Assembly of Gold Nanoparticles by Quadruple Hydrogen-bonded Ureidopyrimidinone-thiol Dimer as a New Type of Crosslinker

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Quadruple hydrogen-bonded networks between gold nanoparticles and a new ureidopyrimidinone-thiol **1** were constructed and the remarkably stable layered films of redox-active gold nanoparticles crosslinked by **1** were formed on a gold electrode.

There has been a rapidly growing interest in the assembly of metal nanoparticles into self-organized nanoscale architectures.[1] Self-assembly based on the spontaneous control of functionalized gold nanoparticles as building blocks through noncovalent interactions (e.g., hydrogen bonding) provides a powerful method for constructing mesoscopic assemblies.[2] On the other hand, interfacial assembly of gold nanoparticles on metal electrode surfaces is of fundamental technological interest because of their potential in the molecular design of interfacial nanostructure and reactivity.[3] Such assembly of gold nanoparticles on gold electrode has been accomplished by the adsorption of gold nanoparticles on the electrode coated with 2-mercaptoethylamine or dithiols as bifunctional crosslinkers of gold nanoparticles.[3a] Dithiols have also been used for fabricating multidimensional gold nanoparticle assemblies.[4]

Recently, self-assembled supramolecular structures have been constructed via quadruple hydrogen-bonding motif using Meijer's self-complementary 2-ureido-4(1*H*)-pyrimidinones with extremely high dimerization constants.[5] The quadruple hydrogen-bonding motifs lead to an increased stability of such self-assembled dimers relative to those formed from the triple hydrogen-bonding motifs. Although self-assembly of gold nanoparticles through three-point hydrogen-bonded networks has been reported,[2] there is no report concerning assembly of metal nanoparticles mediated by quadruple hydrogen-bonding interaction.

We are investigating the utility of 2-ureido-4(1*H*)-pyrimidinone derivatives as crosslinkers of metal nanoparticles. This paper reports the preparation of the first, noncovalent thiol-dimer system of ureidopyrimidinone-thiol **1**, in which both thiol groups are linked by a self-complementary DDAA (donor–donor–acceptor–acceptor) array of hydrogen bonding and the three-dimensional crosslinked gold nanoparticle aggregates by thiol **1**. We also describe that the redox-active gold nanoparticles assemble with thiol **1** on a gold electrode affording the remarkably stable layered films. The thiol bearing ureidopyrimidinone unit has not been previously reported.

A new thiol **1** was synthesized by the methods as illustrated in Scheme 1.[6,7] The ^{1}H NMR spectrum of thiol **1** in $CDCl_3$ showed the resonances for the four dimer bonding hydrogen atoms of **1** at δ 11.78 (H_b) and δ 10.06 (H_c), a signal at δ 13.09 for the intramolecularly bonded H_a, and one at δ 5.74 for the vinylic proton H_d (Figure 1). This finding is consistent with four DDAA hydrogen bonds in the noncovalent thiol-dimer system.[5]

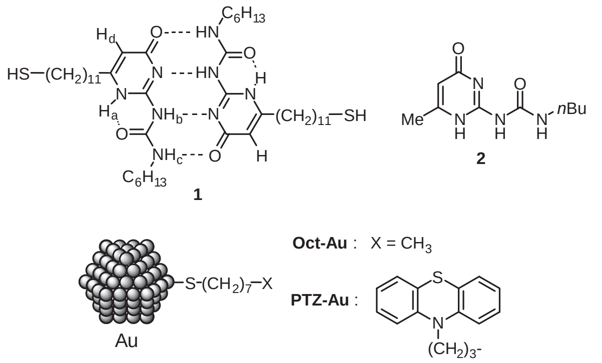
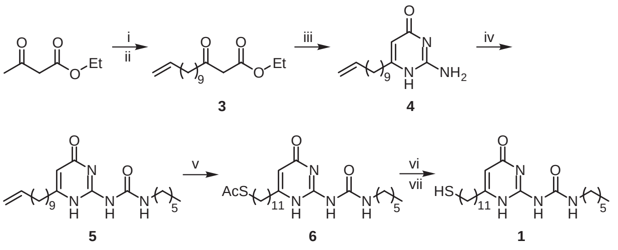


Figure 1. Structure of ureidopyrimidinone-thiol **1** and 2-ureido-4(1*H*)-pyrimidinone derivative **2**. Octanethiol-stabilized gold nanoparticles (Oct–Au) and redox-active phenothiazine-thiol-stabilized gold nanoparticles (PTZ–Au).



