

Support information

Hollow Porous Organic Nanospheres for Anchoring Pd(PPh₃)₄ through Co-hyper-crosslinking Mediated self-assembly strategy

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Experimental Section

Materials

Tetrakis(triphenylphosphine)palladium (0) (99%, Energy), Styrene (99%, Aldrich) was purified by passing through a basic alumina (Al_2O_3), 2,2'-Azobis(2-methylpropionitrile) (AIBN, >99%) and D,L-lactide was recrystallized from ethanol prior to use. S-1-Dodecyl-S'-(α,α' -dimethyl- α'' -acetic acid) trithiocarbonate (TC) was synthesized according to literature procedures.¹

Synthesis of PLA-b-PS

PLA₁₅₈-TC initiator was synthesized as described in the literature.¹ The further RAFT copolymerization of styrene with PLA₁₅₈-TC is as follow. PLA₁₅₈-TC (300 mg, 0.025 mmol), AIBN (0.417 mg, 0.003 mmol), St (1.163 ml), were mixed in a vessel and degassed by three freeze-pump-thaw cycles. Then the polymerization was conduct at 70 °C for 12 hours and the reaction was stopped by cooling down to the room temperature in the air. The resulting polymer was precipitated from DCM towards methanol for three times and dried under vacuum for 24 hours. Yield =581mg (40%). GPC (**Figure S2**) Mn=62kg/mol Mw/Mn=1.14 ¹H NMR: N(St)=233.

Preparation of H-PONs-Pd(PPh₃)₄ catalyst

One typical example, PLA₁₅₈-b-PS₂₃₃ (100 mg), and Pd(PPh₃)₄ (12.44 mg) were added to 10 ml CHCl₃. After dissolving, anhydrous FeCl₃ (419.2 mg) was added into the above solution. Then the vessel was sealed and transferred into 90 °C oil bath for 24 hours without stirring. The resulting product was washed by ethanol/water=4/1 solution for a few hours and then filtering off by decompressional filtration. The obtained black powder was dried under vacuum at 25 °C for 24 hours. Yield=121mg.

Preparation of contrast catalysts

Route A: (H-PONs-PPh₃-Pd): PLA₁₅₈-b-PS₂₃₃ (100 mg), PPh₃ (11.29 mg) (The molar ratio of the PPh₃ to the benzene ring on the diblock polymer was 1/15) and anhydrous FeCl₃ (419.2 mg) were dissolved in CHCl₃ for cross-linking. The obtained solution was heated

in 90 °C oil bath for 24 hours. After washing and filtering, the resulting solid (107mg) was added to acetonitrile solution (3ml) containing PdCl₂ (10 mg 0.056 mmol) and stirring under reflux at 80 °C for 12 hours. The solid was separated by centrifugation and then washed repeatedly by acetone. The final catalyst was dried under vacuum at 25 °C. The as-prepared catalyst was named as H-PONs-PPh₃-Pd.

Route B: (Ph-PPh₃-Pd): Firstly, styrene and [TC] with the 800:1 molar ratio were mixed in a vessel and polymerized in oil bath at 120°C for 12h. The resulting polymer was precipitated from DCM towards methanol for three times. ¹H NMR: N(St)=256. Secondly, PS₂₅₆ (100 mg) and Pd(PPh₃)₄ (13.67 mg) (The molar ratio of the Pd(PPh₃)₄ to the benzene ring on the polystyrene was 1/15) and anhydrous FeCl₃(419.2 mg) were dissolved in CHCl₃ and operated in the same way of route A. The obtained catalyst was denoted as Ph-PPh₃-Pd.

General procedure of Suzuki-Miyaura coupling reaction²

In a 20ml vessel, aryl halide (0.5 mmol), boronic acid (0.75 mmol), K₂CO₃ (1.5 mmol), H-PONs-Pd(PPh₃)₄ (0.12 mol% Pd), solvent (EtOH/H₂O=3/2 v/v, 2ml), were mixed and sealed. Then it was heated in an oil bath at 80 °C under a N₂ atmosphere for 40 min-4h. After the reaction was completed (monitored by TLC), the mixture was filtered, the small amount of liquid for GC analysis. And the solid part was washed by water for one time and ethanol for three times. For catalyst recycle experiments, the washed solid was dried under vacuum for 24 hours and used into the new circle. The liquid part was dried and purified by column to obtain pure coupling product.

