One-Pot Synthesis and Characterization of Mn$^{2+}$-Doped Wurtzite CdSe Nanocrystals Encapsulated with Carbon

Sayan Bhattacharyya,† D. Zitoun,‡ and A. Gedanken*,†

Department of Chemistry and Kanbar Laboratory for Nanomaterials at the Bar-Ilan University Center for Advanced Materials and Nanotechnology, Bar-Ilan University, Ramat-Gan 52900, Israel, and ICGM-AIME, Université Montpellier II, CC15, Place Bataillon 34095 Montpellier, France

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Mn-doped CdSe nanocrystals encapsulated in carbon (Cd$_{1-x}$Mn$_x$Se @ C) were synthesized by the one-pot RAPET (reaction under autogenic pressure at elevated temperature) approach. The nanocrystal core was 27–51 nm encapsulated by a 9–18 nm carbon shell, as evidenced from electron microscopic analysis. The efficient replacement of Cd by Mn in the hexagonal wurtzite Cd$_{1-x}$Mn$_x$Se lattice, until Mn/Cd = 0.099, was confirmed from electron paramagnetic resonance (EPR) experiments. For Mn/Cd = 0.143 nanocrystals, manganese was found to be expelled to the nanocrystal surface. The magnetic measurements evidenced the appearance of antiferromagnetic clusters (manganese rich) that exhibit a superparamagnetic behavior with a blocking temperature of 28 K. Raman experiments revealed that the shell consisted of continuous linear chains of carbon. The formation of the core–shell nanocrystals in the absence of any templating agent was a kinetically controlled process of Cd$_{1-x}$Mn$_x$Se nucleus formation and carbon encapsulation. Mn replaces Cd mainly in the (100) plane and catalyzes the formation of nanorods and tripod nanostructures.

Introduction

In recent years, extensive research has been focused on cadmium selenide (CdSe) nanocrystals because of their technological applications in light-emitting diodes, lasers, and biological labels. However, major efforts have been devoted to the use of CdSe nanocrystals as the host material for doping transition metal ions for the realization of diluted magnetic semiconductors (DMS) in spintronics applications. However, among the II-VI semiconductor materials such as CdS, ZnS, and ZnSe, manganese doping into CdSe nanocrystals is very difficult and controversial due to the self-purification process, whereby Mn has a tendency to be expelled to the CdSe nanocrystal surface. It is of prime importance that manganese is actually embedded inside the nanocrystals in order to obtain high quality DMS nanocrystals for use in spin electronics and quantum information technology. In the Mn$^{2+}$-doped II-VI semiconductor nanostructures, an sp–d exchange interaction exists between the electron/hole band states of the semiconductors and the Mn$^{2+}$ 3d$^5$ electron states, whereby Mn$^{2+}$ acts as a paramagnetic center ($S = 5/2$).

From the application point of view, cadmium chalcogenides, especially CdSe, are highly toxic to biological tissue. Hence, to make them biocompatible and water-soluble, various surface modifications have been tried such as coating them with mercaptopropionic acid, polymers, and silica. In this respect, carbon in its various forms such as diamond, graphite, disordered, or amorphous has been used as a successful coating material to increase biocompatibility for biological/biomedical applications. This prompted us to encapsulate our CdSe nanocrystals in a carbon layer and to study their physical properties. Indeed, a survey of the experimental literature reveals that carbon-encapsulated, Mn-doped CdSe nanocrystals have not been previously reported. Moreover, the carbon shell over the Cd$_{1-x}$Mn$_x$Se nanocrystals was formed without the use of any template by the one-pot, solvent-free RAPET (reaction under autogenic pressure at elevated temperature) approach, which is also much cheaper and easier than all the other previously reported methods.

Experimental Section

Cadmium acetate dihydrate [Cd$_2$(OAc)$_2$·2H$_2$O, Aldrich, 98%], manganese(II) acetate tetrahydrate [C$_4$H$_6$O$_4$Mn·4H$_2$O, Fluka, ≥99%], and selenium powder [100 mesh, Aldrich, 99.99%] were used as received. In a typical synthesis of Mn-doped CdSe nanostructures coated with carbon, 1 g of Cd$_2$(OAc)$_2$·2H$_2$O, 0.31 g of Se, and a stoichiometric amount of C$_4$H$_6$O$_4$Mn·4H$_2$O (according to Mn/Cd atomic ratios of 0, 0.015, 0.06, 0.1, and 0.15) were mixed and introduced into a 2 mL stainless steel Swagelok reactor at room temperature. The filled Swagelok reactor was tightly closed with the other plug and placed at the center of tube’s furnace. The temperature of the furnace was raised to 800 °C at a rate of 10 °C/min and maintained for 10 h. The Swagelok reactor was gradually cooled (~5 h) to room temperature and opened. The yield of the gray colored Cd$_{1-x}$Mn$_x$Se @ C product was ~72%. The Cd$_{1-x}$Mn$_x$Se @ C products with Mn/Cd atomic ratios of 0, 0.014, 0.052, 0.099, and 0.143 were determined by inductively coupled plasma (ICP) analysis, and they will be referred to as M0, M1, M2, M3, and M4, respectively, in subsequent discussions.

