

Nanorod shape separation using surfactant assisted self-assembly†

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High quality single size nanorods can be separated from polydisperse samples using surfactant-assisted nanorod self-assembly.

Good quality single shape nanomaterials are essential in larger quantities to study their shape dependent physical and chemical properties.^{1–3} Nanoparticle shape control methods use either nanoporous templates⁴ or manipulate the growth conditions of traditional colloid chemical methods, in order to achieve anisotropic growth.^{5–11} The colloid chemical methods are relatively simple and do not use any nanoporous template, offering the possibility of large scale synthesis. However, the methods presently available often produce mixtures of different sizes and shapes. Recently, we have reported a seeding growth method for silver and gold nanorods with controllable aspect ratio.¹¹ One difficulty of this method is the formation of spherical nanoparticles as side products and for long nanorod synthetic conditions some percentage of short rods and platelets also forms. Depending on the experimental conditions the percentage of spheres, short rods and platelets varies from 30 to 90%. Nanorods can be partially separated from small size spheres by centrifuging but this separation method was not successful for similar size rods, spheres and platelets. Size selective precipitation and extraction methods, commonly used to separate mixtures of different size nanospheres^{12,13} (in the size range 1–10 nm), do not work for nanorod shape separation because of the larger size regime. Nanoporous filter based shape separation also failed as the short axis of nanorods and spheres have the same diameter. Wang *et al.* used size exclusion chromatography to separate rods from spheres but only a partial separation was possible.¹⁴

We developed a relatively simple and efficient method for the isolation of single size rods from a mixture of different size rods, spheres and plates. Surfactant assisted ordering of nanorods in a concentrated dispersion was exploited for the shape separation. In a concentrated dispersion of a mixture of different size rods, spheres and platelets when surfactant (cetyltrimethylammonium bromide, CTAB) was added, we observed that nanorods and platelets precipitate from the mixture leaving the spheres in solution. (Fig. 1 and 2) Under similar experimental conditions the long rods precipitate more easily than short rods, followed by platelets. Experimental conditions can be tuned for the step-by-step separation of different shapes.

Gold nanorods were prepared by our established seeding growth method in aqueous surfactant (CTAB) solution.§ One litre of solution was prepared where the gold concentration was 2.5×10^{-4} mol dm⁻³. The as prepared solution contains 20 aspect ratio rods with a 12 nm short axis (5–10% in terms of number average observed in TEM) and the rest are spheres of 10–50 nm size along with some short rods and platelets.¹¹ The

UV–visible absorption spectrum of this solution shows an intense absorption band at 500–550 nm with a maximum at 525 nm corresponding to a high concentration of nanospheres (Fig. 1) However, the weak absorbance at 1500–1900 nm (that corresponds to the longitudinal absorption band of nanorods) indicates a lower percentage of nanorods. The as prepared solution was first concentrated (~1–5 wt% of gold) and separated from the small spheres by centrifugation.¶ The pink precipitate obtained after centrifugation can be easily redispersed in water and the dispersion is stable for more than a month due the surfactant (CTAB) coating surrounding the particles. The composition of this precipitate was similar to the as prepared sample except for the absence of short spheres of <20 nm. This was confirmed by similar features in the UV–visible spectrum of the redispersed solution and subsequent TEM study. As the spheres, platelets and nanorods are of similar sizes, they could not be further separated by centrifugation, or filtration. Interestingly, if excess surfactant (CTAB) was added from outside, to the concentrated dispersion of these particle

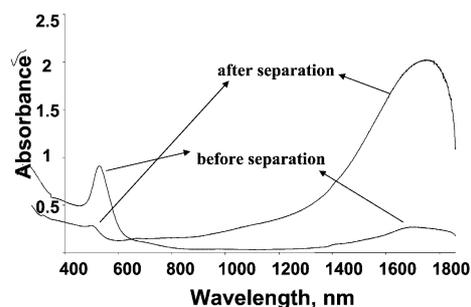


Fig. 1 UV–visible absorption spectra of nanorod solutions before and after shape separation. Concentrations were arbitrary and solutions were diluted for spectral measurements. D₂O was used as the dispersing medium due to the high absorbance of water at NIR region.

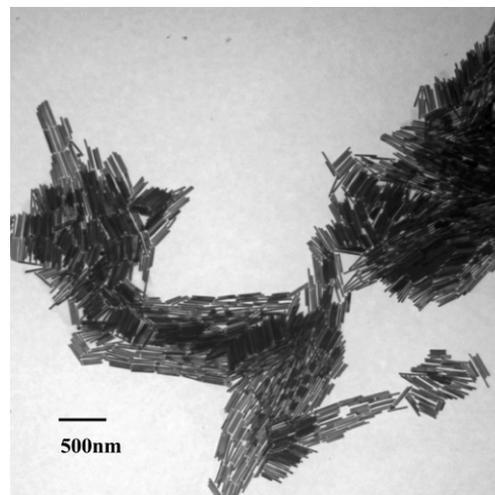


Fig. 2 Transmission electron micrograph (TEM) of shape separated long nanorods.

