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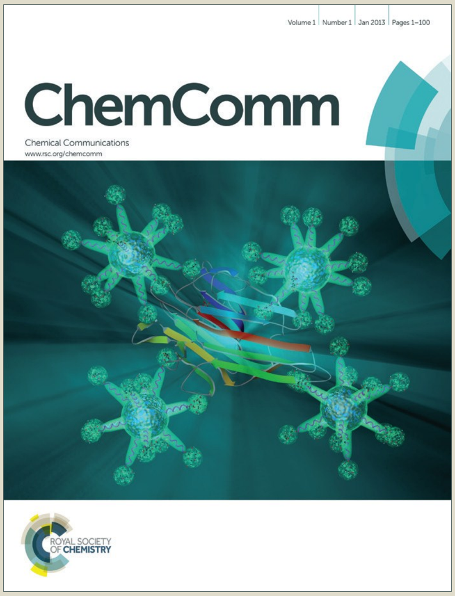

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One-Pot Synthesis with *in situ* Preconcentration of Spherical Monodispersed Gold Nanoparticles using Thermoresponsive 3-(Alkyldimethylammonio)-propyl Sulfate Zwitterionic Surfactants

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Homogeneous solutions of thermoresponsive zwitterionic 3-(alkyldimethylammonio)-propyl sulfate surfactants at elevated temperatures were employed for the synthesis of gold nanoparticles (AuNPs) by the citrate reduction method. Upon cooling at completion of the reaction, the mixture phase separates with the monodispersed AuNPs condensed and concentrated in the small volume surfactant-rich phase.

Gold nanoparticles (AuNPs) exhibit distinctive size dependent characteristics, including unique optical, electrical and mechanical properties, which render them suitable for a myriad of applications ranging from chemical and biological sensors, gene therapy, drug delivery and imaging agents, catalysts, photonic and plasmonic devices and nanoelectronic elements among others.[1] Many such applications require stable concentrated solutions of the nanoparticle.[2] A popular method for preparation of gold nanoparticles (AuNPs) is the citrate reduction synthesis.[3] A disadvantage of this approach is the resultant low concentration of AuNPs.[2c,4] Thus there is a continuing need for rapid and simple synthetic methods for the preparation of concentrated and stable nanoparticle solutions. Here we report utilization of zwitterionic surfactants, such as 3-(decyldimethylammonio)-propyl sulfate ($C_{10}APSO_4$), for the rapid one-pot synthesis, stabilization and in-situ preconcentration of AuNPs. Aqueous solutions of this surfactant class are thermoresponsive and exist as a homogeneous aqueous micellar solution at temperatures above their upper critical solution temperature (UCST) whereas they phase separate at temperatures below the UCST to form a small volume surfactant-rich (coacervate) phase and larger volume aqueous surfactant-lean phase.[5] In the synthesis of AuNP by the inverse citrate method at elevated temperature, the reactants were dispersed in the zwitterionic micelle solution facilitating the synthetic reaction and at the conclusion of the reaction, as the solution cools to room temperature, phase separation occurred with the AuNPs concentrated in the surfactant-rich phase. In addition to serving as the reaction medium for the synthesis of spherical AuNPs and concentration of the AuNP, the surfactant serves as a protective capping agent for the preservation of the AuNP in a dispersed state by preventing their aggregation or agglomeration. Previously, other zwitterionic species (including some micelle-forming surfactants) were shown to function as an effective reaction medium and/or capping agents for the production of stable nanoparticles, including AuNPs.[6] However, in these previous reports, neither this particular class of zwitterionic surfactants nor utilization of their thermoresponsive behavior for the *in situ* concentration of the prepared AuNPs appear to have been considered.

