Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information (SI)

Phosphorus−Doped Ordered Mesoporous Carbons embedded with Pd/Fe Bimetal Nanoparticles for the dechlorination of 2,4−dichlorophenol

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Total number of pages of Supporting Information: 14 (including cover page)

Number of Figures in Supporting Information: 6

Number of Tables in Supporting Information: 2

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Preparation of SBA-15 templates

Mesoporous silicon templates (SBA-15) were prepared as reported by Dongyuan Zhao[1]. In a typical synthesis, P123 (PEO_{20}-PPO_{70}-PEO_{20}, Sigma-Aldrich, 8.0 g) was added into HCl solution (2 mol/L, 312 mL) and the mixture was stirred for 4 h at 35 ℃ until surfactant P123's full dissolution. Next, tetraethyl orthosilicate (TEOS, Fuchen Chemical Regent of Tianjin, 17.2 g) was dropwise added, and followed by 20 h mechanically stirring at 35 ℃. Then, the resulting gels were transferred to the Teflon-lined sealed containers and were kept at 140 ℃ for 24 h under static hydrothermal conditions. The as-synthesized samples were recovered by filtration and washing. Subsequently, the samples were calcined at 550 ℃ in air for 4 h to remove the organic template P123. Thus, the as-synthesized SBA-15 was obtained.

Synthesis of Pd/NZVI@P

Fe was incorporated into the P−OMC via an impregnation method, where 1.44 g of $Fe(NO_3)_3$ $9H_2O$ (Fisher) was melted with deoxygenated deionized water (100 mL) and then mixed with 1 g of P−OMC for 20 min. Nanoscale Fe particles were produced by adding 2 M $NaBH_4$ aqueous solution drop wisely to a 250 mL three−necked flask with mechanical stirring at ambient temperature under nitrogen atmosphere. Ferrous iron was reduced to Fe^0 according to the following reaction:

$$4Fe^{3+} + 3BH^{4-} + 9H_2O \longrightarrow 4Fe^0 + 3H_2BO^{3-} + 12H^+ + 6H_2$$

The NZVI@P were washed three times with deoxygenated deionized water under nitrogen atmosphere, dried by vacuum freeze−drying equipment and then stored in a nitrogen−filled glovebox until required. 0%, 0.5%, 1% and 2% Pd/NZVI@P were then synthesized by adding a desired amount of dried NZVI@P to palladium chloride aqueous solution (50 mL) under nitrogen atmosphere, respectively, and then stirring for 30 min under nitrogen atmosphere according to the following equation:

$$Fe^0+Pd^{2+} \longrightarrow Fe^{2+} + Pd^0$$

The Pd/NZVI@P were then rinsed with deoxygenated deionized water under nitrogen atmosphere to remove chloride ions, dried by vacuum freeze−drying equipment and then stored in a nitrogen−filled glovebox until required.

2,4-dichlorophenol analysis

At selected time intervals, an aqueous aliquot was withdrawn with a 5 mL glass syringe and then passed through a 0.45 mm membrane filter. A drop of 0.5 mol/L NaOH aqueous solution was added into the sample to remove ferrous ions. The sample was then filtered through a 0.22 mm membrane filter for analysis. The concentrations of the parent chlorinated compound and products was analyzed by HPLC. The LC was equipped a Inertsil ODS-SP column (150 mm × 4.6 mm) and a SPD-10Avp UV-Vis detector. A mixture of methanol and water (6/ 4(v/v)) was used as an eluent and the flow rate was 1.0 mL/ min. The size of sample loop was 20 μL. The wavelength of the detector was set at 280 nm. The compounds were qualitatively identified by comparing retention times with standard samples and then quantified with calibration curve method. And the dechlorination rate was calculated by the following equation.

Dechlorination percent (%) = $C_{phenol}/(C_{phenol}+C_{2,4\text{-}DCP}) \times 100$

where C_{phenol} represents the molar concentration of phenol after dechlorination (μmol/L); $C_{2,4\text{-}DCP}$ denotes the molar concentration of 2,4-DCP after dechlorination (μmol/L).

The dechloriniation kinetics of 2,4-DCP was described by the pseudo-first-order kinetic model. This model is expressed as follows.

$d[C]/dt=-k_{SA}a_s\rho_m[C] =-k_{obs}[C]$

where k_{SA} (L/m^2/min) is a surface-area-normalized rate constant, a_s (m^2/g) is the specific surface area of Pd/NZVI@P, and ρ_m (g/L) is the mass of Pd/NZVI@P in the system. Values of k_{SA} are determined by normalizing the pseudo-first-order rate constant for contaminant degradation (k_{obs}) by the product of a_s and ρ_m.

