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Nanometer Gold Clusters Protected by Surface-Bound Monolayers of Thiolated Poly(ethylene glycol) Polymer Electrolyte

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Metal nanoparticles that are stabilized in solutions by polymer surfactants or are imbedded in polymer composites have been of intense recent interest[1] with regard to their fabrication and potential application in areas as diverse as catalysis, nonlinear optics, and magnetic polarizability. Surfactant stabilization does not, however, lend itself to isolation of dry, nonaggregated nanoparticles that can be redissolved without change. Bonding of a monolayer of alkanethiolate ligands to a Au nanoparticle[2] has greatly facilitated their further chemical and physical study[3] as large, polyfunctional molecular entities.

This paper describes a monolayer-protected Au cluster (PEG-S-MPC) based on a monolayer of thiolated *polymer*, α-methoxy-ω-mercapto-poly(ethylene glycol) (PEG-SH, MW 5000), selected for its potential to yield improved core stabilization as well as to induce aqueous solubility. Clusters protected by alkanethiolate- and modified alkanethiolate-monolayers (MPCs) are water insoluble, which limits their biological sensing applications, a topic in which nanoparticle technology offers great promise.[4] The PEG-SH ligand was also selected because dissolution of $LiClO_4$ electrolyte in solvent-free PEG-S-MPC provides, in line with our interests[5] in new polymer electrolyte media, a semisolid having an ionically conductive nanophase around a metallic core.

The PEG-S-MPC was synthesized in a modified Brust[2] reaction using a $^1/_{12}$ polymer thiol/$AuCl_4^{-1}$ reactant ratio. Transmission electron microscopy (TEM) shows that the product (Figure 1 inset, see Supporting Information for a larger image) has modestly polydisperse Au cores of avg. 2.8 ± 1 nm diameter. Combining this core size with a 79% organic fraction determined by thermogravimetric analysis (TGA) and an assumed truncated octahedral shape, as done before,[6] yields an average Au_{807}(PEG-S)$_{98}$ composition.

Au MPCs with bonded polymeric monolayers have not been previously described; therefore, comparisons of their properties with those of alkanethiolate-MPCs are useful, and reveal consequences of the bulkiness of the PEG-S ligand. Table 1 shows that Brust[2] synthesis of a dodecanethiolate-MPC using a $^1/_{12}$ thiol/$AuCl_4^{-1}$ ratio produces an average Au core size (5.2 nm) larger than that of PEG-S-MPC. A much larger reactant ratio is needed to produce alkanethiolate-MPCs with 2.8-nm core diameters, which suggests that the PEG-SH ligand is a better passivant of core growth in the MPC synthesis. Table 1 shows, second, that the PEG-S-ligand has a “footprint”(0.35 nm^2) somewhat larger than the dodecanethiolate ligand (0.21 nm^2) but far smaller than the footprint[7] inferred, assuming that the attached PEG-S ligand is a random coil. The latter difference implies that the PEG-S ligand is distorted into, probably, a cone-shaped volume (Figure 2 inset).

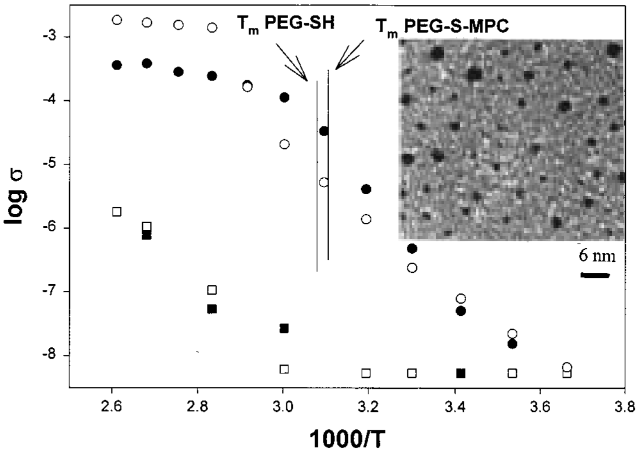

Figure 1. Ionic conductivity of PEG-SH(●) and of PEG-S-MPC (○) with $LiClO_4$ (16:1 polymeric oxygen to $LiClO_4$). Ionic conductivity of PEG-SH (■) and of PEG-S-MPC (□) with no $LiClO_4$. Inset is TEM image of PEG-S-MPC, showing a regular core edge−edge spacing of ca. 7 nm, which is similar to the PEG end-to-end chain length (l).

