Supplementary information

Palladium single-atom catalysts synthesized by gas-assisted redispersion strategy for efficient benzaldehyde hydrogenation

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Experimental

2.1 Chemicals

Pd precursor ($Pd(NO_3)_2$ solution), benzaldehyde, benzyl alcohol, n-octane was purchased from Alfa Aesar. Isopropanol, ethanol, tetrahydrofuran, nitric acid, sodium carbonate was purchased from Sinopharm Chemical ReagentCo., Ltd. Dodecane，absolute ethanol，methanol was purchased from Aladdin.

2.2 Synthesis of catalysts

Synthesis of Pd_{NP}/G： Pd_{NP}/G was synthesized by deposition precipitation. First, weigh 200 mg of graphene in a flask and add 30 mL of deionized water and disperse it by ultrasonic for half an hour to make it well dispersed, adjust the pH value to 10 with 0.25 M of Na_2CO_3 solution. Then measure 50 μL of $Pd(NO_3)_2$ solution (8 mg/mL) into a 5 mL centrifuge tube, dilute with 4 mL of deionized water, sonicate for 2-3 min and add Na_2CO_3 solution to adjust the pH value to neutral. $Pd(NO_3)_2$ solution was slowly added dropwise to the graphene dispersion at room temperature, then heated to 100 °C and reacted for 1 h. After it cooled to room temperature, it was filtered, washed with deionized water to neutral, and dried at 60 °C for 24 h. The sample was reduced by H_2 at 200 °C for 2 h.

Synthesis of Pd_{SA}/G: (Pd_{SA}/G) were prepared by the nitric acid vapor method under mild conditions. Weigh Pd_{NP}/G (80 mg) flat on the bottom of the quartz evaporation cup, measure 5.5 mL of HNO_3 into the Teflon liner, and put the quartz evaporation cup into the Teflon liner, and then put the liner into the hydrothermal reactor. Then react at 80 °C for 3 h, cool to room temperature and take out. dry at 60 °C for 12 h, and reduce H_2 at 200 °C for 1 h.

Synthesis of Pd/ZnO and Pd/CeO₂: Pd/ZnO and Pd/CeO_2 is prepared in the same way as Pd_{NP}/G. except that it is reacted at 90°C for 2 h.

Synthesis of ND@G: The ND@G hybrid support with unique structure was obtained by the calcination of pristine nanodiamonds, as illustrated in our previous studies.the ND@G nanocarbon had core-shell structure with the nanodiamond core covered by few layers defect-rich graphene shell. Nanodiamond (ND) powders (Beijing Grish Hitech Co., China) were annealed at 1100 °C for 4 h in Ar flow (100 mL min^{-1}) and then purified with hydrochloric acid.

Synthesis of Pd$_{NP}$/ND@G: Pd$_{NP}$/ND@G is prepared in the same way as Pd$_{NP}$/G.

Synthesis of Pd$_{SA}$/ND@G: Pd$_{SA}$/ND@G is prepared in the same way as Pd$_{NP}$/G.

2.3 Characterization

Prior to characterization and catalytic testing, all catalysts were reduced by H$_2$ at 200 °C. The reduced catalyst samples were characterized by transmission electron microscopy (TEM) and the high-resolution TEM (HRTEM), TEM and HRTEM images were collected on a FEI Tecnai G2 F20 microscope. Aberration-corrected high-resolution transmission electron microscopy images (AC-HADDF-STEM) were obtained on a JEOL JEM ARM 200CF aberration-corrected cold field-emission scanning transmission electron microscope operating at 200 kV. X-ray absorption spectra (XAS) at the Pd K-edge were obtained at the BL14W1 station in Shanghai Synchrotron Radiation Facility, China. The electron storage ring was operated at 3.5 GeV with a maximum current of 250 mA. Diffuse reflectance infrared Fourier transform (DRIFT) spectra were collected on Thermo Scientific Nicolet IZ10 Fourier transform infrared spectrometer equipped. For example, the catalyst diluted with KBr (mass ratio is about 1:45) was placed in the in-situ pool and pre-treated in hydrogen gas (10% H$_2$/He) at 200 °C for 1 h. Cooling to 303 K under He flow, adsorbent (10% CO/He) was introduced to the chamber until adsorption saturation. DRIFTS were continuously recorded with 64 scans at 4 cm^{-1} resolution during the He flow purging.

