Bimetallic Ni−Pt nanoparticles immobilized on mesoporous N-doped carbon as highly efficient catalysts for complete hydrogen evolution from hydrazine borane

Wei Wang[a], Xiaoling Hong[a], Qilu Yao[a], Zhang-Hui Lu*[a]

[a]*Institute of Advanced Materials (IAM), College of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang, 330022, P.R. China*

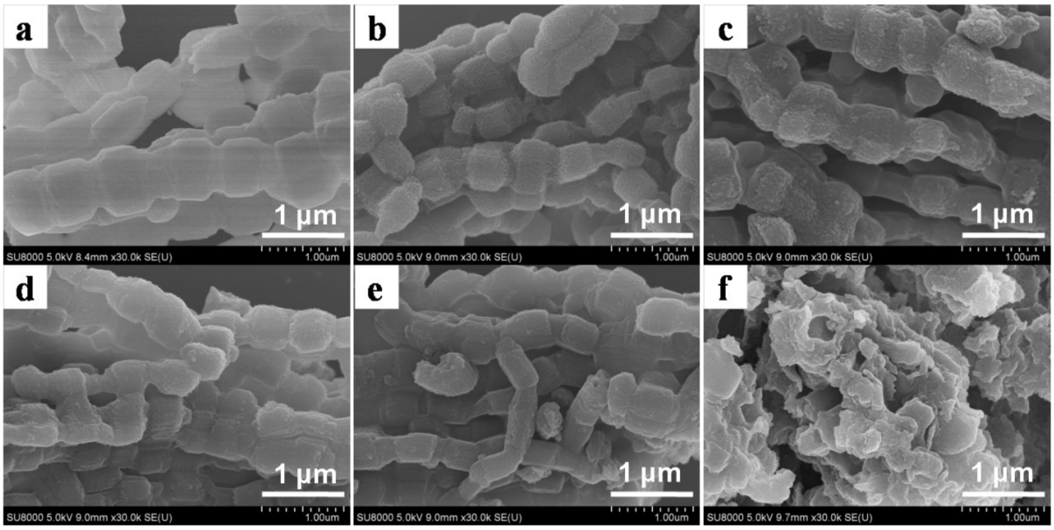

Figure S1. SEM images of (a) SBA-15, (b) MNC-500, (c) MNC-600, (d) MNC-700, (e) MNC-800, and (f) MNC-900.

