

## Preparation of Gold Nanoparticles from a Polyelectrolyte Complex Solution of Terthiophene Amphiphiles

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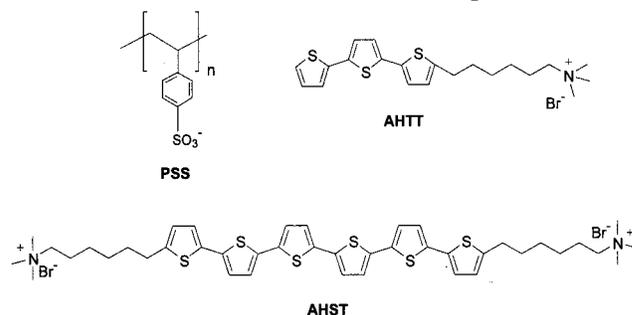
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### Introduction

The synthesis and characterization of gold nanoparticles have attracted great attention due to their potential applications in optoelectronics, electronics, catalysis, and other areas.<sup>1</sup> Gold nanoparticles are commonly prepared from tetrachloroauric acid (HAuCl<sub>4</sub>) as a precursor using various in situ chemical and photochemical reduction methods. For the preparation of gold nanoparticles with small sizes, narrow size distributions, and stability, the use of various stabilizers such as *n*-alkanethiols, *n*-alkylamines, dendrimers, and homopolymers or block copolymers has been extensively studied.<sup>1–8</sup> Stabilization and separation of the particles is often associated with micellar formation and stability in solution. Mayer and Mark<sup>4</sup> suggested that sulfur-containing polymers, especially polythiols, would be of great interest due to the high affinity of the thiol groups for gold surfaces. Also, polymers having pendant reducing groups would be suitable because the additional step of introducing a reducing agent would not be necessary. Hempenius et al.<sup>9</sup> prepared gold nanoparticles inside well-defined polystyrene–oligothiophene–polystyrene triblock copolymer (PS–OT–PS) micelles without the additional step of introducing a separate reducing agent. During stirring of the PS–OT–PS solution in toluene (1 mg/mL) with HAuCl<sub>4</sub>, they observed a rapid color change from red to blue, which they described as evidence for the transport of the gold salt to the thiophene core, followed by an electron transfer from the oligothiophene to the gold salt and the deposition of gold nanoparticles in the core.

Oligothiophenes have attracted much interest as promising organic materials for electronic devices such as light emitting diodes, transistors, and materials for photoelectric conversion.<sup>10–12</sup> Various types of substituted oligothiophene derivatives have been synthesized and charac-

Chart 1. Materials used in the experiment



terized in order to increase their solubility and eventually achieve liquid-phase processibility.<sup>13–16</sup> To create a new type of photo- and electroactive polymers, a novel family of polymers having pendant oligothiophenes with well-defined structures such as terthiophene, quaterthiophene, quinquethiophene, and sexithiophene was synthesized by the Shirota group.<sup>17–22</sup> Their electrochemical doping and dedoping were extensively studied. It is assumed that the redox behavior of these oligothiophenes can be used for the reduction of HAuCl<sub>4</sub> to gold nanoparticles. In this study, we report for the first time the preparation of gold nanoparticles in aqueous solutions using a polyelectrolyte that possesses pendant reducing groups. A polyelectrolyte complex (PEC) with water-soluble terthiophene derivative was used for the reduction of HAuCl<sub>4</sub> to gold nanoparticles.

