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Measurement platforms fabricated by layer-by-layer assembly of crown ether functionalized gold nanoclusters

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Abstract Mixed-ligand monolayer-protected gold nanoclusters (MPCs) with crown ether (CE) and carboxylate functionalities were synthesized and used as components of layer-by-layer (LBL) electrostatic assemblies on gold and indium tin oxide (ITO) electrodes. The purpose of using MPCs was to provide a supramolecular anchor for a functionality, CEs, of interest to sensor and solid-phase extraction design; the carboxylate provided the charged sites needed for electrostatic assembly. With 15-crown-5 as the CE, the capture of 2.8×10^{-10} mol Pb^{II} cm^{-2} per monolayer of MPC was demonstrated by voltammetry and by electrochemical quartz crystal microbalance measurements. The diffusion of ferrocene through these LBL assemblies was investigated. The presence of MPCs and/or generation-4 poly(amidoamine) dendrimers allowed facile transport of ferrocene to the underlying electrode, presumably because these supramolecular assemblies provided a quasi-porous structure.

Keywords Gold nanoparticles · Crown ethers · Lead · Modified electrodes · Layer-by-layer assembly

Introduction

The fabrication of surface layers that have organization at the atomic or molecular level and have controlled functionalities are of interest for a wide range of applications including analytical platforms for separation science and sensing, electronics, photonics, catalysis, and corrosion inhibition. One approach to forming films for these applications is a layer-by-layer electrostatic assembly of supramolecules [1, 2, 3, 4, 5, 6]. In a typical

procedure an electrode surface is modified with a monolayer of a charged substance. For example, we fabricated an electrocatalytically active layer-by-layer assembly on gold by first modifying the electrode with a positively charged self-assembled monolayer of 4-aminothiophenol and then alternating its immersion in an anionic supramolecule, phosphomolybdate (PMA), and a cationic supramolecular spacer, generation-4 poly(amidoamine) dendrimer [7]. In an analogous manner, quartz was modified with LBL assemblies containing either phosphotungstate or PMA; here, the initial monolayer was formed by reaction with poly(diallyldimethylammonium chloride) [8].

Feldheim et al. [9] used an LBL assembly to prepare multilayers that contained citrate-protected colloidal gold particles with diameters in the 1–4 nm range. The intermediate layers comprised insulators that gave an insignificant amount of short circuits between gold layers in a 1 cm^2 array. Indeed, the general topic of electron and ion transport, including quantized charging, with assemblies that contain monolayer-protected gold nanoclusters (MPC) has been a focus of several studies, typified by citations [10, 11, 12, 13, 14]. A complication relative to the LBL fabrication of multilayers of conventional supramolecules is that exposure of a surface of a charged polyelectrolyte to an oppositely charged MPC solution does not necessarily result in a single monolayer. For example, Hicks et al. [12] found that these nanoclusters, when converted to mixed-ligand MPCs using either mercaptoundecanoic acid (MUA) or mercaptophenylamine (ATH), electrostatically assembled with poly(allylamine hydrochloride), PAH, and poly(styrene sulfonate), PSS, respectively, in a manner that resulted in the deposition of about 3.7 ± 1.3 monolayers of MPC for each exposure. They compared the ability of these two assemblies to transport charge by investigating the voltammetry at electrodes thereby modified to contain similar quantities of MPC. The combination of cationic PAH and MUA/MPC provided facile charge transport, whereas the LBL assembly, containing PSS and ATH/MPC, was sufficiently less

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conductive and of more dense structure to virtually block the voltammetry of ferrocene.

