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Research Article

Origin of Ferromagnetism in Ru and N Codoped TiO_2 Nanotubes: Experiments and Theory Investigations

Jing Xu,[1] Zhongpo Zhou,[1,2,3] and Haiying Wang[1]

[1]*College of Physics and Material Science, Henan Normal University, Xinxiang 453007, China*
[2]*Henan Key Laboratory of Photovoltaic Materials, Xinxiang 453007, China*
[3]*Key Laboratory of Artificial Micro- and Nano-Structures, Ministry of Education and School of Physics and Technology, Wuhan University, Wuhan 430072, China*

Correspondence should be addressed to Zhongpo Zhou; paul@whu.edu.cn and Haiying Wang; wanghaiy@whu.edu.cn

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The room temperature ferromagnetism (RTFM) of the undoped, N doped, Ru doped ,and Ru-N codoped anatase TiO_2 nanotubes (TNTs) films are investigated combined with experiments and first principles approaches. The experiments are highly consistent with the theory calculations. All samples display anatase structures and ferromagnetism at room temperature. The values of the saturation magnetization (Ms) of undoped TiO_2, N doped TiO_2, Ru doped TiO_2, and Ru-N codoped TiO_2, respectively, are 0.065 emu/g, 0.015 emu/g, 0.155 emu/g, and 0.073 emu/g. The calculated net moment is in the order of Ru doped > Ru-N codoped > undoped > N doped. The oxygen vacancies play an important role in RTFM of TNTs. Moreover, the hybridization of Ru 4d, N 2p, and O 2p led to the spin-spilt of Ru 4d, N 2p, and O 2p which is devoted to the system magnetism.

1. Introduction

Diluted magnetic oxide semiconductors (DMOSs) have been extensively studied because of the combined transport properties and magnetic properties, which are desirable for spintronic application [1]. The investigations mainly focus on metal doped and nonmetal doped TiO_2, specially for transition metal doping which contains unpaired d electron configuration, such as Mo [2], Co [3], Fe [4], Mn [5], and V [6], and for nonmental elements doping, such as C [7], N [8, 9], and S [10]. There are several models to explain the ferromagnetic origin, for example, Stoner-type model [11] and band coupling model [12]. However, the origin of the RTFM is still controversial.

Recently, the studies about the influence of oxygen vacancy (Vo) on RTFM are paid more and more attention [6, 13]. The weak magnetic moment was observed in TiO_2 films due to abundant Vos [14]. Yang et al. [15] ascribed it to the magnetic Ti^{3+}, which views the Vo as free electron donator that causes Ti ion valence change contributing to magnetic moment.

In this work, we report the RTFM in Ru and N codoped TiO_2 nanotubes by experiments and theoretical calculations. The experiment results show that the saturation magnetization values are in the order of Ru doped > Ru-N codoped > undoped > N doped. The first principles calculations results imply that all the samples exhibit ferromagnetism except for Vo and N codoped anatase TiO_2. The hybridization between the Ru 4d electron states, N 2p electron states, and the O 2p electron states, nearest to the doped Ru atom, leads to the spin-polarized states of electrons. The origin of ferromagnetism is discussed based on the experiment and calculation results.

2. Experiments

The titanium (1 mm thick, purity 99.9%) foils were cut in a size of 2 cm × 2 cm and polished with abrasive papers. These titanium foils were cleaned in deionized water and ethyl alcohol by ultrasonication. The TiO_2 samples were synthesized by a two-step anodic oxidation method. Firstly, the titanium and graphite sheets were put in the electrolyte (including 0.5 wt% NH_4F, 5 mL H_2O, and 195 mL ethylene glycol) as

anode and cathode, respectively, with a 40 V direct current (DC) voltage. After 30 minutes of anodic oxidation, the titanium sheets were taken out to wash away the electrolyte by the ultrasonic cleaner for about 15 minutes. Secondly, the amorphous TNTs films were obtained by the second anodic oxidation treatments. Generally, the completely different growth morphology can be obtained, if fluoride ions are present in electrolytes and suitable anodization conditions are used. Ordered nanotubular/nanoporous structures of TiO_2 or other transition metal oxides can be formed. The morphology and the structure of porous layers are affected strongly by the electrochemical conditions (particularly the anodization voltage) and the solution parameters (in particular the HF concentration, the pH, and the water content in the electrolyte). In this work, the anodic oxidation voltage of 40 V was chosen purposefully to get TiO_2 nanotubes with demanding diameters.