Materials measurement

All ¹H NMR spectra were recorded with a Bruker AVANCE III 500 spectrometer (500 MHz) with use of the deuterated CHCl₃ as the lock. ¹³C and ³¹P CP/MAS measurements were performed using a Bruker 400 M MAS system with Adamantane and NH₄H₂PO₄ as internal reference for C and P respectively. Fourier transform infrared spectroscopy (FT-IR) was performed on a Thermo NICOLET is50. GPC data were obtained from Waters GPC system equipped with two Waters HPLC columns, a 1515 isocratic HPLC pump, and

a Waters 2414 refractive index (RI) detector. Transmission electron microscopic images (TEM) of the samples were recorded on a high-resolution electron microscope JEM-2100F TEM instrument. The samples were prepared by dip-coating a 400-mesh carbon-coated copper grid from the dilute sample solution allowing the solvent to evaporate. A Quantachrome Autosorb IQ surface area and porosity analyzer was utilized to study the pore structure of the samples. Before measurements, the polymer samples were degassed for more than 10 h at 120 °C. The Brunauer-Emmett-Teller (BET) surface area and the micropore surface area were determined by the BET equation and the t-plot equation, respectively. The pore size distribution was analyzed by the DFT method. X-ray photoelectron spectroscopy (XPS) spectra were obtained on an ESCALAB 250Xi spectrometer.

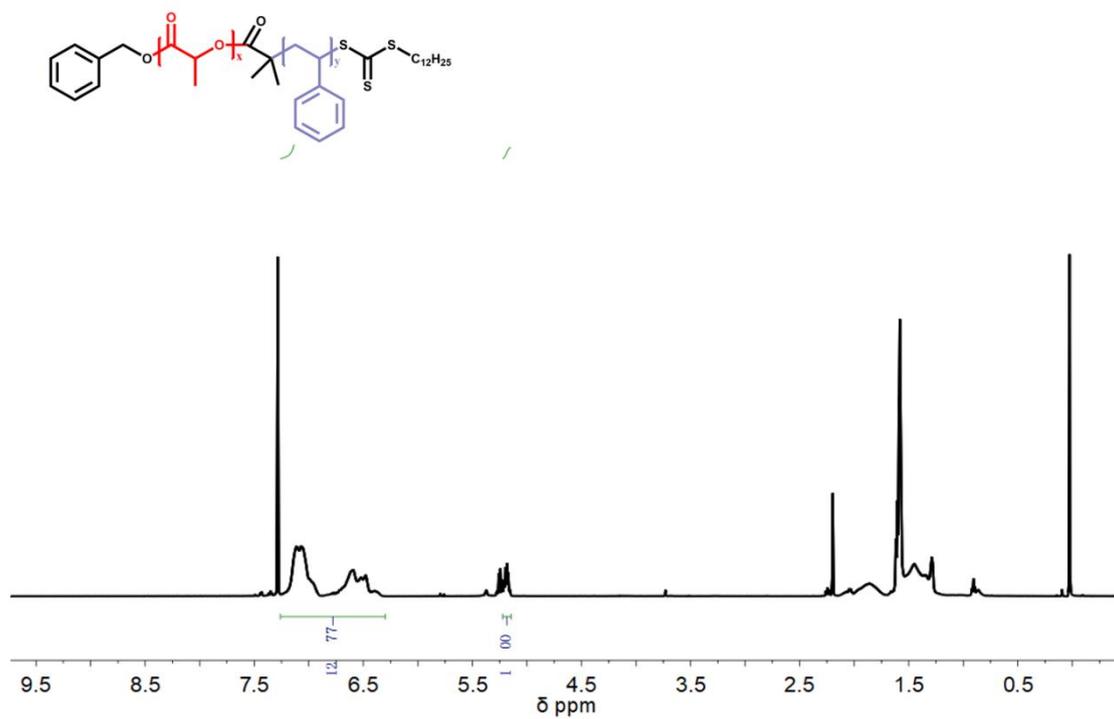


Figure S1 ^1H NMR of PLA-b-PS.

