


sp–d Exchange Interactions in Wave Function Engineered Colloidal CdSe/Mn:CdS Hetero-Nanoplatelets

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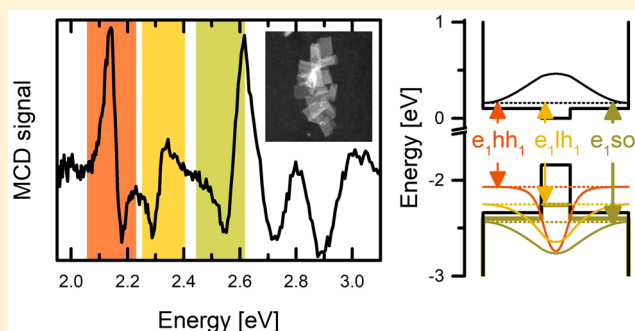
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Supporting Information

ABSTRACT: In two-dimensional (2D) colloidal semiconductor nanoplatelets, which are atomically flat nanocrystals, the precise control of thickness and composition on the atomic scale allows for the synthesis of heterostructures with well-defined electron and hole wave function distributions. Introducing transition metal dopants with a monolayer precision enables tailored magnetic exchange interactions between dopants and band states. Here, we use the absorption based technique of magnetic circular dichroism (MCD) to directly prove the exchange coupling of magnetic dopants with the band charge carriers in hetero-nanoplatelets with CdSe core and manganese-doped CdS shell (CdSe/Mn:CdS). We show that the strength of both the electron as well as the hole exchange interactions with the dopants can be tuned by varying the nanoplatelets architecture with monolayer accuracy. As MCD is highly sensitive for excitonic resonances, excited level spectroscopy allows us to resolve and identify, in combination with wave function calculations, several excited state transitions including spin–orbit split-off excitonic contributions. Thus, our study not only demonstrates the possibility to expand the extraordinary physical properties of colloidal nanoplatelets toward magneto-optical functionality by transition metal doping but also provides an insight into the excited state electronic structure in this novel two-dimensional material.

KEYWORDS: Colloidal nanoplatelets, colloidal heterostructures, semiconductor nanocrystals, wave function engineering, transition metal doping, diluted magnetic semiconductor (DMS)



Recently novel two-dimensional (2D) colloidal nanoplatelets (NPLs), the so-called “colloidal quantum wells”, evoke increasing research interest as functional materials in next-generation optoelectronic and photonic devices, such as light-emitting diodes^{1,2} and lasing applications,^{3–5} thanks to their outstanding electronic and optical properties.^{6–8} These semiconductor nanocrystals, which are precisely tunable in thickness on a monolayer scale, combine short fluorescence lifetimes and high ensemble color purities⁹ with a distinct 2D electronic structure,¹⁰ large absorption cross sections,¹¹ and quasi-zero Stokes shift. In addition, due to their two-dimensional shape NPLs exhibit a potential for an improved charge transport compared to their spherical counterparts,¹² which has been utilized in photodetectors¹³ and transistors.¹⁴ The lately developed technique of the colloidal atomic layer deposition (c-ALD)¹⁵ allows the synthesis of complex core/shell heterostructure architectures. This opens up access to various material combinations enabling precise tuning of the

band alignment and thus the charge carrier wave functions in, e.g., type I,¹⁶ quasi-type II^{17,18} and type II^{19,20} heterojunctions.

Doping, the selective introduction of impurity atoms on lattice sites, represents a powerful approach to tailor the optical, electrical, and magnetic properties of a semiconductor and has successfully been adapted in various colloidal nanocrystals.^{21–25} Embedding transition metal ions like manganese into semiconductors is known to introduce magnetic sp–d exchange interactions between the magnetic moments of the dopants (carried by their d orbitals) and the spins of the charge carriers, i.e., the (s-type) electrons and the (p-type) holes, which results in extraordinary optical and magneto-optical properties.^{26,27} This concept of diluted magnetic semiconductors (DMS) experiences a boost since its adaption to colloidal synthesized

