Supplementary Information

One-pot Approach to Pd-loaded Porous Polymers with Tunable Properties by Oxidation State of Phosphorus Core

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1. Experimental Section

Synthesis of tris-(4-formylphenyl)amine:[1] Phosphorus oxychloride (46.6 mL, 0.5 mol) was added dropwise to a solution of 20 g (0.08 mol) of triphenylamine in 100 ml DMF at 0 ℃. After addition, the ice bath was removed, and the solution was allowed to warm to room temperature. Then the mixture was heated and stirred at 105℃ for 17 h. Afterwards, the solution was poured into water, and was neutralized to pH =7 with NaOH aqueous solution, and then extracted with dichloromethane. The combined organic layers were washed with brine. After the organic solvent was removed off at reduced pressure, the resulting residue was purified by chromatography on a silica gel column (ethyl acetate/n-hexane 1:2) to produce 1.35 g of yellowish solid (20% yield). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 9.92 (s, 3H), 7.84 (d, 6H), 7.24 (d, 6H).

Synthesis of tris(4-vinylphenyl)amine:[1] Under the anhydrous and oxygen-free conditions of a Wittig reaction, 17 equiv of NaH was added to the solution containing 1.25:1 equiv of tris-(4-formylphenyl)amine and methyl phosphonium iodide in dry THF. The reaction mixture was refluxed under N$_2$ for 40 h. After removal of the solvent, the residue was quenched with water and extracted with chloroform. The collected organic layer was dried over anhydrous magnesium sulfate. After removing off the solvent by evaporation, the crude product was purified via column chromatography to offer target compound as transparent slurry (Yield: 43.2%). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 5.18 (3H), 5.61 (3H), 6.63 (3H), 7.65 (6H), 6.58 (6H).

Synthesis of tris(4-bromophenyl)phosphine:[2] To a solution of 1,4-dibromobenzene (2.86 g, 10 mmol) in anhydrous THF (100 mL) was added dropwise n-butyllithium (1.13 M in hexane, 4.2 mL, 9.5 mmol) at -78℃. The reaction was kept at this temperature for 2 h, and then 0.63 mL (4.65 mmol) of phosphorus trichloride was added. After the mixture was stirred for 2 h at -78℃, it was allowed to warm to room temperature, stirred overnight followed by quenching with 5 mL of methanol and water. The mixture was extracted with CH$_2$Cl$_2$, washed with water, and dried over anhydrous MgSO$_4$. After the solvent had been completely removed, 30% hydrogen

peroxide (20 mL) and CH_2Cl_2 (40 mL) were added to the obtained residue and they were stirred overnight at room temperature. The organic layer was separated and washed with water and then brine. The extract was evaporated to dryness, and the residue was purified by column chromatography on silica gel to give a white solid. Yield: 30%. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.68-7.60 (m, 6H), 7.54-7.44 (m, 6H).

