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Preparation of Polymer Composites Containing Gold Nanonetworks Using an Amphiphilic Poly(oxyethylene) Brush

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Abstract: We synthesized gold nanonetwork using the amphiphilic polymer brush, poly(oxyethylene) containing decyltri(oxyethylene)thiomethyl ($C_{10}H_{21}(OCH_2CH_2)_3SCH_2$-) side groups, as a stabilizer and/or a template. When tetrabutylammonium borohydride solution in THF was added to a mixture solution of the polymer and $LiAuCl_4$ in THF, 0-D gold nanomaterials were obtained. However, when an aqueous solution of sodium borohydride was added, gold nanonetworks were synthesized. The composites composed of polymer/0-D gold nanomaterials and polymer/gold nanonetworks showed electrical conductivities of $\sim 10^{-9}$ and $\sim 10^{-3}$ S/cm, respectively, which indicated that the gold nanonetworks increased the electrical conductivity.

Keywords: amphiphilic polymer, electric conductivity, gold, composites, nanonetworks.

Introduction

Amphiphilic organic compounds having mesophases in solution or bulk states have been used as templates for the formation of nano-sized materials.[1,2] In particular, amphiphilic polymer brushes are useful for the formation of one-dimensional (1-D) metal and semiconductor nanostructures because metallic ionic precursors are preferentially located in the nano-sized hydrophilic region (usually core part), and the subsequent reduction of the precursors produces nanomaterials with different sized nanorods and nanowires.[3] However, only a few reports on the preparation of the amphiphilic polymer brushes have been made, probably because the synthetic methods involved are normally tedious, with the amphiphilic side chains of the polymer brushes being made using living polymerization techniques, such as atom transfer radical polymerization.[4-6] Previously we reported that the synthesis of amphiphilic comb-like poly(oxyethylene) having decyltri(oxyethylene) side groups (D3OTP) using a relatively easy synthetic procedure including a polymer analogous reaction.[7] D3OTP itself did not show any mesophases; however, when $LiClO_4$ was added to the polymer, a supramolecular layered structure where the polar inorganic salts are located in the hydrophilic backbone region with a *d*-spacing of 2 nm was obtained. In this paper, we report the preparation of gold nanomaterials with zero-dimensional (0-D) nanoparticles and one-dimensional nanocurves and nanonetworks from a mixture of D3OTP and $LiAuCl_4$, gold precursor, in solution via a chemical reduction method using the amphiphilic comb-like polymers as a stabilizing agent and/or a template.

Experimental

Materials. All reagents were purchased from Aldrich. Tetrahydrofuran (THF) was dried by refluxing it with sodium and benzophenone followed by distillation to obtain anhydrous THF. Since the amount of water affects the shapes or morphologies of gold nanomaterials, the anhydrous THF was intentionally used in this experiment. All other reagents and solvents were used as received. Following procedure was used to synthesize D3OTP. Simply, 1-bromodecane (11.1 g, 50 mmol) was added dropwise at 0 °C to a stirred mixture of triethylene glycol (7.50 g, 50 mmol) and sodium hydride (1.20 g, 50 mmol) in *N,N*-dimethylacetamide (DMAc). Decyltri(oxyethylene) was obtained followed by extraction with methylene chloride and 0.5 N aqueous HCl. After the mesylation of decyltri(oxyethylene) (2.90 g, 10 mmol) using triethylamine (2.09 mL, 15 mmol) and methanesulfonyl chloride (1.08 mL, 14 mmol), decyltri(oxyethylene) thioacetate was obtained by substitution reaction with potassium thioacetate (2.29 g, 20 mmol). Decyltri(oxyethylene) thioacetate (1.74 g 5 mmol) was added to a mixture of sodium (104 mg, 4.5 mmol) and ethanol (10 mL). After 30 min stirring at room temperature and evaporating the solvent, a solution of poly(epichlorohydrin) (0.23 g, 2.5 mmol) in 25 mL of DMAc was added quickly. The reaction mixture was stirred at 70 °C for 30 min and then poured into distilled water. The more

