Electronic Supplementary Information

Insights into the nitridation of zero-valent iron nanoparticles for the facile synthesis of iron nitride nanoparticles

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1. Details of the experimental conditions

The details of different experiments carried out and the obtained phase are tabulated in Table S1.

Strategy	Parameters		Phase
Solvothermal method (Ethylenediamine, Diethylenetryamine)	Nitridation temp: 180 ˚C Duration: 24 h		Fe_3O_4
Gas diffusion method (N_2 gas)	Flow rate: 100 ml/min Duration: 4 h 600 ˚C		Fe_2O_3
Gas diffusion method (NH_3 gas)	Flow rate: 100 ml/min Duration: 4 h Nitridation temp:	300 ˚C	Fe^0
		400 ˚C	Fe^0
		500 ˚C	$Fe^0 + \varepsilon\text{-}Fe_3N$
		600 ˚C	$\varepsilon\text{-}Fe_3N$
		700 ˚C	$\varepsilon\text{-}Fe_3N + \gamma'\text{-}Fe_4N$
		800 ˚C	$\gamma'\text{-}Fe_4N$

Table S1 *Experimental conditions of the nitridation process and obtained phases.*

2. XRD pattern ZVINPs after hydrogen reduction process

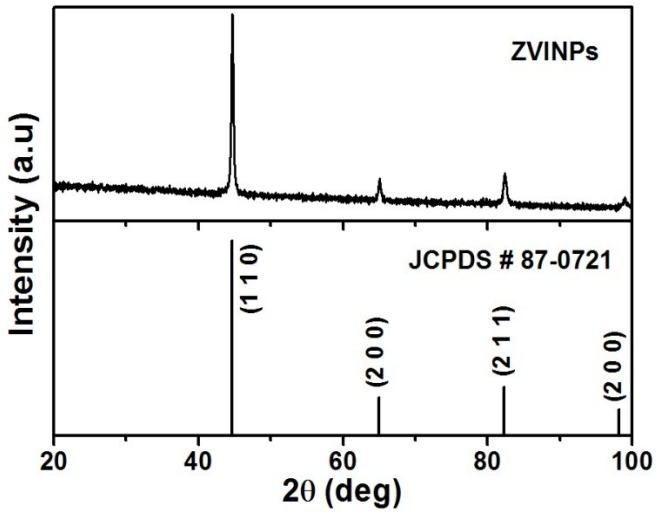


Fig. S1 *XRD pattern of ZVINPs that dried under hydrogen ambience*

3. Cell and refinement parameters

Cell parameters of ε-Fe_3N and γ'-Fe_4N phases that obtained from Rietveld refinement analysis and the corresponding refinement parameters are tabulated in Table S2

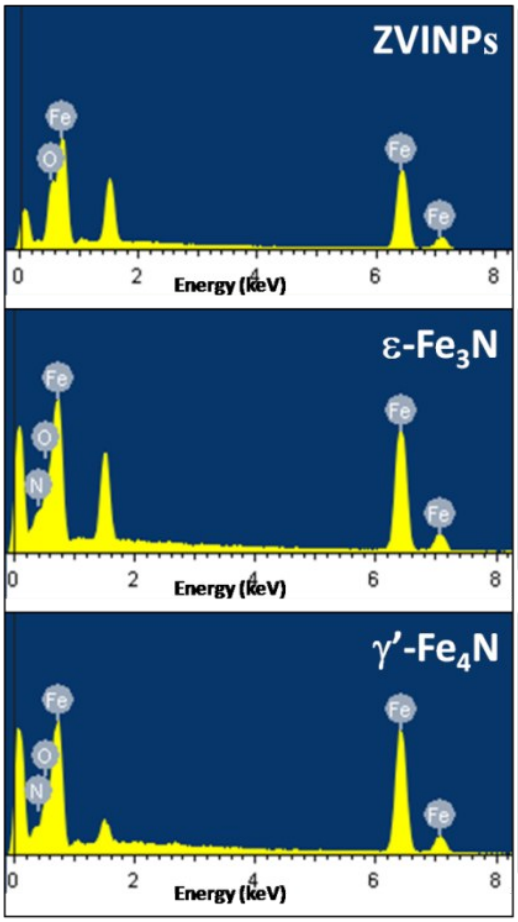
Parameters	**ε-Fe_3N**	**γ'-Fe_4N**
Space group	P312	Pm-3m
A	4.761306	3.800840
B	4.761306	3.800840
C	4.410150	3.800840
A	90	90
B	90	90
Γ	120	90
Volume	86.584	54.908
Atomic position	**(x, y, z)**	**(x, y, z)**
Fe[1]	(0.33905, 0.33942, 0.25424)	(0.50000, 0.00000, 0.00000)
Fe[2]		(0.50000, 0.50000, 0.50000)
N[1]	(0.33330, 0.66670, 0.50000)	(0.00000, 0.00000, 0.00000)
N[2]	(0.66670, 0.33330, 0.00000)	
Occupation no.	**Fe[1]**-0.7201, **N[1]**-0.1822, **N[2]**-0.1523.	**Fe[1]**-0.7201, **Fe[2]**-0.1822, **N[1]**-0.1523.
χ'	0.7950	0.8094
R_p	2.18	3.21
R_{wp}	2.63	4.02
R_{exp}	5.81	8.71

