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Optimized colloidal chemistry for micelle-templated synthesis and assembly of silver nanocomposite materials

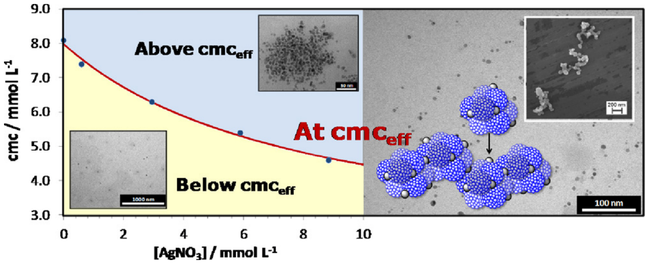
Anna L. Garden[a,b,1], Kerstin Scholz[a,b], Donald R. Schwass[c], Carla J. Meledandri[a,b,*]

[a] Department of Chemistry, University of Otago, P.O. Box 56, Dunedin 9054, New Zealand
[b] The MacDiarmid Institute for Advanced Materials and Nanotechnology, University of Otago, P.O. Box 56, Dunedin 9054, New Zealand
[c] Department of Oral Rehabilitation, Faculty of Dentistry, University of Otago, Dunedin 9054, New Zealand

HIGHLIGHTS

- A cmc boundary for sodium dodecyl sulfate with silver nitrate is reported.
- The implications of this boundary for silver nanoparticle synthesis are discussed.
- Stable assemblies of micelle aggregates with Ag nanoparticles have been prepared.
- Optimized synthetic conditions for the formation of the assemblies are presented.
- Mechanism of assembly formation: at, above and below the cmc boundary is discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work we identify an effective cmc boundary for a model ionic surfactant/metal salt system (sodium dodecylsulfate/silver nitrate; SDS/$AgNO_3$), and demonstrate the importance of this boundary with respect to surfactant- and/or micelle-templated synthesis of metal nanoparticles. By preparing SDS-stabilized silver nanocomposite materials using an SDS/$AgNO_3$ ratio at the identified cmc boundary, we observe the formation of silver nanocomposite assemblies; the extent of assembly can be varied by altering the initial $AgNO_3$ concentration. Finally, we describe the mechanism of formation and morphology of the nanocomposite materials when the structures are prepared *at*, *above* and/or *below* the effective cmc boundary.

1. Introduction

The controlled synthesis of metal and metal oxide nanoparticles is at the forefront of nanomaterials research due to the fact that the properties of nanoscale materials not only differ significantly from those of bulk materials, but they are critically dependent on particle size, shape, surface chemistry and inter-particle interactions [1]. Metallic silver nanoparticles (Ag NPs), in particular, have found use in a broad range of applications in areas as diverse as catalysis [2], biosensing [3], water treatment [4] and medicine [5].

Abbreviations: Ag NPs, silver nanoparticles; Ag NCs, silver nanocomposites; SDS, sodium dodecylsulfate; cmc, critical micelle concentration; *cmc$_{eff}$*, effective critical micelle concentration; ICP-MS, inductively coupled plasma-mass spectrometry.

[*] Corresponding author at: Department of Chemistry, University of Otago, P.O. Box 56, Dunedin 9054, New Zealand. Tel.: +64 3 479 5378; fax: +64 3 479 7096.

E-mail address: cmeledandri@chemistry.otago.ac.nz (C.J. Meledandri).

[1] Present address: Science Institute, VR-III, University of Iceland, IS-107, Reykjavik, Iceland.

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The interest in Ag NPs for applications in health care and medicine is due in part to increasing bacterial resistance to classical antibiotics [6]. Ag NPs offer novel modes of action and target different cellular structures compared with existing antibiotics, and have vastly increased reactivity over ionic silver, as a result of their large surface area to volume ratios. Several areas of medical care have already benefitted from the ongoing development of Ag NP-based materials [7,8].

The antimicrobial activity of Ag NPs has been reported to be critically dependent on the dimensions of the particles. Specifically, many studies have revealed that smaller sized particles impart greater antimicrobial activity, on the basis of equivalent silver mass content [9,10]. The consequence of these findings is that there has been significant recent emphasis on designing synthetic routes that enable a high level of control over Ag NP size and size distribution and prevent particle aggregation in suspension. Many versatile methods have been investigated for the size-controlled synthesis of Ag NPs [11–15]; the chemical reduction method is a common and advantageous strategy for metal nanoparticle synthesis, as it is simple, straightforward, reliable, relatively inexpensive, can be carried out under mild conditions and is well-studied. Perhaps most notably, however, this synthetic approach is extremely versatile, and can be adapted and tailored to enable the rational design and development of more advanced functional nanocomposite materials [16–18]. This typically involves solution-phase chemical reduction of a metal salt and precipitation of the particles within a continuous matrix. This process is commonly performed in the presence of stabilizing molecules (e.g., surfactants, lipids, polymers) in order to prevent unwanted aggregation of the nanocrystals, and to control the growth, size and shape of the particles, as well as impart some control over their surface chemistry, functionality and dispersibility in a specific solvent system.

