Supporting Information

Atomically dispersed Ni as the active site towards selective hydrogenation of nitroarenes

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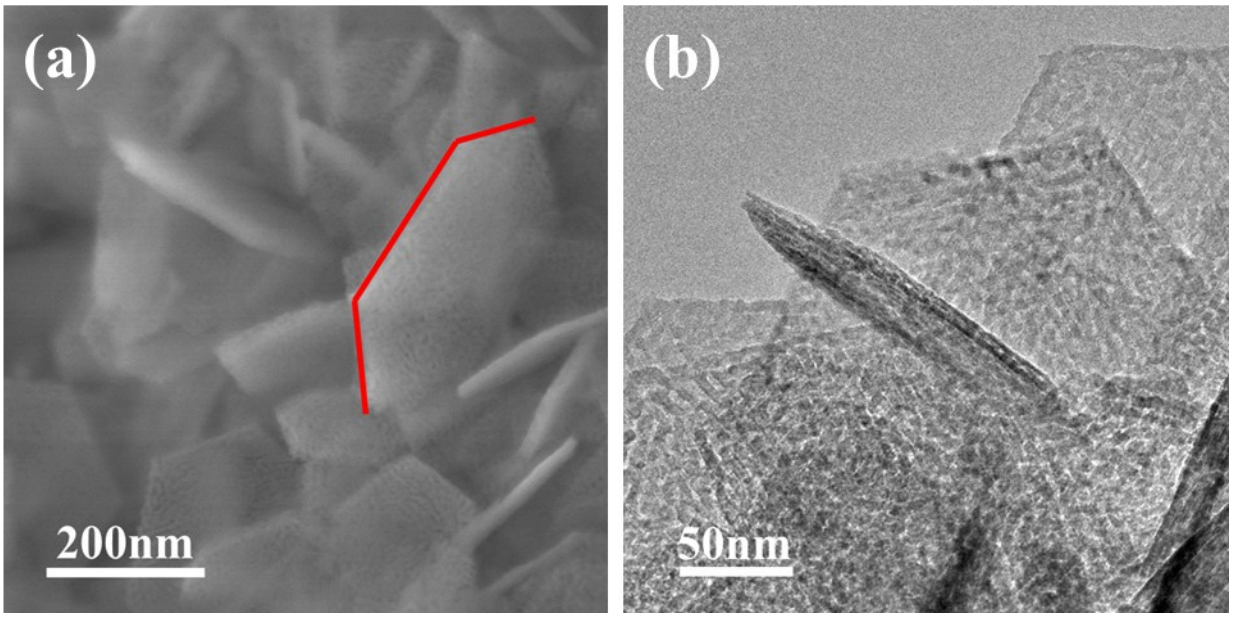


Fig. S1 (a) SEM image and (b) TEM image of MgO.

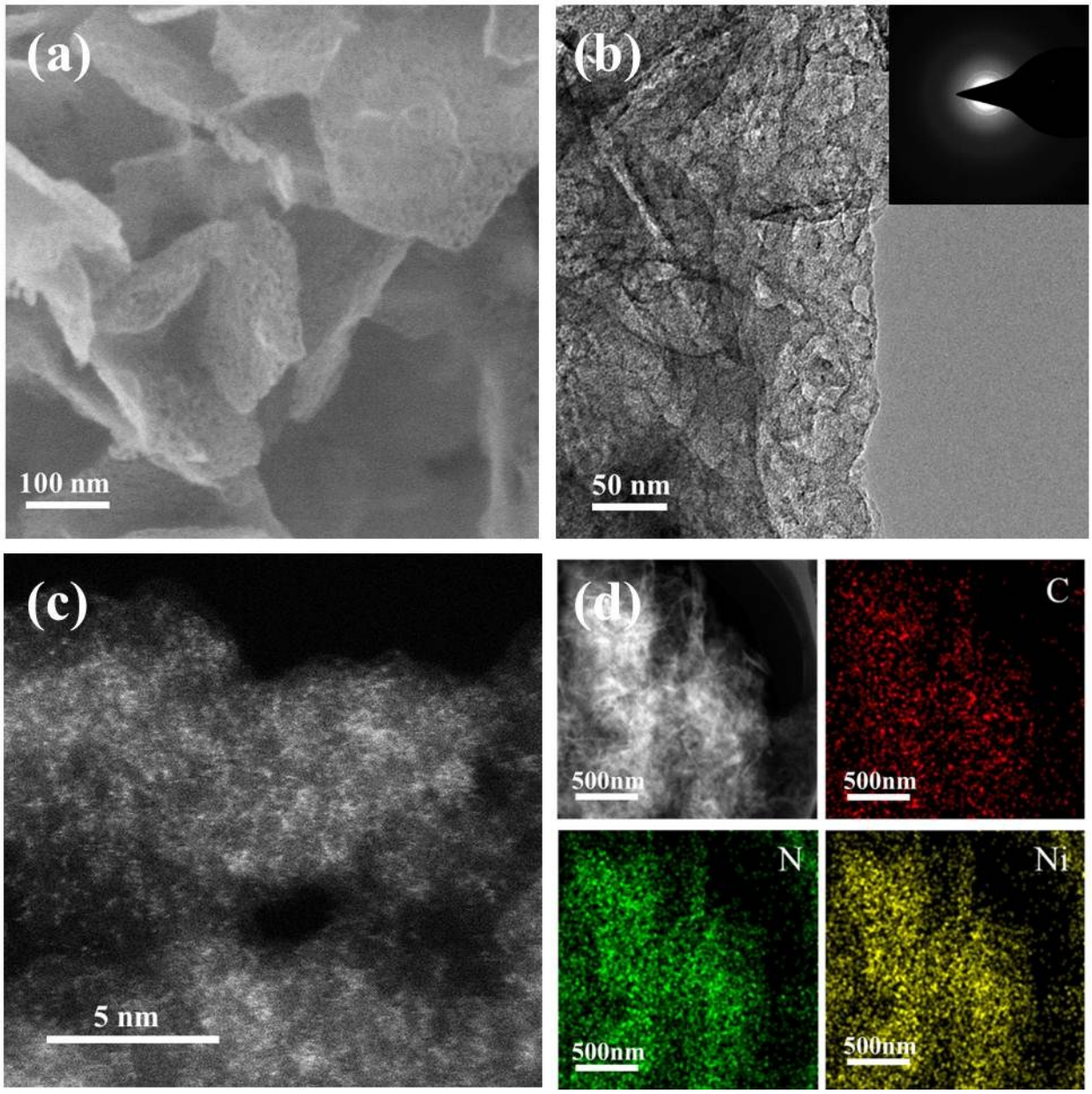


Fig. S2 (a) SEM image, (b) TEM image (inset: the corresponding SAED pattern), (c) HAADF-STEM image and (d) EDS mapping of Ni-N-C-600.

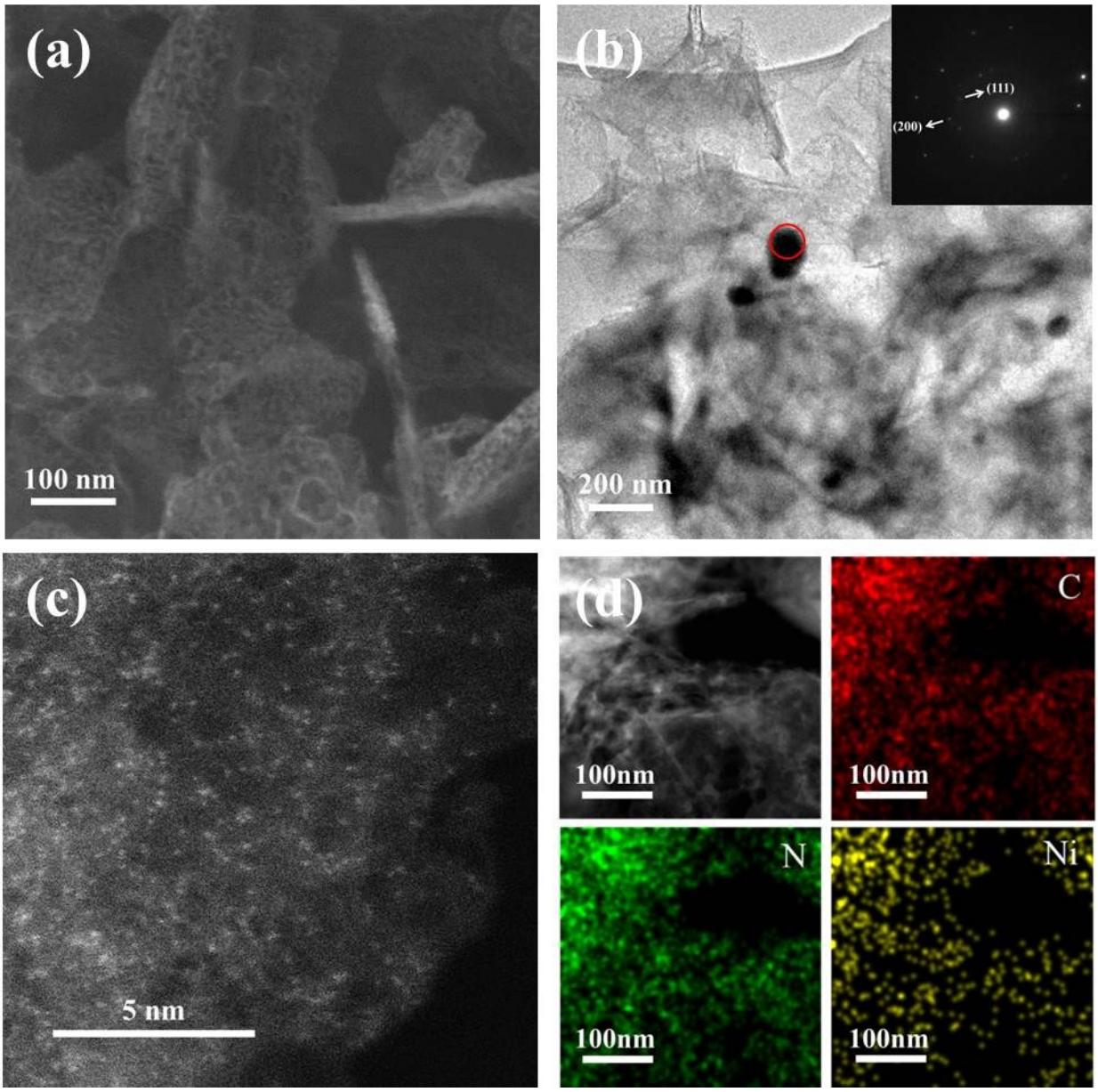


Fig. S3 (a) SEM image, (b) TEM image (inset: the SAED pattern of the region marked with red cycle), (c) HAADF-STEM image and (d) EDS mapping of Ni-N-C-800.