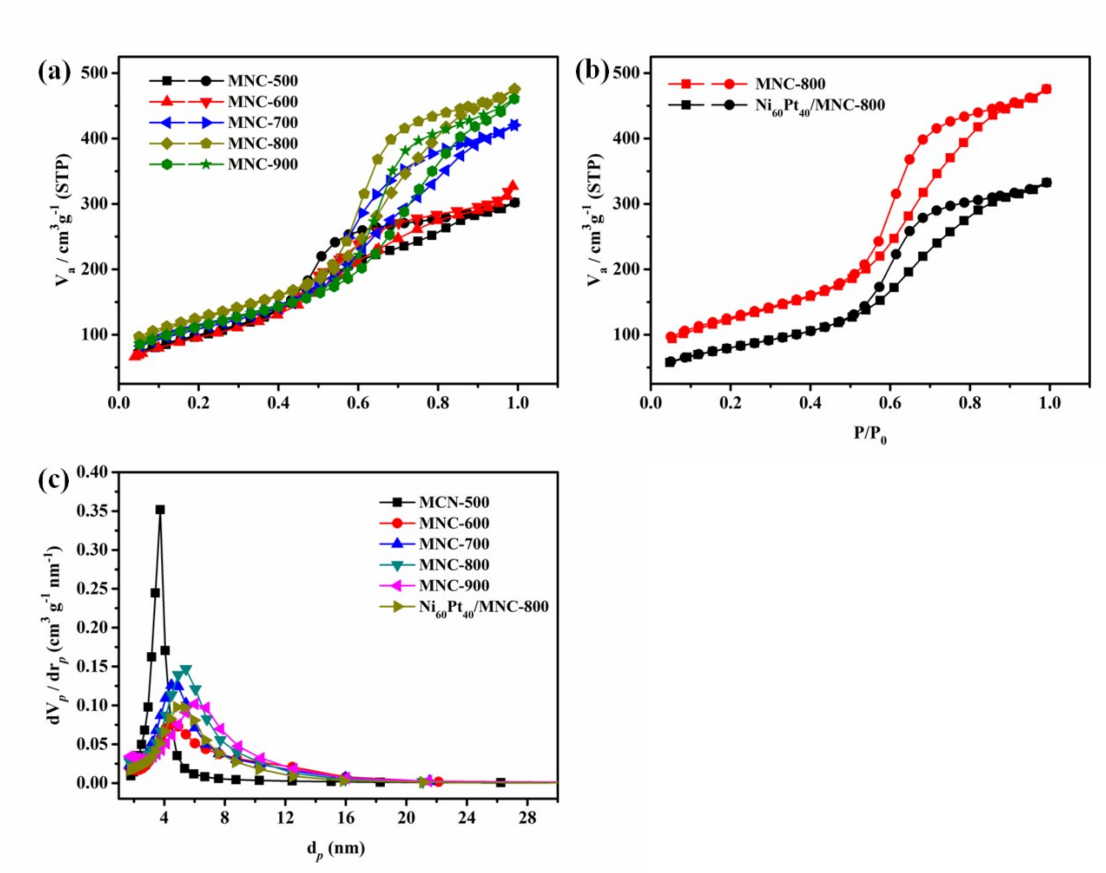

Figure S2. Nitrogen adsorption-desorption isotherms of (a) MNC-500, MNC-600, MNC-700, MNC-800, MNC-900, (b) $Ni_{60}Pt_{40}$/MNC-800; (c) the corresponding pore size distribution.

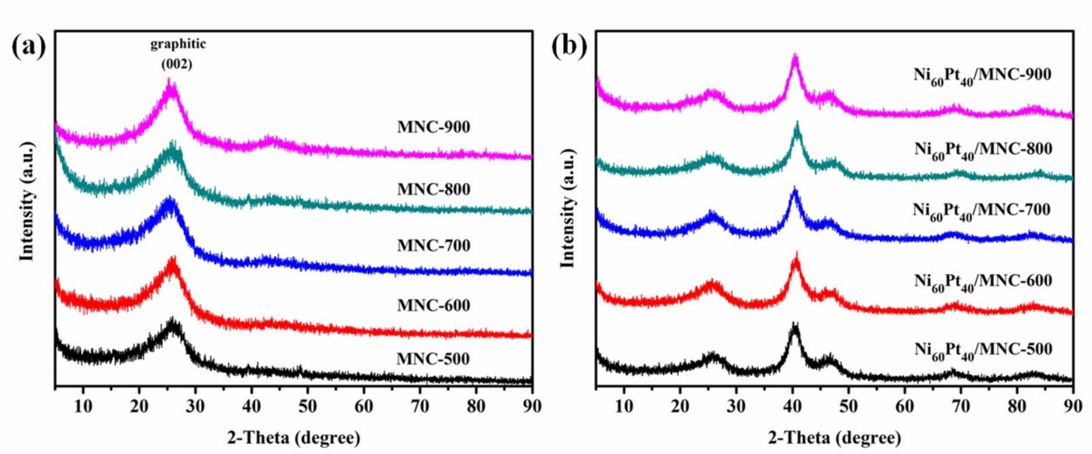

Figure S3. XRD patterns of (a) MNC-500, MNC-600, MNC-700, MNC-800, and MNC-900; and (b) $Ni_{60}Pt_{40}$/MNC-500, $Ni_{60}Pt_{40}$/MNC-600, $Ni_{60}Pt_{40}$/MNC-700, $Ni_{60}Pt_{40}$/MNC-800, and $Ni_{60}Pt_{40}$/MNC-900 NCs.

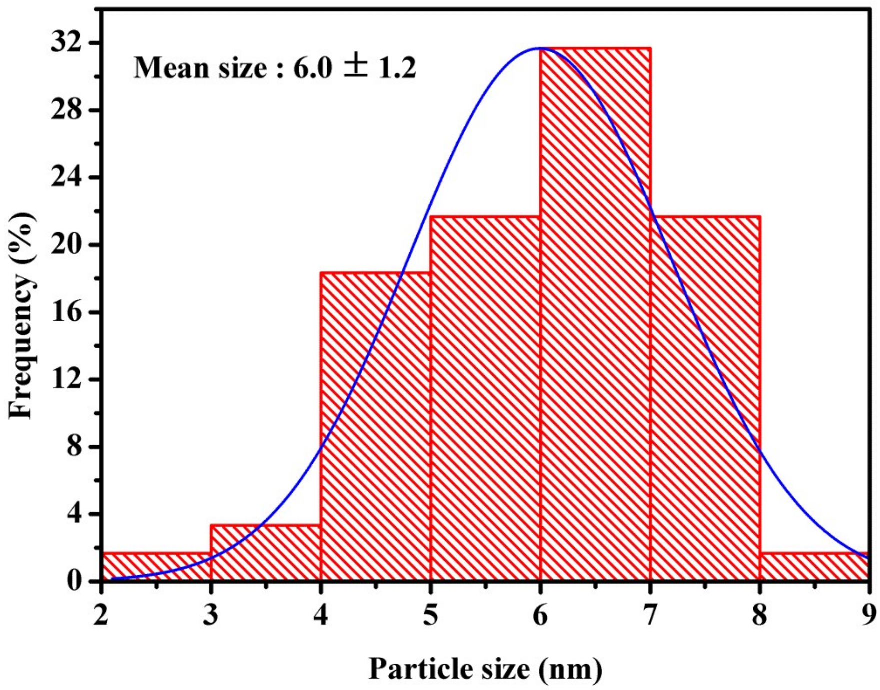

Figure S4. The corresponding distribution size histogram of $Ni_{60}Pt_{40}$/MNC-800.

