

## Structural and magnetic properties of Ni doped titanate nanotubes synthesized by hydrothermal method

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A new method, hydrothermal method, to synthesize Ni doped rutile TiO<sub>2</sub> nanotube (TNT) powders is introduced. This method is more scalable than ones used before. Interestingly, our Ni doped TNTs' structures show different characteristics and properties than ones fabricated by other methods. We report these resulting structural and magnetic properties here. Ni doped nanotubes contained H<sub>2</sub>Ti<sub>2</sub>O<sub>5</sub>H<sub>2</sub>O doped with trivalent Ni. The layered structures had six nm inner and ten nm outer diameters, aspect ratios of seven, and exhibited ferromagnetism at room temperature (undoped nanotubes were diamagnetic). Contrary to earlier versions of Ni doped TNTs, we found that trivalent Ni atoms substituted H<sup>+</sup> in the nanotubes and thus interacted with titanate's 3d electrons to produce ferromagnetic activity. This opens the possibility to achieve ferromagnetic activity in TNTs in a new way.

**Key words :** TNTs, Magnetic properties, Ni doping, Hydrothermal method.

### Introduction

Conventional semiconductor design and processing technology will soon reach its limitations in device fabrication processes and electrical interference. Therefore, researchers worldwide are actively seeking new technological approaches to break through such barriers and continue making ever smaller and smaller electronic devices [1]. In the last decades, ferromagnetic materials and alloys in thin films were of particular interest for sundry uses in data storage and device fabrication [2, 3]. Common devices, e.g. hard disk drive (HDD) read head and magnetic random access memory (MRAM), utilize such materials. Consequently, various thin film deposition techniques developed for both laboratory research and industry applications, and pure magnetic materials and magnetic material doped metal oxide composites were intensively investigated.

Next generation semiconductor devices known as spin transport electronics, or spintronics, currently attract much interest for research and development. Spintronics is a new breed that can potentially fulfill the miniaturization trend by controlling and utilizing both the electron's charge and spin [4, 5]. Examples include high density MRAM, spin field effect transistors (FET), and spin light-emitting diodes (LED) [6-9]. Spintronic devices use various magnetic materials, but right now, most attention goes to the synthesis and characterization of nickel, iron, cobalt, and their many

alloys because these are ferromagnetic archetypes with high magnetic constants [10]. Continued miniaturization in device fabrication will require controllable nanosized magnetic material synthesis processes and a detailed understanding of the nanocomposites' structural and electro-magnetic characteristics.

Direct nanostructure syntheses of pure magnetic materials have been tried. However, mechanical/structural stability still needs improvement, and the processes are not cost effective. Meanwhile, other efforts have been made to dope well-known 1D carrier structures, e.g. carbon nanotubes and titanium oxide (TiO<sub>2</sub>) nanotubes (TNTs), with magnetic materials. We explored a novel fabrication method, hydrothermal method, for doped and undoped TNTs and examined the resultant structural and magnetic characteristics. We used TiO<sub>2</sub> because its compatibility to magnetic material doping is well known [11]. Early reports on the magnetic properties of doped TNTs exist; but the origin of magnetism and its relationship to structural characteristics are not fully understood. Our experiments illumine the structural characteristics of Ni doped TNTs and the effects of doping and temperature on magnetism with regard to hydrothermal method fabrication. Unexpectedly, our hydrothermally synthesized Ni doped TNTs exhibited much different structural and magnetic characteristics than those previously fabricated with other methods.

### Experimental

Rutile powders were prepared by HPPLT method using TiCl<sub>4</sub> as a starting material while Ni was doped

