High dispersed Pd nanoparticles anchored on carbon nitride for hydrogen production of formic acid

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Experimental

Synthesis of CN-UW

20 g urea was dissolved in 20 mL of deionized water. The solution was then transferred to a 100 mL capped ceramic crucible and calcined at 823 K for 4 hours. After cooling the crucible to ambient temperature, a light-yellow product of ultrathin CN nanosheets was formed, designated as $CN-U_1W_1$. Finally, $CN-U_1W_x$ were produced by varying the mass ratio of urea in solution (m_{urea}: m_{water} =1:2, 1:3, 1:5, and 1:7), and the corresponding products were labeled as $CN-U_1W_3$, $CN-U_1W_5$, and $CN-U_1W_7$, respectively. The same procedure was used to make CN-U without the need of water.

Synthesis of Pd/CN-UW

Ultrasonic treatment was used to disperse 0.27 g of $CN-U_1W_1$ in 60 mL of H_2O. Next, 0.065g of the metal precursor $Pd(NO_3)_2$ was added to the suspension, which was then magnetically stirred for three hours. The mixture was injected with 10 mL (0.3M) of $NaBH_4$ solution and vigorously stirred for four hours prior to centrifugation and washing with deionized water three times. The catalysts were then dried for 24 hours at 353 K. A series of Pd/CN- U_1W_x catalysts were also synthesized using the same method, and the resulting products were labeled $Pd/CN-U_1W_1$, $Pd/CN-U_1W_3$, $Pd/CN-U_1W_5$, $Pd/CN-U_1W_7$ and Pd/CN-U, respectively.

Characterizations

Using a Bruker D8 Advance diffractometer equipped with Cu Kα radiation at 40 kV and 50 mA over a scanning range of 3-80° (2θ), X-ray diffraction (XRD) patterns of the test samples were acquired. Using a Tecnai G2 TF30 transmission electron microscope (TEM) with an acceleration voltage of 300 kV, the morphologies and particle sizes of the samples were examined. The materials were analyzed by X-ray photoelectron spectroscopy (XPS) using a VGA ESCALAB 250 spectrometer (Thermo Electron, UK) equipped with a non-monochromatic Al Kα X-ray source (1486 eV). As a reference for calibrating the binding energies, the carbonaceous C 1s line (284.8 eV) was used. On the Agilent 5800, the inductively coupled plasma-optical emission spectrometer (ICP-

OES) was measured.

Catalytic activity tests for FA dehydrogenation (FAD)

For the catalytic experiment, 50 mg of catalyst was dissolved in deionized water in a round-bottom flask. The reaction flask was attached to the water-filled gas burette in order to measure the amount of gas produced. FA/SF (sodium formate) reaction liquid (n_{FA}/n_{SF} = 1:8; FA = 2 mmol) was fed into the flask with magnetic stirring at 348 K in an ambient environment and gas production commenced.
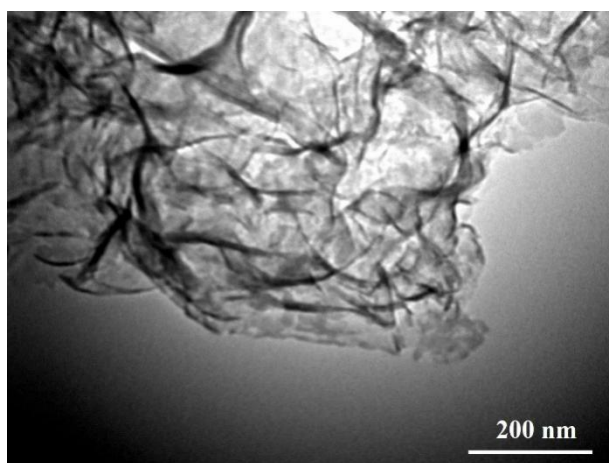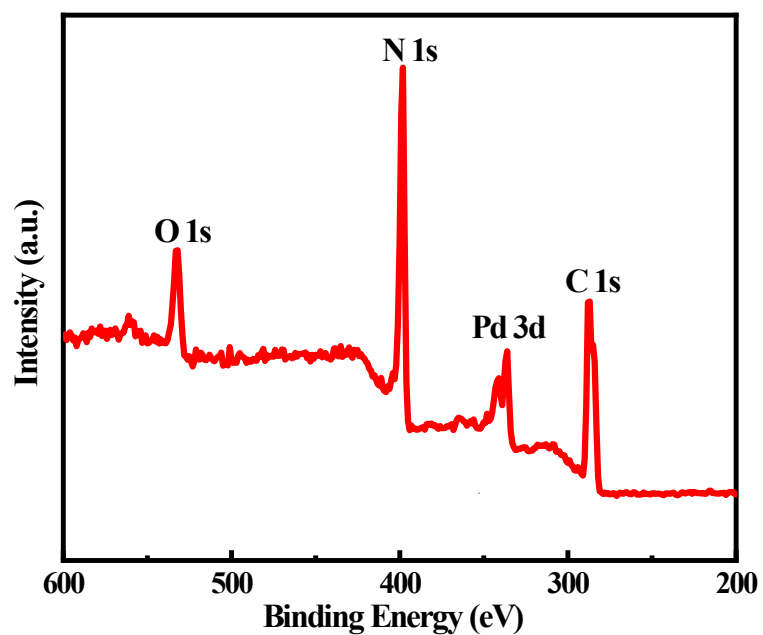

