Microfluidic routes to the controlled production of nanoparticles†

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A microfluidic procedure for the controlled production of cadmium sulfide nanoparticles is described

Nanocrystalline semiconductors are of considerable scientific and commercial interest owing to their tuneable optical and electronic properties, and potential applications in a wide range of electronic devices.[1] Physical characteristics of nanocrystallites are determined primarily by spatial confinement effects with properties such as the optical band gap often differing considerably from the bulk semiconductor. As these properties are ultimately determined by the physical size and shape of the crystallites, there is considerable interest in processing routes that yield nanoparticles of well-defined size.[2]

To date, techniques for producing highly monodisperse nanoparticles have been relatively complex and of a *post-hoc* nature[3–5] (A good review article by Trindade *et al* describes various approaches to synthesis of nanocrystalline semiconductors[6]). They are commonly produced in two stages: a poly-disperse sample is first obtained using standard synthetic routes, and nanoparticles of a given particle size are then isolated by means of repeated recrystallisations. This approach, whilst appropriate for small-scale production of nanoparticles, may not be ideally suited to large-scale production owing to the low product yield and the time consuming nature of the recrystallisation process.[3] At the time of writing there have been few—if any—*direct* (single-stage) approaches to the fabrication of monodisperse nanocrystallites. Fischer and Giersig[7] have previously used a fast flow (~ 1 ml min^{−1}) mixing chamber in conjunction with a chromatographic column to produce ultrasmall CdS nanoparticles. In this paper, we take an established synthetic procedure for cadmium sulfide nanoparticles and demonstrate how adaptation to a continuous flow microfluidic format leads to an immediate reduction in polydispersity. The procedure may offer an effective approach to synthesising nanoparticles *directly* and without recourse to subsequent recrystallisations.

Following Lakowicz *et al.*, nanoparticles of cadmium sulfide were obtained by mixing aqueous solutions of cadmium nitrate and sodium sulfide.[8] In conventional approaches to nanoparticle synthesis, the reactions are carried out in static macroscopic reaction vessels. Any variations in physical conditions across the reaction chamber (*e.g.* concentration or temperature gradients) are liable to influence the nature of the chemical product and in particular are likely to affect the size of the crystallites. In order to improve polydispersity, it is therefore necessary to eliminate local variations in reaction conditions, which is not trivial in a bulk reactor. Miniaturisation on the other hand affords a direct means of eliminating these local variations as the entire reaction volume can be held at a constant (uniform) temperature with near-absolute chemical homogeneity pertaining throughout.[9]

For bulk production of chemicals, the miniature reaction vessel must be used in a continuous flow format with the product being continuously extracted and the reactants con-

tinuously replenished. In order to preserve chemical homogeneity, it is essential that the entrant reagents should mix rapidly (faster than the time-scale of the reaction). Owing to the absence of turbulence in microengineered structures efficient mixing is a non-trivial process.[10] Mixing in microstructures is mediated almost exclusively by molecular diffusion and can be relatively slow. This leads to departures from chemical homogeneity and in the present context increases the polydispersity of the nanoparticles produced. To overcome this problem, a fast micromixer must be used (see ESI†). Specifically, we use the continuous flow micromixer developed by Bessoth *et al.*, which has been described in detail elsewhere.[11] In short, two inlet flows (containing either sodium sulfide or cadmium nitrate) are split into a series of separate multichannel streams (16 partial flows) before bringing them into final contact; as the diffusion time is proportional to the diffusion distance, splitting each reagent stream into *n* substreams of similar width decreases mixing times by a factor n^2. After mixing, the channels are sequentially combined in a reverse network until all partial flows are united in one outlet channel. The entire mixing volume for the micromixer is less than 600 nl.

An additional cause of polydispersity is coalescence of the newly formed nanoparticles to form larger crystallites. This may be discouraged to some extent by stabilising the nanoparticles with another semiconductor or chemical species.[12] However it is nevertheless important to extract the nanoparticles from the reaction volume as quickly as possible. It is therefore to be expected that varying the flow rate of the reagents through the micromixer will have a considerable influence on the size distribution of the nanoparticles.

To summarise the overall experimental procedure: CdS nanoparticles were obtained by directly mixing 4×10^{-4} M aqueous solutions of $Cd(NO_3)_2 \cdot 4H_2O$ and Na_2S. To aid stabilisation of the resulting nanoparticles, an equal quantity of sodium polyphosphate was added to the cadmium nitrate solution prior to mixing. A syringe pump was used to deliver the reagents into the microfluidic channel network at various flow rates (10–300 µL min^{−1}). The outlet flow from the mixer chip was coupled to a quartz flow cell (10 mm path length) and absorption spectra were obtained using a Perkin-Elmer, Lambda 15 UV–Vis spectrometer.

The inset of Fig. 1 shows an absorption spectrum for CdS nanoparticles obtained by mixing bulk (750 µL) solutions of Na_2S and $Cd(NO_3)_2 \cdot 4H_2O$. The shallow profile of the absorbance—which shows a gradual increase from 2.4 to 3.6 eV rather than a sharp onset at a specific energy—indicates that a broad range of crystallite sizes are present in the sample. A simplistic application of Brus' Equation would suggest that the nanoparticles range in size from roughly 12 nm ($\equiv$2.4 eV) to roughly 3.2 nm ($\equiv$3.6 eV); however we stress the highly approximate nature of this calculation. (In passing we note that, as with all the data reported here, no attempt was made to optimise the synthesis procedure. Reaction concentrations of 4×10^{-4} M were taken directly from the literature,[8] and it is likely that systematic variation of reaction conditions might yield nanoparticles of lower polydispersity.)

