Magnetism of Layered TiO$_2$

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Abstract. Room temperature ferromagnetism with large saturation magnetism was first observed in layered TiO$_2$ (LT). The LT is in rich of oxygen vacancy and free of magnetic transition metal elements. The temperature dependence of magnetism indicates that carrier mobility and carrier number of LT are larger than that of anatase TiO$_2$ (AT) and amorphous TiO$_2$ (AMT). The room temperature ferromagnetism is an intrinsic property of LT since there are no magnetic transition metal elements in LT. LT is a good platform to study two-dimensional (2D) magnetism.

1. Introduction  
Much attention has been paid to the two-dimensional (2D) magnetism of layered material [1-7]. Due to the reduced crystal symmetry and the intrinsic magneto-crystalline anisotropy of layered structures [1], layered magnets provide a platform for studying 2D magnetism [1]. 2D magnetism has advantageous for low-power digital applications and for eliminating short channel effects [2]. Many projected applications would involve the use of 2D magnetism by forming quantum wells, multilayers, superlattices, or heterostructures [3]. The low-dimensional nanostructures, high Curie temperature ($T_C$) and large magnetic moments are the long time quest to develop magnetic material into nano-electronics [3]. However, $T_C$ of most layered magnetic materials is far below room temperature [4-7]. For example, $T_C$ of K$_2$CuF$_4$ is only about 8K [4]. Although 2D Ti$_{0.8}$Co$_{0.2}$O$_2$ has a $T_C$ of about 350 K and ferromagnetism with strong spin polarization and spin-orbit-induced anisotropy [3], the origin of ferromagnetism in magnetic transition element doped oxide semiconductors is still under debate as the magnetic elements doping suffers from problems of cluster, precipitates or secondary phase formation [8-9].

The segregation and nanocluster of magnetic transition metal is a major concern about the origin of ferromagnetism in magnetic transition metal doped oxides [9]. The magnetism of material free of magnetic transition metal can prevent these problems happening as much as possible, and has been widely studied because of its potential application as diluted magnetic semiconductor [10-12]. In order to obtain intrinsic ferromagnetism, materials without magnetic transition metal dopants were investigated by calculations and experiments [10-12]. Furthermore, it was proved that Mn doping indeed does not play any key role in introducing FM in TiO$_2$ thin films [13]. $T_C$ of TiO$_2$ monolayer is predicted to be much higher than room temperature [2]. Moreover, Spontaneous direct band-gap, high hole mobility, high carrier mobility anisotropy and huge exciton energy were expected in atomic-thin TiO$_2$ nanosheet [14]. To our knowledge, there is no experimental report about the magnetism of layered TiO$_2$ up to now.

Recently, LT nanostructure consisted of multilayers nanostructure of repeating unit of (CH$_3$)$_4$N$^+$/titania with the thickness of titania about 0.63 nm was obtained [15]. The band gap of LT is close to that of monolayer TiO$_2$ [15]. The magnetism of LT was studied in this paper. It was found that the LT has room temperature ferromagnetism.
2. Experiments
The detail of LT and AT samples fabrication was reported in reference [15]. The AMT samples were available from Tianjin Zhiyuan Reagent co., Ltd. The room temperature magnetic hysteresis was measured by lake shore-735 vibrating magnetometer. The temperature dependence of magnetism was measured using PPMS-9 magnetometer with an applied field of 1000 Oe. The samples’ stoichiometry was measured by x-ray photoelectron spectroscopy (XPS; Kratos X SAM 800). The morphology was measured with a transmission electron microscope (TEM, TECNAL G2 F20). The composition analyses were conducted by the x-ray energy dispersive spectroscopy (EDS) equipped on the SEM and TEM.

3. Results and Discussion
The LT samples consisted of multilayer nanostructure of repeating unit of $(\text{CH}_3)_4\text{N}^+$/titania. The thickness of titania is determined to be about 0.63 nm [15]. The other dominant TiO$_2$ phases in LT are the brookite and anatase TiO$_2$[15]. Besides the brookite and anatase TiO$_2$, there may be AMT in LT. Room temperature magnetism of AT [10-12] and AMT [16] are often reported in literatures. However, the brookite phase TiO$_2$ was reported to be related to the absence of ferromagnetism in TiO$_2$ films [17]. Therefore, the magnetism of LT, AT and AMT was compared in this paper.

Figure 1 shows TEM of LT. The shape and size of particle is not uniform. Some particles have the spindle-like shape with a length of about 60 nm.

