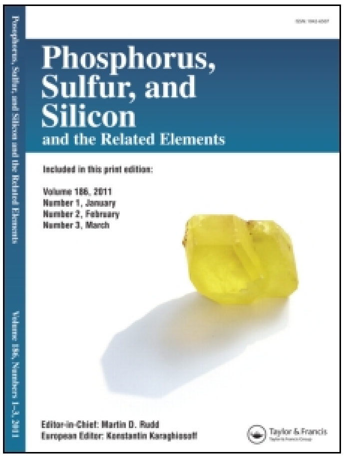

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SELF-ORGANIZATION OF SILSESQUIOXANE-MODIFIED GOLD NANOPARTICLES AND IMMOBILIZATION OF THEIR POLYTHIOPHENE NANOCOMPOSITE FILMS ONTO ELECTRODE SURFACE

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The reduction of tetrachloroaurate with sodium borohydride in the presence of mercaptopropyl-isobutyl-polyhedral oligomeric silsesquioxane (POSS) (1) gave the stable POSS-functionalized gold nanoparticles (POSS-Au). Transmission electron microscopy (TEM) investigation of POSS-Au showed the self-organization of two-dimensional hexagonal packing with a core size of 5.4 nm. The ligand-exchange reaction of POSS-Au with a terthienyldecanethiol (2) having polymerization site led to the new nanocomposite (POSS-TP-Au, core size 4.1 nm), which exhibited a characteristic band at 350 nm due to the terthiophene and a plasmon resonance at 520 nm in the UV-vis spectrum. The novel polythiophene-POSS-Au nanocomposite films were immobilized on metal electrode by electropolymerization of POSS-TP-Au.

Keywords Gold nanoparticle; nanocomposite film; polythiophene; silsesquioxane

INTRODUCTION

The study of metal nanoparticles has received increasing interest in recent years because of their unique optical, electronic, and catalytic properties.[1] A number of gold nanoparticles containing functional units have been synthesized.[2,3] Functionalization of the gold nanoparticles with self-assembled monolayers provides a method for introducing diverse functionality to the nanoparticle surface. Monolayer-functionalized nanoparticles that act as building blocks have been fabricated into ordered architectures. An intriguing further development in this area involves the attachment of electropolymerizable groups at the periphery of metal nanoparticles taking advantage of the electropolymerization process to prepare electrodes modified by electroactive poly(metal nanoparticles). Electrochemical polymerization is an elegant strategy for the immobilization of redox-active groups on the

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surface of electrodes and the preparation of conductive polymer thin films.[4] The surface modification of electrodes with electroactive polymer-metal nanoparticle films has been performed from the electrochemical polymerization of pyrrole-modified gold nanoparticles.[5] However, the literature on polymer thin films of metal nanoparticles by the electropolymerization method is quite limited.[6] There has been a rapidly growing interest in the fabrication of thin films of metal nanoparticles from both a fundamental and a practical application point of view.[7]

