹⁹ Moreover, it is possible to have a homogeneous distribution of one or more active sites due to their high crystalline degree.²⁰ MOFs can also be used as host matrices to support the catalysts, as in the case of mesoporous silicates.²¹ Most efforts have focused on encapsulation of metal NPs inside the cavities of MOFs (metals@MOFs), which can be synthesized in solution- or gas-phase loading methods, which depend on the different metal precursors. In particular, the incipient wetness impregnation is a mostly used method for this fabrication, because common inorganic salts are adoptable as precursors.²¹ The mechanically robust walls of the frameworks can be utilized to confine metal NPs and restrict their growth.²² The good dispersivity of NPs within the frameworks leads them more accessible to reactants, thereby exhibiting excellent catalytic activity.²² Additionally, a variety of structural features can engender catalytic activity in MOFs, such as open metal sites at framework nodes, which often have unique coordination environments, and metal or organic centered catalytic units that are integrated, as well as active metal NPs that are grown and stabilized within the cavities.²³ Moreover, combination of active metal NPs with the functionalities within the host, multifunctional catalysts capable of promoting different reactions or one-pot cascade reactions can thus be realized.²⁴ The Pd@MOFs was firstly tested for C–C coupling reaction in 2008, Kuwang and Fe'rey et al.²⁵ demonstrated the Pd@ED-grafted-MIL-101(Cr) and Pd@APS-grafted-MIL-101(Cr), which were obtained by anionic exchange reactions followed by NaBH₄ reduction, had obviously high activities during the Heck reaction of acrylic acid with iodobenzene, and their activities were comparable with that of a commercial Pd/C catalyst (1.09 wt% Pd) after a certain induction period (0.5–1h). The good recyclability of Pd-loaded MIL-101(Cr) verified the heterogeneous catalysis nature.

Prussian blue analogues (PBA) have been paid growing attention for their applications in hydrogen molecular magnetics,²⁶ storage,²⁷ optics,²⁸ and soon.²⁹ However, employing PBA as catalyst or catalyst supports in liquid reactions has not been reported. According to our previously work,^{30–31} nanosized Co₃[Co(CN)₆]₂, which can serve as efficient adsorbents for adsorbing heavy metal ions³² and organic dyes³³ from aqueous solutions, with ultrahigh specific surface area and abundant micropores was achieved at room temperature via a one-step process. Herein, we demonstrate the construction of easily separable and high activity Pd nanocatalysts through deposition of Pd NPs on the surface of PBA nanocrystals. To evaluate the activity and stability of the supported Pd nanocatalysts, Suzuki coupling reactions were chosen as the model reaction for test. The results indicate that this catalyst not only shows outstanding activity especially for aryl chlorides reactions, but also can be easily separated from the reaction medium and reused several cycles without obvious decrease of conversion rate.

Results and discussion

The crystallinity and phase composition of the resulting products were investigated by X-ray powder diffraction (XRD). Figure 1 shows the XRD patterns of the samples. Compared with the XRD patterns of the pure MOF nanoclusters reported previously, new reflection peaks which corresponded to the 111 and 220 of face-centered cubic Pd nanocrystals were observed. According to the Debye-Scherrer equation, the diameter of Pd NPs is calculated to be 3 nm, which is well in agreement with that observed from TEM.

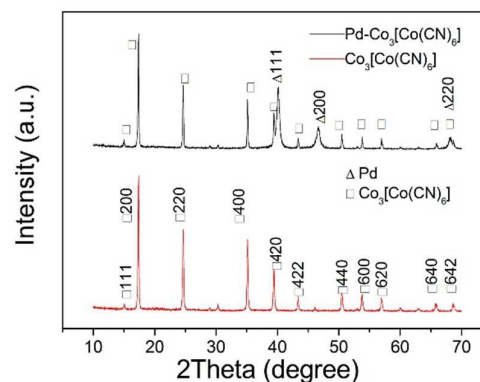


Figure 1. XRD pattern of Pd–Co₃[Co(CN)₆]₂ hybrid NPs and Co₃[Co(CN)₆]₂ NPs.