Figure 2 shows the room temperature magnetic hysteresis of LT, AT and AMT. As indicated in figure 2, LT and AT have clear hysteresis with the coercivity of about 70 Oe and 95 Oe, respectively. The magnetism of LT is saturated under a field of about 5000 Oe. The magnetism of AT is not saturated and increases linearly with magnetic field in the higher field region (>1000 Oe). This behavior of AT is due to that some magnetic moments is not coupled ferro-magnetically and acts as para-magnetism. On the other hand, AMT shows a diamagnetism dominant behavior besides a small hysteresis. It is not suprised to see a little magnetic hysteresis in AT [10-12] and AMT [16] samples. As shown in Figure 2, the diamagnetism is dominant for AMT sample at high magnetic field (>1000 Oe). The saturation magnetism of LT and AT is about $6\times10^{-3}$ and $2.4\times10^{-3}$ emu/g, respectively. The saturation magnetization of AT is determined by subtraction the paramagnetic part. The paramagnetic part increases linearly with magnetic field with the coefficient of about $4\times10^{-7}$ emu g$^{-1}$Oe$^{-1}$. The saturation magnetism of LT is similar as that of TiO$_2$ heated in reducing atmosphere, but about ten times of that of TiO$_2$ nanoparticles heated in air [18]. The magnetization of LT is much larger than that.
of AT and AMT. The magnetic hysteresis of LT, AT, and AMT were measured by the same method. The background contribution should be same for them. The difference in magnetic hysteresis of these three samples should be due to the structural difference of samples. This result means that LT is beneficial for obtaining room temperature ferromagnetism. Since the LT is consisted of ultrathin TiO$_2$ layer with the thickness of about 0.63 nm, the presence of room temperature ferromagnetism in monolayer of TiO$_2$ is confirmed by our experiments. Further study will be stimulated for the study of magnetism in monolayer TiO$_2$.

![Figure 3](image1.png)

**Figure 3.** M(T) for LT, AT and AMT

![Figure 4](image2.png)

**Figure 4.** The XPS of LT, AT and AMT

The temperature dependence of spontaneous magnetization (M(T)) depends on the probability distribution of the coupling between magnetic moments [19]. Concavity in M(T) is a signature for small free-carrier density ($n_c$) and small mean free path ($r_0$), while convex profiles appear deep in the large $n_c$ and large $r_0$. For intermediate $n_c$ and $r_0$, it is possible to obtain a linear M(T) curve [19]. As shown in figure 3, the $M(T)/|M(300)|$ (M(T) is the magnetization measured when temperature is T. $|M(300)|$ is the absolute value of magnetization measured at 300 K) has a convex, linear and concavity profile for LT, AT and AMT, respectively. This means that the free carrier density and mean free path is reduced from LT, AT to AMT. The electric transport property of carrier uncovered by M(T) behavior is in accordance with the calculation [14]. The calculation indicated that the hole mobility of TiO$_2$ atomic-thin nanosheets is much larger than that of bulk AT [14]. On the other hand, the electron mobility of TiO$_2$ atomic-thin nanosheets is smaller than that of bulk AT [14]. Since the thickness of TiO$_2$ of LT is only about 0.63 nm [15], the hole mobility in LT should be much higher than that of AT and AMT. It was reported that the ferromagnetism in TiO$_2$ was induced by the carrier transfer interactions created by the Ti$^{3+}$ and Ti$^{2+}$ [20]. The ferromagnetism of LT should be related to the carrier-mediated exchange interaction among the magnetic moments [19]. The magnetic moments dependence of carrier density shows that the magnetic moment value increase linearly and then reaches a maximum with hole concentration increasing. When the excited electrons are introduced into this system, those electrons will pair with the Ti atoms and weaken the original spin polarization [2]. Therefore, high hole mobility in LT should be beneficial for large magnetic moment.

In order to further explore the mechanism of magnetism in LT, the XPS of LT, AT and AMT was shown in figure 4. As seen in figure 4, no magnetic transition metal is detected in LT, AT and AMT.
samples by XPS measurements. The XPS have similar peaks for the LT, AT and AMT samples except the N1s peak in LT. The N1s peak is from (CH$_3$)$_4$N$^+$ absorbed in LT.

![Figure 5](image.png)