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nanocrystals,^{22,28,29} as herein the magnetic exchange interactions, scaling with the wave function overlap of the charge carriers with the dopants, can be greatly enhanced due to the strong geometrical and dielectric confinement achievable in comparison to their epitaxial counterparts. This has led to, e.g., the observation of giant zero field exchange splitting in single-Mn-doped CdSe quantum dots (QDs)³⁰ and light induced magnetism up to room temperature in Mn:CdSe QDs,³¹ making colloidal DMS nanostructures attractive for the incorporation in tomorrow's spintronic devices.³² In various magnetically doped colloidal nanostructures of different shapes (including spherical quantum dots,³³ magic sized clusters,³⁴ and anisotropic nanoribbons³⁵), sp-d exchange interactions persist up to room temperature.

Very recently, magnetic doping has been realized in CdSe/Mn:CdS/CdS multishell nanoplatelets,^{36,37} extending the versatile outstanding properties of NPLs toward magneto-optical functionality. Hereby, clear evidence of the sp-d exchange interactions for band charge carriers has been missing up to date, as those previous reports are based on magnetoluminescence studies, which are unable to exclude contributions from localized states. The distinct two-dimensional electronic structure allows one to selectively address individual excitonic transitions with a well-defined hole character. This is in contrast to spherical magnetically doped core/shell quantum dots,^{38,39} which are strongly affected by valence band mixing.

In this work, we utilize magnetic circular dichroism (MCD) spectroscopy to directly evidence sp-d exchange interactions in shell-doped CdSe/(MnS)/Mn:CdS core/shell nanoplatelets. By exploring the degrees of freedom provided by c-ALD, we show the possibility to tune the s-d and p-d exchange interactions via wave function engineering. By variation of the core and shell thickness in CdSe/Mn:CdS nanoplatelets with atomic monolayer precision, we are able to adjust the p-d exchange interactions. Integration of a high band gap MnS interlayer enables us to confine the heavy hole wave function in the undoped core, giving access to tune the s-d exchange interactions. Excited state MCD spectroscopy reveals a variety of excitonic resonances. They could be successfully identified and assigned via wave function calculations, providing valuable insights into the excited state electronic structure of this novel class of materials.

Magnetically doped nanoplatelets of a zinc blende type were synthesized following the synthesis described in ref 36. For our study, we prepared two sets of samples allowing us to tune either the hole (p-d) or the electron (s-d) exchange interaction with magnetic dopants. For studying the former (i.e., the p-d exchange interaction), an undoped CdSe core of 2 or 3 monolayer (ML) thickness was coated with a manganese-doped shell of 6 or 8 ML thickness (3 or 4 ML on each side, respectively). In order to tune the s-d exchange interaction, we prepared samples based on a 2 ML CdSe core surrounded by a 2 ML (one on each side) MnS interlayer and an additional 6–10 ML (3–5 ML on each side) Mn:CdS. The doping concentration in the Mn:CdS shell is approximately 1.2% (Supporting Information). A list of all doped samples can be found in Table 1.

Figure 1b compares the MCD signal from (2) CdSe/(8) Mn:CdS NPLs with data from an undoped reference sample at 1.6 T and cryogenic temperatures, revealing a bunch of excitonic signatures for the doped sample. Typically, an A-type MCD feature has a deviated-Gaussian line shape, with its zero crossing coinciding with the peak position in zero-field

Table 1. List of Samples Used in This Study

samples	composition		
	CdSe core	MnS interlayer	Mn:CdS shell
(2) CdSe/(8) Mn:CdS	2 ML		2 × 4 ML
(2) CdSe/(6) Mn:CdS	2 ML		2 × 3 ML
(3) CdSe/(8) Mn:CdS	3 ML		2 × 4 ML
(2) CdSe/(2) MnS/(6) Mn:CdS	2 ML	2 × 1 ML	2 × 3 ML
(2) CdSe/(2) MnS/(8) Mn:CdS	2 ML	2 × 1 ML	2 × 4 ML
(2) CdSe/(2) MnS/(10) Mn:CdS	2 ML	2 × 1 ML	2 × 5 ML

