Research Article

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DC magnetization of titania supported on reduced graphene oxide flakes

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Abstract: DC magnetization of a series of titania nanocomposites modified with reduced graphene oxide (rGO) has been investigated. Hysteresis loops observed at room temperature disappeared at low temperatures. At a temperature of about 100 K, a phase transition to the superferromagnetic order state was observed, probably due to the linear expansion and self-reorientation of the magnetic moments. Processes associated with magnetic moment reorientation can cause a hysteresis loop to disappear at low temperatures as well as superferromagnetic ordering. It was suggested that the isolated nanoparticle in the nanopore could be used to create a "compass" at a nanometer-sized level that would be many times more sensitive than the conventional one. Measurements of the zero-field cooling and field cooling modes do not exclude the possibility of the coexistence of a superparamagnetic state.

Keywords: magnetism, nanocomposites TiO_2/rGO, phase transition

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1 Introduction

A semiconducting material, $TiO_{2-\delta}$ with ferromagnetism up to 880 K, without the introduction of magnetic ions were obtained [1]. They can be also applied to spintronics devices. According to the calculations, a stable ferromagnetic ground state [2] can occur in Cr-doped rutile TiO_2. Enhanced ferromagnetic properties were observed in N-doped TiO_2 [3]. The saturation magnetization at room temperature was in the order of Fe + N doped TiO_2 > N-doped TiO_2 ≫ Fe-doped TiO_2 > undoped TiO_2.

Density functional theory calculations were done for copper-doped titania (anatase and rutile) [4]. Ferromagnetism is predicted to be stable well above the room temperature with long-range interactions prevailing in the anatase phase and short-range interactions in the rutile phase.

Choudhury and Choudhury [5] investigated room temperature ferromagnetism exhibited by nonmagnetic metal oxide semiconductor nanostructures, considering an example of air and vacuum annealed titania nanoparticles. According to the obtained results, ferromagnetism is a nanoscale surface phenomenon in titania NPs, correlated with the presence of paramagnetic Ti^{3+} and F^{+} (oxygen vacancies) centers.

Ferromagnetic ordering at room temperature has been induced in the rutile phase of the TiO_2 polycrystalline sample by O ion irradiation [6]. The structural, electronic and magnetic properties of intrinsic defects in anatase-type ultrathin TiO_2 nanotubes have been investigated systematically by first-principles calculations [7]. This work offers a possible route toward high Curie temperature ferromagnetism in TiO_2 materials. Undoped and Ni-doped TiO_2 (xNi = 0.00, 0.50, 1.00, 1.50, 2.00 and 2.50 wt%) at room-temperature ferromagnetism has been investigated [8]. The addition of Ni did not affect the crystallinity of the samples but influenced the ferromagnetic behavior, which allows for potential spintronic applications of Ni-doped TiO_2 diluted magnetic semiconductors.

Recently, a new generation of nanocomposites for electronic circuit applications has appeared, based on titania modified with rGO [9–13]. Scientists dealing with these nanocomposites approve the importance of dynamic and static magnetic interactions by localized magnetic centers and the formation of magnetic aggregates (clusters) magnetic in physical processes. The most effective methods to study these phenomena are EPR/FMR (electron paramagnetic resonance)/(ferromagnetic resonance) and DC magnetization measurements by SQUID.

In our previous paper [14], EPR/FMR measurements of the whole series of titania nanocomposites modified with reduced graphene oxide (rGO) were reported. A ferromagnetic ordering and localized magnetic moments originating from oxygen defects in nanocomposite particles as well as from free radicals and trivalent titanium ions were observed, and their number depended on the calcination temperature. The application of appropriate proportions of these species improved the photocatalytic properties of the nanocomposites. The aim of the present work is to continue the previous studies [14] of magnetic properties by supplementary and in-depth investigation through the DC magnetization method (the same series of samples). Depending on calcination temperature, we can observe magnetic phase transitions, superparamagnetic state or the appearance of the hysteresis loop.

2 Experimental

Preparation of the titania-based nanocomposites modified with reduced graphene oxide (rGO) and their characteristics were previously described [14]. In the previous work, an attempt to correlate the magnetic properties of the titania/rGO nanocomposites with their photocatalytic activity has been made.

DC magnetization measurements were carried out using an MPMS-7 SQUID magnetometer in a 2–300 K temperature range and under a magnetic field up to 70 kOe, both in the zero-field cooling (ZFC) and field cooling (FC) modes.