Fig. S1 TEM image of CN-U$_1$W$_5$.

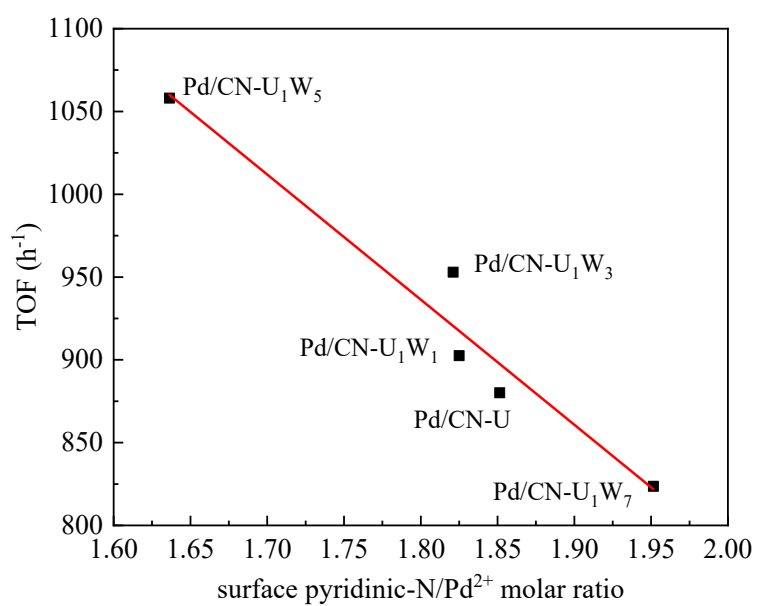Fig. S2 XPS survey spectra of Pd/CN-U$_1$W$_5$.

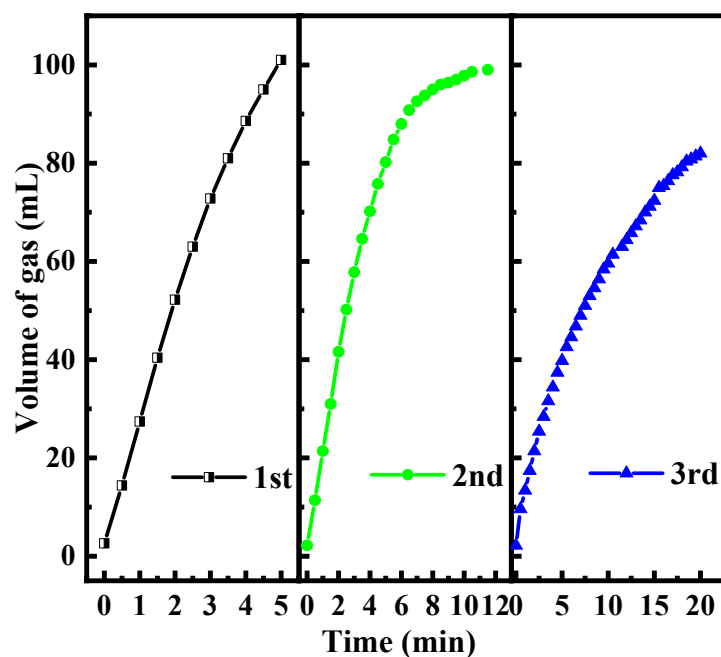Fig. S3 The relationship of the TOF and surface pyridinic N/Pd molar ratio