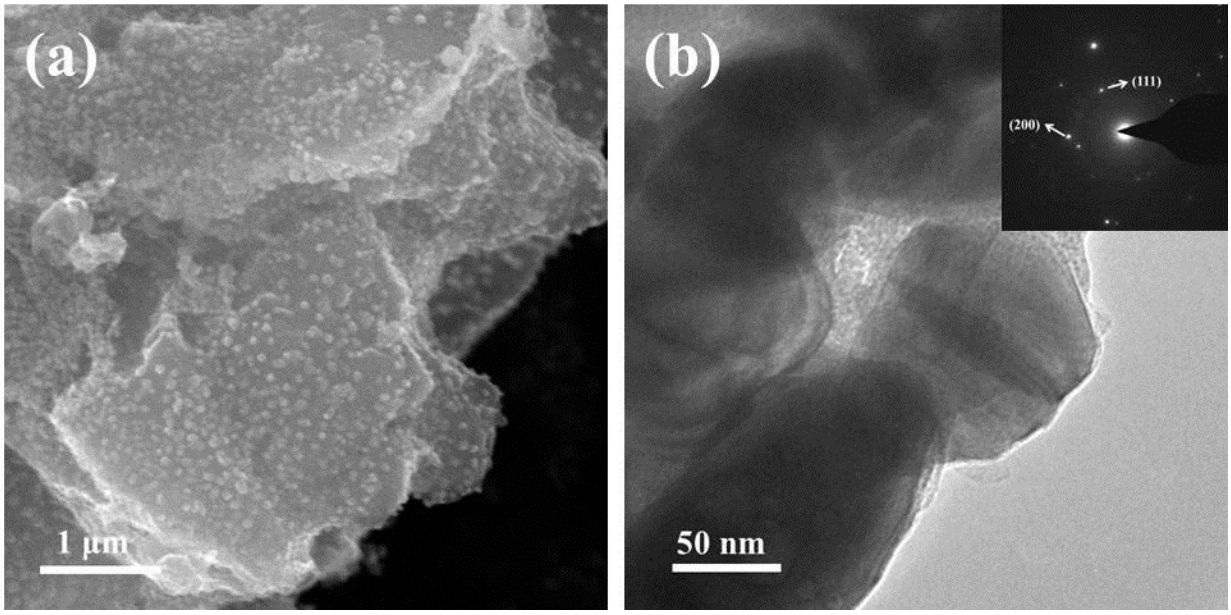


Fig. S4 (a) SEM image and (b) TEM image of Ni-NC (inset: the corresponding SAED pattern).

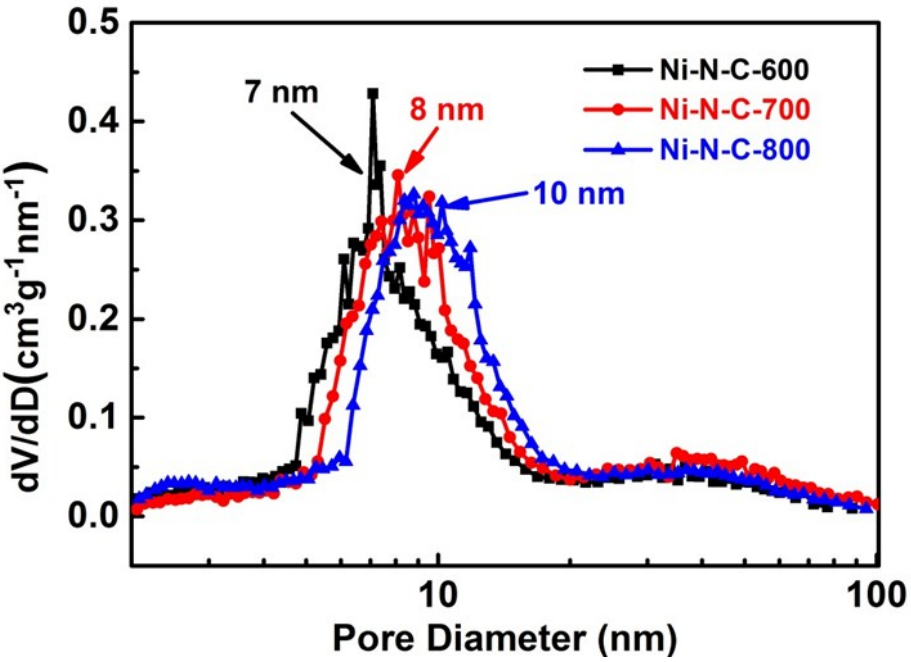


Fig. S5 Pore size distribution of Ni-N-C-600, Ni-N-C-700, and Ni-N-C-800.

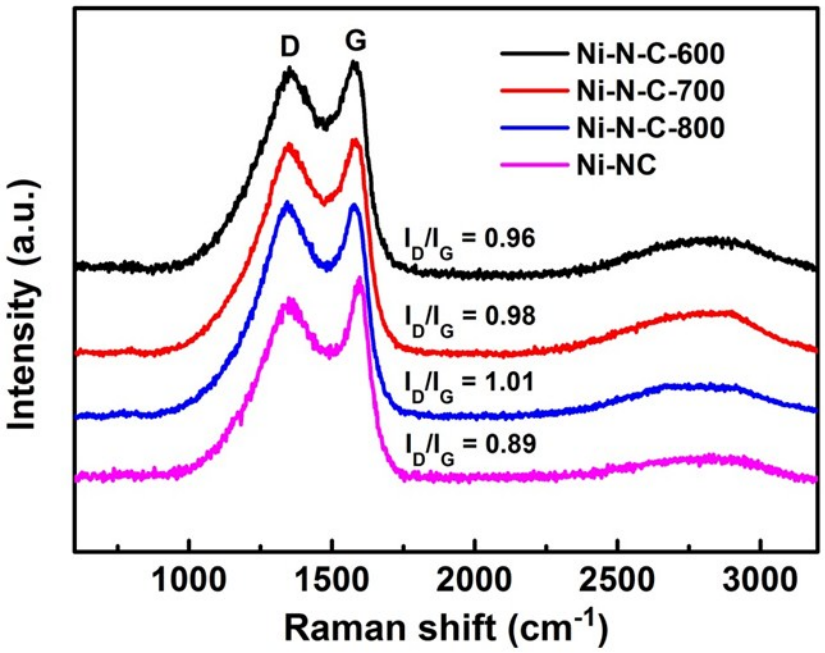


Fig. S6 Raman spectra for Ni-N-C-600, Ni-N-C-700, Ni-N-C-800 and Ni-NC.

