Role of Oxygen Defects on the Magnetic Properties of Ultra-Small Sn$_{1-x}$Fe$_x$O$_2$ Nanoparticles

Kelsey Dodge  
*Boise State University*

Jordan Chess  
*Boise State University*

Josh Eixenberger  
*Boise State University*

Gordon Alanko  
*Boise State University*

Charles B. Hanna  
*Boise State University*

*See next page for additional authors*
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Kelsey Dodge  
Department of Physics  
Boise State University  
Boise, Idaho 83725, USA

Jordan Chess  
Department of Physics  
Boise State University  
Boise, Idaho 83725, USA

Josh Eixenberger  
Department of Physics  
Boise State University  
Boise, Idaho 83725, USA

Gordon Alanko  
Department of Physics  
Boise State University  
Boise, Idaho 83725, USA

Charles B. Hanna  
Department of Physics  
Boise State University  
Boise, Idaho 83725, USA

Alex Punnoose*  
Department of Physics  
Boise State University  
Boise, Idaho 83725, USA

*Correspondence author; Contact email: apunnoos@boisestate.edu

Abstract

Although the role of oxygen defects in the magnetism of metal oxide semiconductors has been widely discussed, it’s been difficult to directly measure the oxygen defect concentration of samples to verify this. This work demonstrates a direct correlation between the photocatalytic activity of Sn$_{1-x}$Fe$_x$O$_2$ nanoparticles and their magnetic properties. For this, a series of ~2.6 nm sized, well characterized, single-phase Sn$_{1-x}$Fe$_x$O$_2$ crystallites with x=0-0.20 were synthesized using tin acetate, urea, and appropriate amounts of iron acetate. XPS confirmed the concentration and 3+ oxidation state of the doped Fe ions. The maximum magnetic moment/Fe ion, $\mu$, of $1.6 \times 10^{-4} \mu_B$ observed for the 0.1% Fe doped sample is smaller than the expected spin-only contribution from either high, or low spin Fe$^{3+}$ ions, and $\mu$ decreases with increasing Fe concentration. This behavior cannot be explained by the existing models of magnetic exchange. Photocatalytic studies of pure and Fe-doped SnO$_2$ were used to understand the roles of doped Fe$^{3+}$ ions and of the oxygen vacancies and defects. The photocatalytic rate constant $k$ also showed an increase when SnO$_2$ nanoparticles were doped with low concentrations of Fe$^{3+}$, reaching a maximum at 0.1% Fe, followed by a rapid decrease of $k$ for further increase in Fe%. Fe doping presumably increases the concentration of oxygen vacancies, and both Fe$^{3+}$ ions and oxygen vacancies act as electron acceptors to reduce $e^- \cdot h^+$ recombination and promote transfer of electrons (and/or holes) to the nanoparticle surface, where they participate in redox reactions. This electron transfer from the Fe$^{3+}$ ions to local defect density of states at the nanoparticle surface could develop a magnetic moment at the surface states and leads to spontaneous ferromagnetic ordering of the surface shell under favorable conditions. However, at higher doping levels, the same Fe$^{3+}$ ions might act as recombination centers causing a decrease of both $k$ and magnetic moment $\mu$.

Metal oxide semiconductors such as SnO$_2$, ZnO and TiO$_2$ have been investigated extensively in recent years following theoretical predictions that doping with transition metal (TM) ions could produce ferromagnetism at room temperature [1,2]. Room temperature ferromagnetism (RTFM) has been reported in several oxide semiconductor systems [3], not only in those that contain transition metal dopants [4], but even in undoped oxides [5,6]. Even after a decade-long research, the actual mechanism of ferromagnetism in these materials is still not understood, although hints about some of the key factors that contribute to the magnetism have been revealed. RTFM was observed in several undoped oxide semiconductors, however, their magnetization increased systematically when doped with increasing concentrations of TM ions [4,7], thus highlighting that TM ions still play a role. RTFM in these oxides are mostly observed in samples that are prepared in nanostructured form, with no ferromagnetism when bulk crystals are doped with TM ions. It is believed that oxygen vacancies and defects play a major role in the RTFM of semiconductor oxides; however demonstration of a direct correlation between the magnetism, dopant concentration and oxygen vacancies/defects has been difficult. Because of
these reasons, in this work, we made an effort to investigate the true role of TM ions and oxygen vacancies on the magnetic properties of ultra-small (~2.6nm) SnO$_2$ nanoparticles by doping them with Fe ions.