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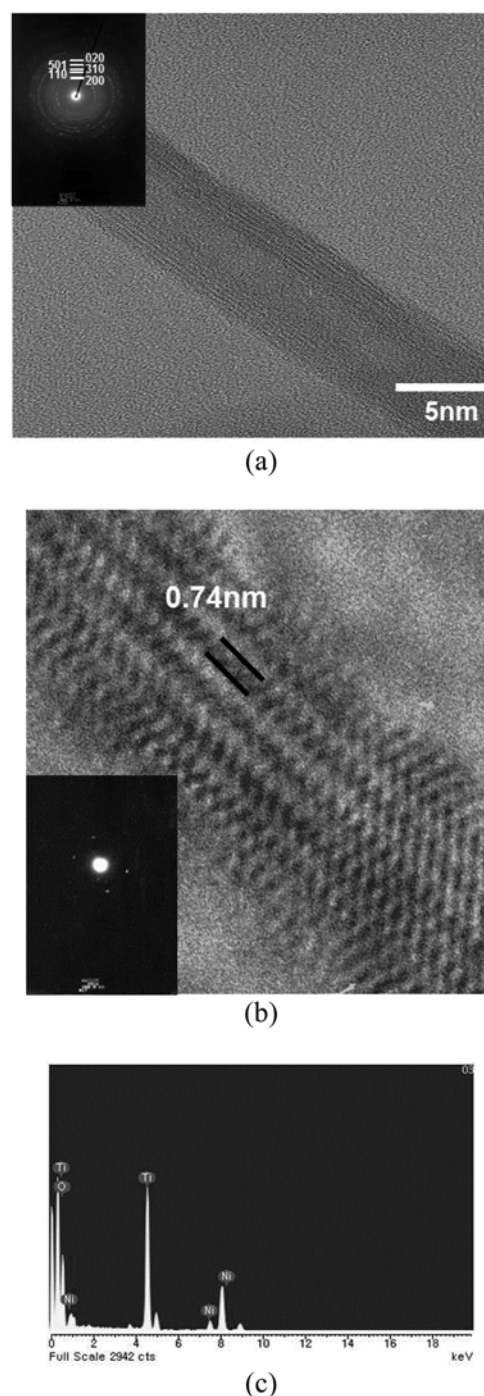
by mechanical alloying with 8 wt% metal Ni element (Kojundo Chem. Co., LTD, 99.9%) for 14 hrs using a planetary ball mill (Fritz mill, P-5). [8, 9] The alloyed powder (0.8 g) and 14 mL of 10 M NaOH aqueous solution were mixed by stirring for one hour, placed in a Ni-lined stainless-steel autoclave at 120 °C for 24 hrs, then cooled to room temperature. Next, 0.1 M HCl aqueous solution was added and washed repeatedly with distilled water until the solution's pH reached 7. Finally, powders were collected by the centrifugal separator (Oak ridge tube) operated at 15,000 rpm for 30 min.

Microstructural features were characterized by X-ray diffraction (Cu-K $\alpha$ , Rigaku D-MAX 3000, Japan) and high-resolution transmission electron microscopy (HRTEM, 400 kV, JEM 4010, Japan). The chemistry was analyzed using atomic emission spectrometer (ICP-AES). Geometry of electronic structures around Ti and Ni in the materials was characterized with X-ray absorption fine structure (XAFS). X-ray absorption measurements were conducted at beam-line 3C1 of PAL (2.5 GeV; stored current of 130 ~ 180 mA). Radiation was monochromatized using Si(111) double crystal monochromator, and the incident beam was detuned by 15-30% using a piezo-electric translator to minimize contamination from higher harmonics (especially third order reflection of silicon crystals). Data were collected at room temperature in transmission mode. Incident intensities and transmitted beams were measured by ionization chamber detectors where N<sub>2</sub> gas flowed. The energy was calibrated by measuring X-ray absorption spectrum of Ni and Ti metal foil and by assigning the first inflection point in the rising portion of the absorption spectra as 8333 and 4966 eV respectively. Obtained data were analyzed using IFEFFIT suite of software programs [10]. Magnetic properties of the nanotubes were determined by vibrating sample magnetometer at room temperature (VSM, Lakeshore 7304) and superconducting quantum interference device (SQUID) measurement.

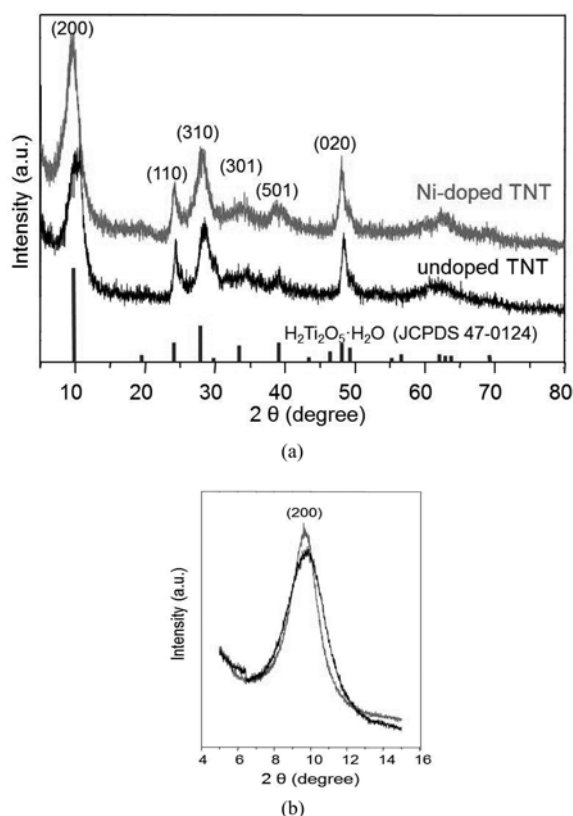
Crystal structure of pristine titanate nanotubes was investigated using density functional theory (DFT) calculations with SEQUEST software [12], a fully self-consistent Gaussian-based linear combination of atomic orbitals (LCAO) DFT method with double- $\zeta$  plus polarization basis sets [13]. All calculations were based on the Perdew-Burke-Ernzerhof (PBE) [14] generalized gradient approximation with PBE pseudo-atomic potentials and spin polarization within three-dimensional periodic boundary conditions. The k-point sampling of  $6 \times 6 \times 6$  in the Brillouin zone and the real space grid interval of  $138 \times 23 \times 19$  in the x-y-z box were carefully determined by energetic convergence. The initial crystal structure was used with a H<sub>2</sub>Ti<sub>2</sub>O<sub>5</sub> · H<sub>2</sub>O crystal structure reported by Tasi and Teng [15], in which the structure's unit cell consisted of four Ti, twelve O, and eight H atoms. The structure was then fully optimized through the DFT calculation.

