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# Synergistic effect of La and Co co-doping on room-temperature ferromagnetism enhancement of $TiO_2$ nanoparticles

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ABSTRACT

The synergistic influence of lanthanum and cobalt co-doping on room temperature ferromagnetism (RTFM) of $TiO_2$ system is investigated. A series of $Ti_{0.97-x}Co_{0.03}La_xO_2$ nanoparticles were prepared and their structures and properties were systematically studied with X-ray diffraction (XRD), scanning electron microscopy (SEM), photoluminescence (PL) spectroscopy, UV–vis spectrophotometer, Raman spectra and magnetic measurement techniques, respectively. Detailed experimental characterizations indicate that the as-prepared La and Co co-doped samples exhibit single anatase phase, and all the samples exhibit strong visible photoluminescence associated with oxygen vacancies and a clear ferromagnetic hysteresis loop, both of which were dramatically enhanced with La and Co co-doping, and the maximum saturation magnetization ($M_s$) reaches 1.38 emu/g at the La content of 6 mol%. It is speculated that oxygen vacancies modulated by ionic La play an important role in the enhanced RTFM, which can be attributed to the bound magnetic polarons (BMPs) formed via ferromagnetic coupling between two neighboring $Co^{2+}$ ions mediated by oxygen vacancy ($F^+$ center). Our results present an alternative method to obtain high performance RTFM.

## 1. Introduction

Dilute magnetic semiconductor (DMS) oxides have gained widespread interest due to the remarkable magnetic properties for the potential application in electronic and microelectronic devices, which combine both the semiconducting and magnetic properties [1–3]. The significant feature of DMS is the accurate adjustment of the exchange interactions between s, p-band and d-band electrons by modulating their band gap via doping with transition magnetic elements, resulting in a modified electronic structure without a change in macro structure [3].

Nanoscale $TiO_2$ has been studied for photocatalysis [4], photoelectrochemical solar cells [5], and sensors [6]. Since Matsumoto *et.al.* discovered that Co-doped $TiO_2$ (Co: $TiO_2$) anatase demonstrated RTFM [7], the study on $TiO_2$-based DMS has become an attractive topics [8]. In the last decade, a notable effort has been directed towards the influence of doped transition metals (TM), such as Mn [2], Co [8], Fe [9,10], V [11], Ni [12], etc., due to their stable RTFM. Among these transition metals, Co was demonstrated to be the most promising metal in modulating the magnetic properties of $TiO_2$-based dilute magnetic semiconductor, due to its excellent ferromagnetism, stability, and high n-type carrier mobility. For example, Srinivas et al. [3] investigated the magnetic performance of nanocrystalline $Ti_{0.95}Co_{0.05}O_2$-DMS, and they obtained a maximum saturation magnetization ($M_s$) of 0.041 emu/g. Kaushik et al. [13] conducted a systematic study using Co:$TiO_2$ polycrystalline samples, and it was found that Co:$TiO_2$ exhibits RTFM with 65 Oe coercivity and a 0.937 emu/g $M_s$. Likewise, other Co:$TiO_2$ systems also showed improved RTFM [14].

The single anatase phase of Co:$TiO_2$ is more suitable for the potential application in future spintronic and magneto-optic devices, and it is because the electron mobility is predicted to be higher in anatase phase than that in rutile phase [3]. Additionally, it is preferable for spin injection with Si [15] or carbon nanostructures. As a result, more efforts are especially focused on fabricating of a single anatase phase of Co:$TiO_2$.

Oxygen vacancies have been claimed to play a decisive role in ferromagnetism behavior at room temperature [16], and maintaining proper oxygen vacancy levels with suitable exchange media is beneficial for making favorable ferromagnetic DMS. Duhalde et al. [17] performed theoretical and experimental studies and they confirmed that ferromagnetic interaction was facilitated by oxygen vacancies in Cu doped $TiO_2$ films. Song et al. [18] investigated the influence of