We are interested in the development of modified electrode surfaces that can selectively interact with substances ranging from metal ions to biological models. The present study is focused on the former. Crown ethers are functionalities that are well known to have the ability for selective complexation of metal ions. A challenge is to fabricate electrode surfaces of defined structure that contain controlled quantities of these reagents. One approach is to tag a crown ether with an alkanethiol and subsequently form a self-assembled monolayer, SAM, of the product on an electrode. Using a method reported by Flink et al. [15], we synthesized 2-[(6-mercaptohexyl)oxy]methyl-15-crown-5 and formed a SAM of this compound on Au [16]. The functionalized assembly was used to trap Pb^{2+} from solution. An important finding was that the SAM was formed with a surface coverage of 0.97 ± 0.01 in 30–90 s. Because of the rapid re-formation of the SAM, it was practical to release the trapped lead ion (and the entire functionalized SAM) into a flow stream by oxidizing the gold thiolate bond. A detection limit of 6 pmol Pb was thereby achieved by amperometry at a down-stream electrode.

Flink et al. [15] used a similar SAM on Au to sense electrochemically inactive cations such as Na^+ ; here, either impedance spectroscopy or attenuation of the cyclic voltammetric current of an electroactive complex in the contacting liquid phase was used to generate the signal. Moore et al. [17] used a somewhat different approach in that electroactive sites, tetrathiafulvalene, were incorporated into the macrocyclic ligand; complexation by cations such as Li^+ was signaled by a shift in the TTF voltammetry. Zhang and Echegoyen assembled calixarene derivatives of a crown ether and sensed Cs^+ by impedance spectroscopy in a study that demonstrated the influence of conformational change on the recognition chemistry [18].

A limitation of these approaches is that a single monolayer has a limited uptake capacity. A premise of this study is that the same chemistry that yields a functionalized SAM on Au is applicable to forming functionalized MPC, which in turn can be assembled into multilayers, thereby increasing the uptake capacity. Others have incorporated chemical trapping agents into multilayer assemblies of gold nanoparticles. Namely, Shipway et al. [19] prepared multilayers of citrate-stabilized gold colloid and incorporated a tetra-cationic cyclophane as an electrostatic crosslinking agent. The ability of the cyclophane to form pi-donor complexes was employed to subsequently trap *p*-hydroquinone. Cyclic voltammetry demonstrated that the quantity of *p*-hydroquinone that was trapped increased with the number of Au particle layers. The present study is not only aimed at testing the premise of trapping by functionalized multilayers of MPC, but also is intended to characterize the assembly process, to establish whether the resulting films have a sufficiently open structure to

permit facile ion transport therein, and to test whether the conformation and density of the crown ether groups on the CE-MPC will permit complexation of a metal ion via a sandwich mechanism.

Experimental

Chemicals and materials

Unless otherwise stated, the chemicals were ACS Reagent Grade from Aldrich Chemical Company (Milwaukee, WI). The 2-(hydroxymethyl)-15-crown-5 (95%); 1,12-dibromododecane (98%); tetrabutylammonium fluoride, TBAF, 1.0 M solution in tetrahydrofuran, THF; hydrogen tetrachloroaurate (III) trihydrate (99.9%), 1-hexanethiol (95%), tetraoctylammonium bromide (98%); sodium borohydride, 12% wt solution in aqueous conc. sodium hydroxide; toluene (99.5%); poly(amidoamine), generation 4 (G4-PAMAM), 10 wt % solution in methyl alcohol; 3-aminopropyl triethoxysilane (3-APTES); 4-aminothiophenol (4-ATP) (97%); tetrabutylammonium hexafluorophosphate, Bu_4NPF_6 (98%); and ferrocene, Fc (98%), also were purchased from Aldrich. The hexamethyldisilathiane (98%) was from Sigma-Aldrich Inc. (St Louis, MO). Poly(4-styrene sulfonate), PSS, (MW ca. 70 000) was from Johnson Matthey (Ward Hill, MA). Glass slides with indium tin oxide (ITO) coated one surface were from Delta Technologies Limited (Stillwater, MN). Solutions were prepared with house-distilled water that was further purified with Barnstead NANOpure II system (Boston, MA).

