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Doping effect on the local structure of metamagnetic Co doped Ni/NiO:GO core-shell nanoparticles using X-ray absorption spectroscopy and pair distribution function†

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U. P. Gawai[a*], D. K. Gaikwad[b], M. R. Bodke[c], H. A. Khawal[d], K. K. Pandey[e], A. K. Yadav[f], S. N. Jha[f], D. D. Bhattacharyya[f] and B. N. Dole[d]

Supplementary Information

Synchrotron X-ray diffraction study

The synchrotron X-ray diffraction (SCXRD) patterns of samples S1 to S4 are shown in Fig. S1. The powder diffraction data were collected at a higher wave vector Q=9.52 Å^{-1}, which was recorded in the transmission mode using a shorter X-ray wavelength of 0.439 Å at high energy ~28 keV from beamline BL-11, AD/ED-XRD at RRCAT, Indore. The SCXRD measurements were achieved with a highly monochromatic synchrotron beam using a Si (111) channel cut monochromator. SCXRD patterns revealed the high resolution diffraction data for the structural refinement. The entire diffraction peaks of the sample can be readily indexed as a face centered cubic (fcc) structure of Ni and NiO with space group Fm-3m. It can be specify, the eight peaks for samples S1-S4 to be assigned to (111), (200), (220), (311), (222) (400), (131) and (402) reflections of cubic Ni (JCPDS No. 65-2865), and respectively and peaks of (111), (200), (220), (311), (222) (400), (131) and (402) for reflections of cubic Ni (JCPDS No. 71-1179) respectively. For samples S2 and S3 there are less reflection for NiO whereas at the samples S2 hexagonal Ni also present. There is no secondary phases and extra peaks of the alloy or oxide phases were detected in the samples. The present of Ni and NiO phases in the samples were evaluated by Rietveld refinement (RR), it is shown in figure S2. The Rietveld refinement was extracted from FullProf program, as a Pseudo-Voigt function profile. The obtained values from RR is given in table 1. The lattice constant 'a' was increases from samples S1 to S4. The volume percentages of Ni and NiO phases obtained by using the FullProf program are as 63.7, 36.3; 89.65, 5.8; 98, 2; 65.8, 34 for S1 to S4 respectively. Also in samples S2 volume percentage was found to be for hexagonal Ni of 4.4. The volume percentage is calculated using the integrated intensity for each phase. Also the atomic ratios or at% of Ni, O and Co were found with consistent in the EXAFS as well as EDAX analysis. From the volume percentage of Ni and NiO phase in samples S1 and S4 evidenced that the more contribution of these phases. While from samples S2 and S3 the volume percentage of NiO phase is very less that the Ni phase. The core-shell structure of samples is responsible for the interfacial interactions (interface between Co/Ni and NiO, and Co/NiO and graphene oxide). This kind of interaction causes two types of strains in the lattice. One is the macro strain, which increases the interplanar spacings (d_{hkl}), and the other is the micro strain, which induces a peak broadening. In such small Ni/NiO core-shell type particles, a slightly modified intensity distribution of X-ray diffraction peaks lies in comparison to reported distribution in bulk Ni and NiO. Nevertheless, in either case, (111) reflection lies as the most intense peak in the Ni core, with the second and third most intense peaks of (200) and (220) reflections, respectively.

Table S1. Structural parameter evaluated from Rietveld refinement.

Samples	Lattice parameters		Bragg R-factor		RF-factor		Chi^2	Volume (%)	
	Ni	NiO	Ni	NiO	Ni	NiO		Ni	NiO
S1	3.523	4.174	8.97	4.70	0.962	1.11	1.07	63.7	36.3
S2	3.545	4.195	8.63	1.27	1.20	8.48	1.9	89.65	5.8
S3	3.524	4.176	8.71	4.01	7.44	5.50	2	98	2
S4	3.524	4.179	3.83	3.58	1.98	3.09	1.25	65.8	34