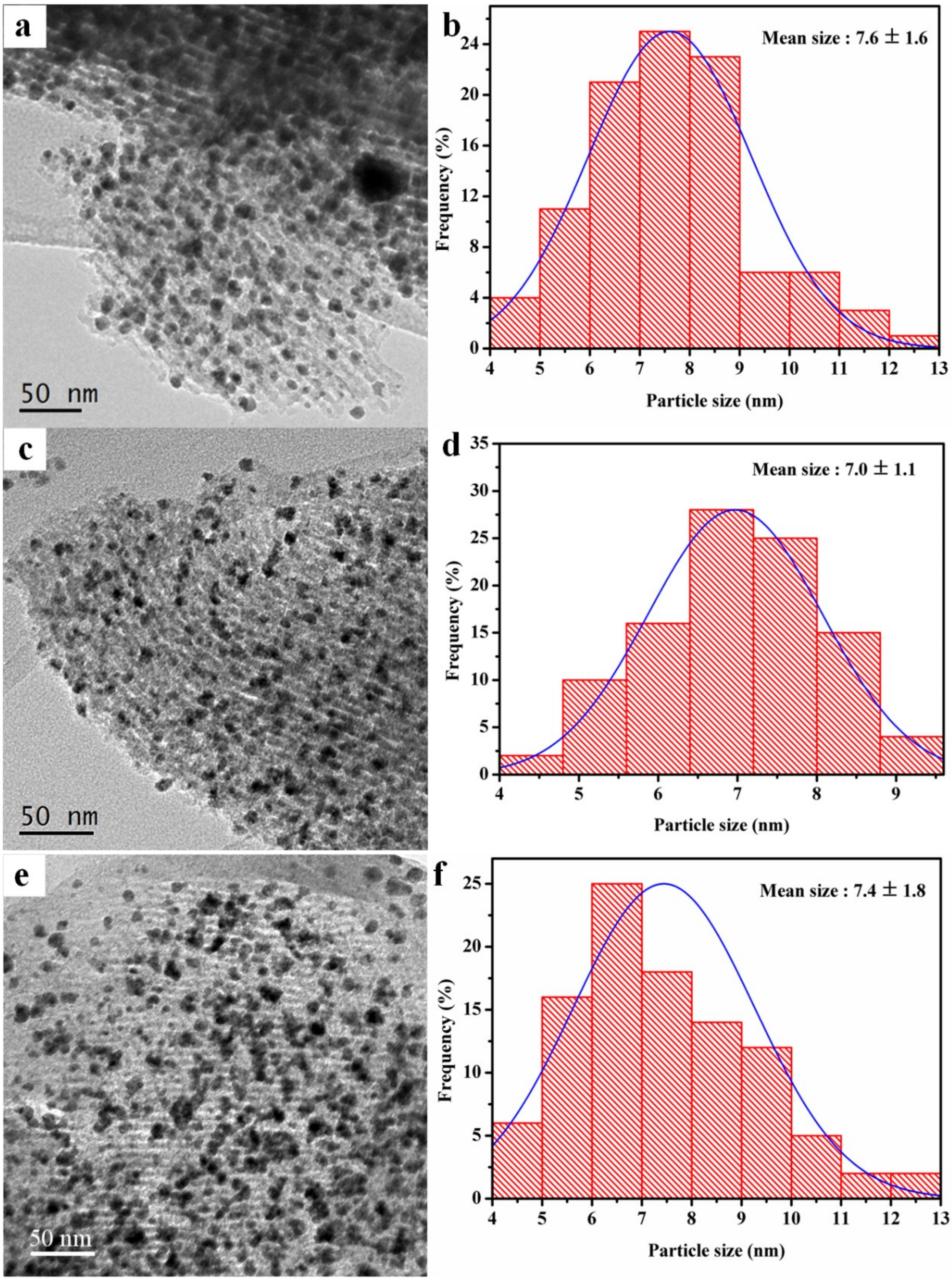

Figure S5. Representative TEM images and the corresponding distribution size histograms of (a and b) $Ni_{60}Pt_{40}$/MNC-600, (c and d) $Ni_{60}Pt_{40}$/MNC-700, and (e and f) $Ni_{60}Pt_{40}$/MNC-900.