The obtained products were structurally characterized using a high resolution scanning electron microscope (HRSEM, JSM, 7000F), a low/high resolution transmission electron microscope (TEM/HRTEM, JEOL, 2010), powder X-ray diffraction (Cu Kα = 1.5418 Å radiation, Bruker AXS D8), inductively coupled plasma atomic emission spectroscopy (ICP-AES; Spectroflame Module E), and energy dispersive X-ray spectroscopy (EDS,
The electron paramagnetic resonance (EPR) spectrum was recorded on a Bruker EPR spectrometer (ER083 CS) operating at an X-band (ν = 9.77 GHz) with a 100 kHz magnetic field modulation. An Olympus BX41 (Jobin-Yvon-Horiba) Raman spectrometer was employed, using the 514.5 nm line of an Ar ion laser as the excitation source to analyze the nature of the core as well as that of the carbon shell. The photoluminescence (PL) spectra were recorded on an Aminco-Bowman-Series-2 luminescence spectrophotometer equipped with a 150 W xenon lamp as the excitation source. Magnetic properties were measured using a Super Quantum Interference Design (SQUID) magnetometer MPMS XL7 in the temperature range of 2–350 K and fields varying between 0–5 T. The temperature-dependent susceptibility was measured using a DC procedure. The sample was cooled to 2 K under a zero magnetic field. A low magnetic field (5 mT) was applied, and data were collected from 2 to 350 K (zero-field-cooled, ZFC). Field-cooled (FC) measurements were performed from 2 to 350 K with an applied field during the cooling.

Results and Discussion

High/low resolution SEM/TEM images for the prepared products were measured in order to investigate and determine the morphological changes as a function of the Mn/Cd atomic ratio. Figure 1 shows the HRSEM images of the products, where the core–shell morphology is clearly distinct. The particles are nearly spherical in shape, where the Cd$_{1-x}$Mn$_x$Se core is 35–51 nm and the carbon shell is 7–14 nm. The detailed dimensions of the spherical core–shell particles are presented in Table 1. A gradual increase in the nanocrystal size is observed with the increase in Mn concentration. In the case of higher Mn concentration, M2, M3, and M4 nanorods coexist along with the spherical nanoparticles (see Figure 1d, f, and i). The nanorods in M2 are ∼300 nm long, and the core and shell across the diameter are 23 (±2 and 15 (±2 nm, respectively (Figure 1d). Figure 1f (sample M3) shows the nanorods having an average diameter of 67 nm (core $= 53$ ± 2 nm; shell $= 14$ ± 2 nm) and a length of >250 nm. The core–shell structure is not distinct in the nanorods of M4 (Figure 1i), where the diameter is 44 (±20 nm and the length is 154 ± 30 nm. In addition, tripod structures are observed for M3 (Figure 1g), where the arms are 64 nm in diameter (core $= 53$ ± 2 nm; shell $= 11$ ± 0 nm) and have a length of ∼161 nm.

The TEM images corroborate the spherical core–shell morphologies of HRSEM (Table 1 and Figure 2a–e). The selected area electron diffraction (SAED) of M3 in Figure 2f shows the
The HRTEM image of the nanocrystal core of M3 (Figure 2g) further verifies the identification of the nanocrystalline hexagonal phase with a perfect arrangement of the atomic layers. The distance measured between the (100) lattice planes is 0.372 nm (as shown with arrows) and matches well with the JCPDS card no. 77-0046. The ordered lattice planes of carbon at the shell of the M3 nanocrystals have an interlayer spacing of ∼0.382 nm, which is slightly larger than that of the graphitic layers (JCPDS card no. 41-1487). Careful observation of the TEM image in Figure 2j reveals the 44 nm core and ∼6 nm shell of the 143 nm long nanorods of M2. The tripod structure of M3 (Figure 2k) mirrors the HRSEM image of Figure 1g. Its HRTEM image in Figure 2l shows the interlayer (100) lattice spacing of 0.372 nm (JCPDS card no. 770-0046). Hollow cages (spheres) surrounded by a carbon shell have been observed in all the products. In Figure 2c, a few hollow spheres are observed, and a large number of them are presented for M3 in Figure 2i. It is highly probable that the DMS nanocrystals escape out of the carbon shell due to the wear and tear of the carbon shell at elevated temperatures. Such a torn shell is shown in the inset of Figure 2i. However, the carbon shell is strong enough to retain its original shape even after the elimination of the DMS core and thus resembles a hollow sphere.

