Polymerization

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CdSe Nanoplatelets: Living Polymers

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Abstract: *Colloidal CdSe nanoplatelets are considered to be excellent candidates for many applications in nanotechnology. One of the current challenges is to self-assemble these colloidal quantum wells into large ordered structures to control their collective optical properties. We describe a simple and robust procedure to achieve controlled face-to-face self-assembly of CdSe nanoplatelets into micron-long polymer-like threads made of up to ~1000 particles. These structures are formed by addition of oleic acid to a stable colloidal dispersion of platelets, followed by slow drying and re-dispersion. We could control the average length of the CdSe nanoplatelet threads by varying the amount of added oleic acid. These 1-dimensional structures are flexible and feature a "living polymer" character because threads of a given length can be further grown through the addition of supplementary nanoplatelets at their reactive ends.*

The organization of colloidal assemblies of nanocrystals (NC) over large areas and volumes is of great interest in nanotechnology because it is required for elaborating artificial solids and functional devices.[1–3] NC superlattices have been proposed for a wide range of optoelectronics, thermoelectric and chemical sensing applications.[4–7] In the field of semiconducting NC, nanoplatelets (NPL), also called "colloidal quantum wells", have recently received much attention owing to their outstanding optical properties such as tunable, very sharp emission wavelengths, carrier recombination faster than that of quantum dots and rods, and low-threshold lasing properties.[8,9] These features make NPL ideal candidates for diverse applications ranging from optoelectronics[10,11] to gas sensing.[12] Various examples of NPL assembly have been reported in the literature.[7,13,14] In the case of CdSe NPL, we have reported their self-assembly into long anisotropic needles, but control over the lateral dimensions and the size of the self-assembled structures remains poor.[15] This aspect is important in the perspective of exploiting the optical properties of NPL, such as ultra-fast FRET, where accurate relative nanoparticle positioning is required.[16,17] Furthermore, stacking of CdSe nanoplatelets can significantly affect their optical emission properties.[15,18–20] Thus, better control of the spatial organization of colloidal NPLs is of crucial importance for their future studies both from applicative and fundamental standpoints.

Examples of spontaneous assembly of metallic colloidal particles in one-dimensional (1D) polymer-like structures have been reported recently.[21–23] The most common geometry is (possibly branched) chains that are called "plasmonic polymers" because they give rise to a shift in the plasmon resonance of the nanocrystals.[21,24] The spontaneous assembly of particles into chains has been achieved by chemical crosslinking, physical attraction between ligands, or oriented attachment of nanocrystals.[25–28] The aggregation number of these polymeric assemblies is usually between 5 and 20. However, there are no reports to date of polymeric 1D assembly for colloidal quantum wells.

Herein, we demonstrate a simple strategy to induce the self-assembly of CdSe NPL into micron-long threads by adding small amounts of oleic acid (OA) to a NPL dispersion, followed by slow drying. The concentration of added OA is a critical factor that controls the assembly and the length of the threads. Furthermore, the threads can be used as seeds for further growth, such as in living polymers where monomers can be added to the reactive ends of an already polymerized chain.

4-Monolayer (4ML) CdSe NPLs were synthesized by slightly modifying a previously reported synthesis[15] (see the experimental section for details). An excess of OA was used at the end of the synthesis so that all of the faces of the NPL were fully covered by ligands. After thorough purification through repeated precipitation/redispersion cycles, the NPL were dispersed in hexane. The absorption and emission spectra (Figure 1 a) show that only one 4ML population was found in solution. Transmission electron microscopy (TEM)

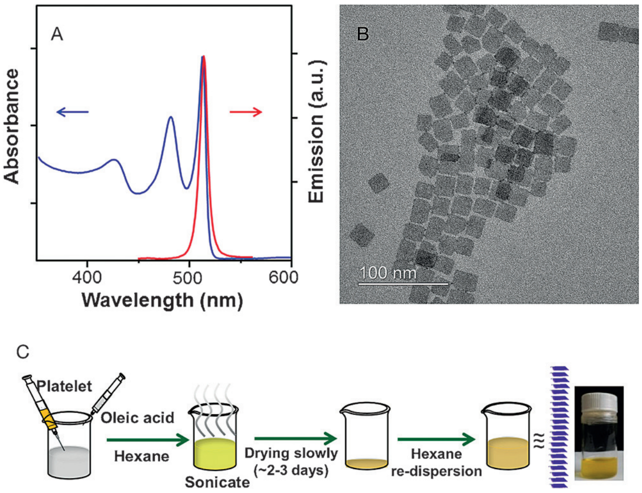

Figure 1. A) Absorbance and emission spectra of 4ML nanoplatelets. B) TEM image of the NPLs used for the self-assembly. C) Procedure for preparing self-assembled threads of CdSe platelets.

