# Effect of Pyrene Additive on the Growth of Gold Nanoparticles in Aqueous Sodium Alkyl Sulfate Micellar Solutions

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Gold nanoparticles (NPs) were synthesized by chemical reduction in sodium octyl sulfate (SOS), sodium decyl sulfate (SDeS) and sodium dodecyl sulfate (SDS) solutions. Gold NPs prepared in SDS solutions have the smallest size and the highest stability among them. The stability of gold NPs was reflected in the hydrophobic property of the protecting surfactant. Size-controlled synthesis of gold NPs was further achieved with the addition of pyrene in all surfactant solutions. Experimental results indicated that the combination of SDS and pyrene has the extraordinary effect in decreasing the size and narrowing the dispersity of gold NPs. Micellar electrokinetic capillary chromatography (MEKC) showed that the chemical reaction between pyrene and gold complexes was attributed to the formation of gold NPs inside the micelles at the embryonic stage.

**Keywords:** Nanoparticle; Gold; Surfactant; Pyrene and electrophoresis.

## INTRODUCTION

The preparation of metal nanoparticles (NPs) with a great degree of control over size and morphology is necessary to study their unique properties.[1] For gold NPs, a lot of time has been spent on developing the methods for the preparation of monodisperse colloidal gold.[2-5] Gold NPs with well-controlled sizes and shapes created many new applications. For example, size-sensitive catalysis by gold NPs deposited on metal oxides is reported for the oxidation of CO to $CO_2$.[3] Gold nanorods have showed anisotropic chemical reactivity with cyanide.[4] Gold NP aggregates provide a rough surface which is suitable for surface enhanced Raman scattering (SERS).[5]

In general, the size and dispersity of metal NPs could be determined by controlling the relative rate of nucleation and growth of metal NPs. In addition to the reductants, the stabilizer used in the preparation is also important for controlling the particle size and shape. Organothiols,[6] polymers,[7] and surfactants[8] have been employed as the capping agents for the synthesis of gold NPs. Currently, negatively charged gold NPs are mostly made by the classical citrate method where citrate ions are used both as a weak reductant and weak surface protecting agent.[9] For producing smaller gold NPs, a stronger reductant and a strong capping agent are usually employed, such as $NaBH_4$ and thiol molecules.[6]

In this study, we would like to explore the combination of a stronger reductant such $NaBH_4$ and a weaker protecting agent such as sodium alkyl sulfate, a typical anionic surfactant, to synthesize gold NPs in aqueous micellar solutions. The reason for making these kinds of gold NPs is that we are developing gold NPs as nanocatalysts where reactants are accessible to the surface of gold NPs. Strong capping agents would block adsorption of other molecules. Three anionic surfactants ($C_nH_{2n+1}SO_4Na$, n = 8, 10 and 12), sodium octyl sulfate (SOS), sodium decyl sulfate (SDeS) and sodium dodecyl sulfate (SDS), were used.[10] Further, pyrene as a size-control additive was solubilized in the above micellar solutions and its influence on the formation of gold NPs will also be reported. At the same time, we employed micellar electrokinetic capillary chromatography (MEKC) to analyze the size distribution of gold NPs and investigate the formation mechanism.

## EXPERIMENTAL SECTION

### Chemicals

Sodium borohydride was obtained from Alfa Aesar and used as supplied. Sodium tetraborate was purchased

We dedicate this article to the late Professor Tong-Ing Ho who was a devoted colleague and friend.

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from Sigma. All other materials and reagents were purchased from Acros.

**Gold Nanoparticle Synthesis**

For the preparation of gold NPs in the SOS system, 5 mL of 0.2 M SOS solution was used as the mother solution. The preparation involves repeating the same mixture action for two runs. In each run, 0.01 mL of aqueous solution of 25 mL $HAuCl_4 \cdot 3H_2O$ was added to the mother solution. Next, 0.03 mL of aqueous solution of 11 mM NaBH4 was added. Finally, UV-vis absorption spectrum is taken. For the preparation of gold NPs in the pyrene-SOS system, an adequate amount of pyrene was added to a 0.2 M SOS solution with stirring until the pyrene powder was completely dissolved. Then, 5 mL of the solution was used as the mother solution, followed by the same procedure mentioned above in the SOS system. UV-vis absorption spectrum is taken between each run of adding reactants. For the SDeS and SDS systems, the concentrations of the mother solutions were 0.1 M and 20 mM, respectively.

