

## Room temperature ferromagnetism in Mn-doped CdS nanorods

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Mn-doped CdS nanorods synthesized by solution phase chemistry demonstrate robust ferromagnetic properties at and above room temperature. The nanorods show large coercivity, possibly originating from the shape anisotropy. The hysteresis measurements reveal strong temperature dependence. Possible origin of the ferromagnetism is discussed. © 2008 American Institute of Physics. [DOI: 10.1063/1.2982583]

Manipulation of carrier spins in semiconductors for spintronics applications has received much attention driven by the promise of new or improved functionalities and higher speed/lower power operation.<sup>1,2</sup> To this end, ferromagnetic semiconductors form an important component of the spintronic devices. Magnetic semiconductors can be made by substituting cations in compound semiconductors with transition metal ions.<sup>3</sup> A well known example is III–V compounds, such as GaAs doped with Mn, with the Curie temperature as high as 170 K.<sup>4</sup> The mechanism responsible for ferromagnetism in III–V magnetic semiconductors is known as the *sp-d* exchange interactions of the band carriers with localized magnetic ions.<sup>5</sup>

By comparison, II–VI materials doped with magnetic ions are known to show diverse magnetic phases, ranging from paramagnetic spin-glass-like antiferromagnetic to ferromagnetic at very low temperatures.<sup>6</sup> There has been little work on high temperature ferromagnetism in such systems. In this study, we report the magnetic properties of Mn-doped CdS nanorods synthesized by high temperature organic solution phase technique. These nanorods demonstrate above room temperature ferromagnetism. Compared to typical diluted magnetic semiconductors (DMS), such as Ga(Mn)As, the coercivity ( $H_c$ ) is found to be much larger and shows strong temperature dependence.

Monodisperse Cd(Mn)S nanorods were synthesized by anisotropic growth catalyzed by Au nanoparticles in solution phase.<sup>7</sup> Detailed synthesis will be published elsewhere. Figure 1(a) shows a low magnification transmission electron microscopy (TEM) image of Mn-doped CdS nanorods, with nominal doping concentration of 10%. The dimensions of the nanorods are  $10 \pm 1$  nm in diameter and  $120 \pm 4$  nm in length. Detailed crystal structures of single nanorods were characterized by high-resolution transmission electron microscopy (HRTEM), as shown in Fig. 1(b). Nearly all nanorods are single crystals, with surface roughness less than 0.5 nm. The lattice spacing is identified to be 0.336 nm, corresponding to the (002) plane of the wurzite CdS structure parallel to the long axis of the nanorods. The inset is a fast Fourier transform pattern from the single nanorod, which clearly shows that the nanorods are single crystals, and the

pattern can be indexed to be [100] zone axis of the wurzite structure, suggesting that the growth direction is along the *c* axis. No secondary phase can be identified from the electron diffraction patterns. Careful examination of HRTEM images of about 50 randomly chosen nanorods also does not show clusters of a different structure. This suggests that the formation of Mn clusters with a different crystal structure can be excluded within the spatial resolution limit of the TEM, although Mn composition variations within the nanorod cannot be ruled out.

The growth mechanism of Cd(Mn)S nanorods is expected to be consistent with the solution-liquid-solid process.<sup>8,9</sup> From the TEM results, about 95% of the nanorods are free of Au nanoparticles, suggesting that Au nanopar-

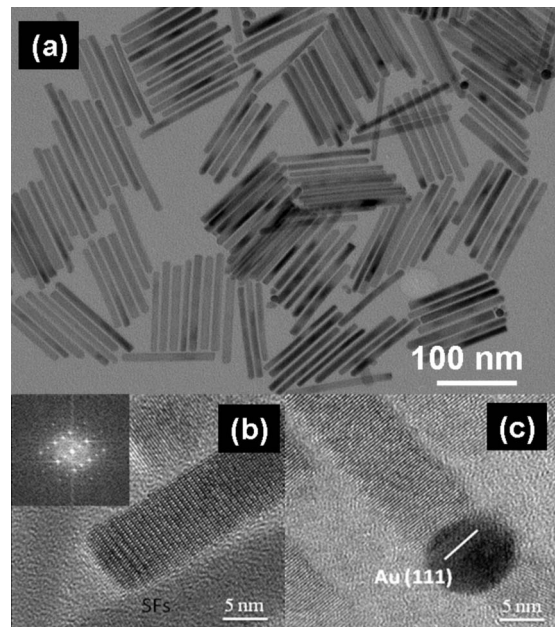


FIG. 1. (a) A low magnification TEM image showing the Mn-doped CdS nanorods prepared by the anisotropic growth using 10 nm Au seed particles with a typical diameter of 10 nm and length about 120 nm; (b) A HRTEM image of Mn-doped CdS nanorods prepared by the anisotropic growth on 10 nm Au seed particles. The inset fast Fourier transform pattern can be indexed as [100] of wurzite CdS. Stacking faults can be observed at the end of the CdS nanorod; (c) A HRTEM image of the Cd(Mn)S nanorod with Au attached at one end. The white line represents the plane of Au fcc structure. The heteroepitaxial relationship at the interface is identified to be Au(111)//CdS(001).