Table S2 *Unit cell and refinement parameters of ε-Fe_3N and γ'-Fe_4N phases.*

The average The average particle size of these nitride phases is estimated as ~ 50 nm; while their crystallite size is about 38.3 and 28.8 nm for ε-Fe_3N and γ'-Fe_4N respectively that deduced using Scherrer's formula.

4. Elemental analysis using EDX

Elemental analysis of ZVINPs and iron nitride phases was carried out using energy dispersive X-ray spectroscopy and the corresponding spectrum and the atomic percentage of the compositions are given in Fig. S2.



Element	Atomic %
Fe	53.99
O	46.01

Element	Atomic %
Fe	40.50
N	32.03
O	27.47

Element	Atomic %
Fe	47.43
N	24.04
O	28.54

Fig. S2 *EDX spectrum of ZVINPs, ε -Fe_3N and γ'-Fe_4N phases, and atomic percentage of elements present in the respective phase.*

The oxygen peak present in all samples represents the adsorbed oxygen species on the surface of the particles whereas the extra peak at 1.5 keV of all samples represents the aluminum, which is from the aluminum substrate used for sample preparation for FESEM analysis.

5. Chemical state analysis using XPS

The XPS full survey spectrum of ZVINPs as shown in Fig S3(a) confirms the presence of zero valent state iron. Similarly, Fig S3(b) and (c) shows the XPS survey spectrum of ε-Fe_3N and □'-Fe_4N phases respectively and confirms the characteristic compositional presence of the Fe and N in the respective phases. The observed peaks corresponding to the oxygen and carbon could be due to the adsorbed species on the surface of these nanoparticles, where it may be ascribed to the XPS technique, where it fundamentally analyzes the chemical composition of the substances on the surface of the particles within the depth of 10 nm.