The morphology of the hybrid NPs shows a core-shell like feature with fine Pd particles deposited on Co₃[Co(CN)₆]₂ surface, as shown in **Fig.2a**. It is easily observed that the diameter of the as-prepared MOF NPs are about 100 nm in size. It can also be found that the surface of Co₃[Co(CN)₆]₂ NPs are decorated with several nanometers diameter NPs. The high-resolution TEM image of a single core shell hybrid nanoparticle from **Fig.2b** suggests that palladium NPs are encapsulated within the micropores; it is easy to find that the Particle size was about 3 nm. Energy dispersive analysis of X-rays (**Fig.2c**) of selected areas further reveals their elemental composition, including Pd, Co, C, N and Cu. The Pd signal shows that the palladium chloride has been successfully reduced and deposited on the surface of MOF nanoclusters. The clear 2D lattice fringes of Pd nanocrystals are shown in **Fig.2d**. The inter planar distance is about 0.2 nm, which corresponds well to the (111) lattice plane of Pd. Elemental mapping of Co, N and Pd (**Figure 2e–2h**) also revealed that the nanostructures were composed of different segments. In particular, the as-prepared Pd-MOF nanocrystals are essentially cube-like nano structures in which Pd encircles a pure Co₃[Co(CN)₆]₂ core.

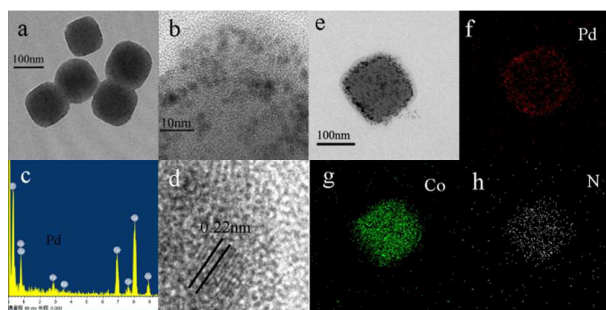


Figure 2. Characterization of Pd-Co₃[Co(CN)₆]₂ hybrid NPs: (a) TEM image; (b) HRTEM image of a Co₃[Co(CN)₆]₂ hybrid nanoparticle (c) EDAX of Pd nanoparticle; (d) lattice fringe and electron diffraction (ED) of a single Pd nanoparticle. (e) HAADF-TEM image of a single nanostructure. (f) Elemental map of Pd on the nanostructure shown in e. (g) Corresponding elemental map of Co. (h) Corresponding elemental map of N.

Figure 3 exhibits the FT-IR spectra of Pd-Co₃[Co(CN)₆]₂ and Co₃[Co(CN)₆]₂ NPs synthesized in this work. In the spectrum, the characteristic peaks at round 2170 cm⁻¹ are assigned to be C≡N bound stretching. The presence of crystal water can be deduced from the occurrence of a sharp ν(O-H) band due to water incorporated in a crystalline lattice (3645 cm⁻¹) and from the occurrence of the δ(OH₂) vibration (1610 cm⁻¹). Compared with two spectrums, there is not too much difference between Pd-Co₃[Co(CN)₆]₂ and Co₃[Co(CN)₆]₂ spectra, which indicated that there is no obviously group change in the prepared section.

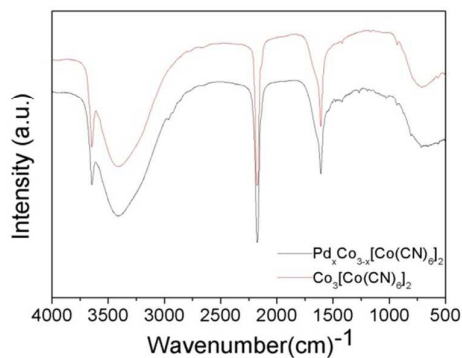


Figure 3. FT-IR spectra of Co₃[Co(CN)₆]₂ NPs and Pd-Co₃[Co(CN)₆]₂ hybrid NPs.