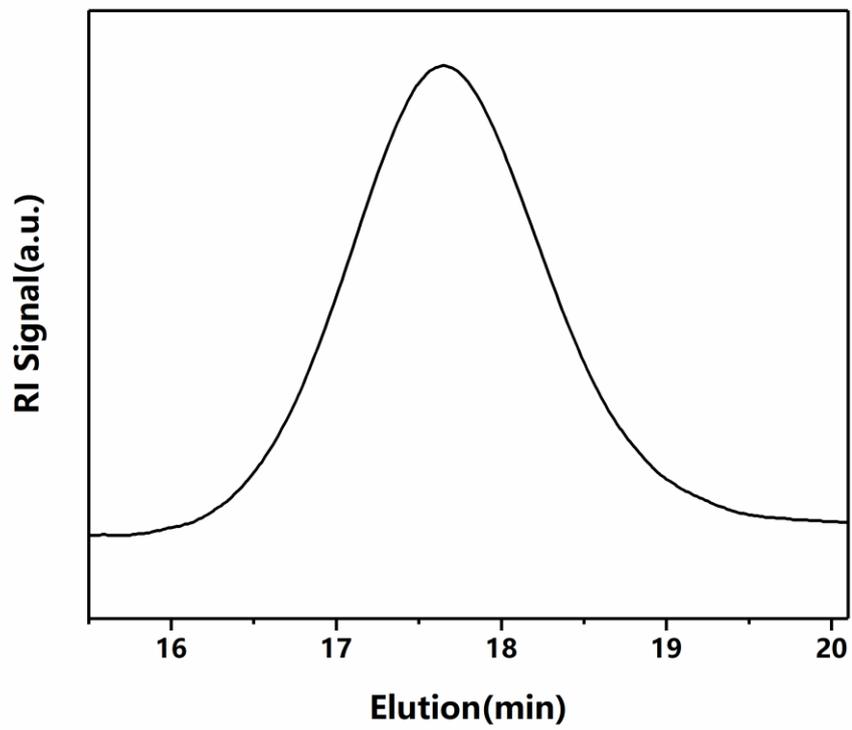


Figure S2 GPC trace of PLA-b-PS diblock copolymer.