Table 1. Results from TGA and TEM Analysis of PEG-S-MPCs and Alkanethiolate-MPCs

ligand/ synthetic prep[a]	av core diam (nm)[b]	no. Au atoms (shape)[c]	no. surface atoms/area (nm^2)[c]	% organic[d]/ % coverage[e]/ no. chains	ligand footprint[f] (nm^2)
PEG-SH (1/12)	2.8	807 (TO$^+$)	348/34	79/28/98	0.35
Alkanethiol (1/3)	2.8	807 (TO$^+$)	348/34	17/47/163	0.21
Alkanethiol (1/12)	5.2	4794 (TO$^+$)	1230/108	9.7/41/506	0.21

[a] Syntheses as in ref 6; parentheses denote mole ratio of thiol to $AuCl_4^-$ employed. [b] Determined by TEM. [c] Number of gold atoms, cluster shape, surface atoms, and surface area for particular diameter clusters is calculated as in ref 6 (TO$^+$ refers to a truncoctahedron where $0 < n - m \leq 4$, n equals the number of atoms between (111) faces and m is the number between (111) and (100) faces). [d] From TGA results. [e] Percent of surface Au atoms with thiolate ligands. [f] Au surface area per ligand.

There are chemical as well as dimensional distinctions between PEG-S-MPC and alkanethiolate-MPCs. Cyanide, known to destroy colloidal gold,[9] has been shown[3b] to decompose alkanethiolate-MPCs at rates decreasing with increasing alkane chain-

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(6) Hostetler, M. J.; Wingate, J. E.; Zhong, C.-J.; Harris, J. E.; Vachet, R. W.; Clark, M. R.; Londono, J. D.; Green, S. J.; Stokes, J. J.; Wignall, G. D.; Glish, G. L.; Porter, M. D.; Evans, N. D.; Murray, R. W. *Langmuir* **1998**, *14*, 17−30. (b) Combining TGA and TEM analysis yields the formula Au_{807}(PEG-S)$_{122}$. The structure reported is Au_{807}(PEG-S)$_{98}$; however, because NMR spectroscopy of the PEG-S-MPC sample shows that ca. 20%, or 24, of the PEG chains are present as disulfides that are not bonded to the Au. The disulfides are detected by $\propto$-CH$_2$ triplet (δ 2.75 ppm) that is not broadened as typical for $\propto$-CH$_2$ units on core-bonded thiolates and that disappears following dialysis of the PEG-S-MPC.

(7) The 5 000 MW PEG-SH ligands have an average 112 monomers/chain. A random coil model[8] gives an end-to-end distance $l \approx 8$ nm and a radius of gyration, $R_g \approx 3$ nm. The cross-section of a sphere of this radius is 28 nm^2. A smaller value (but still ≫ than the experimental result) results from assuming the relevant footprint cross-section is a circular plane lying 0.18 nm (the van der Waals radius of sulfur) into the 3-nm radius sphere.

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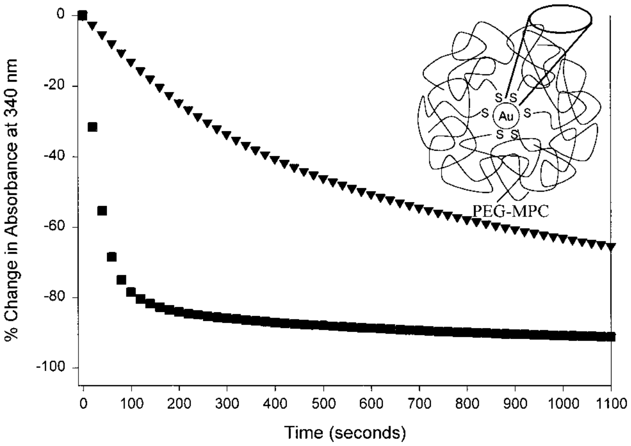