2.4 Catalytic evaluation

In the reaction of selective hydrogenation of benzaldehyde, 50 µL of benzaldehyde and 20 mg of catalyst were added to a Schlenk glass vessel tube containing 10 mL of ethanol and 50 µL of n-octane mixed solvent. The reaction was performed at 60 °C with a stirring speed of 800 rpm. The product was analysed by a gas chromatograph (Agilent 7890A) with a HP-PLOT AL/S (HP-plot 19091J-413, Agilent, 30 m× 320 µm× 0.25 µm) capillary column with N$_2$ as the carrier gas and n-octane as internal standards.

Benzaldehyde conversion and selectivity to benzyl alcohol were calculated as follows:

$$\text{Conversion} = \frac{n_{initial\ benzaldehyde} - n_{residual\ benzaldehyde}}{n_{initial\ benzonitrile}} \times 100\%$$

$$\text{Selectivity}_{benzyl\ alcohol} = \frac{n_{produced\ benzyl\ alcohol}}{n_{converted\ benzaldehyde}} \times 100\%$$

Reaction mass rate of target product was calculated by the formula as follows:

$$\text{Reaction rate} = \frac{1}{m} \cdot \frac{dn_p}{dt} [\text{mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}]$$

n_p is Amount of increase in target product over the dt time (mol), m is the catalyst quality(g), t is reaction time(h),
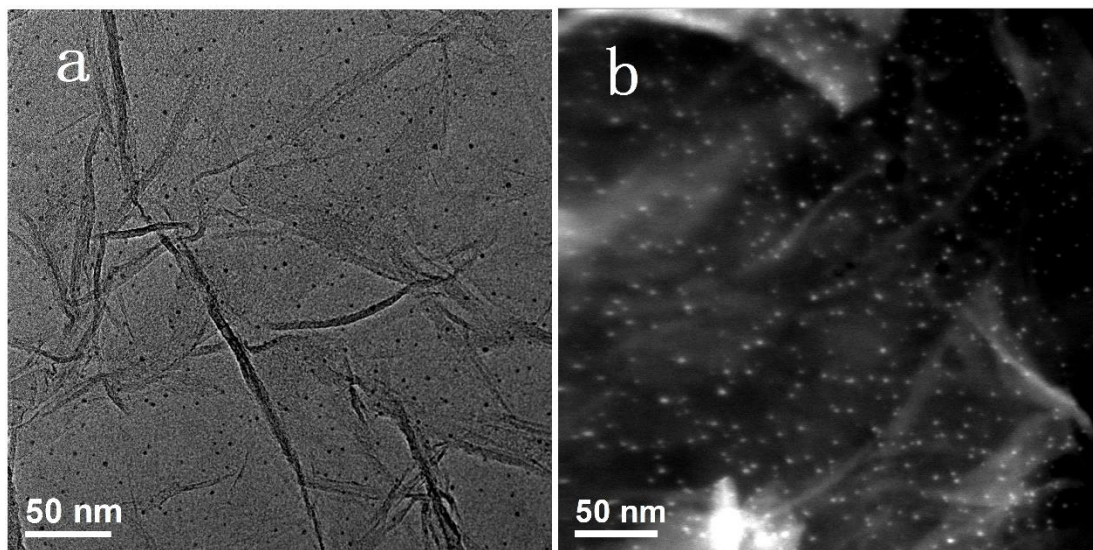
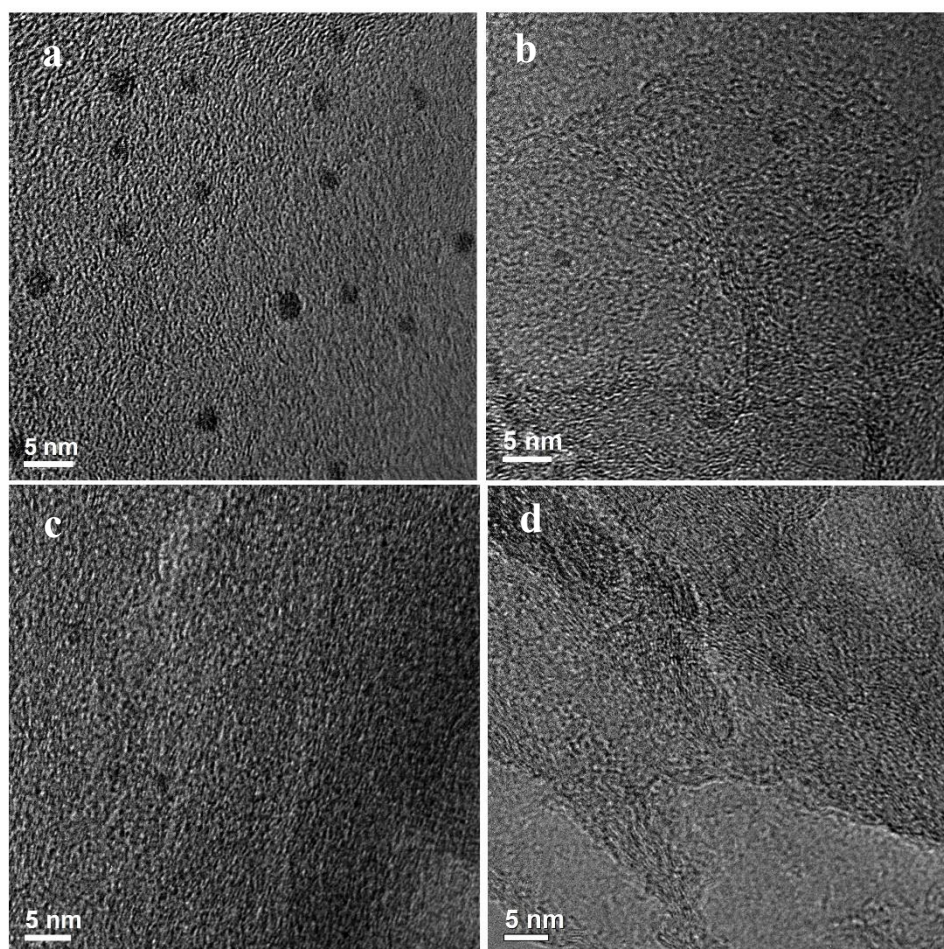**Figure S1.** HRTEM (a) and HAADF-STEM (b) images of as-prepared Pd-NPs supported on Graphene (0.2 wt.%Pd$_{NP}$/G).

