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Magnetism of ZnO Nanoparticles: Dependence on Crystallite Size and Surfactant Coating

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Abstract

Many recent reports on magnetism in otherwise nonmagnetic oxides have demonstrated that nanoparticle size, surfactant coating, or doping with magnetic ions produces room-temperature ferromagnetism. Specifically, ZnO has been argued to be a room-temperature ferromagnet through all three of these methods in various experimental studies. For this reason, we have prepared a series of 1% Fe doped ZnO nanoparticle samples using a single forced hydrolysis co-precipitation synthesis method from the same precursors, while varying size (6 – 15 nm) and surface coating concentration to study the combined effects of these two parameters. Size was controlled by modifying the water concentration. Surfactant coating was adjusted by varying the concentration of poly acrylic acid (PAA) in solution. Samples were characterized by x-ray diffraction, transmission electron microscopy, x-ray photoelectron spectroscopy, optical absorbance spectroscopy, and magnetometry. No clear systematic effect on magnetization was observed as a function of surfactant coating, while evidence for a direct dependence of magnetization on the crystallite size is apparent.

Introduction

Over the last decade, many theoretical and experimental reports have been published regarding room temperature ferromagnetic semiconducting materials [1-11]. More recently, nanoparticles have received attention with articles showing pure oxides [12-19] or oxides coated with thiols or amines [20-22] to display ferromagnetic behavior at room temperature. However, there is a mixture of techniques employed to produce the particles which could result in changes in stoichiometry, morphology and/or structure of the nanoparticles that may affect the observed magnetic behavior. For this reason, we have synthesized a series of Fe doped ZnO nanoparticles using a single chemical method to study the combined effects of crystallite size, surfactant coating and dopant concentration. We have previously reported on the influence of Fe dopant concentration on the magnetism of ZnO nanoparticles, prepared at a single size (6.8 nm) and without surfactant coating.[23] This work now focuses on the variation of the magnetic properties of 1% Fe doped ZnO as a function of crystallite size and surfactant coating concentration. A fixed Fe dopant concentration of 1% is chosen for this work because this is well below the solubility limit of Fe in ZnO, reducing the possibility of secondary or impurity phase formation. A total of 36 nanoparticle samples of $\text{Zn}_{0.99}\text{Fe}_{0.01}\text{O}$ are studied here to investigate their magnetic properties as a function of crystallite size in the 6 to 17 nm range and coating with poly acrylic acid (PAA) surfactant in the 0 to 10 mg/mL range.

Experimental

Fe doped ZnO nanoparticles with dopant concentrations in the 0 to 15% range were synthesized following a previously reported forced hydrolysis procedure.[23] To coat the samples with a surfactant, poly acrylic acid (PAA), a portion of each sample was dispersed in 1 mM of NaCl solution, to which solutions of 0.25 mg/mL or 10 mg/mL PAA solution in 1 mM NaCl was added. These concentrations were chosen to produce differing amounts of PAA coverage. Crystallite structure and size were characterized using a Philips X'Pert MPD diffractometer using a Cu K_α wavelength of 1.5418 Å. X-ray diffraction (XRD) was performed on loose powders mounted horizontally and smoothed using a glass slide. Transmission electron microscopy (TEM) was performed to investigate primary particle size and the effects of the PAA coating on secondary particle size. X-ray photoelectron spectroscopy (XPS) measurements were performed on powders that were hand-pressed into In foil using a Physical Electronics Versaprobe. Samples were irradiated with a 100 W Al K_α x-ray beam rastered over a 1.4 x 0.1 mm area. Charging of the insulating powders was minimized using low energy electrons and Ar^+ ions. The binding energy scale of high

resolution spectra was shifted referencing the Zn $2p_{3/2}$ peak of ZnO at 1021.9 eV[24]. Optical absorption spectra were collected using a Cary 5000 spectrophotometer. Samples were dispersed in nanopure water at a concentration of approximately 70 $\mu\text{g/mL}$ in a quartz cuvette prior to being placed into the spectrophotometer. Magnetic measurements were performed on a LakeShore 7404 vibrating sample magnetometer (VSM). For these measurements, samples were packed into a clear plastic straw and mounted vertically to the sample rod.