**MEKC Electrophoresis**

All the capillary electrophoresis experiments were carried out on the P/ACE-MDQ Capillary Electrophoresis System (Beckman Coulter Inc., Fullerton, CA) with photodiode-array detector. The 100-μm-i.d. and 365-μm-o.d. fused-silica capillary (Polymicro Technologies, Phoenix, AZ) with 10-cm effective length was used. The components of the separation buffer were 0.1 M SDeS, 10 mM sodium tetraborate and 10 mM sodium dihydrogen phosphate. The sample was hydrodynamically injected into the capillary for 3 s at 0.5 psi. Separations were performed with the anode at the sample injection end by applying an electric field strength of 300 V/cm; the capillary was maintained at 25 ºC.

**Instruments**

The absorption spectra were recorded on a Hitachi model U-3310 UV/Vis scanning spectrophotometer. For transmission electron microscopy (TEM) studies, a drop of gold NPs solution was placed on a carbon-coated copper grid. Specimens were examined on a Jeol JSM-1200EX II transmission electron microscope operating at 80 K eV.

## RESULTS AND DISCUSSION

Fig. 1 is the UV-vis absorption spectra of SOS (0.2 M), SDeS (0.1 M) and SDS (20 mM) solutions after the consecutive 2 runs of adding $HAuCl_4$ and $NaBH_4$. The surface plasmon resonance (SPR) band of gold NPs is clearly discernible at 530 nm. The visible absorption of the gold-SDS colloidal solution (solid line) gives its characteristic pink color. Fig. 2a shows TEM images of gold NPs in the SDS reaction solution. These particles are nearly spherical and have a size from 4 to 10 nm. Compared with the SDS reaction solution, it is apparent in Fig. 1 that gold NPs in the SDeS solution have stronger absorptions between 600 and 700 nm (dashed line). The stronger absorption in the range usually indicates that gold NPs are aggregated. It was confirmed by the TEM images of gold NPs in the SDeS reaction solution, as shown in Fig. 2b. The size of those gold NPs was widely distributed from 5 to 16 nm. On the other hand, although the visible spectrum of the SOS reaction solution (dotted line in Fig. 1) was similar to that of the SDeS reaction solution at first, gold NPs in the former were deposited on the stirring bar later. The absorption spectrum of the SOS reaction solution in Fig. 1 (dotted line) was taken twenty minutes after 2 runs. Fig. 2c shows the TEM images of gold NPs in the SOS reaction solution (Fig. 1, dotted line), indicating the aggregation is much more serious. Most of the particles would eventually be precipitated in the solution. The result shows that gold NPs in the solution could not be effectively stabilized by SOS.

On the other hand, pyrene was solubilized in the micellar solutions to study its influence on the formation of gold NPs. Pyrene was added to the aqueous 0.2 M SOS solution at first, the same procedure of mixing was then fol-

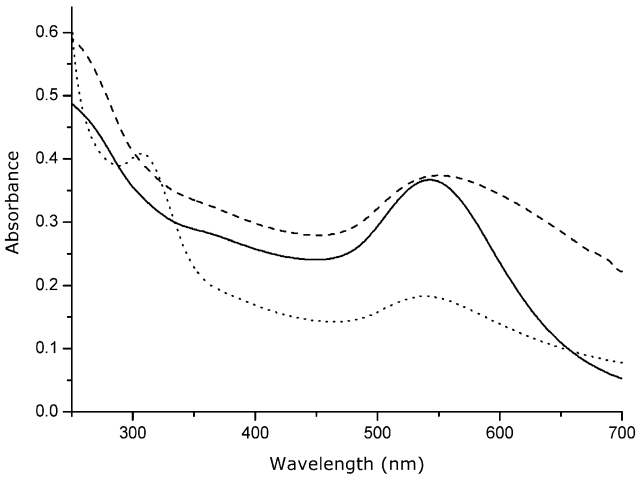



Fig. 1. Absorption spectra of solutions of SOS (dotted line), SDeS (dashed line) and SDS (solid line) after 2 runs.