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*Corresponding Author. E-mail: jongchan@snu.ac.kr detailed synthetic procedures and characterizations including ^1H NMR, ^{13}C NMR, and FT-IR results of D3OTP were reported before.[7]

Characterization. ^1H NMR spectra were obtained on a JEOL JNM-LA 300 spectrometer at 300 MHz. UV visible spectra were obtained on a Perkin Elmer Lambda 20 UV-visible spectrometer. Gold nanoparticles were imaged using transmission electron microscopy (JEOL JEM-200CX). For TEM measurements, the purified products were re-dissolved in THF and then a few droplets of the solutions were dropped onto carbon-coated copper grids. Thermal gravimetric analyses were performed on a TA TGA 2050 at a heating rate of 10 °C/min. The electric conductivities of the composites were measured by the conventional two-probe method. The two-probe cell having the electrode coated by the completely dried composites was connected with a computer-controlled Keithley 2400 digital source meter unit at room temperature. To examine the reasonable results for electric conductivities of the composites, 10 times measurements were performed, and similar values were obtained in every case, respectively.

Preparation of 0-D and 1-D Gold Nanomaterials in D3OTP. To a vial containing 36.5 mg of D3OTP (0.1 mmol) in THF (10 mL), 13.8 mg (0.04 mmol) of $LiAuCl_4$ were added. After stirred vigorously for 1 h, a solution composed of D3OTP and $LiAuCl_4$ (Au(III)@D3OTP) was obtained and used for the reduction. Sodium borohydride ($NaBH_4$) and tetrabutylammonium borohydride (TBABH) were used as reductants in the preparation of the gold nanomaterials. $NaBH_4$ (15.1 mg, 0.4 mmol) and TBABH (103 mg, 0.4 mmol) were dissolved in H_2O (0.3 and 2 mL) and THF (2 mL), respectively, before use. When the $NaBH_4$ solution in 2 mL of H_2O was added to the THF solution (10 mL) of Au(III) @D3OTP with vigorous stirring, the mixture briefly turned black, then within a few seconds, a black precipitate was obtained. The precipitate was purified by repetitive precipitation in methanol. When TBABH/THF solution and $NaBH_4$ solution in 0.3 mL of H_2O was added to the THF solution (10 mL) of Au(III)@D3OTP, the solution color changed instantly to wine red and black, respectively, with no precipitation being observed. The solution was then concentrated (< 2 mL) using an evaporator, and distilled water was added to the solution to give precipitated mixtures of polymer and nanomaterials. The mixtures were purified by re-precipitation several times in methanol.

Results and Discussion

The amphiphilic core-shell polymer, poly[oxy(decyltri-(oxyethylene)thiomethyl)ethylene] (D3OTP) was synthesized via a polymer analogous reaction from poly(epichlorohydrin).[7] The number average molecular weight (M_n) and the polydispersity index (M_w/M_n) of D3OTP calculated using polystyrene standards by gel permeation chromatography (GPC) were 156,000 g/mol and 1.65, respectively. Theoretically, it is well-known that the comb-like polymer has a more compact hydrodynamic volume compared with that of corresponding linear polymer having identical molecular weight.[8,9] Therefore, M_n of D3OTP obtained from GPC calibrated with linear polystyrene standards might be lower than true molecular weight of D3OTP. Since the sulfide group ($-CH_2-S-CH_2-$) which is located in the hydrophilic core region of D3OTP has an affinity to gold,[10] this polymer should have the ability to stabilize gold nanomaterials.