3 Results and discussion

Figure 1 shows the temperature dependence of DC magnetic susceptibility $\chi(T)$ (here, χ is defined as $\chi = M/H$, where M is the magnetization and H an external magnetic field) and the reciprocal magnetic susceptibility $\chi - 1(T)$ of the nanocomposites TiO_2/rGO-8-400, TiO_2/rGO-8-500 and TiO_2/rGO-8-600 in the ZFC mode. The samples under study were registered in an external different magnetic field H in ZFC (zero-field cooling) and FC (field cooling) modes. The nanocomposite TiO_2/rGO-8-400 under a low applied external magnetic field showed the highest magnetic susceptibility (Figure 1). For higher values of the applied external magnetic field, the obtained dependencies were similar to those for other samples.

At the nano and macro levels, the magnetic moments are subject to the laws of classical physics. There is a well-known case of two compasses: when we bring them closer to an appropriate distance (depending on the magnetization of the needles), they positioned themselves anti-parallelly, while by applying an external magnetic field of appropriate intensity, they can line up parallelly. By applying magnetic nanoparticles in a small concentration, we can obtain a superparamagnetic state and there is a strong dependence of magnetic susceptibility in ZFC and FC modes [15,16]. Magnetic susceptibility decreases with increased calcination temperatures in the ZFC modes at low values of the transferred magnetic fields and, in both cases, at higher fields, this process disappears. We can note that GO and rGO DC measurements of magnetization showed a strong paramagnetic relationship [16]. When modifying titanium dioxide with rGOs, a resulting magnetic state is diametrically more complex. In all investigated nanocomposites, hysteresis loops were observed at room temperature (Figure 2) and disappeared at lower temperatures. At temperature 2 K, we can see in Figure 2 that remanent magnetization and coercive field are almost equal to zero so we can state that there is no hysteresis loop at 2 K. Table 1 lists the parameters describing the hysteresis loops at room temperature. So, we can assume that we have sparse "compasses" in the studied nanocomposites.

When high magnetic fields are applied to nanocomposites TiO_2/rGO-8-400 and TiO_2/rGO-8-600, a diamagnetism dominates at room temperature (Figure 2). In the case of nanocomposite TiO_2/rGO-8-500, we have a greater amount of trivalent titanium ions [14] and hence the behavior of magnetization is opposite. Some differences in reaching the diamagnetic state may be due to the different concentrations of localized magnetic moments. In all nanocomposites, paramagnetic behavior at low temperatures is dominant, and hence, we have a similar magnetization behavior under the influence of the applied magnetic field.

Figure 3 shows the dependence of inverse magnetic susceptibility on temperature for a nanocomposite TiO_2/rGO-8-400 in ZFC and FC modes at an applied magnetic field H = 100 Oe. There is a significant difference in inverse magnetic susceptibility at lower values of the