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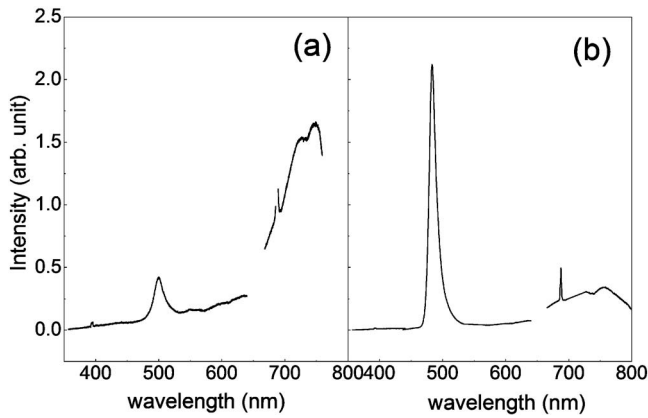


FIG. 2. The PL spectrum of Mn-doped CdS nanorods measured at (a) 300 K and (b) 75 K; the sharp lines at  $\sim 680$  nm are laser lines.

ticles detach from the nanorods due to the strain energy resulting from lattice mismatch. The heteroepitaxial interface between the Cd(Mn)S nanorod and Au nanoparticle can still be clearly identified, however, from the HRTEM images of a small fraction of the nanorods with Au still attached. An example of the heteroepitaxial interface between Au (111) and Cd(Mn)S (001) is shown in Fig. 1(c). Another indirect evidence of the heteroepitaxial growth is that extended defects, most prominently stacking faults are commonly observed at one end of the free nanorods as shown in Fig. 1(b), resulting from the lattice mismatch between Au seeds and Cd(Mn)S.

CdS is a II-VI semiconductor with a Bohr radius of 2.4 nm and a direct band gap of 2.4 eV.<sup>10</sup> UV-vis measurement (not shown here) gives the absorption edge to be about 490 nm, which is slightly blueshifted from the bulk band gap value of CdS at 517 nm due to the quantum confinement in the transverse direction.<sup>11</sup> Figure 2(a) shows the room temperature photoluminescence (PL) spectra of Cd(Mn)S nanorods. The PL spectrum shows a sharp peak at  $\sim 500$  nm corresponding to band edge emission and a broad peak centered at 750 nm, due to Mn defect emission. As the measuring temperature is lowered to 75 K, the band edge emission is significantly enhanced and its position slightly blueshifted to 484 nm, as shown in Fig. 2(b).

Undoped CdS nanorods show diamagnetic properties, which can be seen from the supplemental figure.<sup>12</sup> After doping with Mn, the nanorods demonstrate ferromagnetism. Shown in Fig. 3(a) are hysteresis loops measured from 300 to 10 K for CdS with nominally 10 at. % Mn doping. It can be seen that the samples are ferromagnetic at all measuring temperatures.  $H_c$  at 10 K is 3400 Oe, which is much larger than what is typically observed in DMS materials. It is plausible that the shape anisotropy plays an important role in determining the  $H_c$  for the nanorods with high aspect ratio.  $H_c$  shows strong temperature dependence, decreasing from 3400 Oe at 10 K to 460 Oe at 300 K. If the anisotropy is of shape origin with weak temperature dependence, the temperature dependence of  $H_c$  should come mainly from the thermal effects, i.e., the thermal energy decreases the effective energy barrier for magnetization reversal.