The complex of D3OTP and $LiAuCl_4$ was prepared by adding 0.04 mmol of $LiAuCl_4$ into the 0.1 mmol of D3OTP in THF (10 mL). Since there are four oxygen atoms in a repeating unit in D3OTP, the $[Au^{3+}]/[O]$ ratio was 0.1 and there is one gold atom per 2.5 repeating units of polymer. This complex was named as Au(III)@D3OTP, where 'III' designates the oxidation number of the gold ion, 3. Comparing the ^1H nuclear magnetic resonance (^1H NMR) spectrum of Au(III)@D3OTP with that of D3OTP, all the signals except the resonances of the protons ($-CH_2-S-CH_2-$, c and d) on the α-carbons to the sulfur are identical in terms of chemical shift and integration within experimental error as shown in Figure 1. The relatively sharp peaks from the α-protons of D3OTP at around 2.7 ppm changed to two new broad peaks shown at around 2.8 and 3.3 ppm when the gold salt is complexed. It has been known that chemical shift and intensity of the α-proton resonance change when metals are coordinated with the sulfur group.[11,12] Therefore, it is probable that the core-shell structure of the Au(III)@D3OTP is formed, where gold salt ($AuCl_4^-$) is located near to the sulfide group in the polymer core part in the THF solution as a complex form. Previously, we found that the hydrophilic core part of D3OTP could be complexed with metallic salt to form thermotropic liquid crystalline phases as mentioned in the introduction part.[7] Similarly, it was also reported that the lyotropic liquid crystalline phases could be obtained from

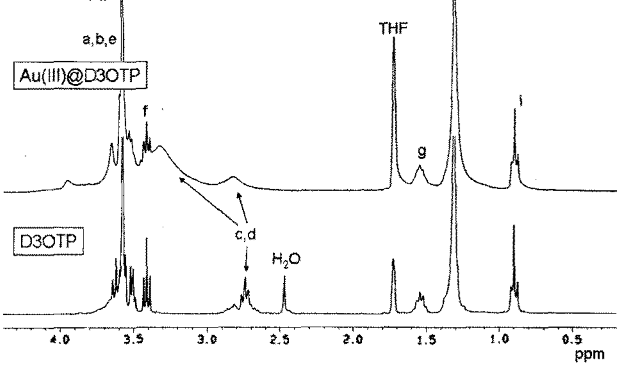

Figure 1. ^1H NMR spectra of D3OTP and Au(III)@D3OTP in THF-d_8.

the mixtures of nonionic surfactants that have oligo(oxyethylene) units and transition metal salts through the interactions between the oxyethylene units and the metallic salts.[13,14] We attempted to observe core-shell structures of the D3OTP and Au(III)@D3OTP using atomic force microscopy (AFM) as others.[15,16] Unfortunately, we could not get such images from AFM probably due to the very small dimension (2-3 nm) (in a height mode) and the indistinguishable morphologies of the hydrophilic oxyethylene and hydrophobic (alkyl groups) regions (in a phase mode) with the resolution of our AFM equipment. Further AFM studies of the polymer and the complex are being conducted.

Tetrabutylammonium borohydride (TBABH) solution in THF and sodium borohydride ($NaBH_4$) solution in H_2O were used to reduce the Au(III)@D3OTP. When the TBABH/THF (10 equivalent to Au atoms) solution was added to the THF solution of Au(III)@D3OTP (10 mM, 10 mL) and stirred vigorously, the solution turned the color of wine red immediately. This red mixture showed an absorption band at ~530 nm from a UV-visible spectrum shown in Figure 2(a), which indicates that spherical gold nanoparticles were formed.[17] Figure 3(a) shows a transmission electron microscopy (TEM) image of the solution after several re-precipitations; spherical gold nanoparticles with the mean diameter of 2.95 nm were observed.

