Interesting magnetic behavior from reduced titanium dioxide nanobelts
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The magnetic behavior of reduced titanium dioxide nanobelts has been investigated with and without Co doping. Room temperature ferromagnetism was observed when the Co-doped titania nanobelts were prepared via vacuum annealing of 2.5 at.% Co-doped nanobelts, while annealing in air resulted in paramagnetic ordering. Interestingly, by vacuum annealing the undoped nanobelts under the same conditions, superparamagnetic ordering was observed in the resulting nanobelt. The electron paramagnetic resonance of this latter sample shows a strong symmetrical signal at g=2.003 suggesting some sort of exchange interactions among the localized electrons’ spin moments from single electron trapped in oxygen vacancies. © 2008 American Institute of Physics. [DOI: 10.1063/1.2944141]
show that both the air and vacuum annealed Co-doped nanobelts contained stable active species residing on bulk and surface defect sites as well as on oxygenated sites primarily on the surface. The EPR signals with $g$ value of $2.001-2.005$ are due to single-electron trapped in oxygen vacancies, while surface plus bulk Ti $3^+$ species have $g$ values of $1.99-1.93$. The latter reduced titanium species was also observed by Ti $2p$ core-level x-ray photoelectron emission spectrum of Fig. 1b. Compared to the fully oxidized undoped TiO$_2$ nanobelts, a shoulder is clearly observable on the lower binding energies side of the XPS Ti $4^+$ peak at 459.3 eV, which can be attributed to the presence of Ti $4^{\text{v}}$ species. The broad EPR signals on the left side of the sharp peak are most likely due to those of surface oxygenated active species. This assignment is consistent with our experimental observations where the intensities of these signals are always higher in all air annealed samples, but relatively lower in all samples that were prepared under vacuum annealing.

Nanostructural titanium oxides are well known for their high defect content that are able to trap electrons which contributes to their enhanced functional behaviors. As previously mentioned, the report on room temperature ferromagnetism on nanoparticles metal oxides attributed to the exchange interactions among localized electron spin moments originated from electrons trapped on surface oxygen vacancies is of great interest, since unlike diluted magnetic semiconductors these nanoparticles contained no magnetic impurities. With this in mind, we investigated the magnetic behaviors of undoped TiO$_2$ anatase nanobelts prepared from vacuum annealing of titanate nanobelts. EPR Fig. 2(a)] of these reduced TiO$_2$ nanobelts shows a single sharp symmetrical signal ($g=2.003$) which can be attributed to single-electron trapped on oxygen vacant sites, also known as singly occupied $F^+$-centers. Studies carried out on Co-doped titanate nanotubes have shown the importance of this type of oxygen vacancies in mediating room temperature ferromagnetism, with the widely accepted view of $F$-centers induced ferromagnetic coupling between Co$^{2+}$ via a donor impurity band exchange model. The enlarged plot of the same graph (inset) also reveals the presence of active species trapped on Ti$^{4+}$ sites ($g=1.933$) but the amount of these species is significantly smaller compared to that of the former.
The magnetization curve of the reduced TiO$_2$ nanobelts recorded at room temperature [inset of Fig. 2(b)] shows that these nanobelts exhibit superparamagnetic behavior. This was further confirmed via zero-field-cooled (ZFC) measurement where a transition from the thermally agitated “random” state to a state where the magnetic moments are blocked below the “blocking temperature” ($T_b$) at 56.6 K was observed. A hysteresis loop was clearly observed when the $M$-$H$ curve was measured below the blocking temperature, as shown in Fig. 2(b). Owing to the presence of a large amount of singly occupied $F^+$-centers, and with the absence of any impurities, it is therefore very likely that the observed superparamagnetic ordering is due to some sort of exchange interactions among the unpaired electron spin moments of these $F^+$-centers. Since the shape of these TiO$_2$ nanobelts is highly anisotropic with preferential exposed faces, it is therefore worth further investigation into the size and shape dependence of TiO$_2$ nanostructural materials in order to elucidate the influence that these factors may have in governing the interactions among the electron spin moments, and therefore the resulting magnetic behavior.

In summary, we have shown the importance of the presence of certain type of oxygen vacancies in governing the magnetic behaviors of Co-doped and undoped TiO$_2$ nanobelts. In the former case, the presence of these vacancies together with cobalt doping mediated ferromagnetic ordering at room temperature. In the case of vacuum reduced undoped anatase TiO$_2$ nanobelts, it is proposed that the exchange interactions among the spin moments of the unpaired electrons occupying in this type of oxygen vacancies, in forming $F^+$-centers, mediated superparamagnetic ordering in the sample.

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