On the other hand, the saturation magnetization ( $M_s$ ) exhibits weak temperature dependence from 10 to 300 K, suggesting that the Curie temperature ( $T_C$ ) is much higher than 300 K. Thermal magnetic measurement shown in Fig. 4

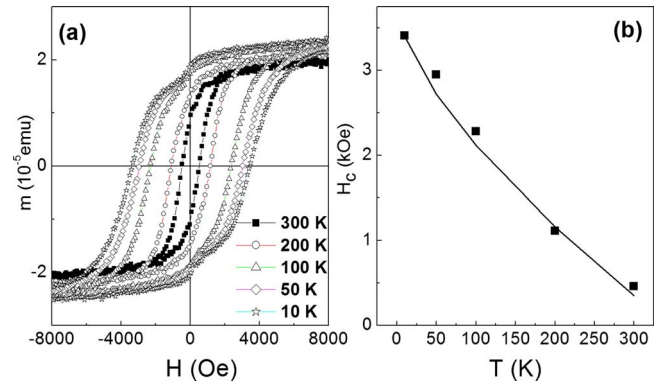


FIG. 3. (Color online) (a) The magnetic hysteresis loops of Mn-doped CdS nanorods measured from 10 to 300 K and (b) the coercivity as a function of temperature; the dots are experimental data and the line is the fitting curve using Eq. (1).

suggests a  $T_C$  of about 700 K. However, this value should not be taken as the true  $T_C$  of the as-synthesized sample, due to aggregation, Mn dopant diffusion, and redistribution of defects. A direct measure of  $M_s$  is difficult due to the presence of organic surfactants. If we assume that the magnetization reversal mechanism is dominated by thermally-assisted coherent spin rotation, the temperature dependence of  $H_c$  can be fitted by Sharrock's formula [Eq. (1)],<sup>13</sup> from which the anisotropy constant and  $M_s$  can be estimated.

$$H_c = H_K \left[ 1 - \left( \frac{k_B T \ln(f_0 t)}{H_K M_s V} \right)^{2/3} \right], \quad (1)$$

where  $H_K$  is the anisotropy field,  $f_0$  is the attempt frequency  $\sim 10^9$  Hz,  $t \sim 100$  s is the measurement time, and  $V$  is the volume of the nanorod.  $H_c$  as a function of temperature is shown in Fig. 3(b) and fitted by Eq. (1), from which we obtain  $H_K = 3600$  Oe using the dimensions measured by TEM as the input for  $V$ . We can then get a crude estimate of  $M_s$  to be  $\sim 25$  emu/cm<sup>3</sup>, which corresponds to an average of  $1.3m_B/\text{Mn}$  ion, assuming 10% doping. This is consistent with the  $M_s$  value obtained directly from magnetic hysteresis measurements. In reality, the Mn doping concentration would be smaller than the precursor ratio, and the expected Mn moment should be higher. For 5% Mn doping, the obtained  $M_s$  is lower but the estimated Mn moment is very similar.

We have carefully ruled out contaminations as the source of the observed ferromagnetic behavior. Metal precursors, surfactants, substrates, and Au nanoparticle catalysts have

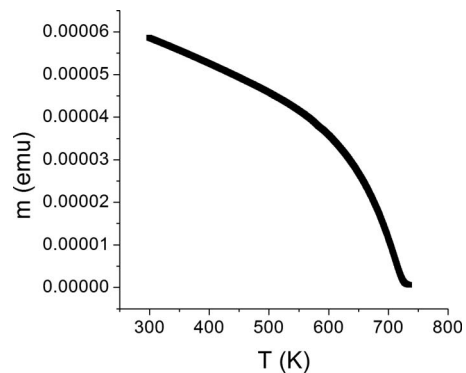


FIG. 4. Magnetization as a function of temperature for Mn-doped CdS nanorods measured at  $H=200$  Oe.

been carefully checked. It is also unlikely that the ferromagnetism originates from Mn-containing clusters. For clusters with sizes greater than 2 nm, they can be easily identified by HRTEM and electron diffraction; if the clusters are so small that they are not discernable by HRTEM, it would require them to possess unrealistically high anisotropy ( $>10^8$  erg/cm<sup>3</sup>) to be ferromagnetic at room temperature. We therefore suggest that the ferromagnetism is a global property of the nanorod.