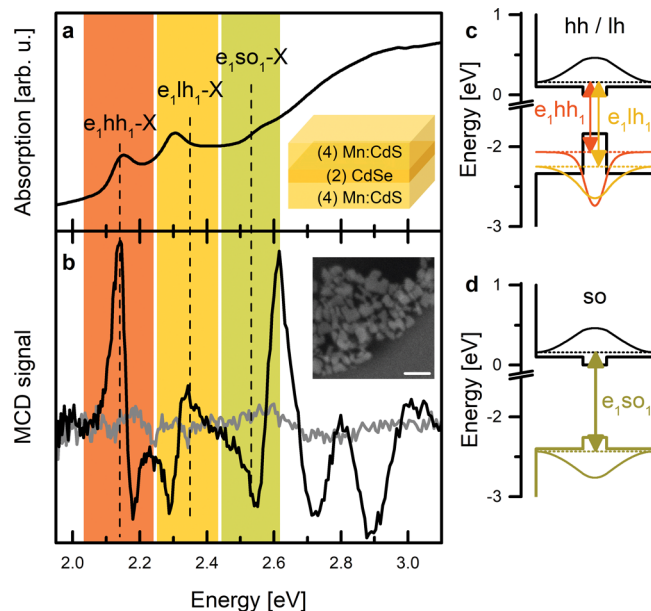


Figure 1. Absorption (a) and MCD spectra (b) of (2) CdSe/(8) Mn:CdS (black) nanoplatelets at 5 K and under 1.6 T. For comparison, the magneto-optical response of an undoped reference (gray line) with the same architecture ((2) CdSe/(8) CdS) is depicted. The spectral range of the e_1hh_1-X , e_1lh_1-X , and e_1so_1-X transitions are highlighted in red, yellow, and olive, respectively, while dashed lines represent the calculated transition energies considering exciton binding energies. (See the Supporting Information for details.) The insets depict a scheme of the sample (top) and a SEM image of nanoplatelets deposited on a Si substrate (bottom, scale bar 50 nm). Parts c and d depict calculated energies and probability density functions for the e_1 electron (black) and the hh_1 (orange), lh_1 (yellow), and so_1 (olive) hole states. Arrows denote the respective optical transitions.

absorption, while the sign of the corresponding Zeeman splitting is revealed in the shape of the signal. (For a positive Zeeman splitting, a maximum follows a minimum in energy and vice versa, following the conventions of refs 29 and 40.) As the MCD and absorption spectra were compared (Figure 1a), the first two energetically lowest transitions can be directly assigned to the first heavy and light hole excitonic transitions (e_1hh_1-X and e_1lh_1-X , respectively), as they coincide with the prominent absorption features commonly observed in literature.^{10,41} These assignments were confirmed with double-potential quantum well calculations (Figure 1c), similarly as often applied to core-only,^{10,41} core-shell,⁴² or core-shell and core-crown colloidal nanoplatelets.⁴³ Here we neglect as a first order approximation nonparabolicity effects and coupling between different states. (See the Supporting Information for calculation details and all

parameters involved.) The calculated transition energies (shown in Figure 1 as dashed lines) nicely resemble the experimental data. The Zeeman splitting can be extracted according to ref 29 and is at $B = 1.6$ T in the range -1 ± 0.5 meV for the e_1hh_1 -X, thus comparable to the previously observed Zeeman splitting in shell-doped multilayer nanoplatelets with a similar architecture.³⁶ The ratio between the e_1hh_1 -X and the e_1lh_1 -X splitting was determined to be $\frac{\Delta E_{hh}}{\Delta E_{lh}} = -0.54 \pm 0.08$. On the basis of our calculations (compare Figure 1d), we assign the third resonance at 2.57 eV to the first spin-orbit split-off exciton (e_1so_1 -X) transition.