Highly concentrated AuNPs was fabricated as follows: Typically 0.50 mL of an aqueous 0.010 M trisodium citrate solution and 1.00 mL of an aqueous 10 % (w/w) zwitterionic surfactant $C_{10}APSO_4$ ($C_{10}H_{21}(CH_3)_2N^+(CH_2)_3OSO_3^-$) solution (both preheated to 95°C in a thermostatted oil bath) were mixed together in a conical bottom centrifuge tube (tube) to prepare a homogeneous micellar solution (the UCST of this surfactant under these conditions is ca. 68°C and at temperatures above this, it forms a homogeneous micellar solution[5]). The resultant solution was adjusted to pH 7.0 using 0.10 M NaOH (typically 0.10 mL addition; solution also at 95.0 °C). Next, 2.50 mL of 1.02 × 10^{-4} M gold ion ($HAuCl_4$) was added to this solution and after mixing, the resultant reaction mixture kept static at 95°C for 8.0 minutes (this time was sufficient for completion of the reaction as determined by monitoring the disappearance of $AuCl_4^-$ at 312 nm; and longer reaction times such as 20-30 min. resulted in formation of agglomerated or aggregated AuNPs). The tube was then removed from the oil bath, placed in a centrifuge and centrifuged for 8 min. at 1500 rpm (x 367.1 g) at room temperature. During this step, the solution cooled and phase separated. The AuNPs were concentrated in the surfactant-rich phase (90 µL) (see Electronic Supplementary Information (ESI†) section for more

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details). The maximum possible enrichment factor for this *in-situ* preconcentration step is 44 (i.e., AuNPs originally in 4.0 mL reaction mixture are condensed into the 0.090 mL surfactant-rich phase). The top surfactant-lean phase was completely removed using a Pasteur pipette. The bottom surfactant-rich phase containing the AuNPs was kept in the tube for storage or appropriately diluted with methanol prior to the visible absorption, dynamic light scattering (DLS) or transmission electron microscopy (TEM) characterization studies (ESI† gives extended experimental).

The AuNPs prepared by this protocol were wine red (burgundy) colored and exhibited their surface plasmon resonance (SPR) absorption band at 529.5 nm (Fig. 1). The mean diameter of the AuNPs was 21.1 ± 4.8 nm as determined from TEM images while the hydrodynamic diameter obtained from DSL was 45.8 ± 5.8 nm (Fig. 2). The TEM images indicated that the AuNPs were monodisperse and roughly spherical shaped. A commercial sample of 20 nm sized AuNPs prepared by the citrate reduction method (obtained from NANOCS, Inc., NY)[7] had an absorption maximum at 521 nm (Fig. 1, right panel). The absorbance of this commercial AuNP preparation (concentration reported as 7.0 x 10^{11} particles/mL)[7] was less compared to the AuNPs prepared by the proposed method. For the typical preparation of AuNPs by the citrate method, concentrations of 1.7 x 10^{-8} M AuNP have been reported in the literature.[3d,8] As calculated using Leff's equation[9] (Eq. 1 in ESI† section), the concentration of the AuNPs in the $C_{10}APSO_4$ surfactant-rich phase was 6.44 x 10^{12} particles/mL (equivalent to 1.07 x 10^{-8} M AuNPs). This concentration is 9.2 times greater than that of the commercial NANOCS sample. The maximum capacity of AuNPs in the surfactant-rich phase was 1.77 x 10^{14} particles/mL (equivalent to 2.91 x 10^{-7} M AuNP) (as determined by repeating the synthetic procedure but using greater initial concentrations of the gold precursor). This latter concentration is 250 times greater than that of the commercial preparation. In addition, if this AuNP saturation capacity in the surfactant-rich phase is exceeded, the excess AuNPs formed remain in the surfactant-lean phase (probably due to excluded volume effects) with no aggregation observed (Fig. S4, ESI†) which is in contrast to many other synthetic systems. The proposed protocol thus allows for the preparation of highly concentrated and dispersed AuNPs. In addition, the $C_{10}APSO_4$ capped AuNPs in the surfactant-rich phase exhibited good stability as no visual change in their wine red color nor their visible absorption spectrum was noted even after more than 3 months storage at room temperature.