After the two-step anodic oxidation, the samples were annealed at 500°C in air atmosphere and at 500°C in NH_3 atmosphere to produce undoped TiO_2 and N doped TiO_2, respectively. To obtain Ru doped TiO_2, the samples were immersed in the $RuCl_3$ solution for one hour. Following the same procedures, similar with undoped TiO_2 and N doped TiO_2, the Ru doped TNTs films and Ru-N codoped TNTs films were obtained.

The structure and morphology of the samples were analyzed by means of X-ray diffraction (XRD, Bruker AXS D8) using Cu Kα radiation and field effect scanning electron microscope (SEM, S-4800). To investigate the electronic structures of ions contained in the samples, the X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi) was employed. The photoluminescence (PL) spectra were conducted by using the 325 nm He-Cd laser (20 MW) as an excitation light source. The magnetic properties were measured by a vibrating sample magnetometer (VSM) with the magnetic field from −10 KOe to 10 KOe.

3. Results and Discussions

The XRD patterns of the samples are shown in Figure 1. The peak positions of all the samples are similar with each other. It indicates that the elements N or Ru are doped into the TiO_2 crystal lattice. The peaks appearing around 35.1°, 38.4°, 40.2°, 53.0°, 62.9°, 70.7°, 74.2°, and 76.2° are indexed to titanium (100), (002), (101), (102), (110), (103), (112), and (201) peaks. The peaks around 25.3°, 37.8°, 48.1° and 53.9° are indexed to TiO_2 anatase (101), (004), (200), and (105) peaks. No evidence of other peaks, such as rutile or impurities, is detected. It is noticed that the XRD diffraction intensity varied a little for the different dopants for Ru doped TiO_2, N doped TiO_2, Ru-N codoped TiO_2, and undoped TiO_2. It is indicated that the TiO_2 crystallizations, which is sensitive with the XRD diffraction intensity, fractionally changed by the TNTs films synthesis procedures and the different dopants.

To obtain the samples morphological feature, SEM measurements were conducted. Figure 2 shows the SEM images of nanotubes film cross-sectional view, nanotubes film bottom view, and nanotubes film top view, respectively. In Figure 2(a), the length of the nanotubes is about 1000 nm. Figure 2(b)

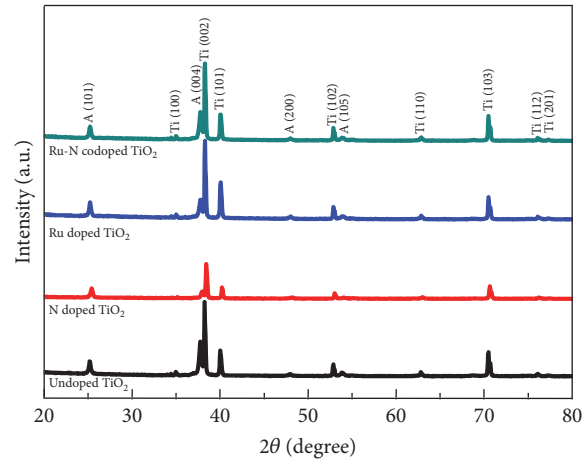
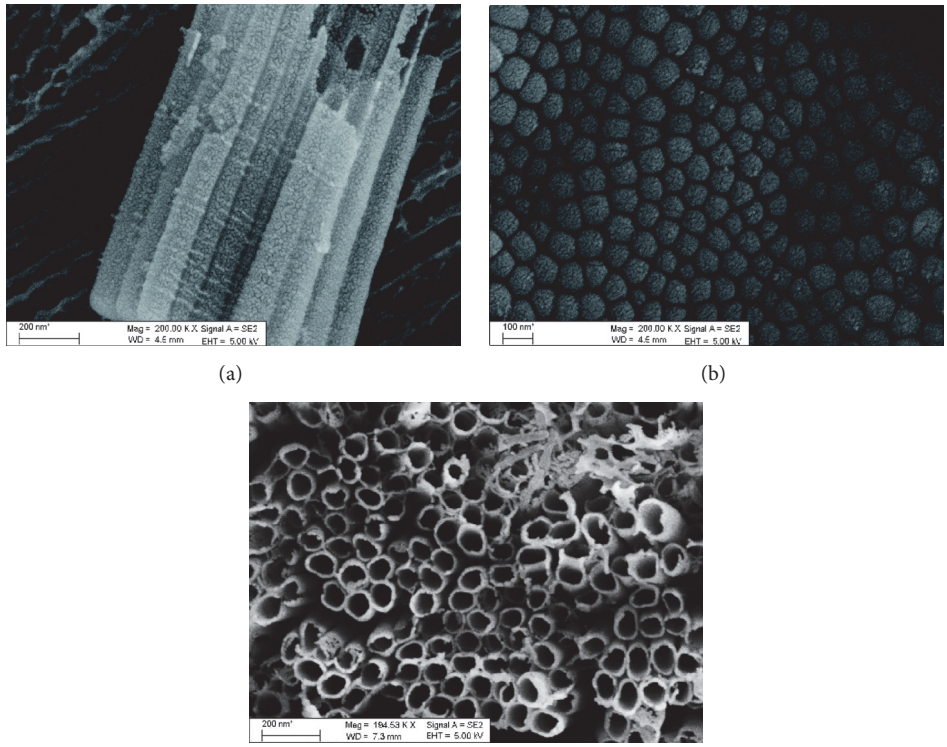


