Electronic Supplementary Information

Trimetallic NiFePd nanoalloy catalysed hydrogen generation from alkaline hydrous hydrazine and sodium borohydride at room temperature

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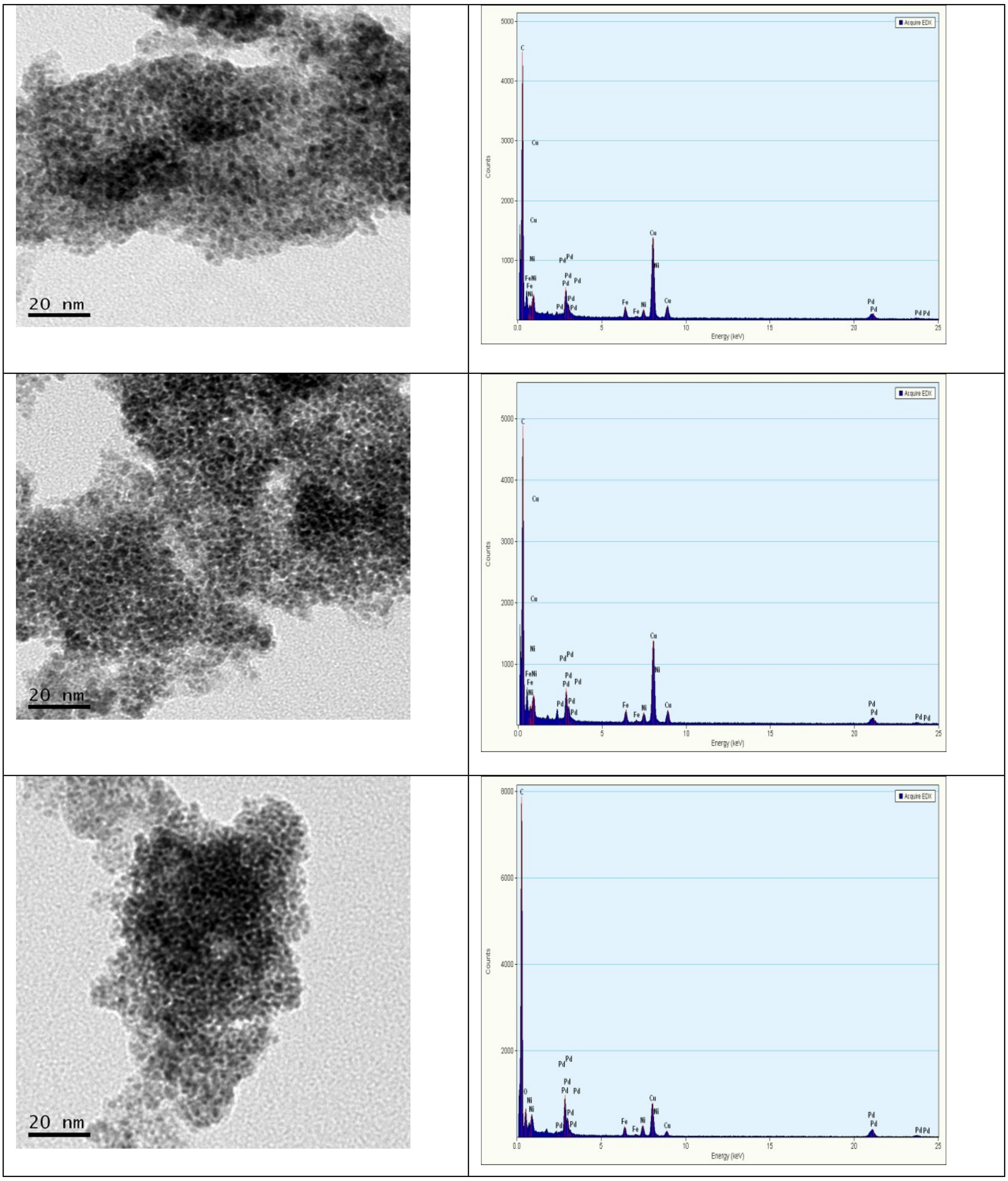

Fig. S1 EDX analysis of $Ni_{30}Fe_{30}Pd_{40}$ NPs shows uniform composition throughout the sample.

