## **Supporting Information**

## Hydrogenation of perfluoroolefins catalyzed by palladium nanoparticles anchored on layered carbon nitride

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## **Preparated Catalyst**

g-C<sub>3</sub>N<sub>4</sub> was prepared as follows: 100 mL deionized water and 6 g ammonium chloride was placed to a beaker, followed by the addition of 3 g melamine after complete dissolution. The mixture was ultrasonicated for 30 min, then heated and stirred in a water bath at 80°C until all the water evaporated to obtain a white solid. The white solid was placed in a vacuum dryer at 80 °C for 12 hours. After drying, the white solid was grinded into powder, then transferred to a porcelain boat, and calcined at 550 °C for 4 hours with a heating ramp of 4 °C / min under nitrogen atmosphere. The obtained product was donated DCN-x, where "x" represents the dosage (g) of NH<sub>4</sub>Cl (herein, x = 0.33, 0.50, and 1.0). Dicyandiamide-derived cyano-rich g-C<sub>3</sub>N<sub>4</sub> and melamine-derived cyano-rich g-C<sub>3</sub>N<sub>4</sub> MCN were prepared via the aforementioned route by selecting dicyandiamide as the precursor, respectively. Cyano-free g-C<sub>3</sub>N<sub>4</sub> (BCN) was prepared via the aforementioned route without adding NH<sub>4</sub>Cl. Weigh a certain amount of sodium chloride and dissolve it in water, then add palladium chloride and ultrasonicate for 2 hours. Obtain Na<sub>2</sub>PdCl<sub>4</sub>.

Various Pd-loaded  $g-C_3N_4$  catalysts were prepared. t 1g  $g-C_3N_4$  was weighed and dispersed in 200 mL deionized water by ultrasonication for 30 minutes. 1mL Na<sub>2</sub>PdCl<sub>4</sub> (1.67g/L) was added and stirred at 80°C for 2 hours. Then 1mL NaBH<sub>4</sub> (16g/L) was added and the suspension was stirred t overnight. The separated product was washed thoroughly with deionized water to remove the adsorbed Pd species, followed by drying at 60°C overnight. One sample of Pd-loaded  $g-C_3N_4$ catalyst was obtained, named Pd-DCN. All samples were prepared following this procedure.

Analyzed via a gas chromatography instrument Shimazu (GC2030). The analysis conditions were as follows: DB-624 capillary column, hydrogen flame ionization detector (FID), high-purity nitrogen as carrier gas, split ratio of 50:1, vaporizer pressure of 101.6 KPa, detector temperature of 150 °C, column box starting temperature of 35 °C, retention time of 8 min, then heating to 250 °C at a rate of 30 °C/min, retention time of 5 min, and total running time of 20.17 min.



Figure S1 XRD patterns of the intermediates obtained by hydrothermal treatment of Melamine, MCS, and DCN.





Figure S3 The pore size distribution of DCN, BCN, and MCN.

The mesopores in the samples were not uniformly distributed and were mainly concentrated at 15 nm, DCN samples had significantly more holes than BCN and MCN.



Figure S4 Thermogravimetric decomposition curves of MUS and Melamine

The figure S6 shows the thermogravimetric analysis of melamine and melamine-tricarbonate polymer (MCS) in which it can be seen that melamine starts to decompose at 190-200°C and the weight loss ends at around 320°C with a remaining mass fraction of 0.63% of the sample, whereas MUS starts to decompose at 280-300°C and the weight loss ends at around 330°C with a remaining mass fraction of 2.5%. The reason was that the aqueous solution was weakly acidic after the addition of ammonium chloride in the preparation process, and the acidity became stronger when subjected to heat, and the amino group on the melamine was subsequently replaced by the hydroxyl group to produce cyanuric acid diamide, which was subsequently hydrolyzed to produce cyanuric acid monoamide, and finally cyanuric acid. Carbon nitride prepared by thermal decomposition of melamine-cyanuric acid is more resistant to high temperature. It maintains a better morphology at high temperatures above 330°C, and the melting point of ammonium chloride is 337°C. When the temperature reaches, ammonium chloride begins to melt, and the undecomposed portion can be regarded as a hard stencil, which serves to separate the MUS and the product in space and inhibits the formation of the tris-s-triazine ring. The decomposed Cl- undergoes a deprotonation process with -C-NH<sub>2</sub> at the end of the MUS to form cyano(-C≡N) by deprotonation, and in the process of continuing to raise the temperature to 550°C, the aromatic C-N bond in the structure is opened, which in turn leads to the formation of the N defects in the heptazine in g-C<sub>3</sub>N<sub>4</sub>.