The results obtained from energy dispersive X-ray spectroscopy (EDS) coupled with TEM are shown in Figure 3a–c. The EDS spectra were recorded at five different locations of the Cu grid to ascertain the homogeneity of the Mn incorporation in the nanocrystals. The Mn/Cd atomic ratios obtained from the EDS results are 0.012 (3), 0.05 (2), 0.099 (1), and 0.14 (1) for M1, M2, M3, and M4, respectively. These values match well with the quantitative analysis by ICP measurements. Elemental line scanning of a single nanocrystal of M3 (placed on the Si wafer) was performed to investigate the core–shell morphology (Figure 3d). The C-line shows a small hump at the edge of the nanocrystal, due to an excess of carbon at the shell of the nanoparticle. A steady rise in the intensities of the Cd, Mn, and Se signals is observed within the nanocrystal region, although the Se signal has the strongest leap. Nevertheless, the average ratio of Cd/Se is determined to be 1:0.83 from ICP analysis of all the products. The precise content of the nanocrystals in M3 was confirmed by employing a highly sensitive, wave dispersive X-ray analyzer (WDX), which is coupled to the HRSEM instrument. The sample was dispersed on the Si wafer. The selected area for the elemental dot mapping (WDX) is shown in Figure 3e. The contents of Si, C, Cd, Mn, and Se are presented in Figure 3f–j, respectively. The Cd, Mn, and Se signals are detected within the position of the nanocrystals. The C signal is observed over the nanocrystals, since the carbon encapsulates...
the nanocrystal core. Manganese is found to be uniformly distributed within the nanocrystals.

The XRD patterns of the Cd$_{1-x}$Mn$_x$Se @ C products are shown in Figure 4. All the reflection peaks in the products could be readily indexed to the hexagonal wurtzite CdSe (P6$_3$mc space group), which agree well with the reported data in JCPDS card no. 77-0046. The reaction conditions were controlled and optimized to eliminate any impurity phase formation such as cadmium oxide, manganese oxide, and metallic selenium, and such peaks were not detected in the XRD patterns. Carbon XRD peaks were not observed, which might be due to the amorphous or semicrystalline nature of the encapsulating shell. In addition, MnSe diffraction peaks were not detected, since the Mn ions replaced the Cd in the CdSe unit cell.

In the XRD patterns, an interplay between the relative intensities of (100), (110), and (103) reflections are observed. A similar interplay is observed between the (002) and (101) reflections. This might occur due to the replacement of Cd$^{2+}$ by Mn$^{2+}$ at different sites of the Cd$_{1-x}$Mn$_x$Se lattice. The (100) reflection peak is negligibly shifted by +0.0006° with the increase in Mn concentration in the lattice from M0 to M1. From M1 to M2, the shift ($\Delta \theta$) of the (100) peak is +0.0989°, which again shifts to a lower angle by ~0.0016° from M2 to M3. In the case of M4, the (100) peak position is same as that of M1. The lattice parameter $a$ was calculated as 0.43021, 0.43019, 0.42845, 0.42848, and 0.43019 nm and $c$ is 0.70136, 0.70149, 0.70135, 0.70136, and 0.70136 nm for M0, M1, M2, M3, and M4, respectively. Accordingly, the $c/a$ ratio increases from 1.63 (M0, M1) to 1.64 (M2, M3) and again decreases to 1.63 (M4). Thus, Mn$^{2+}$ occupies the CdSe lattice mainly along the c-axis. However, it is clear that in M4 all the Mn$^{2+}$ ions are not fully embedded inside the CdSe crystal lattice, and hence, the lattice parameters revert back to those of M0 and M1.