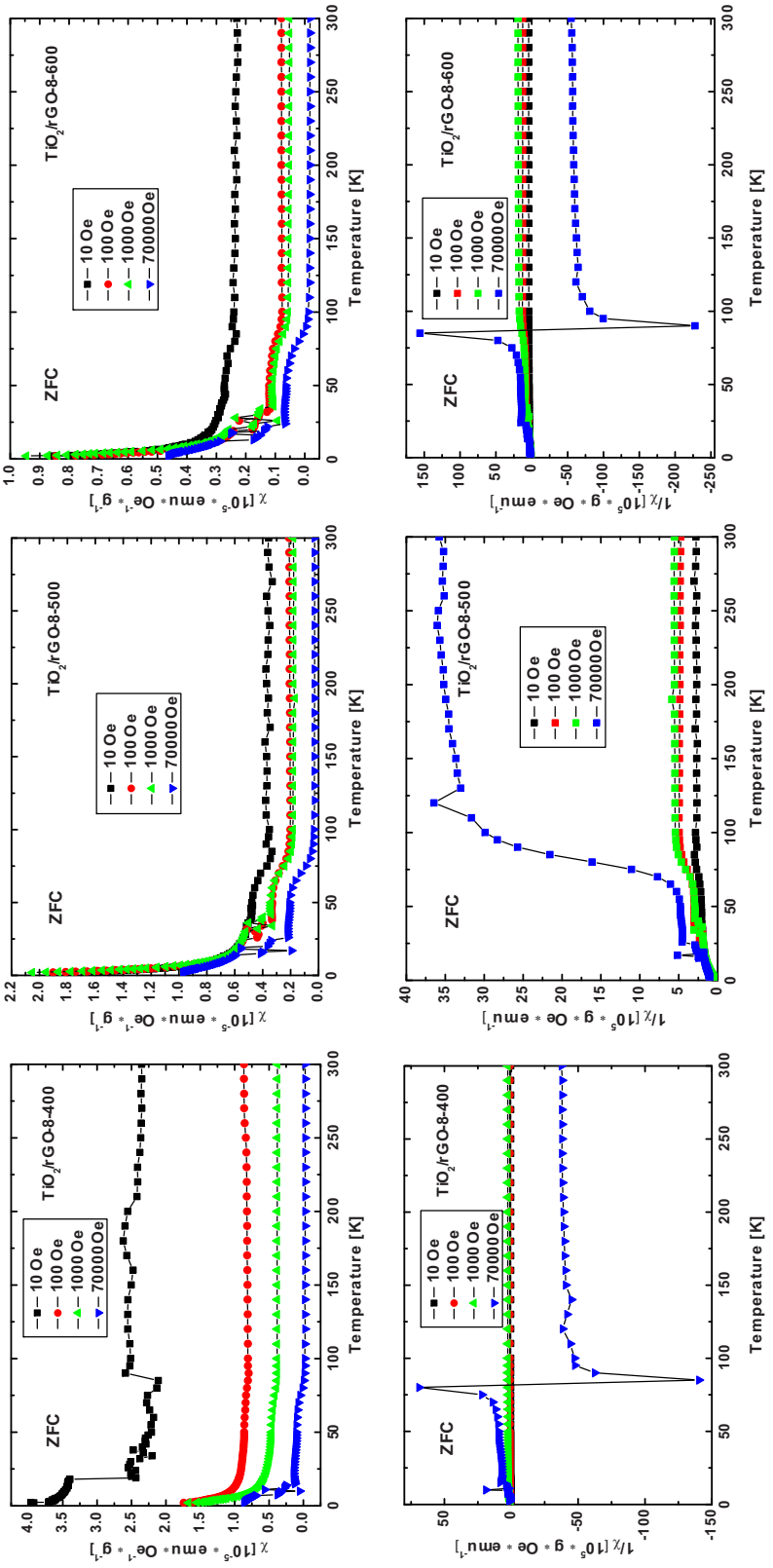

Figure 1: Temperature dependence of magnetic susceptibility and its inverse, ZFC mode.