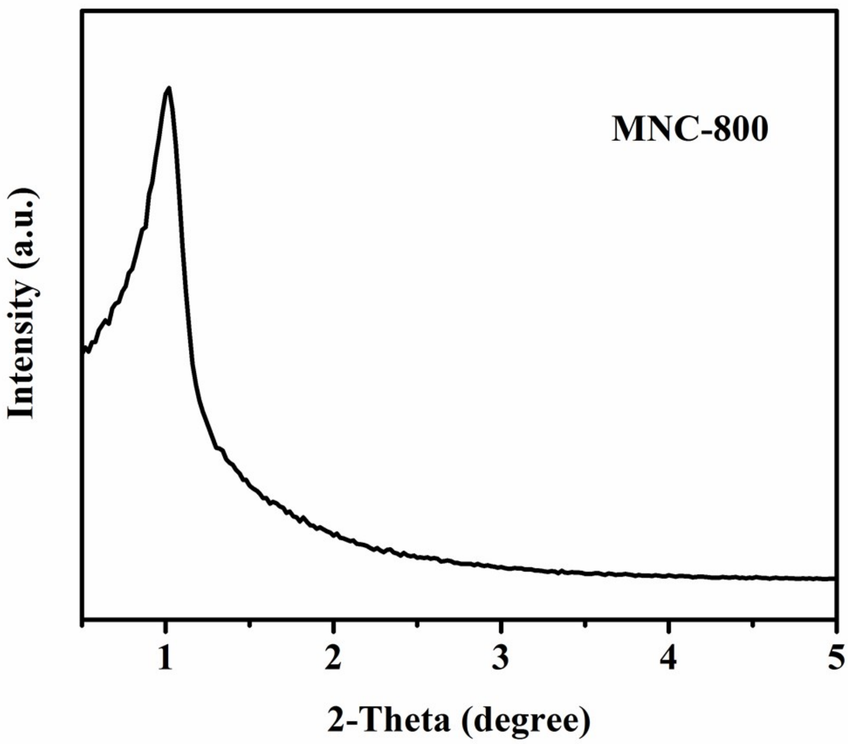

Figure S6. Low-angle XRD pattern of MNC-800.

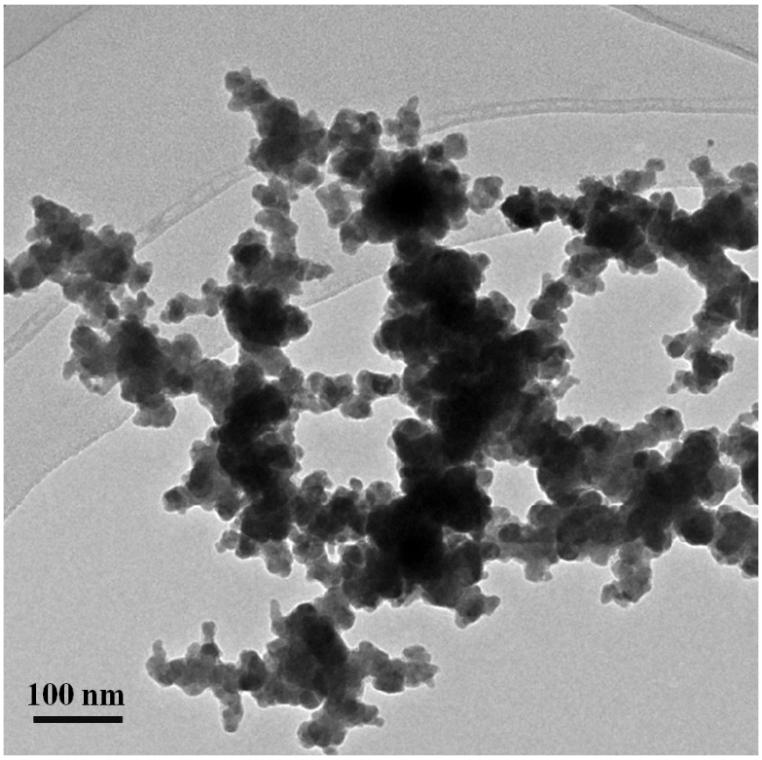

Figure S7. Representative TEM image of MNC-free $Ni_{60}Pt_{40}$ NPs.

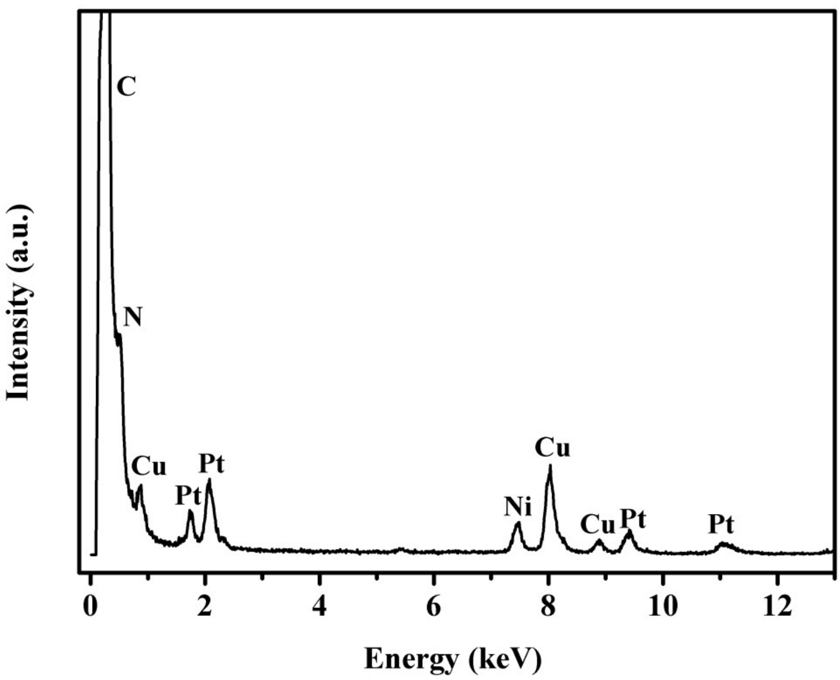

Figure S8. EDX spectrum of $Ni_{60}Pt_{40}$/MNC-800 NCs. The Cu signal originates from Cu grid.