The target product 3,4-2H-perfluoro-2-methyl-pentane ( $C_6F_{12}H_2$ ) exhibits several characteristic absorption peaks in Figure S1. The peak at 2972 cm<sup>-1</sup> corresponds to the C-H stretching vibration absorption peak. The absorption peaks in the band from 1353 to 1112 cm<sup>-1</sup> are attributed to the stretching vibration of C-F bonds in both -CF<sub>3</sub> and -CFH- to varying degrees. The absorption peak appearing at 1042 cm<sup>-1</sup> is likewise caused by the stretching vibration of the C-F bonds under the influence of the side groups. The absorption peak at 991 cm<sup>-1</sup> may originate from the -C-F stretching vibration caused by the stretching vibration of the C-F bond under the influence of the side group. The absorption peaks at 687 cm<sup>-1</sup>, 664 cm<sup>-1</sup>, and 528 cm<sup>-1</sup> are mainly attributed to the bending vibration of C-F bonds in the -CF<sub>3</sub> group. Unaccounted peaks can be attributed to C-F structures.



Figure S6 <sup>1</sup>H NMR spectrum of C<sub>6</sub>F<sub>12</sub>H<sub>2</sub> (700MHz in CDCl<sub>3</sub>)

3,4-Dihydroperfluoro-2-methylpentane ( $C_6F_{12}H_2$ ): <sup>1</sup>H NMR (700MHz, CDCl3),  $\delta$ 5.26 (1),  $\delta$ 5.02 (2) ppm.



Figure S7 GC-MS

Five peaks at retention times of 4.065, 5.649, 5.843, 6.694, and 7.198 can be seen in the figure, and the molecular weights were inferred by GC-MS.

The peak at retention times of 4.065 corresponds to perfluoro-4-methyl-2-pentene (C<sub>6</sub>F<sub>12</sub>) D1-

Е 命中#:1 输入:162735 谱库:NIST20-1.lib SI:93 分子式:C6F12 CAS:0-00-0 摩尔质量:300 保留指数:0 组分名称:1,1,1,2,3,4,5,5,5-Nonafluoro-4-(trifluoromethyl)pent-2-ene 100-80-60-40-20-124 162 300 330 390 30 60 90 120150180 210 240 270360 420 450 480

The peak at retention times of 4.192 corresponds to perfluoro-4-methyl-2-pentene ( $C_6F_{12}$ ) D1-

The peak at retention times of 5.649, 5.843 the substance is the major by-products 2-H-perfluoro-4-methyl-2-pentene ( $C_6F_{11}H$ ) and 3-H-perfluoro-4-methyl-2-pentene ( $C_6F_{11}H$ )

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The peak retention times of 6.694 is the target product 3,4-2H-perfluoro-2-methyl-pentane  $(C_6F_{12}H_2)$ 



Figure S8 diagram of the reactor system



Figure S9 XRD patterns of small palladium loading catalyst



Figure S10 Catalyst evaluation results at different space velocities and particle sizes

Table S1 The result of ICP-MS

Samples	Theoretical load capacity	Icp test results
Commercial catalysts 5wt%	5wt%	3.9329wt%
Commercial catalysts 3wt%	3wt%	2.0280wt%
Commercial catalysts 1wt%	1wt%	0. 7252wt%
Pd-C 0.1wt%	0.1wt%	0.0810wt%
Pd-BCN 0.1wt%	0.1wt%	0.0865wt%
Pd-MCN 0.1wt%	0.1wt%	0.0988wt%
Pd-DCN 0.1wt%	0.1wt%	0.0982wt%
Pd-DCN-0.5 0.1wt%	0.1wt%	0.0923wt%
Pd-DCN-0.33 0.1wt%	0.1wt%	0.0955wt%