Surface Defects: Possible Source of Room Temperature Ferromagnetism in Co-Doped ZnO Nanorods

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Supporting Information

ABSTRACT: Contradicting results about the origin of room temperature ferromagnetism (RTFM) from measurements on different forms of transition metal (TM)-doped ZnO nanostructured materials lead to strong debates on whether RTFM could be an intrinsic property to TM-doped ZnO or not. Through careful synthesis and extensive characterizations, we have excluded the extrinsic contaminations as the cause of RTFM. Our experimental study confirms that defects such as oxygen vacancies lie on surface of nanorods and are likely a source of RTFM. X-ray absorption and emission spectroscopy (XAS and XES) suggest that the doped Co ions, primarily in the divalent state,



replace the Zn ions inside the tetrahedral without introducing Co clustering or Zn-related defects. Band gap narrowing upon Co doping is observed in both optical reflectance and O K-edge XAS/XES and is in agreement with the presence of oxygen vacancies and strong sp-d hybridization. Furthermore, such a trend can be nicely reproduced in GGA+U band structure calculations. Calculations also suggest that these oxygen vacancies are likely to congregate at low-energy (101) and (100) surfaces, instead of inside the bulk. Our findings highlight the importance of using the nanocrystalline surfaces to enhance the impurity concentrations and stabilize the ferromagnetism without post-sample annealing in an oxygen-deficient environment.

INTRODUCTION

ZnO has a large band gap (3.3 eV) and high exciton binding energy (~60 meV), giving it a wide range of applications in UV detectors, field emission transistors, short wavelength lasers, highly sensitive chemical sensors, and nonlinear varistors.¹⁻⁴ After doping with transition metal (TM) ions, ZnO has been shown to exhibit weak room temperature ferromagnetism (RTFM). The presence of RTFM makes this material a promising candidate for device applications, such as high performance read heads, nonvolatile memories, and other stateof-the-art storage devices. Although the existence of RTFM in Co-doped ZnO was first predicted on the basis of doubleexchange interaction between Co ions, the experimental confirmations remain heavily debated. For example, measurements done on thin film samples produced by pulse laser deposition (PLD) method gave contradicting results. Nanocrystalline samples synthesized through different chemical routes could show the RTFM with varying magnitude, while bulk crystals only showed the paramagnetic Curie-Weiss behavior. In addition, some of the early reports supporting the RTFM had been discarded due to contaminations from extrinsic sources. In short, there is still no consensus on whether the RTFM is an intrinsic property to TM-doped ZnO or not. $^{\rm 5-10}$

Amidst these controversial findings, it is important not only to confirm the existence of RTFM but also to exclude the extrinsic contaminations as its origin. Without such effort, it is highly doubtful that TM-doped ZnO can be reliably used in the device applications. Unlike thin films where contaminations from external sources can vitiate the results,¹¹ high-quality nanocrystals can often be produced consistently by a variety of chemical routes, and defects such as oxygen vacancies can be well-controlled through surface capping and annealing.^{12–17} It has been shown that ferromagnetism and its magnitude in nanocrystalline materials can be tune by annealing samples in different atmospheres.^{17–21} We have followed a rigorous procedure in the synthesis of $Zn_{1-x}Co_xO$ nanorods (see Experimental Method section) to avoid any known contami-

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Figure 1. (a) SEM micrograph showing the $Zn_{0.96}Co_{0.04}O$ nanorods. The 200 nm length scale is denoted by a white bar. (b) X-ray diffraction (XRD) curves of $Zn_{0.96}Co_{0.04}O$ (top) and ZnO (bottom). Similarity between these two curves implies no change in the wurtzite structure after Co doping. (c) Room temperature magnetization curve of ZnO (open squares) and $Zn_{0.96}Co_{0.04}O$ (filled circles) showing the diamagnetic and ferromagnetic behavior, respectively. $Zn_{0.96}Co_{0.04}O$ nanocrystal synthesized following the exact procedures as outlined in ref 17 shows paramagnetic behavior. (d) A zoomed-in view (dashed box in panel c) showing the coercive field of $Zn_{0.96}Co_{0.04}O$ and the calculated magnetic moment per doped Co atom. (e) Reflectance spectra of ZnO (dashed line) and $Zn_{0.96}Co_{0.04}O$ (solid line, multiplied by a factor of 2).

nations. Through extensive characterizations, we have demonstrated the existence of RTFM in these nanorods, and the findings are in agreement with theoretical models that involve intrinsic defects, such as oxygen vacancies on the surface of nanorods. Band structure calculations using density functional theory (DFT) with generalized gradient approximation (GGA) and GGA+U suggest that these oxygen vacancies are likely to congregate at low-energy (101) and (100) surfaces, instead of inside the bulk, which is an important factor in stabilizing the RTFM without further sample annealing in oxygen-deficient environment.