Although $C_{10}APSO_4$ is overall neutral, the zeta potential of the AuNPs in the surfactant-rich phase was determined to be negative; i.e., -9.6 mV. This value is in the general range of zeta potentials reported for AuNPs coated with other zwitterionic species (e.g., -8.6 to -17.9 mV).[6f,10] The negative charge for the AuNPs in the zwitterionic surfactant-rich phase could arise as follows. It has been demonstrated that ions can bind to the bipolar head group of zwitterionic surfactant micelles[6a,6i,11] and if anions bind that creates a negatively charged micelle surface. Increases in the anion concentration were found to cause the zeta potential of zwitterionic sulfonate surfactant solutions to become more negative.[11c]

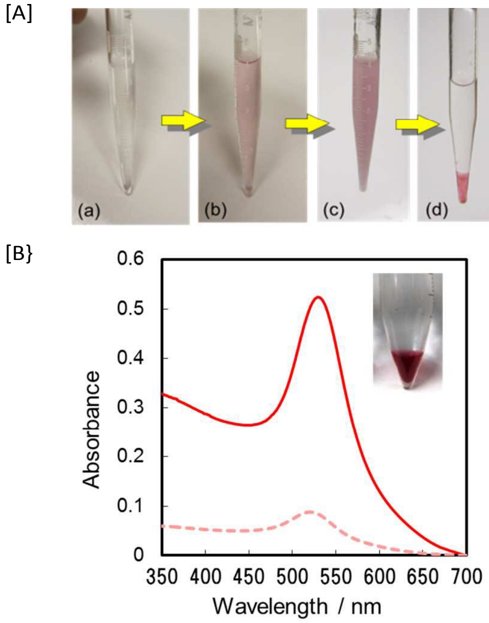

Fig. 1. The panel [A] shows photographs of the reaction solution during the stages of the AuNP synthesis: (a) clear homogeneous solution of $C_{10}APSO_4$ surfactant and citrate ion at 95.0°C, (b) wine red colored solution after $AuCl_4^-$ addition due to formation of AuNP, (c) turbid solution due to phase separation of reaction mixture upon cooling below UCST and (d) phase separated system after centrifugation with AuNPs concentrated in the bottom, small volume surfactant-rich phase. The panel [B] gives the visible spectrum with the absorption due to the AuNP SPR band. Pink dotted line is of a commercial AuNP solution[7] while the red solid line is for a diluted solution of the AuNPs synthesized by the proposed method (surfactant-rich phase was diluted 23.2-fold; i.e., 2.00 mL of methanol was added to the 90.0 µL surfactant-rich phase). Synthetic conditions: $[C_{10}APSO_4]_f$ = 2.50 % (w/w); $[\text{citrate}]_f$ = 1.25 mM; $[AuCl_4^-]_f$ = 6.38 x 10^{-5} M; pH = 7.0; reaction time 8.0 min. at 95 °C; followed by centrifugation at room temperature for 8.0 min.

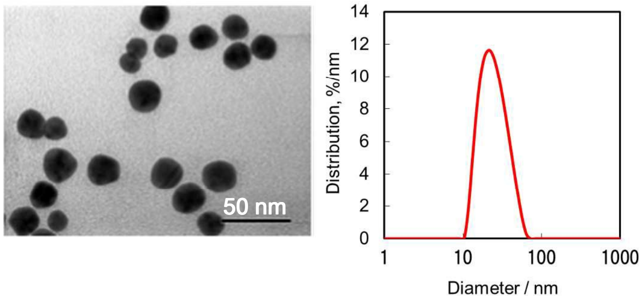

Fig. 2. TEM image (left panel) and DSL profile (right panel) showing the size distribution of the AuNPs synthesized in $C_{10}APSO_4$ (conditions as noted in Fig. 1 legend except that the surfactant-rich phase containing the AuNPs was diluted 11-fold with methanol prior to the measurements).

