Electronic Supplementary Information

A Bifunctional Catalyst for Efficient Dehydrogenation and Electro-oxidation of Hydrazine

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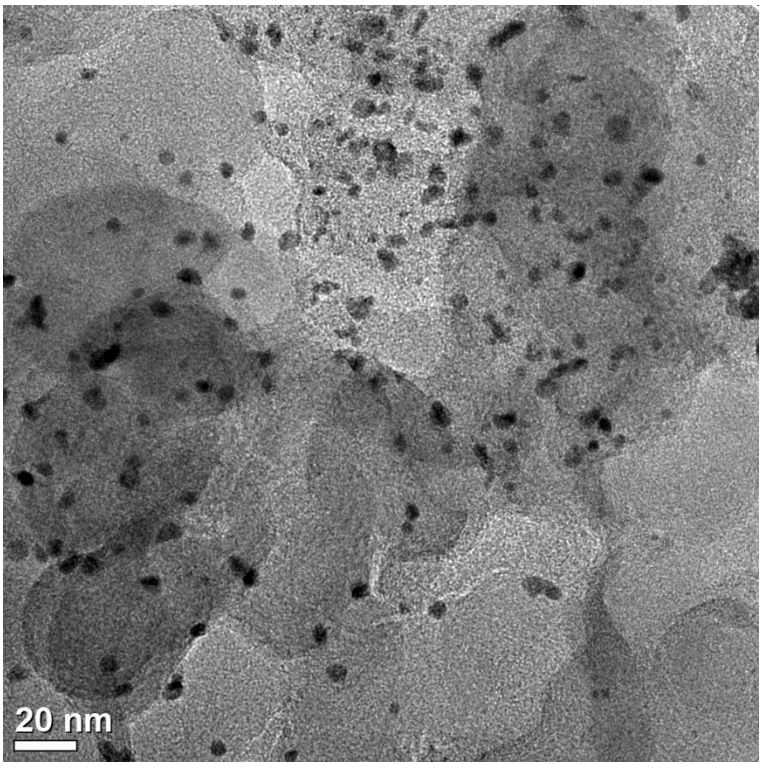

Fig. S1. Overview TEM image of the carbon-black-supported $Pt_{0.2}Ni_{0.8}$-L nanoparticles.

