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Mechanism of defect induced ferromagnetism in undoped and Cr doped TiO_2 nanorods/nanoribbons

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ABSTRACT

We have studied the effect of doping concentrations, growth temperature and calcinations on the structural, optical and magnetic properties of the undoped and Cr doped TiO_2 nanorods/nanoribbons (NR/NRb), in order to develop an improved understanding on the mechanism of room temperature (RT) ferromagnetism (FM) in these nanostructures. Both undoped and doped TiO_2 NR/NRb exhibit RT FM and a ~2.6 fold enhancement in magnetization is observed in 0.3% Cr doped TiO_2 NR/NRb as compared to the undoped NR/NRb, and the magnetization increases considerably after vacuum annealing. However, no measureable FM is observed for the precursor TiO_2 powder, despite the presence of high concentration of oxygen vacancies in it. On the other hand, the magnetization decreases at higher doping concentration (0.7% Cr) as compared to 0.3% Cr doped sample. Thus, our studies revealed that a simple oxygen vacancy and/or Cr ions alone cannot yield the RT FM in TiO_2 nanostructures. We argue that the oxygen vacancy with appropriate charge redistribution and their orbital overlapping, and exchange interaction with the nearby unpaired 3d electron of Ti^{3+} in undoped TiO_2 and/or unpaired 3d electrons of Cr^{3+} dopant with proper charge distribution and occupation inside the host lattice in Cr doped TiO_2 nanostructures play the pivotal role for the ferromagnetic ordering and observed RTFM. The presence of oxygen vacancy related F^+-center and Cr^{3+} are confirmed from the electron spin resonance and x-ray photoelectron spectroscopy measurements.

1. Introduction

Over the past decades, there has been tremendous interest in understanding the origin of room temperature (RT) ferromagnetism (FM) in a variety of transition metal (TM) doped oxide semiconductors. These materials could be useful for future spintronic and magneto-optic devices [1–3], where both spin and charge degrees of freedom can be manipulated and used to transport and store charge, and process information in novel ways. This technology may provide enhanced performance and new functionalities in order to increase both speed and storage capacity in traditional microelectronic devices where only electronic charges are considered. Therefore, intensive attention has been focused on dilute magnetic semiconductors (DMS), such as TM doped ZnO [4,5], SnO_2 [6,7], In_2O_3 [8,9] and TiO_2 [10–13] due to realization of RT FM in these nanostructured non-magnetic semiconductors. In particular, Pereira et al. [14] reported intrinsic ferromagnetism in Co doped TiO_2 anatase nanopowders grown by a hydrothermal method and it was shown that oxygen vacancy (O_v) play an important role in promoting the long-range ferromagnetic order in the material, in addition to the transition metal doping. Later the same group [15] reported a stable ferromagnetism in the $Ti_{1-x}Co_xO_{2-\delta}$ nanopowders (with $0.03 \leq x \leq 0.10$) which provided an evidence of preserved long-range ferromagnetic order in such systems.

Despite several reports on the TiO_2-based DMS [11–13,16–19] since the prediction and discovery of RTFM in Co doped TiO_2 system [3], there is no clear agreement about the nature and origin of the observed FM in the diluted magnetic oxide doped with a few percent of 3d cations. It still remained a subject of intense debate that whether the FM is indeed intrinsic which is mediated by carriers or defects inside the host semiconductor and/or related to the purely extrinsic origin due to formation of ferromagnetic secondary

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phases, metallic clusters or impurities[11–13,16–19]. A wealth of information derived from both experimental and theoretical studies on the FM in Co and Fe doped TiO_2 systems can be found in literature [18–22]. The reported results are controversial regarding the intrinsic and extrinsic nature of Fe and Co doped TiO_2 DMS systems, since these elements themselves are ferromagnetic in nature. Unlike Fe, Co and Ni metals, Cr itself is antiferromagnetic and its clusters/compounds (except nanocrystalline CrO_2) do not contribute to FM. Thus, it would not induce an extrinsic FM even if Cr clustering occurs in the Cr doped TiO_2 (Cr:TiO_2) nanostructures. Moreover, the pure phase ferromagnetic CrO_2 is difficult to synthesize, since it is metastable at atmospheric pressure and generally stable at high oxygen pressure depending upon the method of preparations, process temperatures and precursors [23–25]. An intrinsic FM in annealed Cr:TiO_2 nanorods was reported [12] and it was suggested that ferromagnetic coupling between the O_v and the unpaired 3d electrons of Cr dopant forming bound magnetic polarons (BMP) is the origin of FM signal. Choudhury et al. [13] observed diamagnetism in undoped TiO_2 nanoparticles and FM in Cr:TiO_2 nanoparticles, and suggested that F-center mediated BMP is the active mechanism for induced FM. More recently, Liao et al. [11] reported that O_v plays a critical role in the enhancement of FM in Cr doped anodic TiO_2 nanotubes by comparing the FM behavior of different annealed Cr:TiO_2 nanotubes. Similarly, Xing et al. [8] and Wang et al. [9] demonstrated that O_v defects mediated BMP is responsible for the FM in Cr doped In_2O_3 nanostructures and films, respectively. Recently, Da Pieve et al. [16] reported that F-center mediated exchange mechanism is not active for inducing FM in case of Cr:TiO_2 systems and they proposed a mechanism of super exchange interaction of t_{2g} electrons, which is favored by the presence of structural defects and O_v. Further, the creation of grain boundary defects with O_v at the nanocrystal fusion interfaces was proposed to be the origin of FM in Cr^{3+} doped TiO_2 nanostructures [17]. These contradicting understandings on the RTFM in Cr:TiO_2 materials suggest that the specific mechanism and the physical origin of FM in Cr:TiO_2 is still unclear and it needs further investigation.