Figure 1: XRD patterns of undoped TiO_2, Ru doped TiO_2, N doped TiO_2, and Ru-N codoped TiO_2.

displays the film bottom of the nanotubes which is narrow and neat. The average diameter of the nanotubes bottom is about 70 nm. And Figure 2(c) shows the nanotubes top view. The average tube diameter is approximately 65 nm and the tube wall thickness is about 20 nm.

The optical properties are investigated by PL spectra at room temperature (300 K) and at 250 K which are shown in Figures 3(a) and 3(b), respectively. The horizontal axis is wavelength value with the range from 400 nm to 550 nm. According to the report of Siddhapara and Shah [16], the emission peaks at 468 nm and 482 nm are mainly due to the recombination of electron hole in TiO_2. In Figure 3(b) the peaks that appeared at 450.3 nm, 467.5 nm, and 481.8 nm are the signals of the oxygen vacancies [17]. There are several weaker peaks appearing at 420.1 nm, 439.8 nm, and 492.3 nm. The peak at 420.1 nm is a result of the band edge free excitation. The emission peak at 439.8 nm should be ascribed to self-trapped excitons located on TiO_6 octahedron [9]. The emission peaks at 492.3 nm are attributed singly to the occupied oxygen vacancy [5]. It was noticed that in Figure 3(b) all the peak position sites display a blue shift by the temperature decrease compared with the peak position sites in Figure 3(a). The three "peaks" tagged at 409.1 nm, 508.9 nm, and 546.6 nm in Figure 3(a) are viewed as measurement errors which are not detected at lower temperature.