Beyond their role as stabilizers, surfactants and amphiphilic polymers can also act as structure-directing agents and templates. For instance, when present in solution at the time of metal salt reduction, they can direct the growth of nanocrystals and influence the resulting NP morphology by stimulating anisotropic growth and the preparation of faceted NPs of defined, non-spherical shapes [19,20]. Furthermore, under certain conditions, these molecules can undergo cooperative association to form various colloidal aggregate structures including micelles, bilayers and vesicles, which can subsequently be used as soft templates for NP synthesis [21,22]. This is a powerful, versatile strategy which is increasingly used to control the size, size distribution and morphology of individual NPs, as well as the larger NP-containing structures. In a template-based NP synthesis, the outer surface of the colloidal aggregate is often used to accumulate and sequester synthetic precursors, most commonly metal salts, where they are subsequently chemically reduced, thereby initiating nucleation and growth [23]. This approach enables the resulting metal nanoparticles to remain physically separated from each other, thus preventing the need to completely coat their surfaces with stabilizing molecules, which would subsequently reduce their antibacterial activity.

Ionic surfactant micelles form an important class of NP templating structures, as their inherent surface charge imparts colloidal stability, and facilitates surface adsorption of the precursors via electrostatic interactions. A critical property of surfactant solutions that warrants consideration when used for template-based NP synthesis is the critical micelle concentration, or *cmc*. This is a property which is known to change quite significantly for ionic surfactants upon the addition of electrolytes, which we emphasize includes the addition of metal salts used as NP precursors. The form of the surfactant molecules (monomer vs. aggregated), and thus the morphology of the template, critically depends on whether the surfactant concentration used during NP synthesis is above or below the cmc of the surfactant *in the presence of the corresponding metal salt*. While there is a wealth of knowledge in the colloidal chemistry domain about the effect of various electrolytes on the cmc of ionic surfactants, this is a factor that, to the best of our knowledge, has never been satisfactorily addressed in the context of ionic surfactant-directed nanoparticle synthesis. Furthermore, despite the significant interest in Ag NPs for a myriad of applications and technologies, as well as the existence of a significant body of research focused on their surfactant-templated synthesis, there is a notable lack of data reported to-date on the effect of silver ions on the physicochemical behavior of ionic surfactants. Our work seeks to address this issue using a sodium dodecylsulfate (SDS)/$AgNO_3$ system for the formation of SDS-stabilized Ag nanocomposite (SDS-Ag NC) materials.

In the present work we identify an effective 'cmc boundary' for the SDS/$AgNO_3$ system; i.e., the effective cmc (cmc_{eff}) of SDS at a given $AgNO_3$ concentration (in the range of 0.6–8.8 mM). We demonstrate that this boundary is not only significant because it governs the form of the surfactant molecules, and thus the NP template, but also because it directs the mechanism of formation of SDS-Ag NC materials, the role of SDS in the NP stabilization process, and the morphology of the final nanostructures. In our discussion we identify the SDS/$AgNO_3$ ratio and synthetic conditions for optimum Ag NP loading, high antimicrobial activity and production of nanocomposite assemblies.

2. Materials and methods

2.1. Chemicals

Sodium dodecylsulfate (SDS, 90%), silver nitrate ($AgNO_3$, ≥99.0%), and sodium borohydride ($NaBH_4$, ≥97%) were purchased from Sigma–Aldrich and used as received. Deionized water was of ultrahigh purity (Millipore Milli-Q Plus system).

2.2. Conductivity measurements

Electrical conductivity (κ) of SDS solutions (ranging from 1 to 20 mM) in both the absence and presence of $AgNO_3$ (10, 50, 100, 150 mg) was measured at 25 °C in a high concentration zeta cell using a Malvern Zetasizer Nano (Malvern Instruments; Malvern, UK). Implementation of a technique patented by Malvern (M3-PALS), which combines laser Doppler velocimetry and phase analysis light scattering, enabled the measurement of particle electrophoretic mobility, from which the conductivity data was acquired. The reported conductivity and standard deviation values were obtained from six repeat measurements performed on each sample.

To prepare samples for conductivity measurements, 10 mL of a 0, 10, 50, 100 or 150 mg mL^{-1} $AgNO_3$ solution (which remained in the dark at all times) were added to the required mass of SDS to prepare a series of solutions ranging from 0 to 20 mM SDS, with various amounts of $AgNO_3$ present.

2.3. Synthesis of SDS-stabilized silver nanoparticles

All glassware used in the following procedures was acid washed in a bath of freshly prepared aqua regia (1:3 HNO_3:HCl), thoroughly washed with DI H_2O, then dried before use. A series of aqueous suspensions of SDS-stabilized Ag NPs were prepared as follows. An appropriate amount of SDS was completely dissolved in 100 mL DI H_2O to give a desired concentration between 2.3 and 11 mM (see Table 1). This range spans a wide range of concentrations which fall both above and below the cmc of pure SDS in water, in the absence of any salts, reported to be ~8.0–8.3 mM [24–27]. Silver nitrate (0.06–0.88 mmol) was then added with stirring to the SDS solutions so that the mole ratio of SDS to $AgNO_3$ ranged from 0.3