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Room temperature spontaneous magnetization in calcined trioctylphosphine-ZnO nanoparticles

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In this work, it is demonstrated that capping with trioctylphosphine oxide (TOPO) induces a ferromagnetic response in free-standing ZnO nanoparticles upon calcination without the necessity of metallic doping. Samples were synthesized by precipitation of zinc acetate solutions in a basic medium followed by capping with TOPO and heat treatment in static aerobic conditions. Nanoparticles show a wurtzite-type structure with an average size of 14 nm, and magnetization measurements evidence a spontaneous magnetic moment at room temperature for calcined nanoparticles, in contrast with the diamagnetic response observed in non-calcined TOPO-capped nanoparticles. Giving the absence of any magnetic impurity or metal dopant that could account for the total magnetization, it is proposed that the magnetism would be consistent with a charge transfer mechanism promoted by a phosphorous doping upon calcination of TOPO over the nanoparticles. This situation leads to a spontaneous magnetic moment by the local fulfillment of Stoner's criterion for ferromagnetism at the nanoparticles surface. © 2012 American Institute of Physics. [doi:10.1063/1.3677674]

I. INTRODUCTION

Diluted magnetic oxides constitute a subject of maximum interest in recent years, mainly fueled by both theoretical calculations and experimental results supporting ferromagnetic behavior above room temperature.¹ These claims clearly leave open the possibility of having diluted ferromagnetic semiconductors, showing spin polarization without a continuous field supply and allowing, at the same time, a functional concentration of free carriers. Undoubtedly, such an achievement would revolutionize the field of spintronics, leading to faster and low-maintenance computers no longer requiring a permanent transfer of information between microprocessors and memories. Among some prominent achievements in this field for the time being, the magnetic bipolar transistor² and the more recent realization of a bipolar magnetic junction transistor using an InMnAs-based, diluted magnetic semiconductor³ constitute firm steps toward actual technological applications.

Since theoretical calculations predicted that diluted magnetic semiconductors based on transition metal (TM)-doped oxides like ZnO or TiO₂ could fulfill the requirements for a functional spintronic material,⁴ metallic doping in semiconductors has been the main source for inducing magnetic order, although, more recently, defects⁵ and charge transfer promoted by certain organic ligands⁶ have gained a more prominent role. It has been previously reported that the large

magnetic moment exhibited by thin films obtained from Mn-doped ZnO nanoparticles (NPs) could depend on other factors than the metallic doping itself;⁷ calcination of nitrogenated molecules over the particle surface favors the apparition of a ferromagnetic-like response through the incorporation of n-type defects, whereas oxygen ligands yield to a paramagnetic behavior. Nevertheless, the fact that NPs must be incorporated into thin films is an apparent requisite for ferromagnetism in these materials.⁸ Mn-doped NPs continue attracting attention as a model system for testing the origin of magnetic order in doped semiconducting nanostructures both theoretically, as arising from a symmetry breaking of the ground state⁹ or elliptical deformation controlled by gate voltage,¹⁰ and experimentally, coming from the removal of the antiferromagnetic coupling in Mn²⁺-Mn²⁺ pairs by photochemical reduction.¹¹ For undoped oxides, the striking case of ferromagnetic HfO₂ has been interpreted on the basis of the interaction of the 5d states of Hf atoms with the impurity levels to produce the spin-splitting band scheme needed for a local ferromagnetic coupling.¹² A large number of similar examples of unexpected magnetic order in different diluted oxides can be found throughout the recent scientific literature, all of them having a defect-mediated ferromagnetism as a common feature.

In this work, a possible origin for the ferromagnetic behavior observed in calcined ZnO NPs previously capped with trioctylphosphine oxide (TOPO) is discussed. The proposed explanation is based on the occurrence of a superficial phosphorous doping process derived from the calcination of the coating molecules at moderately high temperatures. A charge transfer between P atoms and Zn vacancies triggers

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the spin polarization process, resulting in a ferromagnetic coupling.

II. EXPERIMENTAL

TOPO-capped ZnO NPs were synthesized by the hydrolysis and condensation of zinc acetate ($\text{Zn}(\text{OAc})$) in dimethylsulfoxide (DMSO) through alkaline activation with tetramethylammonium hydroxide ($\text{N}(\text{Me})_4\text{OH} \cdot 5\text{H}_2\text{O}$) following the procedure previously described by Norberg *et al.*⁸ with some slight modifications. After 4–5 days of aging at 50°C , the washed ZnO NPs were subsequently capped with TOPO. Aiming for a more homogeneous size and shape distribution, the NPs were further refluxed at 200°C in fresh TOPO under a constant nitrogen flow. Calcination of the as-obtained NPs was carried out by heat treatment at 500°C in static aerobic conditions, since TOPO starts to decompose at 425°C . The basic structural features and particle size of the samples were determined by x ray diffraction (XRD) using Cu K_α radiation and transmission electron microscopy (TEM), respectively. Magnetic measurements were performed in a superconducting quantum interference device (SQUID) magnetometer at 5 and 300 K.

