Supporting information:

Efficient aqueous hydrodeoxygenation of vanillin over mesoporous carbon nitride-modified Pd nanocatalyst

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Table S1. Structural parameters of Pd-based catalysts.

Catalysts	Particle size (nm)		Mass concentration (%)	
	XRD	TEM	Pd[a]	Pd[b]
Pd/CN-CT	3.8	4.3	2.41	2.39
Pd/CN-CF	2.1	2.4	2.36	2.33
Pd/CN-TE	4.5	4.7	2.48	2.44

[a] Detected in XPS analysis.

[b] Detected *via* ICP analysis.

Table S2. Elemental analysis results of CNs.[a]

Catalysts	Mass concentration (%)				
	C	H	N	N[b]	O (calculated)
CN-CT	71.83	1.67	18.34	18.45	8.16
CN-CF	75.10	1.86	15.55	15.97	7.49
CN-TE	78.02	2.17	12.07	12.21	7.74

[a] Detected by CHNS elemental analysis.

[b] Detected in XPS analysis.

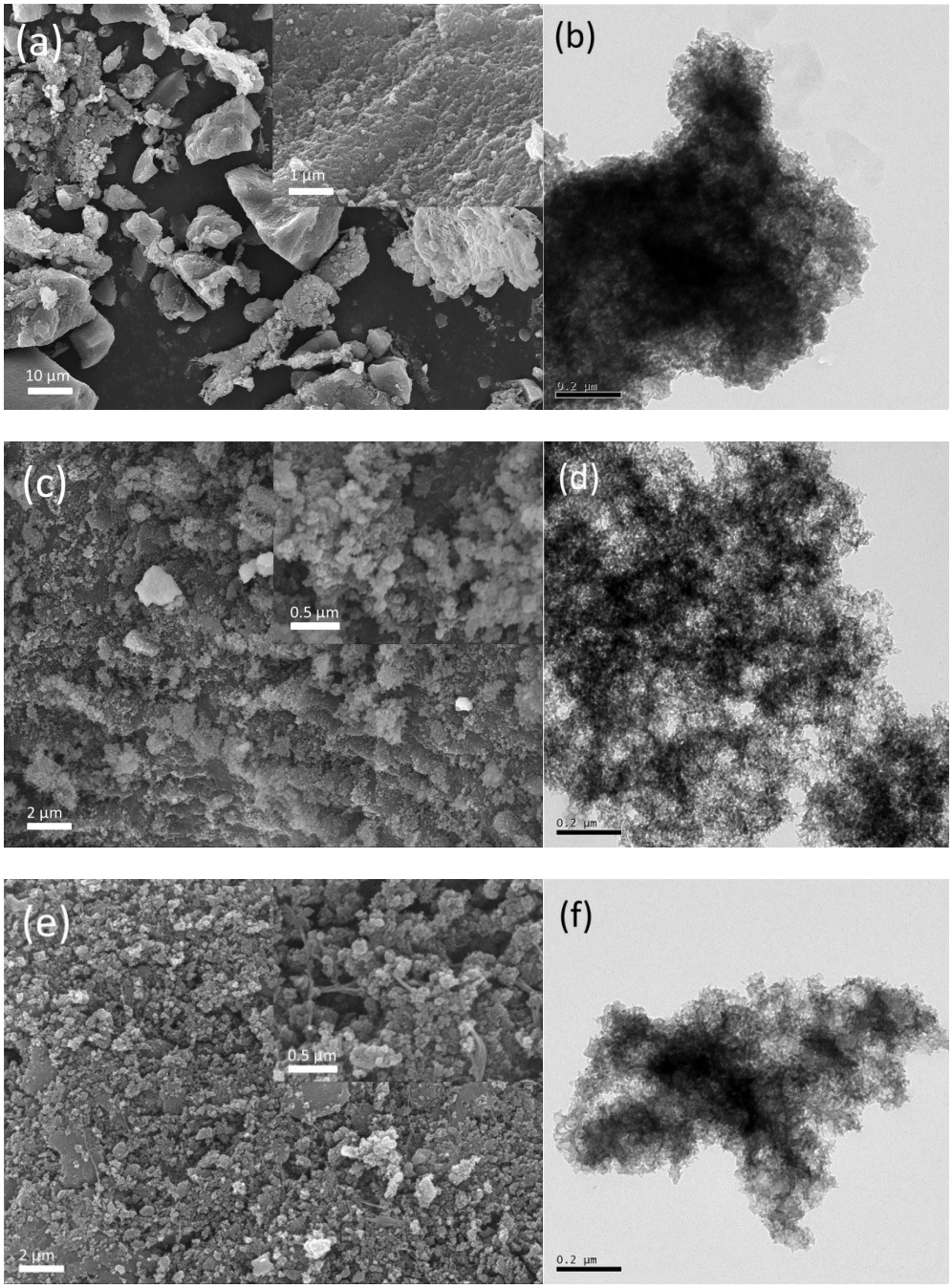

Fig. S1. SEM images of (a) CN-CT, (c) CN-CF and (e) CN-TE; TEM images of (b) CN-CT, (d) CN-CF and (f) CN-TE.

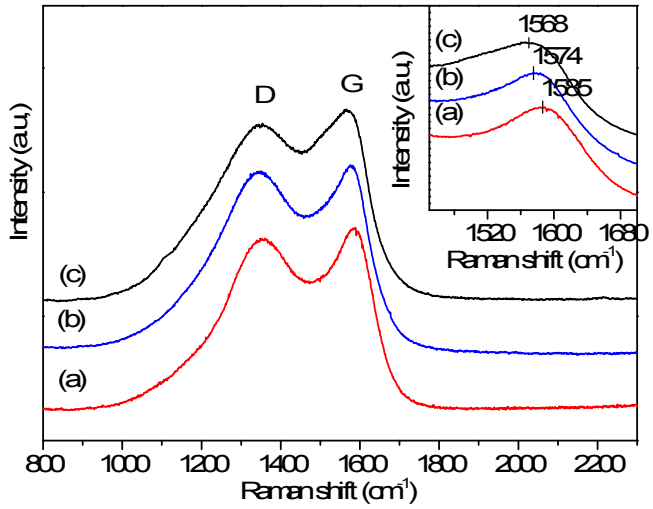

Fig. S2. Raman spectra of (a) CN-CT, (b) CN-TE and (c) CN-CF.

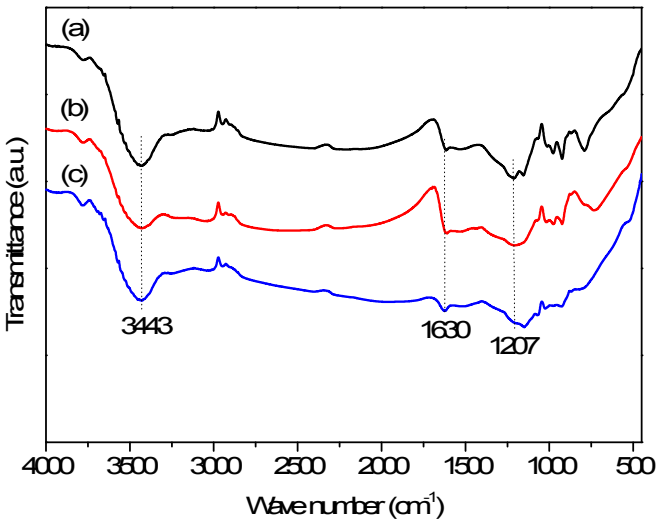

Fig. S3. FTIR patterns of (a) CN-CT, (b) CN-CF and (c) CN-TE.