† Electronic supplementary information (ESI) available: TEM of shape separated shorter nanorods mixed with some spheres and TEM of shape separated plates mixed with short nanorods and spheres. See <http://www.rsc.org/suppdata/cc/b3/b303103a/>

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mixtures, a partial precipitation was observed. The precipitate becomes soluble (leading to a transparent solution), as the solution warms to 40–50 °C and the processes of precipitation and redispersion by alternate cooling and heating were reversible. UV–visible spectroscopy and TEM were performed using both the precipitates and supernatants in order to follow the mechanism of shape separation. The precipitate contains a higher percentage of long rods and the supernatant contains a higher percentage of spheres, platelets and short rods. The precipitated rods form micrometre long rows of ordered nanorods with some spheres trapped or attached with rods. Earlier we reported the similar type of order structures and liquid crystalline properties formed by these nanorods and the role of surfactant in directing such order structures.¹⁵ The separation of single size nanorods from spheres was achieved using this surfactant induced selective precipitation of rods.¶ The separation efficiency can be improved by repeated precipitation and redispersion scheme till complete separation of single size nanorods is achieved.¶ All the supernatants can be further used for the isolation of short rods and plates using a similar protocol.¶

The UV–visible spectra and TEM of shape separated long rods are shown in Fig. 1 and Fig. 2. TEM shows that nanorods are very uniform in length and width (<10% polydispersity in aspect ratio) and free from all other shapes. They have two absorption maxima at 505 nm and 1775 nm corresponding to the longitudinal and transverse plasmon bands. The transverse band was very weak and blue shifted (compared to the absorption maximum at ~525 nm for 10–50 nm spherical gold nanoparticles) but the longitudinal band was very intense.

Recent theoretical and experimental studies have shown that ordered liquid crystalline phases can be formed in concentrated dispersions of anisotropic colloidal particles,^{16–19} as originally proposed by Onsager.¹⁶ These superstructures are thermodynamically stable due to a gain in translational entropy that overrides the loss of orientational entropy associated with particle alignment. Such concentration dependent liquid crystalline ordering is strongly influenced by shape polydispersity.¹⁸ With a higher shape polydispersity, a spontaneous fractionation of shape occurs *via* a nematic–isotropic phase separation, where the nematic phase contain monodisperse particles and the isotropic phase contains more polydisperse particles. We presumed a similar type of mechanism is responsible in the present case of shape separation. In a concentrated dispersion nanorods form liquid crystalline order structures, increase in mass, and precipitate from the solution. Under similar experimental condition, as the liquid crystalline order structure depends on the extent of nanoparticle shape anisotropy; precipitation conditions are different for spheres, plates and short rods and conditions can be manipulated for their successful separation.

Thus a simple shape separation technique has been developed based on the surfactant assisted self-assembly of nanorods. The separation approach used here can be applied to other non-spherical shapes, as the self-assembly depends on the nanoparticle shape anisotropy rather than the nature of the nanoparticles.^{18,19} However, experimental conditions such as concentrated particle dispersion and a suitable particle stabilizer (which can induce a surface charge and/or interdigitation) are important to exploit this separation scheme.^{18,19} As most of the experimental conditions use surfactants as shape inducing agents, different types of self-assembly or ribbon structures are observed for nanorods (BaCrO₄,⁷ Co,⁸ Ni,⁹ CdSe,⁸) and platelets (Co,²⁰ Ag²¹) and our separation scheme may be applied for their further purification.

Notes and references

§ First, a gold seed solution was prepared by borohydride reduction of 20 mL 2.5 × 10⁻⁴ mol dm⁻³ HAuCl₄ in presence of 2.5 × 10⁻⁴ M trisodium citrate and used after 3 h of preparation. The average particle size measured from the transmission electron micrograph was 3.5 ± 0.7 nm. Next, 9 mL,

90 mL and 900 mL of growth solution (containing 0.1 mol dm⁻³ CTAB, 2.5 × 10⁻⁴ mol dm⁻³ HAuCl₄ and 5.0 × 10⁻⁴ mol dm⁻³ ascorbic acid) were placed in each of three conical flasks (labeled **1**, **2**, and **3**) respectively. Next, 1.0 mL of gold seed solution was added to flask **1**. The solution was rapidly stirred for approximately 30 s, then the whole solution of flask **1** was added to the solution of flask **2**. Flask **2** was stirred for 30 s, and then the whole solution of flask **2** was added to the solution of flask **3**. Flask **3** was stirred for 30 s and allowed to stand overnight undisturbed, allowing the rods to form. The solution in flask **3** was used for the shape separation experiments.

¶ Typically, 10–15 mL solution from flask **3** was taken in each centrifuge tube and centrifuged at 6000 rpm for 5 min. The pink precipitate containing rods and large spheres was collected from each centrifuge tube and the pink supernatant containing small spheres and surfactant was discarded. All the precipitates collected from 1 L solution were dissolved in 10 mL of 0.1 mol dm⁻³ hot (40–50 °C) CTAB solution. A brown precipitate along with a pink supernatant was observed upon cooling at room temperature. The precipitate was separated from the supernatant and again dissolved in a fresh 10 mL of 0.1 mol dm⁻³ hot (40–50 °C) CTAB solution and after cooling to room temperature the precipitate was collected and the supernatant was added to the previous supernatant. This precipitation and redispersion can be repeated many times. In the present case we generally repeated 4–5 times for the complete separation of long rods. The precipitate was finally dissolved in 10 mL distilled water and used for all other studies. All the supernatants were collected and used for the further separation of short rods and platelets.

¶ The supernatants collected after separation of long rods were centrifuged at 10000 rpm for 10 min. The colourless supernatant was discarded and precipitates were dissolved in 1.0 mL hot (40–50 °C) CTAB solution. After cooling to room temperature a brown precipitate of shorter rods was observed that was separated and redispersed in distilled water (see ESI Figure 1†). The supernatant was centrifuged at 5000 rpm for 15 minutes and the pink supernatant containing spheres was discarded. The precipitate was deep green in colour and some of the particles make green thin films on the surface of centrifuged tubes. These precipitates were dissolved in 1 mL distilled water to produce a deep green solution containing a mixture of platelets, short rods and some large spheres (see ESI Figure 2†).

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