REDUCED TITANATE NANOTUBES

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Abstract

The preparation of low dimensional redox agents containing titanium oxide was studied by reduction of titania nanotubes with reducing organic compounds. Acid titanium nanotubes were prepared exfoliation in the exchange sodium ions for protons with hydrochloric acid from disodium titanate, which was created by the hydrothermal reaction of nano-titanium oxide in an environment of concentrated sodium hydroxide. Thermal stability of redox nanotubes was analyzed by thermal analysis. Phase composition of nanotubes was determined by roentgen diffraction and nanomorphology was displayed by scanning electron microscopy and atomic force microscopy.

Keywords: titanate nanotubes, reduction, reduction organic compound, hydrothermal reaction

1. INTRODUCTION

For synthesis of partially reduced low dimensional titanate polyacids composited from nonstochiometric titanium oxide in the form nanotubes with titanium ions Ti^{3+} and Ti^{4+} is necessary to modify basic properties of titanate nanotubes, functional surface properties and apply reaction of surface hydroxyl groups with reduction agents of low valence titanium compounds. In the literature have been found no reduction of titanate nanotubes, only high temperature preparation of $M_2Ti_2O_4$ and MTi_2O_4 from titanate compounds, where M = alkali metal. In all samples, only stochiometric compounds was prepared.

2. EXPERIMENTAL

Binary system of titanate nanotubes and low valence titanium compounds was prepared for four compounds of reduced titanate nanotubes. For synthesis of titanate nanotubes was first component the nanosized (21 nm) titanium dioxide P25 Degussa (5 % weight) and second component was sodium hydroxide (10 M) as solvent [1], this preparation is in review [2], other preparation of TiNT is in publication [3]. This systems were homogenized using sonification by power ultrasound (100 W/cm^2) and heated in teflon pressure vessels (100 ml volume) at temperature 130 °C with 24 hours delay. Acid titanate nanotubes was prepared from this system by complete ion exchange of sodium after protons realized 24 h leaching at 0.1 M HCl. Binary systems of titanate nanotubes with low valence titanium compounds was prepared hydrothermal reaction titanate nanotubes (TiNT) with aqueous solution of HCHO, HCOOH, CH_3OH, $C_3H_6O_3$ (molar ratio 1:1).

Table 1. Preparation of reduced low dimensional titanium oxide

Sample	Binary systems	Reduction agents	Reduced systems with TiNT
1	TiNT – HCHO	HCHO	$H_2Ti_2O_{5-x}$+TiO_y
2	TiNT – HCOOH	HCOOH	$H_2Ti_2O_{5-x}$+TiO_y
3	TiNT – CH_3OH	CH_3OH	$H_2Ti_2O_{5-x}$+TiO_y
4	TiNT – $C_3H_6O_3$	$C_3H_6O_3$	$H_2Ti_2O_{5-x}$+TiO_y

3. RESULTS AND DISCUSION

3.1 Roentgen diffraction

X-ray diffraction patterns have shape of envelope for nanotube's morphology for all 4 samples (see Fig. 1). On Fig. 2 can be seen the records of pure TiNT ($nTiO_2$-DA5). In all 4 samples we found the presence of phase $H_2Ti_2O_5*H_2O$ (PDF 47-124) characteristics for titanate nanotubes and next phases (reduction agents).

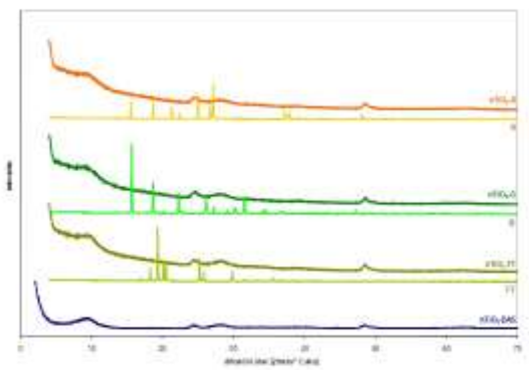


Fig 1. X-ray diffraction patterns of 4 samples

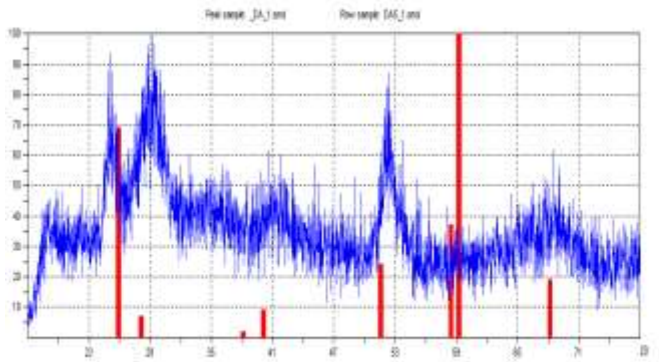


Fig. 2. X-ray diffraction patterns of titanate nanotubes

3.2 Thermal analysis

Reduced TiNT samples with of reduction agents (HCHO, HCOOH, CH_3OH, $C_3H_6O_3$) at thermal decomposition (Fig. 3) are beginning the looses of surface water, it shows endoeffects on DTA curve around 110 °C, weight loses is about 15%. Next exoeffects to 300 °C is transformation titanic acid on TiO_2, weight loses is about 20%.

