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Redox active gold nanoparticles modified with tetrathiafulvalene derivative via direct sulfur bridge

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Abstract

Preparation and redox properties of a new member of gold nano-particles modified directly with tetrathiafulvalene are reported. The nano-particle is very soluble in CH_2Cl_2 and has shown a preliminary response to the concentration of a small molecule 4-hydroxy-2-mercaptopyrimidine.

Keywords: Gold nanoparticle; Gold colloid; Tetrathiafulvalene; Cyclic voltammogram; Electrochemical response

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Applications of gold colloid or gold nano-particles (AuNPs) have been greatly expanded recently in a new generation of optical and electronic devices [1], as well as in biochemical labels or probes for detection and/or recognition of biomolecules [2]. As typical redox active AuNPs, ferrocenyl (Cp or Cp*) derivative alkanethiol-type AuNPs with variation of the chain length and chain types were studied by several groups [3]. Titration of ATP^{2-} with ferrocenyl-dendronized AuNPs showed response of the CV wave with the change of the concentration of the ATP^{2-} anion [3b]. Similar to Cp groups, tetrathiafulvalene and its derivatives (TTFs) are also one of the well characterized redox active organic systems [4]. For this reason, a TTF derivative gold colloid (TTF–$(CH_2)_n$–S–Au) and the electrochemical properties of this system have been first reported [5]. The colloid contains TTF derivative AuNPs and between the gold substrate and TTF group there is/are long alkyl chain or several methylene spacers. We have recently prepared and characterized new AuNPs modified with tetrathiafulvalene derivative via direct sulfur bridge (C_ETTF–S–Au, where C_ETTF–S– = ethylenedithio TTF thiolate) [6]. The differences of the no-spacer system, compared with the spaced system, have been discussed previously. Electrochemistry of the C_ETTF–S–AuNPs was reported in fixed state (adsorbed on a Pt electrode), however, the electrochemistry of the TTF–S–AuNPs in colloid was not measured for the low solubility of the ethylenedithio group substituted TTF–S–AuNP in organic solvents.

In this manuscript, we report the preparation of new gold nano-particles modified with tetrathiafulvalene derivative having long alkanethiol group at outside: C_8TTF–S–Au (C_8TTF–S– = dioctylthio TTF thiolate) and the TTF moiety connects to the Au surface via direct sulfur bridge. The solubility of the TTF–AuNPs is improved when the alkyl group is lengthened. The electrochemistry and electrochemical response with small molecules in dichloromethane have been studied.

The precursor **1**, 2-[4,5-dioctylsulfanyl-1,3-dithiol-2-ylidene]-4-(2-cyanoethylsulfanyl)-1,3-dithiole (informal name: 3,4-dioctylthio-1-cyanoethylthio-TTF, Scheme 1), a new electron donor of TTF derivative with 2-cyanoethylthio group, was synthesized using a previously

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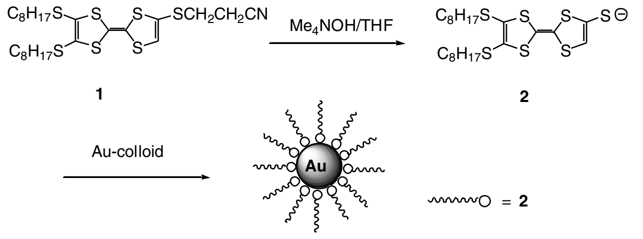

Scheme 1. Preparation of the AuNPs modified with the TTF derivative.

reported method [7,8]. The gold colloid was prepared via chemical reduction of a solution of $HAuCl_4$ in ultra purified water, using the method reported by Natan's group [9]. The preparation of the TTF–S–AuNPs is outlined in Scheme 1 [10]. By removal of the 2-cyanoethyl group from **1**, a mediated anion **2** formed which was stable under argon atmosphere during the experimental period. Subsequently the thiolate **2** was added to an oxygen free gold colloid with vigorous stirring. A stable dark-red **2**-Au colloid (abbreviated as C_8TTF–S–AuNPs) was obtained. The C_8TTF–S–AuNPs in colloid was separated by centrifugation and its IR spectra was measured as KBr pellets. Peaks appear at 1466 cm^{-1}, which is assigned as TTF's C=C vibration, and at 2852, 2923, and 2954 cm^{-1} for the C–H vibrations of the octyl groups. These bands indicate that the TTF derivative has been modified onto the surface of the Au colloid.

