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Magnetic Properties of ZnO Nanoparticles

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ABSTRACT

We experimentally show that it is possible to induce room-temperature ferromagnetic-like behavior in ZnO nanoparticles without doping with magnetic impurities but simply inducing an alteration of their electronic configuration. Capping ZnO nanoparticles (∼10 nm size) with different organic molecules produces an alteration of their electronic configuration that depends on the particular molecule, as evidenced by photoluminescence and X-ray absorption spectroscopies and altering their magnetic properties that varies from diamagnetic to ferromagnetic-like behavior.

Semiconductors and magnetic materials are the basis of most of todays technological devices. While semiconductors are used to develop microprocessors capable of processing information at high speed, magnetic materials are used for information storage due to their ability to maintain the magnetization in a fixed direction without power supply. Materials joining both features into a single one should avoid the continuous transfer of information between semiconductors (microprocessors) and magnetic materials (memories), leading to faster and cheaper devices. In the last years, following the proposal by Ohno[1,2] the research on these magnetic semiconductors has been mainly focused on the so-called diluted magnetic semiconductors (DMS): semiconductors containing a small amount of magnetic impurities. The main challenge for this kind of materials is to preserve their magnetic character at room temperature (RT), that is, Curie temperature (T_C) above 300 K, in order to be useful for technological applications. Despite some initial promising results on Mn:ZnO,[3] it is not clear if DMS can exhibit this required high-temperature magnetism. For most of the experimental results, doubts arose about the real origin of magnetism.[4,5] For some cases it was demonstrated that the magnetism was due to segregation of metallic clusters[6] while in some systems containing transition elements with different valence states it was due to double exchange.[7,8] The most recent and outstanding works on this field showed that the magnetic properties are not exclusively related to the presence of the magnetic ions but strongly determined by the defects.[9−13] For instance, Kittisltved et al.[9,10] showed that Mn:ZnO nanoparticles and thin films only show RT ferromagnetism when capped with molecules that introduce p-type defects, while other capping that introduce n-type defects leads to no RT ferromagnetism. On the contrary, for Co:ZnO films the n-type defects favor the appearance of RT ferromagnetism while p-type defects yield to no RT ferromagnetism. Rubi et al.[11] also found that magnetic properties of Co- and Mn-doped ZnO powder samples are modified by thermal annealing in different atmospheres that favor the presence of p- or n-type defects. Moreover, Coey et al.[12] demonstrated that doping ZnO thin films with 3d nonmagnetic ions (as Ti or V) also leads to RT ferromagnetic behavior and for insulating HfO_2 the effect appears even without doping.[13] Those results, within the fact that superexchange or double exchange interaction cannot account for the observed RT ferromagnetism with a concentration of magnetic ions of few percent, point on the importance of the electronic structure of the semiconductor (modified by both the presence of the magnetic impurity and the defects) in the appearance of the observed magnetism.

Actually, it was recently found that an alteration of the electronic structure of Au nanoparticles and thin films

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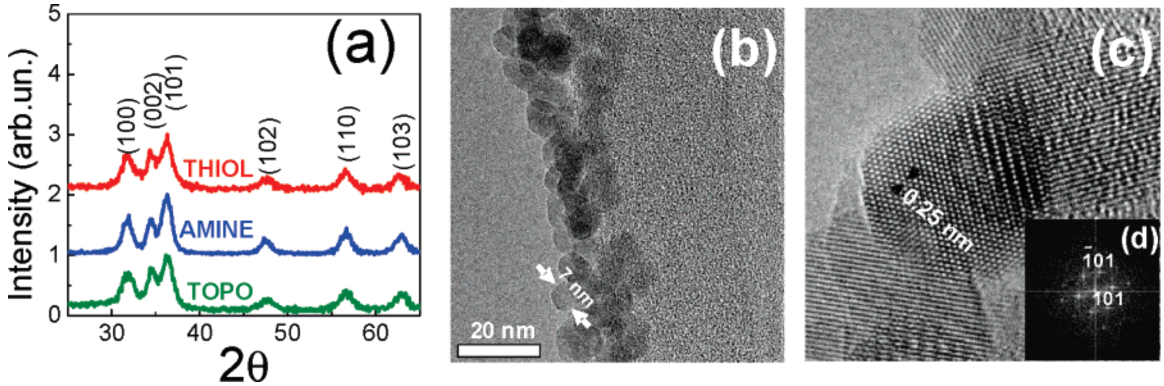