III. RESULTS AND DISCUSSION

Figure 1 shows the room temperature XRD patterns of ZnO NPs before and after heat treatment. The indexation of the peaks evidences the presence of solely hexagonal ZnO with a wurtzite structure. No trace of any other residual phase has been observed. The diffractogram of the TOPO-capped NPs before heat treatment (Fig. 1(a)) shows identical peaks as those corresponding to the heat-treated sample (Fig. 1(b)). A crystallite size of ~ 15 nm was derived by Rietveld refinement of the diffraction profiles after correcting for the instrumental broadening. TEM images (Fig. 2) show relative low-size dispersion in most of the NPs, ranging from 9 to 18 nm with an estimated average size of ~ 14 nm, in good

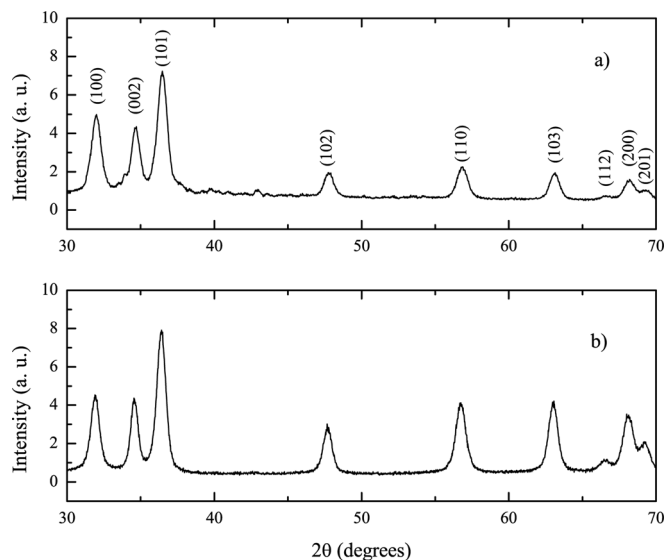


FIG. 1. X ray diffraction patterns of synthesized TOPO-capped ZnO NPs before (a) and after heat treatment (b). Peaks were indexed taking a wurtzite-type ZnO unit cell as reference.

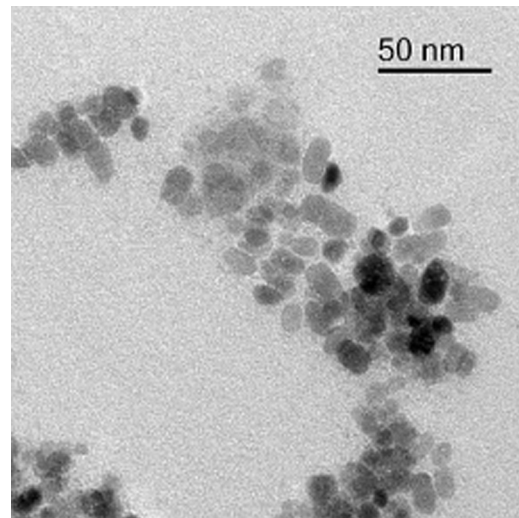


FIG. 2. TEM image of ZnO NPs after heat treatment.

agreement with the crystallite size value calculated from XRD measurements. The images also reveal that NPs are monocrystalline, frequently with oblate shape.

Before the heat treatment, the magnetic response of the TOPO-capped ZnO NPs is diamagnetic (Fig. 3), the same as its bulk counterpart. On the contrary, after the calcination process, the NPs exhibit a clear ferromagnetic contribution superimposed to a main diamagnetic one, with a visible increase of magnetic moment at low temperatures (Fig. 3). The ferromagnetic component saturates at about 2 kOe, the coercive field being 9 Oe at 300 K and 89 Oe at 5 K. The absence of any deliberate magnetic doping or residual magnetic impurity during the preparation stage leads us to confirm that the origin of the observed behavior must be intrinsic to the NPs. Moreover, if the ferromagnetic signal was somehow to be ascribed to the organic capping surrounding the particles, both its relatively low fraction and substantial degradation while exposed at high temperatures in an oxidative atmosphere severely reduce its chances to induce any exchange

