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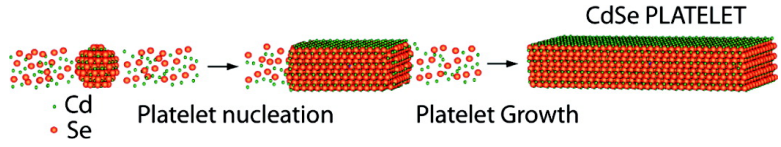

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Quasi 2D Colloidal CdSe Platelets with Thicknesses Controlled at the Atomic Level

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Well documented procedures to grow zero-dimensional systems,[1] dots, and one-dimensional systems,[2] wires and tubes, as colloidal particles in solution have been reported. In contrast, there are no methods of preparation that yield optically active two-dimensional soluble particles. Yet, ultrathin films (quantum wells) of II−VI and III−V semiconductors epitaxially grown on substrates by molecular beam epitaxy for example have proven extremely useful for both fundamental studies and a wealth of applications in optoelectronics.[3] The synthesis of 2D colloidal nanocrystals, nanoplatelets, or nanodisks is limited to a few examples[4] of metal and lanthanide oxide materials as well as CuS and NiS. We extend these studies to show that fluorescent quasi-2D CdSe platelets can be synthesized with different thicknesses quantified by one CdSe monolayer.

The nanoplatelet synthesis is based on the solution phase decomposition of cadmium myristate and selenium mesh precursors in the presence of a noncoordinating solvent and an acetate salt. In a typical experiment, 85 mg (0.15mmol) of cadmium myristate and 12 mg (0.15mmol) of Se mesh were mixed in 15 mL of octadecene in a three-neck flask and degassed under vacuum for 10 min. The mixture was then heated at 240 °C under argon. When the temperature reached 195 °C (the solution is orange), 40 mg (0.15mmol) of cadmium acetate dihydrate were swiftly introduced into the flask. After 10 min at 240 °C, the reaction was stopped by removal of the heating mantle. The particles synthesized were isolated by ethanol precipitation and suspended in hexane. Platelets were separated from polyhedral quantum dots by butanol precipitation and resuspended in hexane. TEM observations of the nanoparticles (Figure 1a) demonstrate the formation of CdSe platelets with lateral dimensions from 6 to 40 nm. The platelets have a zinc-blende crystal structure (see Supporting Information) which is consistent with the zinc-blende formation of CdSe polyhedra when the same syntheses are used without acetate salt.[5] The platelet thickness can be measured when they stack on their edge (Figure 1d and Supporting Information) and is found to be 2.2 ± 0.3 nm. Using TEM images, no difference in the platelet thicknesses could be observed. However, as can be seen on Figure 1b, when platelets lay flat on the TEM grid, different gray levels are distinguishable, suggesting the synthesis of platelets of different thicknesses. The platelet formation is induced by the presence of acetate salt in the reaction medium. All the acetate salts we have tested, including $Mn(Ac)_2 \cdot 4H_2O$; $Zn(Ac)_2$; $Mg(Ac)_2 \cdot 4H_2O$; $Co(Ac)_2 \cdot 4H_2O$, and Na(Ac), allow the formation of CdSe platelets, with somewhat different geometries. In all cases, despite the presence of other metallic ions, elementary analysis indicates that, after the washing step, the platelet shaped crystals contained only cadmium and selenium. When the acetate salt is introduced at the beginning of the synthesis, large CdSe quasi 2D films are obtained (Figure 1f). These films' lateral dimensions can reach the micron, and they can fold in rolls or in sheets. Most of them are not soluble in solvents. When the acetate salt is introduced after the formation of the CdSe crystal seeds, smaller CdSe platelets with a square or rectangular shape or more complex, faceted planes (Figure 1a−e) can be obtained. The shape, aspect ratio, and thickness of the platelets can be systematically controlled by varying the reaction time, the injection, growth temperature, and the ratios between the cadmium myristate, the acetate salt, and the selenium.