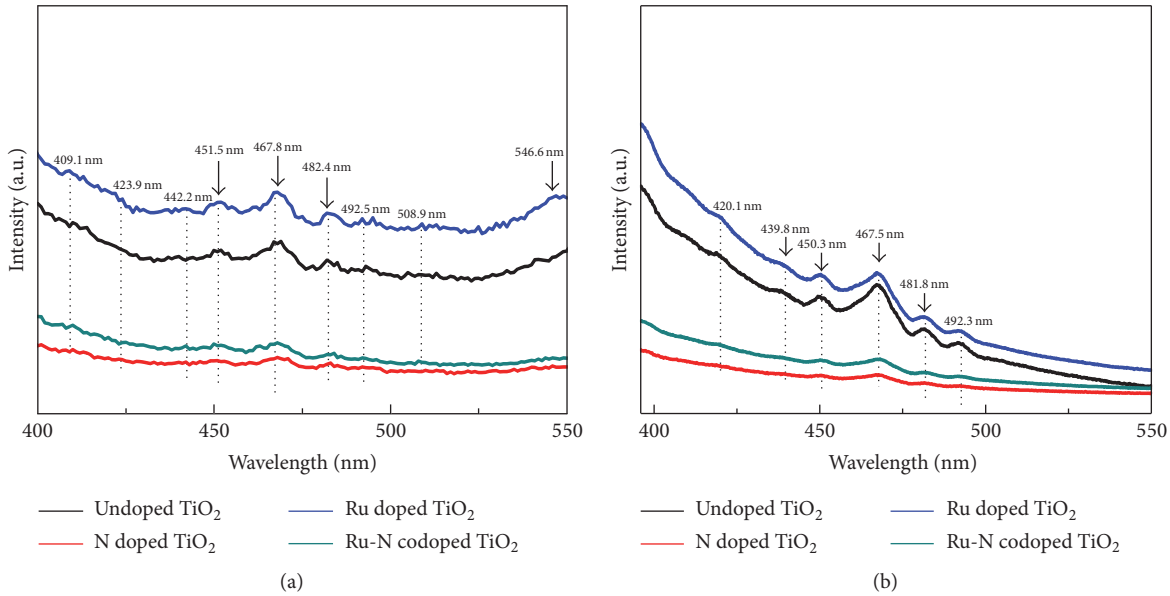
To investigate the chemical state of the ions in the samples, the XPS spectra are demonstrated in Figure 4. It can be seen from Figure 4(a) that the Ti 2p core level spectrum with the peaks is located at 458.47 eV and 464.16 eV. The binding energy (BE) values, which corresponded to TiO_2 Ti $2p_{3/2}$ and Ti $2p_{1/2}$ states, respectively, indicate the existence of Ti^{4+} in all the samples. Figure 4(b) shows the Ru 3d core level spectrum with the peaks positions located at 284.68 eV, 286.24 eV, and 284.94 eV, respectively. The BE peak at 284.68 eV is associated with C 1s [18] which is from air atmosphere during the XPS test procedure. According to the report of Guo et al. [19], the BE peaks observed at 280.5 eV and 283.9 eV are suggested to



(a) (b)

(c)

FIGURE 2: SEM for Ru-N codoped samples (a) nanotubes film cross-sectional view, (b) nanotubes film bottom view, and (c) nanotubes film top view after 500°C annealing.



(a) (b)

FIGURE 3: PL emission spectra of undoped TiO_2, Ru doped TiO_2, N doped TiO_2, and Ru-N codoped TiO_2 (a) at 300 K and (b) at 250 K.

be from Ru^{4+} ions, while higher BE peaks at 285.9 eV and 287.7 eV are ascribed to be the Ru oxidation states, lower than +3 but higher than that of Ru^0. In our results, the BE values of 284.94 eV and 286.24 eV are between Ru^{4+} and Ru^0, which may be assigned as Ru^{3+}, resulting in the forming of Vos. According to the PL spectrum, V_O appears in the crystal lattice. And it is clear that one V_O can provide two free electrons. One electron is trapped by O element, whose outermost electron is $4d^7 5s^1$. Two free electrons were shared by the surrounding N and O atoms. One Ru atom and one