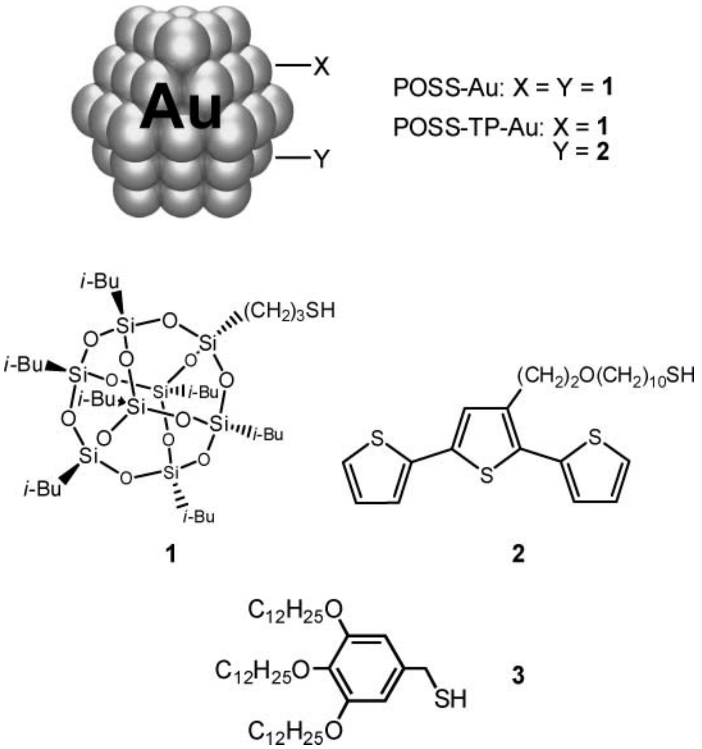
Currently, much attention has been paid to the construction of organic–inorganic nanocomposites based on polyhedral oligomeric silsesquioxane (POSS) as a nanoscale molecular building block (~1.5 nm diameter).[8] Their POSS nanocomposites exhibit improved oxidative and thermal stability, and potential application in a variety of areas, including optoelectronics, sensing, and catalysis.[9] An interesting aspect of POSS derivatives is their strong tendency to crystallize into two-dimensional structure, making them potential "recognition elements" for nanostructured assembly processes.[9c] Although a number of organic–inorganic nanocomposites bearing POSS units have been reported,[9] thus far reports on the synthesis of silsesquioxane-modified gold nanoparticles are quite limited. As such an example, Schmid et al. reported the synthesis of POSS-modified gold nanoparticles from the ligand-exchange reaction of $(PPh_3)_{12}Au_{55}Cl_6$ with a thiol, $(cyclopentyl)_7Si_8O_{12}(CH_2)_3SH$.[10] Interestingly, however, we have succeeded in facile preparation of POSS-functionalized gold nanoparticles (POSS-Au) by a reduction of tetrachloroaurate with sodium borohydride in the presence of a silsesquioxane-thiol (**1**). The ligand-exchange reaction of POSS-Au nanoparticles with a terthienyldecanethiol (**2**) having an electropolymerizable group led to the formation of the terthiophene-functionalized POSS-Au nanocomposites (POSS-TP-Au), which were immobilized on surfaces of metal electrodes by the electropolymerization. This article presents the preparation and self-organization of the POSS-functionalized gold nanoparticles (POSS-Au), and their new electropolymerized conductive polythiophene-gold nanocomposite films containing POSS function (Scheme 1).

RESULTS AND DISCUSSION

POSS-functionalized gold nanoparticles (POSS-Au) were prepared by the reduction of $HAuCl_4$ with $NaBH_4$ in the presence of the thiol **1** and repeatedly isolated from and redissolved in organic solvents (*n*-hexane, benzene, toluene, CH_2Cl_2, $CHCl_3$, THF, diethyl ether, and ethyl acetate) and were extremely stable. Alternatively, Schmid et al. obtained gold nanoparticles having silsesquioxane (POSS) units by a ligand-exchange reaction of triphenylphosphine-stabilized gold nanoparticles, $(PPh_3)_{12}Au_{55}Cl_6$, with a silsesquioxanethiol, $(cyclopentyl)_7Si_8O_{12}(CH_2)_3SH$.[10]

The UV-vis spectrum of the POSS-Au nanoparticles solution in CH_2Cl_2 exhibited a plasmon resonance at 520 nm (Figure 1a). The X-ray photoelectron spectroscopy (XPS) spectrum of POSS-Au showed the Au 4f binding energies at 83.8 and 87.5 eV. There was a feature at 102.6 eV due to Si 2p, 284.8 eV due to C 1s, and 532.6 eV due to O 1s.