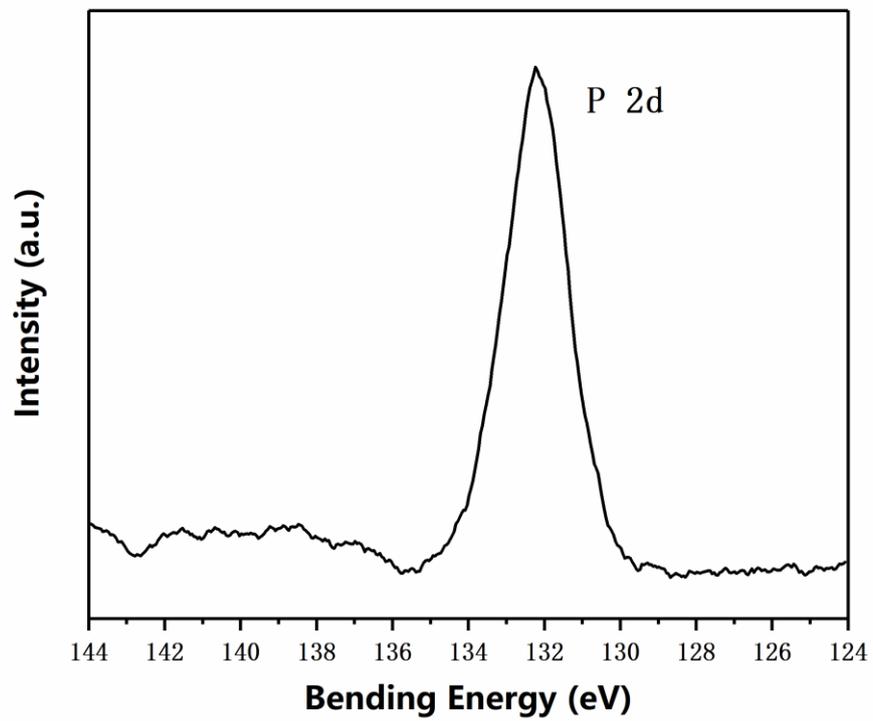


Figure S3 XPS spectrum of the P 2p region for H-PONs-Pd(PPh₃)₄ (1/15).

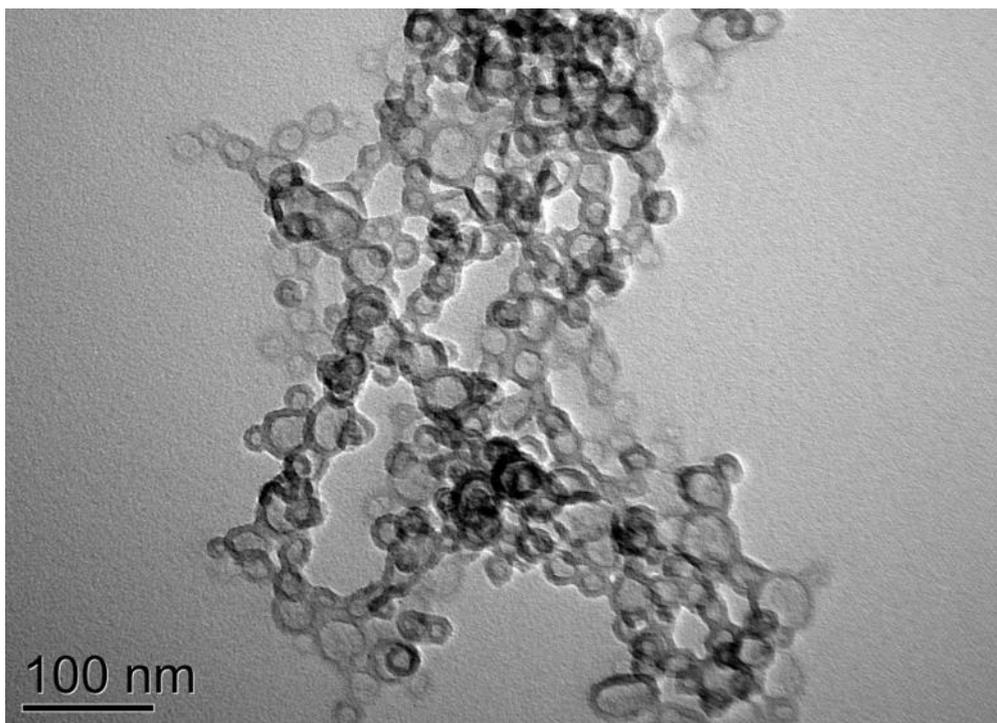


Figure S4 TEM image of H-PONs-PPh₃-Pd.

