Supplementary information

Negative capacitance switching in size-modulated Fe₃O₄ nanoparticles with spontaneous non-stoichiometry: confronting its generalized origin in non-ferroelectric materials

Souvik Bhattacharjee,[†] Anibrata Banerjee,[§] Nilesh Mazumder,^{†,‡} Kausik Chanda,[†] Saikat Sarkar,[†] and Kalyan Kumar Chattopadhyay^{*,†,§}

[†]Department of Physics, Jadavpur University, Kolkata – 700 032, India

[§]School of Materials Science and Nanotechnology, Jadavpur University, Kolkata – 700 032, India

[‡]Present Affiliation: Govt. College of Engineering & Ceramic Technology, Kolkata – 700 010, India

*E-mail: kalyan_chattopadhyay@yahoo.com; Fax: +91 33 2114 6584; Phone: +91 33 2413 8917.

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1. Experimental methods & enumeration

1.1. Synthesis procedure

Spherical magnetite nanoparticles (MNP's) of different size (Sample: S1-S5, in decreasing order) are prepared by a facile one-step solvothermal approach using analytical grade reagents (purchased from SIGMA-ALDRICH) without further purification. In a typical synthesis of 47 nm nanoparticles (S3) 1.50 g (5.55 mmol) FeCl₃. $6H_2O$ is mixed vigorously in a solution of 40 mL ethylene glycol and 40 mL diethylene glycol. Then, 0.35 g (1.52 mmol) hydrated disodium (+) tartrate is added; followed by 3.00 g (36.57 mmol) anhydrous sodium acetate and 3.50 g (0.58 mmol) polyethelene glycol (mol. wt. = 6000). This mixture is ultrasonicated for 10 minutes and magnetically stirred for an hour at 80°C to form a homogeneous dark yellow solution. Thereafter it is put into a teflon-lined stainless steel-autoclave with 100 mL capacity and maintained at 185°C for 12 h. After natural cooling, the black product is precipitated with ethanol followed by thorough centrifugation, washing (in deionized water & ethanol) and vacuum-drying at 65°C to acquire fine Fe₃O₄ powder. The amount of disodium tartrate and PEG-6000 is varied in between 0.05 – 0.65 and 3.00 – 4.00 g respectively to tune particle-size, which obstruct crystal grain growth and act as stabilizer.¹⁻³ A thicker coating around the tinier nanoparticles is apprehended in different surface-characterizations *viz*. XPS, FTIR and Raman spectroscopy.

1.2. Characterization approach & specifications

A high-resolution transmission electron microscope (HRTEM, JEOL-JEM 2100) operated at 200 kV; is employed to observe the smallest MNP's, analyse their crystalline nature & unidirectional growth. The coordinative effect of carboxylate groups in the surface-composition is further verified from FTIR spectra, collected using Shimadzu FTIR-8400S. Micro-Raman (beamdiameter $\approx 1 \ \mu m$) spectra is recorded with $\leq 5 \ mW$ laser power and analyzed by a WITec ALPHA300 RS confocal spectrometer in backscattering configuration. The UHTS 300 spectrograph is connected to a Peltier-cooled back-illuminated charge-coupled device (CCD), operated at -62° C with better than 90% QE in the visible excitation. A solid-state frequency doubled Nd:YAG laser (532.3 nm) is used as the excitation source, having a maximum power of 30mW. Data is acquired using a 50X (N.A. = 0.9) achromatic objective (Zeiss) with 600 groove/mm grating (spectral resolution = $3.3 \ cm^{-1}$) by averaging 10 spectral acquisitions with 6 s of integration-time each to minimize background noise. The wavenumber error is considered ±1.5 cm⁻¹ for our calculations. No polarizers are used, but holographic supernotch filters are employed to reject the Rayleigh and anti-stokes lines.

2. Transmission electron microscopy (TEM) images

The smallest nanoparticles (S5) are dispersed in absolute ethanol and drop-casted on Ted Pella carbon type-B support films on 200 mesh grids for further TEM characterization to perceive their crystalline nature and size-distribution.



Fig. S1 (a) TEM image showing the size-distribution of Fe_3O_4 nanoparticles and dispersion; (b) High resolution TEM image representing lattice fringes and inter-planer spacing of the (311) lattice plane; (c) Selected area electron diffraction (SAED) pattern showing polycrystalline nature of the nanoparticles and growth of particular lattice planes.