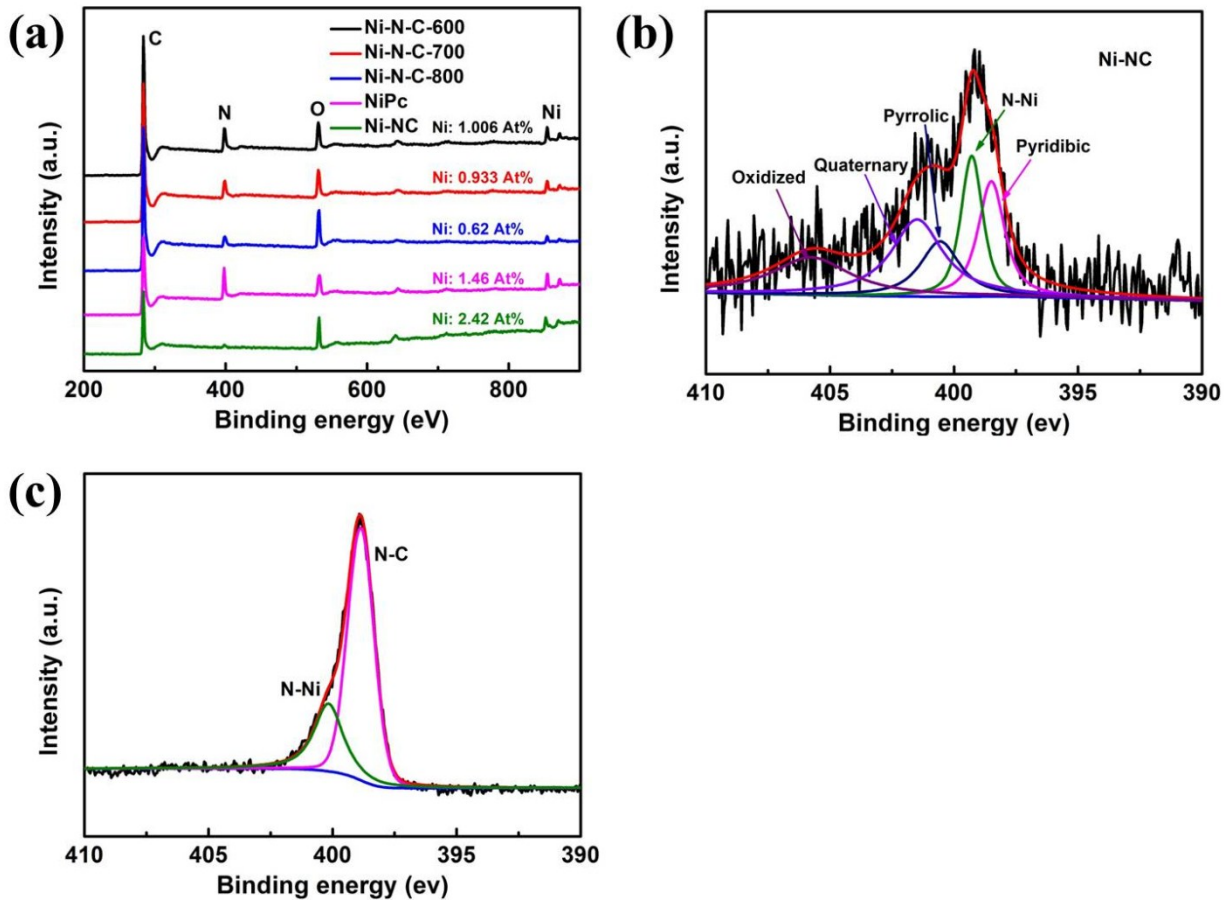


Fig. S7 XPS spectra of the Ni-N-C catalysts. (a) Survey spectra of different Ni-N-C, NiPc and Ni-NC, (b) N1s XPS spectra of Ni-NC, (c) N1s XPS spectra of NiPc.

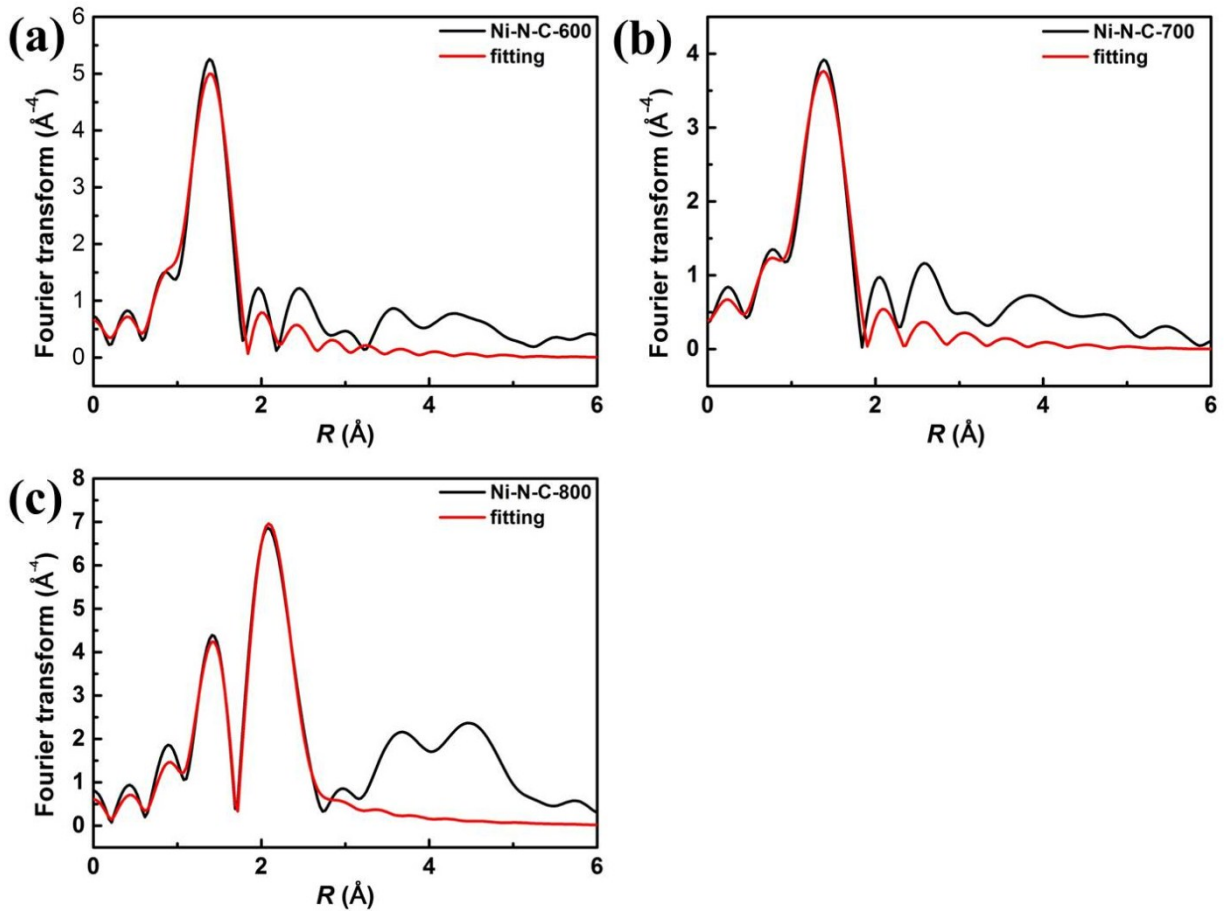


Fig. S8 The corresponding EXAFS fitting curves of (a) Ni-N-C-600, (b) Ni-N-C-700 and (c) Ni-N-C-800.

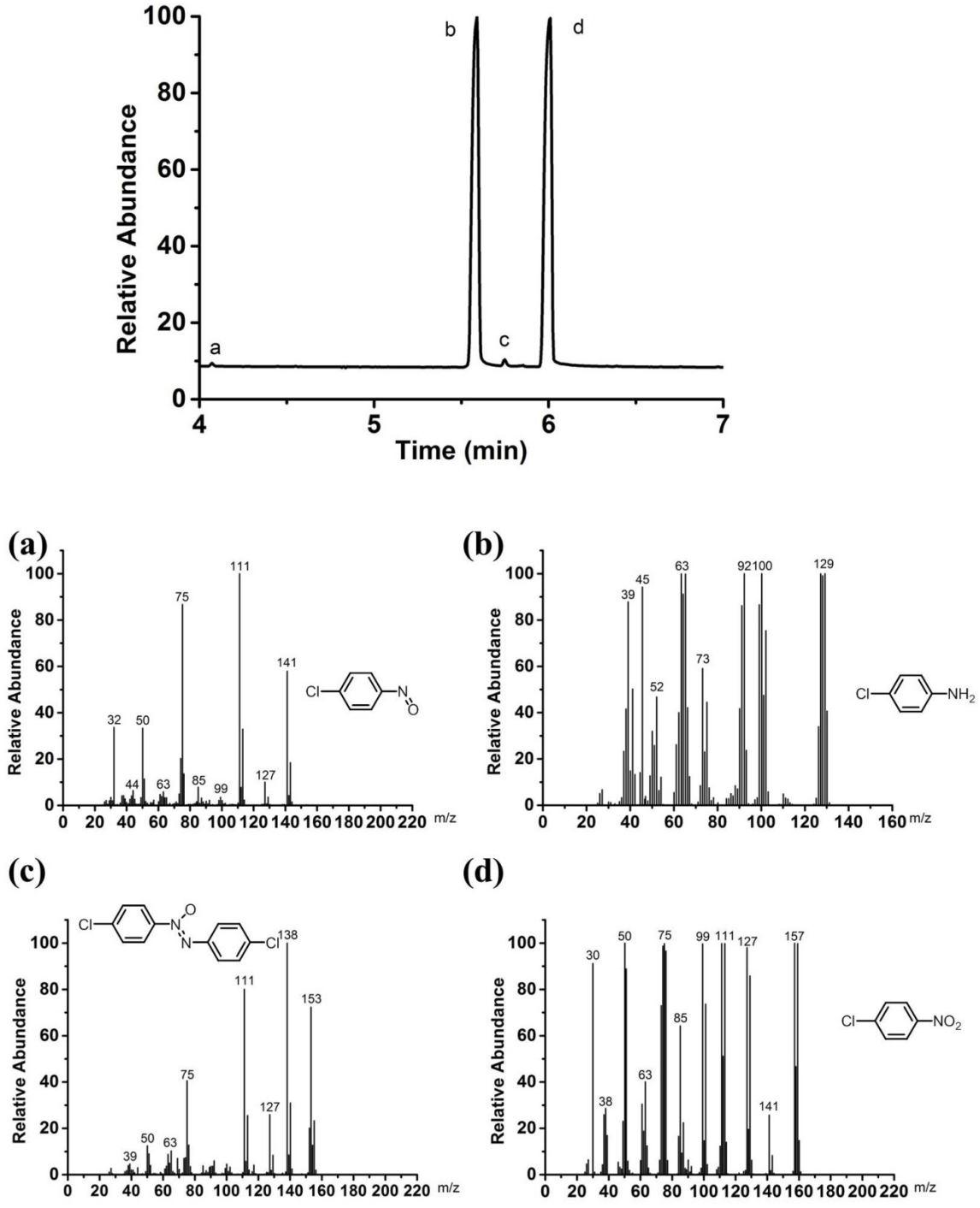


Fig. S9 The GC-MS spectra of reduction reaction intermediate products.