EXPERIMENTAL METHOD

We have adopted and modified the preparation procedure as outlined in ref 17 for $Zn_{1-x}Co_xO$ (x = 0.0, 0.04) nanorods. Appropriate amounts of zinc acetate dihydrate (Zn-(CH₃COO)₂·2H₂O) and cobalt acetate terahydrate (Co- $(CH_3COO)_2 \cdot 4H_2O)$ were dispersed in 200 mL of ethylene glycol while maintaining the overall metal concentration at 0.1 M. Co concentration in the solution was set to 4% to avoid any clustering or impurity phase formation. The suspension was stirred for about 30 min until its color turned pink and then refluxed at 200 °C for 3 h. Precipitates were collected after allowing the mixture to naturally cool down to room temperature. The solid phase was recovered by high-speed centrifugation and washed excessively with deionized water and ethanol. The precipitates were dried under the nitrogen flow at 70 °C for overnight instead of air flow as used in ref 17. Crystalline samples were formed after annealing the solid phase in tubular furnace at 600 °C in air for 8 h. Although the concentration of Co dopants was set to 4% during the synthesis process, it was further confirmed by energy dispersive X-ray spectroscopy (EDX) to less than 4 wt %. The observed change in the morphology was due to the slow speed of stirrer and

drying precipitates in nitrogen flow. The presence of nitrogen during the drying process can assist the formation of oxygen vacancies,²² which led to sufficient energetic sites for the nucleation²³ of ZnO nanorods.

RESULTS AND DISCUSSION

4% Co-doped ZnO nanorods, Zn_{0.96}Co_{0.04}O, were synthesized using the method outlined in the Experimental Method section. Figure 1a shows the micrograph from a Zeiss FESEM-Ultra 55 scanning electron microscope (SEM). These nanorods, with a uniform diameter of 25–35 nm across the entire $\sim \mu m$ length, have hexagonal facets with ends projecting outward. The absence of branching along the entire length indicates a spontaneous nucleation-type growth with high degree of crystalline perfection. The crystal structure and lattice constants are determined by the X-ray diffraction (XRD). Cu K α radiation was used, and XRD curves were recorded by a Bruker D8 Discover X-ray diffractometer. The observed peaks in Figure 1b correspond to those expected for polycrystalline wurtzite ZnO. The results reveal a high crystalline quality for samples with no indication of additional phases within the detection limit of the measurement. There is no significant change in the cell parameters ($a = 3.27 \pm 0.01414$ Å, $c = 5.24 \pm$ 0.02121 Å for ZnO and $a = 3.29 \pm 0.01414$ Å, $c = 5.27 \pm 0.01414$ 0.02121 Å for ZnCoO) as ionic radii of the Co atoms incorporated in the material should be very close to ionic radii of Zn in the ZnO matrix. For the ZnO wurtzite, the Zn is tetrahedally coordinated with valence 2+ and ionic radii (r =0.60 Å). The closest ionic radii assumed by Co is when it is also tetrahedrally coordinated with valence 2+ (r = 0.58 Å).²⁴ Replacing Zn²⁺ ions by Co²⁺ ions leads to the development of three spectral minima (absorption maxima) around 568, 615, and 660 nm in the reflectance spectrum, which was recorded at 300 K by using a PerkinElmer Lambda 950 spectrometer with

integrating sphere attachment and Spectralon standards in the wavelength range of 200–850 nm. These transitions, marked by arrows in Figure 1e, correspond to Co^{2+} d–d crystal field transitions in the tetrahedral symmetry: ${}^{4}\text{A}_{2}(\text{F}) \rightarrow {}^{2}\text{A}_{1}(\text{G})$, ${}^{4}\text{A}_{2}(\text{F}) \rightarrow {}^{4}\text{T}_{1}(\text{P})$, and ${}^{4}\text{A}_{2}(\text{F}) \rightarrow {}^{2}\text{E}_{1}(\text{G})$. The appearance of these transitions supports that the doped Co^{2+} ions are in the high spin (S = 3/2) state.^{7,25}