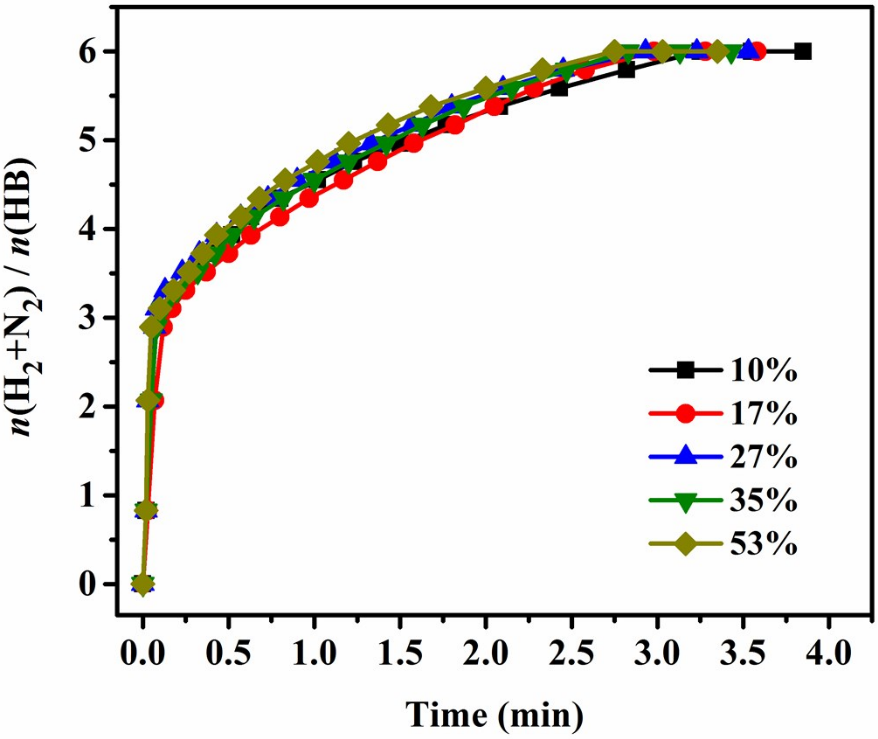

Figure S9. Time course plots for hydrogen generation from HB (200 mM, 5 mL) catalyzed by $Ni_{60}Pt_{40}$/MNC-800 NCs (n_{Pt+Ni}/nHB = 0.1) with different metal loadings at 298 K.

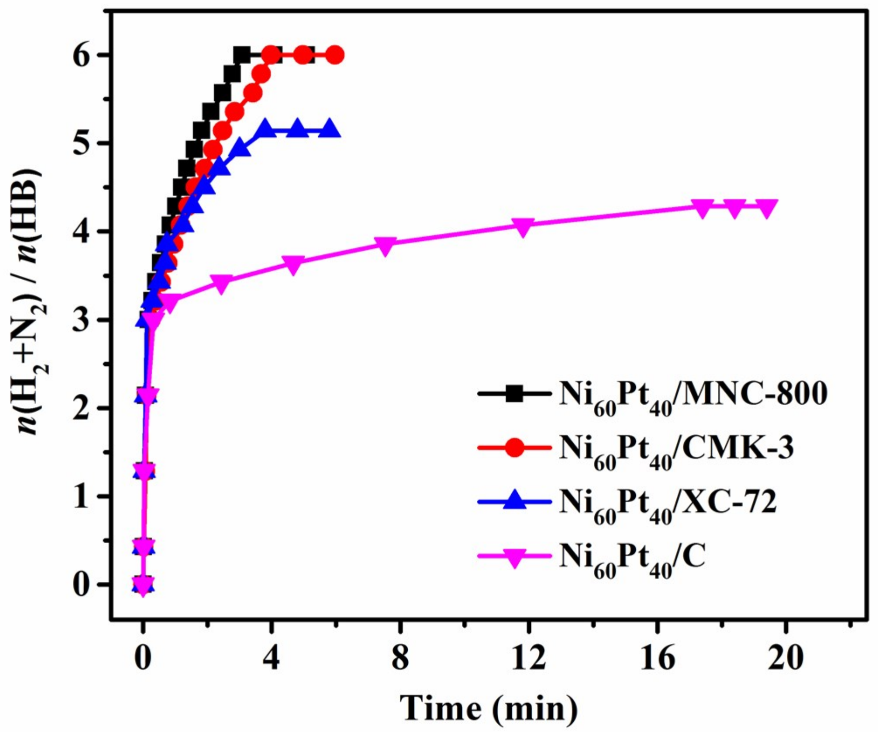

Figure S10. Time course plots for hydrogen generation from HB (200 mM, 5 mL) catalyzed by $Ni_{60}Pt_{40}$/MNC-800, $Ni_{60}Pt_{40}$/CMK-3, $Ni_{60}Pt_{40}$/XC-72, and $Ni_{60}Pt_{40}$/C NCs (n_{Pt+Ni}/nHB = 0.1) at 298 K.