Thermo gravimetric-differential thermal analysis

Figure S-3 shows the thermo gravimetric-differential thermal analysis (DTG-DTA) profiles of P-OMC and Pd/NZVI@P-1% in the ambient air. For P-OMC, it is not difficult to find that there is scarcely any weight loss below 320 °C, which indicates the introduction of phosphorus leads to a small increase in the oxidation resistance of the mesoporous carbon under the conditions with relatively low temperature. However, the mass loss is quite fast at 320-640 °C, and the weight loss can arrive at about 80%. This process is attributed to the atom loss originated from the broken of triphenylphosphine, the decomposition of organic functionalities and carbon skeleton. The weight loss curve of Pd/NZVI@P showed three different thermal events: (i) the first 11% weight loss below 100 °C was attributed to the evaporation of moisture; (ii) the second 9% mass loss at 100-300 °C was assigned to the decomposition of the carbon impurity (such as amorphous carbon); and (iii) when the temperature increased further, the third 60.2% mass loss between 300 and 640 °C corresponded to carbon combustion, which is a decomposition of mesoporous carbon skeleton. Last, the weight loss of P-OMC and Pd/NZVI@P is negligible, and the relative weight can be remained with increasing of temperature from 640-1000 °C. The dramatic decrease in weight loss for P-OMC and Pd/NZVI@P also can be testified in view of their heat flows. The DTA image shows two strong peaks at 400-640 °C, confirming the exothermic reaction of carbon oxidation [2].

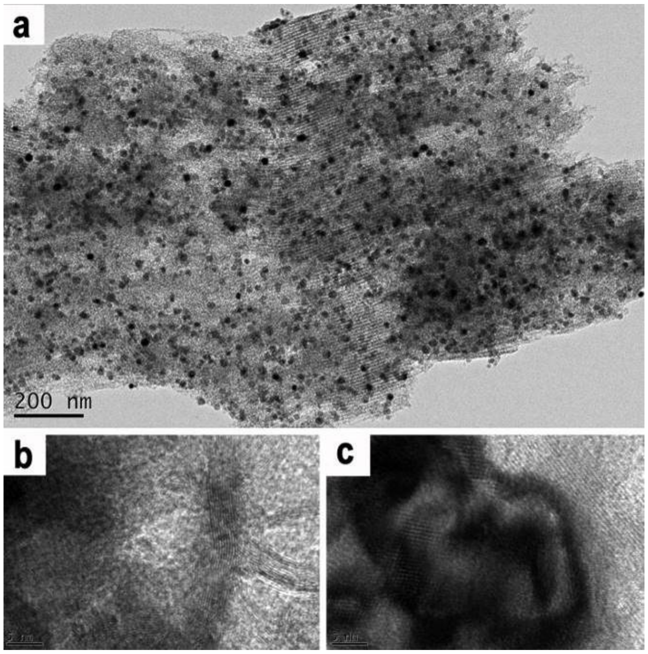

Fig. S-1 TEM of Pd/NZVI@P (a), HR-TEM Pd/NZVI@P (b and c).

TEM images for Pd/NZVI@P confirm the hexagonal ordered mesostructure, and the black nanoparticles dispersed uniformly on the P−OMC were Pd−Fe bimetal nanoparticles. The nanoparticles with an average diameter about 15 nm are well-dispersed and conglutinated by the amorphous substance in the whole framework. High-resolution TEM (HRTEM) images further reveal that the pore system of Pd/NZVI@P is composed of a large number of nanoparticles.

