Nanostructured composite materials based on titanium dioxide doped by Mn: template zol-gel synthesis, structure, properties

V V Zheleznov1,*, A Yu Ustinov1,2, I A Tkachenko1, A A Kvach1, T A Kaidalova1 and A B Podgorbunsky1

1Institute of Chemistry FEB RAS, 159 Pr. 100-letiya Vladivostoka, Vladivostok 690022, Russia
2Far Eastern Federal University, 8 Sukhanova St., Vladivostok 690091, Russia

*E-mail: zheleznov_sergey@mail.ru

Abstract. Nanostructured composites based on TiO2 doped with Mn were obtained by sol-gel template method. The morphology and structure of the composites were studied by x-ray diffraction, scanning and transmission microscopy, X-ray photoelectron spectroscopy. Electrical conductivity and magnetic properties are investigated. It is shown that the doping of TiO2 samples with manganese improves conductivity by two orders of magnitude in comparison with a non-doped sample. Changing the annealing conditions of the nanostructured composite increases the conductive properties four times. It is established that the studied samples have ferromagnetic ordering at room temperature, and the saturation magnetization value and the slope angle of the curve M(H) depend on the annealing conditions, the presence of a magnetic transition in the region of 45 K corresponding to the transition Mn3O4 to the ferrimagnetic state is determined.

1. Introduction

In the last decade, a huge number of works on nanoscale titanium oxides have been published. At least in 2014, Chemical Reviews issued 21 reviews on the production, properties, and applications of nanoscale titanium oxides [1, 2]. Investigation of magnetic properties began intensively after the possibility of obtaining a magnetic TiO2 based semiconductor with room ferromagnetism was shown in [3]. In this paper we investigated the effect of annealing conditions on composition, structure, magnetic and conductive properties of Mn doped nanostructured titanium dioxide microtubes obtained by sol-gel method.

2. Synthesis of materials and methods of study

Nanostructured TiO2 microtubes doped with manganese were obtained according to the procedure described in [4]. The samples were annealed in air at a temperature of 500° C for 2 hours on a titanium substrate (Sample N1). After annealing the carbon template, the sample was additionally annealed for 2 hours in a porcelain crucible in air at 500° C (Sample N2). The Mn content in the samples (in terms of MnO2) was ≈17 wt. %.

The surface morphology was studied on a Hitachi S5500 scanning electron microscope (SEM) (Japan) and a Libra 200FE transmission electron microscope (TEM) (Carl Zeiss, Germany). X-ray phase analysis (XPA) was carried out on a D8 ADVANCE diffractometer (Germany) using the PDF-2
powder database. The magnetic characteristics of the specimens were measured on an MPMS-XL-5 SQUID magnetometer (Quantum Design, United States). X-ray photoelectron spectroscopy (XPS) was carried out using a surface analysis complex of SPECS Company (Bruker, Germany). Electrophysical characteristics of the materials under study were determined by the impedance spectroscopy method (IS) using a Solartron 1260 FRA and DI 1296.

3. Results and Discussion

According to the data of scanning and transmission (Fig. 1a, b) microscopy, the structure of the composite represents micro-sized tubes consisting of nanoparticles. According to the results of X-ray phase analysis, the samples contain anatase, rutile, and also Mn₃O₄ and MnTiO₃ phases.

![Figure 1. SEM-images of Sample N1.](image)

It should be noted that a change in the annealing conditions leads to a change in the ratio of the phases of rutile-anatase in the composite. As follows from the data of X-ray photoelectron spectroscopy (table 1) oxygen has at least two modifications - the dominant metal oxide and “oxycarboxylic”. The content of the metal oxide form is related to the amount of metals and its oxidation states. The presence of carbon is determined by the conditions of template synthesis. Titanium is present in the surface layer in two states: Ti⁴⁺ and Ti³⁺.

