

Hydrothermally synthesized NiFe₂O₄/rGO composites: structure, morphology and electrical conductivity



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Abstract

The effect of thermal treatment on the structural arrangement and pore size distribution of NiFe₂O₄/reduced graphene oxide composite materials has been investigated using X-ray diffraction, Mössbauer spectroscopy, and nitrogen adsorption / desorption technique. Composite materials have been successfully synthesized by the joint hydrothermal method using graphene oxide colloidal solution obtained by the modified Tour method. The electrical properties of the composite materials, as well as the pure component, have been investigated in the frequency range from 0.1 Hz to 1 MHz, in the temperature range from 25 to 175 °C using impedance spectroscopy. A synergetic increase in the electrical conductivity of composite materials in comparison with pure components has been observed. The activation energies of interparticle hopping of charge carriers have been calculated using Arrhenius type conductivity plots.

XRD

The main peak of the rGO sample at 2θ = 19.77° is attributed to a d-spacing of 4.49 Å and corresponds to the (002) reflex of the reduced graphene structure (Fig.1, a). The X-ray diffraction patterns of powders of both N1 and N2 series (Fig.1, b-c) revealed a cubic spinel phase as a major phase and a small amount of hematite (α-Fe₂O₃) as a secondary oxide phase. There is no significant difference in the values of the lattice constant of the spinel phases for N1 and N2 systems, and its changes cause the calcination process. An increase in the integral breadth of the spinel phase with an increase in the calcination temperature (clearly visible for (222) peaks) corresponds to the material dispersion due to the continued reduction of graphene oxide with the evaporation of gaseous reaction products.