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images (Figures 1 b and S1) of the platelets showed that the 4ML NPL are square with ~18 nm edges.

CdSe NPL self-assembly was achieved through a two-step process (Figure 1 c). First, a small quantity of OA was added to the NPL dispersion in hexane. Because we identified the OA concentration as a critical parameter (see below), we confirmed by IR spectroscopy that no free OA was present in solution prior to this addition and that all the OA was bound to the surface of the NPL (Figure S2). Afterwards, the dispersion was slowly dried. The complete drying of the solvent took between 2 and 3 days, after which a yellow deposit was visible at the bottom of the vial and could easily be re-dispersed through gentle stirring. A slightly turbid dispersion was then obtained (Figure 1 c, right), indicating the presence of large objects scattering light in solution. TEM observation of these dispersions revealed the presence of self-assembled threads (Figure 2 a–c) whose length reached up to several micrometers while they were composed of a single platelet along their transverse dimensions (Figure 2 c). Therefore, the NPL are only stacked face-to-face and no edge-to-edge stacking was observed. This contrasts with our previous report[15] where both types of stacking were observed simultaneously.

The small-angle X-ray scattering (SAXS) pattern of the dispersion (Figure 2 e) displays several features consistent with the threaded structure observed by TEM. An intense peak at a scattering vector $q^* = 1.23\ \text{nm}^{-1}$ arises from the stacking of the platelets with a period $d = 2\pi/q^* = 5.1$ nm within the CdSe threads. Because the platelet thickness is 1.2 nm, the faces of neighboring platelets are 3.9 nm apart. This separation is due to partially interdigitated OA molecules bound to the faces of the NPL, as already reported.[18] Interestingly, the fluorescence of CdSe NPL is not quenched by their self-assembly, and the threads on a glass substrate are easily detected by fluorescence microscopy (Figure 2 d). Although the lateral spatial resolution of the confocal microscope is of the order of 200 nm, we can clearly see the elongated character of the threads using this technique. Another interesting feature, shown by both the electron and fluorescence microscopies, is the absence of individual NPLs in solution besides the threads. All of the platelets take part in the self-assembly process and none are present as monomers in solution.

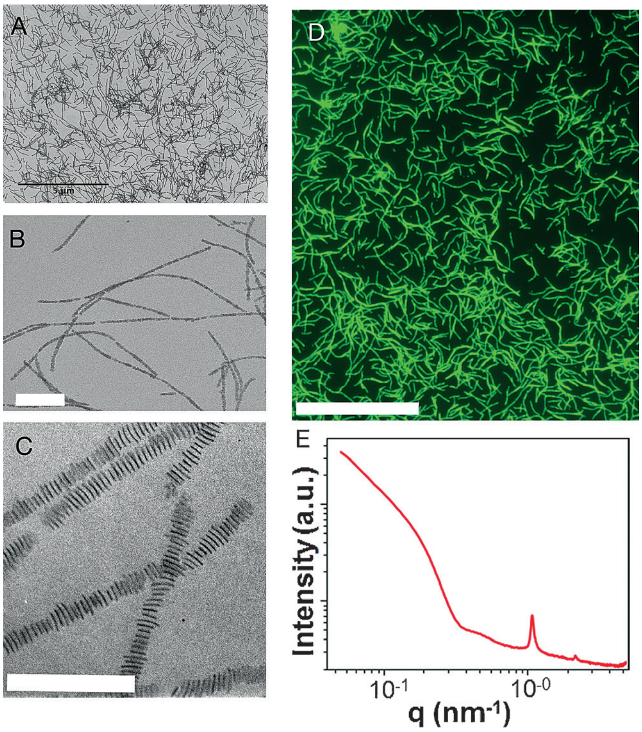

Figure 2. A and B) lower and higher magnification TEM images of threads of 4 ML square platelets. C) High-resolution TEM image of the threads showing the face-to-face stacking of CdSe platelets. D) Fluorescence microscopy images of the threads deposited from solution on a cover slip. E) Small angle X-ray scattering curve of the thread dispersion. Scale bars: 5 µm (A), 200 nm (B), 20 nm (C), 20 µm (D).

Owing to their large aspect ratio, these threads are not completely straight and appear somewhat flexible. Furthermore, in solution, we observed by fluorescence microscopy that the threads occasionally break and reform (Supporting Information, Figure S3 and movie). The threads therefore share this similarity with giant worm-like micelles observed in some surfactant[29] or block copolymer[30] solutions. One noticeable difference is that, in the case of surfactant micelles, monomers (that is, single surfactant molecules) are continuously exchanged between the solution and the aggregates, whereas here, relatively large parts of the threads detach and re-attach dynamically. This is visible in Figure S3 where a thread fragment ~250 nm long (and thus made of ~50 NP) separates from a large thread and then re-merges with it after drifting in solution for a few seconds. This however could be due to flows within the sample cell because the NPL threads are large objects formed by non-covalent self-assembly and they could therefore be very much affected by hydrodynamic stresses.