Table 1. Binding energies (eV) of elements in samples

| Mn (2p⁳/₂) | O (1s) | Ti (2p⁳/₂) | C (1s) |
|-----------|-------|-----------|-------|
| MnOT-2    |       |           |       |
| 641.5     | 531.7 | 529.7     | 288.5 | 286.3 | 285.0 |
| MnOT-4    |       |           |       |
| 641.4     | 531.1 | 529.2     | 458.4 | 456.9 |
| Mn³⁺      |       | TiOₓ      |       |
| COₓ       | Ti⁴⁺  | Ti⁴⁺      | CO₂   | CO    | CH |

According to impedance spectroscopy data, the electrical conductivity of undoped TiO₂ reached 0.8·10⁻¹² S/cm. Doping of TiO₂ samples with manganese improves the conductivity by two orders of magnitude compared to the undoped sample (up to 3.8·10⁻¹⁰ S/cm) - Fig. 2.

One of the reasons for the increase in conductivity may be the presence of the pyrophanite MnTiO₃ phase, which has highly conductive properties compared to the Mn₃O₄ and TiO₂ phases. However, it should not to exclude the possibility of the formation of a substitution solution when doping titanium dioxide with manganese (Ti⁴⁺ → Mn⁴⁺). In this case, if Ti⁴⁺ is replaced by Mn⁴⁺, oxygen vacancies should be formed, which can also lead to an increase in electrical conductivity. Thus, the improvement in electrical conductivity can be associated both with the generation of free charge carriers and with the formation of a highly conductive MnTiO₃ phase.
Changing the conditions of annealing of the nanostructured composite allows us to further increase the conductive properties by more than four times ($\sigma = 3.8 \cdot 10^{-10} \rightarrow 1.6 \cdot 10^{-9}$ См/см) (Fig. 2). The results of the investigation of magnetic properties are shown in figures 3, 4 and 5. A characteristic feature of the magnetization field dependences obtained at room temperature is the presence of hysteresis, indicating a ferromagnetic ordering in the samples (Fig. 3). Moreover, an annealing temperature increasing leads to magnetization values growth and changing the curve angle.

The reason for the ferromagnetic ordering at room temperature in paramagnetic titanium dioxide, doped with 3d metal researchers explain using a widespread model of coupled polarons [5]. However, it was shown in [6] that the presence of ordered defects of various types in the TiO$_2$ structure can also have a strong effect on magnetic properties. The presence of doping manganese ions and defective structure due to annealing makes it possible, in our case, the implementation of the two mechanisms described above for the initiation of ferromagnetic ordering. An increase in the slope of the magnetization curve with a change in the annealing conditions, obviously due to an increase in number of vacancies [7].

The observed peak on the ZFC curve is about 43 K and a sharp increase in the magnetization values in this temperature range on the FC curve (Fig. 4) allows us to say that the samples contain manganese oxide Mn$_3$O$_4$. This is because the transition temperature to the ferromagnetic state for Mn$_3$O$_4$ coincides with the values we obtained.

The observed shift of the hysteresis loop on the M(H) curves obtained at 3 K (Fig. 5) toward negative fields, indicates that in the studied samples there is a ferromagnet / antiferromagnet type interaction.
It was noted in [6], that defective regions with different spin orders could be formed on the surface of TiO$_2$ nanoparticles, leading to strong antiferromagnet / ferromagnet type exchange interactions, which most probably take place in our case.

4. Conclusions

Nanostructured titanium oxides doped with manganese have been obtained. The structure of composites was studied. It is shown that doping and changing the conditions of annealing of a nanostructured composite can increase the conductive properties by several orders of magnitude. It was established that the studied samples have ferromagnetic ordering at room temperature. Moreover, the saturation magnetization value and the slope of the M(H) curve depend on the annealing conditions. A relation between the increase in magnetization below 45 K and the transition to the ferromagnetic state of Mn$_3$O$_4$ was established. Variation in electrical conductivity values and ferromagnetic ordering at room temperature can be due to the presence of defects in the surface layers with a high probability.

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6. References

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