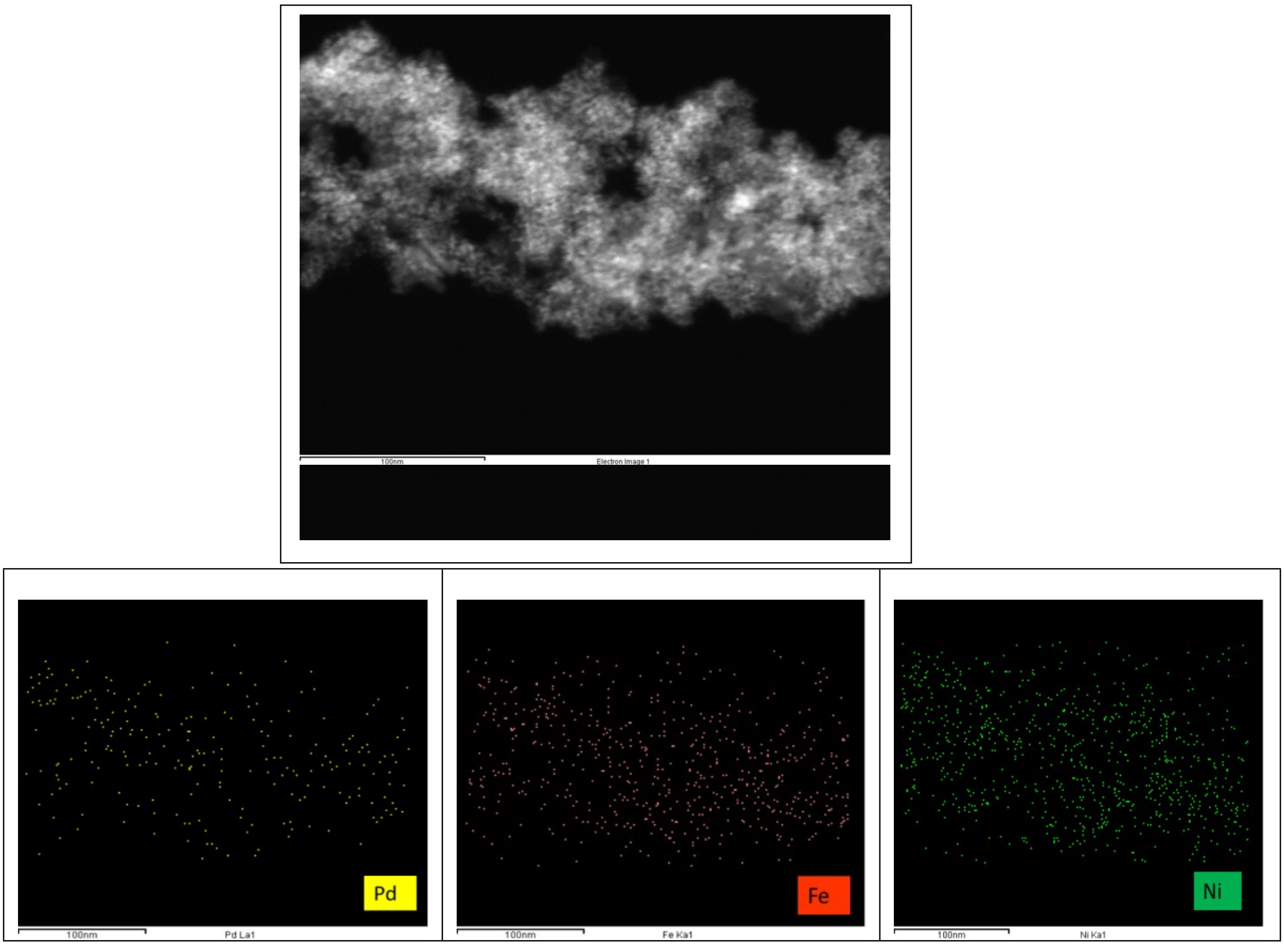

Fig. S2 HAADF-STEM image of $Ni_{30}Fe_{30}Pd_{40}$ NPs; corresponding map-scan profiles of Pd, Fe and Ni are shown. These confirm the uniform composition of the NPs.