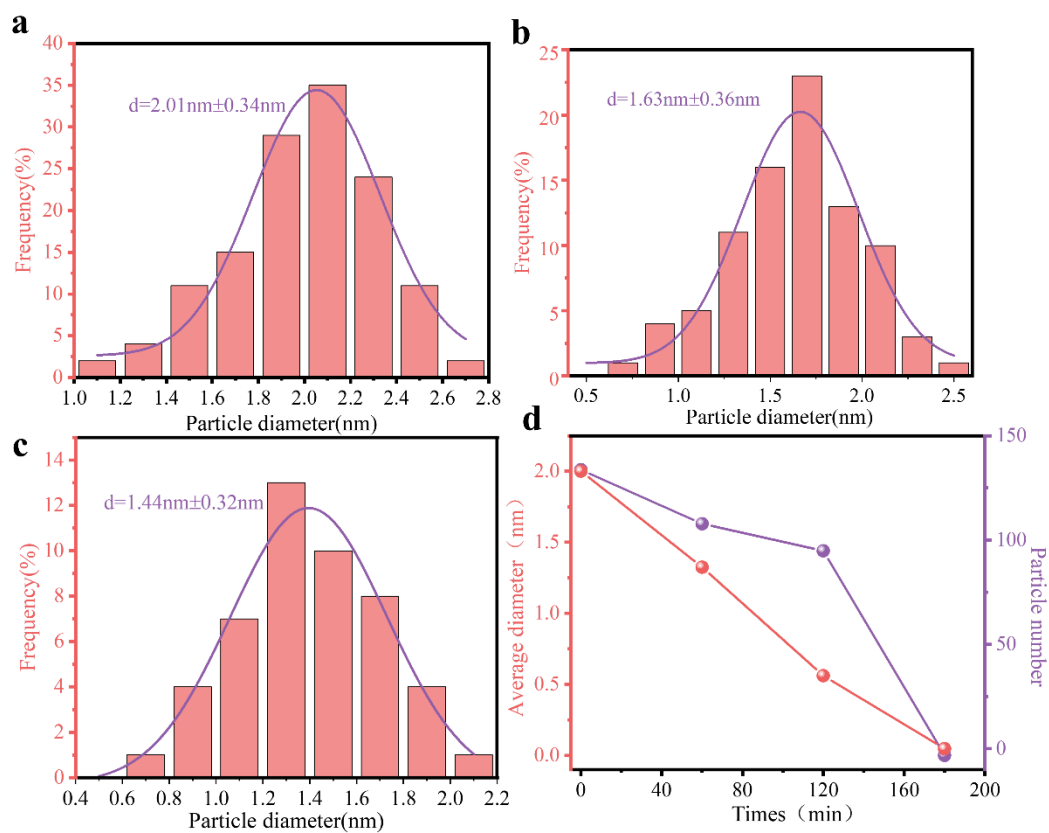**Figure S2.** HRTEM images of Pd_{NP}/G (a), Pd_{NP+SA}/G (b), Pd_{C+SA}/G (c) and Pd_{SA}/G (d).