Apparatus

The voltammetry experiments were performed with a CHI Model 750 electrochemical workstation or a CHI Model 800 electrochemical detector (CH Instruments, Austin, TX). The mass change experiments were carried out on a CH Instruments Model 400 electrochemical quartz crystal microbalance, EQCM, with an 8.000 MHz reference crystal. UV-Visible spectrophotometry experiments were done on a Hewlett Packard 8453 system (Agilent Technologies, Palo Alto, CA).

Synthetic methods

2-(12-bromododecyloxy)methyl-15-crown-5 ether (Compound A) was prepared by a modification of a procedure reported by Fox and Wooten [20]. Briefly, 2-(hydroxymethyl)-15-crown-5 (1 g, 4 mmol), 3.75 eq. 1,12-dibromododecane (5.08 g, 15 mmol), 1.1 eq. potassium hydroxide (0.246 g, 4.4 mmol), *t*-butyl alcohol (32.2 ml) and water (4 ml) were refluxed for 24 h. Water (50 ml) was added and the crude product was extracted with CH_2Cl_2 (50 ml). The organic layer was washed with

water, and the solvent was removed *in vacuo*. Excess 1,12-dibromododecane was separated from the product by column chromatography on silica with hexane as the eluent, and Compound A was eluted off the column with methanol/chloroform (1:9) as light-yellow oil (0.45 g).

2-(12-mercaptododecyloxy)methyl-15-crown-5 ether (Compound B) was synthesized by preparing a 0.5 M solution of A in dry THF (1.654 ml) under argon [21]. The solution was cooled to $-10\text{ }^{\circ}\text{C}$, and 1.1 equivalents of hexamethyldisilathiane and 1.2 equivalents 1.0 M TBAF in THF (10% H_2O) were added and stirred for 30 min. The solution was brought to room temperature and stirred for an additional 24 h. Saturated ammonium chloride (10 mL) was added, and the crude product was extracted with CH_2Cl_2 (50 ml). The organic layer was dried over Na_2SO_4 , and the solvent was removed *in vacuo*. The crude product was purified by column chromatography (SiO_2 , hexane/ethyl acetate 1:1) to yield Compound B as a yellow oil (0.209 g, 58%). The ^1H NMR (200 MHz, CDCl_3) was identical to that reported by Flink et al. [15]

The synthesis of the crown-ether functionalized monolayer-protected gold clusters was accomplished in two steps. First, preparation of hexanethiolate MPC with an average core radius of 1.7 nm was done by the method of Hostetler et al. [22]. Specifically, to a vigorously stirred solution of 1.5 g of tetraoctylammonium bromide in 80 ml of toluene (room temperature) was added 0.8 mmol of HAuCl_4 in 25 ml of water. The organic layer was separated, and 0.8 mmol of 1-hexanethiol was added. The resulting solution was stirred for 1 h at room temperature. A solution of 0.38 g of NaBH_4 in 25 ml of water was added over 10 s. This solution was further stirred for 4 h at room temperature. The organic phase was collected and the solvent was removed *in vacuo* (the temperature was kept below $50\text{ }^{\circ}\text{C}$ to minimize product decomposition). Methanol (100 ml) was added and the black solid was recovered by filtration and washed with methanol.

Subsequently, the crown-ether functionalized monolayer-protected gold clusters (CE-MPC) were prepared from the above MPC using a ligand place-exchange reaction in a modified procedure of Murray and co-workers. [23]. A solution of 160 mg of the hexanethiolate MPC, 14.18 mg of B, and 6.9 mg of MUA were dissolved in 80 ml CH_2Cl_2 . The mixture was stirred at room temperature under argon for 120 h. The solvent was removed *in vacuo*, and the resulting precipitate collected by vacuum filtration.