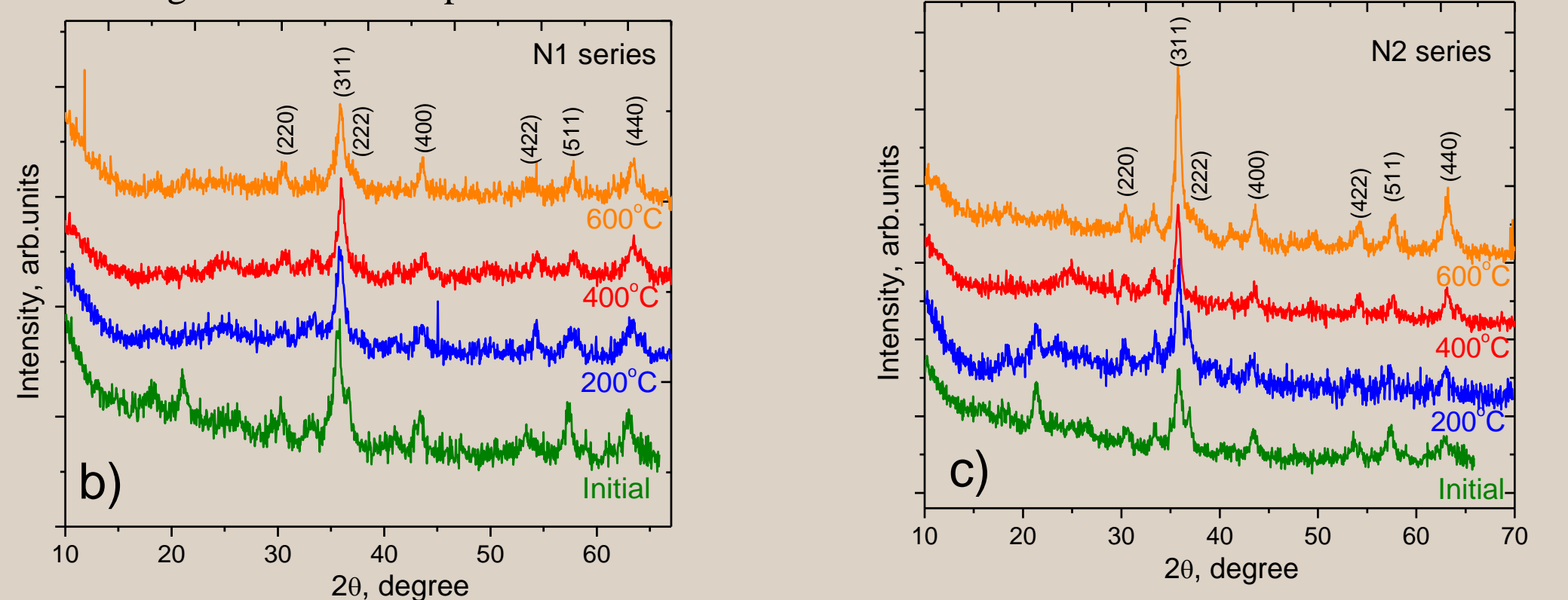


Fig. 1. XRD patterns of (a) – N0 and rGO samples, (b) and (c) – composite of N1 and N2 series

Electrical conductivity

The electrical conductivity (σ) increases with a change in frequency in the range of 10²-10⁵ Hz for sample N0 (Fig. 2, a). The conductivity spectra of N1 sample exhibit metallic behavior (a low-frequency plateau and a sharp decline with frequency increasing above 10⁴ Hz due to skin effects) and can be described by the Drude model

$$\sigma(T, f) = \frac{\sigma_{dc}(T)}{1 + \omega^2 \tau^2(T, f)}$$

where σ_{dc} is the DC conductivity and τ is the relaxation time between two electron-phonon collisions (Fig. 2, b). An increase in the rGO content in sample N2 leads to a decrease in electrical conductivity (Fig. 2, c) by approximately three times, which can be explained by the higher dispersion of the composite material.

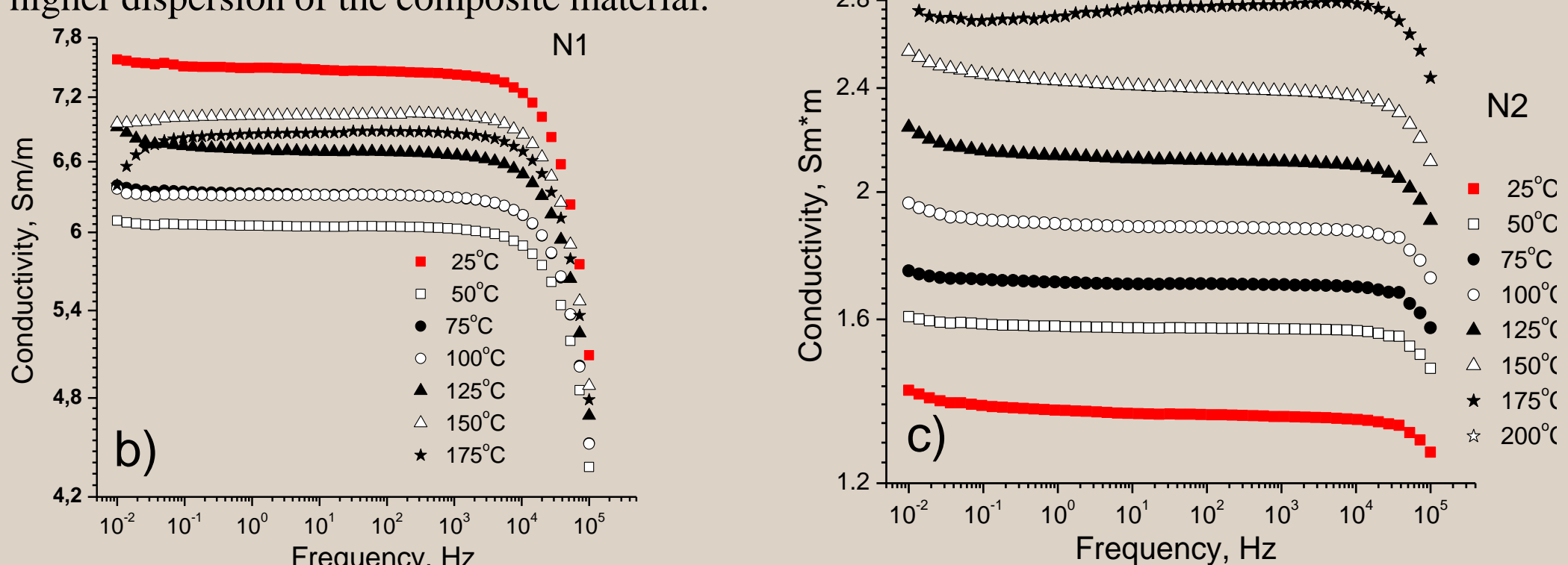


Fig. 2. (a-c) Temperature dependences of the electrical conductivity for the samples (hydrothermally synthesized spinel NiFe₂O₄)