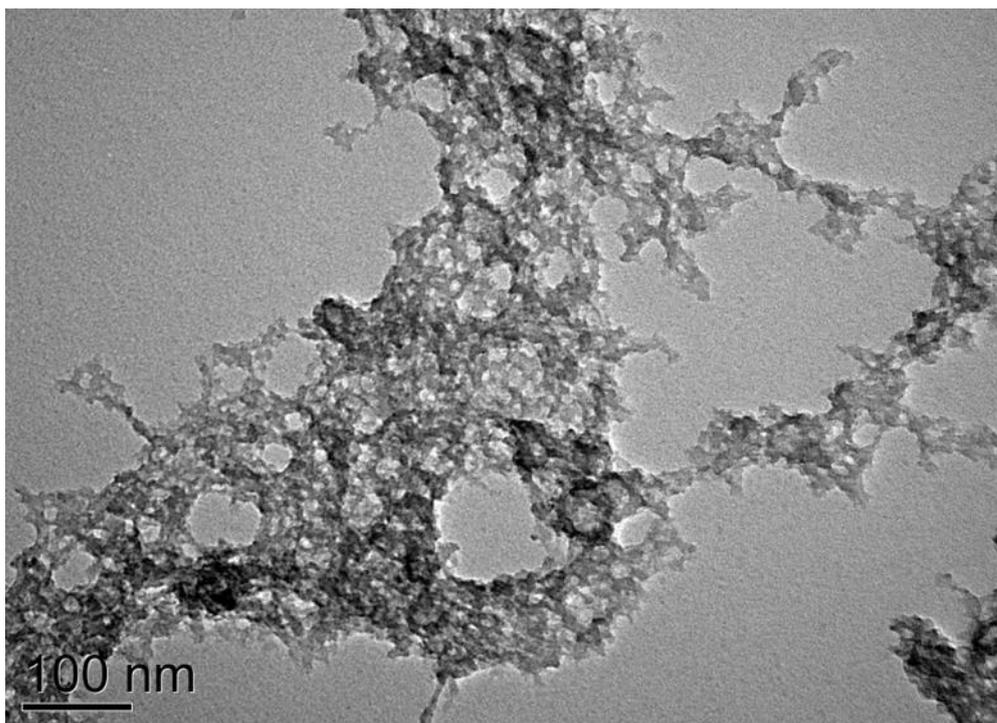


Figure S5 TEM image of Ph-PPh₃-Pd.

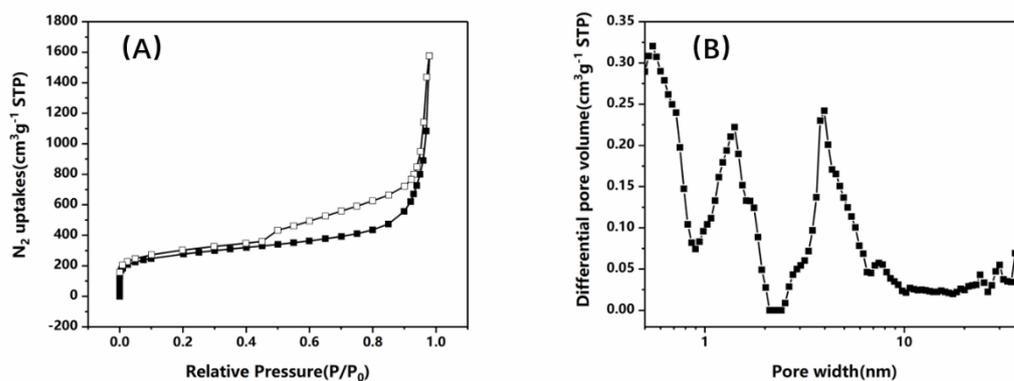


Figure S6 (A) Nitrogen adsorption (solid) and desorption (open) isotherms of H-PONs-PPh₃-Pd; (B) Pore size distribution calculated by density functional theory (DFT) method of H-PONs-PPh₃-Pd.

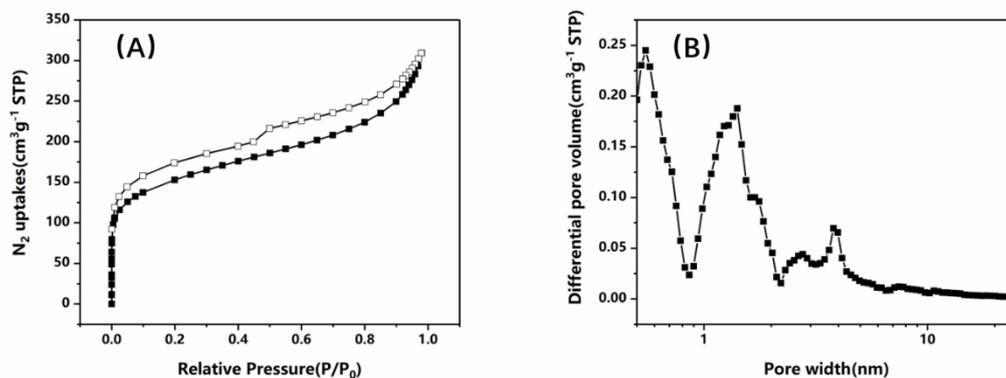


Figure S7 (A) Nitrogen adsorption (solid) and desorption (open) isotherms of Ph-PPh₃-Pd; (B) Pore size distribution calculated by density functional theory (DFT) method of Ph-PPh₃-Pd.

