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ELECTRONIC SUPPORTING INFORMATION (ESI)

Pd supported on g-C_3N_4 nanosheets: Mott-Schottky heterojunction catalyst for transfer hydrogenation of nitroarenes using formic acid as hydrogen source

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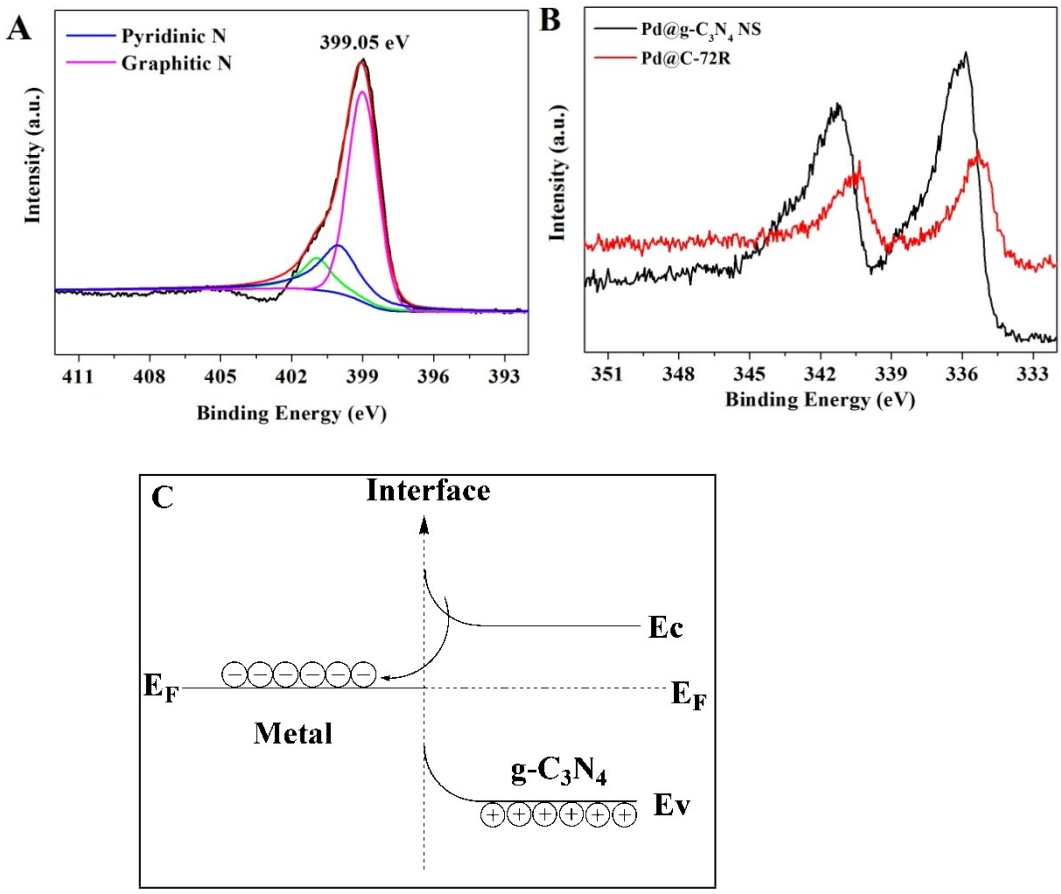

Fig. S1 Mott-Schottky effect on the catalytic performance of the Pd@g-C_3N_4 NS catalysts. (A) N 1s of Pd@g-C_3N_4 NS, (B) Pd XPS spectra of Pd@g-C_3N_4 NS and Pd@C-72R and (C) Schematic illustration of Mott-Schottky-type contact of Pd@g-C_3N_4 NS.