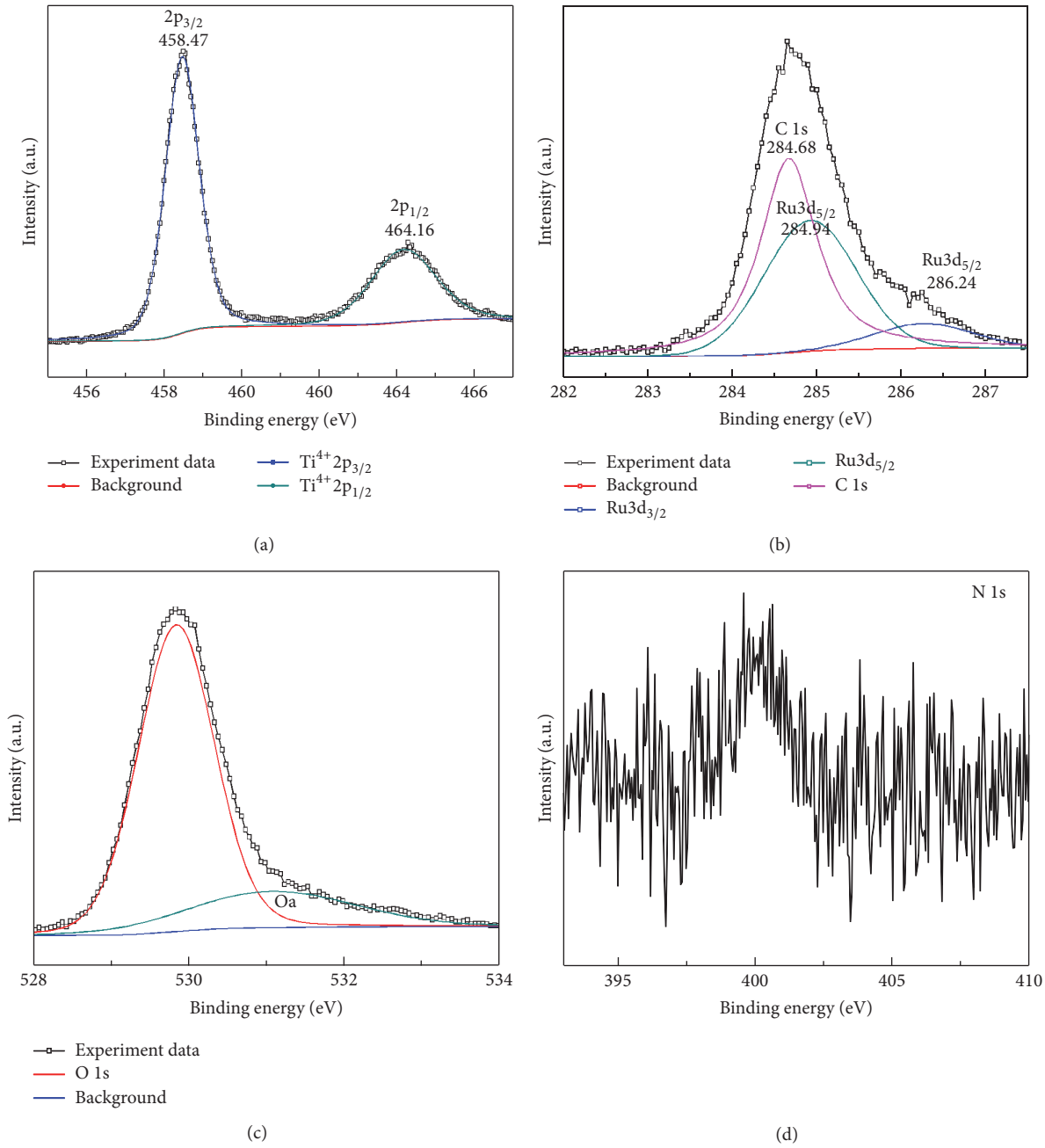


Figure 4: XPS of (a) Ti 2p, (b) Ru 3d, (c) O 1s, and (d) N 1s for Ru-N codoped TiO_2 nanotubes.

Ti atom will lose four electrons and the balance state is Ru^{3+} and Ti^{4+}, respectively. Figure 4(c) shows O 1s core level peak with two fitted peaks located at 529.8 eV and 531.2 eV, respectively. It is noticed that Oa peak is attributed to the oxygen of hydroxyl groups, which were chemisorbed on the sample surface [20]. Figure 4(d) demonstrates the core level XPS spectrum of N 1s with a weak peak at 399.3 eV. This peak observed around 399 eV is often attributed to the anionic N- in O-Ti-N linkages by many researchers [21], because the electronegativity of nitrogen doped into TiO_2 lattice is lower than that of oxygen.

Figure 5 shows magnetic hysteresis (M-H) loops of undoped TiO_2, N doped TiO_2, Ru doped TiO_2 and Ru-N codoped TiO_2. Clear saturation and hysteresis are observed which strongly suggest that all samples are ferromagnetic even at room temperature. The saturation magnetization (Ms) is the state reached when an increase in applied external magnetic field H cannot increase the magnetization of the material further. The saturation magnetization values of undoped TiO_2, N doped TiO_2, Ru doped TiO_2, and Ru-N codoped TiO_2, respectively, are 0.065 emu/g, 0.015 emu/g, 0.155 emu/g, and 0.073 emu/g. It is obvious that the Ru doped TiO_2 has the largest Ms, while N doped TiO_2 has the lowest Ms value. The Ms of undoped TiO_2 is larger than that of the N doped, which is consistent with the report [22]. The undoped TiO_2 and Ru-N codoped TiO_2 samples have similar hysteresis