Synthesis details

Graphene oxide (GO) has been synthesized by the modified Tour method using synthetic graphite (Aldrich, # 282863) as a starting material. The starting materials used in this study to obtain the spinel phases were nickel nitrate (Ni(NO₃)₂·6H₂O) and iron nitrate (Fe(NO₃)₃·9H₂O) (all from Aldrich, 98%), and sodium hydroxide (NaOH, Merck). Two variants of composite samples, marked as N1 and N2, were prepared using the same procedure with the estimated mass ratio of spinel and rGO phases of 3:1 and 3:2, respectively. The phase composition and crystallinity of the synthesized samples were analyzed by powder X-ray diffraction with 2θ angles from 10° to 80°. The pore sizes and their distribution were calculated using DFT slit pore model.

Mössbauer spectra were measured at room temperature on an MS1104Em spectrometer with a ⁵⁷Co (Cr) radiation source. Frequency dependences of electrical conductivity σ were measured by impedance spectroscopy in the temperature range of 20-200 °C.

Mössbauer spectroscopy

Mössbauer spectroscopy provides independent information on the ratio of the Fe-contained phases even at low crystallinity of the material (Fig. 3). The NiFe₂O₄ microcrystal has a mixed inverse spinel structure, which can be described as



The Mössbauer spectra of N0 sample consist of two split well-defined sextet components corresponding to Fe³⁺ ions in tetrahedral (A) and octahedral (B) sites (Fig3, a). The isomeric shift for iron ions located in the A-sites is usually smaller as a result of the correspondingly stronger covalent bonds FeA-O, which allow the identification of the tetrahedrally and octahedrally coordinated Fe³⁺ (Table 1).

Site	Is, mm/s	Qs, mm/s	H, kOe	S, %	G, mm/s
N0					
A	0.24±0.02	-0.03±0.02	449±3	49.5	0.38±0.02
B	0.34±0.02	-0.01±0.02	505±2	50.5	0.57±0.04
N1-400					
H	0.40±0.02	-0.16±0.01	496±2	17.4	0.56±0.04
A	0.28±0.03	0.02±0.02	407±3	28.6	0.78±0.07
B	0.48±0.02	0.01±0.02	460±3	35.6	2.33±0.12
D	0.35±0.03	0.64±0.05	–	12.4	0.51±0.04
N1-600					
H	0.39±0.02	-0.16±0.02	488±3	16.5	0.30±0.05
A	0.36±0.02	0.00±0.02	430±3	34.3	0.72±0.05
B	0.42±0.03	-0.02±0.03	465±2	49.2	0.86±0.04
N2-400					
H	0.38±0.02	-0.21±0.01	506±2	18.4	0.40±0.04
A	0.32±0.03	0.01±0.02	450±4	38.0	0.38±0.07
B	0.36±0.03	-0.07±0.03	491±3	43.6	0.38±0.07
N2-600					
H	0.37±0.02	-0.23±0.02	511±2	9.0	0.29±0.04
A	0.29±0.02	0.01±0.02	472±3	42.6	0.72±0.05
B	0.35±0.03	-0.04±0.04	508±2	48.4	0.86±0.04