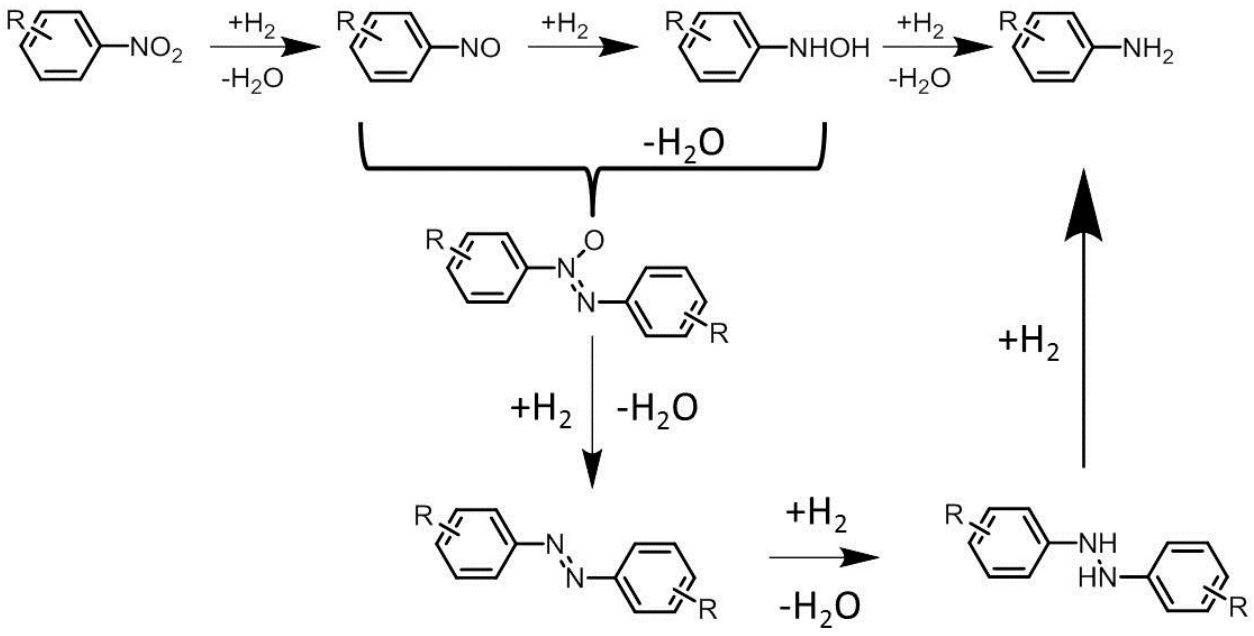


Fig. S10 A proposed reaction mechanism for Ni-N-C-700 catalyze reduction of nitroarene

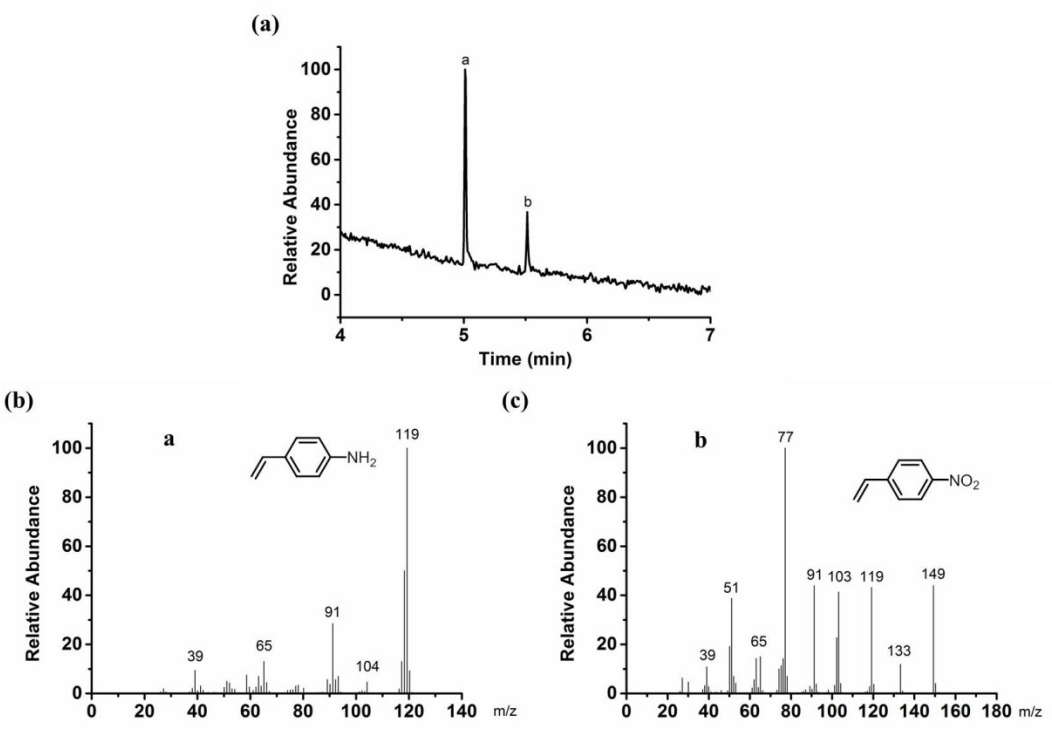


Fig. S11 The GC-MS spectra of hydrogenation of 4-nitrostyrene reaction. Reaction condition: 0.25 mmol nitrostyrene in 5 ml ethanol, 4 mg catalyst, 120 ^{o}C, 3Mpa H_2, 10 h.

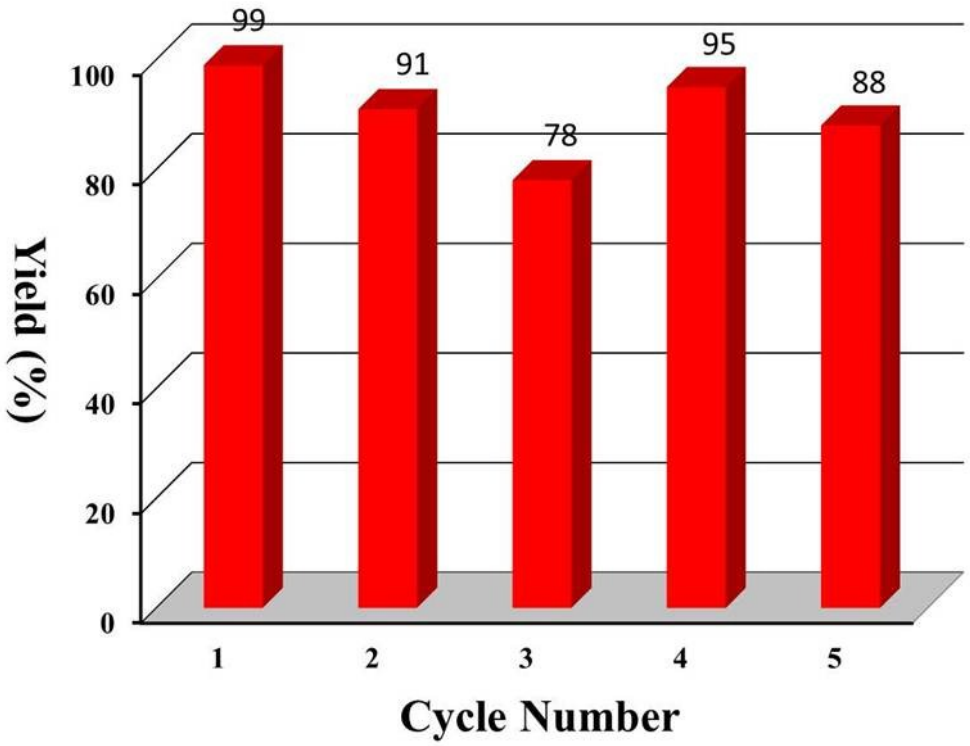


Fig. S12 Catalytic stability and selectivity of Ni-N-C-700 catalysts. Reaction condition: 0.25 mmol 4-nitrochlorobenzene in 5 ml ethanol, 4 mg catalyst, 120 ^{o}C, 3Mpa H_2, 10h up to 3th recycle and 16h for 4th and 5th recycles.