When $NaBH_4$ (10 equivalent to Au atoms) in 0.3 mL of H_2O was added to Au (III)@D3OTP (10 mM) in THF (10 mL), the mixture instantly turned black. The UV-visible spectrum of the product (Figure 2(b)) shows a broad plasmon band in the >600 nm range, which possibly arises from the overlap of the transverse surface plasmon band (~530 nm) and longitudinal surface plasmon resonance bands of 1-D nanostructures of various lengths.[18] Similar plateau was observed from other one-dimensional gold nanomaterials having different lengths or gold nanonetworks.[19-21] In the TEM images of the sample, nanostructures, such as curved rods, cylinders, and spherical nanoparticles were observed (Figure 3(b)). On the other hand, when $NaBH_4$ (10 equivalent to Au atoms) in 2 mL of H_2O was added into the THF (10 mL) solution of Au(III)@D3OTP (10 mM), the mixture instantly turned black, then in a few seconds, black precipitates were formed while the solution changed to colorless indicating gold nanomaterials are preferentially located in the precipitates. Since H_2O is a nonsolvent for D3OTP, the addition of a large amount of H_2O (2 mL) forces D3OTP to precipitate. Figure 3(c) and 3(d) show the TEM images of the networks of 1-D nanowires with ~5 nm diameter after several re-precipitations. Therefore the amount of water (0.3 or 2 mL) affects the shape of the gold nanostructures when $NaBH_4$ in water was used as a reducing agent.

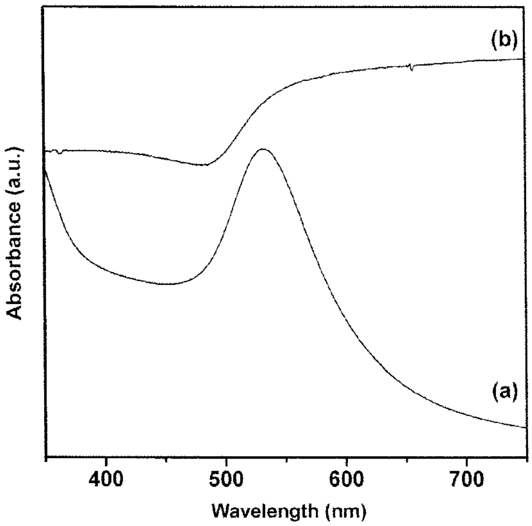

Figure 2. UV visible spectra of (a) gold nanoparticles prepared using TBABH/THF and (b) a mixture consisting of gold nanorods, curved nanorods, and nanoparticles prepared using $NaBH_4$/0.3 mL of H_2O.

The formation of such curved 1-D gold nanostructures (curved rod, cylinder, and network, etc.) has not been commonly observed. Schmidt *et al.* noted that the cylindrical structure of the polymer brush micelle containing gold salts in the core part facilitates the formation of asymmetric 1-D gold nanostructures through the aggregation of the reduced gold atoms in the core part.[3] Ramanath *et al.* prepared gold nanonetworks through a templateless method where the coalescence of hydrophobically passivated spherical nanoparticles in a bi-phasic (water/toluene) solution derives the formation of the network structures.[20] Similar templateless synthesis of gold networks through the adhesion of gold nanoparticles was also reported.[21] In our case, the reduced gold crystals in the core part of D3OTP in the solution or in the precipitate possibly lead to the formation of the 1-D nanomaterials. When the reducing agent ($NaBH_4$) in a small amount of water (0.3 mL) was added to the Au (III)@D3OTP solution, the core-shell structure of the complex was maintained, then the Au^{3+} species in the core part are reduced to Au(0) to form curved or cylindrical 1-D nanorods. When the reducing agent in a larger amount of H_2O (2 mL) was added the solution, the 1-D nanorods formed in the core part of the polymer precipitated, followed by the fusion of the nanorods to form the nanonetworks. This can be further confirmed by the shape of gold nanostructure obtained using $NaBH_4$ in 1 mL of water where gold nanonetworks have some disconnected parts as shown in Figure 3(e). It suggests that a relatively large size of the core part in D3OTP compared to the one in 2 mL of H_2O case should lead the incomplete fusion between the 1-D gold nanorods, resulting in disconnected gold nanonetworks. The diameters of our 1-D nanostructures (~10 nm for curved structures and ~5 nm for nanonetwork) are larger than the possible hydrophilic domain size of the Au(III)@D3OTP complex. This mismatch between the products and the soft templates has been reported.[22] On the other hand, when TBABH in THF