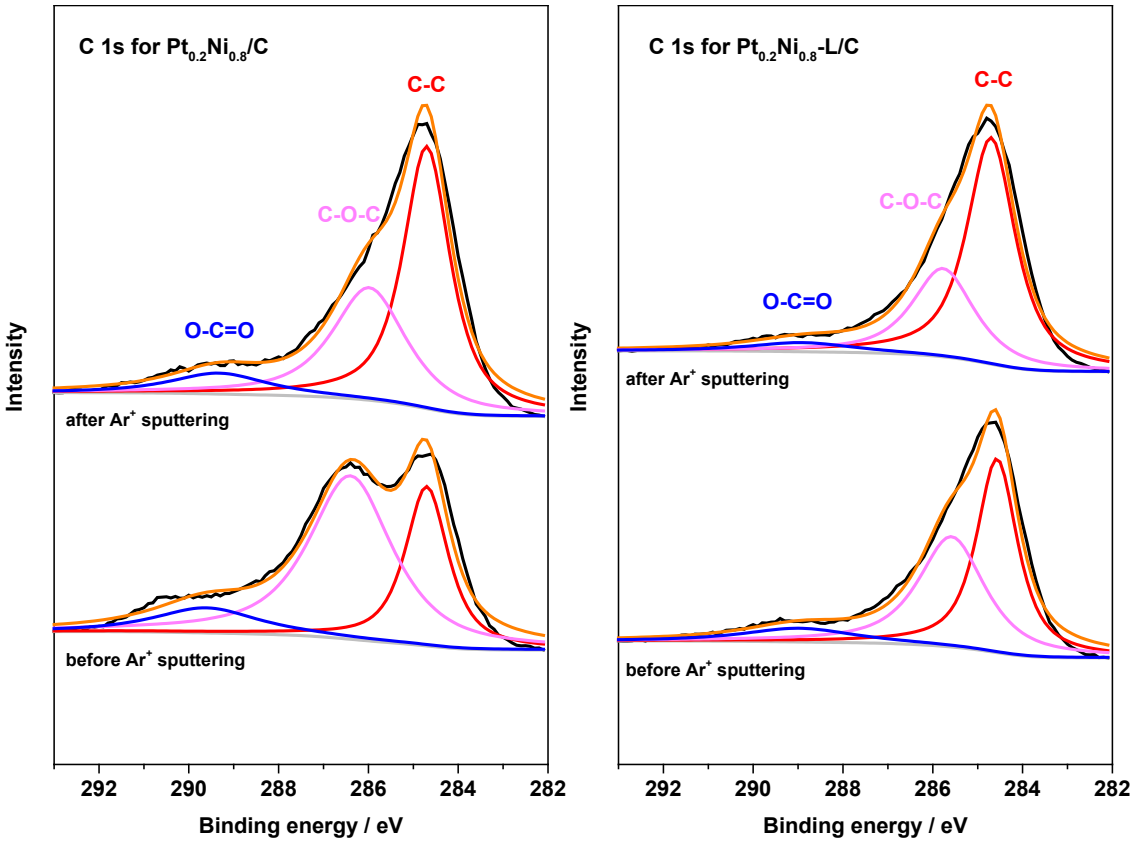

Fig. S2. XPS C 1s spectra of carbon-black-supported $Pt_{0.2}Ni_{0.8}$ and $Pt_{0.2}Ni_{0.8}$-L catalysts before and after Ar^+ sputtering, respectively. Deconvolutions of the peaks are provided; in addition to the C-C peak at 284.8 eV, two additional features are present at ~286 eV and ~289 eV in all spectra in positions consistent with the typical O-containing carbonaceous species among other possibilities (that is, C-O-C and O-C=O, respectively). The carbon black support of the $Pt_{0.2}Ni_{0.8}$ catalyst appears to contain a greater abundance of more readily removed terminal functional groups in the "C-O-C" designated binding energy region relative to the $Pt_{0.2}Ni_{0.8}$-L sample.