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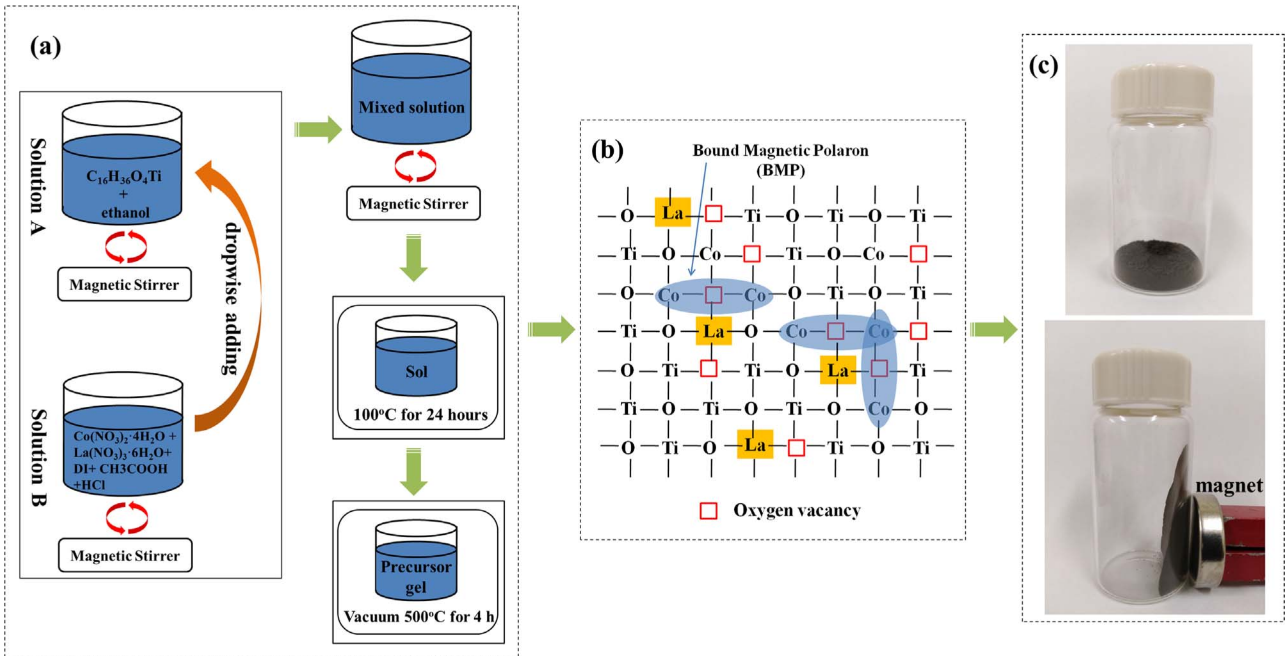


**Fig. 1.** Schematic representation for the preparation of $Ti_{0.97-x}Co_{0.03}La_xO_2$ for enhanced room temperature ferromagnetism: (a) fabrication of $Ti_{0.97-x}Co_{0.03}La_xO_2$ nanoparticles by sol-gel process; (b) oxygen vacancies manipulated by La dopant and BMPs yielded through $Co^{2+}$-□-$Co^{2+}$ ferromagnetic coupling; (c) the as-prepared sample and the enhanced RTFM.

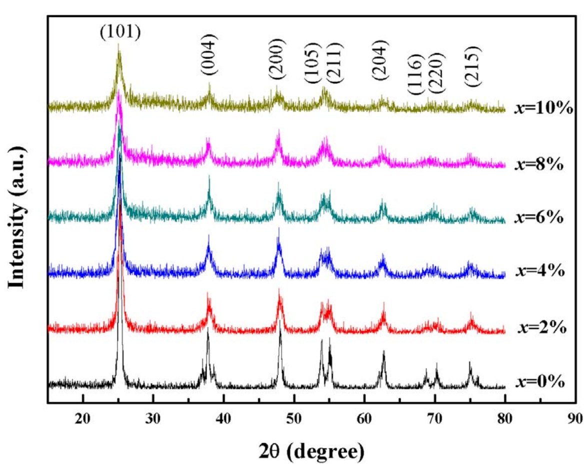


**Fig. 2.** XRD patterns for all the $Ti_{0.97-x}Co_{0.03}La_xO_2$ samples.

**Table 1**
Variation of parameters corresponding to (101) crystal planes and lattice parameters ($a$ and $c$) of anatase for all the samples with La concentration; The shifting of 150 $cm^{-1}$ Raman peaks and Coercive field ($H_c$) determined from *M-H* loops.