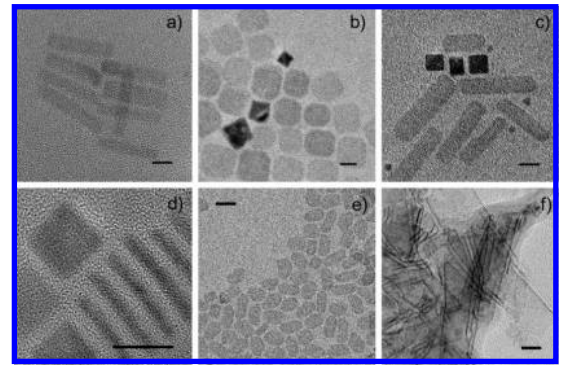

Figure 1. Transmission Electron Microscopy (TEM) images of CdSe colloidal platelet shaped nanocrystals synthesized with different methods. (a) Injection of cadmium acetate at 195 °C and heating at 240 °C for 10 min. (b and c) Same as in (a) with a second precursor injection at 240 °C and heating for 20 min. (d) High resolution TEM of (b). (e) Same as (a) using manganese acetate in place of cadmium acetate. (f) Cadmium acetate is injected at room temperature with the other precursors prior to heating. Scale bars: (a−d) 10 nm, (e, f) 20 nm.

We studied the optical properties of the CdSe platelets (Figure 2). All the CdSe platelet syntheses we have tested so far produce fluorescent populations that emit with maxima exactly at 462 ± 2, 512 ± 2, and 550 ± 2nm. The quantum yield of a platelet solution can reach 30%. Depending on the synthesis conditions, one population or the other can be obtained in large excess compared to the other, and size selective precipitation can be used to further isolate the subpopulations.[1] The emission spectra for each platelet population have full width half-maximums (fwhm) < 10 nm and the Stokes shift between the first exciton and the platelet emission is <10 meV, in contrast with the large Stokes shifts observed for quantum dots and quantum rods. The very narrow fwhm measured in spite of the large lateral platelet size variations observed in TEM images (Figure 1) implies that the platelet aspect ratio has only little influence on their emission wavelength. The major difference between the platelet populations seems to be their thickness.

Interestingly, both the emission and the photoluminescence excitation spectra of the platelets (Figure 2) can easily be interpreted using the model of infinite one-dimensional potential quantum wells. In this framework, the absorption coefficient has a step-like structure[3] with each step at the threshold energy for the n^{th} transition between the heavy hole and the electron (eq 1)

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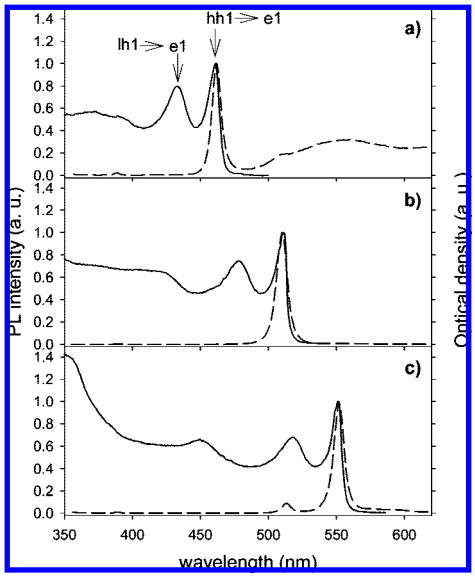

Figure 2. Room temperature emission (dash line) and photo luminescent excitation (solid line) spectra of different platelet syntheses. (a) Cadmium acetate injected at low temperature, (b) cadmium acetate injected at 195 °C. (c) Same as in (b) with one additional injection of precursors at 240 °C.

$$\hbar\omega_n = E_g + E_{hhn} + E_{en} = E_g + \hbar^2 n^2 \pi^2 2m^*_{hh} d^2 + \hbar^2 n^2 \pi^2 / 2m^*_e d^2 \quad (1)$$

and the luminescence spectrum consists of a peak of spectral width $\sim k_B T$ at energy $\hbar\omega = E_g + E_{hh1} + E_{e1}$, where E_g is the semiconductor bandgap, n is the number of the interband transition, m^*_{hh} and m^*_e are the heavy hole and electron effective masses, and d is the thickness of the quantum well.

For each PLE spectra in Figure 2, both the heavy-hole and the light-hole transitions for $n = 1$ are clearly visible (see Supporting Information). Using eq 1 with $n = 1$ with numerical values for zinc-blende CdSe $E_g = 1.67$ eV (ref 6a), $m^*_e = 0.11m_0$, and $m^*_{hh} = 1.14m_0$ (ref 6b), we compute the thickness of each platelet population and find $d = 1.93$, 2.24, and 2.55 nm. The thinner the platelet, the higher its emission energy. The same operation using the light-hole transition and an effective mass of $m^*_{hh} = 0.31m_0$ (ref 6b) gives a thickness of $d = 1.97$, 2.25, and 2.54 nm. The good agreement between the two sets of values confirms the attribution of the light-hole and heavy-hole transition. The thickness difference between the three populations is 0.31 ± 0.01 nm, almost exactly half the lattice parameter of zinc-blende CdSe crystals ($a = 0.608$ nm). This suggests that the CdSe platelets we synthesize have thicknesses quantified by one CdSe monolayer. The small Stokes shift observed for each platelet population is characteristic of quantum wells with precisely controlled thicknesses[7] and suggests that within a platelet population the thickness is indeed precisely controlled.