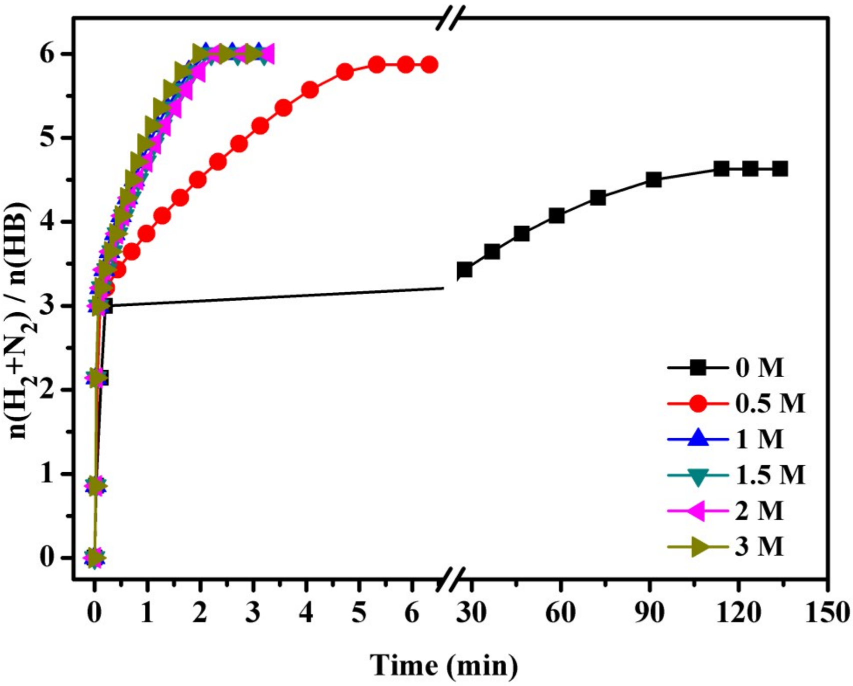

Figure S11. Time course plots for hydrogen generation from HB (200 mM, 5 mL) catalyzed by $Ni_{60}Pt_{40}$/MNC-800 NCs (n_{Pt+Ni}/nHB = 0.1) with different molar concentration of NaOH at 298 K.

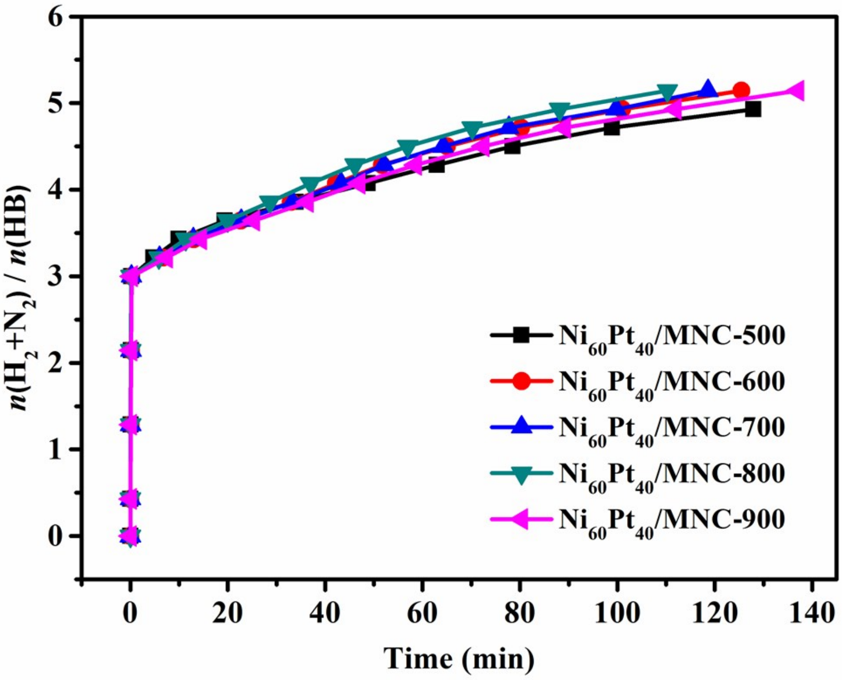

Figure S12. Time course plots for hydrogen generation from HB (200 mM, 5 mL) catalyzed by $Ni_{60}Pt_{40}$/MNC-500, $Ni_{60}Pt_{40}$/MNC-600, $Ni_{60}Pt_{40}$/MNC-700, $Ni_{60}Pt_{40}$/MNC-800, and $Ni_{60}Pt_{40}$/MNC-900 NCs (n_{Pt+Ni}/nHB = 0.1) without NaOH at 298 K.