Procedures

Layer-by-layer (LBL) electrostatic deposition of multilayers of CE-MPCs and G4-PAMAM on ITO glass slides was done using solutions of 10 mg CE-MPC in 10 ml of dry ethanol and 1 wt % G-4 PAMAM in water. Sufficient HCl was added to each to give nominal pH 1 solutions. The ITO glass slide was first sonicated in dry

ethanol and functionalized with 0.06 M 3-APTES in methanol for 2 h. The slide was washed with methanol and dried with a helium gas stream. The first layer of CE-MPCs was assembled on the ammonium-functionalized surface by contacting the ITO to the above solution for 30 min. By repeating the rinsing (dry ethanol), drying (helium stream), and immersions in the CE-MPC and the G4-PAMAM solutions, multilayers were deposited. The LBL assemblies of PSS | G-4 PAMAM were fabricated in the same manner except ca. $14\text{ }\mu\text{M}$ PSS was used instead of the CE-MPC solution.

The trapping of Pb^{II} on the CE-MPC assemblies was based on the projected formation of sandwich complexes with the crown ether. In order to minimize the additional complexation with the carboxylates, the outer layer of the film was G-4 PAMAM. The coated ITO was immersed in a 1.0 mM $\text{Pb}(\text{NO}_3)_2$, 0.1 M HNO_3 solution for 10 min, washed with water and dried with helium gas.

Characterizations by QCM measurements were performed by first modifying the gold surface of the crystal with 1 mM 4-ATP in ethanol and then fabricating CE-MPC | G-4 PAMAM multilayers as described above. The only difference was that instead of dipping the crystal into the solutions, 1 one drop of the selected solution was put onto the surface, and the crystal was kept in the chamber of saturated vapor of selected solvent to prevent evaporation. The trapping of Pb^{II} was the same as described above except that the sample was now was a drop of solution on the surface with and the vapor chamber was used to block evaporation.

Electrochemical measurements were in a conventional three-electrode cell. With Pb^{II} as the test species, the supporting electrolyte was 0.1 M tetraethylammonium chloride. With 0.5 mM ferrocene as the test species, the solution was 0.1 M Bu_4NPF_6 in CH_2Cl_2 , and the working electrode was ITO. All potentials were recorded and reported vs. a $\text{Ag}|\text{AgCl}$ reference electrode.

Results and discussion

The previous study that used a functionalized MPC in a LBL assembly employed the functional group as a crosslinking agent in the formation of the film [19]. In this case, the functional group on the MPC, namely a crown ether (CE), was neutral, so the LBL assembly required the attendant citrate in the mixed-ligand MPC to provide the necessary electrostatic charge without interference from the tethered CE. Spectrophotometric measurements (Fig. 1) demonstrated the formation of $\text{ITO}|3\text{-APTES}(\text{CE-MPC})|\text{G4-PAMAM}_n$ with $n = 16$, at which point the experiment was terminated. A linear least squares curve fit of the absorbance to n (at 520 nm) gave an r -value of 0.993.

Previously, Hicks et al. [12] used spectrophotometry to determine the number of monolayers of a MPC deposited per dipping cycle. Here, their approach was adapted to the case of the CE-MPC. That is, the

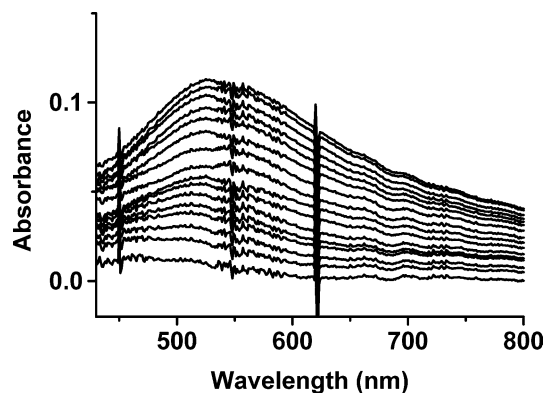


Fig. 1 Layer-by-layer assembly of ITO|3-APTES|(CE-MPC)|G4-PAMAM)_n monitored by spectrophotometry