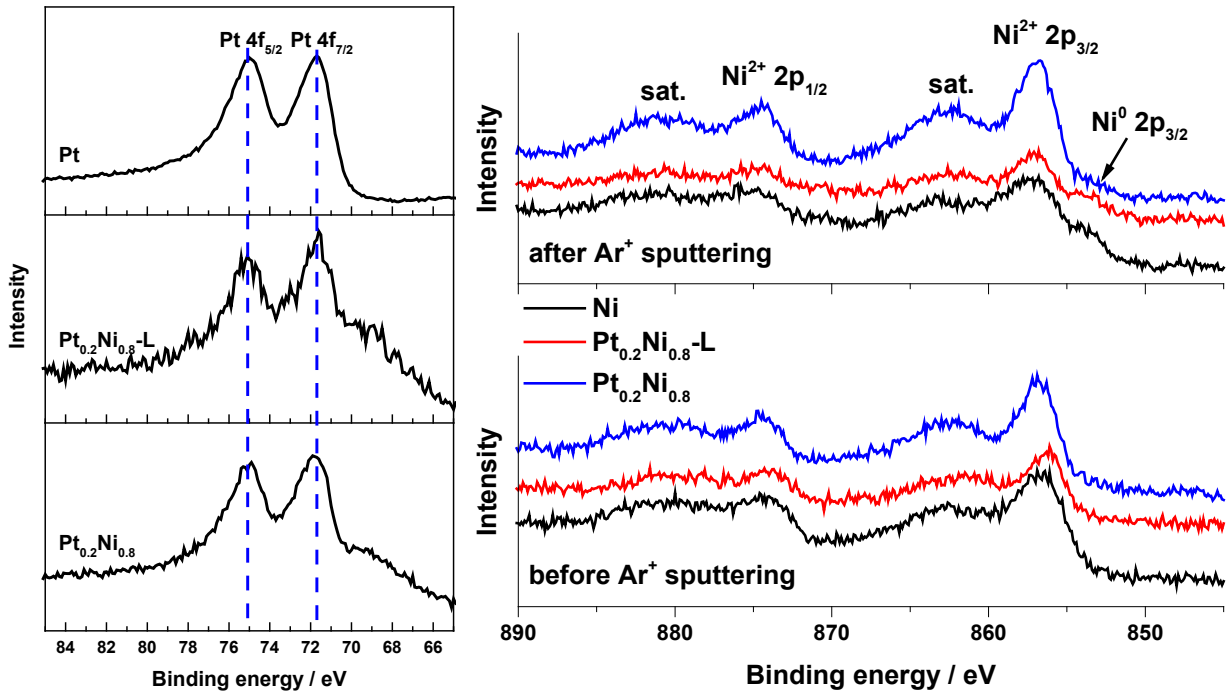

Fig. S3. XPS spectra in the Pt 4f and Ni 2p regions for $Pt_{0.2}Ni_{0.8}$ and $Pt_{0.2}Ni_{0.8}$-L samples. In the Pt 4f region, two peaks with binding energies of 71.7 and 75.0 eV are observed, corresponding to the $4f_{7/2}$ and $4f_{5/2}$ levels of metallic Pt^0. Unlike Pt, the Ni on the surface is not detected in a metallic state after transfer through air into the XPS vacuum system (lower frame), but is instead present in an oxidized form consistent with Ni^{2+}. After mild sputtering with 2 kV Ar^+ (upper frame), a Ni^0 shoulder shows up, which is more likely due to the exposure of subsurface metallic Ni within the supported particles.