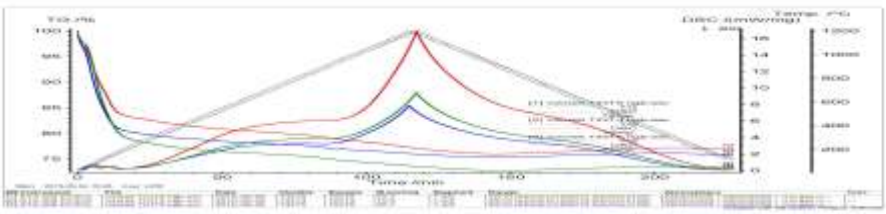


Fig. 3. - DTA – HCHO, HCOOH, CH_3OH, $C_3H_6O_3$

3.3 Scanning electron microscopy

Multi-wall TiNT can be seen in SEM (Figure 5 - 8) with multiwall structure. This structure is reflected in low intensity and large extension of x-ray diffractional lines

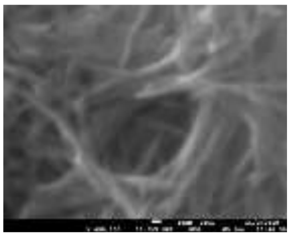
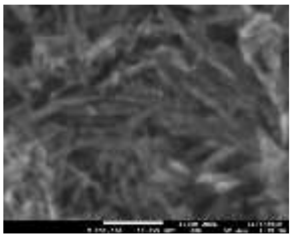
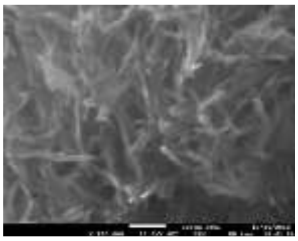
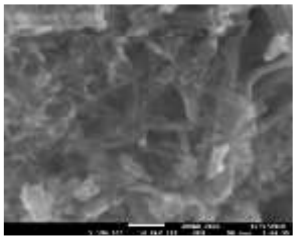
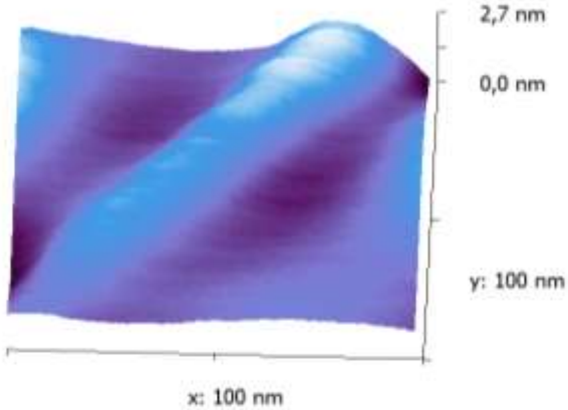





Fig. 5. TiNT-HCHO **Fig. 6.** TiNT-HCOOH **Fig. 7.** TiNT-CH_3OH **Fig. 8.** TiNT- $C_3H_6O_3$

3.4 Atomic force microscopy

Atomic forced microscope has been used to display of surface nanocylinder structure (Fig. 9, 10) of titanate nanotubes (pure TiNT) on graphite (HOPG). Nanotubes were adhesed only on graphite and after the sonolysis of nanotubes in water. The nanotubes become swabbed by AFM tip on micaceous basis.

3.5 Optical spectroscopy



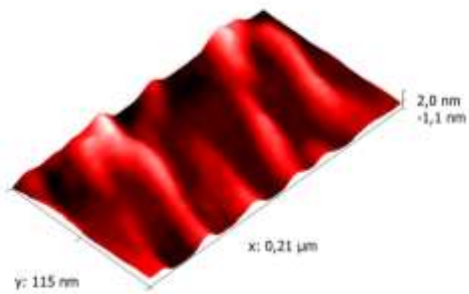


Fig. 9. AFM of pure titanate nanotubes **Fig. 10.** AFM of pure titanate nanotubes

The spectrum of reflected and scattered light was measured by fibre spectrometer. Samples have the color gray to black in dependence on the type of the reducing agents. In UV area can be seen the bands around photon energy 3.4 and 4.4 eV, corresponding with bands of valence titanium compounds.

CONCLUSION

The description of preparation of reduced titanate nanotubes by reduced organic compounds was presented. In our research we realized basic measurements for characterization redox low dimensional titanium oxide compounds.

ACKNOWLEDGEMENT

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LITERATURE

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