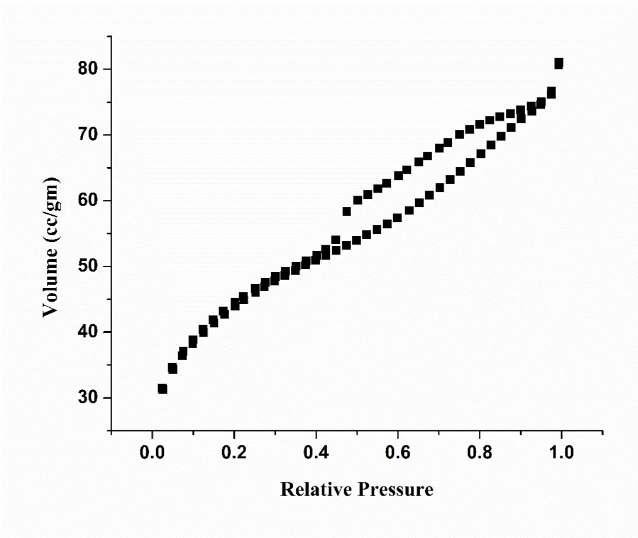

Fig. S3 N_2 adsorption/desorption isotherms of the trimetallic $Ni_{30}Fe_{30}Pd_{40}$ NPs having surface area of 156 m^2g^{-1}.