XPS spectroscopy, one of the most important techniques to determine the oxidation state of surface element in materials, was used to characterize the Pd-Co₃[Co(CN)₆]₂ composites. The inset figure of **Figure 4** shows the survey spectrum of the Pd-Co₃[Co(CN)₆]₂ composites. The signal of Pd element is nearly the same as that of Co element, which implies that Co₃[Co(CN)₆]₂ is almost fully covered by Pd NPs. This phenomenon is well in agreement with what have observed in TEM. The XPS spectrum of Pd 3d can be fitted into two main doublet peak, as shown in Figure 4. The binding energy of the doublet peaks at 335.4 eV (assigned to Pd⁰3d_{5/2}) and 340.7 eV (assigned to Pd⁰3d_{3/2}) can be attributed to the Pd(0) state. The above results indicate that Pd species on the surface of Co₃[Co(CN)₆]₂ nanospheres was elementary Pd(0). The other two peaks are related to Pd(II) species, which may be due to some Pd²⁺ doping into Co₃[Co(CN)₆]₂. Especially, the value of binding energy is similar to K₂Pd₂(CN)₄, which Pd⁰3d_{5/2} state

equals to 338.8 eV and Pd^{II}3d_{3/2} state is 334 eV, indicated that Pd was combined with C≡N.^[34] The above results indicate that some Pd atoms were doped into lattice of Co₃[Co(CN)₆]₂ nanocubes. To ensure Pd²⁺ was not adsorbing but doped, the nanocatalyst was washed by deionized water several times and then dissolved by nitromurlatic acid to ICP test. The ICP test results show the Pd-Co molar ratio is 2.94:1, while the Pd-Co molar ratio of reactant was 5:4, which demonstrate that the Pd²⁺ was not adsorbing but doped in the nanocatalyst. Moreover, in the preparation stage, we use EtOH as reducing agent. Thus, if some Pd²⁺ ions were absorbed, they will be reduced to Pd NPs.

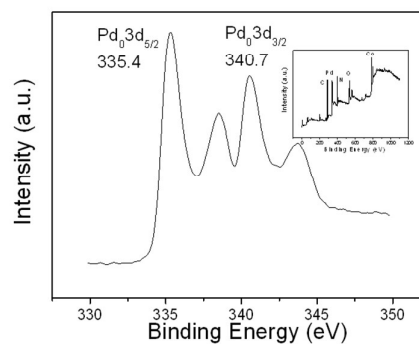


Figure 4. XPS of Pd 3d spectrum in Pd-Co₃[Co(CN)₆]₂, the inset is survey XPS spectrum of Pd-Co₃[Co(CN)₆]₂ hybrid NPs

The porous properties of the samples were analyzed by nitrogen sorption analysis. Before measurement, the sample was heated at 60 °C for 10 h under vacuum to dehydrate completely according to the results of thermo gravimetric analysis. The BET surface area of Co₃[Co(CN)₆]₂ was found to be 459.6 m²/g and that of Pd-Co₃[Co(CN)₆]₂ was 470.8 m²/g. Due to the contribution of small NPs with 5nm in size, the BET surface area of Pd-Co₃[Co(CN)₆]₂ was slightly larger than Co₃[Co(CN)₆]₂. As shown in **Figure 5a and 5b**, the adsorption and desorption isotherms of Co₃[Co(CN)₆]₂ and Pd-Co₃[Co(CN)₆]₂ are also quite similar. The adsorption isotherms display steep nitrogen gas uptake at low relative pressures ($P/P_0 < 0.001$) reflecting abundant micropore structure, a slight hysteresis loop implying a spot of mesopore and a sharp rise at medium and high pressure regions ($P/P_0 = 0.8-1.0$) indicating the presence of size of MOF. The pore size distribution of the Co₃[Co(CN)₆]₂ and Pd-Co₃[Co(CN)₆]₂ can be gained from the supplied results by using the sorption apparatus, as shown in **Fig. 5c and 5d**. The results demonstrate that the narrow porous volume distribution is about 3 nm in the pore size, which indicates that the NPs which formed the nanocubes are porous in structure. Additionally, another narrow porous volume distribution is about 0.5 nm, which is consistent with the pore size of M^{III}₃[M^{III}(CN)₆]₂ porous framework structure.³⁰ Actually, the heterogeneous porous structure is favorable for catalysis process. The macroporous