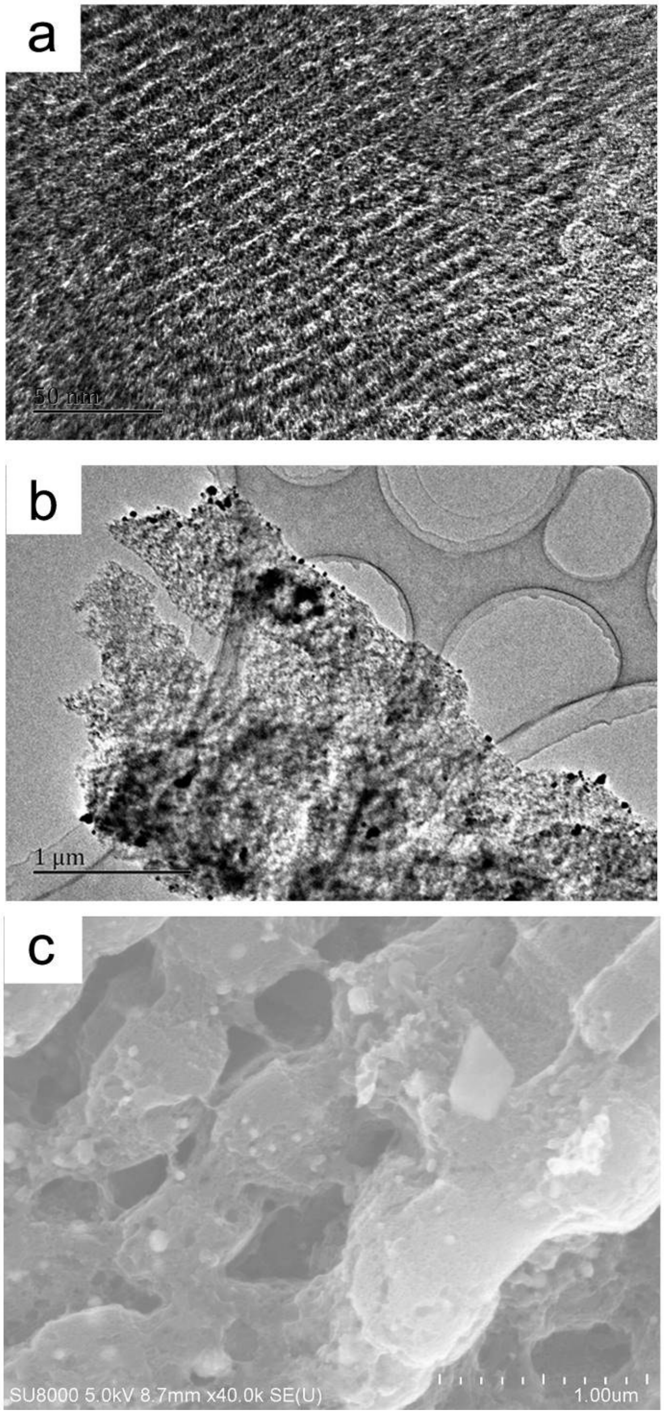

Fig. S-2 TEM of OMC (a), Pd/NZVI/OMC (b), and SEM of Pd/NZVI/OMC (c).

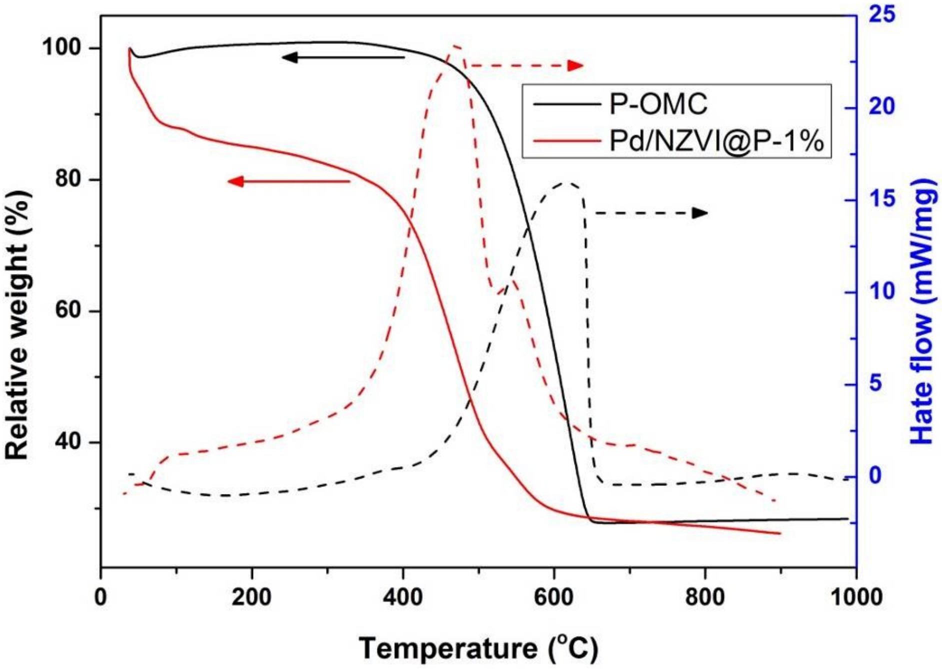

Fig. S-3 TGA-DTA curves of P-OMC and Pd/NZVI@P-1%.