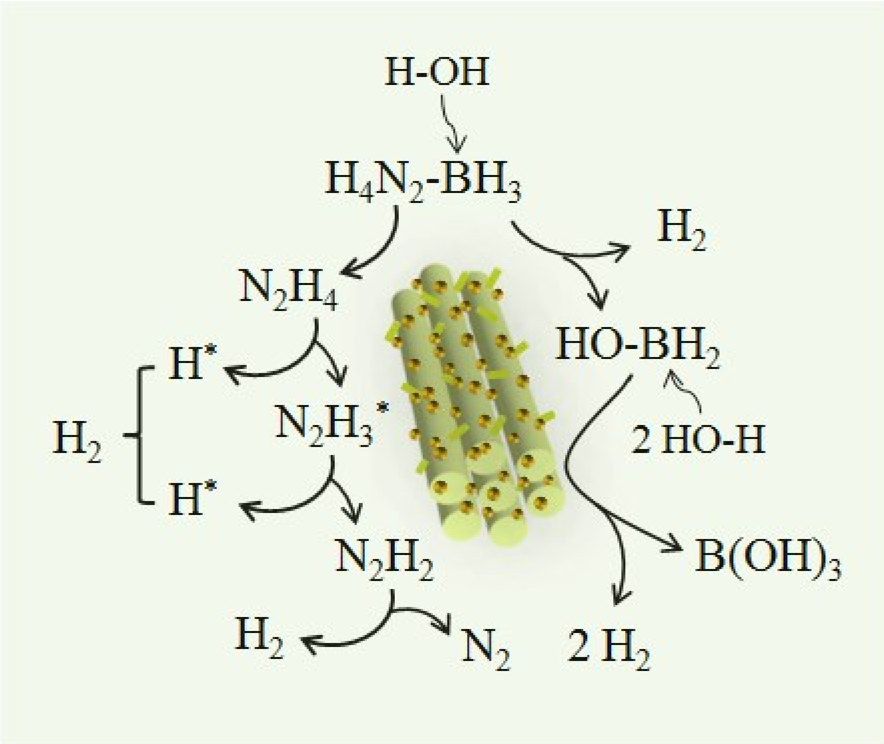

Figure S13. Schematic representation of H_2 generation from HB over $Ni_{60}Pt_{40}$/MNC-800 catalysts.

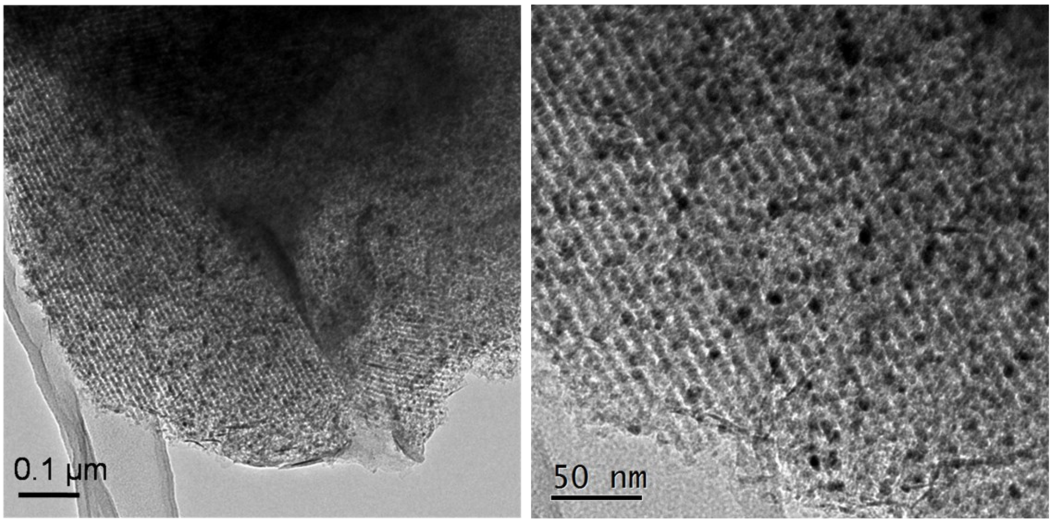

Figure S14. TEM images of the $Ni_{60}Pt_{40}$/MNC-800 NCs after the reusability test.