## Results and Discussion

Analysis begins with the structural characteristics of Ni doped and undoped TNTs. Fig. 1(a) and 1(b) show high resolution transmission electron microscopy (HRTEM) images of Ni doped TNTs. Tubular morphology was similar to undoped TNTs reported in previous studies [16]. Ni doped TNTs' diameters ranged from 6 to 11 nm, and the TNTs were several tens to hundreds nanometers long. They were open on both



**Fig. 1.** (a) HRTEM image, (b) SAED pattern and (c) EDS analysis peaks of Ni doped TNTs.

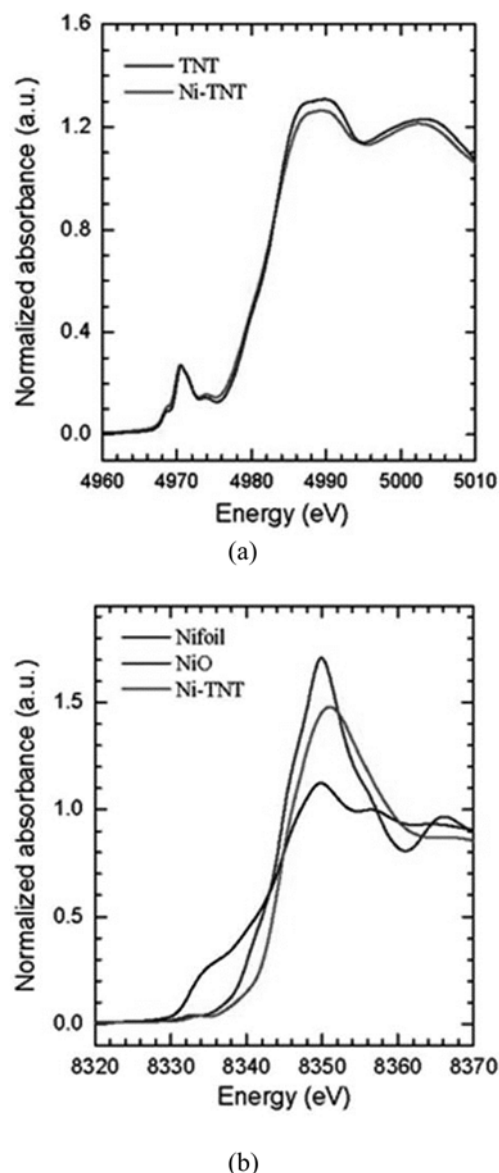


**Fig. 2.** (a) XRD patterns and (b) high resolution reflected XRD patterns of N- doped and undoped TNTs.

ends, and the ends exhibited reflections characteristic to nanotubular axes [17]. Nanotubes showed four to five layered structures, and interlayer spacing averaged 0.74 nm. Though this is inconsistent with XRD data that follows, we assume it is because the electron beam irradiation during TEM analysis dehydrated the samples, yielding shrinkage of the interlayer spacing.

Selected area electron diffraction (SAED) patterns of the central area of single Ni doped nanotubes are also shown in Fig. 1(a). The patterns correspond well to following XRD diffraction data of  $H_2Ti_2O_5 \cdot H_2O$  from individual spots (200), (110), (310), (501), and (020). Fig. 1(c) shows a typical EDS pattern collected from Ni doped TNTs. The average over five different points of analysis confirmed that the nanotubes contained about 7 wt% Ni. ICP analysis further verified that 6.87 wt% metallic Ni atoms remained in the nanotubes. Analytical results indicated that most of the Ni dopant dissolved into the interlayer spacing of the nanotube structure, although a small loss of Ni occurred during the hydrothermal process [18].