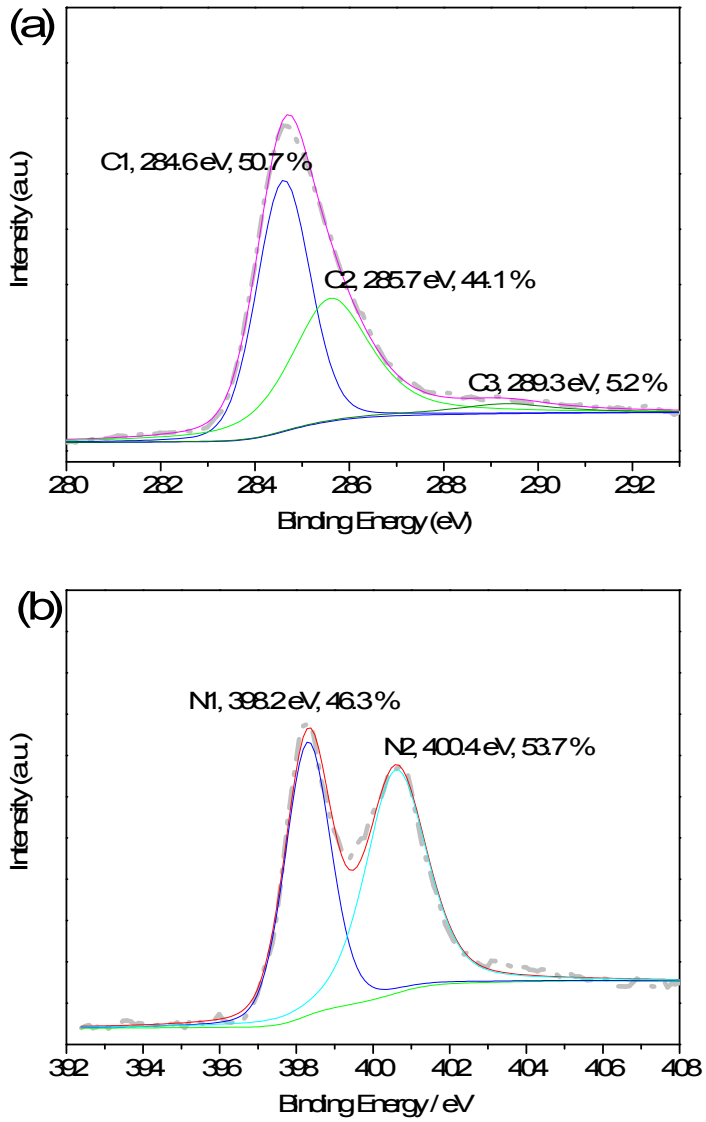

Fig. S4. (a) C1s and (b) N1s spectra of CN-CF.

The C1s peak was deconvoluted into three peaks with binding energies of 284.6 (C1), 285.7 (C2), and 289.3 eV (C3), assigned to pure graphitic sites in the amorphous CN matrix, the sp^2 C atoms bonded to N inside the aromatic structure and the sp^2-hybridized carbon in the aromatic ring attached to the NH_2 group, repectively. N1 (398.2 eV) and N2 (400.4 eV) represent N atoms bonded with the graphitic carbon atoms and N atoms trigonally bonded to all sp^2 carbons, respectively.