3. Fourier-transform infrared (FTIR) spectra

FTIR spectra of MNP's show characteristic absorption peaks at 581 and 1370 cm⁻¹ due to Fe-O bending and stretching vibrations respectively.^{1,2} The peak at 979 cm⁻¹ is assigned to the bending vibrations of =C-H and C-C-O groups, whereas the 1083 cm⁻¹ peak is due to CO-C axial deformation and aliphatic bending vibrations of C-C-H groups. The peaks at 1598 and 1685 cm⁻¹ are attributed to –COO stretching, bending vibrations of chemisorbed water molecules and C=O stretching. The symmetric and asymmetric stretching of the methylene (=CH₂) group and C-H stretching cause peaks at 2888 and 2987 cm⁻¹. Finally, the bands at 3430 and 3733 cm⁻¹ appear due to the stretching and bending vibrations of the –OH groups, which are also the characteristic peaks of PEG.³ Hence, these results confirm the core-shell structure of tartrate coated-PEGylated Fe₃O₄ nanoparticles. The surfactant contributions get enhanced for smaller particles having wider shells around the core to control growth.



Fig. S2 FTIR spectra of Fe_3O_4 samples (S1 – S5).

4. Raman spectra

As magnetite (Fe₃O₄) and maghemite (γ -Fe₂O₃) exhibit near-similar XRD patterns due to similar spinel structure (except for vacancy-states), the composition of the as-synthesized MNP's is further verified by Raman spectroscopy, which is practically capable of characterizing the finger-print vibration-modes of the molecules. Choice of laser power and data acquisition-time are vital parameters for Raman spectroscopy of Fe₃O₄, as thermal phase-changes by partial oxidation are easily induced by the excitation laser in open air. For acquisition times longer than a minute with \geq 5mW laser power; features of maghemite, followed by hematite may be observed. Magnetite's irreducible normal modes of vibration, considering its inverse cubic spinel structure for the first Brillouin zone-centre are given by, $\Gamma_{vib} = A_{1g} + E_{1g} + T_{1g} + 3T_{2g} + 2A_{2u} + 2E_u + 4T_{1u} + 2T_{2u}$.^{4,5} The pronounced peak near 670 cm⁻¹ is attributed to the A_{1g} mode, whereas the features at 201, 318 and 542 cm⁻¹ are very weak in all spectra and are assigned to the three T_{2g} vibrational modes.⁶



Fig. S3 Raman spectra of Fe_3O_4 samples (S1 – S5).

5. Electron delocalization profile



Fig. S4 (a) ELF at (111) plane in pristine Fe_3O_4 ; (b) Electron cloud delocalization and drop in charge-density in the vicinity of the removed central octahedral Fe atom.

6. Further information from impedance spectroscopy

The fitting parameters ($\alpha \& \beta$) in the Harvriliak-Negami model as obtained from the Cole-Cole plots of all the samples are listed below.

			α			β				
Bias	0.0 V	0.1 V	0.3 V	0.6 V	1.0 V	0.0 V	0.1 V	0.3 V	0.6 V	1.0 V
S1	0.985	0.985	0.986	0.988	0.990	0.692	0.693	0.699	0.703	0.708
S2	0.970	0.972	0.975	0.979	0.984	0.635	0.638	0.643	0.649	0.651
S3	0.975	0.976	0.979	0.982	0.988	0.561	0.565	0.569	0.572	0.577
S4	0.992	0.995	0.998	0.998	1.000	0.599	0.601	0.604	0.607	0.613
S 5	0.990	0.991	0.996	0.997	0.999	0.617	0.620	0.621	0.623	0.624

Table S1 Values of the fitting parameters ($\alpha \& \beta$) for all samples in different bias

7. Afterword

- The double-well energy landscape in Landau description of ferroelectrics predicted mathematical possibility of negative capacitance (NC), which today has been well-implemented in overcoming fundamental limits of power dissipation suggested by Boltzman tyranny. However, classical electrodynamics do not include any theory related to NC in non-ferroelectric materials. Although since 1969, after the first official report in amorphous chalcogenide films, there are numerous observations of NC in an extensive variety of materials, among which at least forty cases are not at all related to parasitic effects or erroneous measurement protocol; and severely represent material properties. Absence of strong and pre-defined theoretical grounds compelled researchers to explain the observations using versatile and apparently uncorrelated ideas. But, there ought to be some generalized mechanisms associated, which we have attempted to explore.
- Here, Jahn-Teller distortion surrounding $V_{Fe_{oct}}^X$ has not been taken into account.⁷
- A shifting of switching-frequency (f_0) in hot and humid weather is observed, probably for inciting partial oxidation at the NP-surface and electron donating nature of adsorbed water-vapour⁸ (which is detrimental for the formation of heavy dipoles) respectively.
- The applicability of Debye theory⁹ and the updated models proposed by Cole,¹⁰ Davidson,¹¹ Harvriliak and Negami^{12,13} vary from system to system.
- In some aspects, the phenomenon of capacitive switching is analogous to oxygenvacancy assisted resistive switching.¹⁴

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