Figure 1. (a) X-ray diffraction patterns of the AMINE, THIOL, and TOPO samples. Diffraction maxima (labeled) are indexed on the basis of a ZnO wurtzite type unit cell. (b) Low-magnification image of the AMINE sample, showing the size distribution. (c) HREM image along [010] zone axis and (d) corresponding FFT in agreement to the wurtzite unit cell.

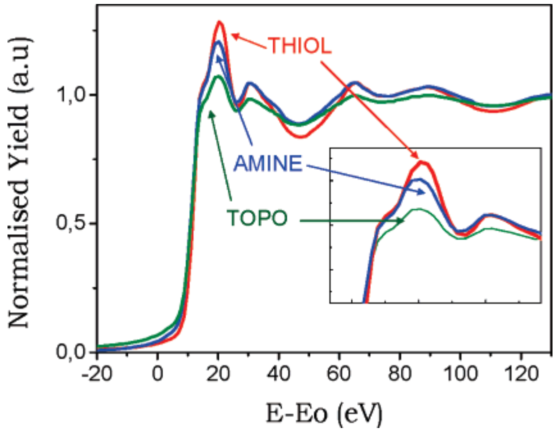

Figure 2. XANES spectra at the Zn K-edge for the ZnO NPs capped with different molecules. Inset shows detail of the white line region.

produced by capping them with organic molecules also leads to the appearance of RT ferromagnetism despite the diamagnetic character of bulk Au.[14−16] When thiols are chemisorbed on Au surface, there is a charge transfer from the Au to the S[14,17] generating holes at the 5d orbital of Au involved in the bond, initially full, arising a magnetic moment. These moments result strongly fixed along the bond direction and the system exhibit giant anisotropy. Thus, the ferromagnetic behavior is observed even at RT. For thiol-capped thin films the magnetization curves are fairly different upon applying field parallel or perpendicular to the surface (hence confirming the huge anisotropy) and the magnetic moments are giant.[15,16] Similar features (giant magnetic moments and huge anisotropy) have been observed for DMS thin films.[12,13,18] Moreover, in both cases (Au and semiconductors) orbital magnetism has been invoked to explain the observed ferromagnetic behavior.[13,19,20] Thus, it is still to be elucidated if the effect found for Au surfaces (nanoparticles (NPs) and thin films) can also be present in semiconductors, that is, if an alteration of the electronic structure of the semiconductor by capping with certain molecules can yield the appearance of RT ferromagnetic behavior even in absence of magnetic ions.

In this work we experimentally show that capping ZnO NPs with a variety of organic molecules modifies its electronic structure resulting in ferromagnetic-like behavior up to 300 K. This result can be helpful in order to understand the current controversy about the origin of magnetic properties in DMS.

ZnO NPs were prepared by sol−gel following the method described in refs 9, 21, and 22 and subsequently capped with three different organic molecules: tryoctylphosphine (TOPO), dodecylamine (AMINE), and dodecanethiol (THIOL), which bond to the particle surface through an O, N, and S atom, respectively.

