Synthesis, structural and electrical properties of nanotubular Ni-doped $Na_2Ti_3O_7$ as a novel functional material

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Introduction

In recent years, ternary $A_2Ti_nO_{2n+1}$ (A = Li, Na, K; n = 2–9) oxides systems, in particular, sodium trititanate ($Na_2Ti_3O_7$) has received considerable attention due to its potential technological applications in various fields. A large number of titanate nanostructures (i.e., nanotubes, nanowires, and nanobelts) have been widely obtained by a simple hydrothermal treatment of TiO_2 particles in NaOH solution. Due to the high-performance ion-exchange properties of $Na_2Ti_3O_7$, it may be used for removal and recovery of heavy metal ions from industrial wastewaters, metal-ion batteries and hydrogen storage materials, as well as photocatalysts, bioactive ceramics and sensors.

	Market share in 2021	Sales growth for 2021
CATL	32,6%	167,1%
LG Energy Solution	20,3%	75,5%
Panasonic	12,2%	33,7%
BYD	8,8%	168,4%
SK On	5,6%	106,2%
Samsung SDI	4,5%	55,3%
China Aviation Lithium Battery	2,7%	132,4%
Guoxuan High-Tech	2,1%	166,7%

Global leaders in rechargeable batteries manufacturing

Highlights

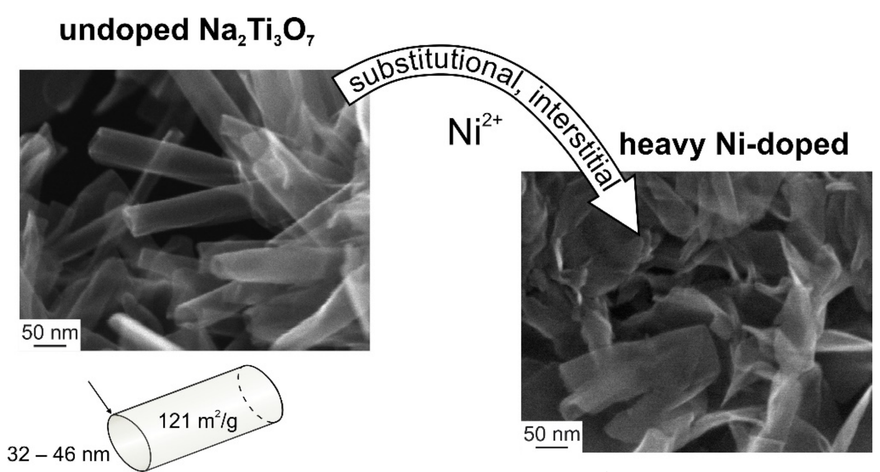

Fig. 1. SEM images and schematic representation of the unfolding process of Ni-doped $Na_2Ti_3O_7$ nanotubes

Objectives, methods

In this work, the effect of nickel doping on the structural and electrical properties of $Na_2Ti_3O_7$ layered ceramics obtained in the form of mesoporous nanotubes is studied by XRD, XPS, SEM, impedance spectroscopy, EPR methods and UV-Vis spectroscopy. Sodium trititanate doped with nickel (1.2–6.9 at.%, denoted as NTO-Ni-25, 75 and 150, respectively) was obtained by hydrothermal treatment of titanium(IV) chloride and nickel(II) chloride (25, 75 and 150 mL) in an alkaline medium in the presence of hydrogen peroxide.

Results and discussion

It was found that the resulting material is nanotubes with a diameter of 30–50 nm and a wall thickness of 3–10 nm. The nanotubular composition is represented by crystallites 14–12 nm in size, while nickel is successfully incorporated into the sodium trititanate lattice. When Na^+ ions are replaced by Ni^+ ions in low concentrations, the $(Ti_3O_7)^{2-}$ layers tend to bend, rolling into nanotubes; the introduction of a significant amount of nickel leads to a "simplification" of the structure and "unfolding" of nanotubes (Fig. 1).