structure accelerates the mass transfer of reactants and products, and micropore of suitable size is beneficial for anchoring metal catalysts. It should be noted that the peak at 3 nm of figure 5d was almost disappeared, which indicated the 3 nm pore of $\text{Co}_3[\text{Co}(\text{CN})_6]_2$ was almost covered by Pd NPs.

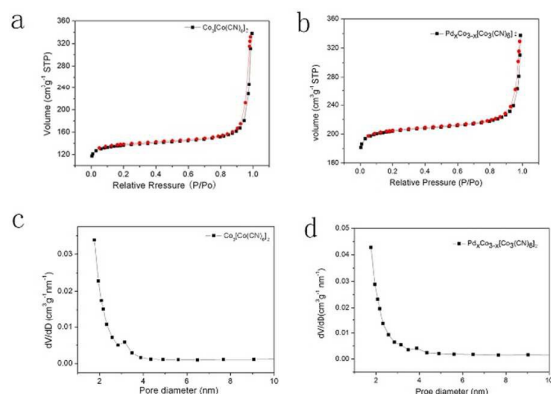


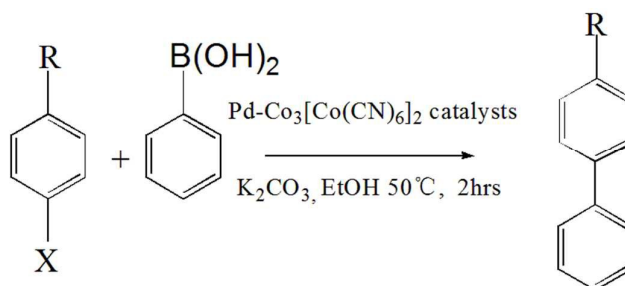
Figure 5. Nitrogen adsorption (black) and desorption (red) isotherms of: a) $\text{Co}_3[\text{Co}(\text{CN})_6]_2$ and, b) $\text{Pd-Co}_3[\text{Co}(\text{CN})_6]_2$. Pore size distributions of: c) $\text{Co}_3[\text{Co}(\text{CN})_6]_2$ and, d) $\text{Pd-Co}_3[\text{Co}(\text{CN})_6]_2$.

The possible formation mechanism of hybrid NPs can be inferred by previous results. Firstly, Pd^{2+} ions were absorbed by MOF supports in the cavities and channels. Secondly, Pd^{2+} ions replaced Co^{2+} and became to $\text{Pd}_3[\text{Co}(\text{CN})_6]_2$ due to the lower k_{sp} of $\text{Pd}_3[\text{Co}(\text{CN})_6]_2$. Finally, redundant absorbed Pd^{2+} ions were reduced by EtOH to Pd element, which assembled and nucleated in the cavities and channels of MOF supports. To evaluate the catalytic ability of the MOF supported Pd NPs, Suzuki cross-coupling reaction was carried out as a model reaction. The reactions were conducted using ethanol as the solvent and K_2CO_3 as the base. As shown in Table 1, iodobenzene and bromobenzene shows good results due to their high reactivity even at room temperature. (Table 1, entry 1-3). Then, 4-bromotoluene was used instead of bromobenzene to confirm the biphenyl was cross coupled by arylhalides and phenylboronic acid rather than self-coupling of phenylboronic (Table 1, entry 4). The result shows that the yield of 4-Phenyltoluene was up to 99%, with very little biphenyl generated. As for chlorobenzene and 4-chlorotoluene (Table 1, entries 5-6), the effect of substituted groups in substrates was also investigated. Although the whole tendency shows that the conversion of substituted substrates is lower than unsubstituted ones, most of reactions can get satisfactory yields by increasing reaction temperature and time (Table 1, entries 7-8). For example, as high as 86.2% yield can be obtained by increased reaction temperature to 80 °C and time up to 4hrs for chlorobenzene reaction. These results can reach the performance of Pd catalysts with organic phosphine ligands and be much better than Pd NPs'. To investigate the universality of aryl chlorides, substituents of $-\text{NO}_2$, $-\text{COOH}$, $-\text{OH}$, $-\text{NH}_2$, were employed (Table 1, entries 9-12). These results demonstrate that both aryl chlorides bearing electron-withdrawing groups such as $-\text{NO}_2$, $-\text{COOH}$ and aryl chlorides