X-ray Absorption Spectroscopic investigations

The normalized EXAFS spectra are shown in figures 4 and 5 at Ni and Co K-edges respectively. In order to take care of the oscillations in the absorption spectra, $\mu(E)$ has been converted to absorption function $\chi(E)$ defined as follows,

$$\chi(E) = \frac{\mu(E)-\mu_0(E)}{\Delta\mu_0(E_0)} \qquad (1)$$

Where E_0 is the absorption edge energy, $\mu_0(E_0)$ is the bare atom background and $\Delta\mu_0(E_0)$ is the step in $\mu(E)$ value at the absorption edge. The energy dependent absorption function $\chi(E)$ has been converted to the wave number dependent absorption function $\chi(k)$ using the relation[1],

$$k = \sqrt{\frac{2m(E-E_0)}{\hbar^2}} \qquad (2)$$

Where m is the electron mass, $\chi(k)$ is the weighted by k^2 to amplify the oscillation at high k and the $\chi(k)k^2$ functions are Fourier transformed in R space to generate the $\chi(R)$ versus R spectra (or the FT-EXAFS spectra) in terms of the real distances from the center of the absorbing atom. The set of EXAFS data analysis software available within IFEFFIT package has been used for EXAFS data analysis.[1] This includes background reduction and Fourier transform to derive the $\chi(R)$ versus R spectra from the absorption spectra (using ATHENA software), generation of the theoretical EXAFS spectra starting from an assumed crystallographic structure and finally fitting of experimental data with the theoretical spectra using ARTEMIS software.

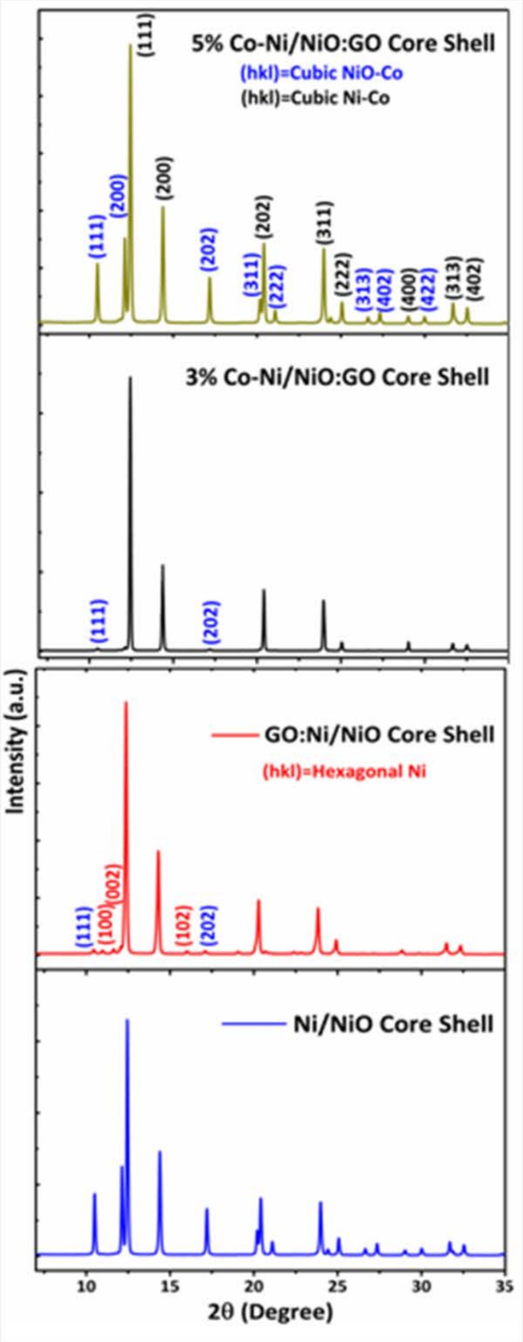

Fig. S1: The SCXRD patterns of as synthesized core-shell Ni/NiO nanoparticles samples.

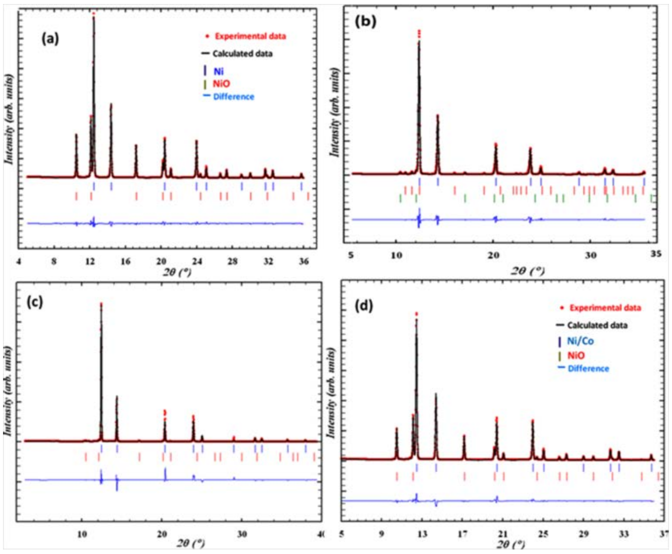

Fig. S2: The Rietveld refinement SCXRD patterns of as synthesized core-shell Ni/NiO nanoparticles samples.