The Fe doped SnO$_2$ nanoparticles were prepared by reacting Tin (IV) acetate (Sn(C$_2$H$_3$O$_2$)$_2$), Urea (C$_2$O$_2$N$_2$), and appropriate amounts of Iron (II) acetate (Fe(C$_2$H$_3$O$_2$)$_2$) as discussed in detail elsewhere [5]. The Fe dopant concentrations were 0.1, 0.5, 1.0, 2.5, 5.0, 7.5, 10.0, 15.0, and 20.0 atomic %. After synthesis, samples were characterized using X-ray diffraction (XRD), transmission electron microscopy (TEM) and x-ray photoelectron spectroscopy (XPS). All XRD patterns were recorded using a Phillips X’Pert x-ray diffractometer equipped with a CuK$_\alpha$ x-ray source (1.5418 Å) in Bragg-Brentano geometry. Samples were mounted by flattening the powder onto a metal dish, and placed on a fixed horizontal platform. TEM was carried out on a JEOL JEM-2100HR microscope with accelerating voltage of 200kV. Samples were prepared by dispersing in water, then dropping onto carbon coated copper grids. XPS measurements were conducted using a Physical Electronics Versaprobe with Al K$_\alpha$ radiation following procedures discussed elsewhere [4]. Room temperature magnetic data was collected on a Lakeshore 7404 vibrating sample magnetometer (VSM) with approximately 50mg of tightly packed sample powder mounted vertically in a clear plastic straw. For the photocatalytic studies, samples were prepared in solution of Rhodamine B (RhB) and nanopure water at about 10$^{-4}$M. Liquid samples were extracted from the reactor and placed in a centrifuge at 12,100g for 60 seconds to separate nanoparticles from the RhB solution. The supernatant was then transferred to a quartz cuvette and optical absorbance was measured on a Cary-5000 UV-Vis Spectrophotometer. This process continues with a fresh aliquot of solution every half hour for 2.5 hours, or until no absorption peak is visible.