bearing electron-donating substituents such as $-\text{CH}_3$ and $-\text{OH}$, $-\text{NH}_2$ at the para position gave the desired products in moderate yields. Also, the mass balanced based on GC results indicated no side reaction involved. Pure MOF supports were not able to catalyze the reaction (Table 1, entry 13).

Table 1. Suzuki Reactions Catalyzed by $\text{Pd-Co}_3[\text{Co}(\text{CN})_6]_2$ catalysts

Reaction conditions: 1 mg of $\text{Pd-Co}_3[\text{Co}(\text{CN})_6]_2$ catalysts (Pd 47.9wt%), 1 mmol arylhalide, 1.2 mmol phenylboronic acid, and 3 mmol K_2CO_3 , EtOH(30)ml, at 50 °C or 2hrs. ^aIsolated yield. ^bat room temperature. ^cat 80 °C. ^dPure $\text{Co}_3[\text{Co}(\text{CN})_6]_2$ as catalyst.



entry	R	X	time (h)	yield(%) ^a	TOF (h ⁻¹)
1	H	I	2	>99	111
2	H	Br	2	>99	111
3	H	Br	12 ^b	>99	9.3
4	CH ₃	Br	2	>99	111
5	H	Cl	2	39.4	44
6	CH ₃	Cl	2	32.6	36
7	H	Cl	4 ^c	86.2	48
8	CH ₃	Cl	4 ^c	83.1	46
9	NO ₂	Cl	4 ^c	77.3	43
10	COOH	Cl	4 ^c	73.8	42
11	OH	Cl	4 ^c	75.4	42
12	NH ₂	Cl	4 ^c	80.4	44
13	H	I	2 ^d	-	-

Separation, reusability, stability, and leaching of the catalysts are crucial for practical applications for nanocatalyst. Firstly, the catalysts can be easily separated and recovered by centrifugation due to the MOF supports with size on the nanometre scale. Secondly, this nanocatalyst can be reused eight times with no obvious decrease of conversion rate (Figure 6a). Moreover, the kinetic studies of four cycles showed that the initial rates and the subsequent rates of each cycle were not reduced even for chlorobenzene reaction at high temperatures (Figure 6b). Thirdly, this catalyst demonstrated great thermal stability with high activity at elevated temperatures (Table 1, entry 7-8). The XRD pattern (Figure S1a) and SEM image (Figure 7a and Figure S1a) of the catalyst after reaction at reflux condition indicated that phase composition and the surface morphology of nanocatalysts were not changed. Compared with previous result, the XPS spectrum (Figure 7b) of the catalyst after high temperature reaction shows that no oxidation reaction happened. Lastly, Pd leaching and dropping from the catalysts into the reaction mixture was not observed. The Pd content in the filtrate after the first reaction as well as after five cycles were all

determined to be lower than 100 ppb by ICP-AES, indicating less of Pd loss even after five cycles. Furthermore, the catalysts after eight cycles were analyzed by ICP-AES. The molar ratio of Pd and Co was not changed which indicated that few Pd NPs dropped from MOF supports. The results suggested that Pd element loss was due to element leaching in Suzuki reaction rather than dropping of MOF supports.³⁵

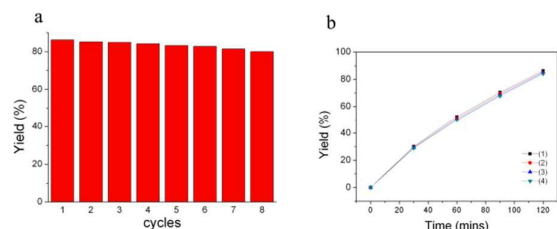


Figure 6. Catalytic results of Suzuki reaction of chlorobenzene (reaction condition similar to Table 1, entry 7). (a) the yield in different cycles. (b) Kinetic profiles for coupling reactions of five cycles.