Scheme 1. *Reagents*: i, NaH, *n*-BuLi; ii, $CH_2{=}CH{-}(CH_2)_8{-}Br$, THF; iii, $(NH_2)_2CNH$, EtOH; iv, $CH_3{-}(CH_2)_5{-}NCO$, pyridine; v, AIBN, CH_3COSH, benzene; vi, K_2CO_3, EtOH; vii, Zn, CH_3COOH, EtOH.

The assembly of gold nanoparticles with thiol **1** was characterized by transmission electron microscopy (TEM). The size and shape of octanethiolate-stabilized gold nanoparticles, Oct–Au (2.8 ± 0.4 nm), did not depend on addition of 2-ureido-4(1*H*)-pyrimidinone derivative **2** (as shown in Figure 1) without thiol group on a carbon-coated copper TEM grid as evidenced by TEM (Figure 2a).[8] Interestingly, however, Figure 2b shows that the aggregation of Oct–Au ($2\,mg\,mL^{-1}$ in $CHCl_3$) was observed by addition of thiol **1** (0.5 mg). This result indicates that the networked aggregates of the gold nanoparticles were readily formed through quadruple hydrogen bonding of thiol **1**.

In order to confirm interfacial assembly of gold nanoparticles with thiol **1** on a gold electrode, the redox-active phenothiazine ω-functionalized decanethiolate-stabilized gold nanoparticles (PTZ–Au as shown in Figure 1) have been prepared and their electrochemical properties were studied by cyclic voltammetry.[9] The cyclic voltammogram of PTZ–Au in CH_2Cl_2–0.1 M Bu_4NPF_6 at a glassy carbon electrode showed the reversible redox peak due to the phenothiazine oxidation/reduction at

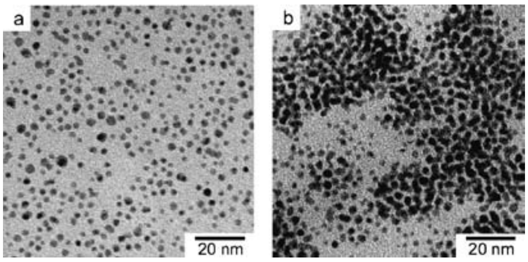


Figure 2. TEM micrographs of (a) Oct–Au and **2**, and (b) the aggregates formed from addition of **1**.

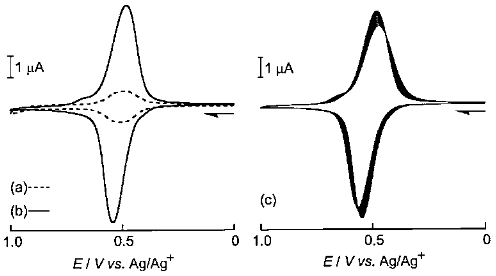


Figure 3. Cyclic voltammograms of (a) the PTZ–Au adsorbed on a gold electrode, (b) the first scan and (c) the multiple scans for the layers of thiol **1**-linked PTZ–Au adsorbed on gold electrode. 0.1 M Bu_4NPF_6–CH_2Cl_2; scan rate 100 mV s^{-1}.

$E_{1/2} = +0.48$ V (vs Ag/0.1 M $AgNO_3$). When a clean gold electrode was immersed for 24 h at room temperature in a solution of PTZ–Au in CH_2Cl_2,[10] rinsed copiously with the same solvent, and inserted into a new CH_2Cl_2–0.1 M Bu_4NPF_6 solution, one reversible wave at $E_{1/2} = +0.51$ V (vs Ag/0.1 M $AgNO_3$) with anodic–cathodic peak separation (ΔE) of 29 mV was observed in the cyclic voltammogram (Figure 3a: dotted line). This result demonstrates that PTZ–Au was slightly adsorbed on gold electrode, however, the PTZ–Au adsorbed on gold electrode was readily desorbed by repeated electrochemical oxidations. In contrast, the layered films of PTZ–Au crosslinked by thiol **1** were remarkably stable under repeated electrochemical cycling (vide infra).