Structural characterization, by means of X-ray Diffraction (XRD) and transmission electron microscopy (TEM), evidence, for the three cases, the formation of hexagonal ZnO nanoparticles (wurtzite structural type) with average size around 10 nm as Figure 1 illustrates. Figure 1b presents a low-magnification image, characteristic of the AMINE sample, where the NPs average size can be estimated. Figure 1c corresponds to a HREM (high-resolution electron microscopy) image of one of these particles, in which atomic distances and the corresponding FFT (Figure 1d) confirm the hexagonal lattice. Similar results are obtained for THIOL and TOPO samples (see Figure S1 in Supporting Information). EDS (energy dispersive spectroscopy) analysis is in agreement with the presence of ZnO (Figure S2 in Supporting Information). Signals corresponding to impurity phases have not been detected. This fact allows excluding the presence of magnetic impurities within the sensitivity of this technique (0.01).

Figure 2 show the X-ray absorption near edge structure (XANES) spectra at the Zn K-edge measured at RT in the SPLINE (BM25) beamline at ESRF. The deep analysis and interpretation of XANES spectra are complicate tasks that will not be addressed here. However, it is evident that the spectra are clearly different for the three capping molecules. The Zn K-edge, corresponding to the transition Zn 1s → 4p, has been shown to be more sensible to the Zn chemical bonding than L edges.[23] Although the 4p level of Zn isolated atoms is empty, chemical bonding with different chemical species leads to hybridization, resulting in states with a different degree of occupation depending on the features of the bond. In particular, a larger intensity at the first maximum is associated with a larger charge transfer between the Zn

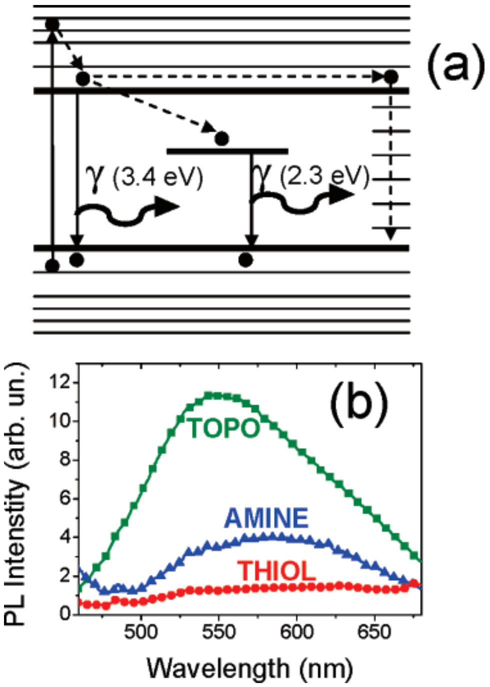

Figure 3. (a) Scheme of the PL process for ZnO as described in the text. (b) PL spectra from the three samples at 300 K upon excitation with 385 nm light.

atoms and the surrounding atoms, which can be due to an increase of the coordination number[24] or changes in the electronegativity of these surrounding atoms. Hence, variations in intensity at the first maximum are related to a different degree of occupation for the outer orbital of Zn atoms (including the hybridized states) for the three samples.

The photoluminescence (PL) spectra of the ZnO NPs are presented in Figure 3. As Figure 3a describes, upon excitation with UV light, electrons are pumped from the valence band (VB) to the conduction band (CB). Those electrons rapidly decay to the bottom of the CB via nonradiative processes. At this stage, there are several paths to return to the ground state, the main ones being (a) creation of an exciton and its subsequent annihilation emitting the excess of energy as a photon with an energy about that of the ZnO gap (3.4 eV) and (b) nonradiative transition to an intermediate level created by a defect and subsequent radiative decay emitting 2.3 eV photons. Although this emission has been reported many times, the nature of the defect is still a matter of discussion, being the oxygen vacancies the most likely candidate.[25] Recently, Shalish et al.[26] demonstrated that this luminescence arises form the surface of the ZnO while Norberg and Gamelin established it is directly correlated with the surface hydroxide concentration.[27] Thus, the study of this emission is a suitable tool to investigate the modification in the surface electronic structure induced by capping the NP with different molecules. (c) Surface states can create intermediate levels in the gap that allow the nonradiative decay of the excited electron to the VB.[28,29]

The 2.3 eV emission (corresponding to photons with 550 nm wavelength) is clearly observed for the TOPO sample, being weaker for the AMINE and absent in the spectrum for the THIOL sample, as Figure 3b shows. The strong dependence of the PL visible emission with the type of capping molecule is in agreement with the surface origin,[26,27] as the molecules can alter only the electronic structure close to the surface. These results can be understood assuming that the kind of molecule controls the number of deep-level recombination centers or that it induces new surface states that provide alternative nonradiative decay paths and, hence, quenching the PL emission.[28] In both cases, it is inferred that the capping molecule alters the electronic structure of the NPs surface, modifying the energy levels.