The size, shape, and dispersity of POSS-Au were determined with transmission electron microscopy (TEM). POSS-Au was redissolved in CH_2Cl_2 (1 mg mL^{-1}), and a drop of the resulting dispersion was placed on a carbon-coated copper grid; its micrograph reveals the formation of dispersed particles with diameter of 5.4 ± 0.6 nm (Figure 2). Significantly, the TEM picture shows a remarkable degree of self-ordering into regular



Scheme 1

arrays. Such self-organization is reflected by large domains of long-range, two-dimensional ordered arrays with a hexagon-type arrangement. The spacing (edge-to-edge distance) of the particles is about 2.1 nm. This distance is close to twice the distance (1.1 nm) of the thiol **1**. It is presumed that the POSS–POSS packing interactions[9c] contribute to the self-organization of POSS-Au. Similar organization of metal nanoparticles was observed in the TEM micrograph of thiol **3**-stabilized gold nanoparticles (**3**-Au). Figure 3 shows that the

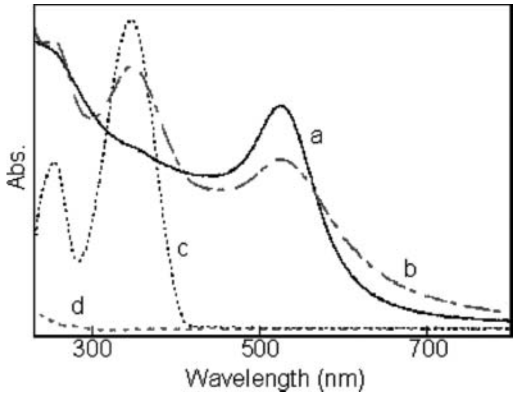


Figure 1 UV-vis spectra of (a) POSS-Au, (b) POSS-TP-Au, (c) thiol **2**, and (d) thiol **1** in CH_2Cl_2.

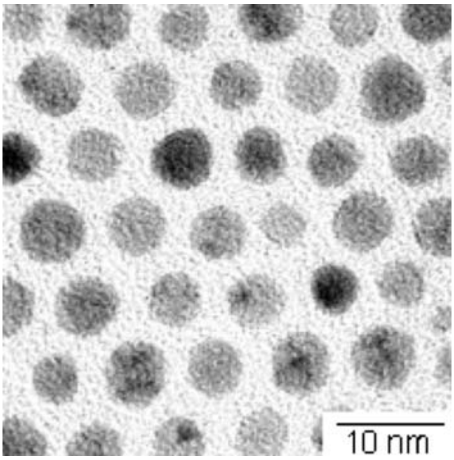


Figure 2 TEM micrograph of POSS-Au.

core size of **3**-Au is 2.2 ± 0.5 nm. The interparticle edge-to-edge distance of the particles is about 2.5 nm, which is somewhat longer than the distance (2.0 nm) of the thiol **3** calculated from a MOPAC simulation. These findings indicate that the shape of metal nanoparticles can be controlled by the nature of protective ligands such as thiols.

Meanwhile, there has been a remarkable increase in interest in the preparation and property of thin films based on polysilsesquioxanes,[11] but there is no report concerning the preparation of polymer films of metal nanoparticles containing silsesquioxane. In order to prepare a new type of polymer films based on silsesquioxane–metal nanocomposite, the POSS-Au bearing terthiophene as a electropolymerization site (POSS-TP-Au) has been prepared by the ligand-exchange reaction of POSS-Au with a terthienylthiol **2**. The UV-vis spectrum of POSS-TP-Au in CH_2Cl_2 showed a characteristic peak at 350 nm due to the terthiophene and significant plasmon resonance at 520 nm (Figure 1b). The TEM micrograph of POSS-TP-Au reveals the core size of 4.1 ± 1.0 nm. The XPS spectrum of

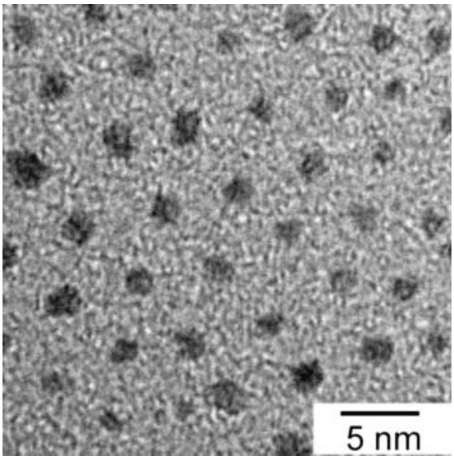


Figure 3 TEM micrograph of **3**-Au.

POSS-TP-Au exhibits 83.8 eV and 87.5 eV for Au, 102.4 eV for Si2p, 163.5 eV for S2p, 285.1 eV for C1s, and 532.7 eV for O1s.