Raman scattering experiments were carried out in order to probe the changes in the atomic arrangement due to the Mn$^{2+}$ doping inside the CdSe lattice, and to investigate the nature of the carbon shell. Figure 5 shows the room temperature Raman spectra of the products, where 100–500 and 1000–3000 cm$^{-1}$ correspond to the spectral regions of the Cd$_{1-x}$Mn$_x$Se core and carbon-containing shell, respectively. In the 100–500 cm$^{-1}$ region for M0, the Raman peaks are observed at 168, 189.6, 205.6, and 408.3 cm$^{-1}$, which are attributed to the transverse
optic (TO), surface optic (SO), longitudinal optic (LO), and 2LO phonon modes of CdSe, respectively. The TO phonon mode is not very distinct in the Mn$^{2+}$-containing products. A minute analysis of the spectra revealed that the SO and LO phonon modes randomly shift by 0.6 and 0.9 cm$^{-1}$ from M0 to M4. However, additional peaks were not observed due to the impurity mode of Mn in CdSe. The Raman modes in the 100–500 cm$^{-1}$ spectral region are not very distinct, probably due to the encapsulating carbon shell.

In the 1000–3000 cm$^{-1}$ spectral region of M0, the distinct peaks at 1326 and 1596 cm$^{-1}$ correspond to the D (Raman-inactive A$_{1g}$ vibration mode of disordered graphite) and G (Raman active optical E$_{2g}$ mode of 2D graphite) bands of the carbon shell. These two bands, although very weakly observed for M1, are totally absent for M2–M4. Instead, strong and broad peaks are observed at 2533, 2388, 2148, 2242, and 2228 cm$^{-1}$ for M0, M1, M2, M3, and M4, respectively. These peaks are in the region of the second order of Raman and are similar to the overtone or combination bands. These peaks cannot be attributed to the C–H stretching, since at 800 °C all the acetate groups were fully decomposed to carbon. The carbon contents in the products, as determined by C, H, N analysis, are 3.4, 4.1, 4.5, 3.1, and 3.8 wt % in M0, M1, M2, M3, and M4, respectively. However, in the literature, the bands in this region were assigned to the characteristic vibration bands of sp$^1$ linear carbon chains. From these data, we can assume that the carbon shell in our case might consist of linearly arranged carbon atoms, forming a continuous stretch along the circumference of the carbon shell similar to carbon fibers encapsulating the DMS core.

In the Mn$^{2+}$-doped products, the changes in the coordination environment of Mn$^{2+}$ modify the crystal field, and hence, EPR spectra act as a probe to study the Mn$^{2+}$ coordination state and Mn$^{2+}$–Mn$^{2+}$ interactions. At 300 K, six line EPR spectra arise due to the hyperfine interaction from the $^{55}$Mn nucleus ($I = 5/2$) and correspond to the allowed transition ($\Delta m_s = \pm 1$, $\Delta m_I = 0$, where $m_s$ and $m_I$ are the electron spin and nuclear spin quantum numbers, respectively). The location of Mn$^{2+}$ at different possible sites (core or surface) present in a nanocrystal can be determined from EPR measurements. The magnitude of the Mn$^{2+}$ hyperfine splitting constant is dependent on the covalency of the site occupied by Mn$^{2+}$, and larger hyperfine constants are exhibited by more ionic sites. The surface sites are more ionic than the bulklike core, and hence, the Mn$^{2+}$ ions at the surface should exhibit larger hyperfine splitting than the internal Mn$^{2+}$ ions embedded within the nanocrystals. This allows the assignment of core doping of Mn into the CdSe lattice.

From Figure 6, we determine hyperfine splitting constants of 64.7 × 10$^{-4}$, 64.5 × 10$^{-4}$, and 61.3 × 10$^{-4}$ cm$^{-1}$ for M1, M2, and M3, respectively, at 300 K. For M4, the six hyperfine lines completely disappear and a single broadened Lorentzian band appears, indicating the domination of Mn$^{2+}$–Mn$^{2+}$ exchange dipolar interactions. Mn has a tendency to form pairs and clusters with an increase in the number of Mn atoms and reduces the hyperfine interactions. This might also indicate the partial segregation of Mn$^{2+}$ at the surface of the CdSe nanocrystals in M4, where a fraction of Mn$^{2+}$ might still be embedded inside the nanocrystals. Hence, the broad line totally dominates the six line spectra. However, for M1 and M2, the symmetry of the six line spectra is hindered by a sharp absorption line at the center. The dipolar interactions between the Mn impurities give rise to a broadening with poor resolution and a broad background signal. From M1 to M3, the EPR line are a bit noisy, and hence, the possibility of weak lines in addition to the six intense lines cannot be ruled out. The weak lines might arise due to double spin transition ($\Delta m_s = \pm 1$, $\Delta m_I = \pm 1$), where $m_s$ and $m_I$ change simultaneously. It is well-known in the literature that Mn$^{2+}$ can be successfully doped into nanocrystals having a zinc-blende crystal structure, while the wurtzite nanocrystals have not been successfully doped, or rather the doping was up to a low concentration (1%) of manganese. This is due to the fact that the binding energy of the [001] facets in the zinc-blende CdSe is ~4–6 eV and is much higher than that of any facets in wurtzite CdSe. In this aspect, it is noteworthy to mention here that we could efficiently dope Mn$^{2+}$ ions into wurtzite CdSe nanocrystals up to a Mn/ Cd atomic ratio of 0.099 via the RAPET approach. To account for the upper limit of doping of Mn$^{2+}$ into the CdSe matrix, the weight ratio of Mn/CdSe is presented in Table 1.