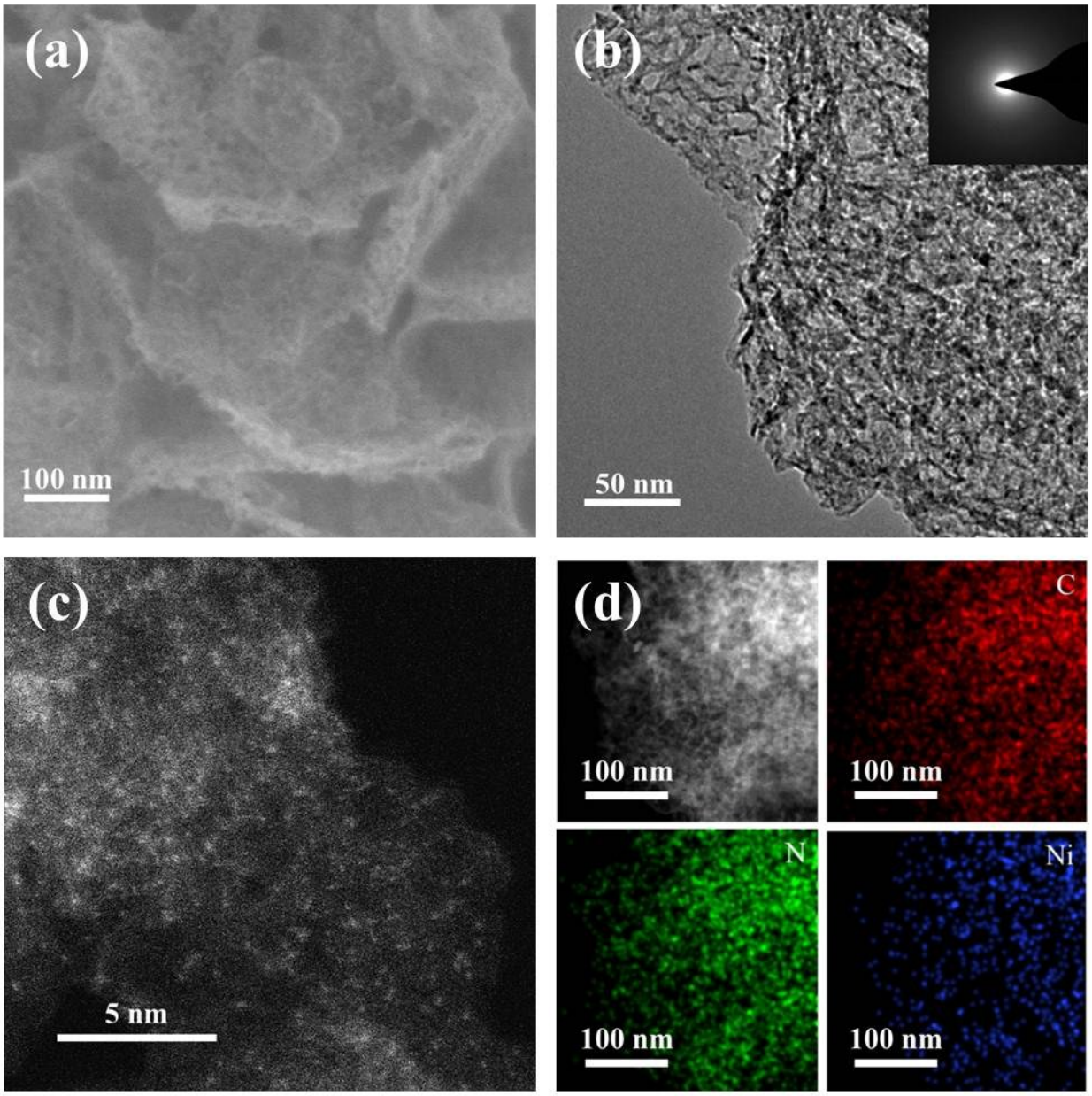


Fig. S13 (a) SEM image, (b) TEM image (inset: the corresponding SAED pattern), (c) HAADF-STEM image and (d) EDS mapping of Ni-N-C-700 after recycle test.

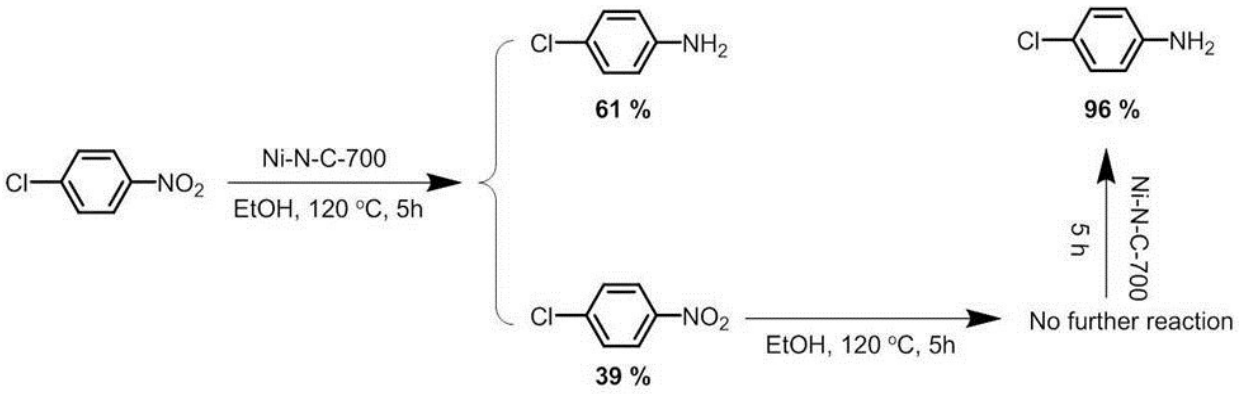


Fig. S14 Schematic diagram of leaching test.

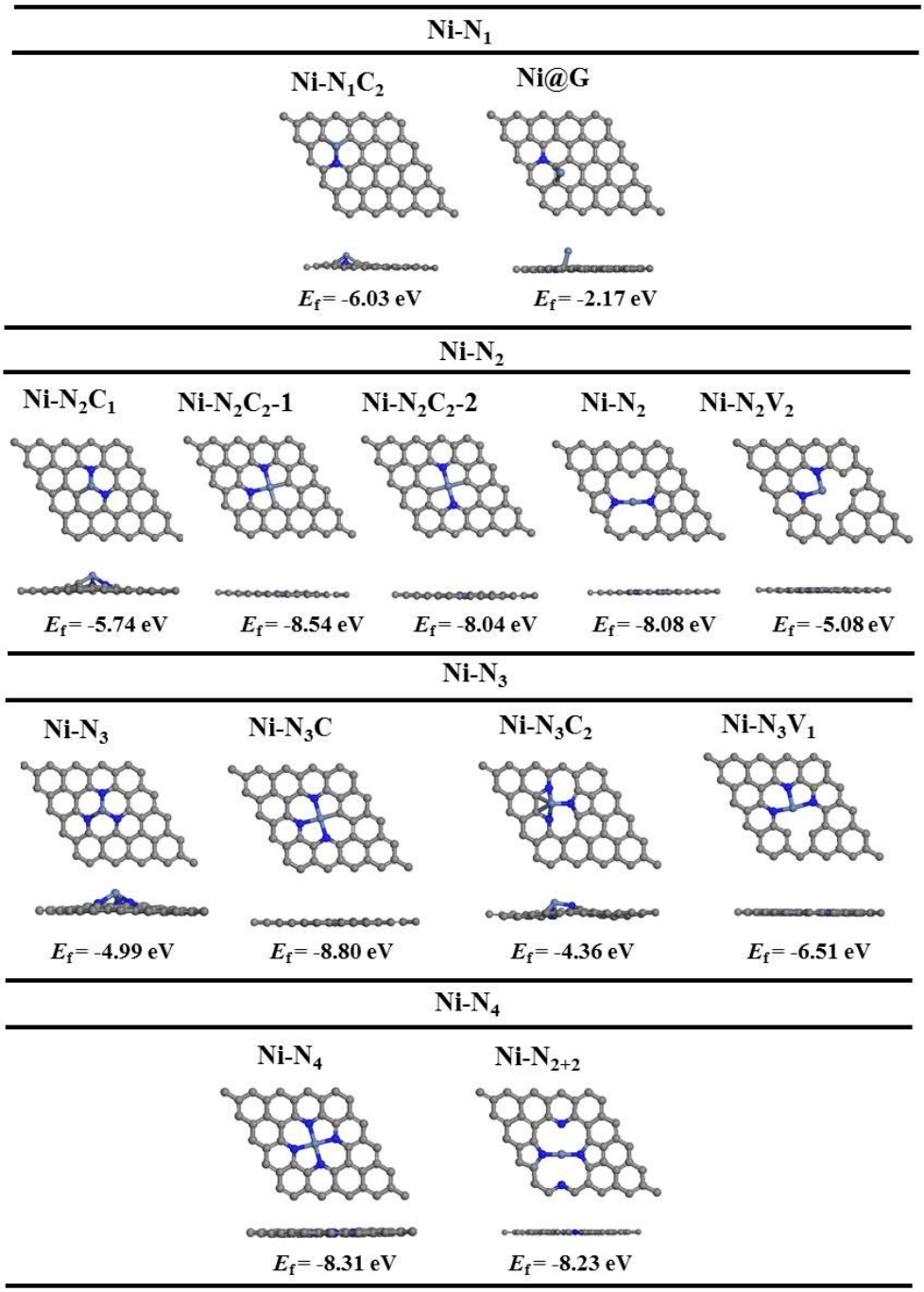
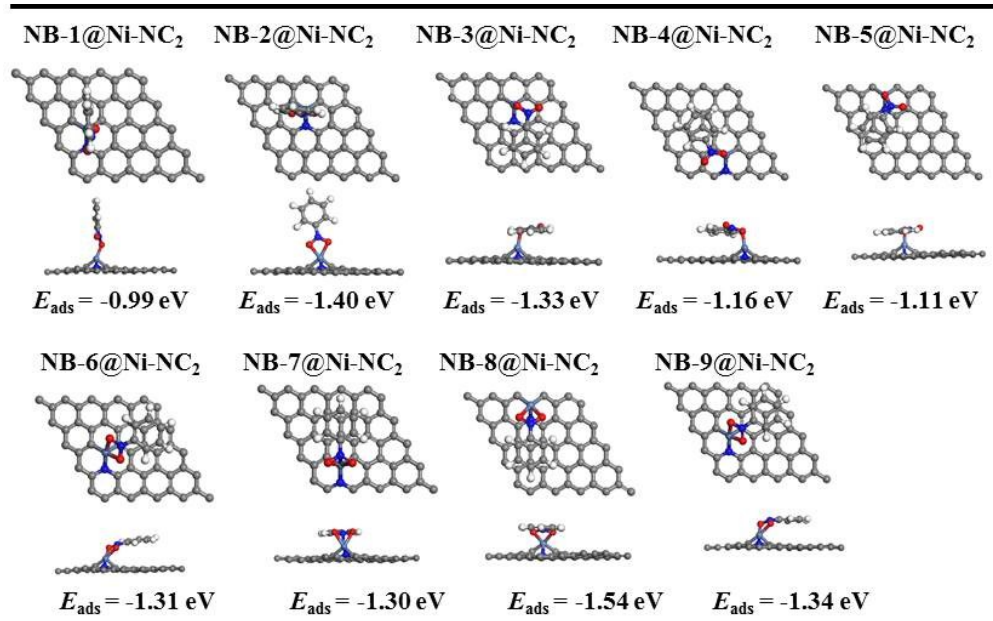
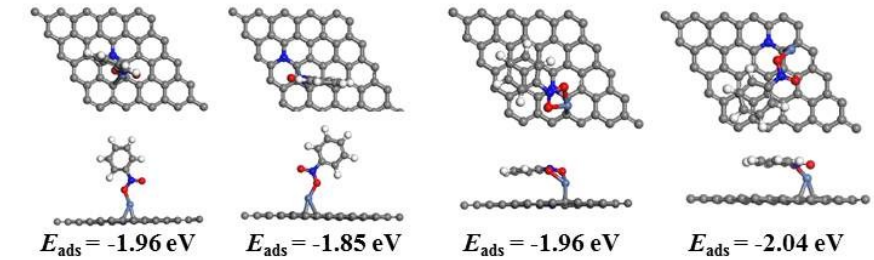