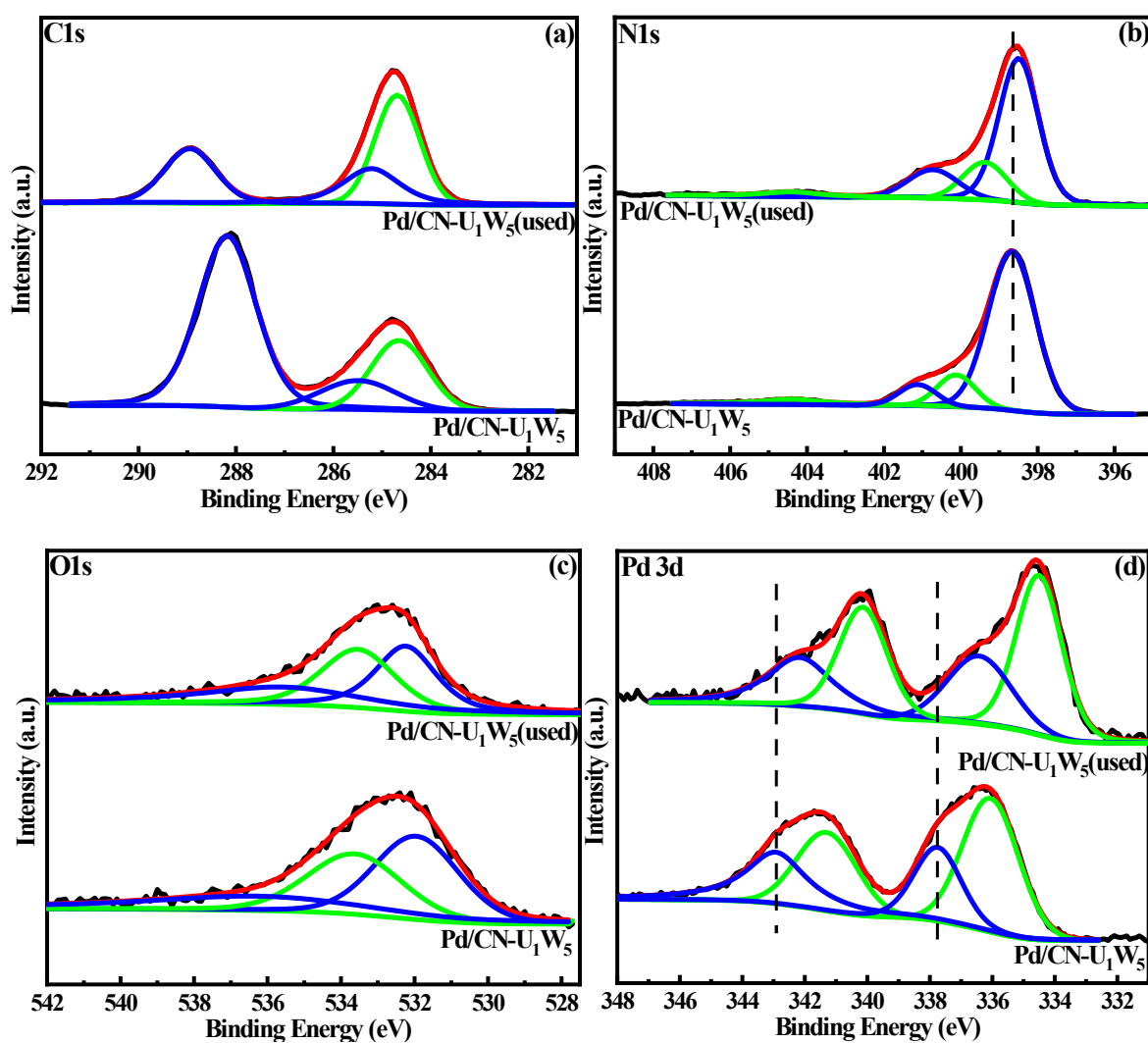Fig. S4 The stability of Pd/CN-U$_1$W$_5$ catalyst at 348 K.

Fig. S5 XPS spectra of (a) N and (b) Pd (c) C 1s and (d) O 1s in Pd/CN-U$_1$W$_5$ after cycling.

Table S1 Comparison of catalytic performance of different catalysts for hydrogen generation from

FA.

Catalysts	T/K	Additive	TOF/h^{-1}	Reference	E_a(kJ/mol)
Ag$_9$Pd$_{91}$/g-C$_3$N$_4$	323	HCOONa	480	[S1]	25.8
PdAg/C–FA	298	HCOONa	90	[S2]	-
C-Pd$_1$Ag$_1$ BNSs	323	HCOONa	378	[S3]	-
Ag$_{18}$Pd$_{82}$@ZIF-8	353	HCOONa	580	[S4]	51.4
AgPd@MIL-100(Fe)	298	-	58	[S5]	-
Pd/mpg-C$_3$N$_4$	298	-	144	[S6]	29.1
Pd/CN-U$_1$W$_5$	348	HCOONa	1058	this work	29.7

Table S2 The content of Pd and N-containing species of Pd/CN-U$_1$W$_5$ catalyst before and after cycling.

Sample	Proportion of peak area					
	Pd^{2+}	Pd^0	pyridinic N	pyrrolic N	graphitic N	π excitation
Pd/CN-U$_1$W$_5$	0.462	0.538	0.756	0.119	0.077	0.047
Pd/CN-U$_1$W$_5$(3 cycles)	0.405	0.595	0.635	0.173	0.149	0.043

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