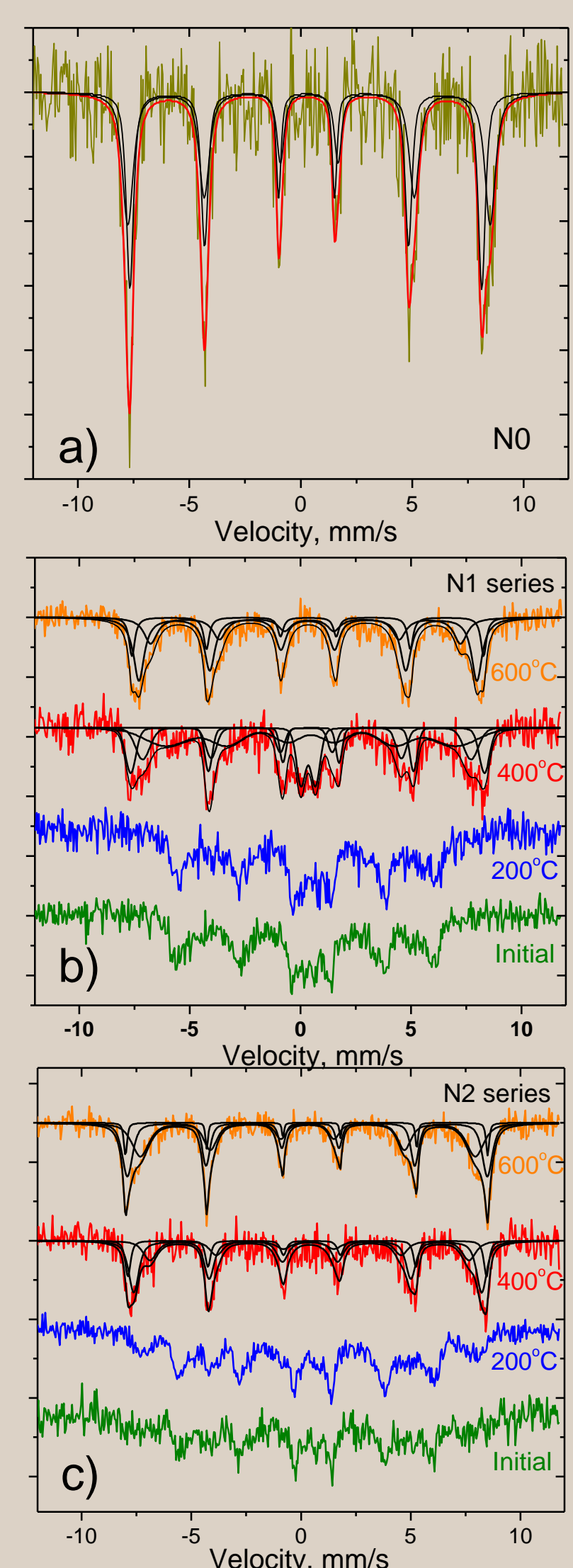


Fig. 3. Mössbauer spectra of the composite of (a) N0 (b) N1 and (c) N2 series as-synthesized and after calcination in air at temperatures of 200, 400 and 600 °C

Conclusion

A comparative study of the temperature and frequency dependences of the electrical conductivity of NiFe₂O₄ / reduced graphene oxide (rGO) composite materials synthesized by the method of joint hydrothermal synthesis is presented. The use of the GO colloidal solution obtained by the modified Tour method as a component in the hydrothermal synthesis of spinel / rGO leads to the formation of α-Fe₂O₃ (up to 20 mol %), an increase in the nonstoichiometry of the material, and a decrease in the average particle size of NiFe₂O₄. The observed increase in the AC conductivity of composite materials relative to pure components corresponds to an increase in the specific surface area for rGO-containing systems. Analysis of the experimental conductivity spectra has shown that the AC conductivity of pure rGO and NiFe₂O₄ is mainly related to the charge hopping mechanism between randomly interconnected semiconductor particles, while composite samples, due to their much higher conductivity, exhibit a skin effect at frequencies above 10⁴ Hz according to Drude's theory. An increase in the specific surface area of composite samples upon annealing at 200 °C (up to 160 m²/g) has revealed increasing values of the activation energy for charge carrier hopping transport. At the same time, a twofold increase in the content of the graphene component in the composite samples leads to a decrease in the conductivity values. Due to the dependence of the electrical properties of NiFe₂O₄ / rGO composites on their morphology, the NiFe₂O₄ / rGO composite can be a suitable material for hybrid electrochemical capacitors application.