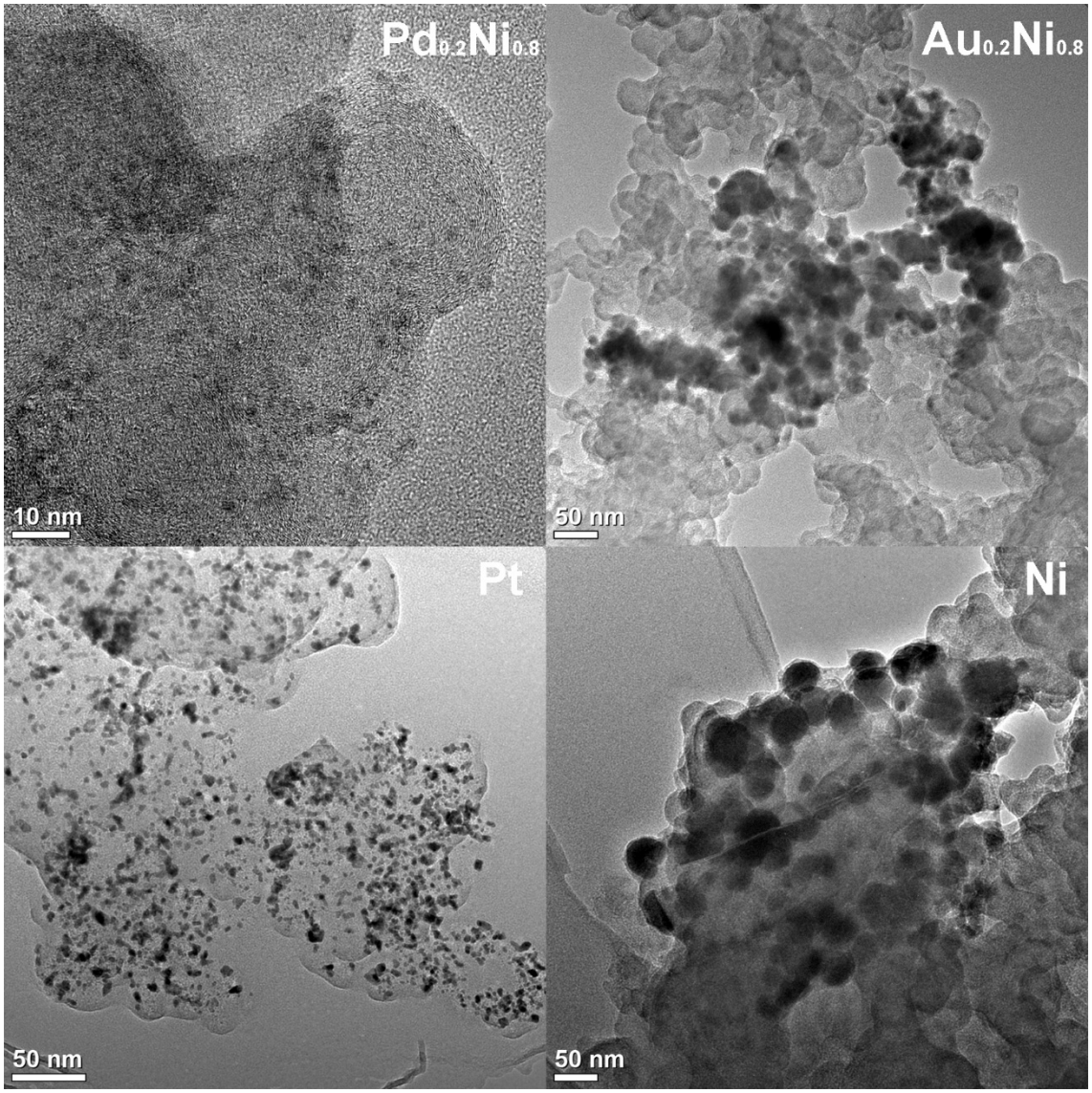

Fig. S4. Representative TEM images of the carbon-black-supported $Pd_{0.2}Ni_{0.8}$, $Au_{0.2}Ni_{0.8}$, Pt, and Ni nanoparticles. A comparison of the images may indicate that the precipitation-reduction method is more effective for the synthesis of ultrafine and homogenous $Pd_{0.2}Ni_{0.8}$ nanoparticles.

Table S1. A summary of the actual metal contents by mass in the catalysts, which were determined by inductively coupled plasma mass spectrometry (ICP-MS).

	M content / wt%	Ni content / wt%
$Pt_{0.2}Ni_{0.8}$/C	14.5	17.2
$Pt_{0.2}Ni_{0.8}$-L/C	14.5	17.2
$Pd_{0.2}Ni_{0.8}$/C	8.1	20.1
$Au_{0.2}Ni_{0.8}$/C	7.5	17.2
Pt/C	49.5	0
Ni/C	0	21.1

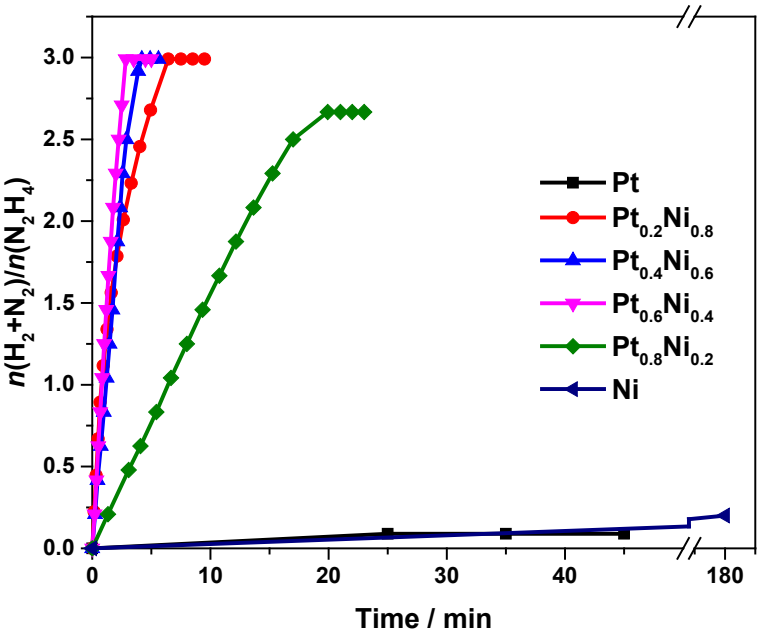

Fig. S5. Time-course plots for the catalytic decomposition of $N_2H_4 \cdot H_2O$ over $Pt_xNi_{(1-x)}$ catalysts in 1 M NaOH solution at 50 ^oC.