Fig. 1 shows, for a variety of flow rates, absorption spectra of fluid streams exiting the micromixer chip after mixing of the

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† Electronic supplementary information ESI available: image of the central portion of the micromixer chip. See http://www.rsc.org/suppdata/cc/b2/b202998g/
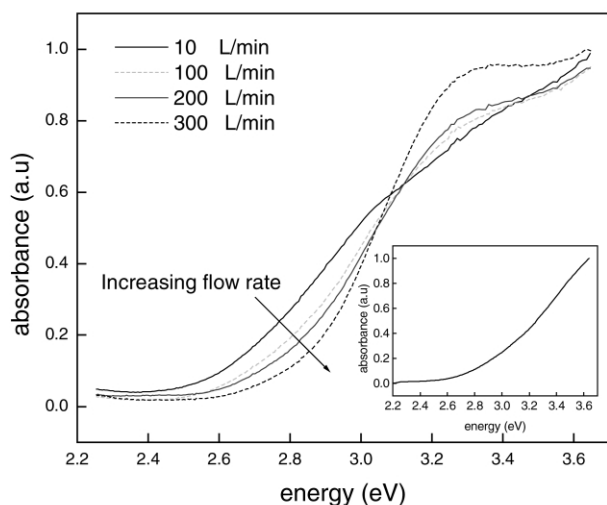
Fig. 1 Absorption spectra of fluid streams exiting the micromixer chip subsequent to mixing of cadmium nitrate and sodium sulfide solutions as a function of volumetric flow rate. Inset: absorption spectrum of nanoparticles produced by mixing bulk solutions.

Fig. 2 Theoretical absorption spectra for samples of nanoparticles obtained by convolving an arbitrary single-particle absorption spectrum (inset right) with three crystallite distributions of similar shape but different second moments (inset left). E_g is defined as the energy at which the absorbance = $\frac{1}{2}$.

cadmium nitrate and sodium sulfide solutions; the reagent concentrations were 4×10^{-4} M in all cases. Two important features are evident: first, the slopes of all absorption profiles in Fig. 1 are steeper than in the inset; and, secondly, there is a progressive steepening of the absorption profile as the volumetric flow rate is increased from 10 to 300 μL min^{-1}. The first observation indicates that the process of miniaturising the reaction volume is sufficient to lower the polydispersity of the crystallites. The second observation illustrates that increasing volumetric flow rates leads to further improvements in crystallite monodispersity. Both observations are consistent with the discussion above: miniaturisation improves homogeneity across the reaction volume; and increasing the flow rate lessens the likelihood of nanoparticle coalescence.

An interesting feature of the data presented in Fig. 1 is the existence of an approximate isosbestic point at 3.12 eV. This (and the variation in absorption profiles) may again be rationalized in terms of the polydispersity of the nanoparticles. If $N(E)$ represents the relative occurrence of particles with bandgap E and $A(E,E_G)$ represents the absorption spectrum of monodisperse particles of bandgap E_G, the average absorption spectrum of the population $\langle A(E) \rangle$ may be approximated as $\langle A(E) \rangle = A(E,E_G) \otimes N(E)$ where $\otimes$ denotes a convolution. (Here we have assumed that the absorption spectra of the variously sized nanoparticles are essentially identical in form, differing only in the location of the band edge.) In principle, if $A(E,E_G)$ is known, the underlying size distribution $N(E)$ may be inferred using deconvolution. In practice though this is seldom possible owing to noise in the input data and hence we make no attempt to extract size distributions here. We note however that the various absorption spectra will yield an isosbestic point only in special circumstances: underlying population distributions must be of similar form—with the same modal energy gap and skewness—but different variances. This is illustrated in Fig. 2 where we have taken an arbitrary non-symmetric absorption profile and performed convolutions with a series of skewed distributions with different second moments but identical first, third and fourth moments. The spectra are all seen to pass through a common point with the steepest absorption profile corresponding to the narrowest size distribution. The exact location of the isosbestic point is close to the modal energy gap of the particle distribution. Importantly, an isosbestic point is
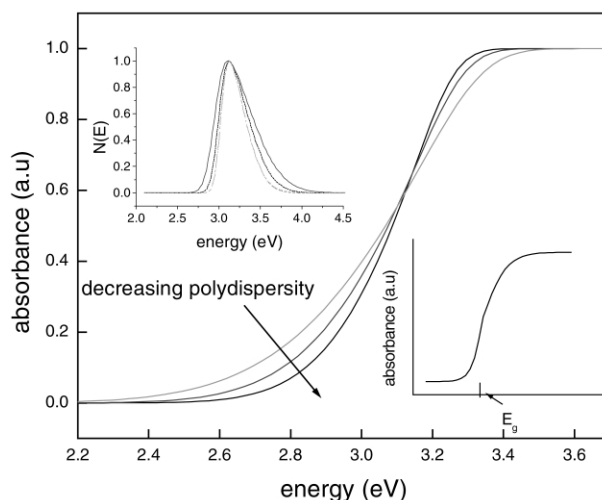
not obtained if the distributions have different third moments (skewness).

Relating this observation to the experimental data, it is apparent that varying the flow rate provides a means of improving monodispersity (reducing the second moment of the size distribution) without affecting the modal energy gap or altering the symmetry of the size distribution.

In conclusion, it can be seen that the use of microfluidic synthesis procedures offers distinct advantages over bulk scale fabrication procedures. The small size of the microreactor ensures that thermal and chemical homogeneity pertain throughout the entire reaction volume, leading to well controlled reaction conditions. Moreover, performing the reaction in a continuous flow format discourages coalescence of the newly formed nanoparticles. It should be noted that no effort has been made to optimise the microreactor in the current application. It is expected that refinements will lead to further improvements in resultant size distributions.

Notes and references

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