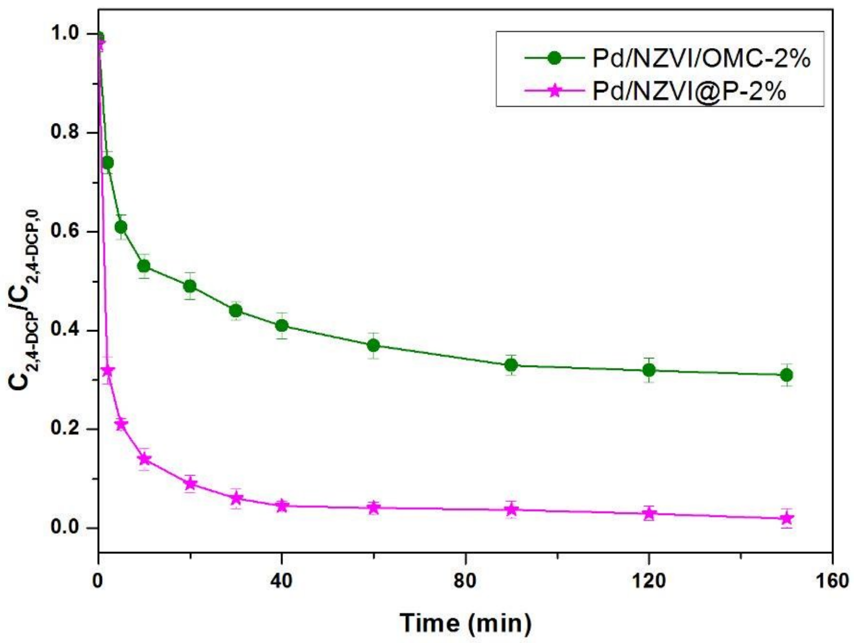

Fig. S-4 Compare Pd/NZVI supported on the OMC with and without P on the same conditions for the dechlorination of 2,4−DCP.

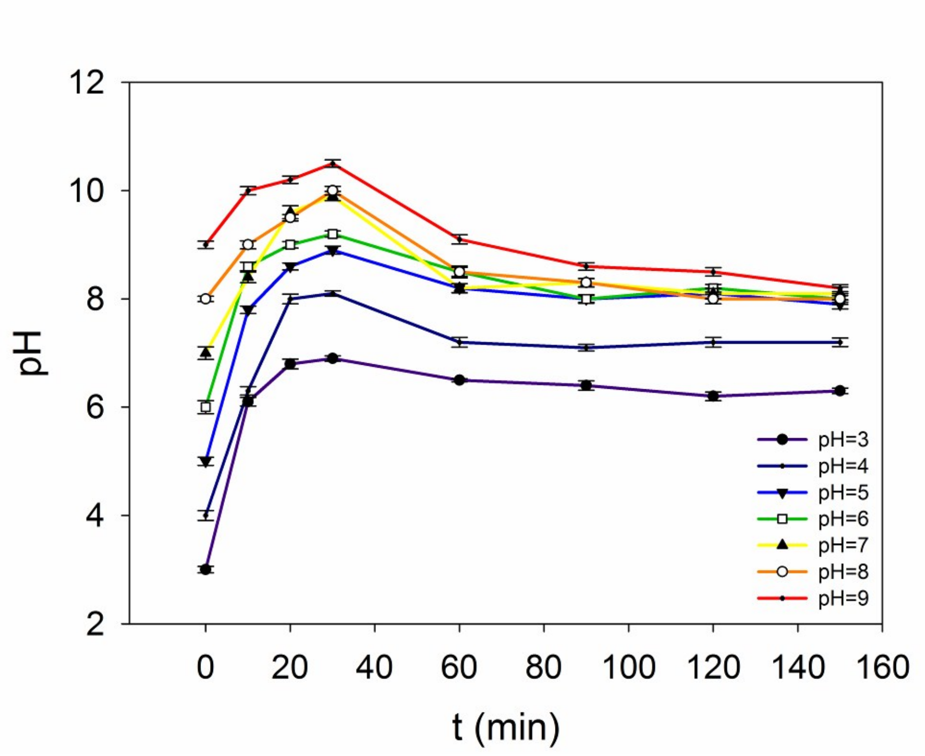

Fig. S-5 The pH change profile in the reaction process.