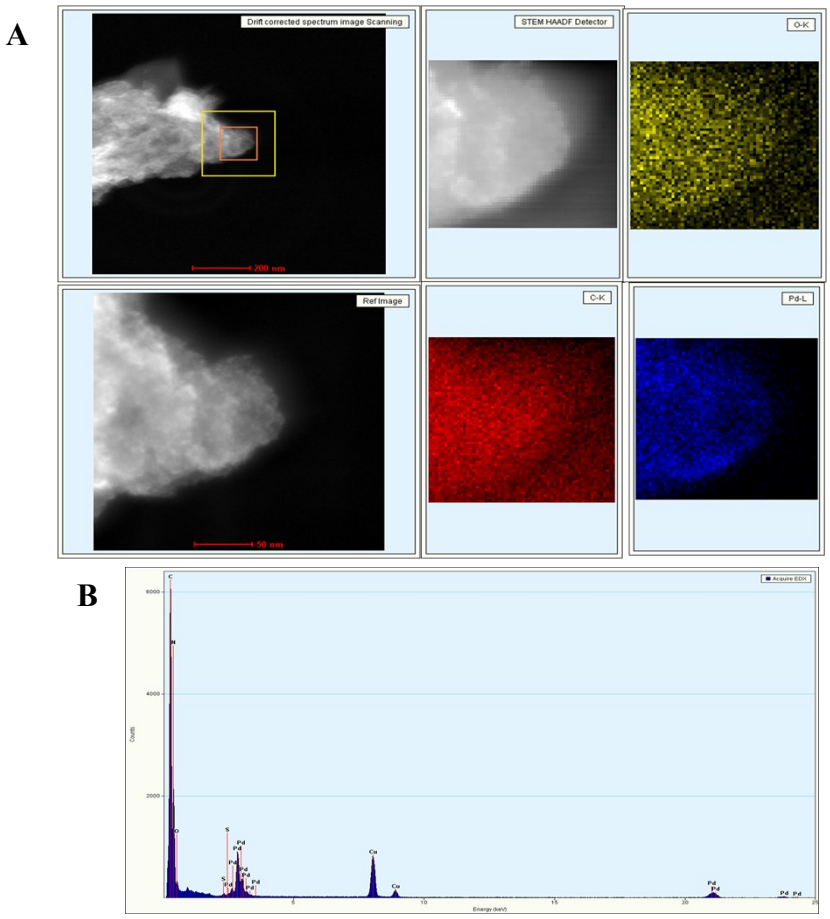

Fig. S2 The EDX mapping of the synthesized Pd@g-C_3N_4 NS (A) and EDX image of Pd@g-C_3N_4 NS (B).

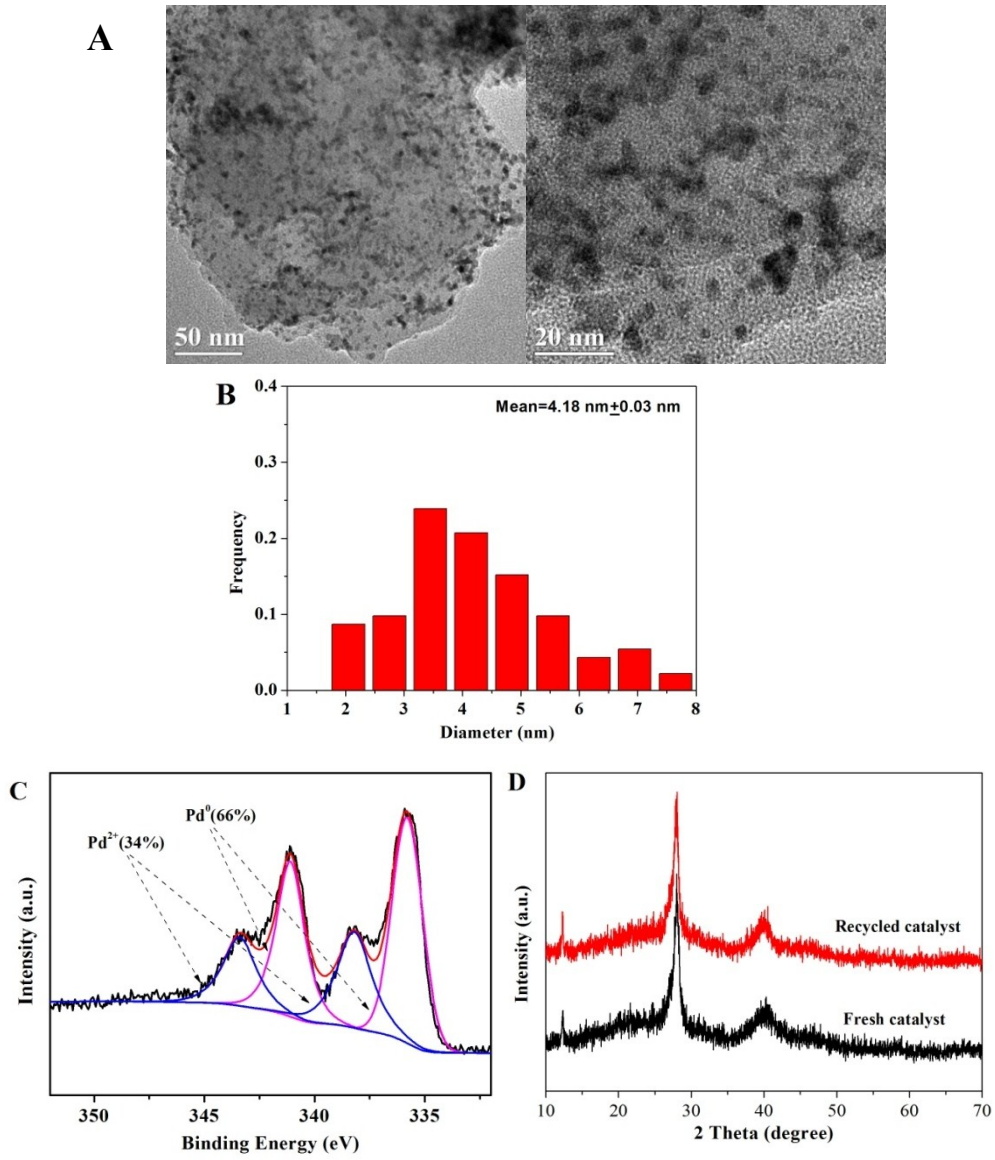

Fig. S3 TEM images (A), Pd particle-size distribution (B), Pd XPS spectra (C), XRD pattern (D) of recycled catalyst**.**