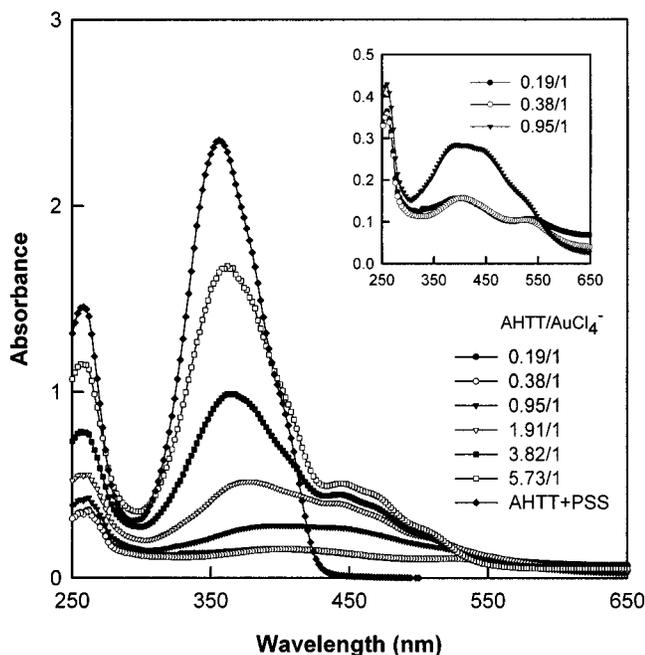
### Experimental Section

All the essential chemicals and reagents were purchased from Aldrich, and all of the reactions were carried out under a nitrogen atmosphere. The structures of the oligothiophene derivatives are presented in Chart 1. 5-(6-Bromohexyl)-2,2':5',2''-terthiophene (BHST) was synthesized according to our previous studies.<sup>24</sup> 5,5''''-Di((6-bromo-hexyl)-2,2':5',2''-terthiophene)-2,2':5',2''-5''',2''''-5''''-sexithiophene (BHST) was synthesized using a Stille coupling reaction. This method has been widely used for the synthesis of other oligothiophene derivatives.<sup>14,25,26</sup> 5-(6-Trimethylamino-hexyl)-2,2':5',2''-terthiophene (AHST) and 5,5''''-di((6-trimethylamino-hexyl)-2,2':5',2''-terthiophene)-2,2':5',2''-5''',2''''-5''''-sexithiophene (AHST) were obtained by an amidation reaction (quaternary amine formation) of BHST and BHST by stirring with an excess of trimethylamine in methanol solution for 2 weeks. UV–vis

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**Figure 1.** UV-vis absorption spectra of the PEC solution for different concentrations of  $\text{HAuCl}_4$ .

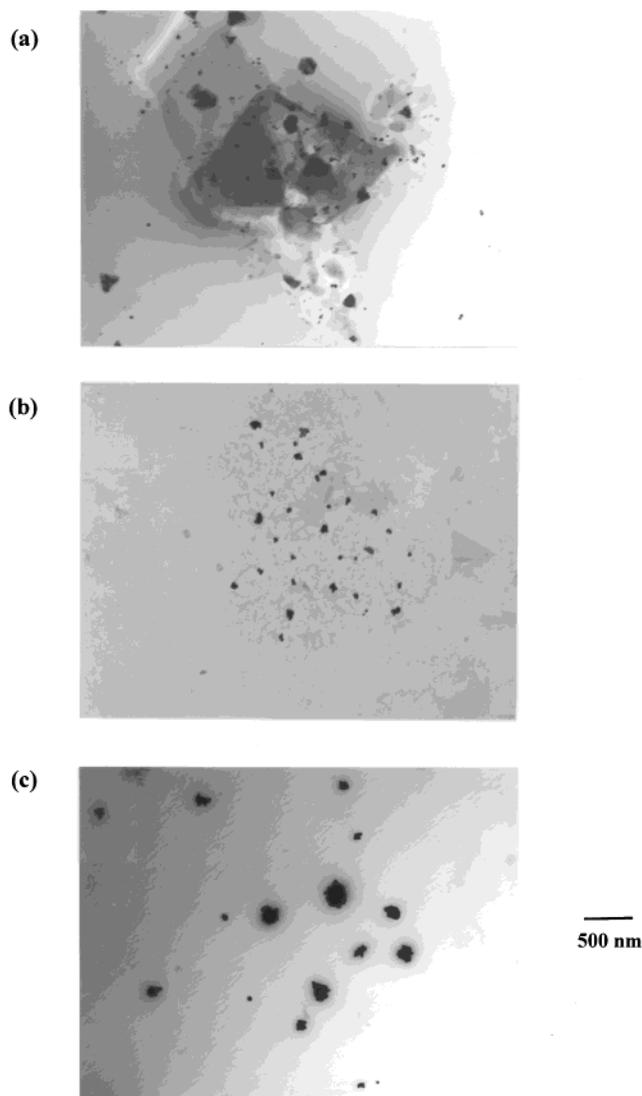
absorption spectra were obtained using a Perkin-Elmer UV-vis spectrometer (Lambda 20). The formation and average particle sizes of gold nanoparticles were determined using a Hitachi transmission electron microscope (TEM) (H-7000).

### Results and Discussion

AHTT was partially soluble in water at room temperature but dissolves well with a solution of poly(sodium 4-styrenesulfonate) (PSS) ( $M_w = 70\,000$ ) (2 mg/mL). The improved solubility of AHTT was due to the formation of a PEC with PSS. More than 40 mol % of the anionic groups in PSS could be complexed to AHTT without precipitation. PECs with various contents of AHTT in PSS solution were prepared to observe the effect of AHTT concentration on the gold nanoparticle formation. Further studies will be made on the interesting PEC behavior of these solutions.

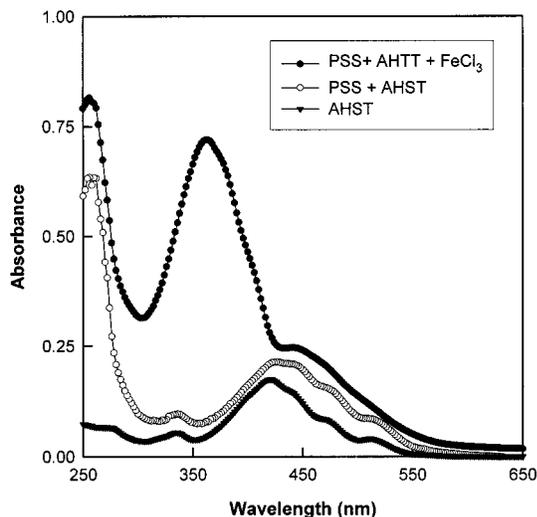
One milliliter of  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  solution ( $1.02 \times 10^{-5}$  mol/mL) was added to 20 mL of PEC solution (2 mg/mL) with vigorous stirring. Upon adding the  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  solution to the PEC solution, the color of the solution changed immediately from yellow to blue. After less than 10 min, the color was blue-black, and after ca. 12 h, a red color appeared. The immediate color change is probably due to the electron transfer from the terthiophene to  $\text{AuCl}_4^-$ . It has been previously reported that vinyl and methacrylate polymers containing pendant oligothiophenes undergo clear color change by the electrochemical oxidation of pendant oligothiophenes.<sup>17-22</sup> Figure 1 shows the UV-vis absorption spectra of PEC solution with different concentrations of  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  after vigorous stirring for 24 h.