Representative XRD patterns of Sn$_{1-x}$Fe$_x$O$_2$ samples (fig. 1) confirm the cassiterite phase with no impurity phases for x ≤ 0.20. Crystallite size determined using the Scherrer equation [4] decreased gradually from 2.6 ± 0.1 nm at 0% Fe to 2.3 ± 0.1 nm at 20% Fe. Wide-scan survey XPS spectrum of pure SnO$_2$ and 20% Fe doped SnO$_2$ samples (fig. 2a) further verify that the samples are free from impurities, especially magnetic or TM ions other than Fe. Although XPS is a surface-sensitive technique that can probe only down to <10nm, the ultra-small size (<3nm) of our Sn$_{1-x}$Fe$_x$O$_2$ crystallites allows the XPS data to be representative of the entire volume of the particles. High resolution XPS spectra of the Fe 3p region (fig. 2b) show gradual increase in the intensity with increasing Fe%. The actual Fe concentration estimated using the Fe 3p peak was slightly lower than the nominal values. This may be due to the use of the relatively weaker Fe 3p peak, chosen instead of Fe 2p which is overlapped by Sn 3p. The binding energy of the Fe 3p peak at 56.1 eV was higher than the reported values slightly lower than the nominal values. This may be due to the use of the relatively weaker Fe 3p peak, chosen instead of Fe 2p which is overlapped by Sn 3p. The binding energy of the Fe 3p peak for x = 0.1% Fe is 553nm, allowing us to monitor its decomposition. Changes in the RhB absorbance peak intensity at different times after treating with nanoparticles of pure, and 10% Fe doped SnO$_2$ are shown in figs. 4b and 4c respectively. Clearly, the pure SnO$_2$ sample shows much faster photocatalytic decomposition of RhB. The photocatalytic rate constant k, given by $k = \ln(C_0/C)$ (where $t =$ time, $C_0 =$ initial concentration of RhB molecules, and $C =$ concentration after UV irradiation) shows a maximum value (k = 0.0697) for 0.1% Fe doping, and then decreases rapidly as x increases (fig. 4). Pure SnO$_2$ nanoparticles showed a fairly high rate constant (k = 0.0182) on its own. In these semiconductor oxides, the primary species responsible for the photocatalytic activity are the electron - hole (e$^-$ - h$^+$) pairs, generated by the UV light irradiation. If the particle has plenty of temporary electron acceptors such as oxygen vacancies to keep the e$^-$ - h$^+$ pairs separate, their tendency for fast recombination can be prevented, and these electrons/holes can reach the nanoparticle surface to participate in redox reaction and destroy organic molecules like RhB. When prepared as nanoparticles, photocatalytic activity of oxides is expected to increase due to the large surface to volume ratio, since oxygen vacancies and defects form predominantly in the surface region. While Fe doping has little influence on the morphology of the samples, it has interesting and important influence in the resultant photocatalytic activity. As x increases from 0 to 0.001, k shows a 4-fold increase. It has been shown both theoretically and experimentally that low levels of Fe doping in oxide semiconductor nanoparticles can strongly reduce the energy for oxygen vacancy formation, resulting in increasing number of oxygen vacancies [11]. This will reduce e$^-$ - h$^+$ recombination rate and result in the higher k. For such low doping levels, the well separated Fe$^{3+}$ ions themselves can act as efficient e$^-$ as well as h$^+$ traps, turning into Fe$^{2+}$ or Fe$^{4+}$ states, respectively [7]. The trapped charges will be released eventually and they migrate to the nanoparticle surface to contribute to increased photocatalytic activity, while the Fe$^{2+}$ and Fe$^{4+}$ states change to the more stable Fe$^{3+}$ state which has a half filled 3d$^5$ orbital. As the Fe dopant concentration increases further, these Fe$^{3+}$ ions get closer to each other and they act as recombination centers for the photo-generated electrons and holes, and this will reduce the photocatalytic activity and k. Thus, the optimal Fe dopant concentration for the strongest photocatalytic activity of SnO$_2$ nanoparticles is 0.1% Fe.
Figure 3 shows the RT hysteresis loops of the Sn$_{1-x}$Fe$_x$O$_2$ samples. Interestingly, the undoped pure SnO$_2$ nanoparticles showed a weak ferromagnetic behavior characterized by a saturation magnetization $M_s = 0.31 \pm 0.01$ memu/g and coercivity $H_c = 91$ G. $M_s$ showed a gradual increase with increasing Fe concentration even up to the highest $x = 0.20$. The magnetic moment per Fe ion, calculated by assuming that the entire magnetization results from the moment of the Fe dopants (except for the undoped SnO$_2$ sample), showed a downward trend with increasing Fe doping percent (See fig. 4). The magnetic moment/Fe ion, $\mu$, was the largest (1.6x10$^{-3}$µB) at 0.1% Fe doping, and the smallest being at 20% Fe. The fact that highly pure undoped SnO$_2$ samples also showed RTFM, the extremely weak $\mu$ of the Sn$_{1-x}$Fe$_x$O$_2$ samples compared to that expected for Fe$^{3+}$, and the decreasing $\mu$ with increasing $x$ makes it less likely that observed magnetism is directly related to the magnetic moment of the doped Fe$^{3+}$ ions. The similar dependence of $\mu$ and $k$ with $x$, shown in fig. 4, may be indicative of a much different role of the doped Fe$^{3+}$ ions in the observed weak ferromagnetic properties. It is likely that the main contribution of the doped Fe$^{3+}$ ions to magnetism might be the creation of additional oxygen vacancies as discussed above. Role of oxygen vacancies in producing RTFM in TM doped oxide semiconductors has been widely discussed in the past [3]. Furthermore, the recent observation of RTFM in undoped oxide semiconductors has been attributed to oxygen vacancies [5,6,12].

To investigate the role of oxygen vacancies in the observed magnetic and photocatalytic properties, a pure SnO$_2$ nanoparticle sample was annealed in flowing Ar gas at 350°C for 1 and 2hrs, and changes in the oxygen stoichiometry was investigated by measuring the XPS intensity of O 1s and Sn 3d peaks. The XPS intensity ratio $I_{O1s}/I_{O2s}$ increased gradually to 0.1562 and 0.1575 after annealing at 350°C for 1 and 2 hours, respectively. Variation of the saturation magnetization $M_s$ and photocatalytic rate constant $k$ of pure SnO$_2$ nanoparticle sample are plotted as a function of the relative XPS intensity $I_{O1s}/I_{O2s}$ in Figure 5. This systematic increase in $M_s$ with decreasing oxygen content supports the role of oxygen vacancies in producing ferromagnetism in SnO$_2$ nanoparticles. However, $k$ shows an opposite behavior with increasing $I_{O1s}/I_{O2s}$. This may be due to the removal of surface redox species when the sample was annealed at 350°C in flowing argon gas. It is also important to note that our experiment points to the oxygen vacancies as the most likely origin of the decrease in photocatalytic activity and magnetic moment but other explanations cannot be totally ruled out [14].