lowed as in the SOS-only solution. Fig. 3a shows the absorption spectra of the SOS-pyrene reaction solution for the various numbers of runs. Compared with gold NPs prepared in the SOS-only solution (Fig. 1, dotted line), the SPR band of gold NPs in Fig. 3a is very much broader at first (runs 1 and 3). It indicated that the size of the newborn gold NPs was very small. The SPR band gradually appeared after several runs. Fig. 3b shows the TEM images of gold NPs for the sample after 7 runs in Fig. 3a. It is apparent that most gold NPs have a size range from 2 to 7 nm although a few particles have a size more than 10 nm. It is possible that the latter could be formed during the preparation of the gold NP sample on a carbon-coated copper grid for TEM experiments. The result shows that pyrene has the effect of decreasing the size of gold NPs in the SOS micellar solution.

At the same time, similar results were also obtained with the SDeS-pyrene system. The SPR band of gold NPs

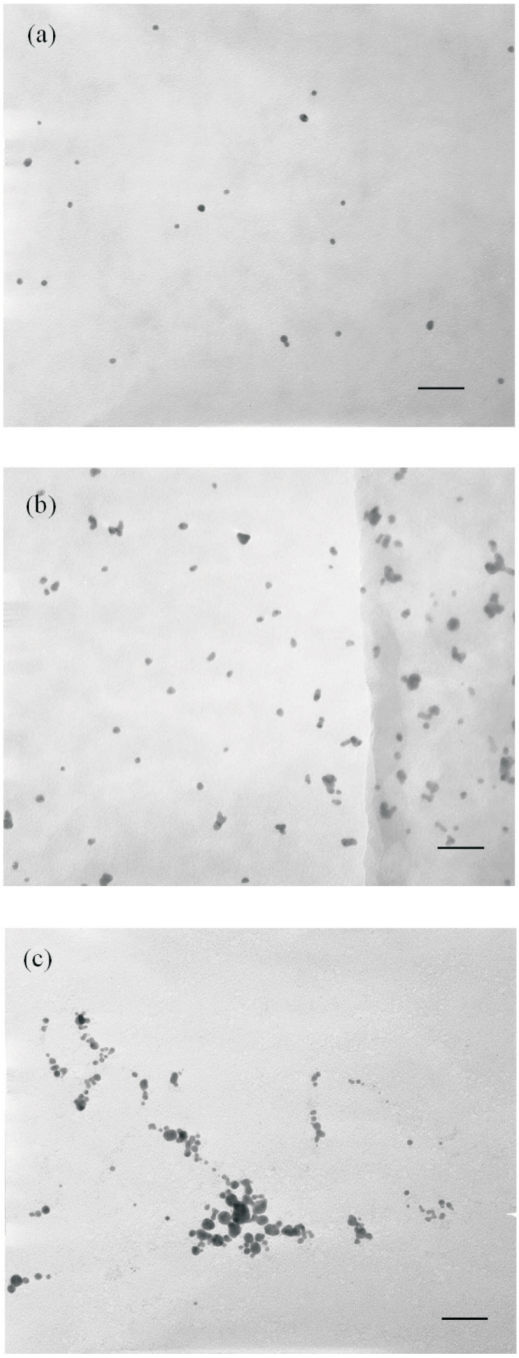
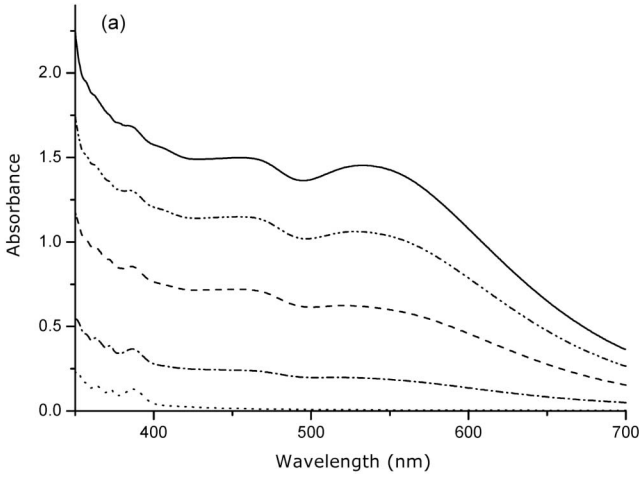