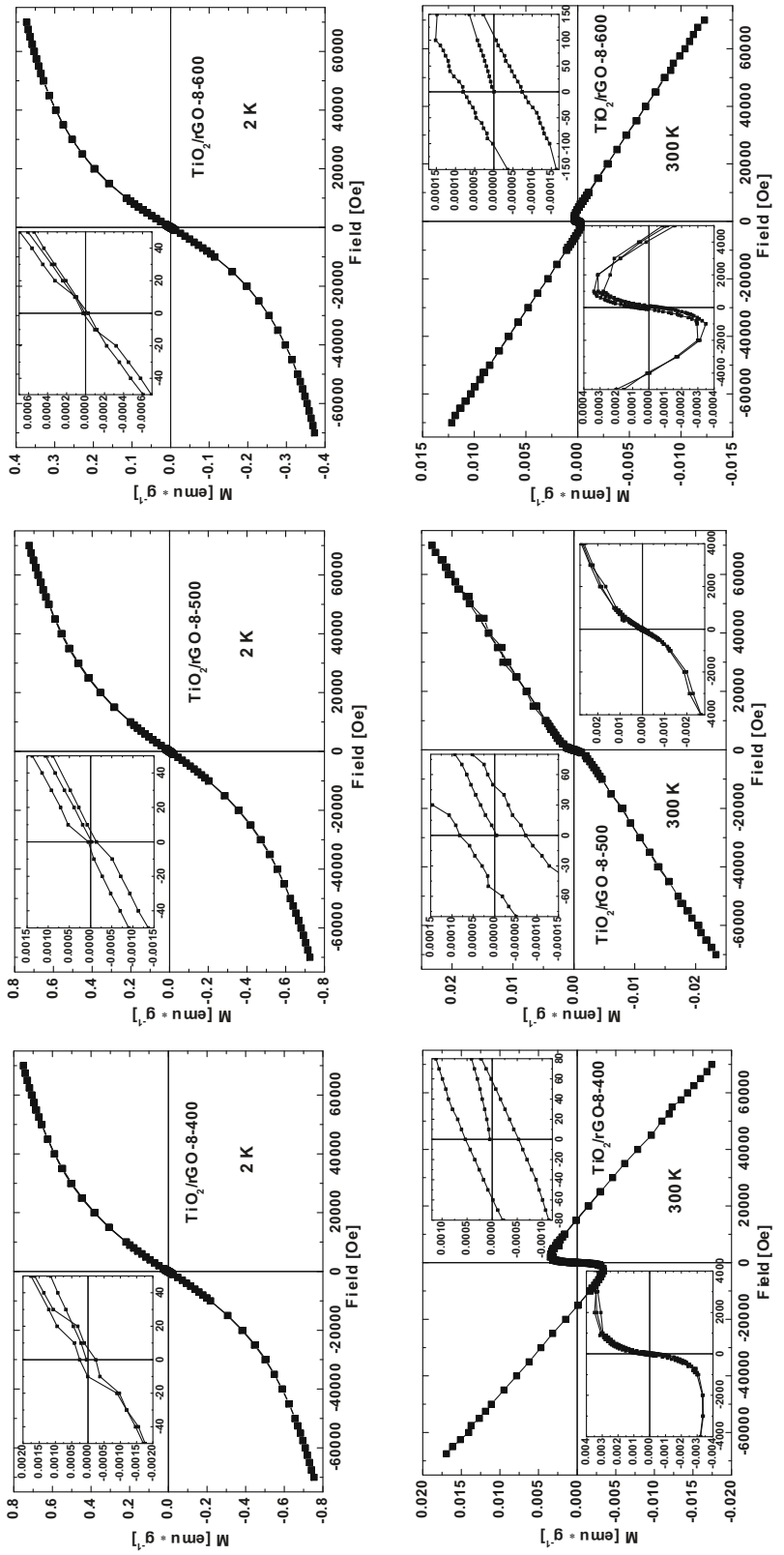

Figure 2: Dependence of magnetization on the magnetic field at $T = 2$ K and room temperature.

Table 1: Parameters of the magnetic hysteresis loop at room temperature

TiO_2/rGO-8-400		TiO_2/rGO-8-500		TiO_2/rGO-8-600	
Hc (Oe)	Mr (emu·g^{-1})	Hc (Oe)	Mr (emu·g^{-1})	Hc (Oe)	Mr (emu·g^{-1})
60	5.3×10^{-4}	50	7.7×10^{-5}	106	7.7×10^{-5}

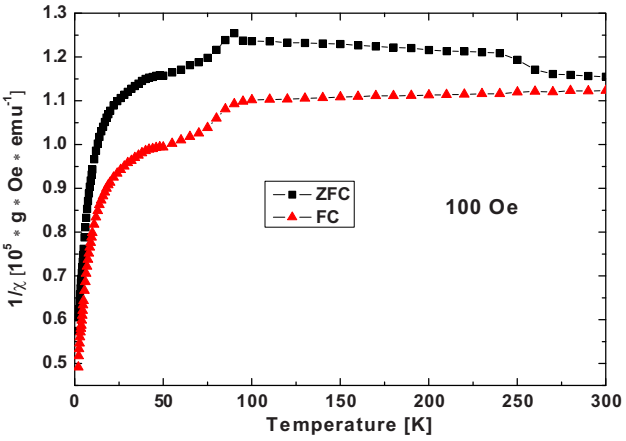

Figure 3: Temperature dependence of inverse magnetic susceptibility in ZFC and FC modes for the nanocomposite TiO_2/rGO-8-400 at an applied magnetic field H = 100 Oe.

applied magnetic field. This is due to the possibility of setting some anti-parallel magnetic moments. Below 100 K, we can observe a transition of magnetic moment systems from anti-parallel to ferromagnetic order, where below 50 K, there is an almost "paramagnetic" state. For a field 1,000 Oe in the FC mode (for all samples) after a linear extension of the 1/χ curve below about 100 K, the extension crosses the positive coordinate of the temperature axis; therefore, we conclude that there is a superferromagnetic order of magnetic moments. Magnetic nanoparticles are smaller in size than the nanopores and hence they are more mobile and the resulting internal magnetic field can act in order. With high values of the intensity of the external magnetic field, the transition to the ferromagnetic state takes place at about 100 K. In the case of nanocomposites TiO_2/rGO-8-500 and TiO_2/rGO-8-600, the transition occurred at about 90–100 K. The lower value of the critical temperature for the nanocomposite TiO_2/rGO-8-500 may be related to the presence of a greater amount of trivalent titanium ions [14].