Interestingly, RTFM has been observed in a wide range of undoped oxides, such as TiO_2 [26–28], HfO_2 [29], In_2O_3 [27], SnO_2 [30] and ZnO [31]. Recently, Hoa and Huyan [32] reported enhanced FM in undoped TiO_2 nanowires as compared to Ni doped TiO_2 nanowires. Some of the outstanding reports revealed no evidence of ferromagnetic ordering in Fe doped TiO_2 (Fe:TiO_2) systems [20,22]. These reports help to address the controversies on the issues related to the role of defects in the ferromagnetic ordering. In fact, recent experimental evidences [26,28] and theoretical studies [33,34] suggest that intrinsic defects are responsible for the ferromagnetic signal in undoped TiO_2. However, unambiguous determination of the nature of defects responsible for the observed FM remains a considerable challenge to researchers. It is unclear whether O_v or Ti-vacancy defects contribute to the magnetic moments, since both titanium and oxygen vacancies were proposed to be responsible for the FM in undoped TiO_2 [28,33–35]. Some reports based on first-principle calculations indicate that Ti-vacancies and Ti-divacancies are ferromagnetically coupled [34], and oxygen vacancies do not produce any magnetic moment in undoped anatase [34,36] and rutile [36] TiO_2. On the other hand, newer theoretical and experimental studies show that ferromagnetic ordering in undoped TiO_2 is strongly related to O_v in TiO_2(B) [28], rutile [28,35] and anatase [28,35] TiO_2, and thus it was thought to be the source of RTFM in undoped semiconducting oxides. Based on first-principles calculations, Wang et al. [33] reported a multi-defects induced FM mechanism, in which one kind of defect (Ti-vacancy) produces local moments while the electrons induced by another kind of defect (O_v) mediate long-range ferromagnetic ordering through exchange interaction, and suggested that O_v alone cannot induce RTFM in undoped rutile TiO_2. These diversities of results and interpretations intensified the controversy related to issue whether O_v or Ti-vacancy defects contribute to the ferromagnetic response in undoped TiO_2. Therefore, it is important to understand the presence of specific defect types and their roles towards the FM. In fact, this may provide the key for interpreting the theoretical predictions and experimental data consistently.

At present, most of the reported FM in undoped TiO_2 systems has been for thin films [27,35] and nanoparticles (NPs) [37,38], while their undoped bulk counterparts are paramagnetic or diamagnetic. This implies that the spatial dimensionality might play an important role in the ferromagnetic ordering. Compared to thin films and NPs, exploitation of TiO_2 one dimensional (1D) nanostructures such as nanowires, nanorods (NRs) and nanoribbons (NRbs) with high surface area make it easier to engineer high availability of defect sites for trapping electrons and may favor the ferromagnetic ordering, thus making them an ideal candidate for the realization of intrinsic enhanced RTFM. Moreover, 1D nanostructures are favored over the 0D nanoparticles in terms of electron transport, storage and information processing that can enhance the performance of spintronic devices at the nanoscale for practical applications. A survey of literature show that RTFM in undoped and doped 1D TiO_2 nanostructures are relatively less studied [11,12,26]. In our earlier study [28], we reported RTFM in undoped TiO_2 NRbs and a direct correlation between the O_v and FM was established from various experimental tools. In another study [39], we examined the individual and combined effect of Fe dopant and O_v defects and clarified the controversial issues related to the long-range ferromagnetic ordering in Fe:TiO_2 systems. A clear demonstration by correlating the RTFM with dopant concentration and O_v defects in the host semiconducting oxide lattice is crucial and it needs a thorough investigation. In this work, we carried out a systematic study on the structural, optical and magnetic properties of undoped and Cr doped TiO_2 1D nanostructures in order to investigate the mechanism of ferromagnetic ordering in these nanostructures. We aim to provide an improved understanding of the mechanism of long-range ferromagnetic ordering in undoped and Cr doped TiO_2 systems by discussing the interplay of specific defects and their interaction in TiO_2 nanostructures, which is essential to control and improve the magnetic properties for practical device applications.

2. Experimental details

2.1. Growth and processing of undoped and doped TiO_2 NRs/NRbs

Anatase TiO_2 powder (particle size ~80 nm), chromium nitrate nonahydrate ($Cr(NO_3)_3 \cdot 9H_2O$) were used as TiO_2 and Cr precursors, respectively. Doubly distilled de-ionized (DI) water was used as solvent for the synthesis of Cr doped TiO_2 nanostructures. The appropriate quantity (0.3 at% and 0.7 at% of Cr) was mixed with TiO_2 powder and ground it for 10 min in a ceramic mortar. The mixed powder was added in 10M NaOH (alkaline water) and stirred for 30 min in a conical flask. Then the solution was transferred into the Teflon-lined autoclave (Berghof, BR-100) for hydrothermal reaction at 170 and 190 °C for 24 h. The precipitates after HCl treatment and washing with DI water were allowed for calcinations in a tube furnace at 500–900 °C temperatures. The undoped sample was prepared under similar condition except adding the Cr precursor. For the simplicity of discussion, the undoped sample grown at 170 °C and calcined at 500 °C is named as A500. The 0.3% Cr doped samples grown at 170 °C are named as “B” series and are named as B500, B700 and B900 after calcinations at 500, 700 and 900 °C, respectively. The sample B500 after vacuum annealing at 300 °C, 2 h under 1.2×10^{-2} mbar pressure is named as B500V. The