Figure S3. Particle size distribution of Pd_{NP}/G (a), Pd_{NP+SA}/G (b), Pd_{C+SA}/G (c) and Average diameter and number of particles versus nitric acid steam treatment time (d).
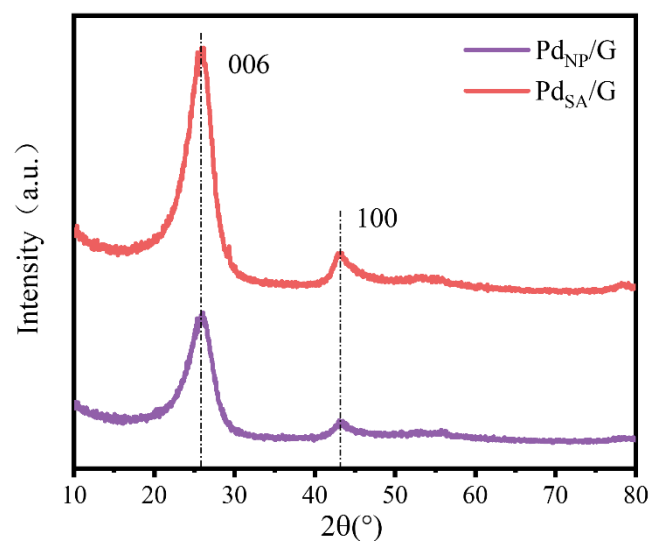
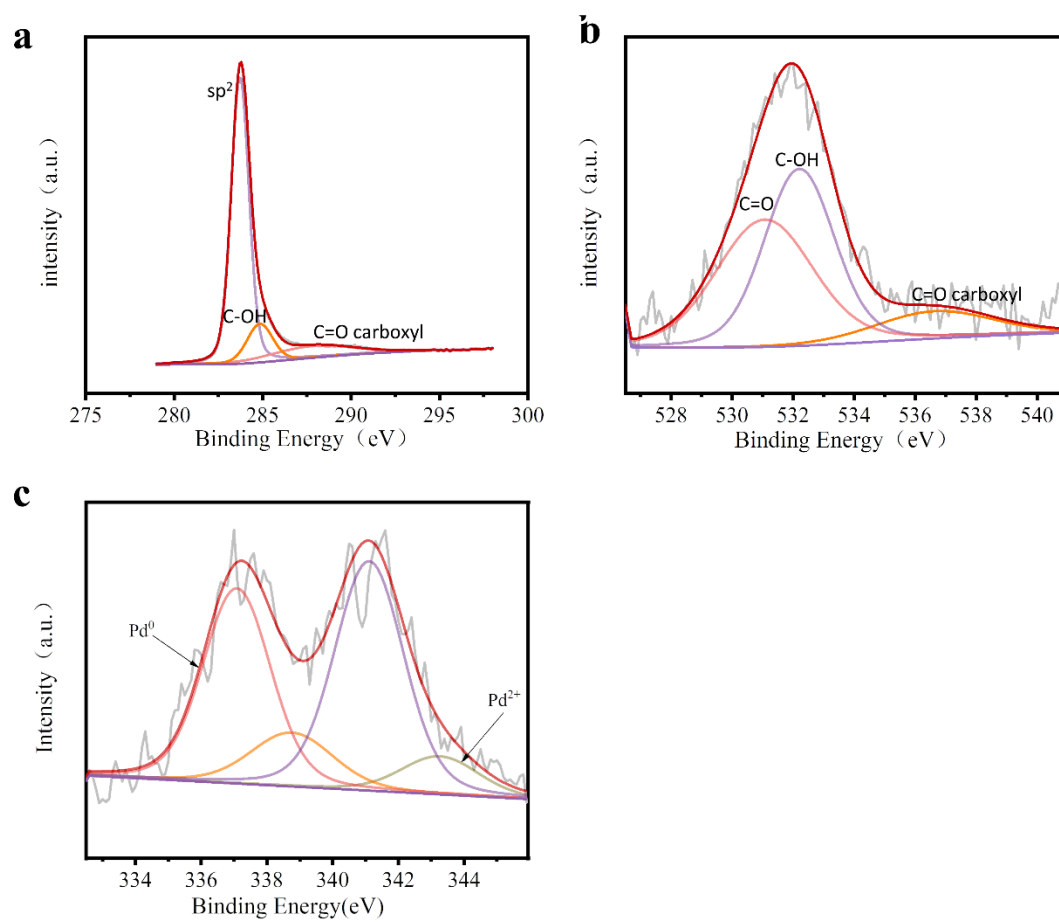**Figure S4.** XRD spectra of Pd_{SA}/G and Pd_{NP}/G