Fig. 2(a) shows XRD patterns of Ni doped and undoped TNT powders. One notices that the main peaks are nearly identical, but interlayer spacing of Ni doped TNT is increased due to Ni substituting for  $H^+$ . Both powders exhibit characteristic peaks at around  $2\theta = 10^\circ$ ,  $24^\circ$ , and  $28^\circ$  (these can be assigned to  $H_2Ti_2O_5 \cdot H_2O$  nanocrystallites' diffraction and bending



**Fig. 3.** (a) Ti K-edge and Ni K-edge XANES of doped and undoped TNTs (b) Ni K-edge XANES comparison of the Ni doped TNTs powder with metallic Ni and NiO and (c) Fourier-transforms spectra of Ti K-edge from undoped and Ni doped TNTs.

of the tubes' atomic planes). Since the diffraction peaks' locations were nearly identical between the two powders, we infer that Ni dopants were incorporated only between the walls, thus expanding interlayer spacing.

As shown in Fig. 2(b), we measured interlayer spacing (200) from reflected XRD patterns [19] of Ni doped TNT as 0.91 nm and undoped TNT as 0.84 nm. We found no Ni elemental peaks in the pattern (Fig. 2(a)) for our 7 wt% Ni doped raw powder because the Ni was completely dissolved in the nanotubes. Most surprisingly, we suggest that the Ni dopant did not substitute Ti sites as previously reported for others [20], but instead ours substituted  $H^+$  in the nanotubes'

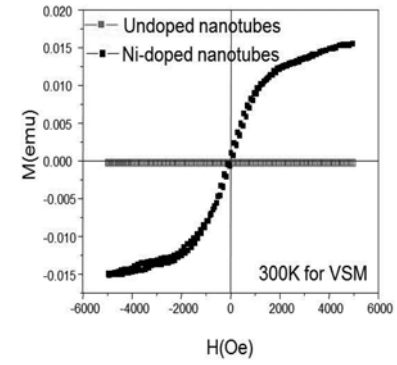
interlayers. This explains why the main peaks of the two powders differ slightly from  $9.56^\circ$  to  $9.95^\circ$  [21]. We confirmed this finding by studying the nickel dopant's detailed oxidation state with XAFS.

Observed absorption properties further illuminate structural details for undoped and Ni doped TNTs. Fig. 3(a) shows Ti K-edge and Ni K-edge X-ray Absorption Near-Edge Structure (XANES) for both. The three weak peaks at 4966-4974 eV indicate forbidden transitions from core 1s level to unoccupied 3d states of  $Ti^{4+}$  in the distorted  $TiO_6$  octahedron [22-24]. This contrasts with the characteristically observed four peaks (depending on energy resolution) of octahedral symmetry [17, 25]. Similar pre-edge structures with and without dopant Ni provide distinct evidence that Ni did not substitute for Ti in the  $TiO_6$  octahedral lattice of  $H_2Ti_2O_5 \cdot H_2O$ , as previously indicated in other doped nanotubes [20]. In a similar manner, structures above 4980 eV differed only minimally in oscillation intensity, which further supports our novel observation.

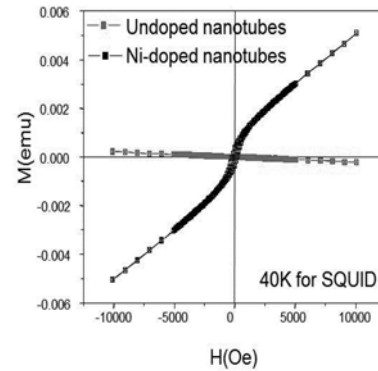
To investigate the chemical state of dopant Ni in TNTs, we compared Ni K-edge XANES of the Ni doped powder with metallic Ni and NiO; results shown in Fig. 3(b). Ni doped TNTs provided a radically different result than Ni metal, and their absorption edges shifted to a higher energy level even than NiO. Ni doped TNT's Ni K-edge conforms to  $Ni_2O_3 \cdot H_2O$ . Thus, we maintain XANES results strongly suggest that dopant Ni atoms are fully dissolved, exist in-between  $TiO_6$  octahedral lattices, and that  $Ni^{3+}$  substitutes for  $3H^+$ .