Fig. 2. TEM images of gold NPS prepared in the SDS (a), SDeS (b) and SOS (c) solutions in Fig. 1. The scale bars indicate 50 nm.



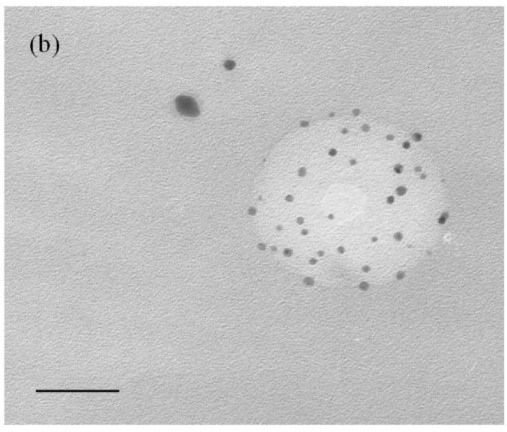




Fig. 3. (a) Absorption spectra of solutions of SOS with pyrene after 7 consecutive runs. The dotted line was obtained before the first run reduction and only the odd number runs are shown: run 1 (dash-dot line), run 3 (dashed line), run 5 (dash-dot-dot line) and run 7 (solid line). (b) TEM images of gold NPs prepared in (a). The scale bars indicate 50 nm.

in Fig. 4a is also broader at first. The major difference in the absorption spectra between Fig. 3a and Fig. 4a is the absence of the two absorption bands at 410 and 470 nm in the SDeS-pyrene reaction solution after 7 runs. In our previous work, it has been shown that the absorption peaks from 400 to 500 nm in the UV-vis spectrum were attributed to the oxidation product of pyrene.[10] Because lots of precipitates were observed in the SDeS-pyrene reaction solution after three runs and then deposited on the wall of the glass container, it is expected that the oxidation product of pyrene was absent from the solution. Fig. 4b shows the TEM images of gold NPs for the above sample in Fig. 4a. The size of the gold NPs prepared in the SDeS-pyrene system was distributed from 3 to 5 nm. Compared with the size distribution in Fig. 3b (SOS-pyrene) and Fig. 4b (SDeS-pyrene), it seems that the dispersity of gold NPs is narrower in the more hydrophobic surfactant. The stronger confinement effect could be observed in the more hydrophobic SDS-pyrene system. Fig. 5 shows the TEM images of gold NPs prepared in the SDS-pyrene reaction solution after 14 runs. The dispersity of those particles which have diameters from 5 to 7 nm was still narrow even after 14 runs reduction.

MEKC can be applied for the characterization of the analytes on the basis of their difference in charge-to-mass ratio, so it was employed to investigate the formation of gold NPs and analyze their size distribution. Fig. 6-1 shows