Figure S5. XPS spectrums for the (a) C 1s, (b) O 1s, (c) Pd 3d regions of Pd$_{SA}$/G.
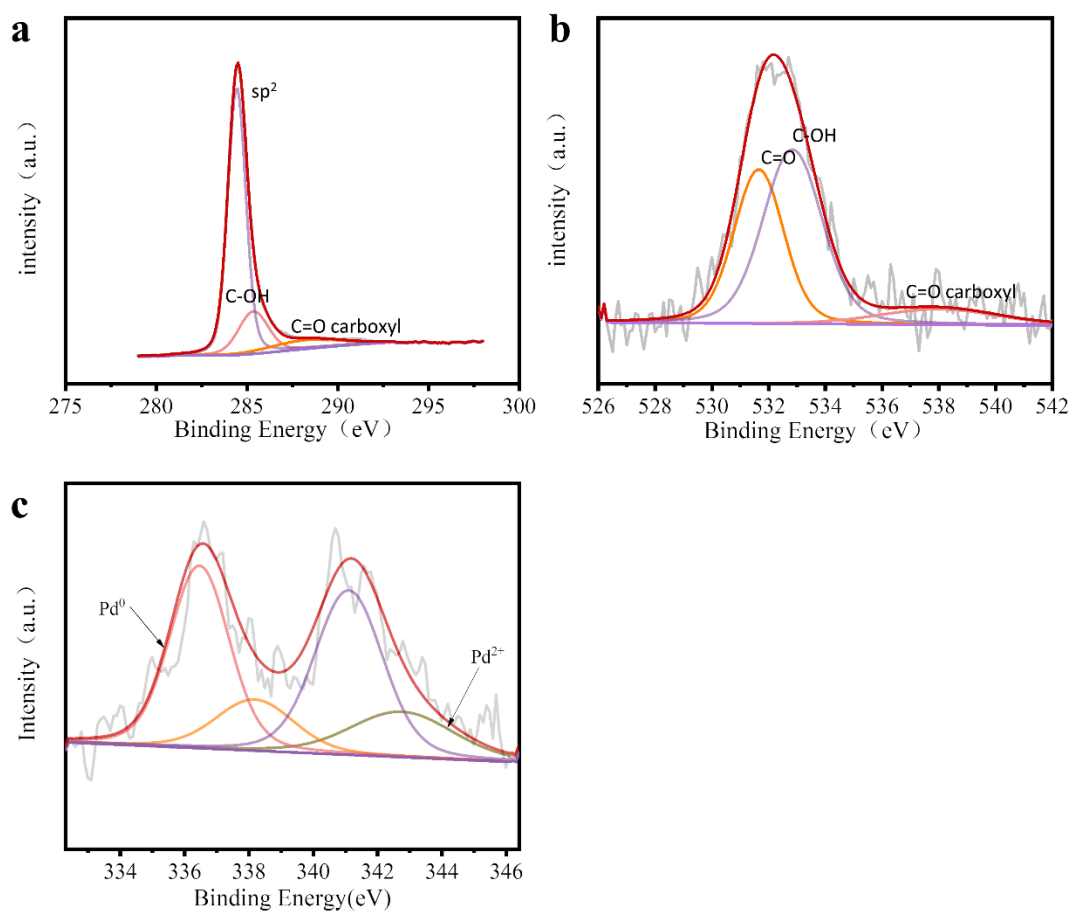
Figure S6. XPS spectrums for the (a) C 1s, (b) O 1s, (c) Pd 3d regions of Pd_{NP}/G.

Table S1. Pd 3d XPS data of Pd_{NP}/G and Pd_{SA}/G.