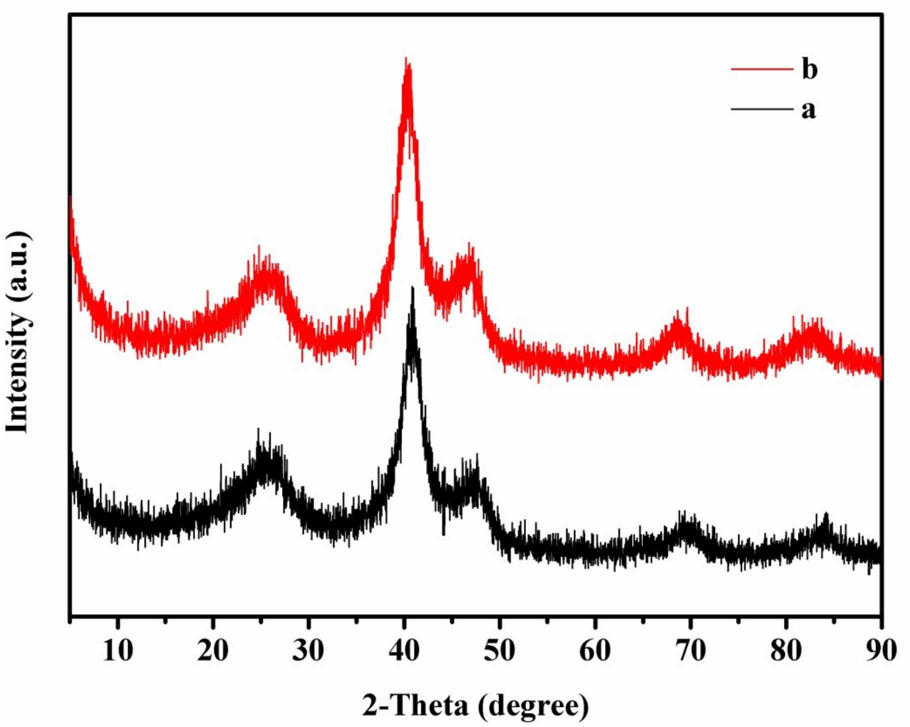

Figure S15. Powder XRD patterns of (a) fresh synthesized $Ni_{60}Pt_{40}$/MNC-800 NCs and (b) the $Ni_{60}Pt_{40}$/MNC-800 NCs after the durability and reusability test.

Table S1. Texture Parameters of MNC-500, MNC-600, MNC-700, MNC-800, MNC-900 and $Ni_{60}Pt_{40}$/MNC-800.

sample	S_{BET} (m^2 g^{-1})	pore volume (cm^3 g^{-1})	pore size (nm)
MNC-500	354	0.47	4.44
MNC-600	364	0.51	5.56
MNC-700	385	0.65	5.78
MNC-800	438	0.74	5.82
MNC-900	396	0.71	6.49
$Ni_{60}Pt_{40}$/MNC-800	289	0.51	5.78

Table S2. Element analysis of MNC-500, MNC-600, MNC-700, MNC-800, and MNC-900.

Sample	N wt%	C wt%	C/N mole ratio
MNC-500	18.46	61.70	3.85
MNC-600	18.07	65.90	4.17
MNC-700	13.62	71.82	6.25
MNC-800	9.75	73.02	9.09
MNC-900	8.67	78.26	10.52

Table S3. The catalysts composition determined by inductively coupled plasma atomic emission spectroscopic (ICP-AES).

Catalysts	Ni (wt%)	Pt (wt%)	Ni/Pt initial composition	Ni/Pt final composition
Ni/MNC-800	9.2	-	-	-
$Ni_{80}Pt_{20}$/MNC-800	7.0	6.1	80:20	79:21
$Ni_{70}Pt_{30}$/MNC-800	6.2	9.0	70:30	69:31
$Ni_{60}Pt_{40}$/MNC-800	5.3	11.8	60:40	60:40
$Ni_{50}Pt_{50}$/MNC-800	4.3	14.4	50:50	50:50
$Ni_{40}Pt_{60}$/MNC-800	3.4	16.9	40:60	40:60
$Ni_{30}Pt_{70}$/MNC-800	2.5	19.4	30:70	30:70
Pt/MNC-800	-	26.2	-	-
$Ni_{60}Pt_{40}$	31.6	68.4	60:40	61:39
$Ni_{60}Pt_{40}$/MNC-800 after five cycles	5.2	11.7	60:40	60:40

Table S4. The relationship between the performance of the catalyst and the C/N mole ratio and the mean particle size of the metal particles.

Sample	C/N mole ratio	Mean particle size / nm	TOF / h^{-1} (298K)
$Ni_{60}Pt_{40}$/MNC-600	4.17	7.6	508
$Ni_{60}Pt_{40}$/MNC-700	6.25	7.0	882
$Ni_{60}Pt_{40}$/MNC-800	9.09	6.0	1111
$Ni_{60}Pt_{40}$/MNC-900	10.52	7.4	857

Calculation method for *TOF*:

The total turnover frequency (*TOF*) reported in this work is an apparent *TOF* value based on the number of metal atoms in catalyst, which is calculated from the equation as follow:

$$TOF = \frac{n_{H_2}}{n_{metal} \times t}$$

Where n_{H_2} is the mole number of generated H_2, n_{metal} is the mole number of metal (Ni and Pt) in catalyst and t is the completed reaction time in hour.