Synthesis of tris(4-bromophenyl)phosphine oxide:[3] The 30% H_2O_2 (0.28 ml, 2.64 mmol) was slowly added to a solution of tris(4-bromophenyl)phosphin (1.20 mg, 2.42 mmol) in 50 ml of CH_2Cl_2, and stirred overnight at room temperature. The organic layer was separated and washed with water and then brine. The extract was evaporated to dryness, and the residue was purified by column chromatography on silica gel using dichloromethane/methanol (30:1 by vol) as the eluent to give a white solid (1.13 mg yield: 93%).
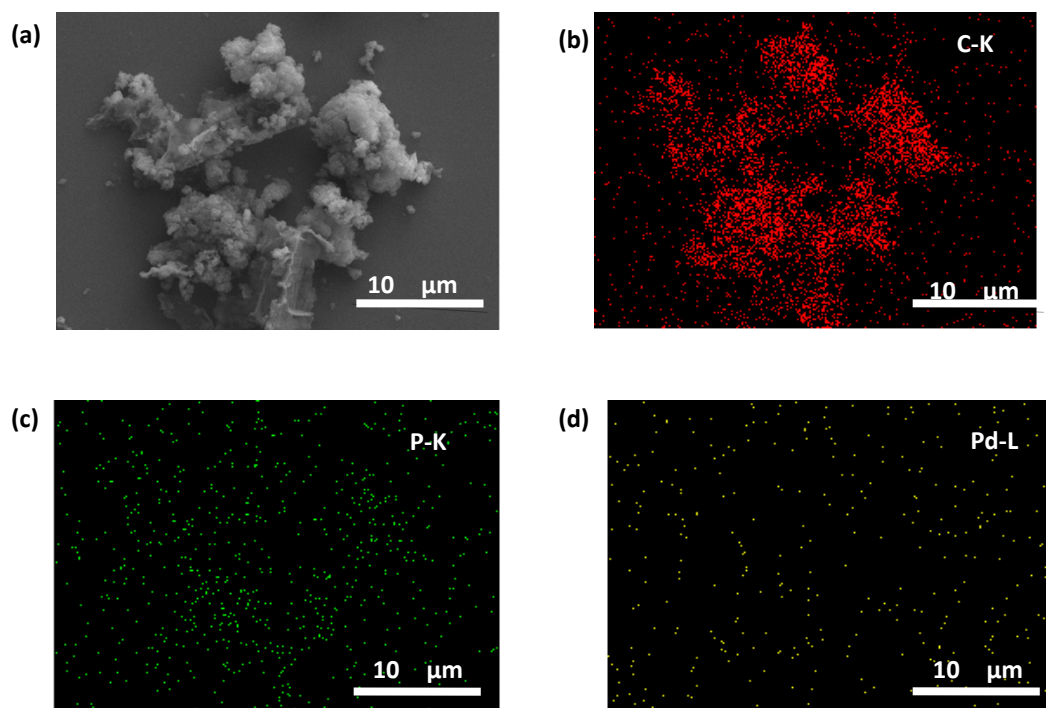
2. Figures