The existence of RTFM in our samples is confirmed by the magnetic measurements at 300 K with the Quantum Design Physics Properties Measurement System (QD-PPMS). During the measurements, a maximum 1 T magnetic field was applied onto the samples, and the diamagnetic behavior of sample holder was subtracted from all magnetization curves to retrieve only signal from samples. The magnetization curves from three different types of samples are shown in Figure 1d. Unlike ZnO (open squares, diamagnetic behavior) and Zn_{0.96}Co_{0.04}O nanocrystals fabricated using the exact procedures outlined in ref 17 (cross symbols, paramagnetic behavior), the M-H curve of our Zn_{0.96}Co_{0.04}O samples (filled circles) dried under nitrogen flow condition (see method section) shows a clear ferromagnetic behavior. The ferromagnetism is very weak, with saturation moment (M_s) and the coercive field (H_c) around $(0.0049 \pm 2.12132) \times 10^{-4}$ emu/g and 160 Oe, respectively (Figure 1d). The estimated 0.06 \pm 0.003 $\mu_{\rm B}$ moment per Co atom (with 4 wt % Co doping) is smaller than previously reported values, and such small value points strongly to the absence of Co clustering, which is an unrelated extrinsic source that could show ferromagnetism and mask the intrinsic signal.

Further information can be obtained by using X-ray-based techniques, e.g., X-ray absorption (XAS) and emission (XES) spectroscopy, to directly probe the unoccupied and occupied electronic structures with elemental, bonding, and chemical selectivity. The XAS/XES measurements were carried out at BL 8.0.1 at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory. During the measurements, the overall energy resolution was maintained around 0.2-0.4 eV for XAS and 0.5-0.8 eV for XES. A channeltron with front bias grid to repel the photoelectrons was used to record the total fluorescence yield (TFY) signal, and the sample-to-ground drain current was used for the total electron yield (TEY) signal in the XAS spectra. The TFY method can be considered as mostly a bulk method because it has the probing depth of \sim 10-100 nm, while TEY gives increased sensitivity to the surface of the layers with probing depth of \sim 3 nm.²⁶ An X-ray emission spectrometer with constant line density spherical gratings (150, 380, and 925 lines/mm) and CsI-coated multichannel plate detector was used to record the XES spectra. The spectrometer was placed at 90° scattering geometry to suppress the reflection at π -polarization. The multiplet features A, B, and C in the XAS spectrum in Figure 2b, which are caused by the Coulomb and exchange interactions between Co 2p core holes and 3d electrons, and the overall line shape of XES spectrum in Figure 2c taken with an excitation energy well above the Co L-edge absorption threshold (810.0 eV) are in good agreement with previously reported results.²⁷ The combined XAS and XES findings suggest that the majority of Co dopants, predominantly the Co(II), reside at Zn sites and are indeed tetrahedrally coordinated with ligand O atoms. The line shape of Zn Ledge XAS spectrum from Zn_{0.96}Co_{0.04}O in Figure 2a is almost identical to the one from ZnO, implying the absence of Znrelated defects like Zn interstitials or Zn antisite defects and



Figure 2. (a) X-ray absorption spectrum around Zn L_3 (feature A) and L_2 (feature B) edges. (b) X-ray absorption spectrum around Co L_3 and L_2 edges. The multiplet features A, B, and C are in good agreement with previous results.²⁷ (c) X-ray emission spectrum taken at 810 eV above Co L edge thresholds.