Figure 4 shows the magnetization curves of the samples, exhibiting diamagnetic character as bulk ZnO does. However, for the AMINE- and THIOL-capped NPs there is a ferromagnetic-like contribution that can be clearly observed after subtracting the diamagnetic background (parts c and d of Figure 4). Identical results were found at 5 K and 300 K. Actually the magnetization resulted thermally independent in the range 5−300 K as Figure 5 shows. By "ferromagnetic-like" behavior we mean that the magnetization curves of these samples show most of the typical features of ferromagnetic materials (remanence, coercivity, saturation) but not the presence of exchange interaction responsible of the magnetic order that is hard to understand in these materials.

For an average nanoparticle size of 10 nm, the magnetic moment per surface atom resulted $2 \times 10^{-3}\ \mu_B$ and $0.5 \times 10^{-3}\ \mu_B$ for THIOL and AMINE sample, respectively. These values are calculated assuming that no precursors are present in the sample; they represent therefore a lower limit. Chemical analysis provided by the suppliers of the precursors showed that possible traces, lower than 0.5 ppm, cannot account for the magnetic moment experimentally measured. Moreover, we measured the magnetization curves for the precursors used in the NP synthesis to check any contamination in the measuring procedure and we found no magnetic signal up to the detection limit of our equipment (Figure S3 in Supporting Information). Thus, possible contribution of magnetic impurities should be 2 orders of magnitude below that measured for THIOLS and 1 order below that measured for AMINE.

Beyond and above the value of the magnetic moment, the thermal dependence of the magnetization allows us to discard the magnetic impurities as the origin of the magnetic properties of ZnO nanoparticles. It is well-established that magnetic impurities dispersed in a nonmagnetic matrix behave as paramagnetic and its magnetization decreases with temperature while the magnetism we present here is thermally independent. For the case of thiol-capped Au nanoparticles, we confirmed that intentional doping with Fe impurities enhances the magnetic moments but the magnetization decreases fast with *T*, while in pure Au NPs it is thermally independent.[30] Actually some recent experiments found magnetism in nanostructures of nonmagnetic materials in bulk state as proton irradiated graphite[31,32] or HfO_2 films,[13] which are also thermally independent in the range 5−300 K. Thus, our results seem to belong to this new kind of magnetism without typical magnetic atoms as the thermal behavior cannot be explained as due to magnetic impurities. A nice hint that suggests that 3d ions are not necessary is

