Novel Effects of Twin-tailed Cationic Surfactants on the Formation of Gold Nanorods

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The effects of using twin-tailed ammonium surfactants with different spacer-chain lengths between their alkyl tails on the formation of gold nanorods (NRs) were studied. The NRs were obtained using considerably lower concentrations of these surfactants than that of the commonly used surfactant $R_{16}Q$.

Synthesis of metal nanoparticles via wet-chemical approaches is one of the promising routes for their cost-effective and large-scale production. As to gold nanoparticles, gold nanorods (NRs)–rod-like gold nanoparticles–have attracted much attention in photonics,[1] analytical chemistry,[2] and so on, because they have unique optical properties which are not expected in spherical particles. Several wet-chemical approaches for the preparation of NRs have been reported, including templating,[3–5] electrochemical,[6,7] seeding,[8–11] and photochemical[12–14] methods. For all except the template method, a large excess of hexadecyltrimethylammonium bromide (CTAB, $R_{16}Q$) is indispensable for the preparation of NRs with high yield. This has led to certain drawbacks, such as the need for troublesome separation procedures (e.g., repeated centrifugation) and the unproductive flocculation of NRs. Therefore, it is desirable that the concentration of surfactants, if used, be as low as possible.

In this paper, we have found novel effects of twin-tailed ammonium surfactants on the formation of NRs, and have synthesized NRs in high yield using very low surfactant concentrations.

The following ammonium surfactants were used in this study: $R_{16}Q$, dimethyldihexadecylammonium bromide ($2R_{16}Q$), 1,2-bis(hexadecyldimethylammonio)ethane dibromide ($2R_{16}enQ$), and bis(2-hexadecyldimethylammonioethyl)methylamine dibromide ($2R_{16}amQ$), and are shown in Figure 1. The formation of NRs using these surfactants was compared under the seed mediated method.[15] A typical procedure was as follows: for the aqueous seed solution, 0.18 mL of an aqueous 0.01 M solution of $HAuCl_4\cdot4H_2O$ was added to 5 mL of a 0.10 M $R_{16}Q$ solution in a glass tube. Next, 0.48 mL of an ice-cold aqueous 0.01 M $NaBH_4$ solution was added all at once, followed by rapid mixing for 2 min. The color of the solution turned from yellow to pale brown, and then finally to pale brownish yellow. Size of seed particles somewhat depended on the surfactants: about 4, 10, 20, and 5 nm for $R_{16}Q$, $2R_{16}Q$, $2R_{16}enQ$, and $2R_{16}amQ$, respectively. The aqueous growth solution was prepared separately as follows: 0.20 mL of 0.01 M $HAuCl_4\cdot4H_2O$ and 0.03 mL of 0.01 M $AgNO_3$ were added into 4.75 mL of aqueous 0.10 M $R_{16}Q$ solution, followed by gentle mixing. The color of the solution at this stage was pale yellow. Next, 32 µL of 0.10 M L-ascorbic acid (AA) was added to the growth solution, which turned colorless upon mixing. Finally, 0.01 mL of the above-described seed solution was added, and the reaction mixture was gently mixed for several seconds and left undisturbed at 25 °C.

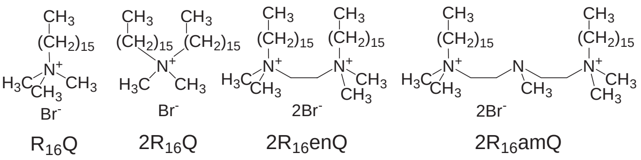

Figure 1. Structures and abbreviations of ammonium surfactants.

Transmission electron microscopy (TEM) observations and UV absorption measurements from the ultraviolet (UV) to the visible (vis) and near-infrared (NIR) regions were carried out by a JEOL JEM-2000FX electron microscope and a conventional JASCO V-530 spectrophotometer, respectively.

The formation of NRs under these various surfactant conditions is summarized in Table 1 and Figure 2. For $R_{16}Q$,

Table 1. Comparison of ammonium surfactants on the formation of NRs

	Surfactant	Conc./mM	cmc/mM	NR formation[a]	Dimension (length × width)/nm	Average aspect ratio	Yield/%
(a)	$R_{16}Q$	100	1.0	○	25 (±5.0) × 6.8 (±1.1)	3.7	99
(b)	$R_{16}Q$	10	1.0	×			
(c)	$2R_{16}Q$	0.1	7.8×10^{-5}[b]	×			
(d)	$2R_{16}enQ$	0.1	2.0×10^{-2}[c]	×			
(e)	$2R_{16}amQ$	10	6.3×10^{-2}	○	31 (±4.8) × 9.9 (±0.58)	3.1	71
(f)	$2R_{16}amQ$	8	6.3×10^{-2}	○	28 (±4.6) × 9.7 (±0.51)	2.9	70
(g)	$2R_{16}amQ$	2.5	6.3×10^{-2}	×			

[a]○: Predominant products were NRs; ×: NRs were hardly detectable (see Fig. 2 for clarification). [b]Ref 16. [c]Ref 17.