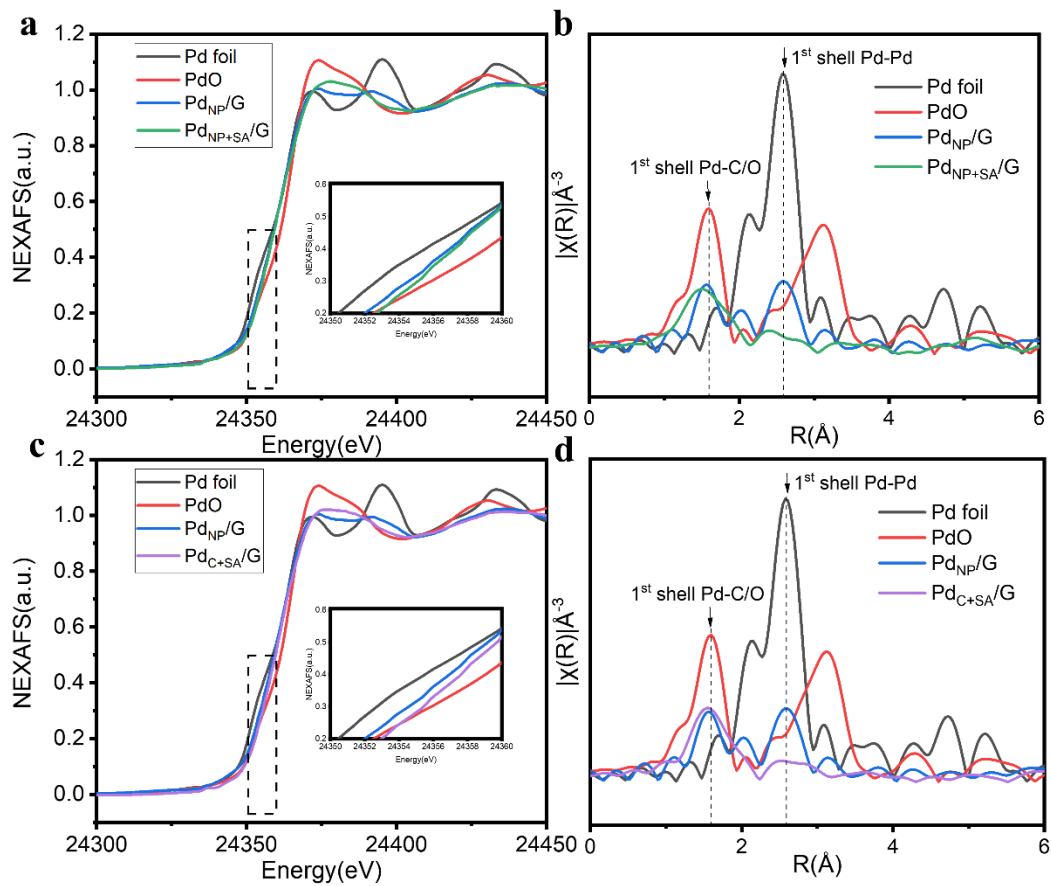| Sample	Pd^0(eV)		Pd^{2+}(eV)	
PdNP/G	336.4	341.0	338.2	342.8
PdSA/G	337.1	341.2	338.6	343.2

Figure S7. Pd K-edge XANES spectra (a) and FT k^3-weighted Pd K-edge EXAFS spectra (b) of Pd foil, PdO, and Pd_{NP}/G, Pd_{NP+SA}/G. Pd K-edge XANES spectra (c) and FT k^3-weighted Pd K-edge EXAFS spectra (d) of Pd foil, PdO, and Pd_{NP}/G, Pd_{C+SA}/G.

Table S2. EXAFS parameters of different samples

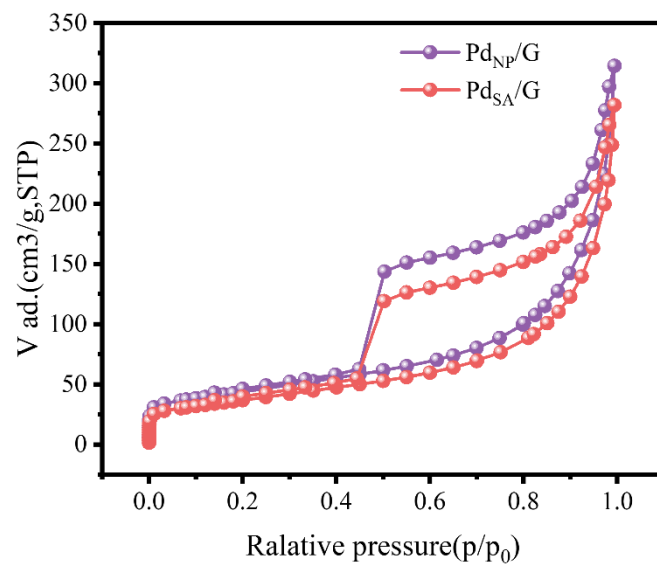| Sample	Shell	Bond length (Å)	Coordination Number	σ^2 (Å2)	E0 shift (eV)	R-factor (*10-3)
Pd foil	Pd-Pd	2.74	12	0.005	8.5	2.5
PdO	Pd-O	2.01	4	0.001	2.0	8.9
Pd_{NP}/G	Pd-O/C	1.99	1.5	0.006	7.9	19.9
	Pd-Pd	2.73	3.7	0.006		
Pd_{NP+SA}/G	Pd-O/C	1.99	2.1	0.009	10.1	6.5
	Pd-Pd	2.72	2.3	0.004		
Pd_{C+SA}/G	Pd-O/C	2.01	2.5	0.004	8.6	6.0
	Pd-Pd	2.74	1.5	0.005		
Pd_{SA}/G	Pd-O/C	2.01	3.1	0.003	4.3	3.1
	Pd-Pd	2.74	0.7	0.008		