For various zinc blende bulk DMS materials, it is known that the hh excitonic transition splits according to

$$\Delta E_{hh} = x_{\text{eff}} \langle S_z \rangle (\gamma_{hh} N_0 \beta - \gamma_e N_0 \alpha) \quad (1)$$

with $N_0 \alpha$ and $N_0 \beta$ representing the electron and hole exchange coupling constants, x_{eff} the concentration of paramagnetic active Mn dopants, $\gamma_{e/hh}$ the wave function overlap between the charge carriers and the Mn ensemble, and $\langle S_z \rangle$ the Mn spin expectation value.^{26,27} Since the values of the exchange coupling constants usually have different signs ($N_0 \alpha = 0.22$ eV and $N_0 \beta = -1.8$ eV for Mn: CdS),²⁶ the giant Zeeman splitting of the e_1hh_1 -X is always negative and maximal in amplitude. This relation remains valid in quantum wells as long as both the quantization axis and the direction of the external magnetic field are parallel and point in the direction of light propagation.^{26,44} This is the case in our experiment with the majority of the nanoplatelets being oriented parallel to the substrate (as apparent from the inset of Figure 1). The expected sign of the Zeeman splitting is in accordance with our experiment exhibiting a negative splitting for the e_1hh_1 -X transition.

The e_1lh_1 -X and e_1so_1 -X transitions in zinc blende bulk DMS materials are known to split according to²⁷

$$\Delta E_{lh} = x_{\text{eff}} \langle S_z \rangle \left(\gamma_e N_0 \alpha + \gamma_{lh} \frac{N_0 \beta}{3} \right) \quad (2)$$

and

$$\Delta E_{so} = x_{\text{eff}} \langle S_z \rangle \left(\gamma_e N_0 \alpha - \gamma_{so} \frac{N_0 \beta}{3} \right) \quad (3)$$

As for the e_1so_1 -X the electron and hole contribution to the Zeeman splitting both have a positive sign, the e_1so_1 -X is expected to consistently exhibit an opposite sign as compared to the e_1hh_1 -X even in anisotropic systems.^{45,46} The positive splitting of the third transition (at around 2.57 eV) observed in our experiments thus represents a strong indication for the assignment as e_1so_1 -X. In the case of e_1lh_1 -X, both exchange components compensate each other in great part,^{26,27} leading to a small negative splitting in cubic bulk DMS,^{47–49} which can be inverted in sign in materials with anisotropic perturbations, e.g., a wurtzite lattice,^{45,50} strain,⁵¹ and quantization.³⁵ Hence, the observed positive splitting of the e_1lh_1 -X transition in the nanoplatelets might be due to the influence of the strong quantization combined with strain in the nominally zinc blende structured Mn: CdS shell. For excited state transitions, we accordingly expect any transition with positive splitting (i.e., a minimum followed by a maximum in MCD) to involve either an lh or a so hole state, while transitions involving an excited hh state should be characterized by a negative splitting.

As the MCD signal is highly sensitive to excitonic features,⁵² it reveals a bunch of distinct transitions above 2.6 eV. These features cannot be identified in the absorption spectrum, as it represents a superposition of excitonic transitions with inter-sub-band transitions of free electrons and holes and a scattering background. Thus, through the MCD signal, magnetic doping provides a unique path to resolve the upper excitonic transitions in the 2D quantum well. The whole MCD spectrum up to 3.1 eV can be reproduced with two additional higher excitonic transitions (compare Figure S2) at 2.68 and 2.93 eV, respectively, which can be related to excited hole states. As discussed in the Supporting Information, we hypothesize the former to be correlated with the e_1hh_3 -X, while the latter transition cannot be assigned definitely. Similar assignments (e_1hh_1 -X, e_1lh_1 -X and e_1hh_3 -X) have been drawn in epitaxial CdMnTe quantum wells.⁴⁴