The magnetic measurements were performed at low and high fields as a function of manganese concentration on samples M1, M2, and M3 (M4 was discarded for its heterogeneity). The susceptibility was investigated using a zero-field-cooled/field-cooled (ZFC/FC) routine at a field of $\mu_0H = 0.1$ T. Figure 7 shows the results for different Mn concentrations. The susceptibility was plotted both as a function of temperature and, in the inset, as a function of inverse temperature. All the samples display paramagnetic behavior. The inverse of susceptibility follows the Curie law with Curie–Weiss temperatures of $\theta_1 = -50.9 \pm 0.5$ K, $\theta_2 = -393 \pm 1$ K, and $\theta_3 = -760 \pm 2$ K. This behavior is clear evidence of the strong antiferromagnetic coupling between the manganese atoms.

A detailed analysis of the ZFC/FC data shows a new phenomenon occurring at 25 K. The ZFC/FC routine was also performed at a lower field of $\mu_0H = 0.02$ T to give some insight (Figure 8). Under this low external field, the ZFC curve exhibits a maximum at 28 K. This behavior is typical of the occurrence of a blocking temperature for a superparamagnetic system. Both antiferromagnetic and ferromagnetic systems can display superparamagnetism when the grain size is reduced to the nanoscale.

Additional high field measurements $M(H)$ were performed at low temperature ($T = 2$ K) and room temperature ($T = 300$ K).
The results are plotted in Figures 9 and 10, respectively. All doped samples display a hysteresis at low temperature. The coercive field reaches values of $\mu_0H_{0.5}$, 7.0, and 60 mT for the M1, M2, and M3 samples, respectively. The observed hysteresis results from the antiferromagnetic coupling between the manganese atoms in the CdSe matrix. The magnetic moment does not reach saturation even at an applied field of 5 T. The magnetic moments follow a Langevin function $M(H,T) = M_{ITL}(\mu_0H/k_B T)$. At room temperature, the hysteresis loops do not show a significant coercive field. Nevertheless, the behavior is still not purely paramagnetic.

All magnetic measurements (EPR and SQUID) are consistent with a $^+II$ state of the manganese atoms. The $M/T$ magnetic measurements are evidence of the antiferromagnetic coupling between the spins. This coupling is strong enough to promote the appearance of antiferromagnetic clusters (manganese rich) that exhibit a superparamagnetic behavior with a blocking temperature of 28 K. The pure MnSe is indeed antiferromagnetic with a Néel temperature of 173 K. However, the Curie–Weiss temperature for MnSe is only $\theta_1 = -297$ K, far from the value found for M3 ($\theta_3 = -760$ K). The very low value found can then be attributed to the clustering of manganese at the nanoscale. This effect was recently reported in manganese-doped CdSe. According to the authors, the superparamagnetic behavior was attributed to the ferromagnetic coupling between MnSe clusters upon annealing the pristine materials.