Figure 2. Room-temperature cyanide-induced decomposition of 1.0×10^{-3} M PEG-S-MPC solution in water (▼) and of 2.6×10^{-3} M dodecanethiolate-MPC in THF (■) by the addition of 10× molar excesses of NaCN in water and THF, respectively. First-order analysis of the decays gives rate constants of 1.2×10^{-3} and 9×10^{-3} s^{-1}, respectively. (MPC concentration reported is for gold). Inset illustrates crowding of PEG-S ligands around Au core.

lengths. The decay of absorbance of the cluster solutions in Figure 2 shows that PEG-S-MPC is decomposed more slowly than a dodecanethiolate-MPC, an effect assignable to the former's greater ligand bulkiness. The tight PEG-S-monolayer, second, also shuts off place-exchange reactions with other thiols; such reactions occur[10] quite freely with alkanethiolate-MPCs. PEG-S-MPCs do not exhibit place-exchange reactions (with dodecanethiol) even at elevated temperatures (~35°C), high alkanethiol concentrations, or long reaction times (4 days). PEG-S-MPC is, third, more thermally stable, decomposing (presumably to the polymer disulfide[6]) in a TGA experiment at 318 °C in comparison to 240 °C for a dodecanethiolate-MPC. The overall picture, then, is that the size of the PEG-S-ligand has numerous consequences for cluster properties and behavior and suggests that even more robust MPCs may result by playing on ligand bulk.

A principal aim in preparing this new material was to explore a polymer electrolyte nanophase organized around distributed metallic centers. Dissolution of an electrolyte like $LiClO_4$ in polyethers produces ionically conductive semisolids that have been of great interest in energy storage.[11] In the PEG-S-MPC, the polyether nanophase also dissolves $LiClO_4$ to become ionically conductive. Figure 1 shows the temperature dependence of ionic conductivity (measured by AC impedance) of dry films of PEG-S-MPC (○) and of PEG-SH ligand (●), each containing $LiClO_4$ dissolved in a 16:1 ether oxygen:Li^+ ratio. At lower temperatures, where both PEG-SH and PEG-S-MPC phases are partially crystalline (and where conductivities are classically more difficult to interpret[11]), the ionic conductivities are similar. Strikingly however, above the melting transitions ($T_m \approx 62$ °C, by differential scanning calorimetry), where both polymer electrolytes are in an amorphous state, ionic conductivity is clearly larger (10-fold) in the PEG-S-MPC melt phase. This effect could arise from the distortion of chain conformation in PEG-S-MPC from the random coil expected in a pure PEG-SH phase; the electronic polarizability of the Au cores might also play a role. Further study is needed before an interpretive model is developed.[12] The principal result is that the ionic conductivity of a polyether phase is enhanced when one end of the polymer constituent is immobilized (on the cluster). Changes in the PEG-S-MPC structure such as chain length and core size may lead to even larger ionic conductivity enhancements. Further to this end, studies are ongoing of an ionically associated polymer cluster consisting of thiolated sulfonates ligated to the gold core and having Et_3N-PEG^+ counterions.

Efforts to diversify monolayers that stabilize metal nanoparticles are important to development of MPCs as useful materials. In the present case a polymeric monolayer has led to characteristics uniquely different from alkanethiolate MPCs, notably aqueous solubility, thermal and chemical stability, ligand footprint size, and ionic conductivity.

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Supporting Information Available: Details of PEG-S-MPC synthesis and characterization (NMR, IR, UV−vis, and thermogravimetric) and more information on stability (6 pages, pent/PDF). See any current masthead page for ordering information and Web access instructions.

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[12] The enhanced conductivity is not due to mixed ionic−electronic transport since the conductivity of PEG-S-MPC without $LiClO_4$ (Figure 1) is much smaller, nor is it due to the lessening of crystallinity as caused[12b,c] by the addition of inert filler-salt, since the effect is seen at temperatures above T_M. (b) Capuano, F.; Groce, F.; Scrosati, B. *J. Electrochem. Soc.* **1991**, *138*, 1918−1922. (c) Quartarone, E.; Mustrelli, P.; Magistris, A. *Solid State Ionics* **1998**, *7*, 75−79.