Thiol **1** has been examined to act as a crosslinker for assembling gold nanoparticles on gold electrode. Soaking a gold electrode in a CH_2Cl_2 solution of thiol **1** and PTZ–Au for 24 h at room temperature,[11] followed by copious rinsing in CH_2Cl_2 resulted in the assembly of each PTZ–Au nanoparticle. The cyclic voltammogram for the layers of thiol **1**-linked PTZ–Au adsorbed on a gold electrode in CH_2Cl_2–0.1 M Bu_4NPF_6 displayed one reversible redox peak corresponding to the PTZ–Au at $E_{1/2} = +0.51$ V (vs Ag/0.1 M $AgNO_3$) with peak separation (ΔE) of 61 mV (Figure 3b: solid line). Figure 3b shows that the peak currents were increase compared to those of Figure 3a, which indicates the progressive multilayer growth on the surface of the electrode.[12] The repeated electrochemical cycling of the thiol **1**-linked PTZ–Au films modified gold electrode showed very little diminution of the peak currents due to the PTZ units, indicating that the thiol **1**-linked PTZ–Au films adsorbed on the gold electrode were considerably stable (Figure 3c). Thus, PTZ–Au is strongly immobilized on the electrode surface through quadruple hydrogen-bonding networks.

In summary, we have synthesized the first thiol-dimer linked via quadruple hydrogen bonding and shown that nanoparticle aggregation can be facilitated by thiol **1**, i.e., the thiol **1** works as an effective crosslinker of the gold nanoparticles. The electrochemical study demonstrates the formation of composite layered assemblies of the redox-active gold nanoparticles and thiol **1** on a gold electrode, in which the composite layered films were significantly stable in dichloromethane under repeated potential cycling. Further studies for the nanoparticle assembly and the surface modification with metal nanoparticles based on the quadruple hydrogen-bonding system are in progress.

References and Notes

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7 Thiol **1**: mp. 90.5 °C; FT-IR (cm^{-1}, KBr) 1697, 1664, 1582, 1527; ^{1}H NMR ($CDCl_3$) δ 13.09 (s, 1H, NH), 11.78 (s, 1H, NH), 10.06 (s, 1H, NH), 5.74 (s, 1H, CH), 3.16 (q, 2H, CH_2), 2.44 (q, 2H, CH_2), 2.38 (t, 2H, CH_2), 1.63–1.48 (m, 6H, CH_2), 1.36–1.14 (m, 21H, CH_2, SH), 0.80 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 173.2, 156.6, 154.7, 152.4, 105.8, 40.1, 34.0, 32.7, 31.5, 29.4, 29.3, 29.1, 29.0, 28.8, 28.3, 26.9, 26.6, 24.6, 22.5, 14.0. Exact Mass: Calcd for $C_{22}H_{41}N_4O_2S$: 425.2950. Found: 425.2953.
8 Figure 2a shows the particle size of 2.8 ± 0.4 nm.
9 a) Phenothiazine (PTZ) was chosen in the following reasons. (i) PTZ is known as a good electron-donor. (ii) The electrochemical redox behavior of PTZ is reversible. b) PTZ–Au (2.1 ± 0.4 nm) was prepared from the two-phase reaction of $HAuCl_4$ with sodium borohydride in the presence of the phenothiazinyl-decanethiol.
10 PTZ–Au (5 mg) was dissolved in CH_2Cl_2 (5 mL).
11 PTZ–Au (5 mg) and thiol **1** (2 mg) were dissolved in CH_2Cl_2 (5 mL).
12 The particle aggregates of PTZ–Au with thiol **1** were formed as evidenced by TEM.

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