A synthesis using cadmium acetate reported recently[8] produces particles with emission maxima at 395, 463, and 513 nm with similar emission and absorption spectra as the ones we measured. In contrast with what we observe, the authors interpret their data as the synthesis of magic sized CdSe nanocrystals. Interestingly, the 395 nm population they obtained can be also interpreted as CdSe platelets with a 1.62 nm thickness, which is exactly one CdSe monolayer less than the 462 nm emitting polulation.

Single platelet fluorescence emission is easily visualized using a fluorescent microscope and a mercury lamp as the excitation source. To the eye, they appear as extremely bright sources of light with strong blinking and low resistance to photobleaching, as in the case of CdSe quantum dots.

Colloidal platelets with thickness tuneable at the atomic level and controlled lateral dimensions should be useful to test the predictions made for 2D quantum boxes.[9] For example, the oscillator strength of platelets is predicted to increase strongly as the lateral confinement of the exciton increases. This enhanced oscillator strength gives rise to interesting nonlinear properties[10] and could be applied with these colloidal platelets to make effective nonlinear optical device. The growth of multiple quantum wells lead to the development of several applications including quantum cascade lasers.[11] We expect that stacking of platelets could lead to similar devices, especially if core/shell platelets can be synthesized and electrically coupled.

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Supporting Information Available: Further optical and structural characterization of the CdSe platelets. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706–8715.
(2) (a) Duan, X. F.; Lieber, C. M. *Adv. Mater.* **2000**, *12*, 298–302. (b) Peng, X. G.; Manna, L.; Yang, W. D.; Wickham, J.; Scher, E.; Kadavanich, A.; Alivisatos, A. P. *Nature* **2000**, *404*, 59–61.
(3) Weisbuch, C.; Vinter, B. *Quantum Semiconductor Structures: Fundamentals and Applications*; Academic Press: 1991.
(4) (a) Puntes, V. F.; Zanchet, D.; Erdonmez, C. K.; Alivisatos, A. P. *J. Am. Chem. Soc.* **2002**, *124*, 12874–12880. (b) Xu, R.; Xie, T.; Zhao, Y. G.; Li, Y. D. *Crys. Growth Des.* **2007**, *7*, 1904–1911. (c) Si, R.; Zhang, Y. W.; You, L. P.; Yan, C. H. *Angew. Chem., Int. Ed.* **2005**, *44*, 3256–3260. (d) Sigman, M. B.; Ghezelbash, A.; Hanrath, T.; Saunders, A. E.; Lee, F.; Korgel, B. A. *J. Am. Chem. Soc.* **2003**, *125*, 16050–16057. (e) Ghezelbash, A.; Sigman, M. B.; Korgel, B. A. *Nano Lett.* **2004**, *4*, 537–542.
(5) Yang, Y. A.; Wu, H. M.; Williams, K. R.; Cao, Y. C. *Angew. Chem., Int. Ed.* **2005**, *44*, 6712–6715.
(6) (a) Kim, Y. D.; Klein, M. V.; Ren, S. F.; Chang, Y. C.; Luo, H.; Samarth, N.; Furdyna, J. K. *Phys. Rev. B* **1994**, *49*, 7262–7270. (b) Norris, D. J.; Bawendi, M. G. *Phys. Rev. B* **1996**, *53*, 16338–16346.
(7) Bastard, G.; Delalande, C.; Meynadier, M. H.; Frijlink, P. M.; Voos, M. *Phys. Rev. B* **1984**, *29*, 7042–7044.
(8) Ouyang, J.; Zaman, M. B.; Yan, F. J.; Johnston, D.; Li, G.; Wu, X.; Leek, D.; Ratcliffe, C. I.; Ripmeester, J. A.; Yu, K. *J. Phys. Chem C* **2008**, *112*, 13805–13811.
(9) Bryant, G. W. *Phys. Rev. B* **1988**, *37*, 8763–8772.
(10) Chemla, D. S.; Miller, D. A. B. *J. Opt. Soc. Am. B* **1985**, *2*, 1155–1173.
(11) Faist, J.; Capasso, F.; Sivco, D. L.; Sirtori, C.; Hutchinson, A. L.; Cho, A. Y. *Science* **1994**, *264*, 553–556.

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