By tuning the amount of added OA, it is possible to control precisely the mean thread length (Figure 3). Without any further addition of OA, single platelets and very short platelet stacks are found in suspension. For an OA concentration of 6 mM, the CdSe NPL stack and form small threads of length 100–200 nm. The length of the threads further increases up to a mean length of 1.4 µm for [OA] = 48 mM (Figure 3). This size increase is also clearly observed by fluorescence confocal microscopy although the threads of smallest size only appear as small bright spots since they are smaller than the lateral resolution of the microscope (Figure 3 a–d). It should be noted that, for all values of OA concentrations, the polydispersity index remained low (PDI = 1.05 ± 0.03). After reaching a maximum for an OA concentration of 48 mM, further ligand addition resulted in the precipitation of the colloid. Whatever their length, the width of the CdSe threads always remained equal to the edge length of the platelets.

We now turn to the mechanism by which self-assembly occurs and we try to propose a physical explanation for the influence of OA concentration on the thread length. We consider the simple case of 1-dimensional self-assembly of NPL in threads under the influence of pairwise attractive interactions between platelets at contact and facing each other. There are two types of attractive potentials whose

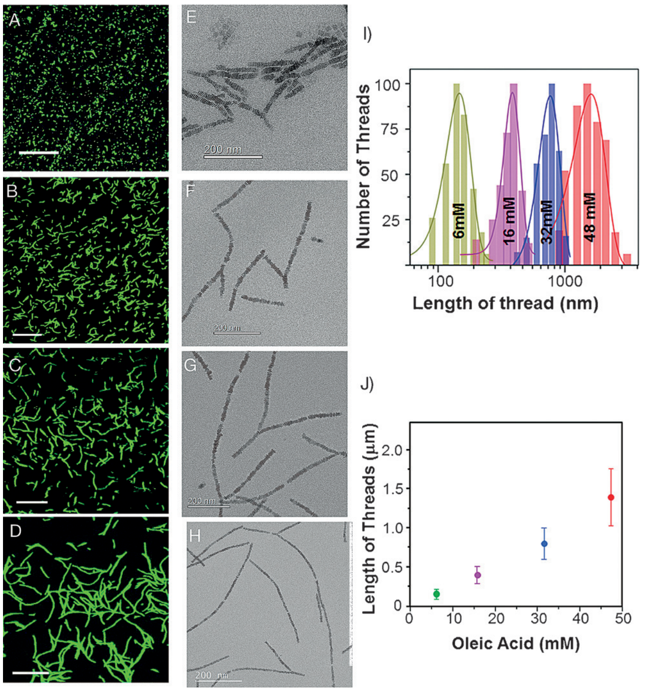

Figure 3. Evolution of threads of square CdSe platelets using different concentrations of added OA. A–D) Confocal fluorescence microscopy images of the threads obtained with different concentrations of OA, 6 mM, 16 mM, 32 mM, and 48 mM, respectively. Scale bars: 5 µm. E–H) Corresponding TEM images of CdSe threads. Scale bars: 200 nm. I) Length polydispersity distributions of CdSe NPLs threads for different concentrations of added OA. J) Dependence of the thread average length on the concentration of OA added to the platelet solution in hexane.

intensities can be larger than kT (where k is the Boltzmann constant and T is the temperature): van der Waals and depletion. Van der Waals attractions are always present and destabilize colloidal suspensions of platelets on a time scale ranging from minutes to days, depending on NPL concentration,[31] but this weak ($\sim 2\,kT$) interaction does not explain the dependence of thread length on OA concentration. On the other hand, the depletion interaction exerted by free oleic acid molecules on the NPL is a much better candidate in this respect. Even though the size of OA molecules is small (~2 nm), their concentration can reach high enough values to induce a strong attractive potential on the NPL, of the order of 10 kT at the beginning of the drying process. Moreover, the intensity of these attractions depends linearly on the OA concentration,[32] which explains the thread length increase with increasing OA concentration.

