Supporting Information for

Cobalt doped ZnO quantum dots in a monolayer: do the bands depend on the alignment of the magnetic domain?

Sudipto Chakrabarti and Amlan J. Pal*
Department of Solid State Physics, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India

Growth of Nanoparticles. Cobalt-doped ZnO nanocrystals were grown following reported routes, which ensured Co$^{2+}$ to be isotropically doped throughout the ZnO nanocrystals. In brief, for a typical synthesis of cobalt-doped ZnO nanoparticles, precursor salts (zinc acetate dehydrate and cobalt acetate tetrahydrate) were dissolved in 15 mL of DMSO (dimethylsulfoxide). The solution was allowed to stir vigorously for 10 min at room temperature. 5 mL (2.5 mM) TMAH (tetramethylammonium hydroxide) in dry ethanol was then added drop-wise to the solution at a rate 2 mL/min. Upon addition of the base, colour of the pink solution slowly turned blue indicating formation of cobalt-doped ZnO nanocrystals. After complete addition of the base, the solution was stirred for a few more minutes. The nanocrystals were precipitated by adding 40 mL ethylacetate. After removal of the supernatant, the nanoparticles were redispersed in 20 mL of ethanol or DMSO.

The synthesized nanoparticles were first washed several times prior to TOPO (trioctylphosphine oxide) treatment to remove DMSO. The nanoparticles along with excess TOPO was taken in a 25 mL flask and was allowed to stir under nitrogen atmosphere at 150 °C. After continuous stirring for 5-6 h, temperature of the solution was lowered down to 60 °C; 5 mL of dry methanol was then added to the reaction flask. The nanoparticles were separated by centrifugation (4000 rpm for 2 min) and were re-dissolved in toluene. Concentration of cobalt as dopants in ZnO nanoparticles was varied between 0 to 4 wt%. To achieve a particular concentration of cobalt in ZnO nanoparticles, concentrations of zinc acetate dehydrate and cobalt acetate tetrahydrate were adjusted so that the total concentration of metal ions remained 100 mM.

Characterization of the Nanoparticles. Cobalt-doped ZnO nanocrystals were characterized through optical absorption, X-ray diffraction (XRD), energy-dispersive X-ray (EDX) analysis, and high-resolution transmission electron microscopy (HR-TEM). Optical absorption spectra of the nanoparticles in dispersed solution are presented in Figure S1(a). Each of the spectra showed a band in the near-UV region that is related to the nanocrystals. With cobalt-doping, there was a blue-shift in the absorption band. The shift was related to a decrease in diameter of the quantum dots. With Co$^{2+}$ doping in ZnO, Schwartz et al. showed that the dopants inhibited nucleation and growth of the nanocrystals leading to a decrease in diameter and correspondingly a blue-shift in absorption band of the doped quantum dots. This decrease in the diameter has been explained in terms of Gibbs-Thompson relationship between lattice strain and crystal solubility. In addition, with cobalt doping, a new band appeared in the lower wavelength region. The band at around 600 nm has been assigned to be due to spin-orbit split ligand field transition of tetrahedral Co$^{2+}$ in the bulk and also in quantum confined size regime.

Incorporation of cobalt as dopants could be observed in EDX analysis. Composition of the nanoparticles for different doping concentrations has been tabulated in Figure S1(b). Crystalline nature of the quantum dots could be observed in XRD spectra. In all the spectra,
as shown in Figure S1(c), we found that the diffraction peaks of ZnO or cobalt-doped ZnO nanoparticles readily matched that of wurtzite phase of pure ZnO (ICPDS file #36-1451). A typical TEM image of doped nanocrystals, as presented in Figure S1(d), showed that the particles were monodispersed and mostly spherical in nature. HR-TEM image of a typical particle, as presented in the same figure, showed that the diameter of the nanoparticles was about 3.4 nm. Lattice spacing of the nanocrystal was about 0.247 nm that matched well with the spacing of <101> planes of ZnO crystals. The image further showed that the nanoparticles were largely single crystalline in nature.

Monolayer formation. Monolayer formation was a part of LbL deposition process. With Co-doped ZnO nanoparticles (doping concentration varied from 0 to 4 wt%), we formed LbL films of the nanoparticles with a polycrystalline.\(^4\) It has been reported that van der Waals interactions played a crucial role in LbL deposition process. To confirm that monolayer was truly formed during the adsorption process, we measured thickness of multilayered LbL films of different bilayers. Since fewer-bilayered films would return too low thickness that could be measured accurately, we relied on higher-bilayered films, such as 2 to 10 layers. We then extrapolated the plot to one bilayer and compared the thickness with diameter of the nanoparticles. In presenting some typical experimental results, we show AFM topography of a 10-bilayered unoriented film in Figure S2(a). Image of an intentional scratch has been presented here so that thickness of the film can be measured from the depth profile of the scratch. While depth profile of the scratch is shown in Figure S2(b), thickness versus number of bilayers plot is shown in Figure S2(c). From the extrapolated region of the plot, we find that the thickness of one bilayer film (5.67 nm) matches reasonably well with the diameter of the particles (3.4 nm). A higher value of the film-thickness as compared to the diameter of the nanoparticle is due to the polycrystalline monolayer involved in the film. Such a thickness of one bilayer film more importantly proves that a monolayer of the nanoparticles was indeed formed on the substrate. It moreover showed that a multilayered film did not form during adsorption of the first layer of the nanoparticles. The thickness neither differed when multilayered films were formed with moments oriented along any particular direction.

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**Table 1.** Content in % obtained from EDXa

<table>
<thead>
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<th>Content in % obtained from EDXa</th>
<th>Co</th>
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<th>O</th>
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<td>21.1</td>
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<tr>
<td>4</td>
<td>3.9</td>
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**Figure S2.** (a) AbsorbanceIntensity of cobalt-doped ZnO nanoparticles. (b) Atomic wt% of cobalt aimed during growth as sintered. (c) XRD patterns of dopant-coated ZnO nanoparticles. (d) HR-TEM images of ZnO nanoparticles.
Figure S1. (a) Optical absorption spectra of different cobalt-doped ZnO nanoparticles in dispersed solution with the longer wavelength part being zoomed in the inset. (b) Composition of nanoparticles, as obtained from EDX analysis, in the form of a table. (c) XRD spectra the nanocrystals. (d) Typical TEM and HR-TEM images of the 2 wt% cobalt doped ZnO nanoparticles.

Figure S2. (a) AFM topography and (b) depth profile of a 10-bilayer film of Co-doped ZnO nanoparticles (doping concentration - 2 wt%, moments unoriented) with an intentional scratch. (c) A plot of film thickness versus number of bilayers of LbL films. While the straight line is a fit to the experimental points, the broken one is the extrapolated plot towards the origin.
Figure S3. Optical absorption of LbL films of cobalt-doped ZnO nanoparticles after adsorption of each monolayer. (a) Spectra for films deposited without any magnetic field, i.e., a conventional LbL film and (b) spectra for films with an assistance from a magnetic field, i.e., when a magnetic field ($\mu_0H = 330$ mT) was applied to the film before adsorption of the next monolayer.

Figure S4. STM topography of a monolayer of Co-doped ZnO nanoparticles on Si substrates showing (a) 2-dimensional and (b) 3-dimensional views. Image in (c) shows topography of a bare silicon substrate under the same approaching condition.