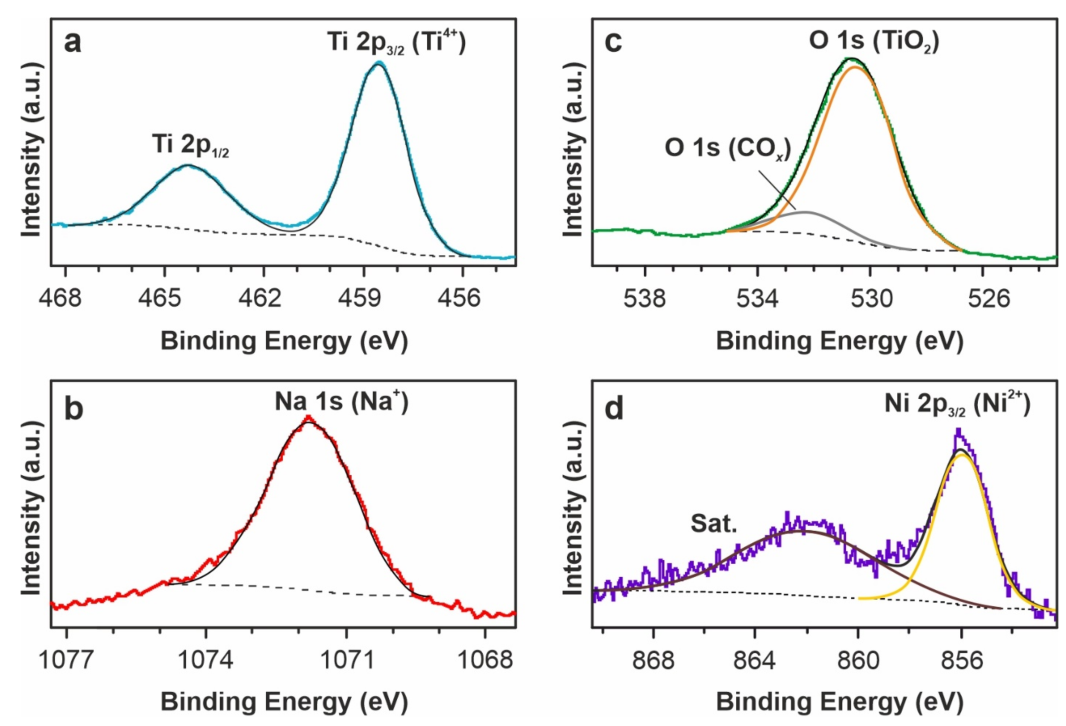

Fig. 2. XPS-spectra of Ni-doped $Na_2Ti_3O_7$: Ti 2p (a), Na 1s (b), O 1s (c), Ni 2p (d)

As shown in Fig. 2d, the Ni $2p_{3/2}$ region of XPS spectrum is represented by the peak near 856.0 eV corresponding to Ni^{2+}. From the quantitative XPS analysis, the content of elements in sample with Ni 3.5 at.% corresponds to the $Na_{2.09}Ti_{2.89}Ni_{0.16}O_{6.86}$ formula (the presence of polyphase TiO_2 in the sample was not taken into account during calculation), which is close to sodium trititanate. Nevertheless, an oxygen deficiency can be observed in doped $Na_2Ti_3O_7$ suggesting the existence of anionic vacancies.

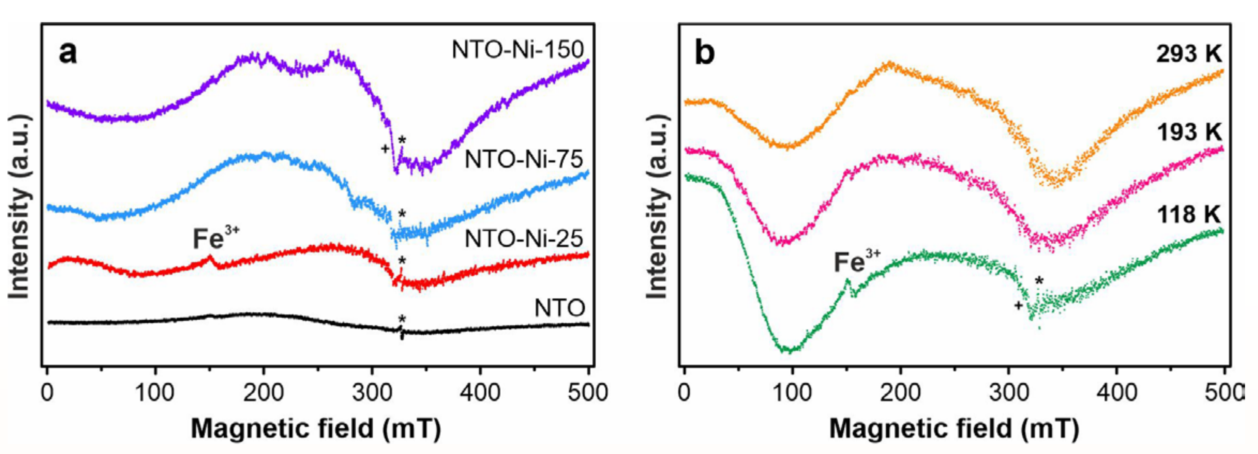

Fig. 3. Magnetic resonance spectra of undoped and nickel-containing $Na_2Ti_3O_7$ materials at the room temperature (a) and a plot of FMR spectra of doped titanate (3.5 at.%) at different temperatures (b). Signs "" and "+" denote, respectively, the EPR signals of F-centers (g=2.0055) and magnetic resonance of unknown origin.*

It is shown that for $Na_{2.09}Ti_{2.89}Ni_{0.16}O_{6.86}$ (nickel alloying 4.6 at.%), a deficiency of oxygen atoms registered. In this case, the most probable location of their location in $Na_2Ti_3O_7$ is the interlayer space. Fig. 3a represents the EPR/FMR spectra of unmodified and Ni-doped sodium trititanate products recorded at the room temperature.
An intense and broad asymmetric line dominates in spectra of the Ni-containing products; some curves are characterized by two-peaked signals.