The temperature dependence of the MCD signal gives additional evidence for the sp-d exchange interaction as the origin of the magneto-optical response. This allows distinguishing between sp-d exchange and intrinsic contributions to the magneto-optical response. In general, the MCD signal is composed of contributions from the sp-d exchange interaction and the intrinsic Zeeman splitting present in any semiconductor ($\text{MCD} = \text{MCD}_{\text{sp-d}} + \text{MCD}_{\text{int}}$). Since the MCD amplitude corresponding to the sp-d exchange interaction scales with the magnetization of the Mn sublattice given by the competition between the alignment along the external magnetic field and the disordering by the thermal energy, it declines with increasing temperature following a characteristic Brillouin function. Figure 2b,c depicts the decrease of the MCD amplitude with temperature for the band edge e_1hh_1 -X transition as well as for the e_1hh_3 -X transition. (Note that the sign of the amplitude is chosen in order to correspond to the sign of the Zeeman splitting.) Both data sets can be described with the same Brillouin function (and different amplitudes for the sp-d and the intrinsic contribution, details in the Supporting Information), which reinforces that the sp-d exchange interaction largely dominates the magneto-optical response for all transitions at low temperatures ($\left| \frac{\text{MCD}_{\text{int}}}{\text{MCD}} \right| < 17\%$ at 5 K for both transitions).

Interestingly, the signal of the transitions involving $n = 1$ hole states vanishes below the signal-to-noise ratio at about 100 K, while the signal of the transitions involving excited hole states persists up to room temperature (compare inset in Figure 2a). This difference is related to different signs of the intrinsic MCD contribution, being positive for the ground state transitions (where the hole is mainly located in the CdSe core), while it is negative for the excited hole states, where the hole wave function strongly extends into the Mn: CdS barrier. It is known that, in CdSe, the intrinsic splitting owns the opposite sign compared to the giant Zeeman splitting (i.e., has a positive g-factor with g_{int} between 1.0 and 1.4⁵³), while it has a negative sign in CdS ($g_{\text{int}} \approx -1.0$ to -1.3 , estimated from ref 54). In our structure, we expect contributions from both materials according to the wave function distribution between the core and the shell. As the observed ground and excited state transitions share the same e_1 electron state, the difference in the intrinsic g-factor between both excitonic transitions is related to the redistribution of the hole, which can be calculated to increase from a probability density of 0.24 in the shell for the hh_1 state to 0.93 for the hh_3 state.