The $C_{10}APSO_4$ surfactant head group could bind either to the citrate ion of the initially synthesized citrate coated AuNPs and/or directly to the AuNP surface. In either case, the surfactant's alkyl tail would be directed outward and away from the AuNP surface such that a double layer forms about the AuNP. The citrate ions present could then also bind to the

$C_{10}APSO_4$ head group on the outer surface of that double layer. Such configurations would explain the observed negative charge and also why the zwitterionic surfactants stabilize the formed AuNPs by preventing their agglomeration or aggregation. Previously, it had been hypothesized that the anionic sulfonate moiety of a sulfobetaine surfactant interacted with the surface of AuNPs and formed a bilayer by interdigitating its hydrophobic alkyl tails[6b] and a similar situation was demonstrated to occur in the stabilization of palladium nanoparticles using an imidazolium-based zwitterionic surfactant.[6i]

The size, polydispersity and stability of AuNPs synthesized by the citrate method are influenced by factors such as the type and concentration of surfactant(s), if present, the initial gold and citrate concentrations as well as the citrate ion to gold precursor concentration ratio, pH, temperature, etc.[3c,4,12] Some of these factors were briefly examined in order to determine their impact on the proposed synthetic method. First, the AuNP synthesis in the absence and presence of different concentrations (1.25, 2.50, 5.00 and 7.50%) of the $C_{10}APSO_4$ surfactant was examined. The UCST for $C_{10}APSO_4$ over this concentration interval ranges from ca. 58 to 80°C[5] while the volume of the surfactant-rich phase after phase separation is in the range from ca. 25 to 180 µL (Fig. S5, ESI†). In the absence of the $C_{10}APSO_4$ surfactant, the average and hydrodynamic diameters of the AuNPs formed were 22.0 ± 1.5 nm and 25.8 ± 5.9 nm as determined by TEM and DLS, respectively. The TEM of the AuNPs formed in the presence of 5.0 and 7.5 % $C_{10}APSO_4$ were similar to that shown in Fig. 2 (left-hand panel) which was obtained using 2.5% surfactant in the synthesis and indicated that they all had very similar average diameters (ca. 21.1 – 22.0 nm). The fact that very similar AuNP sizes were observed at the different $C_{10}APSO_4$ concentrations was surprising in view of prior reports that gold and other metal nanoparticles synthesized in the presence of surfactants indicated that the size and size distribution were a function of the surfactant concentration[13] (see ESI† for discussion). At the lowest $C_{10}APSO_4$ concentration examined (1.25%), flocculation (aggregation) of the AuNPs occurred. This may be due to the fact that the volume of the surfactant-rich phase at this $C_{10}APSO_4$ concentration is only 25 µL and the AuNPs confined in this smaller volume resulted in their aggregation. Such explanation has been proposed for AuNP aggregation in other synthetic systems.[14]

The one-pot synthesis of AuNPs was also successful using 2.5% (w/w) C_9APSO_4 as the surfactant (at this concentration, the UCST is ca. 38 °C[5] and the volume of the surfactant-rich phase is ca. 60 µL). Fig. 3 (left side) gives the absorption spectrum. The average diameter as determined from TEM was 13.4 ± 3.7 nm while the DLS profile yielded a hydrodynamic diameter of 30.2 ± 6.8 nm. Thus, the alkyl chain length of this class of zwitterionic surfactants appears to influence the size of the resultant AuNP with the surfactant having the smaller alkyl chain length yielding AuNPs of smaller size. Previously, in the synthesis of AuNP in reverse and normal micelles, the surfactant alkyl chain length was reported to also influence the size of the produced NPs.[13d,15]

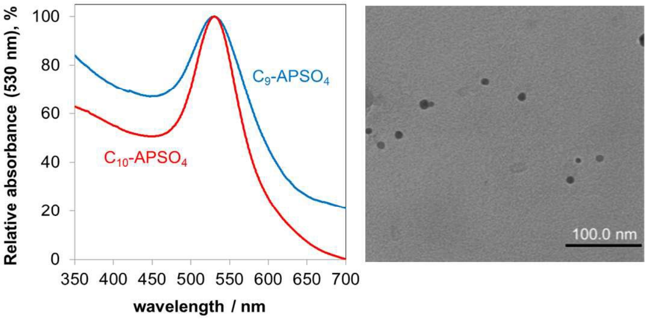

Fig. 3. Visible absorption spectrum (left side panel) showing the SPR band of AuNPs prepared using $C_{10}APSO_4$ (red line) or C_9APSO_4 (blue line) (see ESI†) and TEM image of AuNPs prepared using C_9APSO_4 (right panel) [conditions are as noted in Fig. 1 legend except that C_9APSO_4 was the surfactant and the surfactant-rich phases containing the AuNPs were diluted 11-fold with methanol prior to the respective measurements].