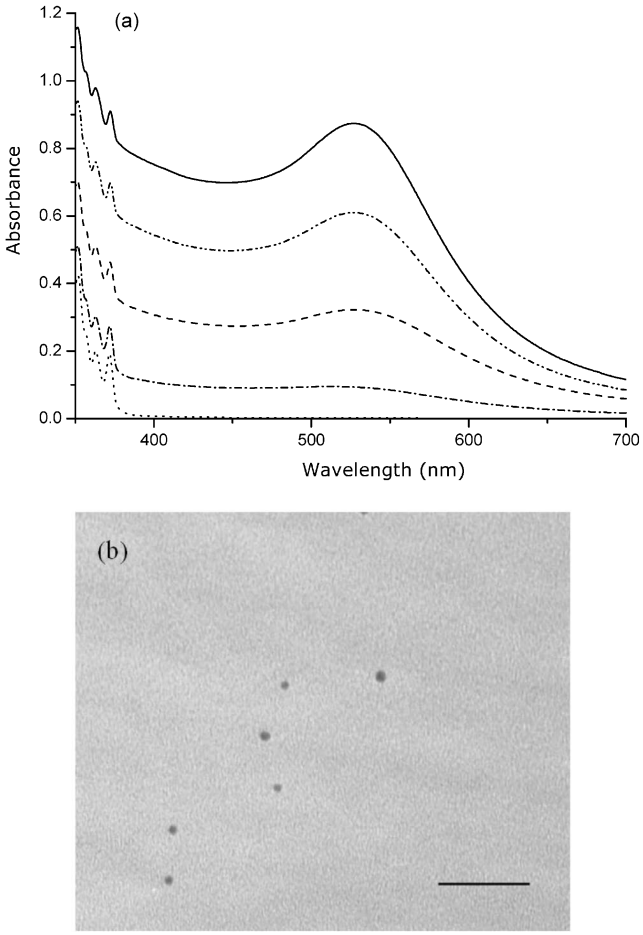



Fig. 4. (a) Absorption spectra of solutions of SDeS with pyrene after 7 consecutive runs. The dotted line was obtained before the first run reduction and only the odd number runs are shown: run 1 (dash-dot line), run 3 (dashed line), run 5 (dash-dot-dot line) and run 7 (solid line). (b) TEM images of gold NPs prepared in (a). The scale bars indicate 50 nm.

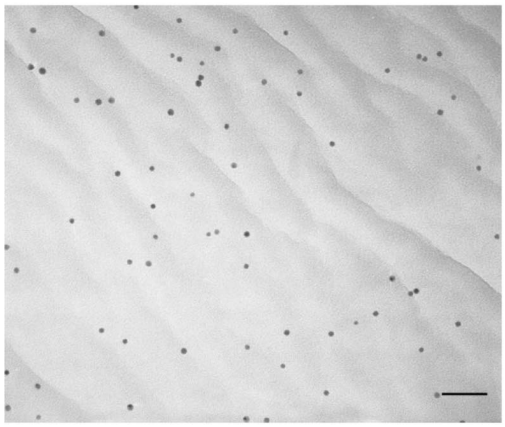


Fig. 5. TEM images of gold NPs prepared in the solution of SDS with pyrene after 14 runs. The scale bars indicate 50 nm.

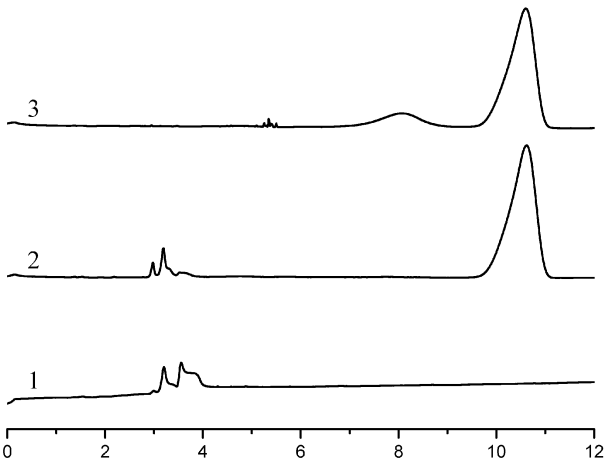



Fig. 6. Electropherograms of the solution of SDeS without (line 1) and with (line 2) pyrene after adding $HAuCl_4$. Line 3 is the electropherogram of the solution of SDeS with pyrene after 7 runs.