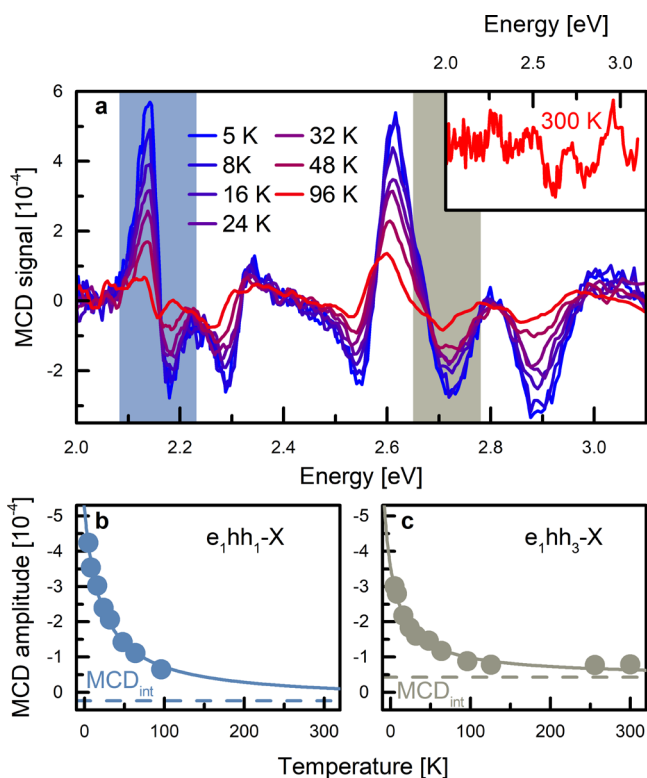


Figure 2. (a) Temperature dependence of the MCD spectra at 1.6 T between 5 and 96 K. The inset depicts the room temperature MCD signal. The spectral range of the e_1hh_1-X and the e_1hh_3-X transition are highlighted in blue and gray, respectively. Parts b and c illustrate the decay of the MCD amplitude with temperature for both transitions highlighted in part a. (For the e_1hh_1-X , the mean amplitude between the minimum and the maximum of the resonance is shown, while, in the case of the e_1hh_3-X transition, which overlaps with the e_1so_1-X feature on the low energy side, the amplitude of the minimum at 2.7 eV is taken.) Dots depict the data, while lines represent the Brillouin fits according to $MCD = MCD_{max} \cdot B_S(a) + MCD_{int}$. Herein, MCD_{max} denotes the maximum MCD amplitude in the case that all Mn^{2+} ions are aligned along the external magnetic field, $B_S(a)$ the Brillouin function with $S = 5/2$, and MCD_{int} the MCD amplitude according to the internal Zeeman effect. (See the Supporting Information for details.)

On the basis of the assignment of the different transitions, we demonstrate exchange coupling engineering by tuning the nanoplatelets architecture exploiting the synthetic degrees of freedom provided by *c*-ALD. In the first series, we concentrate on the manipulation of the hole exchange coupling by changing (i) the shell thickness from 8 to 6 ML and (ii) the core thickness from 2 to 3 ML (compare room temperature absorbance in Figure 3a). Figure 3b illustrates the effect of a decreased shell thickness, shifting the excited hole transitions to higher energies (energies above 2.6 eV in MCD spectra), while the ground hole states are neither affected in the energetic position nor in the MCD amplitude (energies below 2.5 eV in MCD spectra). These observations are reflected in our calculations, as depicted in Figure 3d. While the ground heavy hole state is not shifting at all, the excited states shift toward higher energies with decreasing shell thickness. Extracting the wave function overlap with the doped shell reveals a change of less than 15% for the hh_1 state with varying shell thickness, while the wave function overlap γ_{so} of the so_1 state significantly decreases with decreasing shell thickness.

This is summarized in Figure 3f and is in good agreement with our experimental findings (Figure 3b).

Modifying the core thickness, on the other hand, significantly influences the excitonic transitions involving the ground hole states (compare Figure 3c): While the transitions involving excited hole states slightly shift in energy but retain their magneto-optical activity, the MCD amplitude significantly decreases for the transitions involving $n = 1$ hole states as the core thickness is increased. Wave function calculations (compare Figure 3e) reveal that this is due to the decreasing hole wave function overlap with the doped shell, when increasing the undoped core thickness from 2 to 3 ML (e.g., γ_{hh} decreases by a factor of 2 from 0.24 to 0.12). The wave functions of the excited $n = 3$ hole state, widely delocalized over the whole nanoplatelets thickness, is not affected to the same degree (compare Figure 3g). Changes in the core thickness do only result in a minor variation of the MCD amplitude of excitonic transition involving excited hole states. Thus, we can tune the exchange coupling between magnetic dopants and ground or excited hole states by changing either the core or the shell thickness in these hetero-nanoplatelets.