The experimental UV-Vis absorption spectra (Fig. 4a) demonstrate that the undoped material absorbs UV rays and reflects light in the visible region of spectrum (NTO sample exhibited absorption edge at $\lambda \sim 374$ nm). This is typical behavior for $Na_2Ti_3O_7$, which is known to be a wide-bandgap semiconductor. Doping sodium trititanate with nickel shifts the absorption edge to higher wavelengths (so-called red shift) up to $\lambda \sim 451$ nm and increase the optical activity in both UV and visible regions.

The representation of impedance spectra in Nyquist plots (Z'' vs. Z') reveals a depressed semicircle reflecting the conductivity of material and arc characterizing the interfacial phenomena, as shown in Fig. 5b. On the basis of impedance data fitting, the conductivity of nickel-containing materials was calculated as $1.20 \cdot 10^{-5}$ S cm^{-1} (NTO-Ni-25), $1.91 \cdot 10^{-5}$ S cm^{-1} (NTO-Ni-75), and $2.35 \cdot 10^{-5}$ S cm^{-1} (NTO-Ni-150), whereas for NTO sample it equals to $4.06 \cdot 10^{-6}$ S cm^{-1}. Hence, the conductivity of sodium trititanate increases in 3–6 fold after the incorporation of nickel dopant.

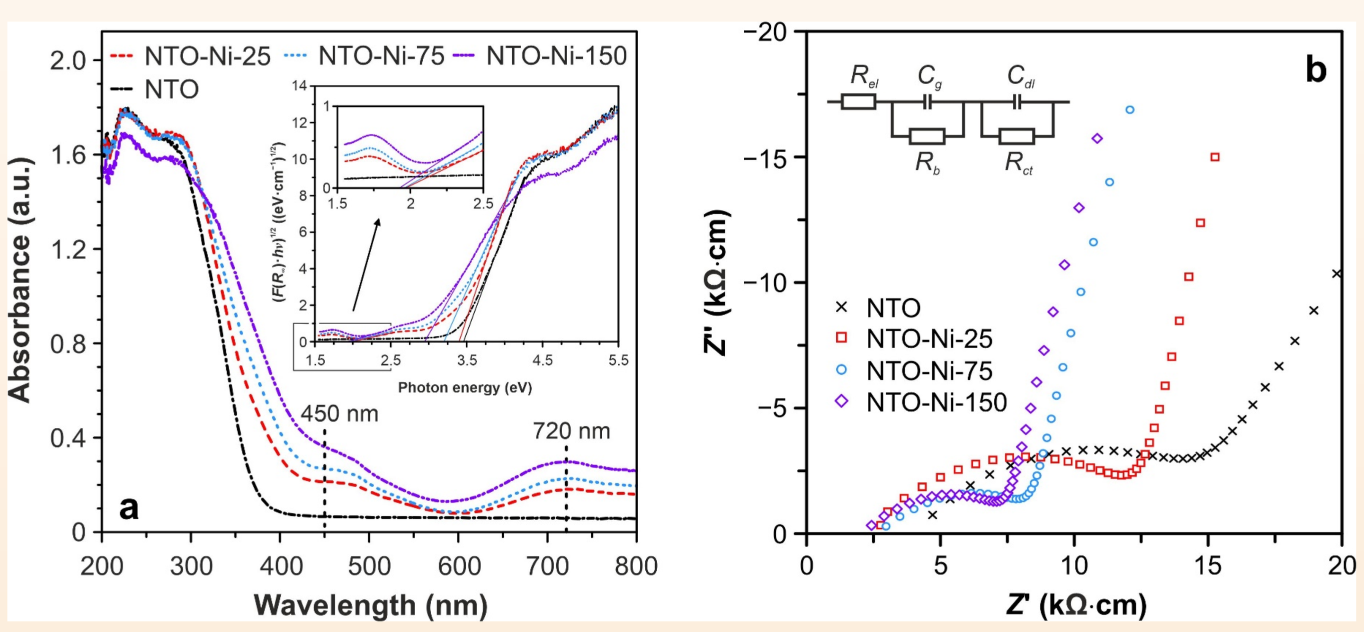

Fig. 4. UV-Vis absorption spectra (a) with a graphical evaluation of E_g (inset) by the Tauc method and EIS spectra (b) with an equivalent electric circuit (inset) used for fitting for unmodified and Ni-doped $Na_2Ti_3O_7$ products

Conclusions

Thus, the paper presents the results of the synthesis and study of mesoporous materials with a tubular nanostructure based on sodium trititanate doped with nickel. It has been established that doping improves the conductive properties of the material, which is associated with the formation of oxygen vacancies resulting from the charge compensation of the nonisovalent substitution of Ti^{4+} ions by nickel ions. «Unfolding» nanotubular structures at the high doping levels reduces the specific surface area and porosity, whereas, both electronic properties (E_g narrowed to 2.43 eV) and conductivity (by more than six-fold) increases.

Acknowledgements

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