In the field of macromolecular synthesis, reactive macromolecules that can grow when supplementary monomers are added in solution can be produced either by the mechanism of "step-growth" polymerization or by that of "living" polymerization. Living polymerization differs from self-growth by the control of the degree of polymerization, with a low polydispersity index, by a linear dependence of the average molecular weight on monomer conversion, and by the fact that further monomer addition only results in chain propagation, with no formation of new polymer chains.[33–37] Because the chain ends are reactive, new monomers attach to existing chains and the mean chain length (polymerization degree) increases while the number of macromolecules remains constant. To investigate whether the CdSe NPL threads feature this property, we prepared small (~300 nm) threads, re-dispersed them in a solution of free platelets, and slowly evaporated the solvent (see the Supporting Information for experimental details). If the new NPLs only attach to the existing threads and do not form new threads, then the contour length will increase by an amount proportional to n_{NPL}/N, where n_{NPL} is the concentration of NPL added and N is the initial number of threads in solution. Thus, if we plot the contour length (propotional to the number of NPL in a thread) as a function of the quantity of added NPLs, then we should obtain a straight line. This is actually what is observed (Figure 4); the threads grew to a predictable extent based on the amount of added NPL. Interestingly, free NPL attach to both ends of the existing threads and do not form new chains. Finally, because one of the most interesting applications of living polymerization is the synthesis of block-copolymers, we tried to synthesize ABA-type triblock copolymers through the addition of 5ML NPLs to already formed 4ML threads. Taking advantage of the different emission wavelengths between the NPLs of different thicknesses, we could localize 4ML and 5ML independently using the confocal microscope. Figure S4 shows that 4 and 5ML NPLs are colocalized on the same threads and that 5ML, added after the formation of 4ML threads, are more likely situated at the extremities of the threads. Together with the low polydispersity index and the re-growth of 4ML threads, this is aditional evidence for a living polymerization mechanism in this system.

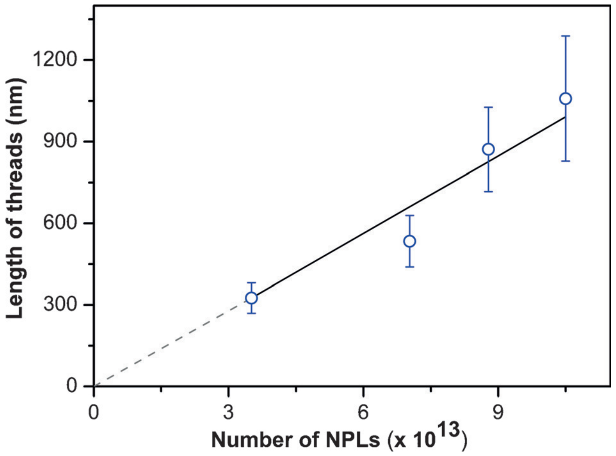

Figure 4. Mean length of threads as a function of added NPL number for re-growth of initial threads.

In conclusion, we have developed a simple method to self-assemble CdSe nanoplatelets into long flexible threads through slow evaporation of colloidal solutions. These threads are composed of hundreds to thousands of individual platelets. We can control the average number of platelets per thread with the concentration of added OA or through subsequent re-growth of existing threads. We expect this control over their self-assembly to yield interesting developments in the study of emerging properties in ensembles of

NPL. In principle, the simple procedure described here could also be potentially generalized to other systems of 2-dimensional colloidal nanocrystals.

Experimental Section

Cadmium acetate dihydrate ($Cd(OAc)_2{\cdot}2H_2O$), myristic acid, technical grade 1-octadecene (ODE), oleic acid (OA), and selenium in powder were purchased from Sigma–Aldrich. Ethanol and hexane were purchased from SDS Carlo–Erba. The preparation of cadmium myristate was performed as reported in the literature.

Synthesis and purification of nanoplatelets: For a typical synthesis, 340 mg of cadmium myristate, 27 mg of selenium powder, and 25 mL of octadecene were introduced into a three-neck round-bottom 50 mL flask, equipped with a septum, a temperature controller, and a condenser, and were kept under vacuum for 30 minutes. Afterwards, the flask was purged with argon and the temperature was set to 230 °C. At 180–190 °C, the selenium started to dissolve and the solution turned clear yellow. When the temperature reached 205 °C, the septum was withdrawn and 160 mg of cadmium acetate was swiftly added into the flask. After the temperature reached 240 °C, the reaction continued for 12–15 minutes, 1 mL of oleic acid was injected at the end and the flask was immediately cooled down to room temperature. At this stage, the reaction product was a mixture of 3 ML NPL, 4ML NPL, and quantum dots in solution. The 4ML NPL were collected using size-selective precipitation by addition of ethanol and redispersion in hexane. This washing procedure was repeated 3 times and the yellow-colored platelets were dispersed in hexane to prepare a stock solution for further self-assembly.

Self-assembly of nanoplatelets: 1 mL of the NPL stock solution ($4\,mg\,mL^{-1}$), the required amount of oleic acid (for example, $15\,\mu l\,mL^{-1}$ for long threads) and 4 mL of hexane were mixed together in a 15 mL vial and sonicated for 30 min at room temperature to obtain a transparent solution. Then, the vial was kept with cap slightly open at room temperature to slowly evaporate hexane. Complete evaporation of hexane took about three days. After complete evaporation, the deposit was re-dispersed in 3 mL of hexane by shaking. The solution looked slightly turbid and remained stable upon further dilution with hexane.

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