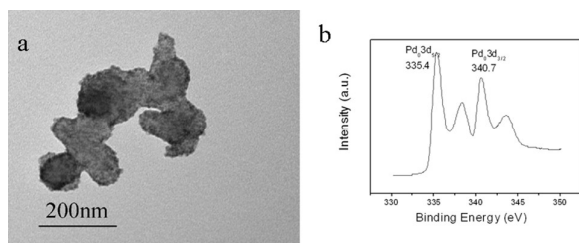


Figure 7. a) TEM image of Pd-Co₃[Co(CN)₆]₂ catalysts after reaction. b) XPS spectrum of Pd nanocatalysts after reaction.

We compared our results with those of Pd-based catalysts reported in recent one year. Taking the reaction of bromobenzene with chlorobenzene as an example; the results were listed in **Table S2**. Compared with other Pd based catalysts such as Pd-PPh₃ and Pd-NHC, our catalyst can reach almost the same catalytic efficiency with the reported ones. Our catalyst enjoys several advantages including simply preparation, excellent separation and reusability. Another hand, our catalysts show much better catalytic performance than the traditional supported Pd(0) NPs in short reaction time and low reaction temperatures.

There are four reasons why our catalyst own high catalytic activity even in the Suzuki coupling of aryl chlorides as following: (1) the Pd NPs almost 3 nm are appropriately small and clean without other organic groups; (2) amounts of cavities and channels of MOF supports are benefited to reagent adsorbing. In tradition catalytic theory, the adsorbing is the first and important step; (3) the metal nodes of MOF usually have catalytic unique coordination environments due to their unique coordination environments. In Co₃[Co(CN)₆]₂ NPs, Co²⁺ ions may provide extra electron to Pd NPs to maintain charge balance. Thus, it is reasonable to expect that the Pd sites with the energetic electrons will exhibit superior catalytic activity to that of pure palladium NPs alone; (4) Two valent states Pd including Pd(0) and Pd (II) exist in the catalyst.

They may be able to convert easily and both states Pd can catalyze Suzuki reaction. Therefore, to understand the synergistic effect of MOF supports and Pd NPs, the performance of different kinds of nanocatalysts' catalyst ability for chlorobenzene reaction were tested (Table S2.). Four types of Pd-based NPs respectively are Pd doped Co₃[Co(CN)₆]₂, whose Pd states were Pd (II), Co₃[Co(CN)₆]₂@Pd (**Figure S3**), whose Pd states were Pd (0), Pd-Co₃[Co(CN)₆]₂, this catalyst, whose Pd states were combine Pd (II) and Pd (II), and Pd-Fe₃O₄@C, which Pd(0) states with low surface area supports. From these results, we can confirm that the channels and cavities of MOF, Pd (II) and Pd (0) were contributed to the reaction, even the MOF supports were not able to catalyze the reaction (Table 1, entry 9).

Experimental

Synthesis of MOF nanocrystals

The typical synthetic experiments were as follows, Solution A: 0.04 mmol K₃[Co(CN)₆]₂ and 0.3 g PVP were dissolved in 10 mL distilled water system under agitated stirring to get an absolute transparent solution. Solution B: 0.075 mmol of Co(CH₃COO)₂·nH₂O was dissolved in 10 mL distilled water. Solution B was added into solution A slowly and regularly using a syringe to form a red colloid solution. The whole reaction process was kept at room temperature with agitated stirring. After 10 min, the reaction was aged at room temperature without any interruption for 24 h. The resulting pink precipitation was filtered and washed several times with absolute ethanol and finally dried in an oven at 60 °C.