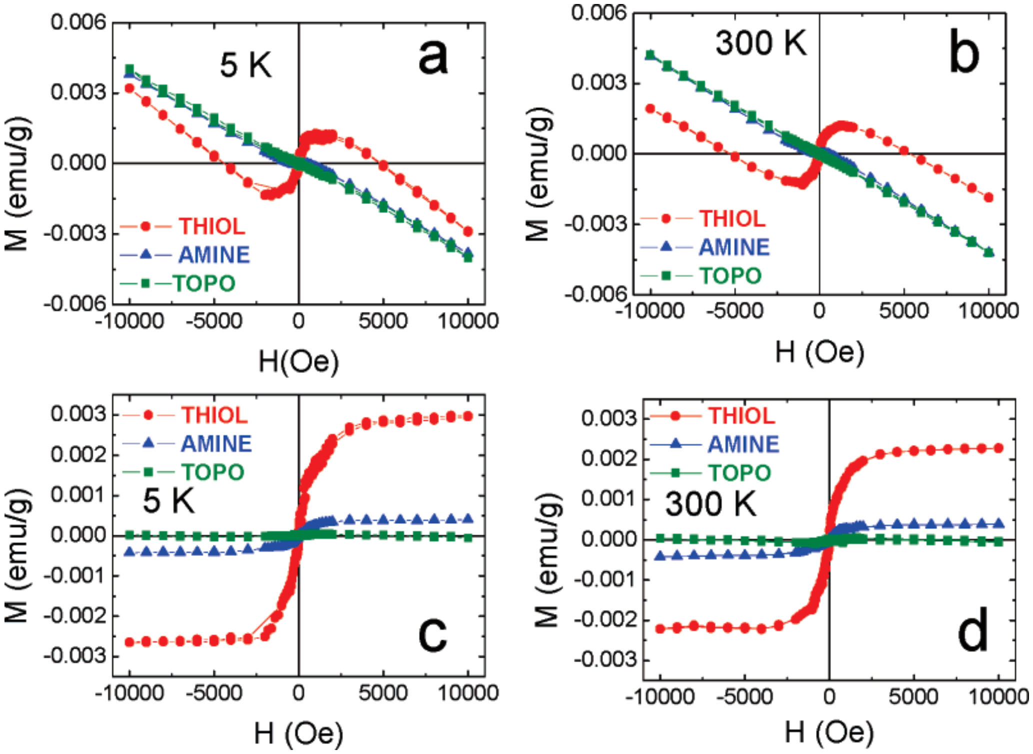

Figure 4. (a, b) Magnetization curves loops for ZnO NPs capped with different molecules. (c, d) The curves alter subtracting the diamagnetic/paramagnetic background.

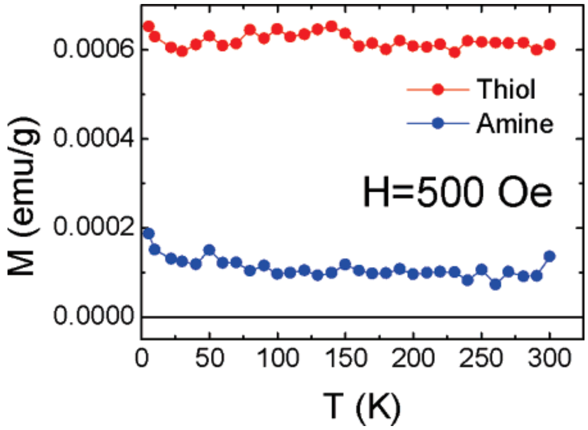

Figure 5. Magnetization vs temperature for the ZnO NPs capped with THIOL and AMINE under an applied field of 500 Oe. The corresponding constant diamagnetic background has been subtracted for clarity.

the experimental dependence of the magnetic moment per 3d ion as a function of 3d impurity content. It abruptly grows as the content decreases indicating that there is a magnetic moment independent of the presence of 3d impurity.[12]

It is worthy to note that structural analysis of the NPs (performed by XRD, TEM, and HREM) showed about identical structure irrespective of the capping molecule but those measurements probing the electronic structure (XANES, PL, and magnetic properties) confirmed that these are strongly dependent on the capping molecule. Moreover, there is a perfect correlation in the evolution of these measured properties with the capping molecule: THIOL sample shows the highest XANES absorption, the absence of PL emission (totally quenched by appearance the new surface states), and the largest magnetic moments (despite the diamagnetic character of ZnO). On the contrary, the TOPO sample presents an electronic configuration more similar to bulk ZnO as confirmed by the smallest XANES absorption (less charge transfer), the most intense PL emission typical of bulk ZnO, and diamagnetic behavior. The AMINE sample presents, in the three cases, an intermediate result. All this results together point out that the capping molecule induces an alteration of the electronic configuration of the nanoparticles that is in the origin of the room-temperature ferromagnetism of those samples.