ruling out the possibility of Zn-related ferromagnetism in the nanorods. 28,29

Doping Co has been shown to change the band gap of ZnO in the thin-film samples, and a similar trend is also observed in the nanorods. The band gap can be determined by using the optical diffuse reflectance spectroscopy (DRS). The reflectance *R* can be used to calculate the Kubelka–Munk function³⁰ F(R)= $(1 - R)^2/2R$, and the gap size is obtained by linear extrapolation of the leading edge of the $F^2(R)$ function to zero. In Figure 3a, an $\sim 0.1 \pm 0.005$ eV red-shift in gap size from 3.24 \pm 0.0324 eV (in ZnO) after Co doping is seen in the reflectance spectrum and has been attributed to changes in the lattice parameters, the sp-d exchange interaction between band and localized 3d electrons of Co²⁺ cation, and the formation of doping-induced defect level.¹⁷ O K-edge XAS and XES spectra can also be used to determine the band gap. Upon Co doping, a spectral feature is developed at the bottom of the conduction band, which can be attributed to the hybridization between O 2p and Co 3d states. By comparing the leading edges of XAS curves of ZnO (dashed line) and $Zn_{0.96}Co_{0.04}O$ (solid line), we can identify the change in band gap Δ around 0.56 \pm 0.028 eV. The reduction of band gap is consistent with the presence of oxygen vacancies which affect the 1s binding energies of surrounding oxygen atoms.²⁸ Interestingly, the change in the band gap size upon Co doping revealed by X-rays, which has a shallower probe depth in the TEY mode, is larger compared to the one from optical reflectance. The difference implies that the surface has very distinct energetics from the bulk and these vacancies are likely to accumulate closer to the surfaces of nanorods.



Figure 3. (a) Band gap of ZnO (open squares) and $Zn_{0.96}Co_{0.04}O$ (filled circles) using the Kebulka-Munk function (see Supporting Information). The red solid and dashed lines are extrapolation showing the red-shift of leading edges. (b) Overlay of O K-edge X-ray absorption and emission spectra from Zn_{0.96}Co_{0.04}O (solid curve, TEY mode for XAS) and XAS of ZnO (dashed curve). (c) A zoomed-in view of XAS/XES spectra around 530 eV. The ZnO XAS curve is shifted (red curve) to overlay with the leading edge of Zn_{0.96}Co_{0.04}O XAS curve, and the change in band gap Δ determined by the offset is around 0.56 eV ± 0.028.

THEORETICAL CALCULATIONS

Our findings suggest that the observed RTFM in high quality nanorods is not caused by extrinsic contaminations, and the data are in agreement with the mechanism involving the oxygen vacancies around the surfaces of nanorods. Such assertion can be further supported by the electronic structure calculations using the generalized gradient approximation (GGA)³¹ to the density functional theory (DFT).^{32,33} The projected augmented wave (PAW) method³⁴ is used, as implemented in the Vienna ab initio simulation package (VASP).^{35,36} All bulk calculations

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Zn atoms replaced by Co atoms to match the desired Co concentration. The convergences of total energy with respect to the plane wave energy cutoff and k-point sampling had been carefully tested. The final series of energies were computed with an energy cutoff of 400 eV and integration using 90 k-point sampling over the supercell irreducible Brillouin zone, which was generated by the Monkhorst-Pack scheme. This scheme was used to ensure that total energy of the system is converged within 5×10^{-6} eV per formula unit.

To properly account for the electronic correlations between TM d states,^{37–39} the GGA+U^{40,41} with $U = 5 \text{ eV}^{42}$ for Co is also used to correctly reproduce the electronic and magnetic states of Zn_{0.96}Co_{0.04}O. The O 2p (blue), Zn 3d (red), and Co 3d (green) partial density of states (PDOS) with two spin species (up and down) are plotted in Figure 4. When Co²⁺ ions are doped into bulk ZnO, besides the successive reduction of the band gap, the O 2p PDOS becomes spin-polarized through the hybridization of the TM d bands. This trend persists to an even higher doping level where the Zn PDOS become spinpolarized and dominates the highest occupied as well as the lowest unoccupied states (Figure 4a).

The electronic structure near the surface is often distinct from bulk due to inversion symmetry breaking at the surface. This is an even more important factor in nanocrystals where the surface-to-volume ratio is large. The same GGA+U scheme was also used to calculate the energies of different surfaces of Codoped ZnO. The unrelaxed structures of (100), (101), (010), and (001) surfaces were carved out of fully relaxed bulk Codoped ZnO structure. A slab⁴³ technique was implemented by periodically repeating the infinite number of layers separated by vacuum layers along the surface normal. The slab was chosen with its two sides having a mirror symmetry with respect to each other. In the calculation, the atoms in the inner layers of the slab were frozen to simulate the bulk properties, whereas the atoms in the top two and bottom two layers were allowed to fully relax until the forces were smaller than 0.02 eV/Å. The thickness of vacuum and slabs were varied to achieve a reasonable convergence in the surface energy in the given direction.