Figure.S1 (a) The SEM image of Pd@N=P and the corresponding elemental mapping images of (b) carbon, (c) phosphorus, and (d) palladium in the full area.
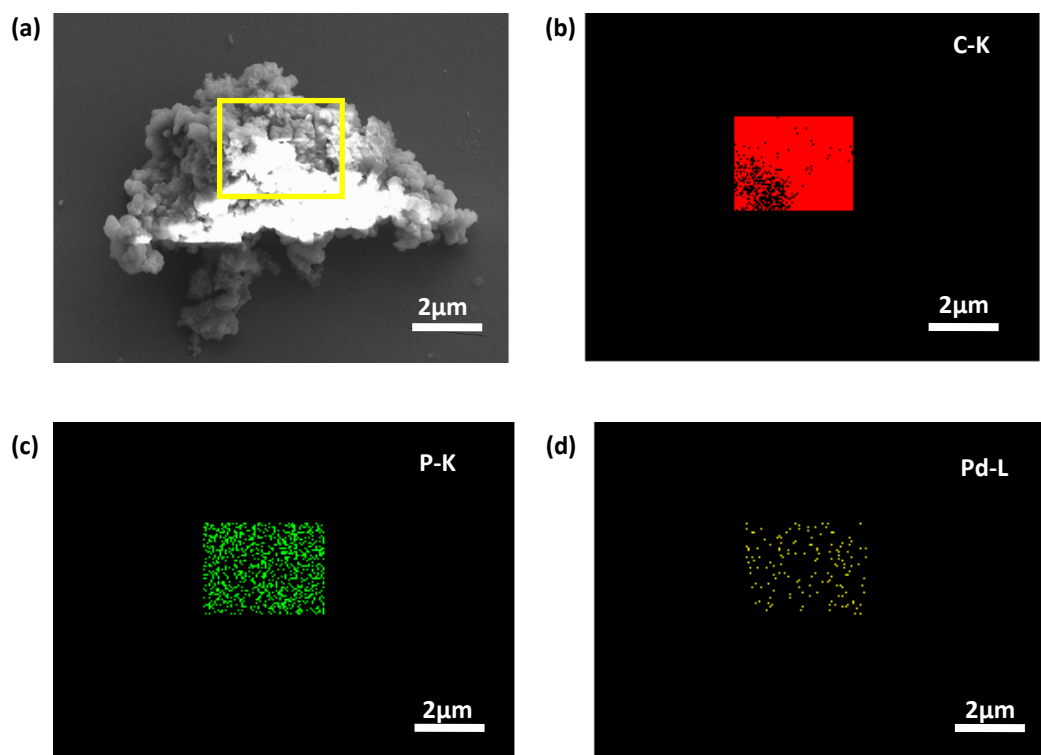
Figure.S2 (a) The SEM image of Pd@N=P=O and the corresponding elemental mapping images of (b) carbon, (c) phosphorus, and (d) palladium in the selected area.
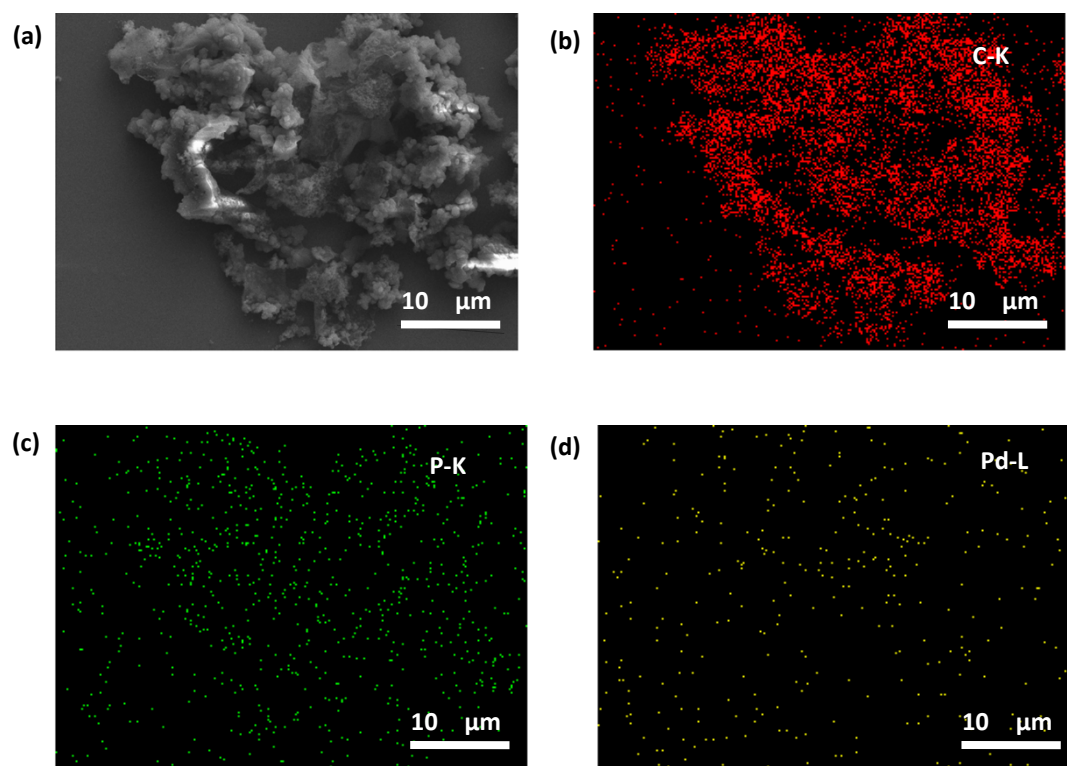