expression $A = \epsilon k \Gamma$ was used where k is a constant (obtained as described below), ϵ is the molar absorptivity of the MPC, and Γ is the surface excess. In order to correct for differences in operational parameters and the molar absorptivities of the MPCs employed, their experiment was first replicated by preparing the hexanethiolate and MUA mixed-ligand MPC they used. An $n = 16$ assembly was prepared on an ITO|3-APTES surface. Relative to the report of 3.7 ± 1.3 monolayers of the hexanethiolate and MUA mixed-ligand MPC per dipping, 1.1 ± 0.3 monolayers of CE-MPC per dipping were deposited.

The deposition of CE-MPC|G4-PAMAM on a Au|4-ATP electrode of a QCM was monitored (Fig. 2). A linear least squares fit of frequency change with bilayer number ($n = 4$) yielded an r -value of 0.992. The importance of the QCM result was that it established the veracity of the experimental approach for the LBL assembly on the QCM crystal. A concern was that solvent evaporation may have caused deposition by other than an electrostatic assembly.

Proposed applications require accessibility of Pb^{II} to the CE functionalities in the inner layers of the assembly. A previous study [12] showed that with a somewhat related MPC, an LBL assembly provided facile charge transport, presumably because of a rather open structure imparted by the presence of these supramolecular assemblies. Hence, the first step in studying transport in the present used assemblies was to investigate the relative diffusion of a non-complexing species, ferrocene,

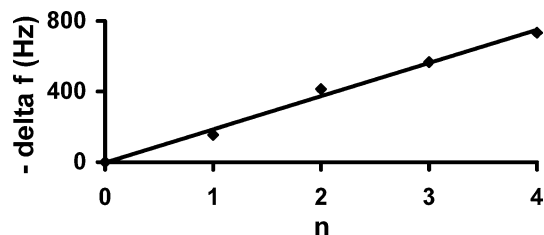


Fig. 2 Layer-by-layer assembly of Au|4-ATP|(CE-MPC)|G4-PAMAM)_n monitored by mass measurement with a QCM

through the LBL assemblies by cyclic voltammetry. Initially, the cyclic voltammetry of 0.5 mM Fc was studied at ITO|3-APTES|(CE-MPC)|G4-PAMAM)₄ and ITO|3-APTES|(PSS)|G4-PAMAM)₄. As shown in Fig. 3, under identical voltammetric conditions the peak currents were comparable. From the ratio in their values, the diffusion coefficients, where the former is denoted D_{MPC} and the latter is denoted D_{PSS} , calculated from the Randles-Sevcik Equation showed that $D_{\text{MPC}} = 1.6D_{\text{PSS}}$. The result is in contrast to one system studied by Hicks et al. [12] in which a bilayer comprised of poly(allylamine hydrochloride) and an MPC with mercaptoundecanoic acid and hexanethiol ligands essentially blocked the voltammetry of Fc. This comparison points to an important role of the G4-PAMAM in facilitating mass and/or charge transport through these LBL assemblies.

That the voltammetry of Fc at ITO|3-APTES|(CE-MPC)|G4-PAMAM)_n was diffusion limited was shown by a study of peak current, i_p , vs. the $v^{1/2}$, where v is the scan rate. Here, the solution was 1.0 mM Fc in CH_2Cl_2 with 0.1 M Bu_4NPF_6 as the supporting electrolyte. The scan rate at the 4.2 cm^2 electrode, upon which 6 bilayers were assembled, was varied over the range 5 – 200 mV s^{-1} . The data were fitted with a $\log i_p$ vs. $\log v$. The r^2 value was 0.9992 and the slope was 0.41. Although the theoretical slope for a diffusion limited process is 0.5, the experimental value supports the assignment of diffusion limited. The difference between experimental and theoretical values is probably due to uncompensated resistance that caused the peak potential difference to increase with scan rate. The results with an identical study on a ITO|3-APTES|(PSS)|(G4-PAMAM)₆ electrode yielded a slope of 0.42.