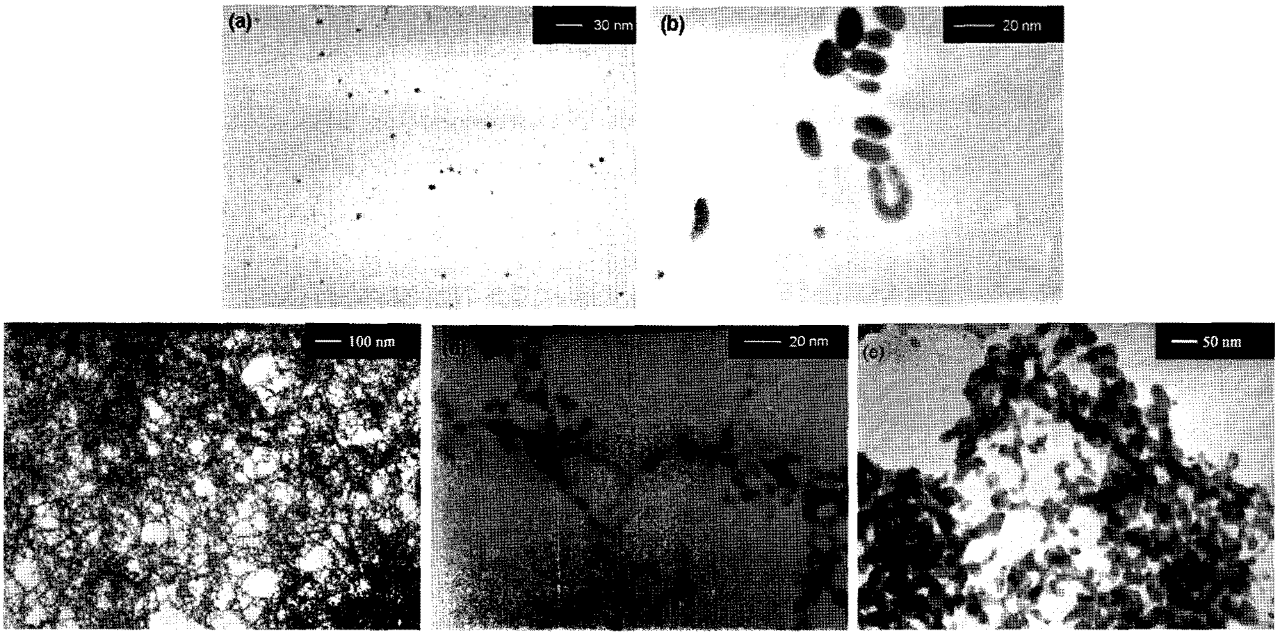

Figure 3. TEM images of (a) gold nanoparticles prepared using TBABH/THF and (b) a mixture consisting of nanorods, curved nanorods, and nanoparticles prepared by $NaBH_4$/0.3 mL of H_2O. (c) Low magnification and (d) high magnification TEM images of 1-D gold nanonetworks prepared using $NaBH_4$/2 mL of H_2O. (e) Disconnected part of gold nanonetworks obtained using $NaBH_4$/1 mL of H_2O.

was used as the reducing agent, symmetrically (0-D) nanocrystals were obtained because tetrabutyl ammonium group in TBABH can work as a surfactant such as a phase transfer catalyst.[23] This might disorganize the core-shell structure of the complex to form a spherical micelle structure. To further confirm the effect of TBABH as a surfactant, we add TBABH in H_2O to an Au(III)@D3OTP solution in THF. Again, only spherical gold nanoparticles were obtained. We also investigated the effect of polymer molecular weight on the shape of gold nanomaterials by preparing D3OTP having M_n about 5,000 g/mol. This low molecular weight D3OTP was synthesized by the similar polymer analogous reaction mentioned in the experimental part using low molecular weight poly(epichlorohydrin) (M_n about 4,700 g/mol) and decyltri(oxyethylene) thioacetate. We found that this low molecular weight D3OTP produced almost the same gold nanonetworks and nanorods when the same reduction conditions were used, respectively. The overall synthetic process of gold nanomaterials is depicted in Figure 4.