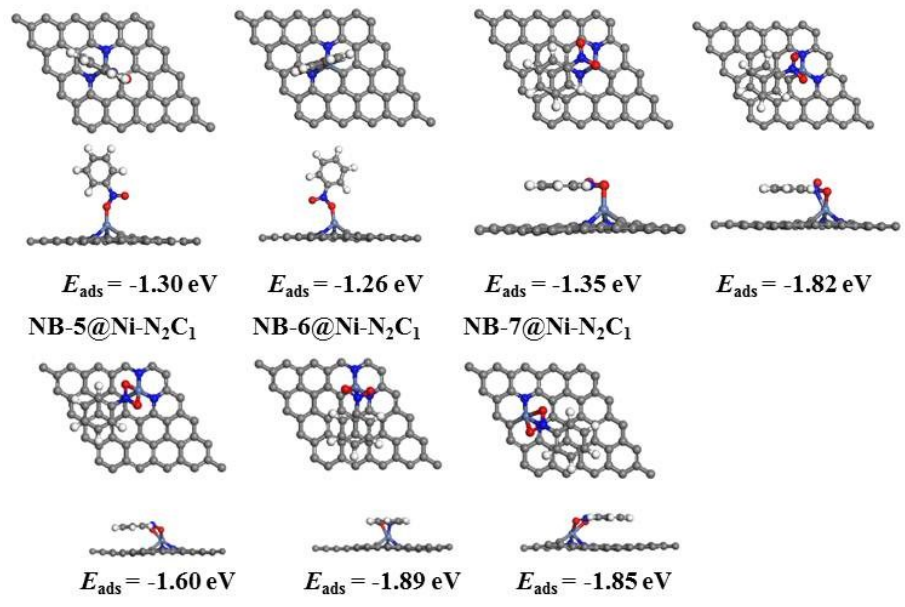
Fig. S15 The models of Ni-N_x (x=1-4).

For NiN_2C_2-1 and NiN_2C_2-2, the former is more stable than the later with the lower energy of 0.50 eV, therefore, in the following nitrobenzene adsorption process, we only consider the case of NiN_2C_2-1 as a substrate.

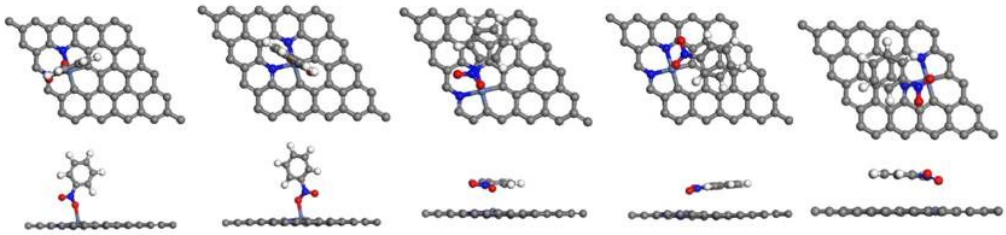
$E_f = E_{Ni\text{-}Nx} - E_{GNx} - E_{Ni}$


NB-1@Ni-NC2
NB-2@Ni-NC2
NB-3@Ni-NC2
NB-4@Ni-NC2
NB-5@Ni-NC2
Eads = -0.99 eV
Eads = -1.40 eV
Eads = -1.33 eV
Eads = -1.16 eV
Eads = -1.11 eV
NB-6@Ni-NC2
NB-7@Ni-NC2
NB-8@Ni-NC2
NB-9@Ni-NC2
Eads = -1.31 eV
Eads = -1.30 eV
Eads = -1.54 eV
Eads = -1.34 eV


NB-1@Ni@G
NB-2@Ni@G
NB-3@Ni@G
NB-4@Ni@G
Eads = -1.96 eV
Eads = -1.85 eV
Eads = -1.96 eV
Eads = -2.04 eV

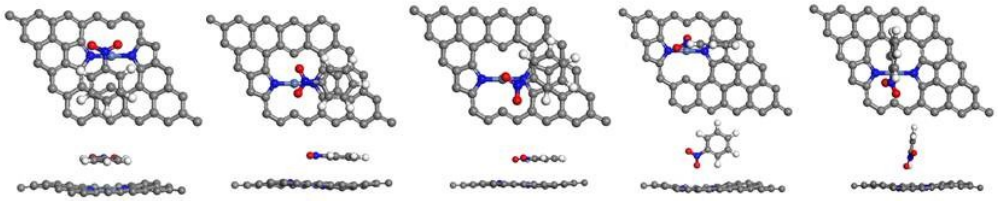

NB-1@Ni-N2C1
NB-2@Ni-N2C1
NB-3@Ni-N2C1
NB-4@Ni-N2C1
Eads = -1.30 eV
Eads = -1.26 eV
Eads = -1.35 eV
Eads = -1.82 eV
NB-5@Ni-N2C1
NB-6@Ni-N2C1
NB-7@Ni-N2C1
Eads = -1.60 eV
Eads = -1.89 eV
Eads = -1.85 eV

NB-1@Ni-N_2C_2-1 NB-2@Ni-N_2C_2-1 NB-3@Ni-N_2C_2-1 NB-4@Ni-N_2C_2-1 NB-5@Ni-N_2C_2-1



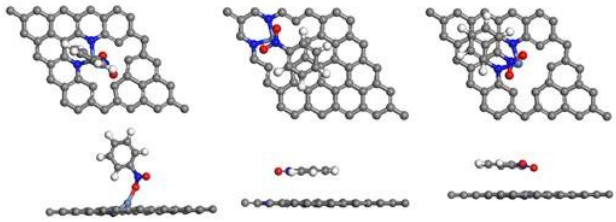
E_{ads} = -0.31 eV E_{ads} = -0.23 eV E_{ads} = -0.68 eV E_{ads} = -0.67 eV E_{ads} = -0.57 eV

NB-1@Ni-N_2 NB-2@Ni-N_2 NB-3@Ni-N_2 NB-4@Ni-N_2 NB-5@Ni-N_2



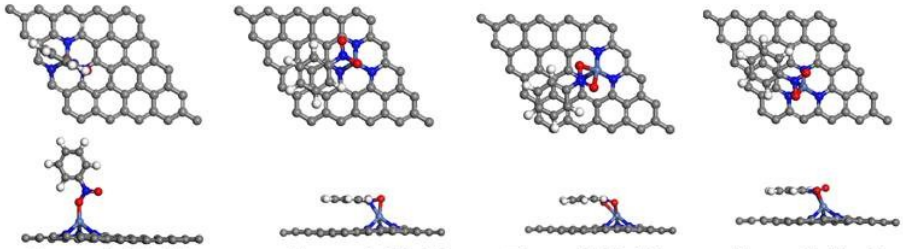
E_{ads} = -0.56 eV E_{ads} = -0.53 eV E_{ads} = -0.57 eV E_{ads} = -0.29 eV E_{ads} = -0.30 eV

NB-1@Ni-N_2V_2 NB-2@Ni-N_2V_2 NB-3@Ni-N_2V_2



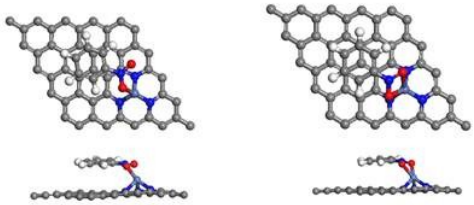
E_{ads} = -0.81 eV E_{ads} = -0.51 eV E_{ads} = -0.60 eV