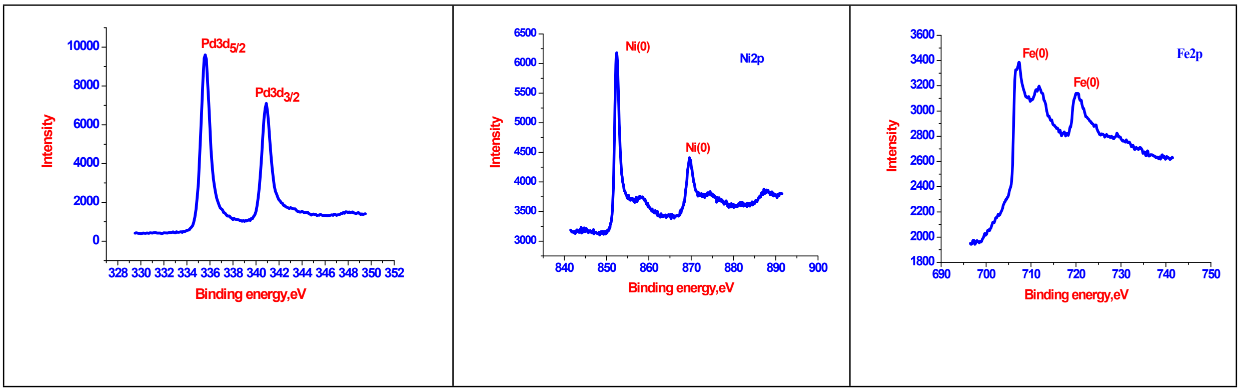

Fig. S4 XPS spectra of $Ni_{30}Fe_{30}Pd_{40}$ NPs after 10mins of Ar sputtering

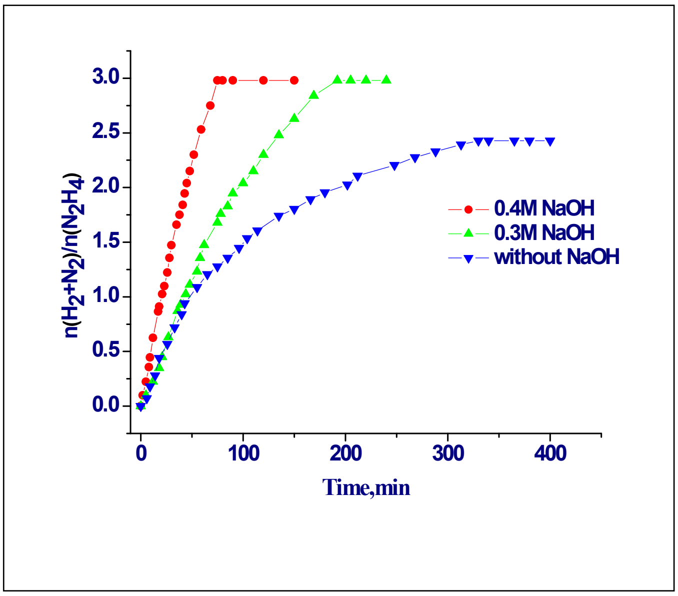

Fig. S5 NaOH variation in the decomposition of 10 mL of 0.5 M hydrous hydrazine (hydrazine: catalyst =10:1) using $Ni_{30}Fe_{30}Pd_{40}$ NPs at 298K.

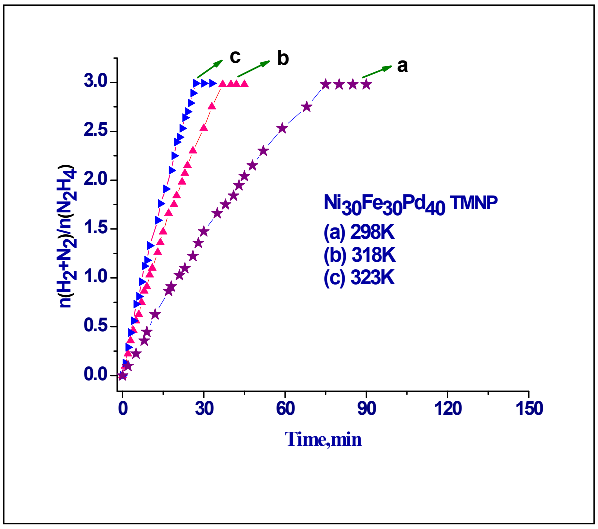

Fig. S6 Time profile for decomposition of 10 ml of 0.5M hydrous hydrazine (hydrazine: catalyst =10:1) using $Ni_{30}Fe_{30}Pd_{40}$ NPs at different temperatures.

Activation Energy graph

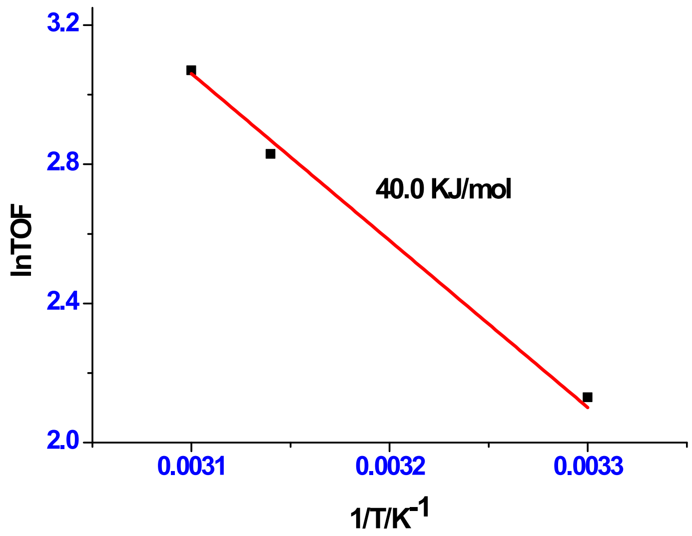

Fig. S7 Arrhenius plot for decomposition of hydrazine catalyzed by $Ni_{30}Fe_{30}Pd_{40}$ NPs.

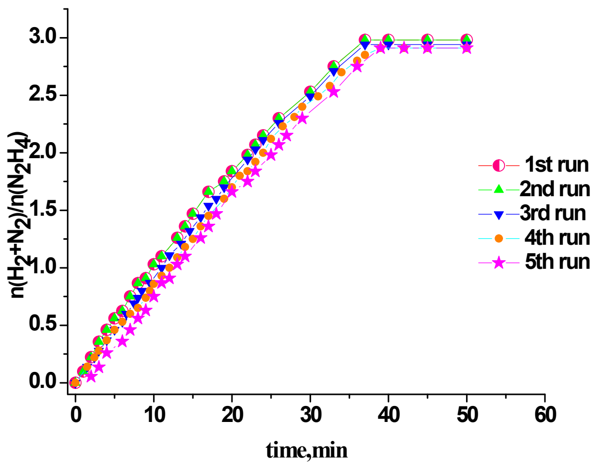

Fig S8 Recycle test of $Ni_{30}Fe_{30}Pd_{40}$ NPs for the decomposition of 10 ml of 0.5M hydrous hydrazine (hydrazine: catalyst =10:1) in 0.4 M NaOH media at 318K. The results show no significant decrease in catalytic activity of $Ni_{30}Fe_{30}Pd_{40}$ TMNPs over 5 cycles.