The electrochemical property of POSS-TP-Au was examined by cyclic voltammetry. The first scan of the cyclic voltammogram (CV) of POSS-TP-Au in CH_2Cl_2–0.1 M Bu_4NPF_6 at a glassy carbon (GC) electrode showed one irreversible oxidation peak at $E\text{p} = +0.74$ V (vs. Ag/Ag^+) due to oxidation of the terthiophene group (Figure 4a). The continuous cycling of the potential at the oxidation peak developed the redox response of the polymer growing on the electrode. After ten scans, the electrode was rinsed copiously with solvent and dipped into fresh CH_2Cl_2 solution. The CV of the poly(POSS-TP-Au nanoparticle) films-modified electrode is shown in Figure 4b. The XPS spectrum of poly(POSS-TP-Au nanoparticle) films showed the Au 4f binding energies at 83.7 and 87.4 eV, corresponding to the Au° state. There was a feature at 102.5 eV for Si2p, 163.4 eV due to S 2p, 284.0 eV due to C 1s, and 532.7 eV due to O 1s. Thus, conductive polythiophene metal nanoparticle films bearing cubic silsesquioxane are readily immobilized on metal electrode surface by electrodeposition. This finding indicates the possibility for the immobilization of metal nanoparticles having several kinds of functional molecules on the

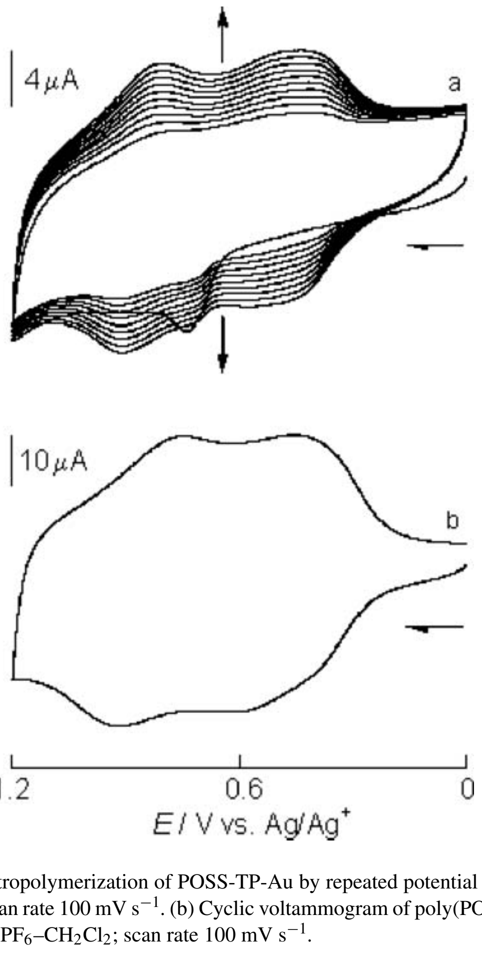


Figure 4 (a) Oxidative electropolymerization of POSS-TP-Au by repeated potential scans on a GC electrode in 0.1 M Bu_4NPF_6–CH_2Cl_2; scan rate 100 mV s^{-1}. (b) Cyclic voltammogram of poly(POSS-TP-Au) films-modified GC electrode in 0.1 M Bu_4NPF_6–CH_2Cl_2; scan rate 100 mV s^{-1}.

metal electrode surface. To our knowledge, this is the first example for the polythiophene nanocomposite films containing silsesquioxane and metal nanoparticles.

CONCLUSION

We have demonstrated that the reduction of Au(III) compound in the presence of the POSS thiol results in the formation of POSS-thiolate-protected gold nanoparticles (POSS-Au), which are converted into the terthiophene-functionalized POSS gold nanoparticles (POSS-TP-Au) by the ligand-exchange reaction of POSS-Au with a terthienyldecanethiol. Thus the ligand-exchange reaction of POSS-Au having a nanoscale molecule such as POSS unit can be achieved without decomposition of the nanoparticles. The POSS-Au nanoparticles show a characteristic property of self-organization assembly of nanoparticles as evidenced from the TEM measurement. The POSS-TP-Au bearing an electropolymerizable site provides a new type of poly(metal nanocomposite)films-modified electrode. Such conductive polythiophene hybrid nanocomposite films are of special interest, as they have applications to sensor devices, catalysis, and nanoelectronics.