Our results can be helpful to clarify the current controversy about the origin of magnetism in DMS: Until today, the magnetic properties of DMS have been explained as due solely to the magnetic moments of the magnetic impurities (of spin character). This leads to great confusion as many results are not reproducible, the magnetic properties strongly depend on the preparation method, and the fact that the magnetic moment per magnetic atom decreases with its concentration. In view of the results presented here, in DMS there can be an additional magnetic component not related to the spin of the magnetic impurities but due to this new contribution related to the alteration of the electronic configuration, similar to that observed in thiol-capped Au surfaces. Such a contribution can be of orbital character, which can be generated by electrons/holes trapped at defects and therefore do not require the presence magnetic impurities as proposed for the case of Au.[19] Actually Figure 4a shows evidence that the appearance of the ferromagnetic-like component is accompanied by and enhancement of the diamagnetic susceptibility, a new hint of the possible contribution of orbital magnetism as in the case of Au surfaces.[16,19,33,34] In this framework, the apparently irreconcilable results about DMS could be understood assuming that that their magnetic properties are originated by two sources: (i) the magnetism arising by the magnetic moments of the 3d impurities that, when isolated, are expected to behave as paramagnetic and rapidly decrease with temperature, and (ii) an additional contribution originated by the alteration of the electronic structure of the semiconductor induced by defects (p or n type) that are thermally independent up to 300 K.

Previous experiments on DMS demonstrate that when both contributions are present they are coupled.[9,10] Actually, the incorporation of magnetic impurities into the semiconductor matrix, besides the presence of its magnetic moment, represents an alteration of the electronic structure. Thus, the final electronic configuration will be determined by both nonmagnetic defects and magnetic impurities, explaining why the RT ferromagnetism depends also on the presence of the magnetic ion. The observation of RT ferromagnetism in DMS without defects can be explained as due to the alteration of the electronic configuration induced by the presence of the impurity. Moreover, the ferromagnetism observed in semiconductors doped with nonmagnetic ions can be also explained within this frame. What we confirmed here is that the magnetism due to the alteration of the semiconductor electronic configuration can be present in the absence of the magnetic ions and that, for nanoparticles, capping with organic molecules may induce such an alteration of the electronic structure. Actually, previous works[35,36] showed that capping DMS with organic molecules, modifies the magnetic properties of semiconductors already containing magnetic ions (Mn), while we confirmed here that the effect exists even in absence of the magnetic ion.

In a recent work, Kittilstved and Gamelin found no RT ferromagnetism in AMINE-capped ZnO NPs in disagreement with the result presented here.[9] It is evident that not just any alteration of the electronic structure of ZnO will result in the ferromagnetism but only under certain circumstances. Actually, we found that slight modifications in the preparation conditions and size of thiol-capped Au NPs lead to important variations in their magnetic properties, and for DMS, small differences in the preparation methods also lead to apparently irreconciliable results, suggesting that a slight variation of the electronic structure can lead to a large variation of the magnetic properties. Thus, it is possible that the different preparation method used by Kittilstved and Gamelin, yield reduced values of magnetization for their samples that make the magnetic moments undetectable (note that the magnetization value we measured for AMINE is fairly small and close to the detection limit of the SQUID). Then, for NPs capped with AMINE and doped with Mn atoms, the electronic structure (modified by both the presence of Mn and the capping molecules) results in a thermally independent magnetization that is superimposed to that due to the magnetic moments of Mn atoms that decreases fast with temperature (Figure 1 in ref 9).

In summary, we have experimentally shown that absorption of certain organic molecules onto ZnO nanoparticles modifies its electronic structure and gives rise to a ferromagnetic-like behavior at room temperature even in the absence of magnetic ions. Identification of the particular electronic configuration that originates this magnetism is an amazing challenge that would open a world of possibilities for the use of these materials.

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Supporting Information Available: Descriptions of materials, chemical synthesis, and characterization and figures showing sample images, EDS spectra, and magnetization curve. This material is available free of charge via the Internet at http://pubs.acs.org.

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