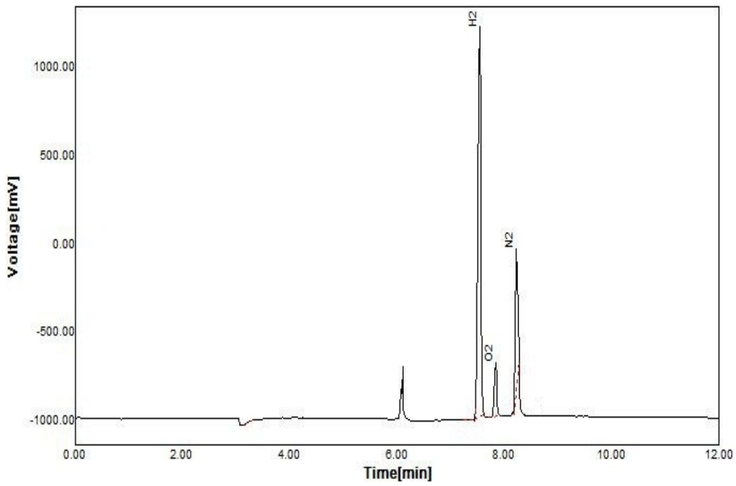

Fig. S9 GC-TCD spectrum of the evolved gas released from complete decomposition of hydrous hydrazine over $Ni_{30}Fe_{30}Pd_{40}$ NPs (hydrazine: catalyst =10:1) in alkaline media at 298K. Small amount of O_2 comes from the air at the time of gas collection.

<u>**TOF calculation method**</u>

The $TOF_{initial}$ is calculated from the formula[1]

$$TOF_{initial} = \frac{P_{atm}V_{H2+N2} / RT}{3n_{metal}t}$$

Where $TOF_{initial}$ is the initial turnover frequency, P_{atm} is the atmospheric pressure, V_{H2+N2} is the volume of the generated gas (H_2+N_2) when the conversion reaches 50%, R is the universal gas constant, T is the room temperature (298 K), n_{metal} is the mole number of metal catalyst, and t is the reaction time when the conversion reaches 50%.

The relationship of the temperature and the initial rate (conversion <50%)[2] followed Arrhenius behaviour. The Arrhenius' reaction rate equation[2] can be written as follows:

$$\ln TOF = \ln A - E_a/RT$$

Where A is the reaction constant

References:

1. L. Yu, X. S. Zhang and L. Y. Yu, *Adv. Mater. Res.* 2012, 396-398,130.
2. A. Boddien, D. Mellmann, F. Gärtner, R. Jackstell, H. Junge, P. J. Dyson, G. Laurenczy, R. Ludwig and M. Beller, *Science*, 2011, 333, 1733.

Table S1: Activities in-terms of TOF values of different nanocatalysts tested for hydrogen generation from the decomposition of $N_2H_4.H_2O$ solution

Catalyst	**Temp (K)**	**Reaction time(h)**	**Selectivity for H_2 (%)**	**$TOF_{initial}$**	**References**
Ni/Al_2O_3	303	1.167	93	2.2 h^{-1}	[43]
$Ni_{0.60}Pd_{0.40}$	323	3.167	82	3.8 h^{-1}	[30]
$Ni_{0.60}Pd_{0.40}$	298	1.0	100	9.15 h^{-1}	[9]
NiFe(1:1)	343	3.167	100	4.2 h^{-1}	[40]
$Ni_{0.6}Fe_{0.4}Mo$	323	0.250	100	28.8 h^{-1}	[14]
$Ni\text{-}CeO_2$	323	0.25	100	51.6 h^{-1}	[44]
$Ni_{0.93}Pt_{0.07}$	298	3.167	100	2.8 h^{-1}	[29]
$Ni_{0.95}Ir_{0.05}$	298	6.5	100	2.2 $h^{-}1$	[28]
RhNi@graphene	298	0.817	100	13.7 h^{-1}	[33]
$Ni_{30}Fe_{30}Pd_{40}$	**323**	**0.61**	**100**	**21.5 h^{-1}**	**This work**