We performed a thermogravimetric analysis (TGA) of D3OTP and the composite composed of D3OTP and nanonetworks to study their thermal stability (Figure 5). The decomposition temperature of the polymer itself (D3OTP) is slightly higher than that of the composite. This implies that the decomposition of composite is catalyzed by the gold nanonetworks, that is, the metal-catalyzed oxidative decomposition is occurred.[24] It has been reported that metal nanomaterials in polymer matrices can decrease the thermal stability of the polymer.[25] When D3OTP was heated to 450 °C, the residual mass was found to be almost 0%, however, the composite was found to have 20.9% of the residual mass at the same temperature; therefore this residual mass should be

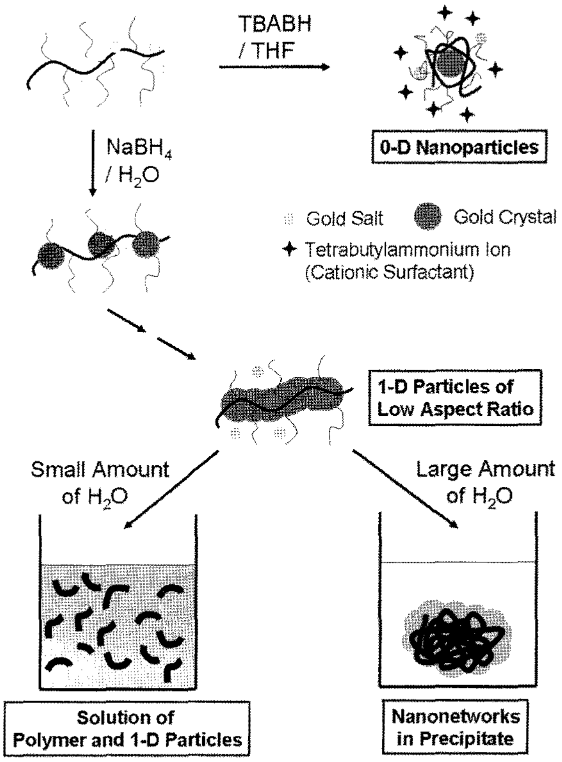

Figure 4. Schematic illustration of the formation of 0-D and 1-D gold nanomaterials from Au(III)@D3OTP.

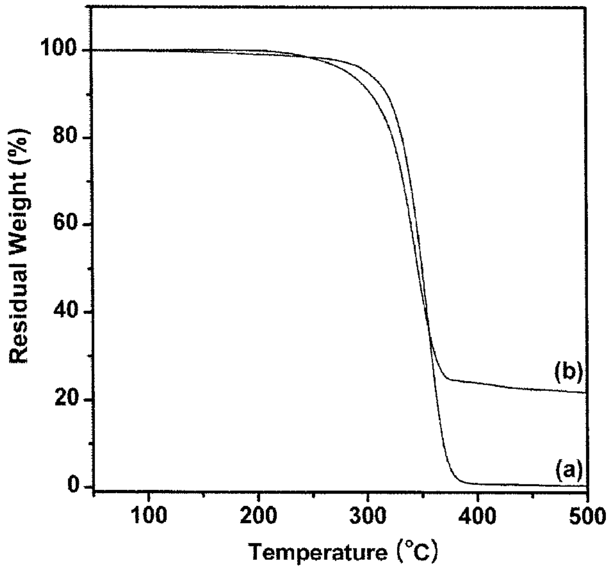

Figure 5. Thermal gravimetric analysis curves of (a) D3OTP and (b) its mixture with gold nanonetworks.