Fourier-transforms [11] spectra of Ti K-edge from undoped and Ni doped TNTs are presented in Fig. 3(c). Peak A, at  $0.6 \sim 2.0 \text{ \AA}$ , can be assigned to Ti-O scatterings, and results were similar for both samples. In contrast, shoulder peak B<sub>2</sub> in undoped TNTs, at  $2 \sim 3 \text{ \AA}$ , disappeared from Ni doped TNTs altogether. To explain why: in the  $H_2Ti_2O_5 \cdot H_2O$  structure, Ti has two types of surrounding titanium atoms, one from in-layer  $TiO_6$  octahedron and another from out-of-layer  $TiO_6$  octahedron. Each has different Ti-Ti bond lengths due to interlayer  $H^+$ ; therefore, two prominent peaks display for undoped TNTs. However, in the doped TNTs, Ni enters the interlayer as presented in our XRD analysis, and interlayer spacing increased. Consequently, Ti scattering in out-of-layer  $TiO_6$  octahedron did not influence in-layer Ti. This again leads us to believe that dopant Ni atoms reside in-between  $TiO_6$  octahedral lattices, not as substitutes for Ti atoms in the lattice.

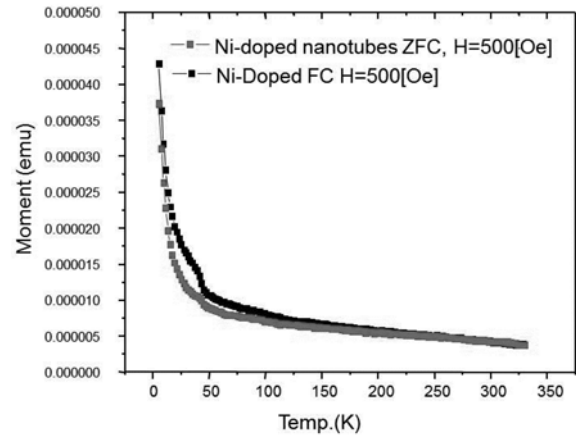
Fig. 4(a) and 4(b) show magnetic hysteresis curves of the Ni doped and undoped TNTs at 300K and 40K. Ni doped TNTs revealed reliable evidence of ferromagnetism at both temperatures, whereas undoped TNTs merely exhibited diamagnetism. Though undissolved Ni dopant or small Ni clusters outside the nanotubes would induce a ferromagnetic response, and others hypothesized that ferromagnetism in Ni doped TNTs comes from an



(a)



(b)



(c)

**Fig. 4.** Magnetic hysteresis curves of the (a) Ni doped and (b) undoped TNTs at 300K and 40K (c) Thermal blocking behavior of Ni doped TNTs (ZFC and FC).

impurity band, or defective interlayer [27], no evidence for impure traces of Ni particles could be found in our structural analyses (described above). Therefore, dopant Ni atoms must exist as a trivalent species, which interact with  $H^+$  in the TNTs' interlayers. To be sure, we tested this idea in yet another way to verify its validity. For nanoclusters of metallic ferromagnetic elements (Ni, Fe, Co, etc.), the superparamagnetic effect should present in the zero-field-cooling (ZFC) experiment.

So, Investigated Ni doped TNT's superparamagnetic limits; thermal blocking behavior was observed by measuring Field-Cooling (FC) and ZFC effects with an applied field of 500 Oe, presented in Fig. 4(c). The two curves bifurcate only slightly. This negligible bifurcation indicates that most TNTs have sizes close to the superparamagnetic effect's critical limit, and that the number of spins to freeze is very small. Others suggested that Ni doped TNTs' superparamagnetism comes from single domain magnetic precipitates in the nanotubes [28], yet our experiment leads us to conclude that for hydrothermally fabricated nanotubes, the superparamagnetic effect is due to the interacting spins with relatively larger Ni-doped TNTs, not smaller impurities of metallic Ni.

## Conclusions

Ni doped titanate nanotubes with outer and inner diameters of ten and six nm were synthesized via the hydrothermal method. This method is advantageous over others in that it is more scalable. The nanotubes showed layered structures of  $\text{H}_2\text{Ti}_2\text{O}_5\cdot\text{H}_2\text{O}$  and revealed reliable evidence of ferromagnetism at room temperature with Ni dopant. Additionally, trivalent Ni atoms substituted  $\text{H}^+$  in the nanotubes. These findings are considerably different than prior reported research. To use magnetic  $\text{TiO}_2$  nanotubes as a building block, ferromagnetic constant (area of the hysteresis curve) should be increased. Doping amount control and effect of other magnetic materials as dopants will remain as future work. To use magnetic  $\text{TiO}_2$  nanotubes as a building block, increase ferromagnetic constant (area of the hysteresis curve) is necessary.

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