NB-1@Ni-N_3 NB-2@Ni-N_3 NB-3@Ni-N_3 NB-4@Ni-N_3

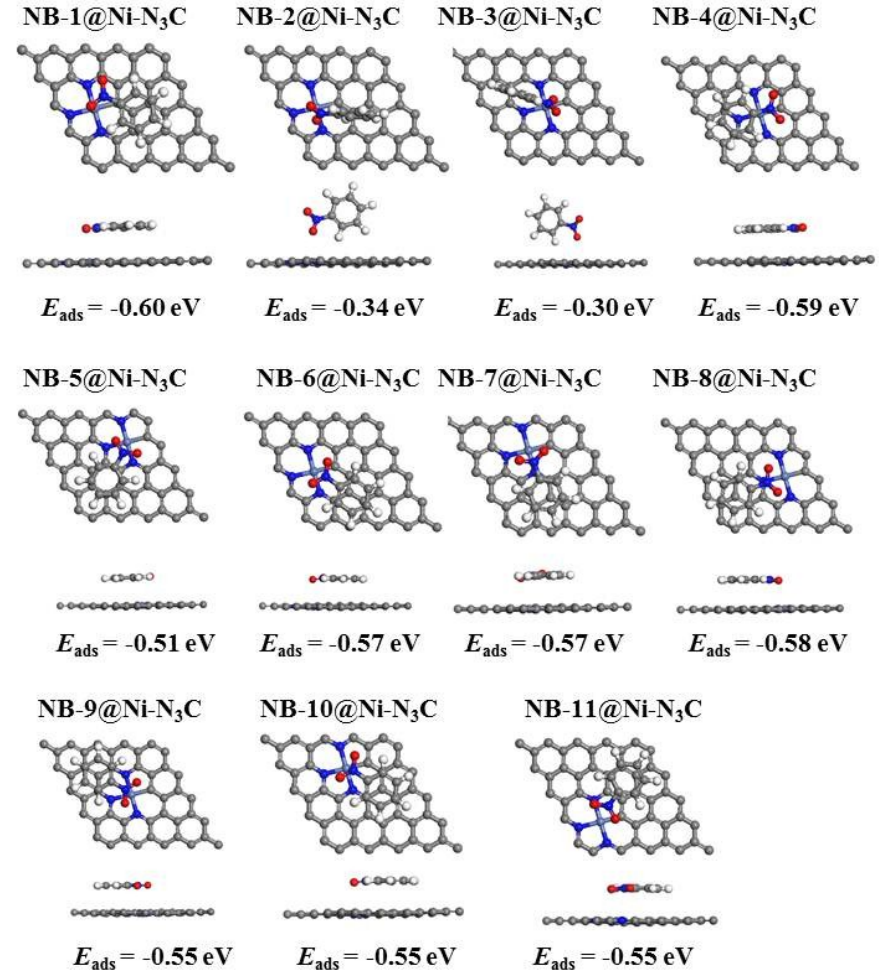


E_{ads} = -1.65 eV E_{ads} = -2.22 eV E_{ads} = -2.03 eV E_{ads} = -2.11 eV

NB-5@Ni-N_3 NB-6@NiN_3



E_{ads} = -1.96 eV E_{ads} = -1.53 eV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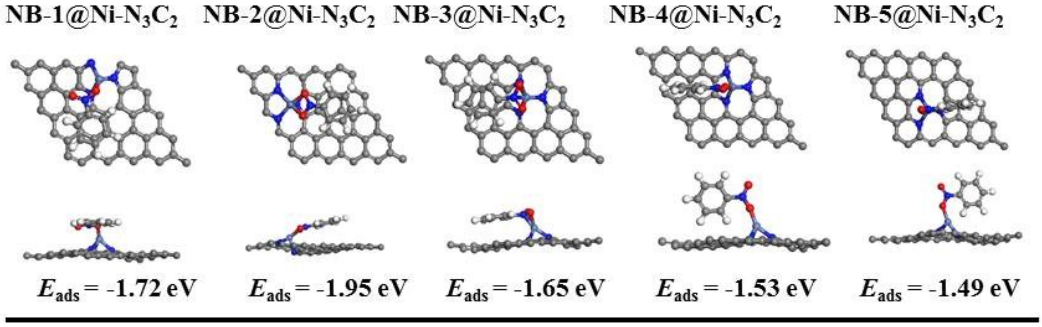
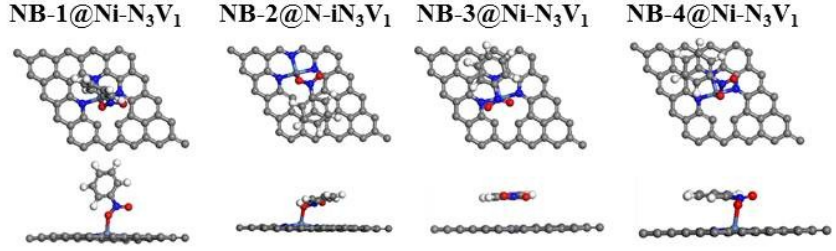
NB-2@Ni-N3C
NB-3@Ni-N3C
NB-4@Ni-N3C
Eads = -0.60 eV
Eads = -0.34 eV
Eads = -0.30 eV
Eads = -0.59 eV
NB-5@Ni-N3C
NB-6@Ni-N3C
NB-7@Ni-N3C
NB-8@Ni-N3C
Eads = -0.51 eV
Eads = -0.57 eV
Eads = -0.57 eV
Eads = -0.58 eV
NB-9@Ni-N3C
NB-10@Ni-N3C
NB-11@Ni-N3C
Eads = -0.55 eV
Eads = -0.55 eV
Eads = -0.55 eV


NB-1@Ni-N3C2
NB-2@Ni-N3C2
NB-3@Ni-N3C2
NB-4@Ni-N3C2
NB-5@Ni-N3C2
Eads = -1.72 eV
Eads = -1.95 eV
Eads = -1.65 eV
Eads = -1.53 eV
Eads = -1.49 eV


NB-1@Ni-N3V1
NB-2@N-iN3V1
NB-3@Ni-N3V1
NB-4@Ni-N3V1
Eads = -0.44 eV
Eads = -0.73 eV
Eads = -0.50 eV
Eads = -0.65 eV

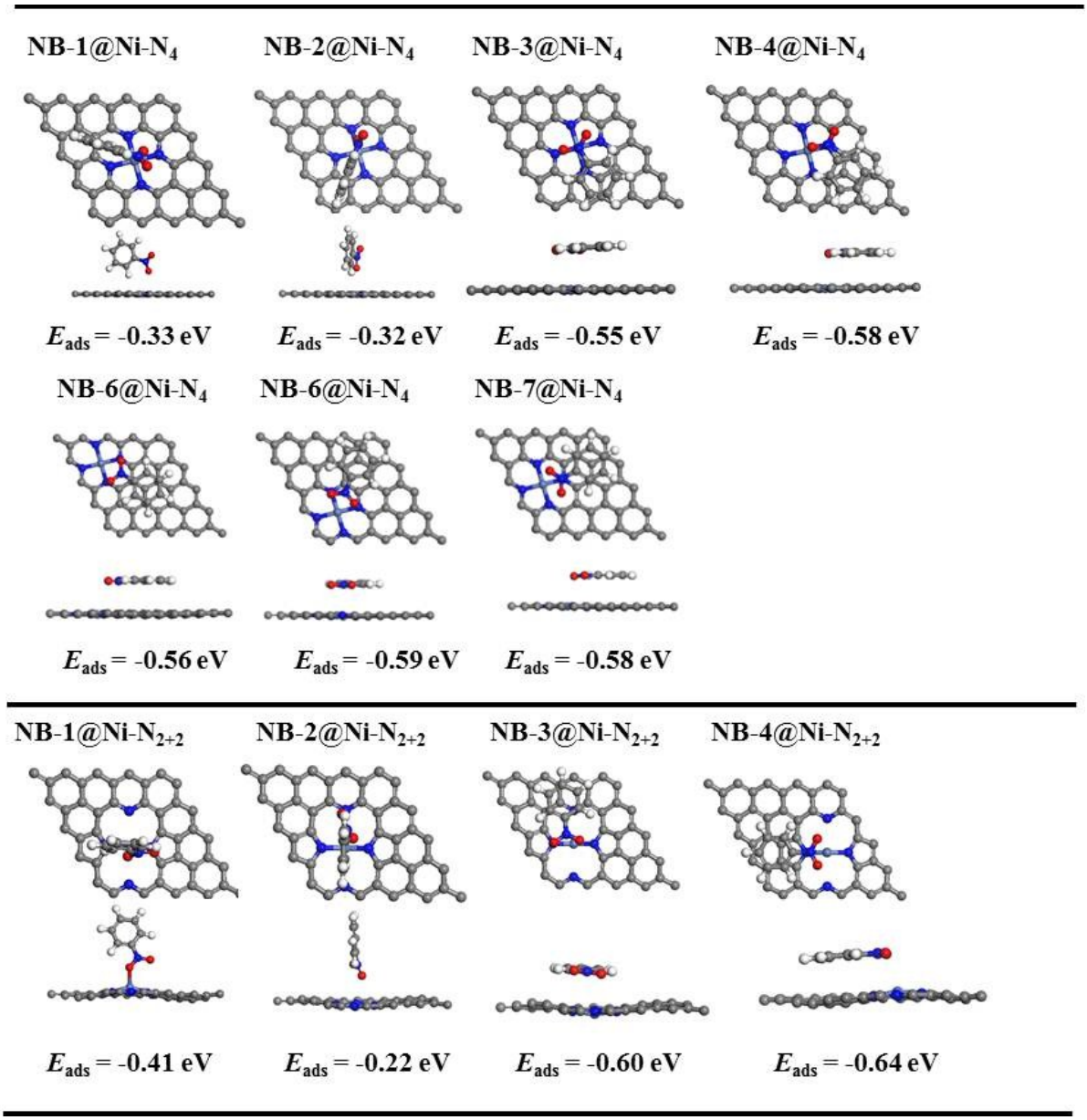


Fig. S16 Adsorption structures of nitrobenzene on Ni-N_x substrates. The gray, blue, light blue, red, and white balls stand for C, N, Ni, O, and H atoms, respectively.