The main absorption band observed at 357 nm is attributed to the terthiophene units in the PEC solution. This was confirmed by the absorbance spectra of a solution of 40 mol % anionic groups of PSS complexed with AHTT. The distinct gold surface plasmon peak at around 530 nm is clearly observed at low concentration of AHTT as shown in the inset in Figure 1. These peaks indicate that electron transfer from terthiophene to  $\text{AuCl}_4^-$  occurred which resulted in a slow reduction of  $\text{AuCl}_4^-$  to gold nanoparticles. However, at low concentrations of AHTT, complete reduction of  $\text{AuCl}_4^-$  does not occur.



**Figure 2.** TEM micrographs of gold nanoparticles obtained from different concentrations of  $\text{HAuCl}_4$  in the PEC solution: (a) 0.38/1, (b) 0.95/1, and (c) 5.73/1.

The formation of gold nanoparticles in PEC solution was also confirmed by TEM. Figure 2 shows TEM micrographs at the concentrations of 0.38/1, 0.95/1, and 5.73/1 ( $\text{AHTT}/\text{AuCl}_4^-$ , mol/mol), in which 2, 5, and 30 mol % of anionic groups on the PSS were complexed with AHTT. The size of gold nanoparticles obtained at the concentrations of 0.38/1 is ca. 15 nm, but as the concentration of AHTT increases, the size of the gold nanoparticle increases. The distribution is heterogeneous. Mayer and Mark<sup>4</sup> successfully prepared gold nanoparticles in the presence of protective polymers including PSS. Their results show that PSS is not as effective as other polymers having hydrophobic backbones to stabilize smaller gold nanoparticles. It was reported that the average size of gold nanoparticles is dependent on the interaction between the stabilizer and gold surface rather than its architecture.<sup>4,7,8</sup> We observed that as the concentration of AHTT increases, more  $\text{AuCl}_4^-$  can be reduced to gold nanoparticles, but they are not effectively stabilized by PSS and terthiophenes at this experimental concentration. For future investigations, we plan to investigate polycation complexes with *anionic* terthiophene derivatives. This would be of interest since it could more effectively stabilize gold nanoparticles, which are known to carry a negative surface charge excess. However, the oxidation potential



**Figure 3.** UV-vis absorption spectra of AHST.

of anionic terthiophene derivatives will need to be considered.

Interestingly, new peaks in the range of 430–530 nm ( $\lambda_{\text{max}} = 443$  nm) were observed at higher concentrations of AHST. It is assumed that in this system, sexithiophenes (AHST) can be formed through a coupling reaction via a cation radical mechanism in terthiophenes.<sup>17–23</sup> This reduction–oxidation reaction result is similar to that reported by Selvan et al.<sup>27–29</sup> They prepared nanostructures of gold–polypyrrole composites within the microdomain of a diblock copolymer, in which pyrrole diffused into the core of the micelles where polymerization of pyrrole and generation of gold nanoparticles occurred simultaneously. To explain the new peaks, an excess of  $\text{FeCl}_3$ , which is well-known as an oxidative polymerization reagent for thiophene and alkythiophene,<sup>30</sup> was added into PEC solution and stirred for 24 h to induce coupling. As shown in the UV-vis absorption spectrum in Figure 3, the same peaks in the range of 430–530 nm were

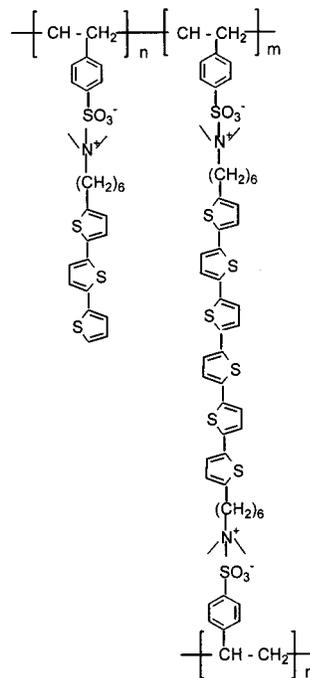
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**Chart 2**



obtained. Furthermore, exactly the same UV-vis absorption peaks were obtained from AHST and its complex with PSS in water, indicating that the new peaks are attributed to AHST formation via an electrochemical coupling reaction of terthiophenes as shown in Chart 2. This interpretation is supported by a report from Ohseido et al.<sup>19</sup> in that the absorption peaks of the pendant terthiophene and sexithiophene were observed in a methacrylate polymer at 375 and 460 nm, respectively.

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