Synthesis of Pd- Co₃[Co(CN)₆]₂ Microspheres

0.01 g of Co₃[Co(CN)₆]₂ was dissolved in 20 ml water solution. 10ml palladium chloride water solution (1g/L) was slowly added into the above mixture solution in 30 °C in 10mins with magnetically stirred vigorously, followed by, the addition of 5ml EtOH. About four hours later, the solid products were collected by centrifuging and were washed with water several times. The products were dried in vacuum. The solid product was dissolved in concentrated nitric acid and analyzed by inductively couple plasma atomic emission spectrometer (ICP-AES) to determine the content of Pd (47.9 wt%).

Catalytic Reaction.

For Suzuki cross-coupling reactions, 1 mg of Pd-Co₃[Co(CN)₆]₂ catalyst, 1 mmol arylhalide, 1.2mmol phenylboronic acid, and K₂CO₃ (3mmol) were added to 30 mL alcohol. The reactions were carried out at 50 °C under reflux condition for 2hrs or at room temperate for 12hrs. Then, the catalysts were collected by centrifuging, and the reaction system was analyzed by gaschromatography (GC).

Conclusions

In summary, we demonstrated a simple approach for the large-scale synthesis of Pd-MOF hybrid NPs by a two steps process. The hybrid composite is composed of a large amount of 3 nm-

sized Pd nanocrystals with a 100 nm-sized $\text{Co}_3[\text{Co}(\text{CN})_6]_2$ nanocluster. The formation process of hybrid NPs is via adsorption and reduction of noble metallic ions, which can be extended to achieve the synthesis of various noble metal- $\text{Co}_3[\text{Co}(\text{CN})_6]_2$ hybrid NPs. The nanocrystals exhibited good activities for various Suzuki coupling reactions especially the coupling of aryl chlorides due to their unique structure. Furthermore, the nanocrystals could be easily separated and could be used repeatedly 8 times with minor variation of catalytic activity. The Pd-MOF catalysts have, the advantages of heterogeneous (e.g., low cost, air-stability, easy separation, and good reusability) and homogeneous systems (e.g., high yield) without using toxic chemicals, potential to be used widely in Pd catalyst systems.

Acknowledgements

Thanks for the help of Dr. Yang Wang at Hefei University of Technology in the area of Transmission electron microscope. This work was supported by the National Natural Science Foundation (Grants 21271163 and U1232211).

Notes and references† Footnotes relating to the main text should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

§
§§
etc.

