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# Covalency, hybridization and valence state effects in nano- and micro-sized $ZnFe_2O_4$

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## SUPPLEMENTARY INFORMATION

Contents

**Table S1: Crystallite size estimated from Scherrer's formula in this work and previous work.**

| Annealing Temperature (°C) | Crystallite size (D), nm | |
|---|---|---|
| | This work | Previous work[1] |
| 300 | 21 | 10 |
| 400 | 21 | 12 |
| 500 | 21 | 16 |
| 600 | 26 | 15 |
| 800 | 48 | 21 |
| 1000 | 58 | 62 |
| 1200 | 62 | - |

**Table S2: Procedure to obtain precursor in this work and previous work.**

| Treatment | Thermal History | |
|---|---|---|
| | This work | Previous work[1] |
| Magnetic Stirring | 90°C, 2hrs | 85°C, 2hrs |
| Heating of viscous solution | 100-200°C, 6hrs | 100°C, Overnight |

**Explanation for Table S1 and Table S2**-It is clear from Table S1 and Table S2 that thermal history for obtaining precursor plays important role in determining crystallite size of zinc ferrite nanoparticle. This clearly envisages that mere controlling of annealing temperature not only provides control over particle size but thermal history also has important effect.

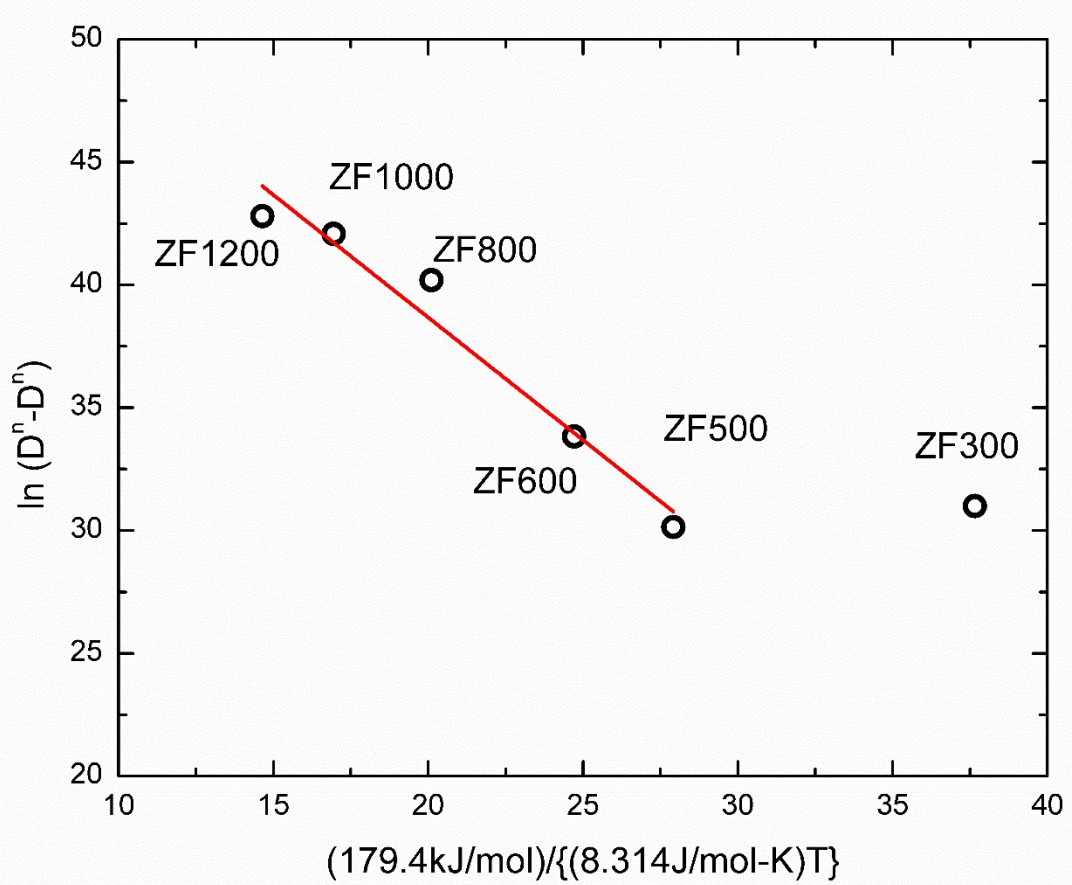


**Figure S1:** A linear fit between ln ($D^n$-$D_o^n$) and (Q/RT) depicting the kinematics of grain growth

**Explanation for Figure S1:** Graph between ln ($D^n$-$D_o^n$) and (Q/RT) was plotted according to phenomenological equation mention in ref 2. Values of n (10.26) and Q (179.4 kJ/mol) are adopted from ref 3. 8.314J/mol-K is the value of R gas constant. Value of $D_o$ is assumed the value of crystalline grain of precursor ZF000. In the figure, ZF300 and ZF500 exhibit almost same value of ln ($D^n$-$D_o^n$) as crystallite size of both materials are comparable. Crystallite size of ZF400 is slightly less than precursor, hence value of ln ($D^n$-$D_o^n$) could not be obtained for this material. Thus, it is clear that when nano-sized $ZnFe_2O_4$ are synthesized with similar thermal history from precursor, crystalline growth occurs only after 500°C.