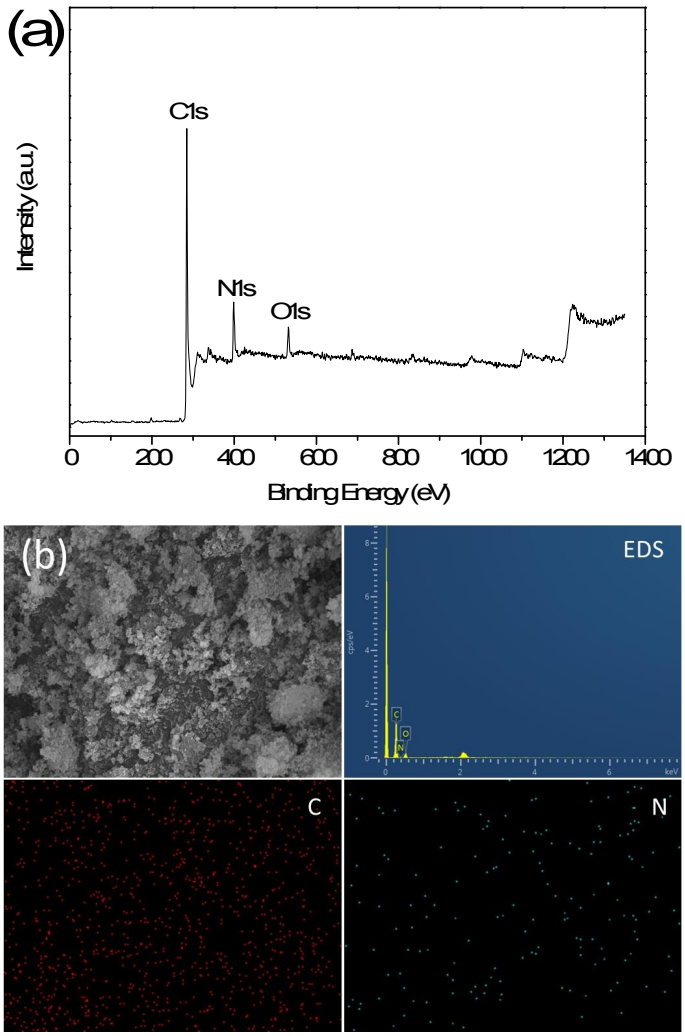

Fig. S5. (a) XPS survey spectra and (b) surface EDS analysis of CN-CF.

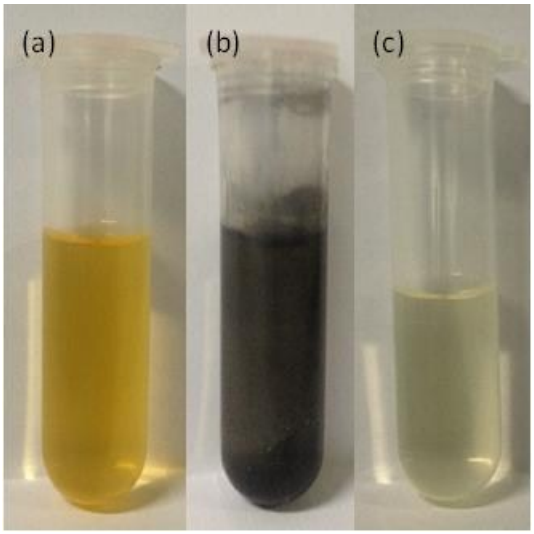

Fig. S6. The reaction solution for preparing Pd/CN-CF. (a) The $PdCl_2$ aqueous solution without CN-CF, (b) the $PdCl_2$ aqueous solution is added with CN-CF and stir at 40 ^oC for 1h, (c) the solution of (b) after removal of CN-CF by centrifugation.

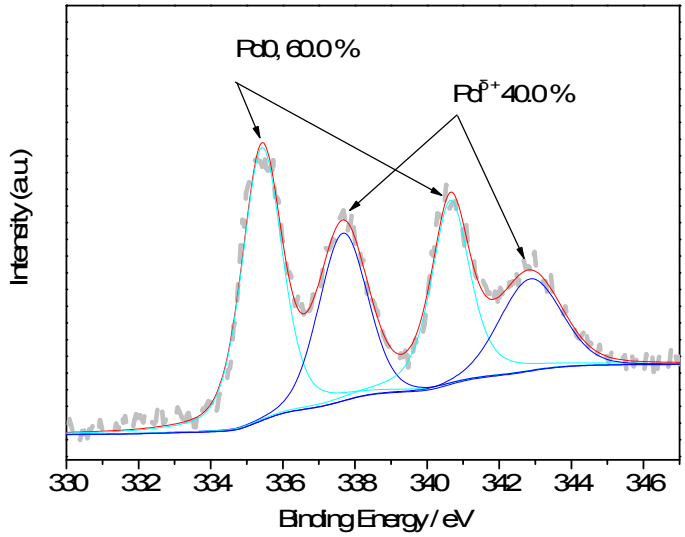

Fig. S7. Pd3d spectra of Pd/CN-CF.