| $x$ | $2\theta$ | $D$/nm | $d$/ Å | $a$/ Å | $c$/ Å | Raman shift ($cm^{-1}$) | $H_c$(Oe) |
|---|---|---|---|---|---|---|---|
| 0.00 | 25.26 | 16.59 | 3.523 | 1.895 | 2.386 | 150 | 215 |
| 0.02 | 25.22 | 13.49 | 3.528 | 1.899 | 2.379 | 152 | 153 |
| 0.04 | 25.18 | 12.06 | 3.534 | 1.901 | 2.373 | 153 | 217 |
| 0.06 | 25.12 | 11.53 | 3.541 | 1.902 | 2.371 | 156 | 51 |
| 0.08 | 25.10 | 11.36 | 3.546 | 1.907 | 2.382 | 153 | 245 |
| 0.10 | 25.04 | 11.33 | 3.553 | 1.911 | 2.376 | 148 | 531 |

oxygen vacancies on the magnetism of gallium-doped $TiO_2$ DMS films, and found that both the enhanced saturation magnetization and the Curie temperature ($T_C$) are related to oxygen vacancies concentration. Similarly, Ahmed [19] synthesized $Ti_{1-x}Mn_xO_2$ powder and found that its ferromagnetic phase derives from the interactions between oxygen vacancies and manganese ions. The above studies support the notion that ferromagnetism in these $TiO_2$-based DMS is strongly related to oxygen vacancies.

Recently, rare earth metals (RE) doping oxide semiconductors have also been reported with prominent magnetic properties. For example, Ma [20] synthesized Gd doped ZnO nanowires which showed remarkable ferromagnetic properties. Sundararaj et al. [21] reported the magnetism of $Sm^{3+}$ doped ZnO thin films greatly depended on Sm concentration and the film thickness. Also, Tseng et al. [22] synthesized Sm-doped $TiO_2$ nanorods with weak RTFM.

The optical properties and photocatalytic behaviors of the La-doped $TiO_2$ systems have been studied [23–25]. The results showed that oxygen vacancies in $TiO_2$ can be manipulated by doping the sample with ionic La [23,25], creating an effective method to regulate the proportion of oxygen vacancies and thus affects the RTFM [26]. Furthermore, it has been reported that the addition of ionic La into $TiO_2$ can be a useful way to inhibit the rutile phase and enhance the crystallization degree of anatase [27,28], a more suitable state for the application of $TiO_2$-based DMS. However, co-doping of both lanthanum and cobalt into the $TiO_2$ system on its RTFM, has been scarcely reported.

The present work is therefore to explore the influence of La doping on oxygen vacancies and the RTFM of Co:$TiO_2$ system, and the synergistic effect of La and Co co-doping on oxygen vacancies and ferromagnetic coupling is expected to enhance the RTFM of $TiO_2$ system. Herein, Co:$TiO_2$ was chosen as matrix, and a series of $Ti_{0.97-x}Co_{0.03}La_xO_2$ nanoparticles were synthesized via sol-gel technology followed by post vacuum annealing, then the influence of La doping on oxygen vacancies in Co:$TiO_2$ as well as the RTFM are investigated in detail. Moreover, the role of La concentration and oxygen vacancies in regulating magnetic moment and the origin and significance of the observed RTFM were analyzed.

## 2. Experimental

### 2.1. Preparation of $Ti_{0.97-x}Co_{0.03}La_xO_2$ nanoparticles

$Ti_{0.97-x}Co_{0.03}La_xO_2$ (nominal La concentration $x$ = 0%, 2%, 4%, 6%, 8%, and 10%) nanoparticles samples were prepared using sol-gel route, by following similar preparation method reported before [9,29]: First, a prescribed amount of tetrabutyltitanate ($C_{16}H_{36}O_4Ti$) was dissolved in