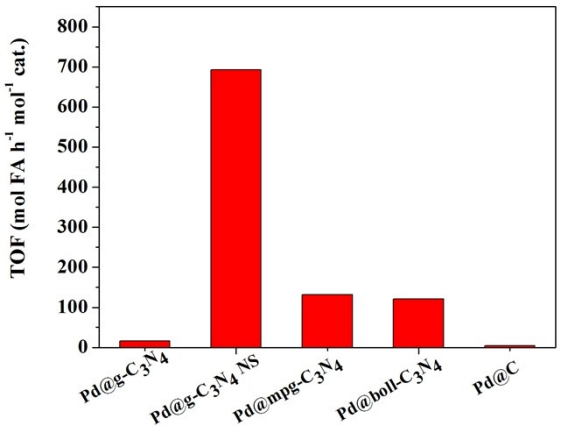

Fig. S4 TOF values of FA for transfer hydrogenation of nitrobenzene over Pd@g-C_3N_4, Pd@g-C_3N_4 NS, Pd@mpg-C_3N_4, Pd@boll-C_3N_4 and Pd@C(commercially available). Reaction condition: water (5 mL), nitrobenzene (1 mmol), FA (5 mmol), catalyst (2 mg), 25 °C.

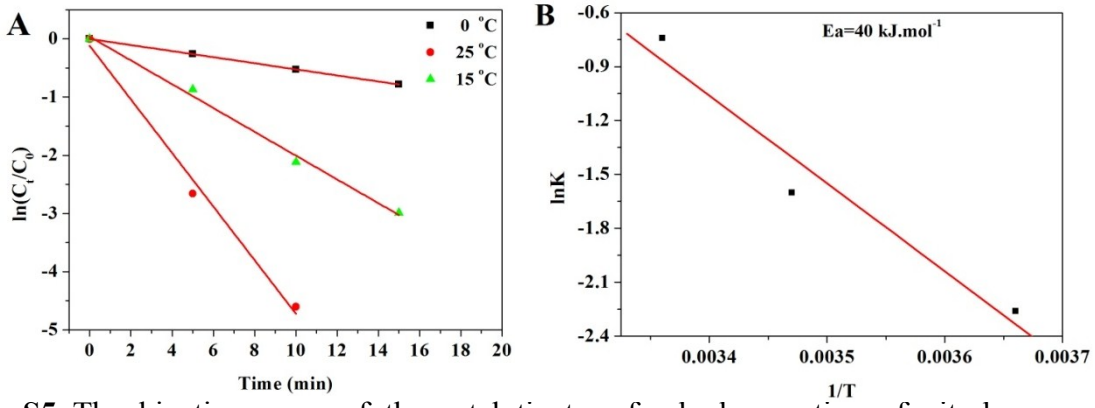

Fig. S5 The kinetic curves of the catalytic transfer hydrogenation of nitrobenzene at different reaction temperatures. Reaction conditions: nitrobenzene (1 mmol), Pd@C_3N_4 NS (0.155 mol%), water (5 mL), FA (5 mmol).

Table S1 Reduction of nitrobenzene to aniline with different amount of formic acid over Pd@g-C_3N_4 NS catalyst.[a]

Entry	FA (mmol)	Time (min)	Conversion (%)	Selectivity (%)
1	0	12 h	0	0
2	1	30	62	95
3	3	30	84	98
4	5	10	100	>99
5	7	8	100	>99

[a] Reaction conditions: nitrobenzene (1 mmol), Pd@g-C_3N_4 NS (0.75 mol%), water (5 mL), 25 °C. GC analysis using *n*-decane as an internal standard.

Table S2 Various reported catalyst tested for reduction of nitroarenes into anilines.

Entry	Catalyst	Hydrogen source	Temp (^oC)	Time (h)	TOF[h^{-1}][a]	Ref
1	Pd/CN-PC[a]	HCOOH	25	0.08-4	15-775	1
2	Au/rutile	HCOOH	60	0.67-4	25-149	2
3	$[Mo_3S_4H_3(dmpe)_3]BPh_4$[b]	HCOOH-Et_3N	70	18	0.54-1.85	3
4	Fe_2O_3/NGr@C	HCOOH-Et_3N	120	20-24	0.74-0.95	4
5	γ-Fe_2O_3@HAP-Pd[c]	$HCOONH_4$	60	3	35-30	5
6	$Fe(BF_4)_2 \cdot 6H_2O/PP_3$	HCOOH	40	1	100	6
7	Fe-MMIO[d]	HCOOH	70	0.67-1	20-25	7
8	Pd@g-C_3N_4 NS	HCOOH	25	0.17-4.5	24-1313	This work

[a] Pd/CN-PC = The Pd/CN-fresh sample was also reduced under the irradiation of commercial lamp (15 W) for one week at room temperature.

[b] dmpe =1,2-(bis)dimethylphosphinoethane.

[c] HAP = hydroxyapatite.

[d] MMIO = micro-mesoporous iron oxide.

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