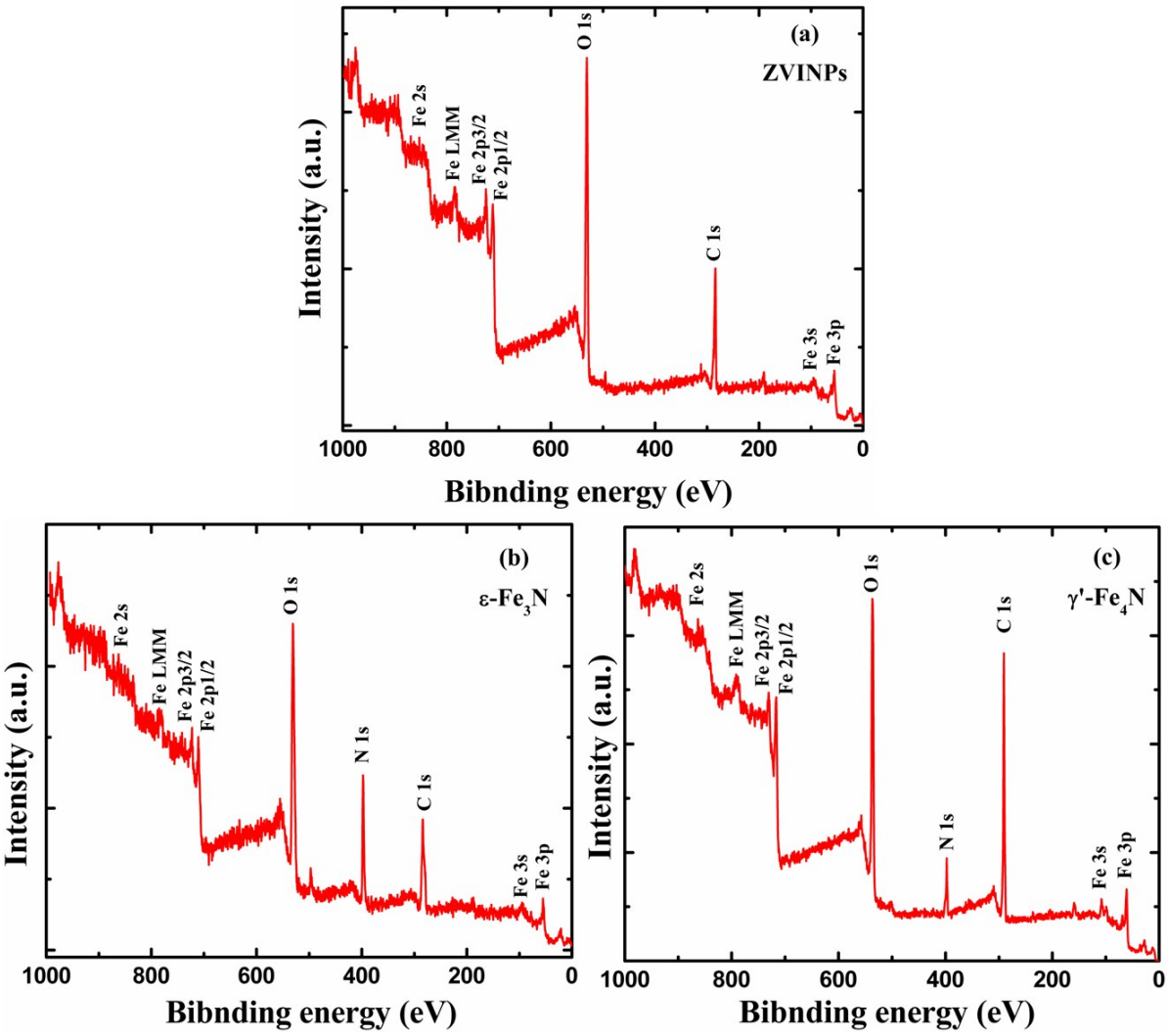


Fig. S3 *XPS full survey spectrum of (a) ZVINPs, (b) ε-Fe_3N and (c) γ'-Fe_4N phases.*

6. Temperature dependent magnetic properties of ZVINPs

The temperature dependent magnetization (zero field cooled and field cooled (ZFC-FC)) of ZVINPs in a constant applied field of 100 Oe is shown in Fig S4, which is obtained over the temperature range from 5 K to 300 K.

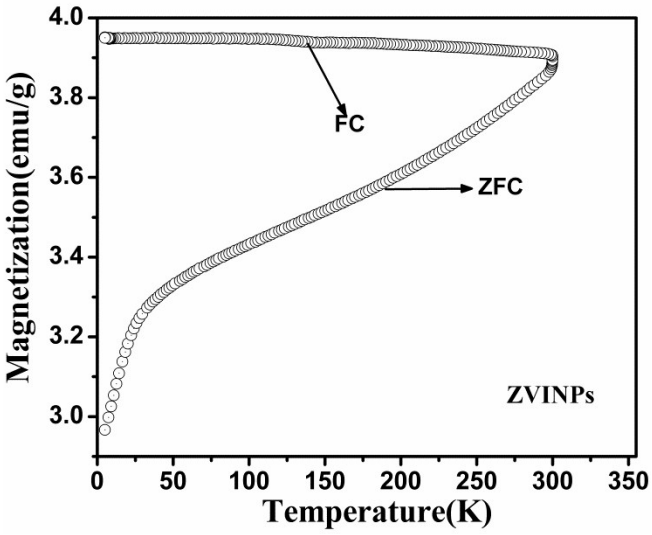


Fig. S4 *M-T (ZFC-FC) curve of ZVINPs at applied field of 100 Oe.*