**Figure 5.** The binding energy of Ti 2p of LT, AT and AMT

XPS of Ti 2p of LT, AT and AMT was shown in figure 5. The binding energy of Ti 2p 3/2 and Ti 2p$_{1/2}$ of LT is about 458.1 eV and 463.8 eV, respectively. The binding energy of Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ of AT and AMT is about 458.6 eV and 464.3 eV, respectively. The binding energy of Ti 2p of LT shows a 0.5 eV shift to lower energy compared with that of AT and AMT. The shift to the low binding energy indicates the formation of Ti$^{3+}$[21-22]. The appearance of Ti$^{3+}$ in TiO$_2$ is mainly due to the maintenance of electrostatic balance because of the formation of oxygen vacancies [21]. By gain electron from surrounding oxygen atoms, the Ti$^{4+}$ is changed to the Ti$^{3+}$ state [22]. Oxygen vacancies will be easily formed on the surface [21]. More amount of Ti$^{3+}$ means more surface oxygen vacancies [21]. Since thinner TiO$_2$ has larger specific surface area [23], the oxygen vacancies are easily formed in the LT. it was reported that the average magnetic moment of one oxygen defect increases to a maximum value of 2.2 $\mu_B$ at 8% oxygen defect concentration [2]. Furthermore, the electrons of the oxygen defect can be transferred into the neighboring Ti atoms, which can lead to spontaneous spin polarization [2]. Therefore, the expected magnetism in TiO$_2$ was triggered by introducing the oxygen defect [2]. These behaviors in figure 2 and figure 5 mean that LT is rich in magnetic moments induced by structure defects like oxygen vacancy.

The XPS of O1s of LT, AT and AMT was shown in figure 6. The XPS of O1s of LT, AT and AMT can be well fitted using two peaks. The fit of O1s XPS of AT and AMT indicates that the peaks are located at about 529.7 eV and 531.8 eV, which can be assigned to the lattice oxygen species (LO) and the surface adsorbed oxygen species (SO), respectively[21]. The fit of O1s XPS of LT indicates that the peaks are located at about 529.8 eV and 532.9 eV, which can be assigned to the LO and the chemically-bonded water (OW), respectively [21]. The OW should be from the fabrication process of LT [24]. The SO presented in AT and AMT is not observed in LT. This should be due to that the surface of AT and AMT is exposed to air directly, but the surface of LT is covered by (CH$_3$)$_4$N. The SO is the low valence oxygen such as O$_2^-$ and O$^-$[25].

The XPS results indicate that there are more Ti$^{3+}$ (more oxygen defects) in LT compared with that of AT and AMT. The existence of Ti$^{3+}$ can be explained by the chemical equation (1):

$$4\text{Ti}^{4+} + \text{O}_2^- \rightarrow 4\text{Ti}^{4+} + 2e^- + 0.5\text{O}_2 \rightarrow 2\text{Ti}^{4+} + 2\text{Ti}^{3+} + \square + 0.5\text{O}_2$$

in which $\square$ represents the oxygen vacancy[26]. It was reported that the magnetic moment in vacuum-annealed TiO$_2$ films decays rapidly as the sample is stored under ambient conditions [27].
The oxygen vacancies producing ferromagnetic order in TiO$_2$ are unstable against excess oxygen[27]. Therefore, it is reasonable to suppose that oxygen vacancy and Ti$^{3+}$ would be absence according to equation (2):

$$2\text{Ti}^{4+} + 2\text{Ti}^{3+} + □ + 0.5\text{O}_2 \rightarrow 4\text{Ti}^{4+} + e^-/□ + 0.5\text{O}_2^- \text{ (or O}^-\text{)} \rightarrow 4\text{Ti}^{4+} + \text{O}_2^- $$

Equation (2) will take place in AT and AMT because the surface of AT and AMT is exposed directly to air. In other hand, it will not take place in LT because the surface of TiO$_2$ layer in LT is covered with (CH$_3$)$_4$N. The calculation reported that magnetic behavior can be generated by oxygen defects [2]. No magnetism could be observed in the pristine system without oxygen defects [2]. The experimental results also indicated that more oxygen vacancies are needed for larger room temperature ferromagnetism in TiO$_2$ [16].

Therefore, the larger ferromagnetism of LT should be related to the larger amount of oxygen defects. Although the Ti 2p and O 1s XPS of AT and AMT has little difference, the magnetic property of AT and AMT has large difference. The difference in magnetic property of AT and AMT should be related to the different carrier transport property as revealed by M (T)/|M(300)| profile in figure 3. The calculation indeed indicated that ferromagnetism in TiO$_2$ monolayer is only presented when hole density is larger than a critical value [28]. Besides the carrier transport property, the crystallinity also plays important role in magnetism [29].

4. Conclusion
The room temperature magnetism, temperature dependence of magnetism (M(T)), and X-ray photo electron spectra (XPS) of Layered TiO$_2$(LT), anatase TiO$_2$(AT) and amorphous TiO$_2$(AMT) were
investigated. The LT and AT samples have ferromagnetism at room temperature. On the contrary, AMT sample has a diamagnetic dominant behavior. The saturation magnetic moment of LT is about three times of that of AT. The $M(T)/M(300)$ of LT, AT and AMT has convex, linear and concavity profile, respectively. This behavior indicates that free carrier density and mean free path of LT are larger than that of AT and AMT. LT is in rich of structure defects like oxygen vacancy, which induces magnetic moments and ferromagnetic interaction.

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6. References
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