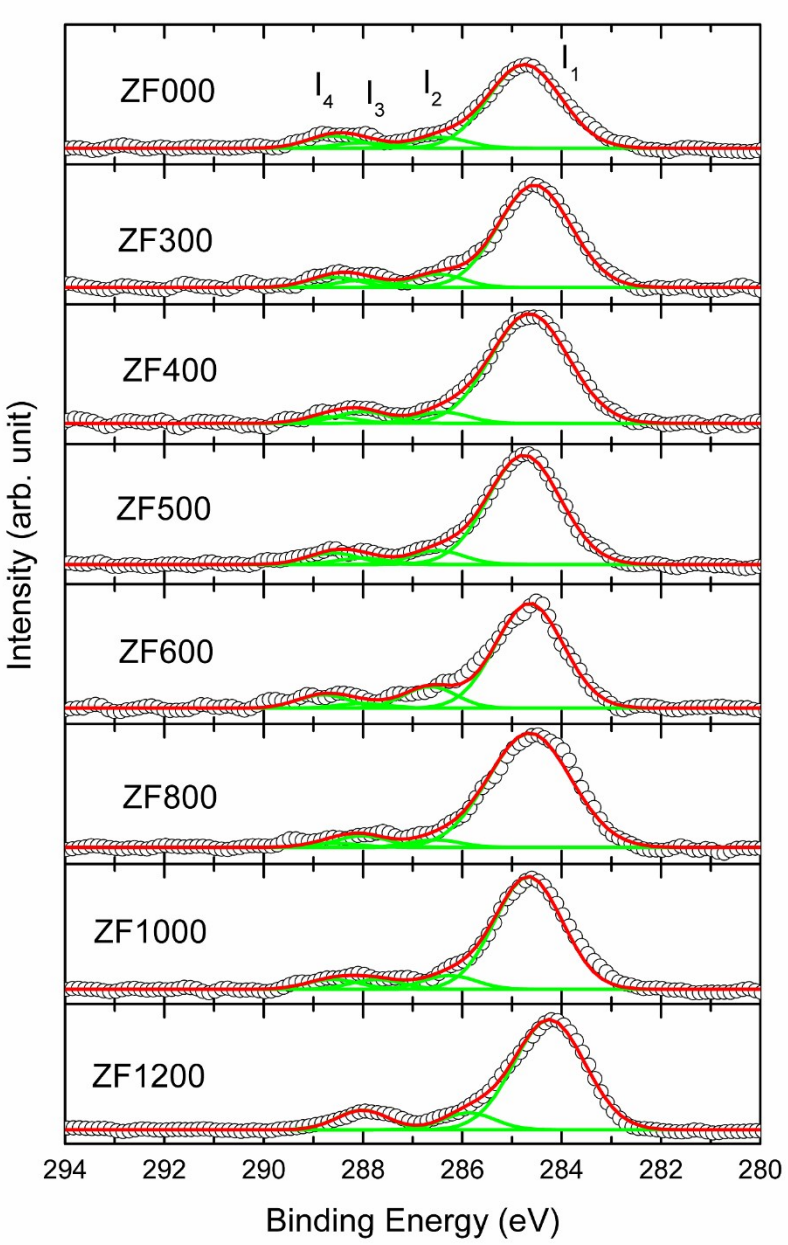


**Figure S2: C(1*s*) spectra for nano-sized zinc ferrite**

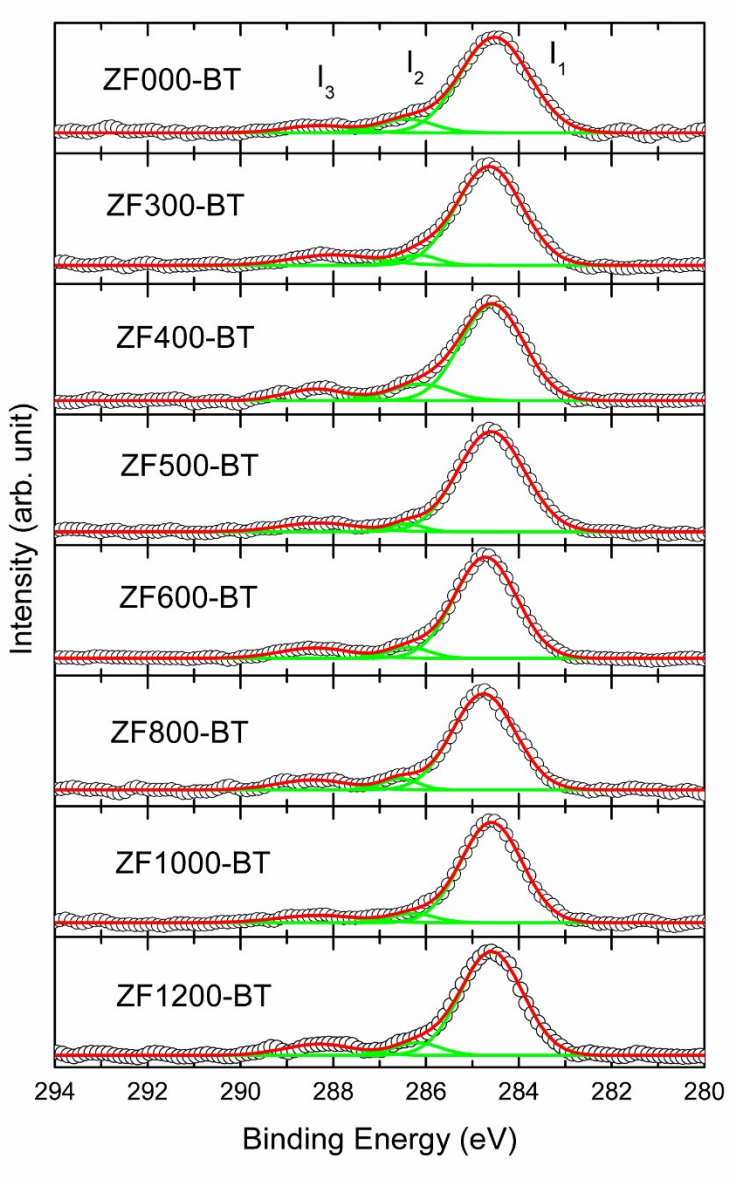


**Figure S3: C(1*s*) spectra for micro-sized zinc ferrite**

**Explanation for observed peaks in C1*s* spectra of nano- and micro-sized $ZnFe_2O_4$-** Presence of peaks $I_1$ (~284.6 eV), $I_2$ (~286.6 eV), $I_3$ (~288.0 eV) and $I_4$ (288.7 eV) is ascribed to the presence of C-C/C-H, C-O, O-C=O and O-C=O$^-$ bonds, respectively adsorbed at material surface[4,5]. Peak $I_4$ is absent in ZF1200 (Figure S2) and micro-sized $ZnFe_2O_4$ (Figure S3). This shows removal of few adsorbed species in effect of high temperature annealing.

**References**

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