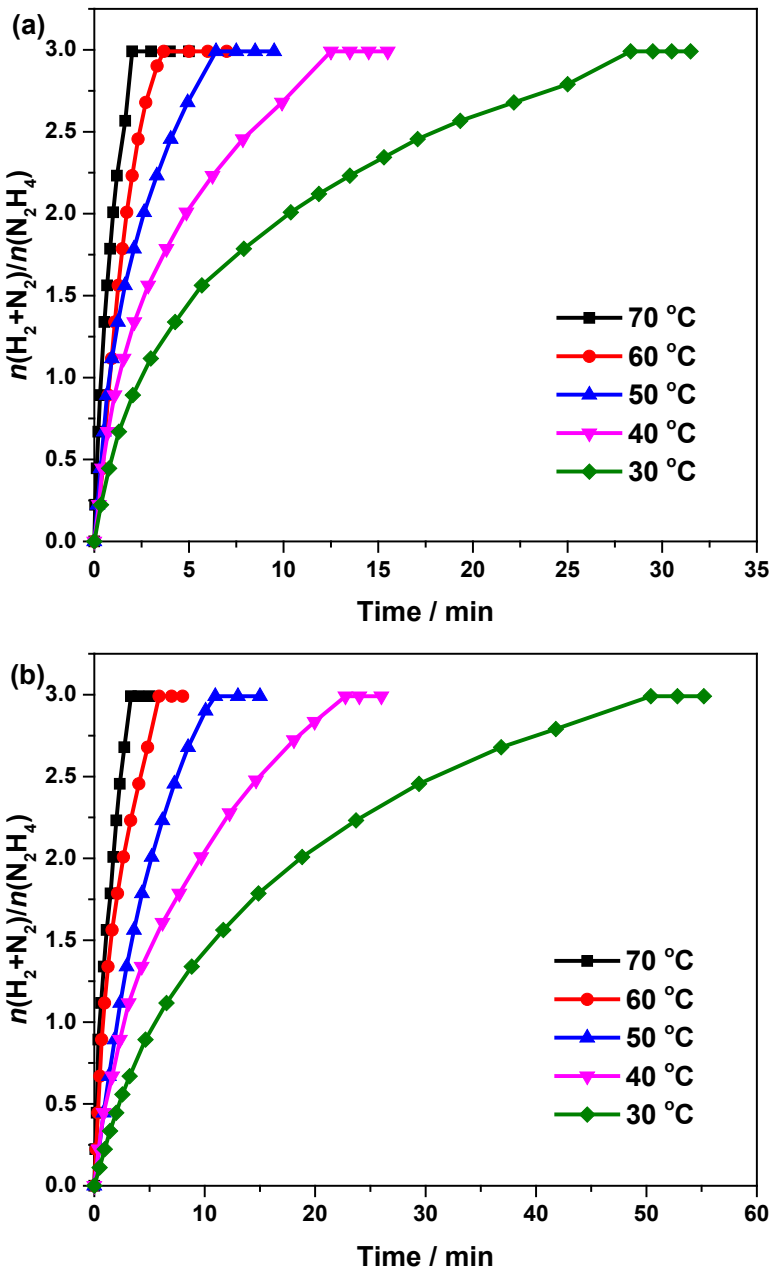

Fig. S6. Time-course plots for the catalytic decomposition of $N_2H_4 \cdot H_2O$ on the (a) $Pt_{0.2}Ni_{0.8}$ and (b) $Pt_{0.2}Ni_{0.8}$-L catalysts in 1 M NaOH solution at different temperatures.

Table S2. Comparison of the activity for hydrazine dehydrogenation over different catalysts.