The particle size of both the original and modified colloids is about 3–8 nm (average 5 nm) in diameter estimated from TEM micrograph (Fig. 1(a) and (b)). Comparing with the original Au colloid, the TTF modified Au particles are well dispersed. Due to the strong Au–S chemical bonding, the thiolate **2** is a very effective stabilizer that forms an organic layer on nano-Au surface and protects the nano-particles from the aggregation.

UV–vis spectrum of the original Au-colloid in purified water shows the plasmon resonance band at 514 nm. It shifts to about 535 nm for the **2** stabilized nano-particles. The phenomena are similar to that of the C_ETTF–S–Au system we have reported [6], but strong background absorption, gradually increasing from visible range to ultraviolet range, is found for the new colloid (see SI). It must cause from the long alkyl group, since the difference of the TTF compounds used in previous system and this system is only the length of the alkylthio groups.

To strictly study the influences of the length of the alkyl group to the properties of the modified Au colloids, TTF–S–Au colloid with short alkylthio group (MeS–) has also been prepared using the same original gold colloid, abbreviated as C_1TTF–S–AuNPs. Besides the difference in UV–vis spectra, we found that the solubility of these two TTF modified colloids in dichloromethane is completely different. The C_nTTF–S–AuNPs

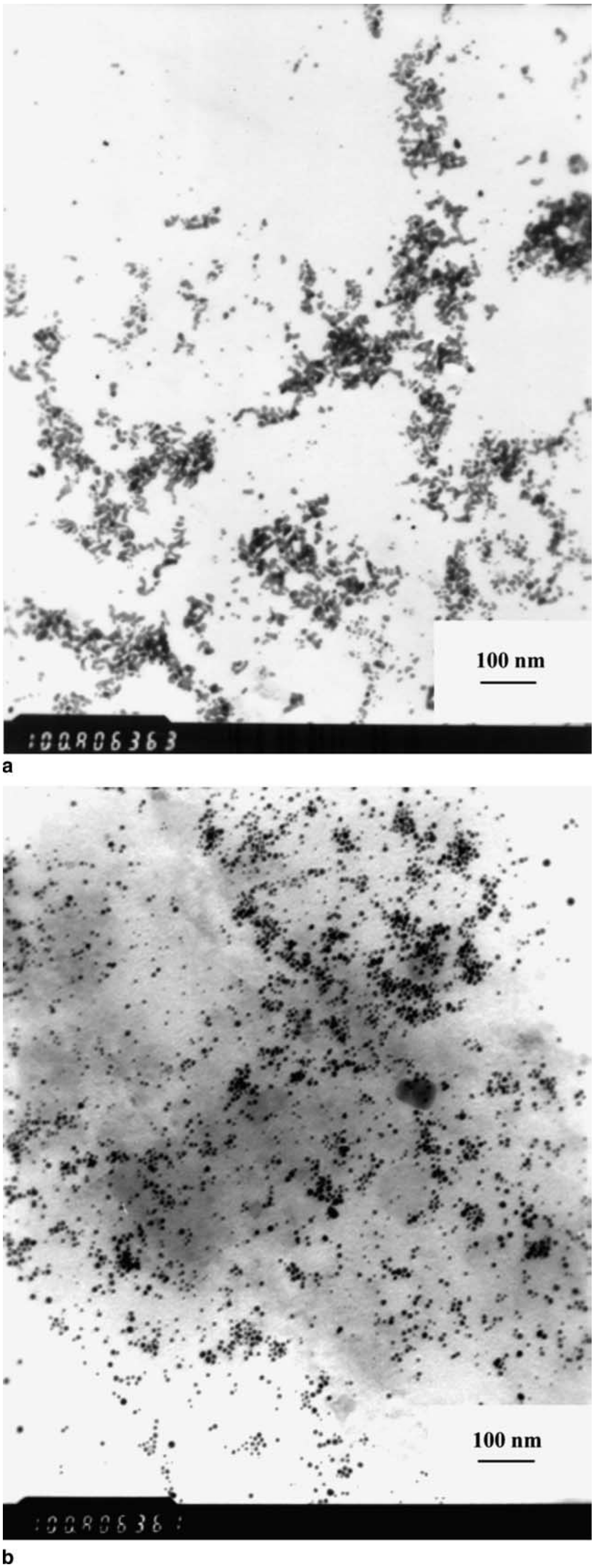

Fig. 1. TEM micrograph of the original AuNPs (a) and **2** stabilized AuNPs (b).