Figure S8. N_2 adsorption/desorption isotherms of Pd_{NP}/G and Pd_{SA}/G.
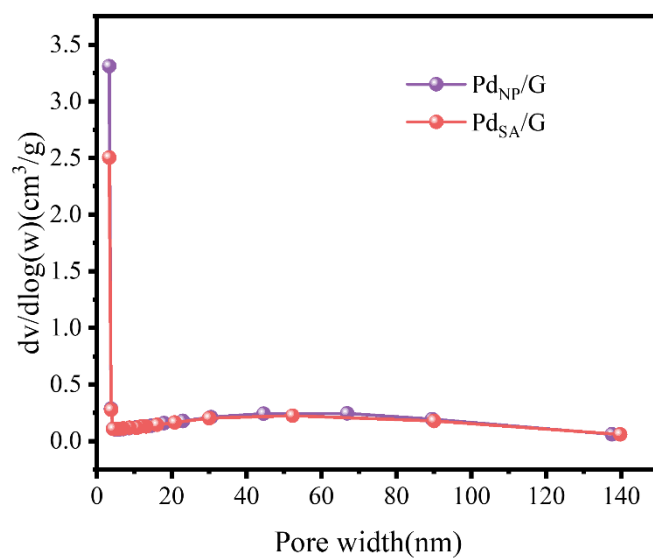
Figure S9. Pore size distribution of Pd_{NP}/G and Pd_{SA}/G

Table S3. Physical properties of Pd_{NP}/G and Pd_{SA}/G.

Sample	$S_{BET}(m^2g^{-1})$	$V_{pore}(cm^{-3}g^{-1})$	Pore size(nm)
Pd_{NP}/G	154.32	0.49	11.2
Pd_{SA}/G	130.93	0.44	11.7
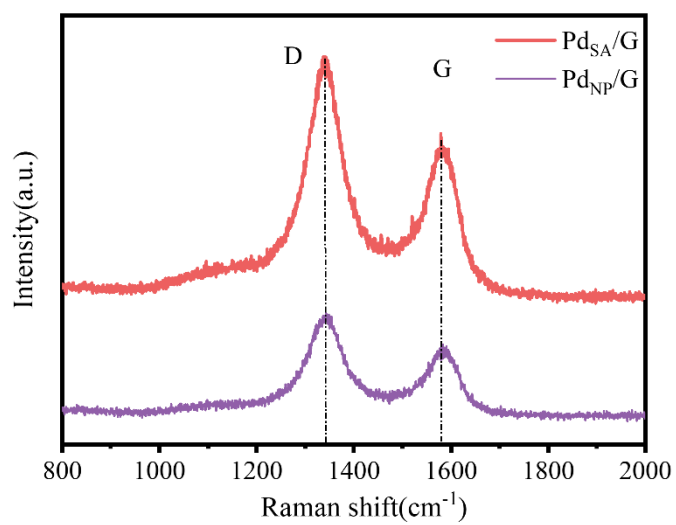
Figure S10. Raman spectra of Pd_{NP}/G and Pd_{SA}/G.