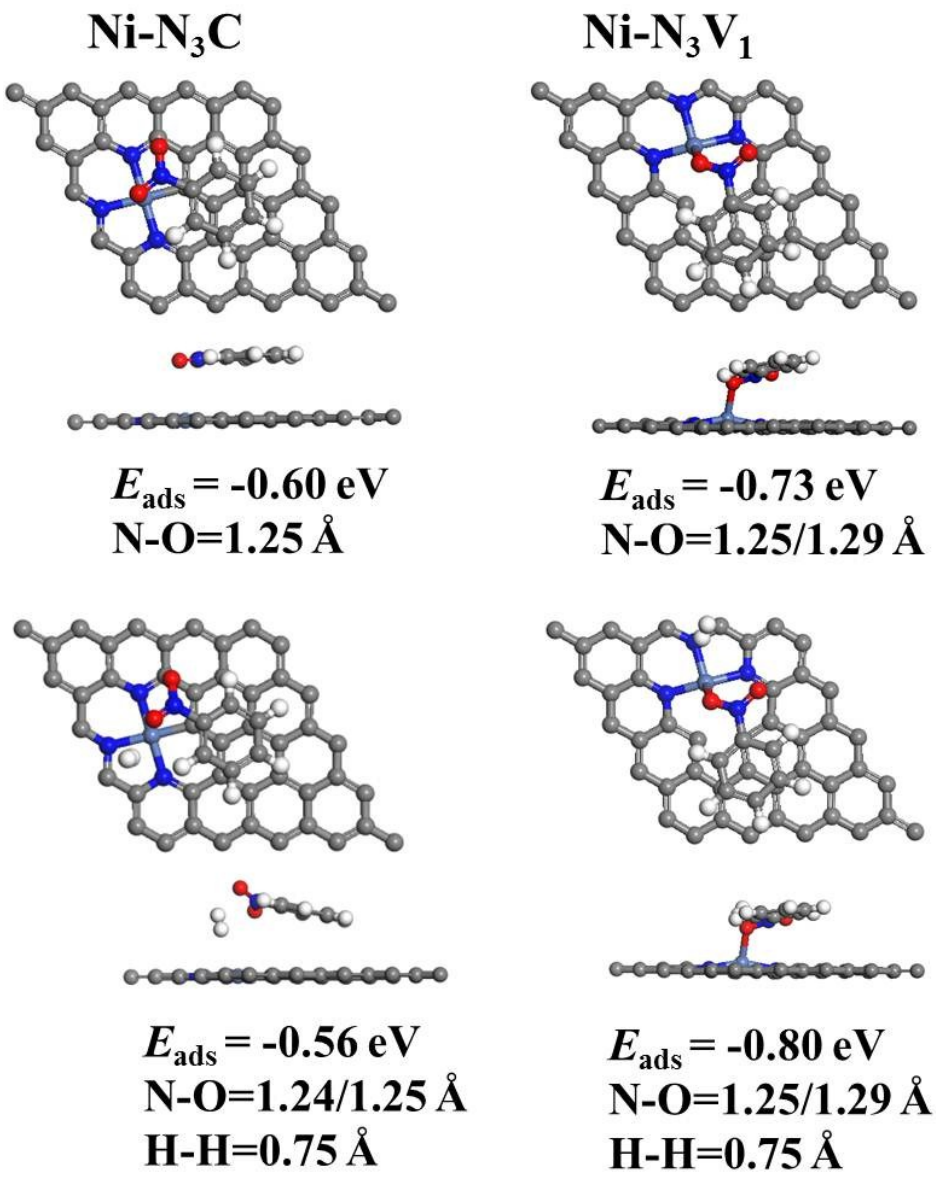


Fig. S17 Co-adsorption structures of nitrobenzene molecules and H_2 on the other optimized Ni-N_3 structures. The gray, blue, light blue, red, and white balls stand for C, N, Ni, O, and H atoms, respectively.

Table S1. EXAFS data fitting results of Ni-N-C-600, Ni-N-C-700, and Ni-N-C-800 for Ni K edge.

Sample	Shell	N^a	R (Å)^b	σ^2(Å^2 10^{-3})^c	ΔE_0 (eV)^d	R factor (%)^e
Ni-N-C-600	Ni-N	3.7	1.86	6.9	-0.2	0.8
Ni-N-C-700	Ni-N	3.3	1.84	6.4	-5.7	0.6
Ni-N-C-800	Ni-N	2.6	1.86	5.0	-9.6	0.4

[a] CN, coordination number; [b] R, bonding distance; [c] σ^2, Debye-Waller factor; [d] ΔE_0, inner potential shift; [e] R factor is used to value the goodness of the fitting

Table S2. Ni content of catalysts

sample	Ni-N-C-600	Ni-N-C-700	Ni-N-C-800	Ni-NC
Ni[a] wt%	4.9	4.4	3.6	10.3
Ni[b] at%	1.006	0.993	0.62	2.42
Ni[c] wt%	4.5	4.2	2.9	9.8

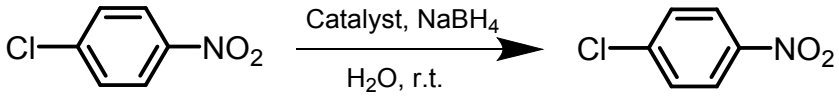
[a] Ni content (wt) of catalysts as measured by ICP-OES. [b] Ni content of catalysts as measured by XPS. [c] It was calculated based on the contents of C, N, O and Ni.

Table S3. The total nitrogen content and percentage of different nitrogen species in Ni-N-C catalysts

Catalyst	At%	pyridinic	Ni–N	pyrrolic	quaternary	oxidized
Ni-N-C-600	10.6	3.65	2.40	2.29	1.12	1.37
Ni-N-C-700	8.5	2.54	1.95	1.34	1.57	1.1
Ni-N-C-800	5.2	1.52	1.14	0.78	0.91	0.85
Ni-NC	3.5	0.68	0.65	0.51	0.96	0.70

[a] It was calculated according to the peak area of different types of N.

Table S4. Evaluation of reaction conditions for the reduction of 4-chloronitrobenzenea[a]



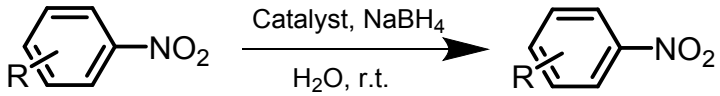
Entry	Catalyst	$NaBH_4$	*T* (h)	Yield[b] (%)
1	Ni-N-C-600			73
2	Ni-N-C-700	5 equiv	0.25	99
3	Ni-N-C-800			46

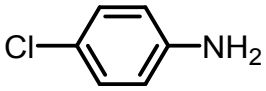
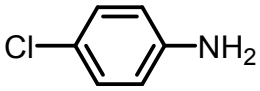
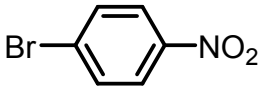
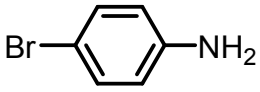
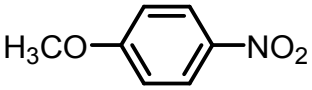
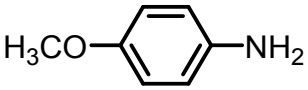
[a] Reaction conditions: 0.25 mmol 4-nitrochlorobenzene in 1 ml H_2O, 2mg Catalyst. [b] isolated yield.

Table S5. Summary of various catalysts in hydrogenation of nitroarenes

Catalyst	$NaBH_4$ (equiv)	Temp ^oC	Time (min)	TOF (h^{-1})	Ref
Ni-N-C-700	5	r.t.	15	667.7	This work
N-G	100	r.t.	21	-	*Energy.Environ. Sci.* **2013**, *6*, 3260-3266.[1]
N-CNTs	100	r.t.	48	-	*Environ. Sci. Technol.* **2014**, 48, 10191-10197.[2]
N-G	10	r.t	300	-	*Green Chem.* **2016**, 18, 4254-4262.[3]
N,P-G	100	35	2.5	-	*J. Catal.* **2018**, *359*, 233-241.[4]
S,N-CNTs	32	r.t	10	-	*Adv. Mater.* **2016**, *28*, 10679-10683.[5]
AA/GO	750	r.t	80	-	*Nano Res.* **2015**, *8*, 3992-4006.[6]
Ni/mZSM-5	4	r.t	-	450	*RSC Adv.* **2015**, *5*, 34398-34414.[7]
Co@NC	-	r.t	-	45	*J. Mater. Chem. A* **2016**, *4*, 7476-7482.[8]
Cu&Fe_3O_4-mC	10	r.t	-	12.5	*Green Chem.* **2014**, *16*, 4198-4205.[9]

Table S6. Results of Hydrogenation of nitroarenes catalyzed by Ni-N-C-700



Entry	Reactant	Product	*T* (h)	Yield[b] (%)
1			0.25 h	99
2				95
3				97
5				96

[a] Reaction conditions: 0.25 mmol 4-nitrochlorobenzene in 1 ml H2O, 2mg Catalyst. [b] isolated yield

Table S7. Comparison of the hydrogenation of nitroarenes activity between Ni-N-C-700 and other nonprecious catalysts in literature.

Catalyst	Reducing agent	Temp ^{o}C	P (MPa)	TOF (h^{-1})	Ref
Ni-N-C-700	H_2	120	3	8.4	This work
Ni-N-C-600	H_2	120	3	6.2	This work
Ni-N-C-800	H_2	120	3	6.4	This work
Ni–$NiFe_2O_4$	H_2	150	1	5	*Green Chem.* **2015**, *17*, 821-826.[10]
Ni/C_{60}-Ac-B-4	H_2	110	2	7.8	*Catal. Commun.* **2017**, *97*, 83-87.[11]
Ni/C	H_2	140	2	10.6	*Chem. Eng. J.* **2015**, 275, 36-44.[12]
Ni/C	H_2	140	0.5	1.9	*Green Chem.*2016, **18**, 3594-3599.[13]
Ni-NiO/NGr@C-800	H_2	110	5	2.5	*ChemCatChem.* 2016, **8**, 129-134.[14]
Ni@SiCN	H_2	110	5	5	*ChemCatChe. 2016, 8, 2461-2465.*[15]
Ni-L/P-CNTs	H_2	140	2	1.5	*Catal. Sci. Technol.* 2013, **3**, 982-991.[16]
Fe_2O_3-NC	H_2	120	5	1.9	*Science* **2013**, 342, 1073-1076.[17]
Co_3O_4/CNT	H_2	110	3	6.2	*Acs Catal.* **2015**, 5, 4783-4789.[18]
Co-Co_3O_4/CN	H_2	110	5	16.7	*Nat. Chem.* **2013**, 5, 537-543.[19]

Table S8. Ni content (wt%) of Ni-N-C-700 catalysts as measured by ICP-OES

Catalyst	Fresh	Recycle
Ni wt%	4.4	2.8

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