In addition, the effect of temperature and pH on the resulting AuNP was evaluated. The results indicated that carrying out the synthetic reaction at 100 or 95 °C resulted in the sharpest SPR band (at 529.5 nm) and very similar AuNP hydrodynamic diameters (48.7 ± 8.4 or 45.8 ± 5.8 nm). Decreasing the reaction temperature (to 90 and 80 °C) resulted in increased AuNP size with greater polydispersity as revealed by broadened SPR bands and the DLS profiles. This is in agreement with literature which indicated that a decrease in the reaction temperature results in formation of larger sized AuNPs.[3f] Also, higher reaction temperatures often result in AuNPs that are more monodisperse due to the more controlled reduction of $AuCl_4^-$.[3e] At the lowest reaction temperature examined, 70 °C, only formation of a sediment of AuNP was visually observed and no SPR band was evident in the visible spectrum.

Neutral pH (7.0) was found optimal for the preparation of mondispersed AuNP in the zwitterionic surfactant media if the buffer concentration range was between 1.25 – 12.5 mM sodium citrate. However, suitable AuNPs could also be prepared under weakly alkaline conditions (pH 8 -9) but the AuNP size distribution broadened with increasing alkalinity, especially at pH 9 or 10. Acidic pH did not result in the formation of suitable AuNPs; i.e., in the pH region 4-6, larger and polydisperse AuNPs formed whereas at pH < 4, no AuNPs formed as evidenced by the colorless reaction solutions and the absence of the SPR band in the visible spectra. Previously, pHs in the range of 6.2 to 7.5 had been reported to be satisfactory for the citrate preparation method of AuNPs depending upon the reaction temperature.[3c,4a,4b,16] The $C_{10}APSO_4$ or C_9APSO_4 surfactants should remain in their zwitterionic state with a net neutral charge over a wide pH region (from 3 to 12); however at pH values lower than 3, they are progressively converted to a cationic surfactant (since the pK_{a2} of hydrosulfuric acid is 1.91).[5b] Prolonged storage of these zwitterionic surfactant solutions in acidic media, especially at elevated temperatures, should be avoided or minimized since hydrolysis with cleavage of the O-S bond linkage of the sulfate moiety is expected to occur.[17]

The effect of alteration of the $AuCl_4^-$ concentration (at a fixed citrate concentration of 2.50 mM) upon the synthesis of AuNPs in 5.0% $C_{10}APSO_4$ was examined. The AuNP particle size determined from TEM images increased from a diameter of 12.1 nm to 22.0 nm as the gold concentration increased from 0.05 mM to 1.25 mM (Fig. S6, ESI†). Increasing the citrate ion concentration from 1.25 mM to 12.5 mM at a constant gold concentration (6.37×10^{-5} M $AuCl_4^-$) resulted in the formation of essentially the same sized AuNPs (diameter only increased from 21.1 nm to 22.0 nm). Use of a much greater citrate concentration (125 mM in the synthesis) resulted in the formation large and agglomerated AuNPs. Previously, it had been reported that the size of the formed AuNPs depended not only upon the ratio of the citrate to gold ion concentration but also upon the specific initial gold and citrate ion concentrations.[3c,4b,4c,12d,12e]

In summary, the preparation of highly concentrated and stable AuNPs in a one-pot synthetic procedure without the need for a separate dedicated preconcentration or extractive step has been demonstrated. The general approach described herein should also be amendable for the synthesis and in-situ concentration of other types of nanoparticles. It is thought that the AuNPs in the surfactant-rich phase could potentially be employed either as is or after suitable dispersion for different applications (see ESI† section).

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