Table S4. I_D/I_G values for Pd_{NP}/G and Pd_{SA}/G

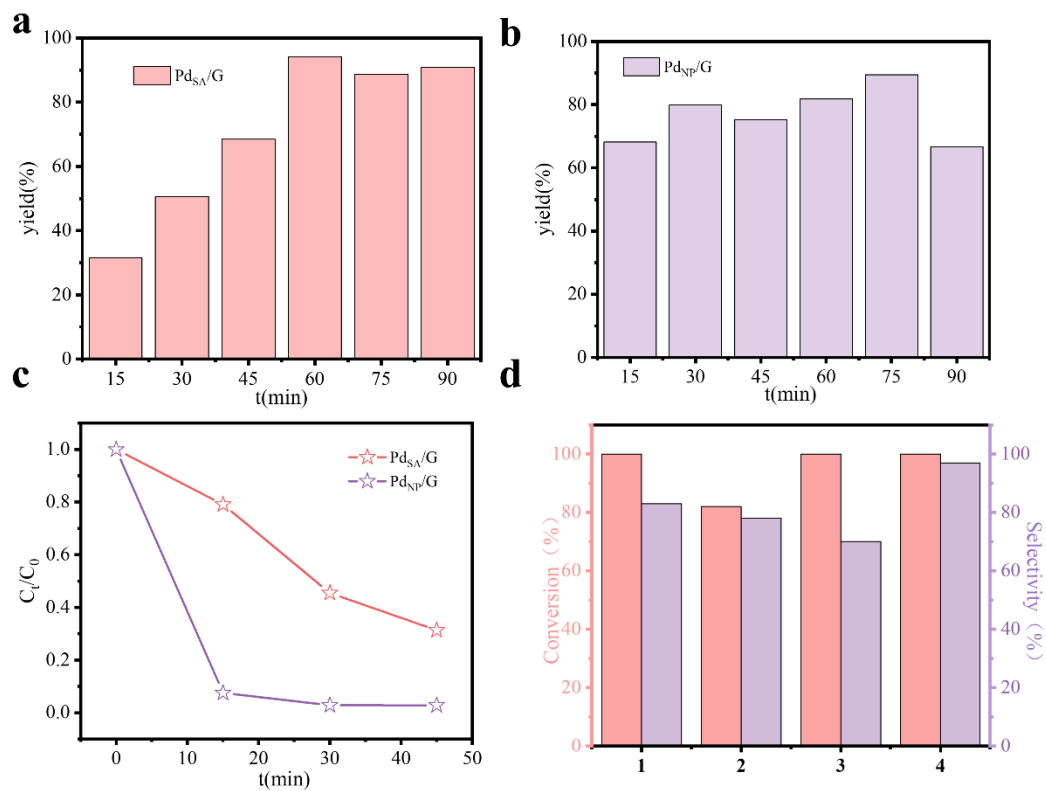| Sample	Pd_{NP}/G	Pd_{SA}/G
Value of I_D/I_G	1.335	1.473

Figure S11. Catalytic performance of samples. Yield of the (a) Pd$_{SA}$/G, (b) Pd$_{NP}$/G,

Hydrodehalogenation kinetics of benzaldehyde by Pd/G(c), Catalytic performance of 1:

Pd$_{NP}$/G, 2: Pd$_{NP+SA}$/G, 3: Pd$_{C+SA}$/G and 4: Pd$_{SA}$/G.

Table S5. Optimization of solvent

Serial number	solvent	Conv. (%)	Sel. (%)
1	ethanol	100	88.56
2	methanol	99.31	87.1
3	Isopropanol	54.83	94.55
4	n-hexane	1.42	89.5
5	Dodecane	17.72	59.01
6	THF	3.8	84.3

Table S6. ICP-OES of different nanocarbon catalysts

Sample	Theoretical Pd loading/wt.%	Actual Pd loading/wt.%
Pd$_{NP}$/G	0.2	0.19
Pd$_{SA}$/G	-	0.09

Table S7. Catalytic performance over various catalysts.

Catalysts	Metal load(wt.%)	T (°C)	P（MPa)	TOF	Conv. (%)	Sel. (%)	Ref.
Pd_{SA}/G	0.09	60	0.7	2959	99	97	This work
Pd_{NP}/G	0.19	60	0.7	2762	100	83	This work
Pd_1/TiO_2	1.5	25	-	1002	100	-	1
Pd_{SA+C}/TiO_2	4.8	25	0.1	16288	100	98	2
$Pd/@-ZrO_2/AC$	1	40	0.7	-	100	98.1	3
Pd/C	5	25	0.1	1062	100	-	4
Rh/C	5	25	0.1	520	100	-	4
Ni/Al_2O_3-SiC	16	90	2	-	99.3	>90	5
Ni/Al_2O_3	16	90	2	-	97.5	>90	5
Pd/GNP	0.5	50	0.2	-	70	94	6
Pd-Ru/NGC	1.63	40	0.5	-	100	89.6	7
Pd/NGC	1.5	40	0.5	-	99.3	41.9	7

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