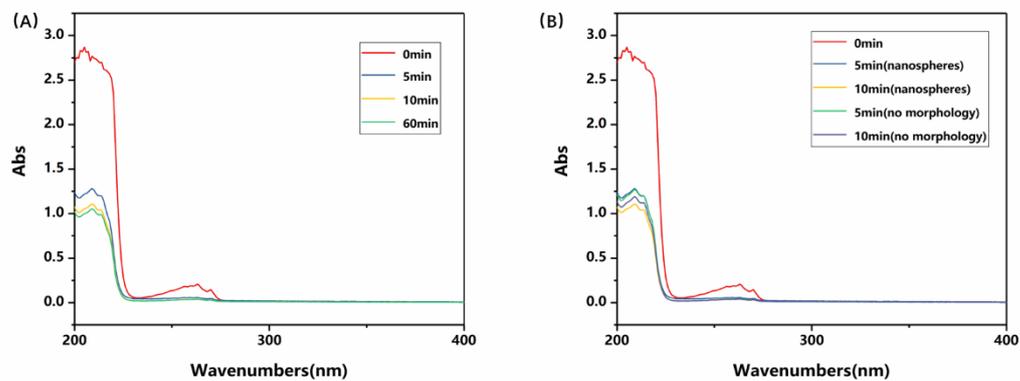


Figure S8 UV curves of phenyl chloride of (A) H-PONs-Pd(PPh₃)₄(1/15) (B) H-PONs-Pd(PPh₃)₄(1/15) and Ph-PPh₃-Pd.