Table 2 shows the values of the magnetic susceptibility at room temperature and at T = 2 K. At a temperature of T = 2 K, the magnetic susceptibility decreased with increasing calcination temperature for small external magnetic fields. By increasing the intensity of the applied external

Table 2: Magnetic susceptibility at temperatures of 2 and 300 K

			T = 2 K			
H (Oe)	TiO_2/rGO-8-400		TiO_2/rGO-8-500		TiO_2/rGO-8-600	
	ZFC	FC	ZFC	FC	ZFC	FC
			(10^{-5} emu·(g·Oe)$^{-1}$)			
10	3.9	4.9	1.8	1.9	0.9	0.9
100	1.7	2.0	1.9	2.0	0.8	0.9
1,000	1.7	1.9	2.1	2.1	0.9	1.0
70,000	0.9	1.0	1.0	1.0	0.5	0.5
			T = 300 K			
H (Oe)	TiO_2/rGO-8-400		TiO_2/rGO-8-500		TiO_2/rGO-8-600	
	ZFC	FC	ZFC	FC	ZFC	FC
			(emu·(g·Oe)$^{-1}$)			
10	2.4×10^{-5}	4.1×10^{-5}	3.6×10^{-6}	3.3×10^{-6}	2.3×10^{-6}	2.3×10^{-6}
100	8.7×10^{-6}	8.9×10^{-6}	2.1×10^{-6}	2.1×10^{-6}	7.9×10^{-7}	8.1×10^{-7}
1,000	3.8×10^{-6}	3.4×10^{-6}	1.8×10^{-6}	1.8×10^{-6}	5.2×10^{-7}	5.3×10^{-7}
70,000	-2.7×10^{-7}	-2.6×10^{-7}	2.8×10^{-7}	2.8×10^{-7}	-1.8×10^{-7}	-1.8×10^{-7}

magnetic field, the magnetic susceptibility decreased. In the case of the TiO_2/rGO-8-400 nanocomposite, the greatest difference in magnetic susceptibility in FC and ZFC modes was noticed (Figure 3). Probably, some of the magnetic moments aligned anti-parallely under the influence of the magnetic field. At room temperature, the lowest magnetic susceptibility value was obtained for the nanocomposite TiO_2/rGO-8-600. The highest value was obtained for the nanocomposite TiO_2/rGO-8-400 after applying a low external magnetic field. These results confirm that the smallest number of magnetic moments was found in the nanocomposite TiO_2/rGO-8-600, where the photocatalytic efficiency was the highest [14].

At very low temperatures, a magnetic susceptibility to oxygen defects related to trivalent titanium ions and free radicals was observed, which at low values of the external magnetic fields were subjected to the Curie-Weiss law with a negative Curie-Weiss temperature value. With higher applied external magnetic fields, the susceptibility followed the Curie law, probably due to the anti-parallel setting of magnetic moments associated with trivalent titanium ions [14].

At lower temperatures, the resonance lines of magnetic nanoparticles significantly shifted, increasing the internal magnetic field [17,18]. In the papers [19,20], a very small occurrence of magnetic clusters in nitrogen-reduced titanium dioxide was determined using the FMR method. In collaboration with the chemical engineering research group, a concept was developed to create a material based on the modified titanium dioxide, an ordering system of magnetic moments, created by the action of the internal magnetic field (superferromagnetic state). As a result of the effect of thermal expansion, a large internal magnetic field was generated at a certain temperature. The generated internal magnetic field affects the magnetic domains that cancel hysteresis loops at lower temperatures.

The materials under study are porous, and hence, we can consider the placement of magnetic moments in the pores as "compasses" at the nano level. By tuning the nanoparticles' size and porosity, we can create in the future a much more sensitive "compass" system.

The observed super-ferromagnetic state occurs significantly above the temperature of liquid nitrogen, which would be important because of the lower cost of future electromagnetic devices. In our previous work, we also showed that such a state was favorable for photocatalytic properties [14]. Since the magnetic ordering is dominated by trivalent titanium ions, creating magnetic hysteresis can influence the photocatalytic processes.

Since the magnetic ordering and the accompanying magnetic hysteresis are related to the trivalent titanium ions, the formation of hysteresis loops has a complex character. Because it is associated with titanium ions at a lower oxidation rate, it causes the disappearance of the hysteresis loop at lower temperatures, for example, due to the change in thermal expansion.

The hysteresis loop disappeared at low temperature; nevertheless, it is not possible to verify if this phenomenon could affect photocatalytic activity, as the photocatalytic process is carried out in water at room (or higher) temperature. The disappearance of the hysteresis loop at low temperatures may be due to the processes of reorientation of magnetic moments.

4 Conclusion

Measurements of the temperature dependence of DC magnetization in the ZFC and FC modes of a series of nanocomposites modified with reduced graphene oxide (rGO) were performed. The conclusions drawn in the previous work on magnetic resonance investigation [14] were confirmed. At room temperature, magnetic hysteresis was observed in all investigated nanocomposites, which disappeared at low temperatures. It is probably related to change of the internal magnetic field due to reorientation of spin systems. In the modified titanium dioxide, a superferromagnetic state was obtained by ordering magnetic moments through the resulting internal magnetic field.

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