originated from the gold nanomaterials. The calculated amount of the gold materials in the composite is 17.7%. The difference (3.2%) between the experimental and the calculated values is possibly because of the loss of polymer during several re-precipitations in the purification process. This result also indicates that most gold nanonetworks in the D3OTP do not separate from the polymer in the purification process. Additionally, we found that the residue from TGA experiment for composite was gold nanonetworks where the morphology was not changed much, if any, as shown in Figure 6.

The electric conductivities of the polymer and the composite were measured by the two-probe method.[26,27] After dried overnight in vacuum, the samples were sandwiched between flat stainless-steel electrodes in the two-probe cell, where the thickness was controlled to be at 100 μm by introducing a Teflon® film spacer. Table I shows the electric conductivity of D3OTP and the composites. The D3OTP was found to be an insulator, while the composites showed the conductivities of semiconductor's level. The conductivities of composites containing the nanonetworks and the nanoparticles were 3.6×10^{-3} and 1.0×10^{-9} S/cm, respectively. Since the mass ratios of gold in both of the composites were very similar (~20 wt% by TGA), the difference of the conductivity obviously originated from the morphology of the gold nanomaterials in the composites. We believe that much higher conductivity can be achieved by obtaining a pure gold nanonetwork film through calcination of the organic moieties or by using conducting polymers as the matrix.[28]

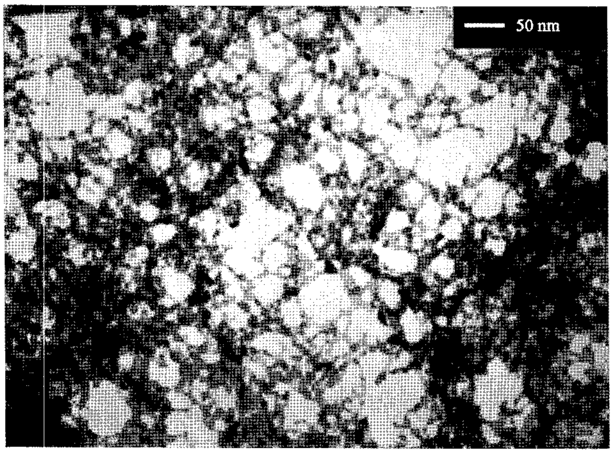

Figure 6. TEM image of residue from TGA experiment for composite.

Table I. Electric Conductivity of D3OTP and the Mixtures of D3OTP and Gold Nanostructures

Sample	Electric Conductivity (S/cm)
D3OTP	Not detected
D3OTP/gold nanoparticles[a]	1.0×10^{-9}
D3OTP/gold nanonetworks[b]	3.6×10^{-3}

[a]Prepared using TBABH in THF as a reductant.
[b]Prepared using $NaBH_4$ in water as a reductant.

Conclusions

A size- and shape-controlled synthesis of 0-D and 1-D gold nanomaterials were accomplished by the reduction of the Au(III)@D3OTP complex using chemical reducing reagents such as a tetrabutylammonium borohydride solution in THF and a sodium borohydride solution in H_2O. We found that our amphiphilic comb-like polymer brush worked as a stabilizer and/or a template in the reduction step. The reduction condition (reductant, solvent, etc.) determined the shapes and sizes of the gold nanocrystals. The D3OTP composite having gold nanonetwork has a higher electric conductivity than the one with gold nanoparticles when the gold content is the same. This indicates that the network structures can produce electrical conducting channels in the polymer matrix. Since the polymer composite of gold nanonetworks is soluble in various solvents including THF, chloroform, DMAc, and so on, various solution processes such as spin coating are possible for future applications.

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