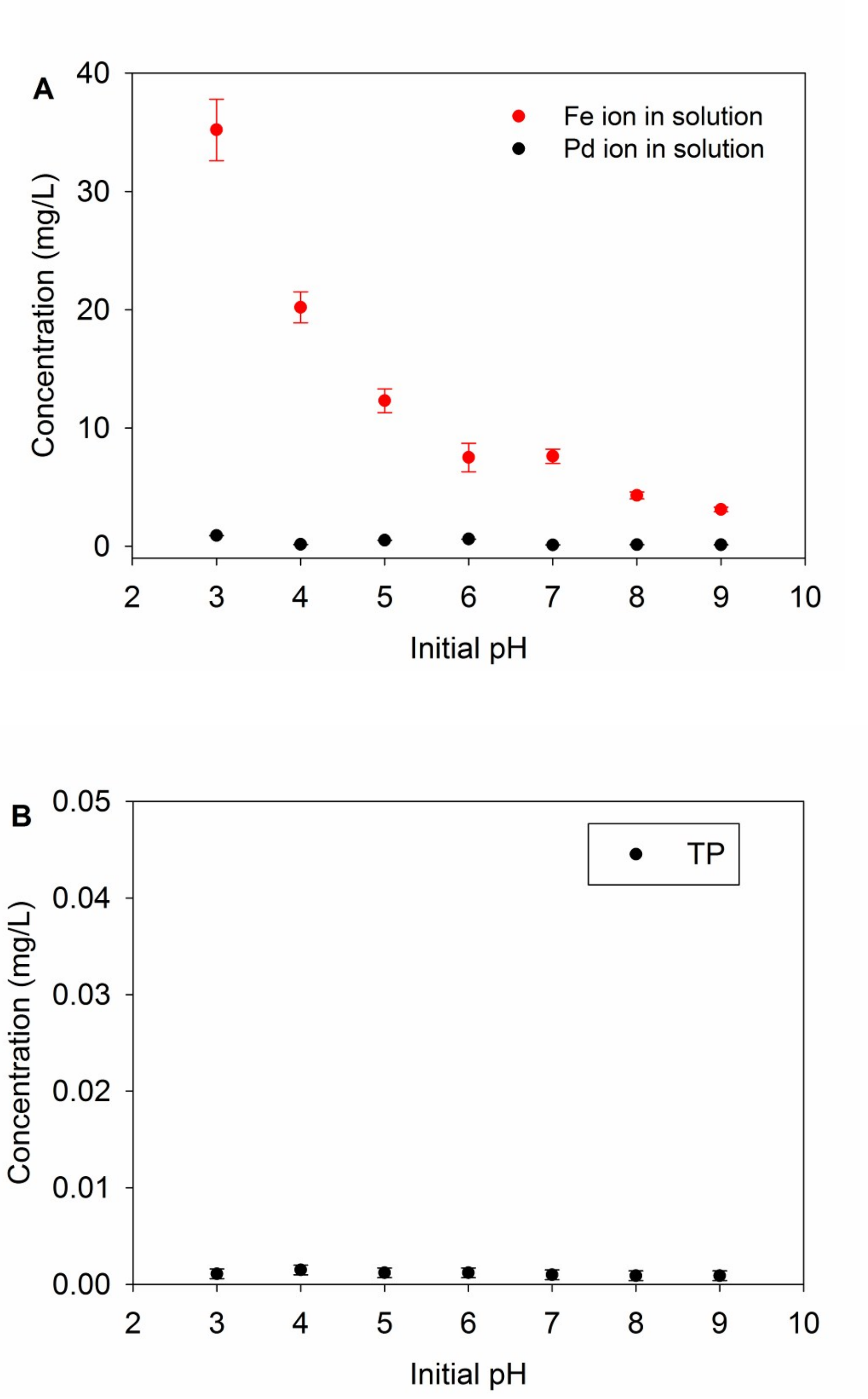

Fig. S-6 Effect of initial pH on the concentrations of dissolved metal ions (A), and total P (TP) (B) in solution after 150 min reaction.

Table S−1 The EDS results of the catalyst of Pd/NZVI@P−2%.

Conditions	Content (wt%)
C	81.58
O	10.22
P	1.15
Fe	5.62
Pd	1.43
Total	100%

Table S−2 Textural properties of composite materials.

sample	surface area ($m^2 \cdot g^{-1}$)	pore volume (cm^3/g)	pore diameter (D_p^a) (nm)
SBA−15	473.897	1.134	9.73
P−OMC	1033.5	1.446	4.935
Pd/NZVI@P−0%	667.746	1.054	5.087
Pd/NZVI@P−0.5%	552.42	0.966	5.058
Pd/NZVI@P−1%	455.53	0.81	5.011
Pd/NZVI@P−2%	344.22	0.72	4.979

Reference

[1] D.Y. Zhao, J.L. Feng, Q.S. Huo, N.G. Melosh, H. Fredrickson, B.F. Chmelka, G.D. Stucky, Science, 1998, **279**, 548–552.

[2] N.P. Wickramaratne, V.S. Perera, B.W. Park, M. Gao, G.W. McGimpsey, S.D. Huang, M. Jaroniec, Chemical of Materials, 2013, **25**, 2803–2811.