Recently, Coey et al [13] proposed a new model for ferromagnetism in oxide semiconductors. They argued that the role of the TM dopants is to act as charge reservoirs from which electrons can be transferred to local defect density of states. Such electron transfer to the defect states such as oxygen vacancies in a nanoparticle could raise the Fermi level $E_F$ to a peak in the local density of states where the Stoner criterion for ferromagnetism may be satisfied. If the energy cost of the charge transfer is lower than the energy gain from spin splitting, surface states could develop a magnetic moment and the surface shell of the nanoparticle that is rich in oxygen vacancies can spontaneously order ferromagnetically. At higher values of $x$, data from photocatalytic measurements indicate that the doped Fe$^{3+}$ ions to magnetism might be the creation of additional oxygen vacancies as discussed above. Role of oxygen vacancies in producing RTFM in TM doped oxide semiconductors has been widely discussed in the past [3]. Furthermore, the recent observation of RTFM in undoped oxide semiconductors has been attributed to oxygen vacancies [5,6,12].

In conclusion, ultra small SnO$_2$ nanoparticles show strong photocatalytic activity, due to the presence of high concentration of surface defects and oxygen species. RTFM observed in these undoped SnO$_2$ nanoparticles are attributed to oxygen vacancies and/or defects. Doping these nanoparticles with low concentrations of Fe$^{3+}$ ions increases both photocatalytic activity and magnetism, presumably due to the creation of additional oxygen vacancies. However, when Fe doping concentration $x$ increases above 0.1%, both photocatalytic activity and magnetic moment of Sn$_{1-x}$Fe$_x$O$_2$ rapidly decreases. Since the decrease in $k$ is attributed to the high rate of $e^- \cdot h^+$ recombination facilitated by the doped Fe$^{3+}$ ions, we tentatively assign the reduction in $\mu$ also to the reduction of charge carriers. High electron/hole concentration is necessary for both carrier-mediated models as well as the charge-transfer ferromagnetism to work.

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References


FIGURE CAPTIONS

Figure 1: XRD data for Sn\textsubscript{1-x}Fe\textsubscript{x}O\textsubscript{2}, with x=0, 0.001, 0.01, 0.05, 0.10, and 0.20.

Figure 2: A) Wide-scan survey XPS spectrum of pure SnO\textsubscript{2}, and 1% doped SnO\textsubscript{2}. B) High-resolution XPS spectrum showing the Fe 3p region of Fe\textsubscript{1-x}Sn\textsubscript{x}O\textsubscript{2}. Samples with x in the 0.1-20% range are shown along with a similarly prepared FeOOH (100% Fe).

Figure 3: Magnetization curve loops for pure SnO\textsubscript{2} and the 1, 7.5, 10 and 20% Fe doped SnO\textsubscript{2} samples measured at room temperature. The inset shows the low field region of the hysteresis loops.

Figure 4: A) Plot showing the variation of magnetic moment per Fe ion (calculated using the saturation magnetization of each sample from Figure 3), and the photocatalytic rate constant of Sn\textsubscript{1-x}Fe\textsubscript{x}O\textsubscript{3} as function of Fe doping percentage. B) and C) show the photocatalytic degradation of RhB dye in nanopure water, treated with pure SnO\textsubscript{2} and Sn\textsubscript{0.9}Fe\textsubscript{0.1}O\textsubscript{2} respectively for 0, 30, 60, 90, and 120 minutes.

Figure 5: Variation of saturation magnetization M\textsubscript{s} and photocatalytic rate constant k of pure SnO\textsubscript{2} nanoparticles as a function of the relative XPS intensity of Sn 3d and O 1s peaks measured from pure SnO\textsubscript{2}. The XPS intensity ratio I\textsubscript{O}/I\textsubscript{Sn} decreased gradually after annealing pure SnO\textsubscript{2} in flowing Ar gas at 350C for 0, 1 and 2hrs, which corresponds to the three data points.