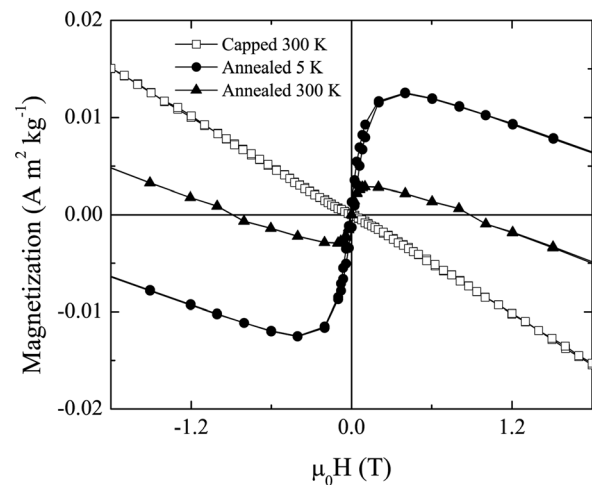


FIG. 3. Magnetization curves of the calcined ZnO NPs at 300 K (full triangles) and 5 K (full circles). The magnetization curve of non-calcined TOPO-capped ZnO NPs at 300 K is shown for comparison (open squares).

interactions resulting in a ferromagnetic coupling. Finally, given the fact that thermal annealing of ferromagnetic diluted oxides in an oxygen-rich atmosphere causes the disappearance of any ferromagnetic response, or at least has an almost negligible effect on it,¹³ and that the mere TOPO coating barely alters the original diamagnetism of ZnO, other factors should be taken into account to disentangle the mechanism underpinning the ferromagnetic order found in the samples under study.

TOPO molecules are expected to covalently bind to the available Zn atoms at the surface of ZnO NPs, with a coverage subjected to the steric hindrances imposed by the alkyl chains bonded to the P atoms. This would reduce the amount of dangling bonds and the associated loss of coordination, but, precisely, this loss of coordination in oxygen atoms at the surface of nanostructured ZnO has been pointed out as the cause of the high magnetic moments generated at 2p holes in the valence band, as shown by *ab initio* calculations.¹⁴ Nevertheless, TOPO molecules decompose during the thermal treatment into phosphorous oxides, such as P₂O₅, known to be a source for producing amphoteric P-doping in ZnO thin films,¹⁵ where P atoms can act as both donors or acceptors. Phosphorous has a low diffusion rate, even at moderately high temperatures, for which the derived dopants would be localized at the topmost surface layers of NPs. Among other possibilities, there are two main relevant paths that P atoms could follow, once they become a part of the ZnO network, for displaying a ferromagnetic order: interacting with Zn atoms or vacancies and interacting with O atoms or vacancies.

In the first case, P atoms can occupy a Zn antisite, as demonstrated from first principle calculations¹⁶ and, due to the energy involved in the process, two Zn vacancies will be spontaneously generated, giving rise to a P_{Zn}-2V_{Zn} complex with a low formation energy. It has to be noted that the formation of this complex is fully compatible with the use of an oxygen-rich atmosphere during the heat treatment. As a consequence of the difference in charge states between the two components of the P_{Zn}-2V_{Zn} complex, there will be a charge transfer of three electrons from the P_{Zn} to the two V_{Zn} defects, which would eventually induce an increase of the Fermi level (E_F). This adds to the narrowing effect that the superficial loss of coordination in NPs has on the bandwidth, related to the density of states at the E_F through the relationship $N(E_F) \simeq n_{imp}/W_{imp}$,¹⁷ where n_{imp} is the fraction of impurity atoms and W_{imp} the bandwidth of the impurity level. This scenario, therefore, would lead to the local fulfillment of the Stoner criterion for ferromagnetism, implying that

$$n_{imp}I_{eff} > W_{imp}, \quad (1)$$

where I_{eff} is the on-site interaction parameter. From Eq. (1), it is evident that the lower the W_{imp} , which can take place at the surface of NPs, the lower the impurity fraction n_{imp} needed to meet the criterion.

Now looking into the possible interaction of P with O atoms, recent calculations made on a hypothetical P-doped ZnO supercell predict a ferromagnetic ground state for the structure, revealing a magnetic moment of 1 μ_B mainly

contributed by the 3p and 2p orbitals of P and O atoms, respectively.¹⁸ In a similar fashion to how other III-V semiconductor materials exhibit ferromagnetic order,¹⁹ substitutional P induces spin splitting impurity states formed by P atoms and their nearest neighboring O atoms close to the top of the valence band.

IV. CONCLUSIONS

The synthesis and characterization of TOPO-capped ZnO NPs with relatively low size dispersion is described. For the as-synthesized NPs, a diamagnetic response is observed, whereas calcination at 500 °C in aerobic conditions induces the apparition of a distinct ferromagnetic signal in magnetization curves measured at both 300 and 5 K. A phosphorous doping process is proposed as a candidate for the presented results. The explanation of the unexpected room temperature ferromagnetism in the studied nanoparticles is partially built on the occurrence of a charge transfer between P atoms and Zn vacancies, as well as on the grounds of recent calculations in P-doped ZnO systems, predicting a spontaneous magnetic moment contributed from the interaction between phosphorus and oxygen p orbitals.

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