Results and Discussion

Representative XRD patterns, shown in Fig. 1a, demonstrate the control of the synthesis method over particle size. Samples coated with PAA show significantly more noise than uncoated samples. Sample sizes from XRD were also slightly smaller than the average from TEM. As an example, TEM images from a 5% Fe doped ZnO sample, shown in Figs. 1b and 1c, which have been coated in 0 and 0.25 mg/mL PAA solution respectively, show primary particle sizes of 10.5 \pm 2 nm while for the same sample the crystallite size from XRD was around 8 nm. The inset of Fig. 1a shows the size distribution. The nanocrystals tend to agglomerate as larger clusters, with a size of approximately 82 nm and this does not appear to depend on the concentration of PAA used to coat the samples.

XPS spectra of the Fe 3p region were recorded from $\text{Zn}_{0.95}\text{Fe}_{0.05}\text{O}$ and are shown in Fig. 2a. The peak position of the uncoated ZnO nanoparticles at 55.7 eV is similar to that reported for hematite, suggesting the Fe ions are in the 3+ state [25]. If Fe^{3+} substitutes for Zn^{2+} , the smaller ionic size of Fe^{3+} should result in a contraction of the lattice and/or reconfiguration of the oxygen stoichiometry for charge balancing. The concentration of carbon on the surface of coated particles increases with increasing PAA concentration, which is expected due to the surface sensitivity of XPS and the carbon content of PAA. The Fe 3p binding energy seems to move towards a lower value with the increasing PAA coating. Since XPS is inherently surface sensitive, typically to the first few atomic layers, this may indicate a reduction of the surface Fe ions as a result of PAA attachment.

Optical absorbance spectra were collected from varying size Fe doped ZnO at 5% focusing on the absorption peak of ZnO (See Fig. 2b) to demonstrate the size effect on optical and electrical properties. As expected, the peak blue-shifts slightly as the particle size decreases[26, 27]. This is illustrated in Fig. 2c showing the inverse squared dependence of absorption peak on crystallite size. The PAA coating did not appear to have a systematic effect on the absorption peak.

Representative M vs. H curves, and their corresponding low-field regions, are shown in Fig. 3a. It can be seen that there is a very weak hysteresis present, which has been observed in other nanoparticle studies of magnetism [14, 15, 18, 28]. For $\text{Zn}_{0.99}\text{Fe}_{0.01}\text{O}$, there does appear to be an increase in saturation magnetization M_s as the particle size decreases, suggesting that the surface to mass ratio and thus the surface itself plays an important role in the magnetic behavior of these particles (See Fig. 3b). No significant variation of the magnetic properties is observed when the surfactant concentration was varied in the 0 to 10 mg/mL range. The three lines plotting the variation of the saturation magnetizations of $\text{Zn}_{0.99}\text{Fe}_{0.01}\text{O}$ samples as a function of crystallite size for three different surfactant concentrations (0, 0.25 and 10 mg/mL) more or less overlap (Figure 3b), suggesting that the PAA coating is having no effect on the magnetization of $\text{Zn}_{0.99}\text{Fe}_{0.01}\text{O}$.

Conclusions

Doping ZnO nanoparticles with 1% Fe ions produces magnetism, in agreement with our previous reports [23, 29]. In this work, we demonstrate strong evidence that this magnetism varies with crystallite size. Saturation magnetization steadily increases with decreasing size or increasing surface area. No appreciable effect is distinguishable when the PAA surfactant concentration was varied, although more work is needed to study the possible effects of coating concentration when using other surfactants. Recently, Straumal et al.[30] have demonstrated that the observed ferromagnetic behavior of doped ZnO nanocrystals may be a grain boundary effect which exists in both pure and doped ZnO. If so, the increase in available surface area with the decreasing particle sizes would cause a higher ratio of grain boundaries to grain volume, thus explaining the resulting relationship between crystallite size and magnetization shown in Fig. 3c. Furthermore, the grain boundary properties combined with the lack of effect from PAA coating on particle coalescence demonstrated by the constant average agglomerate size across samples could be the reason why there was also a lack of change in magnetization with PAA concentration. It should also be pointed out that the adsorption of ZnO at the grain boundaries is higher than free surfaces, allowing for increased solubility limits[31], and so the interaction between particles at their interface may be competing with the PAA coating effect resulting in little difference in the overall magnetization when using PAA. No impurity phases were

detected with XRD or evidence of other elements or states with XPS, so the observed magnetization seems to be of intrinsic origin. The size dependence observed for the 1% Fe doped ZnO samples further support the intrinsic nature of ferromagnetism in ZnO nanoparticles.

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