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Worm-like micelles as templates: Formation of anisotropic silver halide nanoparticles

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ABSTRACT

A novel method is suggested for the formation of anisotropic silver halide nanoparticles by the direct reaction of silver nitrate ($AgNO_3$) with cetyl trimethyl ammonium bromide (CTAB)/chloride (CTAC) and sodium salicylate (NaSal) using worm-like micelles in aqueous solution. It is observed that the presence of a worm-like micellar phase is critical to the formation of anisotropic nanoparticles. Spherical nanoparticles are otherwise obtained when NaSal is absent or below the critical concentration required for the micellar phase. Direct addition of $AgNO_3$ to the surfactant system leads to formation of spherical nanoparticles at short times, which then possibly coagulate and consolidate on a surfactant backbone to form nanorods. Interestingly, when pre-formed spherical nanoparticles are added to a worm-like micellar system, nanorods similar to the proposed method are observed. This technique can possibly be used to synthesize anisotropic nanoparticles of even those materials which do not have an inherent tendency (crystal habit) to form anisotropic structures.

1. Introduction

Surfactant molecules in solution, when present in sufficient concentration and in the right chemical environment, can self-assemble into aggregates of various shapes and sizes. The shape and size of such aggregates depend upon the molecular structure of the surfactant, nature of solvent and additives, and their molar concentration. The morphologies of these aggregates can be of different shapes and sizes; such as spherical micelles, worm-like micelles, lamellar phases depending upon the surfactant and counterion concentrations [1]. Such surfactant stabilized micellar systems, like microemulsions, hexagonal phases, etc., have been successfully used as nanoreactors and templates for the synthesis of nanoparticles [2–6].

Nanoparticle synthesis in surfactant systems allows for better control on particle shape and size distribution compared to other methods. The size and shape of nanoparticles also depend upon the micellar concentration and the nature as well as concentration of ionic or co-surfactant additives [7]. Nanoparticles of varying shapes have been synthesized in nonspherical surfactant templates. The formation of different mesoporous nanostructures, such as 2D hexagonal phase, cubic phase, and lamellar phase, by using different micellar phases as surfactant template has been reported [8–13]. Also, rod-like and reverse rod-like micellar systems have been used to produce nanorods [14–22].

The cetyl trimethyl ammonium bromide (CTAB)–$AgNO_3$ system has recently invoked great interest in anisotropic nanoparticle synthesis. It was found that the formation of gold nanorods, with CTAB as the surfactant, is greatly enhanced (both yield and aspect ratio) in the presence of $AgNO_3$ [23]. The role of $AgNO_3$ and bromide counterion has therefore been a subject of quite a few investigations.

Further, the formation of CTASB spherical nanoparticles is reported to result from the reaction between $AgNO_3$ and Br^- counterion of CTAB, when the CTAB concentration is in isotropic phase [24]. The reaction depends critically on the ratio of concentrations of CTAB to $AgNO_3$, and occurs at room temperature. On heating, transition of layered metastable CTASB complex into anisotropic AgBr particles is observed, with maximum length of around 500 μm.

In the present work, we explore the reaction between CTAB and $AgNO_3$ in the hitherto unexplored worm-like micellar phase, and explore the possibility of a room temperature reaction for one-step synthesis of anisotropic AgBr particles. We then examine the necessity of worm-like micelles for the formation of anisotropic nanoparticles using another surfactant system: CTAC–NaSal worm-like micelles to form anisotropic AgCl particles. These silver halides have several applications in high-speed photographic materials, X-ray films, instant photography and catalysts [25–27], and have been synthesized by various methods: microemulsions [3,2,4], electrospinning [28], on site precipitation [29], direct reaction between silver chloride suspension and potassium bromide [30],

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ion exchange reaction [31], computer assisted double jet [32], *in situ* generation [33], aqueous phase precipitation [34], and an amphiphilic graft copolymerization [35] and even solid-solid reactions [36].

Worm-like micelles are large one-dimensional self-assemblies of surfactant molecules, which are locally cylindrical and behave like semi-flexible polymeric chains. These micelles entangle with each other leading to viscoelastic phases. In the present work, the surfactant system was prepared using CTAB (cetyl trimethyl ammonium bromide) and sodium salicylate (NaSal) salt. This is a well known system for making worm-like micelles [37–39]. The presence of ionic or co-surfactant additives such as NaSal, reduces the repulsions between CTAB micellar head groups and thereby affects structural transitions. In addition, the micellar aggregates can grow anisotropically under appropriate conditions, thus changing their shapes from spheres to rods or highly flexible worm-like aggregates [6].

In this work, we propose a novel and facile method for the synthesis of anisotropic nanoparticles, using worm-like micellar surfactant templates (CTAB/CTAC–NaSal) and apply it to the formation of AgBr and AgCl particles, with the objective of examining the effect of template on the shape of nanoparticles.

2. Materials and methods

2.1. Chemicals

Cationic surfactant cetyl trimethyl ammonium bromide (CTAB, 99%), hexadecyl-trimethyl-ammonium bromide and silver nitrate ($AgNO_3$, 99.9%) were purchased from Sigma–Aldrich Chemicals, GmbH. Sodium salicylate (NaSal, 99%) and cetyl trimethyl ammonium chloride (CTAC, 25%, w/v solution) were purchased from S.D. Fine Chem-Limited. In the preparation of all the samples, Milli-Q water of conductivity 18.2 MΩ cm^{-1} was used and the temperature was kept at 25 °C.