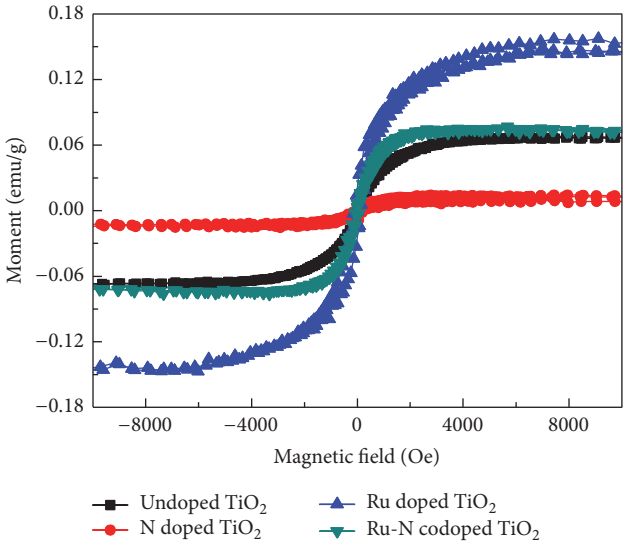


FIGURE 5: M-H loop recorded at room temperature of undoped TiO_2, N doped TiO_2, Ru doped TiO_2 and Ru-N codoped TiO_2.

loop. The values of Ms are in the order of Ru doped TiO_2 > Ru-N codoped TiO_2 > undoped TiO_2 > N doped TiO_2. The results show that a mechanism should be responsible for the enhancement of FM in our experiments.

In order to find out the essential origin of the ferromagnetism in Ru doped TiO_2 and Ru-N codoped TNTs films, the first-principle calculations are performed. The calculations are performed with VASP (Vienna Ab-inito Simulation Package) based on density functional theory. The calculations have been carried out for four cases: (1) one oxygen (O) atom is substituted by a Vo ($Ti_{32}O_{63}$); (2) two O atoms are substituted by a Vo and a N atom ($Ti_{32}O_{62}N$); (3) two O atoms are substituted by a Vo and a Ru atom ($Ti_{32}O_{62}Ru$); (4) a titanium (Ti) atom and two O atoms are substituted by a Ru atom, a V_O and, a N atom ($Ti_{31}RuO_{62}N$). The Monkhorst-Pack scheme k-points grid sampling was set to be $2 \times 2 \times 5$ for the 95-atom anatase supercell. The valence electrons configuration for the O, N, Ti, and Ru are 2s2 2p4, 2s2 2p3, 3s2 3p6 3d2 4s2, and 4d7 5s1, respectively. All the atomic positions are fully optimized until the atom forces drop below the value 0.02 eV/Å. The total density of states (TDOS) and partial density of states (PDOS) of Ru doped TiO_2 and Ru-N codoped TiO_2 are shown in Figure 6. The vertical axis is the value of states density and the horizontal axis is the value of electronic energy. On Figure 6(a)(I), there is an obvious exchange spin-splitting around the Fermi level which indicates the existence of ferromagnetic order in the system. And the calculated value of the magnetic moment is about 1.887 μ_B. Figure 6(a)(II) demonstrates an exchange spin-splitting; and it is observed that Ru 4d impurity states peak appeared in the band gap. From Figure 6(a)(III) to Figure 6(a)(VII), all of the upspin electrons and downspin electrons has spin-split exchange spin-splitting indicating a strong interaction between Ru 4d and O 2p in the Ru doped TiO_2 system. The system magnetic moment mainly comes from Ru atoms about 1.557 μ_B and minor magnetic moment is from the surrounding O atoms with 0.207 μ_B in this system. Besides, little small magnetic moments also appear in the second closed O atoms. It indicates that magnetic orbital center diffused from doped Ru atom to the second closed O atoms.

Figure 6(b)(I) shows the TDOS for the Ru-N codoped TiO_2. The spin-split at the bottom of the conduction band indicates the existence of the ferromagnetism. And the calculated value of the magnetic moment is about 0.955 μ_B. The spin-split around the Femi level exists according to Figure 6(b)(II) to Figure 6(b)(VII). The magnetic moment values of Ru 4d, N 2p, and the nearest four O atoms are 0.734 μ_B, 0.025 μ_B, 0.009 μ_B, 0.041 μ_B, 0.041 μ_B, and 0.023 μ_B, respectively. There is strong hybridization between Ru 4d, O 2p, and N 2p which donates and forms the total magnetism of the system.