- A. Fihri, M. Bouhrara, B. Nekoueshahraki, J. M. Basset, V. Polshettiwar, *Chem. Soc. Rev.*, 2011, **40**, 5181.
- K. C. Nicolaou, P. G. Bulger and D. Sarlah, *Angew. Chem. Int. Edit.*, 2005, **44**, 4442.
- G. C. Fortman and S. P. Nolan, *Chem. Soc. Rev.*, 2011, **40**, 5151.
- J.-P. Corbet and G. Mignani, *Chem. Rev.*, 2006, **106**, 2651-2710.
- A. Zapf, A. Ehrentraut, M. Beller, *Angew. Chem. Int. Edit.*, 2000, **39**, 4153.
- E. A. B. Kantchev, C. J. O'Brien and M. G. Organ, *Angew. Chem. Int. Edit.*, 2007, **46**, 2768.
- L. Botella and C. Nájera, *Angew. Chem. Int. Edit.*, 2002, **41**, 179.
- G. Borja, A. Monge-Marcet, R. Pleixats, T. Parella, X. Cattoën and M. Wong Chi Man, *Eur. J. Org. Chem.*, 2012, **2012**, 3625.
- R. Akiyama and S. Kobayashi, *J. Am. Chem. Soc.*, 2003, **125**, 3412.
- A. Balanta, C. Godard and C. Claver, *Chem. Soc. Rev.*, 2011, **40**, 4973.
- N. B. McKeown and P. M. Budd, *Chem. Soc. Rev.*, 2006, **35**, 675.
- H. Furukawa and O. M. Yaghi, *J. Am. Chem. Soc.*, 2009, **131**, 8875.
- D. Dang, P. Wu, C. He, Z. Xie and C. Duan, *J. Am. Chem. Soc.*, 2010, **132**, 14321.
- G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé and I. Margiolaki, *Science*, 2005, **309**, 2040.
- T. Tozawa, J. T. Jones, S. I. Swamy, S. Jiang, D. J. Adams, S. Shakespeare, R. Clowes, D. Bradshaw, T. Hasell and S. Y. Chong, *Nat. Mater.*, 2009, **8**, 973.
- C. D. Wood, B. Tan, A. Trewin, F. Su, M. J. Rosseinsky, D. Bradshaw, Y. Sun, L. Zhou and A. I. Cooper, *Adv. Mater.*, 2008, **20**, 1916.
- H. Furukawa, N. Ko, Y. B. Go, N. Aratani, S. B. Choi, E. Choi, A. Ö. Yazaydin, R. Q. Snurr, M. O'Keeffe and J. Kim, *Science*, 2010, **329**, 424.
- Z. Y. Gu and X. P. Yan, *Angew. Chem. Int. Edit.*, 2010, **49**, 1477.
- J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen and J. T. Hupp, *Chem. Soc. Rev.*, 2009, **38**, 1450.
- A. Corma, H. Garcia and F. Llabrés i Xamena, *Chem. Rev.*, 2010, **110**, 4606.
- H. R. Moon, D.-W. Lim and M. P. Suh, *Chem. Soc. Rev.*, 2013, **42**, 1807.
- W. Xuan, C. Zhu, Y. Liu and Y. Cui, *Chem. Soc. Rev.*, 2012, **41**, 1677.
- K. K. Tanabe and S. M. Cohen, *Chem. Soc. Rev.*, 2011, **40**, 498.
- M. Zhao and C. D. Wu, *Acc. Chem. Res.*, 2014, **47**, 1199.
- Y. K. Hwang, D. Y. Hong, J. S. Chang, S. H. Jhung, Y. K. Seo, J. Kim, A. Vimont, M. Daturi, C. Serre and G. Férey, *Angew. Chem. Int. Edit.*, 2008, **47**, 4144.
- S.-i. Ohkoshi, Y. Abe, A. Fujishima and K. Hashimoto, *Phys. Rev. Lett.*, 1999, **82**, 1285.
- S. S. Kaye and J. R. Long, *J. Am. Chem. Soc.*, 2005, **127**, 6506.
- S. Ferlay, T. Mallah, R. Ouahes, P. Veillet and M. Verdaguer, *Nature*, 1995, **378**, 701.
- J. G. Moore, E. J. Lochner, C. Ramsey, N. S. Dalal and A. Stiegman, *Angew. Chem. Int. Ed.*, 2003, **42**, 2741-2743.
- L. Hu, P. Zhang, Q.-w. Chen, N. Yan, J.-y. Mei, *Dalton Trans.*, 2011, **40**, 5557.
- L. Hu, P. Zhang, Q.-w. Chen, J.-y. Mei, N. Yan, *Rsc Adv.*, 2011, **1**, 1574.
- L. Hu, J.-y. Mei, Q.-w. Chen, P. Zhang, N. Yan, *Nanoscale*, 2011, **3**, 4270.
- L. Hu, Y. Huang, Q. Chen, *J. Alloys. Compd.*, 2013, **559**, 57.
- G. Kumar, J. R. Blackburn, R. G. Albridge, W. E. Moddeman and M. M. Jones, *Inorg. Chem.*, 1972, **11**, 296.
- Z. Q. Niu, Q. Peng, Z. B. Zhuang, W. He and Y. D. Li, *Chem. Eur. J.*, 2012, **18**, 9813-9817.

TOC

A simple approach for synthesis of Pd-MOF nanocatalyst with high activity for Suzuki coupling of aryl chlorides was reported.