To tune the electron exchange interactions of the e_1hh_1-X , we modified the architecture of the hetero-nanoplatelets by including an additional MnS interlayer between the core and the shell. The MnS band gap can be extrapolated from CdMnSe to be as high as 3.6 eV at cryogenic temperatures.⁵⁵ This interlayer is thus able to confine the heavy hole wave function in the core, avoiding any influence of the outer Mn:CdS shell thickness on the hh_1 wave function distribution, while the electron wave function can be tuned via the number of Mn:CdS monolayers. As the MnS layer is only a monolayer thick on each side and epitaxially grown onto the CdSe core, we expect it to have zinc blende structure. Bulk zinc blende β -MnS is a metastable salt, exhibiting antiferromagnetic ordering among the embedded Mn spins below the Neel temperature (approximately 100 K).⁵⁶ As shown in Figure 4a, the amplitude of the MCD signal decreases among different samples with the same dimension of the core and the interlayer (2 ML CdSe and 2 ML MnS, i.e., 1 ML on each side of the core) but increasing shell thickness. Wave function calculations (compare Figure 4b) reveal that, by increasing the Mn:CdS shell thickness between 6 and 10 ML, we can purposely change the electron wave function distribution, while the heavy hole ground state is not affected at all. The origin for the decreased amplitude of the MCD signal becomes clear upon calculating the wave function overlap of the electron and the heavy hole with the MnS interlayer on the one hand and with the Mn-doped CdS shell on the other hand (compare Figure 4c). This reveals that the heavy hole wave function overlap with the doped regions is not significantly affected by the shell thickness, indicating that the contribution of the p-d exchange interaction is virtually independent of the Mn:CdS shell thickness. On the other hand, the electron wave function extends more and more into the Mn:CdS shell with an increasing shell thickness, while its wave function overlap with the MnS interlayer decreases (see Figure 4c). The change in the magneto-optical activity with Mn:CdS shell thickness can thus be traced back to a modification of the s-d contribution. The decreasing amplitude of the magneto-optical response observed in experiment therefore suggests that the concentration of the magneto-optically active Mn ions is higher in the MnS interlayer compared to the Mn-doped CdS shell. This allows us to conclude that a large amount of Mn spins in the 1 ML thin MnS interlayer does behave

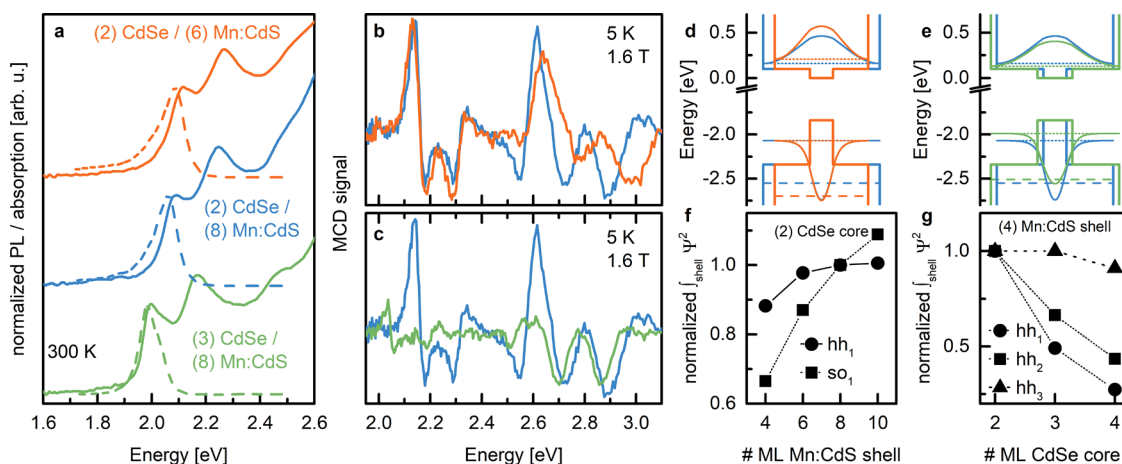


Figure 3. (a) Normalized room temperature PL (dashed lines) and absorption (solid lines) spectra of magnetically doped core-shell nanoplatelets with different core and shell thicknesses: (3) CdSe/(8) Mn:CdS nanoplatelets in green, (2) CdSe/(8) Mn:CdS nanoplatelets in blue, and (2) CdSe/(6) Mn:CdS nanoplatelets in light red, respectively. (b and c) MCD signals at 5 K and 1.6 T of samples with different numbers of ML in the shell ((b) 6 ML compared to 8 ML) and different core thicknesses ((c) 2 ML vs 3 ML). (d and e) Calculated energies of the lowest electron state e_1 in the conduction band (CB) and the hh_1 and hh_3 states in the valence band (VB), respectively. Narrow dotted lines represent the ground states ($n = 1$) and dashed lines the $n = 3$ states. Straight lines represent the probability density function of the electron and the heavy hole in the $n = 1$ state, respectively. Coloring in panels b–e is the same as in panel a. Panels f and g depict the integrated probability densities of selected hole wave functions in the doped shell for (f) different shell thicknesses surrounding a 2 ML CdSe core and (g) different core thicknesses with 8 ML Mn:CdS shell. All values are normalized with respect to the value in the (2) CdSe/(8) Mn:CdS sample.