Chemical Composition Study

Figure S3 shows the compositional analysis of the as synthesized samples from energy-dispersive absorption X-ray spectroscopy EDAX patterns. It can be notice that the peak of Ni, Co, O and C are present. It is confirmed that the cobalt is present in samples. For pure Ni/NiO structure, qualitative analysis reveals that the atomic ratio of Ni to O is very close to 68.79: 31.21. For **0.05mg GO+Ni/NiO**, atomic% of Ni, O and C was found to be 82.01, 17.99, and 0.01 respectively, whereas for 3%Co+0.05mg GO+ 97%Ni/NiO and 5%Co+0.05mg GO+ 95%Ni/NiO the atomic% of the elements of Ni, Co, O and C was found to be 77.11, 2.91, 19.98, 0.5 and 57.72, 2.75, 39, 0.5 respectively. The amount of Co element detected is less than those actually added during synthesis.

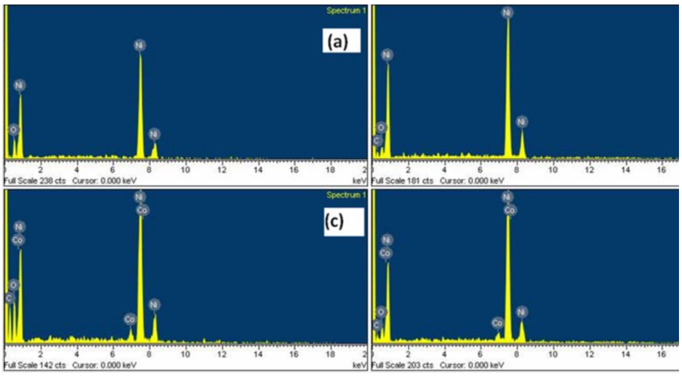

Figure S3: EDAX patterns of S1 to S4 samples.

Synthesis of Graphene oxide:

Graphene oxide (GO) was synthesized using Hummers method, as was reported[1] it was briefly given here. For Hummers' method, concentrated H_2SO_4 was added to a mixture of graphite flakes (3.0 g) and $NaNO_3$ (1.5 g), and the mixture was kept on ice bath. $KMnO_4$ (9.0 g) was added slowly in portions to keep the reaction temperature below 20 °C. The reaction was warmed to 35 °C and stirred for 30 min, at which time water (138 mL) was added slowly, producing a large exotherm to 98 °C. Again additional water and 30% H_2O_2 were added, producing another exotherm. After air cooling, the mixture filtration with multiple washings, centrifugations, decanting and vacuum drying, it gives GO. After preparing, we have taken TEM of the GO it shown in figure 4. It is clearly reflect from Tem image that the sample having sheet like structure.

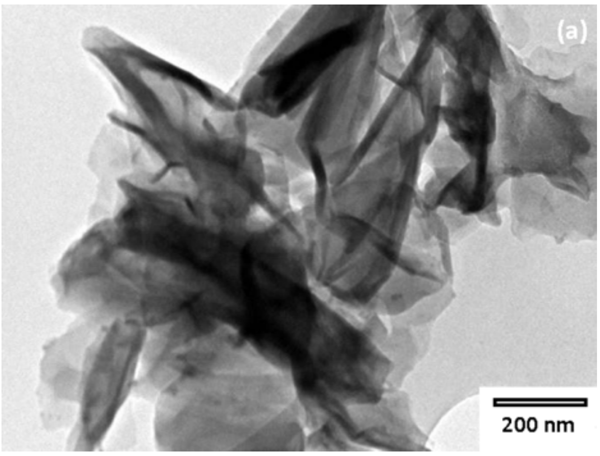

Fig. S4. TEM image reflect the sheet of Graphene oxide.

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