The room temperature photoluminescence (PL) spectra of the products (Figure 11) were measured at an excitation wavelength of $\lambda_{ex} = 473$ nm. The bulk band edge emission occurs at 717 nm. In our case, the band edge emission is blue-shifted to 624, 622, 626, and 624 nm for M0, M1, M3, and M4, respectively. In M2, the band edge emission merges with the intra-Mn$^{2+}$ transition ($^4T_1 \rightarrow ^6A_1$) band at 675 nm. The intra-Mn$^{2+}$ emission occurs at 675, 676, and 676 nm for M2, M3, and M4, respectively, and is not observed for M1. The band edge emission is blue-shifted due to the probable effect of the encapsulating carbon shell on the band structure of the Cd$_{1-x}$Mn$_x$Se nanocrystals. The appearance of the intra-Mn$^{2+}$ emission is strong proof of the successful doping of Mn$^{2+}$ into the CdSe lattice. The weaker peaks at 528–537 and 570–577 nm might relate to the shallow and deep trap emissions, which
are probably due to the surface states and structural defects of the nanocrystals.18 Hence, the luminescence spectra may indicate that in fact there are three structures, according to the increase in Mn content. The spectra of M1 (low Mn2+ content) is almost identical to that of the pure CdSe @ C (M0); the overall optical properties are modified for the uniformly distributed Mn2+ product (M2); and two significant luminescence peaks are observed for M3 and M4, whereby the Mn2+ ions start segregating.

The template-free formation of the nanocrystals with the core–shell morphology proceeds with the initial decomposition of the cadmium and manganese acetates into their gaseous state, along with gaseous selenium, when heated to 800 °C inside the Swagelok reactor. The decomposition of acetates involves the following steps: (i) M(CH3COO)2 + xH2O → M(CH2COO)2 + xH2O; (ii) M(CH2COO)2 → MCO3 + CH4COCH3; (iii) CH3COOH → CO + C2H4; (iv) 2CO + C + CO2 (Boudouard reaction); and (v) MCO3 → Mn + CO2.19 Selenium evaporates above 685 °C and reacts with (Cd1−xMnx)-O to form Cd1−xMnxSe via the following reaction: 2Cd1−xMnxO + 2Se → 2Cd1−xMnxSe + O2. All the products of the dissociation reaction float in the gas phase in a closed Swagelok reactor and solidify right after their formation. A little stoichiometric excess of Se was used, since a lesser amount of Se (and at temperatures of <800 °C) retained <5 wt % Cd1−xMnxO and manganese oxide impurity phases. The formation of the carbon shell over the semiconducting core is a kinetically controlled process.20 The solidification rate of Cd1−xMnxSe is faster than that of carbon, and hence, Cd1−xMnxSe crystallizes initially to form the core, followed by carbon, giving rise to the core–shell structure. From Figures 1 and 2, it can be seen that the thickness of the carbon shell around the nanocrystal core is inhomogeneous in many cases, which might result if the gradient in the carbon density is not uniform during the core–shell formation process. The nanorod and tripod structures in the M2–M4 products owe their formation to the catalytic action of manganese.21 To eliminate the possibility of any catalytic reaction by Fe, Co, Ni, or Cr (Swagelok body components) in the formation of 1D nanostructures, control experiments were carried out in which the reactants were filled in a quartz tube which was again placed inside the Swagelok reactor. No change was observed in the composition, structure, and morphology of the products. This confirms that the Swagelok body has no catalytic role. The relatively higher percentage of the spherical nanocrystals, as compared to the nanorods, is also governed by a kinetic process, whereby the one-dimensional growth competes with the carbon encapsulation process. If the carbon encapsulates the nanocrystal completely before the 1D growth takes place, we obtain spherical nanoparticles. On the other hand, if the 1D growth has taken place appreciably, before the carbon encapsulates the growing end, nanorods and tripod nanostructures are obtained.

Conclusions

In conclusion, carbon-encapsulated Cd1−xMnxSe nanocrystals and nanorods were synthesized via the one-pot RAPET approach. Manganese catalyzes the formation of the nanorod and tripod nanostructures in addition to the spherical nanocrystals. The core of the Cd1−xMnxSe @ C products has a hexagonal wurtzite crystal structure, and Mn2+ is efficiently and uniformly doped inside the CdSe nanocrystals up to a Mn/Cd atomic ratio of 0.099. This is evident from the room temperature EPR measurements. The mechanism for the formation of the core–shell nanocrystals, without the use of any template, is a kinetically controlled process involving Cd1−xMnxSe nucleus formation and carbon encapsulation. The carbon shell is mainly composed of continuous linear chains, as evidenced from Raman experiments. The encapsulating carbon shell influences the Cd1−xMnxSe band edge emission and hence the PL characteristics, which also show the intra-Mn2+ emission. The observed magnetic hysteresis at 2 K results from antiferromagnetic Mn−Mn coupling in the CdSe matrix. The superparamagnetic blocking of the spins occurs at 28 K, below which there is clear evidence for strong antiferromagnetic interactions.

References and Notes

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