Catalyst	Additive	Temp. / K	Selectivity for H_2 / %	TOF / h^{-1}	E_a / kJ mol^{-1}	Reference
$Pt_{0.2}Ni_{0.8}$/C	NaOH	323	100	673	45.7	This work
$Ni_{88}Pt_{12}$@MIL-101	NaOH	323	100	350	55.5	*Int. J. Hydrogen Energy*, 2014, **39**, 9726
$Ni_{66}Rh_{34}$@ZIF-8	NaOH	323	100	140	58.1	*ChemCatChem*, 2014, **6**, 2549
$NiRh_4$	/	298	100	9.6	/	*J. Am. Chem. Soc.*, 2009, **131**, 18032
$NiRh_{4.4}$/graphene	NaOH	298	100	13.7	/	*Energy Environ. Sci.*, 2012, **5**, 6885
$Ni_{0.9}Pt_{0.1}/Ce_2O_3$	NaOH	298	100	28.1	42.3	*J. Mater. Chem. A*, 2013, **1**, 14957
$Ni_{0.95}Ir_{0.05}$	/	298	100	2.2	/	*Chem. Commun.*, 2010, **46**, 6545
Ni/Al_2O_3	/	303	93	2.2	49.3	*Angew. Chem., Int. Ed.*, 2012, **51**, 6191
Rh	/	298	43.8	2.5	/	*J. Am. Chem. Soc.*, 2009, **131**, 9894
$(Ni_5Pt_5)_1$-$(CeO_x)_{0.3}$/NG	NaOH	298	100	408	38.7	*Nano Res.*, 2017, **10**, 2856
$Pt_{0.6}Ni_{0.4}$/PDA-rGO	NaOH	303	100	903	33.4	*J. Mater. Chem. A*, 2015, **3**, 23090
$Ni_{0.58}Pt_{0.42}$/graphene	NaOH	323	100	846	23.9	*J. Alloy. Compd.*, 2017, **695**, 3036

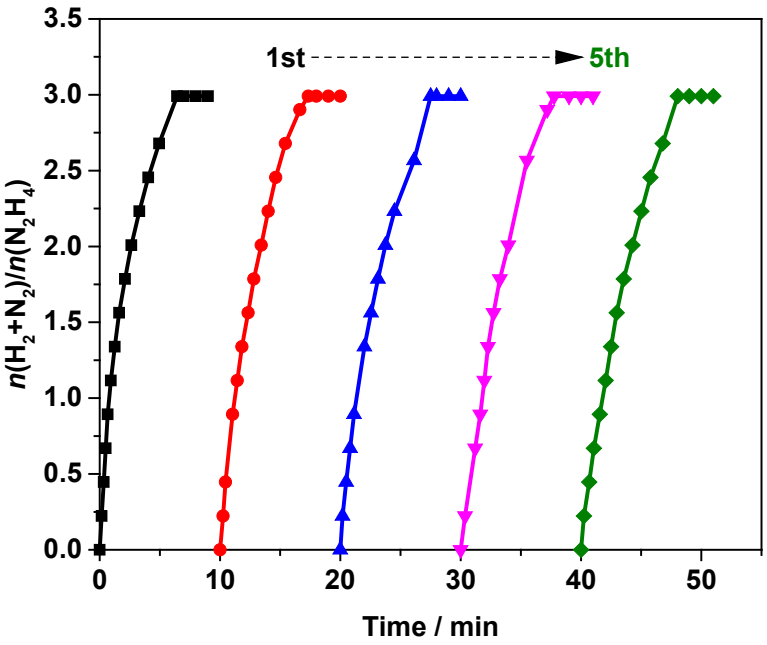

Fig. S7. Durability test of the $Pt_{0.2}Ni_{0.8}$ catalyst for complete decomposition of $N_2H_4 \cdot H_2O$ in 1 M NaOH at 50 °C. Additional aliquot of $N_2H_4 \cdot H_2O$ was introduced into the reaction vessel after the completion of the previous run.

Table S3. The pH values of 0.1 M PBS with different concentrations of N_2H_4.

***c*(N_2H_4) / M**	**0**	**0.1**	**0.3**	**0.5**
pH	7.2	8.6	9.2	9.5