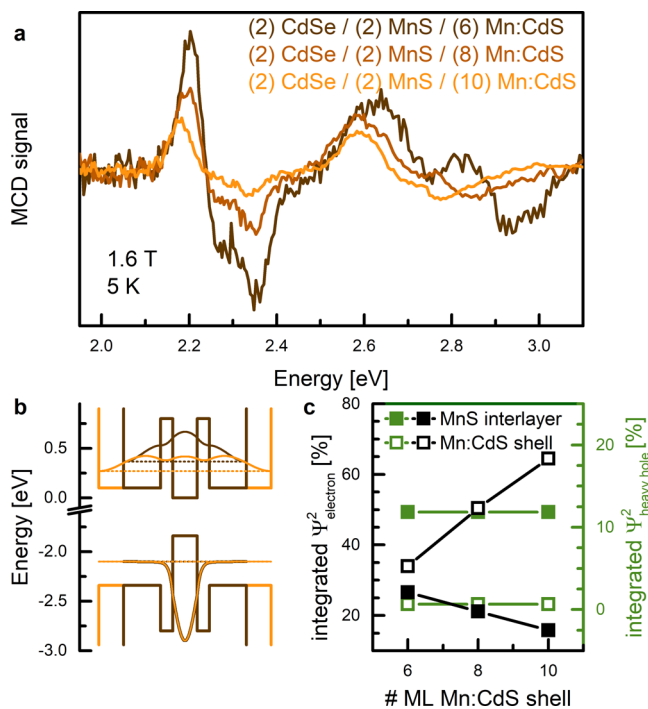


Figure 4. (a) MCD signal of nanoplatelets with a 2 ML CdSe core, 2 ML (one on each side) MnS interlayer, and 6–10 ML (3 to 5 ML on each side) Mn:CdS shell at 1.6 T and 5 K. (b) Energy states and probability density functions calculated for samples with a 2 ML CdSe core, 2 ML MnS interlayer, and 6 (dark brown) or 10 (orange) ML Mn:CdS shell, respectively. (c) Overlap of the electron and hole wave functions with the doped regions in the MnS interlayer and the Mn:CdS shell, respectively.

paramagnetically without dominant antiferromagnetic coupling. Similar tendencies of a decreased Neel temperature have been observed in nanoscaled MnS thin films.⁵⁷ By confining the heavy hole in the core with the MnS interlayers tuning of the

s – d electron exchange interaction by varying the thickness of the Mn:CdS shell is thus demonstrated for the e_1hh_1 -X.

In conclusion, we demonstrated sp – d exchange interactions between electron and hole band states and magnetic dopants in core-shell CdS/(MnS)/Mn:CdS hetero-nanoplatelets. The high sensitivity of MCD spectroscopy for excitonic transitions allowed us to investigate the electronic structure of excited states in core/shell hetero-nanoplatelets. We were able to assign a bunch of higher transitions, including the e_1so_1 -X exciton transition as well as exciton transitions involving the e_1 electron ground state and excited hole states. The electron or hole exchange interactions could be tuned separately by modifying the architecture of the hetero-nanoplatelets, namely, composition, core and shell thickness, and MnS interlayer. This precise tunability of the magnetic exchange interactions by controlling the geometry of the nanoplatelets with monolayer accuracy is novel among the whole family of colloidal DMS nanostructures. Our study not only proves the possibility to furnish chalcogenide nanoplatelets with tunable magneto-optical functionalities but furthermore provides new insights into the electronic structure of this auspicious material class.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.8b00060.

Sample synthesis, experimental section, data analysis, and theoretical section (PDF)

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Notes

The authors declare no competing financial interest.

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