Figure.S3 (a) The SEM image of Pd@N=P=O and the corresponding elemental mapping images of (b) carbon, (c) phosphorus, and (d) palladium in the full area.
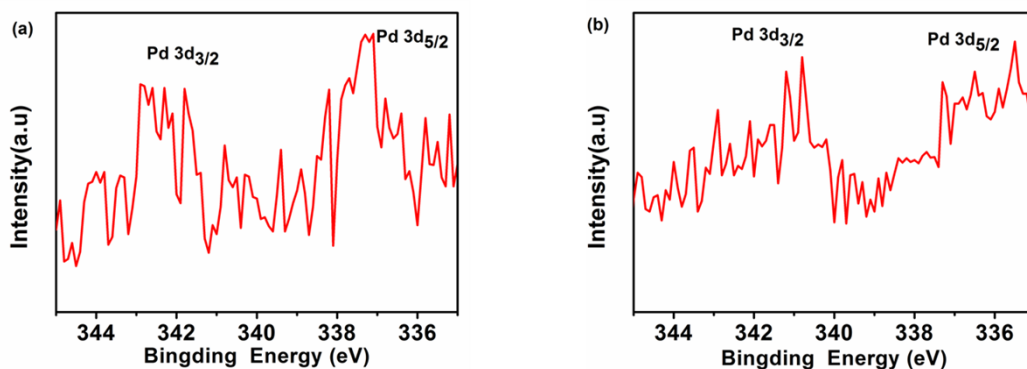
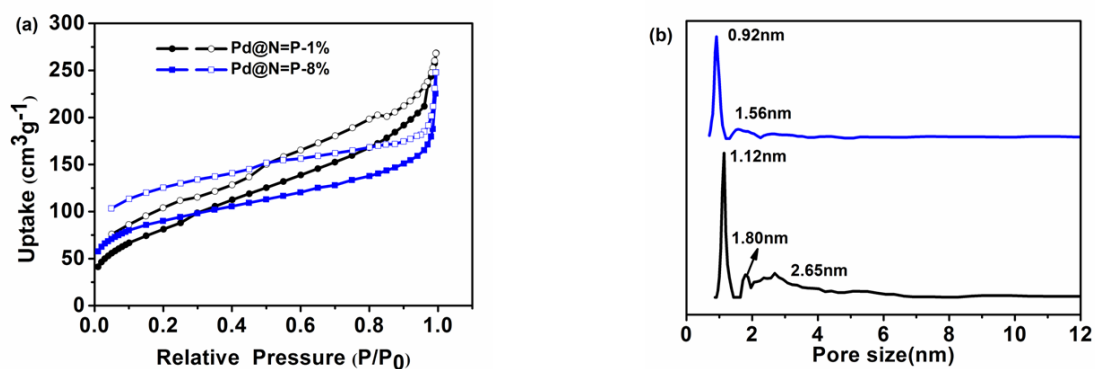**Figure.S4** The Pd XPS spectra of (a) Pd@N=P and (b) Pd@N=P=O.

Figure.S5 (a) Nitrogen adsorption-desorption analysis of porous polymers; (b) Pore size distribution of porous polymers.

3.Table

Table S1 The effects of the amount of the catalyst on the reaction and the porosities of the final porous materials

Entry	Pd(PPh$_3$)$_4$ (mol%)	Pd (wt%)[a]	S_{BET} (m^2/g) [b]	$S_{Langmuir}$ (m^2/g) [c]	Pore size (nm) [d]	Yield (%)
1	1	0.64	300	389	1.12,1.80	65%
2	4	1.0	381	481	0.52,0.98	83%
3	8	4.67	330	422	0.92,1.56	88%

[a] Determined by ICP;[b] Surface areas calculated from the N$_2$ adsorption isotherm using the BET method. [c] Langmuir surface areas calculated from the N$_2$ adsorption

isotherm using the Langmuir method. [d]The pore size distribution was calculated using nonlocal density functional theory (NLDFT).

3. Reference

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2. C. Liu, Y. Li, Y. Li, C. Yang, H. Wu, J. Qin and Y. Cao, *Chem. Mater.*, 2013, **25**, 3320.
3. Y. Wang, M. I. Ranasinghe and T. Goodson, *J. Am. Chem. Soc.*, 2003, **125**, 9562.