Figure 4. DFT with GGA+U calculation showing the O 2p (blue line), Co 3d (green line), and Zn 3d (red line) partial density of states (PDOS) from (a) ZnO bulk with 0% (bottom panel), 6.25% (middle panel), and 12.5% (top panel) Co doping and (b) (100) surface of a 6.25% Co-doped ZnO with 0% (bottom panel), 18.75% (middle panel), and 25% (top panel) oxygen vacancies at the surface layer.

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The surface energies were calculated by subtracting the bulk energy with a specified amount of Co-doped ZnO (per formula units, E_b) from the energy of the slab containing the same amount of Co doped ZnO (E_s) and then dividing by the surface area from both sides of the slab (2S). The energetics of (100), (001), (101), and (110) surfaces, $\gamma = (E_s - nE_b)/2S$, with 6.25% Co doping are given in Table 1. The (100) and (101)

Table 1. Surface	Energies	of ZnO with	Doped Co	o (6.25%)
surface	(100)	(001)	(101)	(110)
energy (J/m ²)	0.80	1.68	0.52	1.84

surfaces have the lowest energies and are the most stable ones, which means that they dominate the formation of nanomaterials under thermodynamic equilibrium conditions. Interestingly, as shown in Figure 4b, simply by going from bulk to the (100) surface with the same 6.25% Co concentration, the band gap is further reduced. The band gaps shown in the Figure 4 are calculated within the error bar of 2%. This finding is consistent with different reduction in gap sizes reported by diffuse reflectance and X-ray measurements in Figure 3. Furthermore, we have investigated the energetics of oxygen vacancies by placing them at top and different sublayers of the (100) surface. As can be seen in Table 2, the presence of oxygen vacancies in

Table 2. Energies of 6.25% Co-Doped ZnO (100) Surface When 3.125% O Vacancies Are Arranged in Different Layers

(100) surface	top layer	sublayer	bulk region
energy (J/m ²)	0.75	0.76	0.79

the topmost (outer) layer the (100) surface lowers the energy of the surface facet. This suggests that oxygen vacancies in the Co-doped ZnO nanorods will eventually move to the outermost layer and increase the stability of the (100) surface. When oxygen vacancies congregate at the (100) surface to minimize the overall energies, O 2p PDOS at the bottom of the conduction band will be greatly enhanced. The GGA+U calculation clearly confirms the experimental findings and highlight the importance of surface oxygen vacancy in stabilizing the RTFM.

The ferromagnetism can be explained by different mechanisms such as carrier-mediated interaction^{44,45} or RKKY exchange interaction.^{46,47} In materials with low carrier densities such as oxides, the magnetic polaron can play an important role. In this scenario, the spins of magnetic dopants (e.g., Co in the current example) incorporated into the semiconductor lattice interact through a donor-impurity band that is formed by overlapping the low-lying triplet states from trapped electrons around lattice defects such as oxygen vacancies (V_{0}) , and such interactions lead to the ferromagnetic ground state.⁴⁸ In this context, not only the dopant concentration but also the number of donor electrons must be large enough to stabilize the ferromagnetism. Nanomaterials, with their large surface-tovolume ratio, often contain defects in the form of unsaturated bonds, and certain surfaces, such as (100) and (101) surfaces in current example, can further concentrate these defects. In this regard, nanorods can stabilize the RTFM without postannealing them in oxygen-deficient environment to introduce additional oxygen vacancies.

CONCLUSION

In summary, we have experimentally demonstrated the existence of RTFM in carefully synthesized high quality $Zn_{0.96}Co_{0.04}O$ nanorods, and used the GGA+U calculations to highlight the importance of nanocrystalline surfaces which help concentrate the oxygen vacancies on the surfaces. This is an important factor to stabilize the ferromagnetism without resorting to postannealing samples in oxygen deficient environment. The distinct energetics of nanocrystalline surfaces may be used to enhance certain physical and chemical properties, e.g. RTFM in current study, which are much weaker or even absent in the bulk and such unique aspect may be useful in developing multifunctional materials.

ASSOCIATED CONTENT

Supporting Information

Sample synthesis method, (2) experimental methods, and
electronic structure calculation. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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