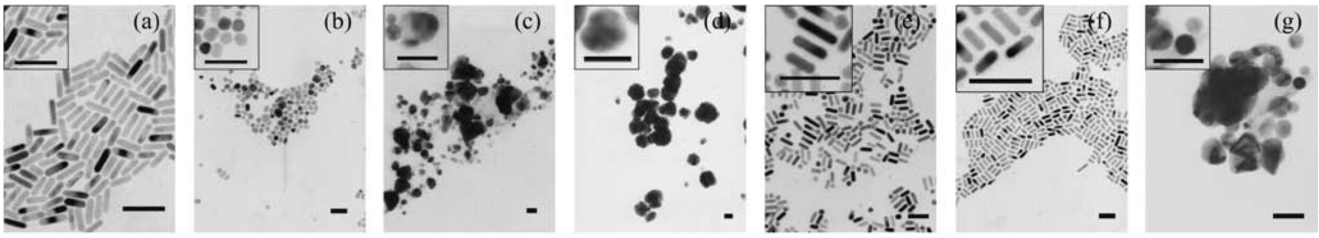

Figure 2. TEM images of gold nanoparticles formed in the presence of various surfactants at different concentrations: (a) 100 mM $R_{16}Q$; (b) 10 mM $R_{16}Q$; (c) 0.1 mM $2R_{16}Q$; (d) 0.1 mM $2R_{16}enQ$; (e) 10 mM $2R_{16}amQ$; (f) 8 mM $2R_{16}amQ$; (g) 2.5 mM $2R_{16}amQ$. See Table 1 for clarification. Insets show respective high-magnification views. All scale bars are 50 nm.

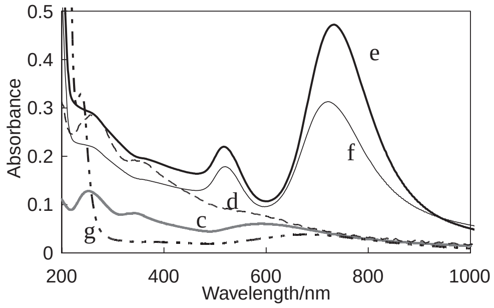

Figure 3. UV–vis–NIR absorption spectroscopy of gold nanoparticles formed in the presence of twin-tailed cationic surfactants: (c) 0.1 mM $2R_{16}Q$; (d) 0.1 mM $2R_{16}enQ$; (e) 10 mM $2R_{16}amQ$; (f) 8 mM $2R_{16}amQ$; (g) 2.5 mM $2R_{16}amQ$ ((c)–(g) here corresponded to images (c)–(g) of Figure 2.)

NR formation was only observed at concentrations higher than the critical micelle concentration (cmc). In this study, we verified that NRs were no longer formed at 10 mM $R_{16}Q$ by the seed method (Figure 2b), in agreement with previous reports.[15] Most importantly, there was a remarkable structural effect on the formation of NRs when using the twin-tailed ammonium surfactants with two hexadecyl groups. If the surfactants acted as templates for NRs, it was expected that they could be prepared at lower concentrations of the twin-tailed surfactants compared with $R_{16}Q$, because the cmc's of the former were considerably lower than that of the single-tailed $R_{16}Q$ (see Table 1).

With this in mind, we first investigated the formation of NRs in the presence of $2R_{16}Q$ or $2R_{16}enQ$. NRs did not form at a concentration of 0.1 mM, which was much higher than the cmc of the former, and close to the cmc of the latter. These surfactants precipitated at concentrations higher than 0.1 mM. However, NRs were obtained in high yield (ca. 70%) using $2R_{16}amQ$ when its concentration was over a hundred-fold higher (8 or 10 mM) than its cmc. However, at concentrations from 8 to 2.5 mM, only spherical nanoparticles were obtained; no NRs were formed. These results suggested that the formation of NRs was substantially influenced by the concentration of the surfactant, even when, for example, the concentration of $2R_{16}enQ$ was up to ten times less than that of $R_{16}Q$. It was not clear at this stage why no NRs formed in the case of $2R_{16}enQ$. Low solubility of $2R_{16}enQ$ may be one of the reasons.

The UV–vis–NIR absorption spectra of the colloidal solutions (Figure 3) were consistent with the TEM observations. The spectra of reaction solutions containing 8 or 10 mM $2R_{16}amQ$ clearly showed a couple of plasmon peaks at around 520 and 730 nm characteristic of NRs in the visible and near-infrared regions, whereas such peaks were not observed in spectra of solutions containing 0.1 mM $2R_{16}Q$, 0.1 mM $2R_{16}enQ$, or 2.5 mM $2R_{16}amQ$.

In summary, we have succeeded in making NRs using the seed mediated synthesis growth method in the presence of a twin-tailed quaternary ammonium compound, $2R_{16}amQ$. NRs were obtained even at concentrations substantially lower than that of $R_{16}Q$ (CTAB). The formation of NRs was profoundly influenced by the concentration of the surfactant, which was used at concentrations higher than its cmc. A quantitative study is under investigation.

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