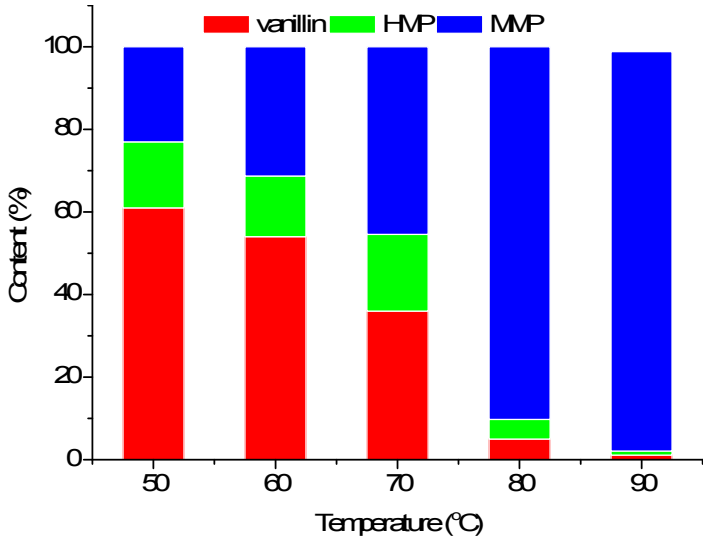

Fig. S8. Temperature-activity profile for the selective hydrogenation of vanillin.
Reaction conditions: vanillin (200 mg), Pd/CN-CF (20 mg), H_2O (16 mL), 1 MPa H_2, 0.5 h.

Reactions at 90 °C or above it are provided complete vanillin conversion and excellent MMP selectivity. When the temperature decreases at or below 90 °C, vanillin conversion starts slightly decreasing (Table 2, entry 5). At 50 °C, vanillin conversion notably decreases to 52 % with a MMP selectivity of 59 %. But longer reaction time (7 h) at 50 °C can help to reach 99.2 % vanillin conversion as well as a MMP selectivity exceeding 98 %.

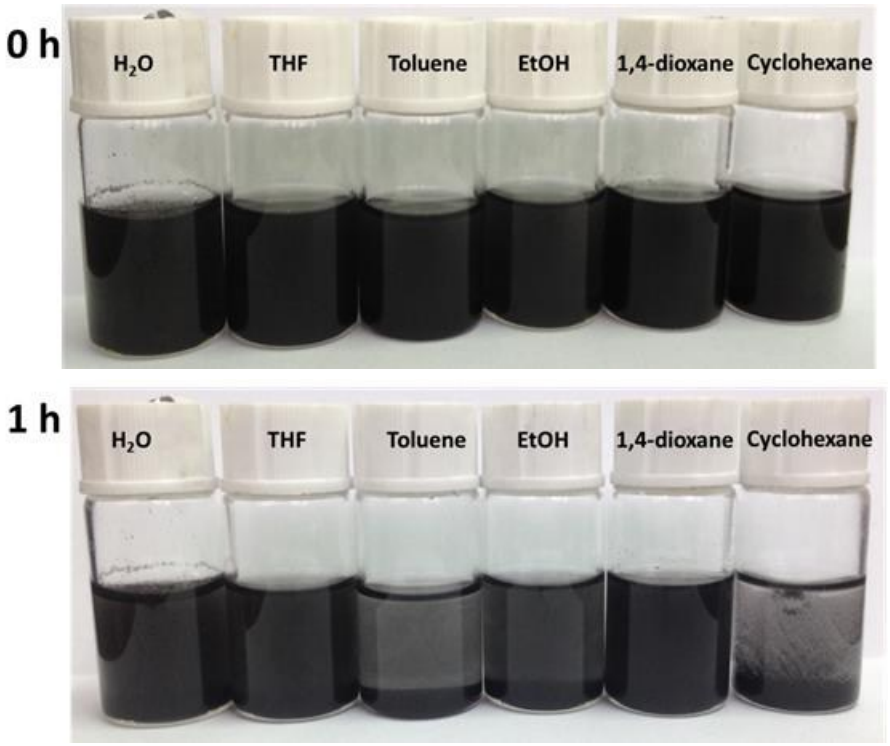

Fig. S9. Dispersibility of CN-CF in various solvents.