Table S2: Activities in terms of rate of gas generation of different nanocatalysts tested for hydrogen generation from the hydrolysis of alkaline sodium borohydride

Catalyst	Temp (^0C)	$NaBH_4$	NaOH (wt%)	Catalyst Activity (mL H_2 $min^{-1}g$ $catalyst^{-1}$)	References
5 wt.% Ru on IRA-400	32.5	7.5 wt.%	1	606	[66]
Ni_2B	20	0.2 g in 20ml of $NaBH_4$	10	18.3	[67]
Co_2B	20	0.2 g in 20ml of $NaBH_4$ solution	10	468	[68]
Ni–Co–B	28	0.16 g of 5 ml of $NaBH_4$ solution	15	2608	[69]
$Pt/LiCoO_2$	22	20 wt.%	10	3100	[70]
$Pt\text{-}Ru/LiCoO_2$	25	5 wt.%	5	2400	[71]
$Pt/LiCoO_2$	20	10 wt.%	10	1250	[72]
Rh/TiO_2	23	15 wt.%	5	210	[73]
Co-B/Pd	30	20 wt.%	4	2875	74]
Co-Ni-B	25	0·95 wt.%	1	1175	[75]
Co-Fe-B	25	0·95 wt.%	1	1300	[75]
Co-Cu-B	25	0·95 wt.%	1	2210	[75]
Co-Cr-B	25	0·95 wt.%	1	3400	[75]
Co-Mo-B	25	0·95 wt.%	1	2875	[75]
$Pt/LiCoO_2$	22	20 wt.%	10	3100	[76]
$Ni_{40}Fe_{40}Pd_{20}$	25	0.19 g in 10ml of $NaBH_4$ solution	20	3343	**This work**

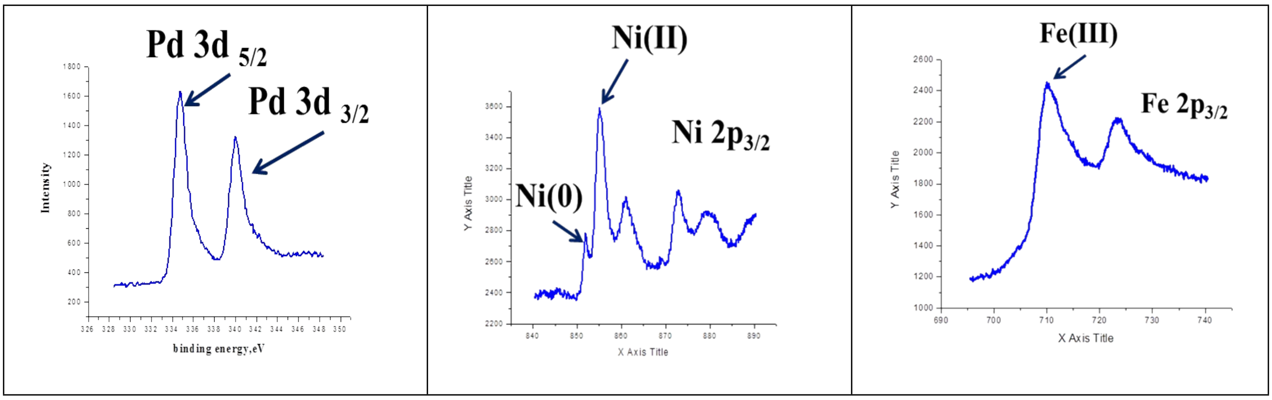

Fig. S10 XPS spectra of $Ni_{40}Fe_{40}Pd_{20}$ NPs.