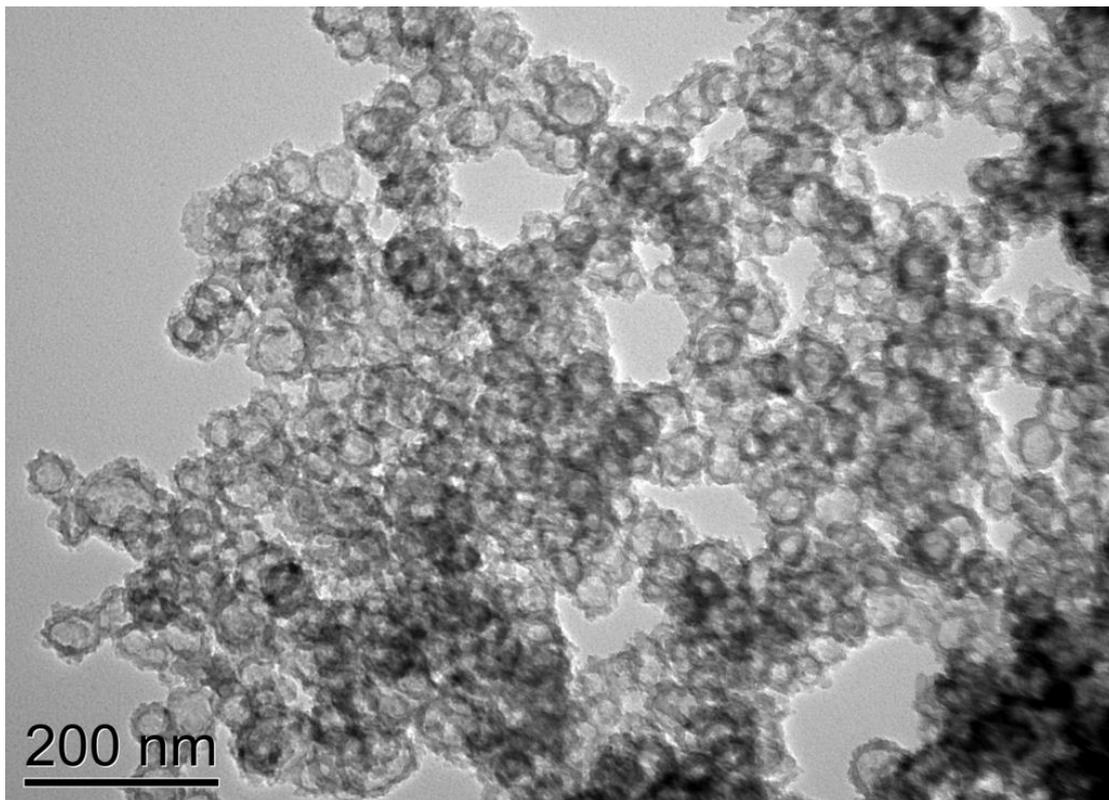


Figure S9 TEM image of H-PONs-Pd(PPh₃)₄ (1/15) after nine catalysis cycles.

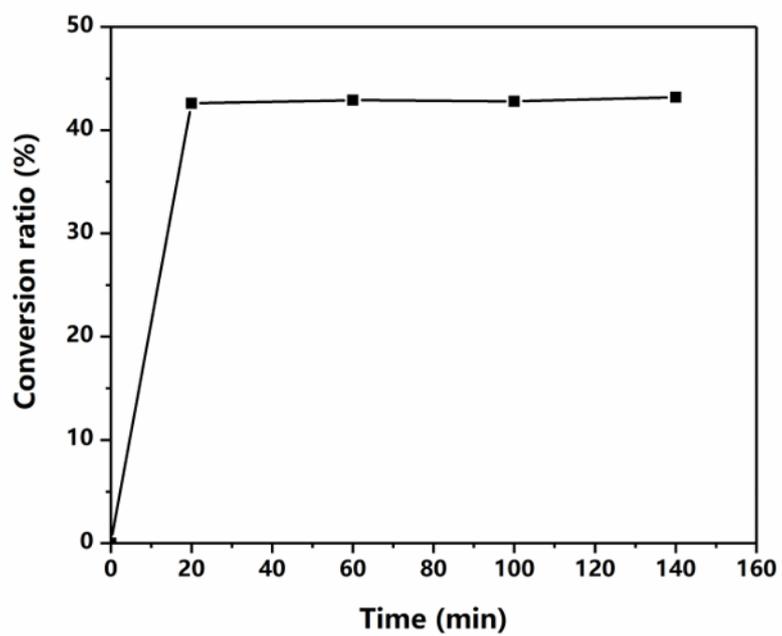


Figure S10 Leaking test of H-PONs-Pd(PPh₃)₄ (1/15) (phenyl chloride).

Table S1 Comparison of the catalytic performance of different heterogeneous catalysts in Suzuki-Miyaura couplings.

Entry	Catalysts	Amount of catalysts (respected to aryl chloride)	Reaction conditions	Yield (%)	TOF(h^{-1})	Ref.
1	$Pd(OAc)_2/Silica-TRIP^3$	0.5mol%	THF,60°C,12 h, P-methyl chlorobenzene	93	16	3
2	$PdCl_2(PhCN)_2/ligand(Pd/P 1:2)^4$	1mol%	THF,40°C,2h, P-methyl chlorobenzene	95(R=tBu)	48	4
3	$KAPs(Ph-PPh_3)-Pd^2$	0.6mol%	2 mL of EtOH:H ₂ O (3:2 v/v), 80°C,3h, under a N ₂ atmosphere	99	55	2
4	$MONFs-PPh_3@Pd-1^5$	0.12mol %	2 mL of EtOH:H ₂ O (3:2 v/v), 80°C,3h, under a N ₂ atmosphere	99	275	5
5	$PPPd^6$	0.2mol%	2 mL of EtOH:H ₂ O (3:2 v/v), 80°C,20h, air	96	24	6
6	$H-PONs-Pd(PPh_3)_4 (1/15)$	0.12mol %	2 mL of EtOH:H ₂ O (3:2 v/v), 80°C,2h, under a N ₂ atmosphere	99	413	This work

Reference

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