The sample was dispersed into various solvents under mild sonication for 5 minutes. CN-CF is dispersible in most polar solvents, such as H_2O, THF, ethanol, 1,4-dioxane and so on.

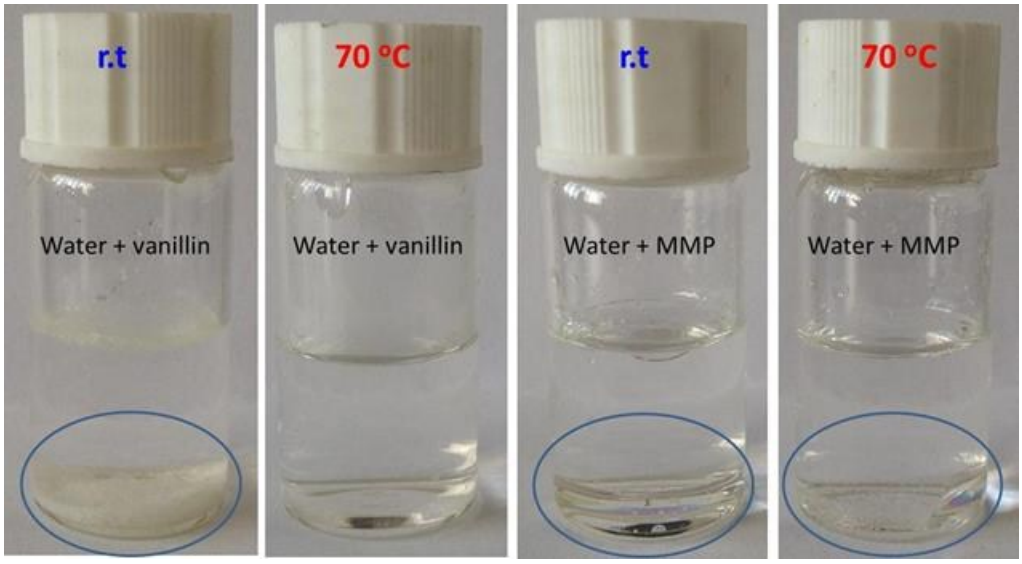

Fig. S10. The solubility tests of vanillin and MMP in water.

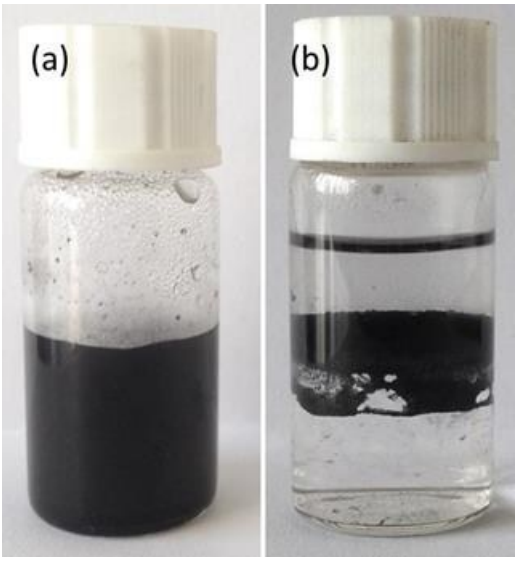

Fig. S11. Digital photos of catalyst and product separation. (a) The reaction mixture, (b) extracted by ethyl acetate. The Pd/CN-CF catalyst disperses in biphasic interface between ethyl acetate and water and can be easily recycled.