We do not understand the origin of the ferromagnetic behavior for Mn-doped CdS nanorods at this stage. Without further experiments to probe the Mn occupancy, we can only postulate several possibilities. For a material to exhibit ferromagnetism, two factors are important: the presence of local magnetic moments and their ferromagnetic coupling. Can the ferromagnetism in our system be carrier mediated? Theoretical work based on carrier mediation predicted that GaN and ZnO may have  $T_C > 300$  K.<sup>5</sup> However, the  $p$ - $d$  hybridization in sulfides is expected to be weaker than nitrides and oxides, due to the more extended nature of the sulfur  $3p$  orbital. Therefore, the exchange energy in sulfides should be smaller than that of nitrides and oxides with similar doping level, and its  $T_C$  should be lower. Hence, we do not believe that carrier mediation plays a significant role inducing ferromagnetism in this system. Can it be due to the direct exchange between Mn ions? At the doping level of 3%–10%, the average distance between Mn ions is about 9–13 Å. At such distances, the overlap between the Mn  $3d$  wave functions would be extremely small and our estimated exchange energy is well below 1 meV, due to the narrow charge density distribution. However, if Mn ions concentration is higher at the nanorod surface than at the bulk interior, Mn  $3d$  electrons may have stronger exchange interactions. Although the direct exchange of Mn ions in bulk is typically antiferromagnetic,<sup>14</sup> it is possible that at the surface, the electronic structure is strongly modified that the exchange interactions become ferromagnetic, leading to above room temperature ferromagnetism. For nanorods with large surface-to-volume ratio, their magnetism can be dominated by surface magnetization. If this is true, it is then reasonable to explain why similar behavior has not been observed in Mn-doped II-VI bulk thin films. Another possibility is that doping may create cation vacancies. Such vacancies may lead to local moment formation from

the sulfur  $p$  orbital. The weakly localized  $p$  orbital may also favor super-long range ferromagnetic exchange interactions.<sup>15</sup> First principle calculations of the density of states are ongoing to validate some of the proposed scenarios.

In summary, Mn-doped CdS nanorods synthesized by high temperature solution phase chemistry demonstrate robust ferromagnetism at room temperature and strong temperature dependent magnetic properties. Both behaviors may be related to the nanoscale size of the system. Opening questions are then the origin of the observed ferromagnetism, and whether the carriers interact with magnetic dopants strong enough to acquire spin polarization.

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<sup>1</sup>S. A. Wolf, D. D. Awschalom, R. A. Buhrman, J. M. Daughton, S. von Molnar, M. L. Roukes, A. Y. Chtchelkanova, and D. M. Treger, *Science* **294**, 1488 (2001).

<sup>2</sup>T. Dietl, *Semicond. Sci. Technol.* **17**, 377 (2002).

<sup>3</sup>H. Ohno, *Science* **281**, 951 (1998).

<sup>4</sup>K. Y. Wang, R. P. Campion, K. W. Edmonds, M. Sawicki, T. Dietl, C. T. Foxon, and B. L. Gallagher, *AIP Conf. Proc.* **772**, 333 (2005).

<sup>5</sup>T. Dietl, H. Ohno, F. Matsukura, J. Cibert, and D. Ferrand, *Science* **287**, 1019 (2000); V. M. Galitski, A. Kaminski, and S. Das Sarma, *Phys. Rev. Lett.* **92**, 177203 (2004).

<sup>6</sup>H. Saito, W. Zaets, S. Yamagata, Y. Suzuki, and K. Ando, *J. Appl. Phys.* **91**, 8085 (2002).

<sup>7</sup>W. L. Shi, Y. Sahoo, H. Zeng, Y. Ding, M. T. Swihart, and P. N. Prasad, *Adv. Mater. (Weinheim, Ger.)* **18**, 1889 (2006).

<sup>8</sup>T. J. Trentler, S. C. Goel, K. M. Hickman, A. M. Viano, M. Y. Chiang, A. M. Beatty, P. C. Gibbons, and W. E. Buhro, *J. Am. Chem. Soc.* **119**, 2172 (1997).

<sup>9</sup>H. Sakai, *Surf. Sci.* **351**, 285 (1996).

<sup>10</sup>G. Z. Shen, J. H. Cho, J. K. Yoo, G. C. Yi, and C. J. Lee, *J. Phys. Chem. B* **109**, 9294 (2005).

<sup>11</sup>K. T. Yong, Y. Sahoo, M. T. Swihart, and P. N. Prasad, *J. Phys. Chem. C* **111**, 2447 (2007).

<sup>12</sup>See EPAPS Document No. E-APPLAB-93-054837 for magnetic hysteresis loops of (a) Mn-doped CdS with 5% nominal doping; (b) CdS nanorods on Si substrate (300 K); (c) Au nanoparticle on Si substrate (300 K); (d) the Si substrate (300 K) and (e) the VSM sample holder (300 K). For more information on EPAPS, see <http://www.aip.org/pubservs/epaps.html>.

<sup>13</sup>M. P. Sharrock, *J. Appl. Phys.* **76**, 6413 (1994).

<sup>14</sup>A. J. Freeman and R. E. Watson, *Phys. Rev.* **124**, 1439 (1961).

<sup>15</sup>P. Dev, Y. Xue, and P. Zhang, *Phys. Rev. Lett.* **100**, 117204 (2008).