the electropherogram of the SDeS solution after adding 70 μL $HAuCl_4$. There were two major peaks with broad shoulders at 3.2 and 3.6 minutes and another smaller peak at 3 minutes. It is known that $HAuCl_4$ in an aqueous solution dissociates into $H^+$ and $[AuCl_4^-]$.[11] The latter was subsequently hydrolyzed into $[AuCl_3(H_2O)]$ and $[AuCl_3(OH)^-]$. Compared with the negative $[AuCl_4^-]$ and $[AuCl_3(OH)^-]$ complexes, the neutral $[AuCl_3(H_2O)]$ complex existed in low abundance. Because the electroosmotic flow (EOF) velocity is high toward the negative electrode (the detection window), the negatively charged complexes having the electrophoretic flow toward the positive electrode are carried toward the neative electrode by EOF, but with a lower velocity than the neutral complex. So, the two major peaks with longer migration time in Fig. 6-1 could be assigned to $[AuCl_4^-]$ and $[AuCl_3(OH)^-]$. The smaller peak at 3 minutes was assigned to $[AuCl_3(H_2O)]$. Therefore, gold NPs were quickly formed when $[AuCl_4^-]$, $[AuCl_3(OH)^-]$ and $NaBH_4$ met in the aqueous phase. Subsequently, the growth of these NPs was terminated by the capping molecules and then stabilized. In our case, the protecting abilities of sodium alkyl sulfates were reduced with the decrease in hydrophobic property. It could be expected that the smallest gold NPs were obtained in the SDS micellar solution (Fig. 2a) because its alkyl chain length is the longest among them, but the aggregates and then precipitates of NPs were formed in the SOS micellar solution (Fig. 2c). Amorphous gold NPs appeared in the case of the intermediate hydrophobic surfactant - SDeS (Fig. 2b).

Fig. 6-2 shows the electropherogram of the SDeS-pyrene solution after adding 70 μL $HAuCl_4$. The ratio of all three gold complexes in Fig. 6-2 was apparently different from that in Fig. 6-1. It suggests that the change could result from chemical reaction between pyrene and gold complexes. Fig. 6-3 shows the electropherogram of gold NPs prepared in the SDeS-pyrene solution in Fig. 4a. The peak at 8 minutes having the absorption band near 520 nm could be assigned to gold NPs. In a previous work, the oxidation of pyrene by the gold complexes gave the products that were subsequently solubilized in the SDS micelles (pyrene $\rightarrow$ pyrene$^+$ + e, $E^\circ$= 1.491 V and $AuCl_4^- + 3\,e \rightarrow Au + 4\,Cl^-$, $E^\circ$ = 1.002 V).[10] But the oxidized products in the SDeS-pyrene solution could not be solubilized and they precipitated out of the solution, so only gold NPs and pyrene were detected in Fig. 6-3. The result is consistent with the absorption spectra in Fig. 4a. At the same time, all the gold complexes were reduced by pyrene and evenly solubilized into the micelles. After adding $NaBH_4$, the newborn small particles could be easily capped and stabilized by the surfactants at the embryonic stage. On the other hand, the intensity of the emission of SDS-pyrene solution was strongly quenched in the fluorescence spectra after the formation of gold NPs, indicating that pyrenes are intimately located on the surface of gold.[10] So, the electrophilic pyrene and its oxidized products on the surface of the newborn gold particles could inhibit further reduction reaction assisted by the gold NPs. The inhibition of growth allows continuous nucleation to form gold NPs with a smaller size. Finally, the narrower size distribution (the inset of Fig. 4) with the symmetrical peak (Fig. 6-3) of gold NPs could be maintained after several runs of reduction. A very broad peak was usually observed for the sample of gold NPs with a wide size distribution. Moreover, it was reported that the effect of the solubilization of pyrene on the critical micelle concentration (CMC) of the surfactants was slight,[12] so the resulting influence on the formation of the smaller gold NPs was insignicant. Based on the size distribution obtained in those three surfactant-pyrene systems (Fig. 5, Fig. 3b and Fig. 4b), it is concluded that SDS with the longest alkyl chain has the best effect in narrowing the size distribution of gold NPs and also decreasing the size of gold NPs.

In conclusion, we used three sodium alkyl sulfates (SOS, SDeS and SDS) to synthesize gold NPs in micellar solutions by chemical reduction. The hydrophobic properties of the three surfactants were reflected in their protecting abilities to stabilize gold NPs. The addition of pyrene in the micellar not only improves the stability of gold NPs, but also results in the formation of gold NPs in smaller sizes and with a narrower size distribution. In particular, the SDS-pyrene system has the best capping effect among them.

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