

Role of oxygen defects on the magnetic properties of ultra-small $\text{Sn}_{1-x}\text{Fe}_x\text{O}_2$ nanoparticles

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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 $\text{Sn}_{1-x}\text{Fe}_x\text{O}_2$ nanoparticles and their magnetic properties. For this, a series of ~ 2.6 nm sized, well characterized, single-phase $\text{Sn}_{1-x}\text{Fe}_x\text{O}_2$ 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, μ , 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 μ 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 $e^- - h^+$ 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 μ .

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) SnO₂ nanoparticles by doping them with Fe ions.

The Fe doped SnO₂ nanoparticles were prepared by reacting Tin (IV) acetate (Sn(C₂H₄OH)₄), Urea (C₂O₂(NH₃)₂), and appropriate amounts of Iron (II) acetate (Fe(C₂H₄OH)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_α 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_α 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 10μM, then solution was placed in a Rayonet RPR-100 UV reactor equipped with 2537 Å UV lamps delivering approximately 3.2mW/cm². Before beginning optical absorption measurements, the samples were equilibrated for approximately 15 minutes, after which an initial sample was taken from the mixture before the lamps were turned on, and then every 30 minutes after illumination. 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_xO₂ 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 SnO₂ and 20% Fe doped SnO₂ 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_xO₂ 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 of metallic Fe (53 eV) and common Fe oxides including Fe₃O₄ (53.9 eV), FeO (54.9 eV), and Fe₂O₃ (55.4 eV) [8], thus ruling out the presence of any of these phases in the Sn_{1-x}Fe_xO₂ samples. This along with the spin-orbit splitting of the Fe 2p peak (not shown) of 13.5eV suggests an oxidation state of 3+ for the Fe ions in our Sn_{1-x}Fe_xO₂ samples.

It has been reported that nanoparticles of metal oxide semiconductors display significant photocatalytic activity [9,10]. The photocatalytic activity of the Sn_{1-x}Fe_xO₂ samples was evaluated using RhB as a model dye because it has a strong absorbance peak at 553nm, allowing us to monitor its decomposition. Changes in the RhB absorbance peak intensity at different time points after treating with nanoparticles of pure, and 10% Fe doped SnO₂ are shown in figs. 4b and 4c respectively. Clearly, the pure SnO₂ sample shows much faster photocatalytic decomposition of RhB. The photocatalytic rate constant k, given by $kt = \ln(C_0/C)$ (where t = time, C₀ = 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 SnO₂ 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 Fe³⁺ ions themselves can act as efficient e⁻ as well as h⁺ traps, turning into Fe²⁺ or Fe⁴⁺ states, respectively [9]. The trapped charges will be released eventually and they migrate to the nanoparticle surface to contribute to increased photocatalytic activity, while the Fe²⁺ and Fe⁴⁺ states change to the more stable Fe³⁺ state which has a half filled 3d⁵ orbital. As the Fe dopant concentration increases further, these Fe³⁺ 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 SnO₂ nanoparticles is 0.1% Fe.

Figure 3 shows the RT hysteresis loops of the $\text{Sn}_{1-x}\text{Fe}_x\text{O}_2$ 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, μ , was the largest ($1.6 \times 10^{-4} \mu_B$) 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 μ of the $\text{Sn}_{1-x}\text{Fe}_x\text{O}_2$ samples compared to that expected for Fe^{3+} , and the decreasing μ 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 μ 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 350C 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 $I_{\text{Sn}}/I_{\text{O}} = 0.1537$ of the as-prepared SnO_2 sample increased gradually to 0.1562 and 0.1575 after annealing at 350C 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 $I_{\text{Sn}}/I_{\text{O}}$ 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 $I_{\text{Sn}}/I_{\text{O}}$. This may be due to the removal of surface redox species when the sample was annealed at 350C 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+} might deplete charge carriers by acting as recombination centers and this could reduce charge transfer, the net magnetization and μ . High electron/hole concentration is a necessary condition for both carrier-mediated models [1,3] as well as the charge-transfer ferromagnetism [13], so depletion of carriers will lead to reduced magnetic moment. Thus, the direct correlation observed between photocatalytic activity and magnetism, might suggest a major role of surface oxygen vacancies and charge carriers. However, we cannot rule out other reasons such as additional interstitial incorporation of Fe ions or other structural changes causing reduction in oxygen vacancies for this opposite trend in magnetism at higher x and more studies are necessary to confirm these.

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 $\text{Sn}_{1-x}\text{Fe}_x\text{O}_2$ rapidly decreases. Since the decrease in k is attributed to the high rate of $e^- - h^+$ recombination facilitated by the doped Fe^{3+} ions, we tentatively assign the reduction in μ 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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FIGURE CAPTIONS

Figure 1: XRD data for $\text{Sn}_{1-x}\text{Fe}_x\text{O}_2$, 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_2 , and 1% doped SnO_2 . B) High-resolution XPS spectrum showing the Fe 3p region of $\text{Fe}_{1-x}\text{Sn}_x\text{O}_2$. 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_2 and the 1, 7.5, 10 and 20% Fe doped SnO_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 $\text{Sn}_{1-x}\text{Fe}_x\text{O}_2$ as function of Fe doping percentage. B) and C) show the photocatalytic degradation of RhB dye in nanopure water, treated with pure SnO_2 and $\text{Sn}_{0.9}\text{Fe}_{0.1}\text{O}_2$ respectively for 0, 30, 60, 90, and 120 minutes.

Figure 5: Variation of saturation magnetization M_s and photocatalytic rate constant k of pure SnO_2 nanoparticles as a function of the relative XPS intensity of Sn 3d and O1s peaks measured from pure SnO_2 . The XPS intensity ratio $I_{\text{O}}/I_{\text{Sn}}$ decreased gradually after annealing pure SnO_2 in flowing Ar gas at 350C for 0, 1 and 2hrs, which corresponds to the three data points.