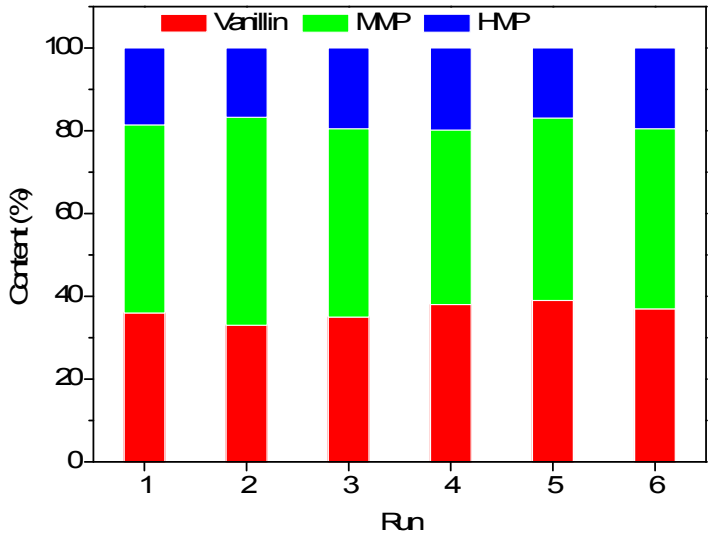

Fig. S12. Re-uses of Pd/CN-CF catalyst for the vanillin hydrogenation.
Reaction conditions: vanillin (200 mg), catalyst (20 mg), H_2O (16 mL), 1 MPa H_2, 70 °C, 0.5 h.

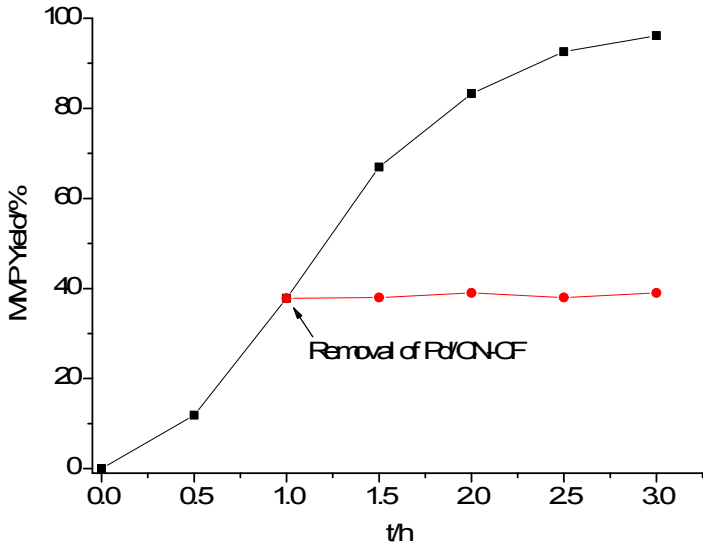

Fig. S13. Effect of removal of Pd/CN-CF on the selective hydrogenation of vanillin.

In order to verify whether the observed catalysis is truly heterogeneous, the reaction is stopped after 60 min by hot filtering Pd/CN-CF from the reaction mixture, and then heats again for 2 h, but no further production of MMP is observed. This result suggests that the observed catalysis is truly heterogeneous in nature.

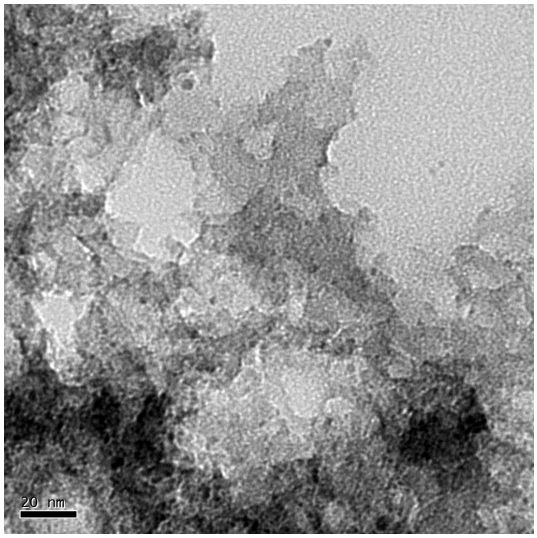

Fig. S14. TEM image of Pd/CN-CF after the 6th run.