For the Vo doped TiO_2 and Vo and N codoped TiO_2 systems, the investigation of the origin of the ferromagnetism has been reported clearly by Wang et al. and Zhou et al. [13, 22]. In the case of the Vo doped TiO_2 nanotubes, it is assumed that the system owns only one Vo, and the Vo contributes two electrons. One electron contributes to its surrounding two equal Ti atoms with downspin and the other electron was contributed to the third Ti atom surrounding the Vo with upspin; therefore the total magnetic moment is zero. According to our calculation results, the calculated magnetic moment is 0.533 μ_B which may come from the lattice oxygen distortion in TiO_2 nanotubes films. For the scenario of Vo and N codoped TiO_2 nanotubes, there are no spin-split exchange which indicates no ferromagnetic order exists in the Vo-N codoped TiO_2. Also one Vo donate two electrons; one is captured by the nearby N atom; and the other is donated to the three equal Ti atoms with zero net magnetic moment. In our calculation, similar results are obtained.

4. Conclusion

The undoped, Ru doped, N doped, and Ru-N codoped TiO_2 TNTs films were synthesized by a two-step anodic oxidation and annealed in air atmosphere or NH_3 atmosphere. XRD patterns show there is no impurity and other phases except the anatase TiO_2 and metal Ti. The Vos that were discussed employed PL spectra. The XPS results show there are Ti^{4+} and Ru^{3+}; and two free electrons donated by a Vo are shared by the surrounding N and O atoms. The VSM result shows all simples exhibit RT ferromagnetic order and the values of saturation magnetization are in the order of Ru doped > Ru-N codoped > undoped > N doped. The results on magnetic properties calculated based on first principles indicate that the Ru doping and Vo doping play an important role in the origin of system magnetism. The system ferromagnetism results in the orbit hybridization of spin-split O 2p states, Ru 4d states, and N 2p states.

Competing Interests

The authors declare that they have no competing interests.

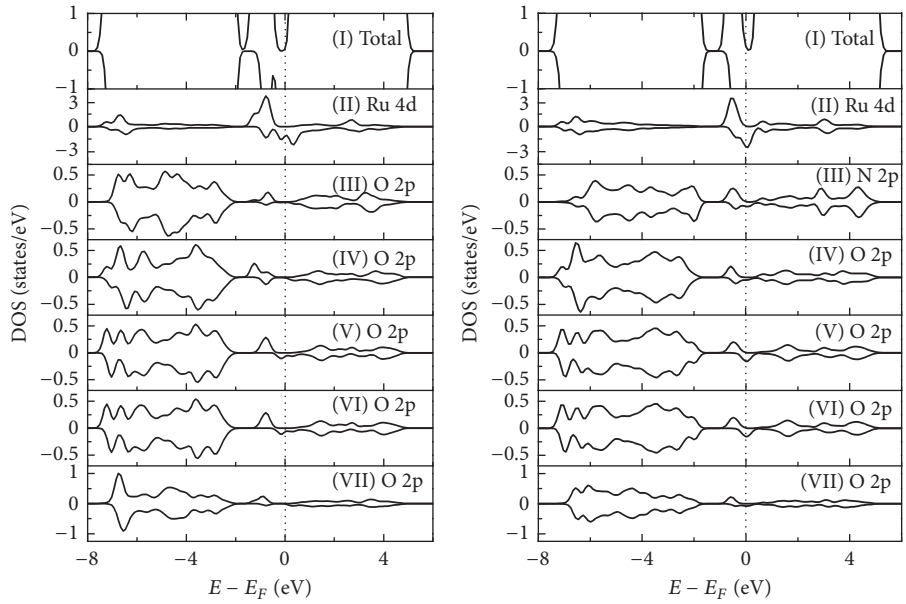


Figure 6: (a) TDOS of Ru doped TiO_2 nanotubes films: (a)(I) the TDOS of Ru doped TiO_2, (a)(II) the PDOS of the Ru 4d electrons and five O 2p electrons (a)(III), (a)(IV), (a)(V), (a)(VI), and (a)(VII) nearest to the defect Ru atom. (b) The total density of states (DOS) of Ru-N codoped TiO_2 nanotube films: (b)(I) the TDOS of Ru-N codoped TiO_2, (b)(II) the PDOS of the Ru 4d electrons (b)(III), the PDOS of the N 2p electrons and four O 2p electrons (b)(IV), (b)(V), (b)(VI), and (b)(VII) nearest to the defect Ru atom.

Acknowledgments

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