2.2. Preparation of surfactant system

The surfactant system, for the synthesis of AgBr nanoparticles, was prepared by adding CTAB to Milli-Q water until the surfactant dissolved completely, followed by the direct addition of NaSal under constant stirring. CTAB concentration was kept constant (50 mM) for various sets of rheological experiments and the NaSal concentration was varied to keep the NaSal to CTAB ratio (S) between 0 and 2. It was observed that on addition of NaSal salt to the aqueous CTAB solution, the surfactant system turned into a transparent soft gelatinous mass which was then used to synthesize anisotropic AgBr nanoparticles. For the synthesis of AgCl nanoparticles, CTAC was used instead of CTAB, in Milli-Q water. A similar method was followed as described above for AgBr nanoparticles. CTAC concentration was kept constant (100 mM) for various sets of experiments and NaSal concentration was varied to keep the NaSal to CTAB ratio (S) between 0.5 and 2.

2.3. Synthesis of nanoparticles

The synthesis of nanoparticles using CTAB–NaSal worm-like micelles was carried out by the direct reaction of an added salt solution with the surfactant counterion. Aqueous solution of $AgNO_3$ was added gradually to the CTAB–NaSal surfactant system with vigorous stirring at room temperature, to produce the AgBr particles. The resulting mass was gelatinous and milky yellow in colour. Similarly, AgCl nanoparticles were prepared using CTAC–NaSal surfactant system. The appearance of the worm-like micellar phase before and after addition of $AgNO_3$ was similar to that of the CTAB–NaSal system.

2.4. Characterization

The UV absorption of the AgBr nanoparticles was measured using SHIMADZU UV–VIS spectrophotometer. The wavelength range was maintained between 200 and 400 nm. The particle-free CTAB–NaSal worm-like micellar solution was used as a reference for UV measurements. For TEM investigations, AgBr or AgCl nanoparticles in the micellar solution were diluted several times, using Milli-Q water. A drop of this solution was taken and placed on carbon coated copper TEM grids and vacuum dried at room temperature for 12 h. Images of the nanoparticles were taken at different degrees of magnification from different locations on the grid using a PHILIPS CM200 transmission electron microscope. For EDS of AgBr and AgCl nanoparticles, a similar sample preparation method as that of TEM was used and EDS taken using JSM-7600F field emission gun-scanning electron microscope. The gelatinous mass, containing AgBr nanoparticles, was washed with water and then used for XRD analysis. The XRD measurement of the AgBr nanoparticles were carried out on a Rigaku D-max 2000/JADE 6.0 copper rotating anode X-ray Diffractometer using Cu $K\alpha_1$ radiation. Reference to the standard diffraction spectrum of AgBr (JCPDF No. 79-0149) indicates that the peaks correspond to that of AgBr. The rheology experiments were conducted using Anton Paar MCR 301 Rheometer 'equipped with temperature control' to measure the elastic and viscous responses to oscillatory shear. IR spectra for AgBr samples were obtained using a Nicolet MAGNA 550 FT-IR spectrometer. The samples were diluted with water and recording made in the transmission mode.

3. Results and discussion

3.1. AgBr nanoparticles in worm-like micellar system

The worm-like micellar phase is best characterized by its rheology and exhibits a single relaxation time that indicates Maxwellian behavior [40]. Rheological properties of the CTAB solution in the presence of NaSal were first investigated as a function of S, the molar ratio of NaSal to CTAB. The CTAB concentration was fixed at 50 mM and the molar concentration of NaSal was varied from 0 to 100 mM to determine the onset of worm-like behavior. The surfactant system of CTAB–NaSal is known to form long elongated micelles when the concentration of NaSal is above a critical value, C^*_{NaSal} (50 mM for 50 mM CTAB in the present study). Below the critical concentration of NaSal, the rheological behavior is non-Maxwellian, which suggests that the solution is predominantly contains individual polymers (non-entangled chains) (Fig. S1, supplementary material). At a concentration of about 50 mM of NaSal, the system shows worm-like behavior with a single cross relaxation time, in agreement with Maxwellian rheology (Fig. S2, supplementary material). Beyond this point, the degree of entanglement of the micelles increases and the solution exhibits viscoelastic properties similar to those observed in solutions of flexible polymers in the entanglement regime [40].

In the Maxwellian rheology regime, the variation of storage modulus G' and loss modulus G'' as a function of frequency ω is given as:

$$G'(\omega) = \frac{G_p\,\omega^2 t_r^2}{1+\omega^2 t_r^2} \quad (1)$$

$$G''(\omega) = \frac{G_p\ \omega t_r}{1+\omega^2 t_r^2} \quad (2)$$

where G_p denotes plateau modulus and t_r denotes relaxation time. Fig. 1 shows the correct scaling for G' and G'' at low and high frequencies, respectively, i.e. $G' \propto \omega^2$ and $G'' \propto \omega$ at low frequencies,