EXPERIMENTAL

All reagents were purchased from Wako Pure Chemical Industries Ltd., Tokyo Kasei Co. Ltd., Fluka Chemical Co., or Aldrich Chemical Co. The reagents used as reaction solvents were further purified by general methods.

NMR spectra were recorded on a JEOL GSX270 and JEOL GSX500 (270 MHz and 500 MHz) spectrometer. UV-vis spectra were measured with a Hitachi U-4000. Mass spectra were recorded on a JEOL JMS-700. Fourier transform infrared (FT-IR) spectra were collected with a JASCO FT-IR-470. Transmission electron microscopy (TEM) measurements were performed on a JEOL JEM-3010.

Cyclic voltammetry was performed at room temperature using a BAS Instrument model 100B/W electrochemical workstation. Platinum wire was used as the counter electrode, and glassy carbon (3.0 mm diameter) was used as the working electrode in a one-compartment cell. Potentials were relative to the system Ag/0.1 M $AgNO_3$ in acetonitrile. Bu_4NPF_6 (Fluka, electrochemical grade) and CH_2Cl_2 (Wako, anhydrous) were used for the preparation of electrolyte solutions.

Preparation of POSS-Au

To a vigorously stirred solution of tetraoctylammonium bromide (1.09 g, 2.0 mmol), $HAuCl_4.4H_2O$ (186 mg, 0.46 mmol) in deionized water (15 mL) in toluene (20 mL) was added. A solution of thiol **1** (370 mg, 0.42 mmol) in 20 mL of toluene was added, and the resulting solution was stirred for 20 min at room temperature. $NaBH_4$ (190 mg, 5 mmol) in deionized water (12 mL) was then added. The mixture was stirred for 3 h at room temperature. After stirring, the organic phase was evaporated to 5 mL in vacuo and mixed with MeCN (200 mL). The resulting precipitate was collected by filtration and washed serially with MeCN. The nanoparticles were redissolved in toluene to purify and precipitated with MeCN, and then the particles were isolated by filtration (yield of POSS-Au: 360 mg). These processes were repeated until no free thiol or phase transfer catalyst remained, as detected by TLC and ^1H and ^{13}C NMR spectroscopy.

Preparation of POSS-TP-Au

The ligand-exchange reaction of POSS-Au with a terthienylthiol **2**[12] was carried out as follows. A mixture of POSS-Au nanoparticles (81 mg) and thiol **2** (160 mg) in toluene (2 mL) was stirred at room temperature for 48 h. To the mixture MeCN (100 mL) was added, and then the resulting precipitate was collected by filtration and washed serially with MeCN. The nanoparticles were redissolved in toluene to purify and precipitated with MeCN, and then the particles were isolated by filtration (yield of POSS-TP-Au: 70 mg).

Preparation of 3-Au

To a vigorously stirred solution of tetraoctylammonium bromide (1.10 g, 2.00 mmol) in deionized water (15 mL), $HAuCl_4.4H_2O$ (191 mg, 0.46 mmol) in toluene (35 mL) was added. A solution of a thiol **3**[13] (280 mg, 0.42 mmol) in 5 mL of toluene was added, and the resulting solution was stirred for 15 min at room temperature. $NaBH_4$ (190 mg, 5.02 mmol) in deionized water (12 mL) was then added. The mixture was stirred for 2 h at room temperature. After stirring, the organic phase was evaporated to 20 mL in vacuo and mixed with EtOH (200 mL). The resulting precipitate was collected by filtration and washed serially with EtOH. The nanoparticles were redissolved in toluene to purify and precipitated with EtOH, and then the particles were isolated by filtration (yield of **3**-Au: 164 mg). These processes were repeated until no free thiol or phase transfer catalyst remained, as detected by TLC and ^1H and ^{13}C NMR spectroscopy.

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