The ITO|3-APTES|(CE-MPC)|G4-PAMAM)_n electrodes were used to extract Pb^{II} as described in the Experimental section. A typical result is shown in Fig. 4. Integration of the current – voltage curve yielded the result that 8.4×10^{-10} mol cm^{-2} were trapped. Thus, in that three bilayers were used, an average of 2.8×10^{-10} mol cm^{-2} per monolayer was obtained, which is comparable to the trapping of $(6 \pm 3) \times 10^{-10}$ $\text{mol Pb}^{\text{II}} \text{cm}^{-2}$ for a

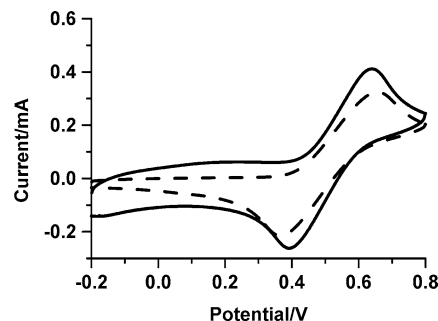


Fig. 3 Cyclic voltammetry of 0.5 mM ferrocene at ITO|3-APTES|(CE-MPC)|G4-PAMAM)₄ (solid line) and ITO|3-APTES|(PSS)|G4-PAMAM)_n (dashed line) electrodes. Supporting electrolyte, 0.1 M Bu_4NPF_6 in CH_2Cl_2 ; scan rate, 100 mV s^{-1} ; initial potential, -0.2 V.

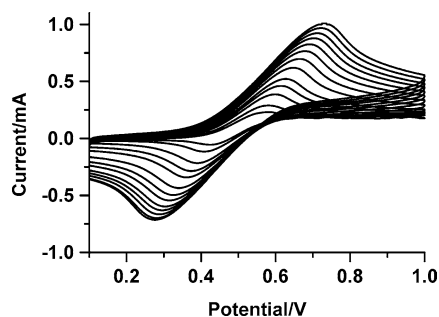


Fig. 4 Influence of scan rate on the cyclic voltammetry of ferrocene at an LBL assembly of CE-MPC. Except for scan rate, the conditions are those in Fig. 3.

self-assembled monolayer (SAM) with a tethered crown ether [16]. Given that the complex between 15-crown-5 and Pb^{II} is a sandwich, the comparison suggested that the CE-MPC has a population density of the crown ethers that can participate in the trapping of the metal to that of the SAM. It was also important that the quantity of the Pb^{II} trapped was proportional to the number of bilayers. Because the study only involved n in the range 1–3 the statistical data are of limited value; the standard deviation of the fit was 30%. After the trapping of Pb^{II} , the LBL assembly was studied by UV-visible spectrophotometry. The spectrum was the same as that reported in Fig. 1, which suggests that the general organization of the network was not altered.

Apparently, the Pb^{II} is complexed by the crown ethers in a given monolayer rather than crosslinked between either crown ethers or G4-PAMAM of adjacent bilayers. To test this postulate, the extraction experiment was repeated with an ITO|3-APTES|(MUA-MPC|G4-PAMAM)₃ electrode that was immersed in a 0.1 M HNO_3 , 1.0 mM $\text{Pb}(\text{NO}_3)_2$ solution for 30 min. Subsequently, cyclic voltammetry was performed at 100 mV s^{-1} . No evidence of the reduction of Pb^{II} was observed, which supports the premise that the Pb^{II} resided on the crown ether in the experiment reported in Fig. 4.

The voltammetric study was supported by QCM results. Using an Au|4-ATP|(CE-MPC)|G4-PAMAM)₃ surface, the average amount of Pb^{II} trapped per monolayer was $2.1 \times 10^{-10} \text{ mol cm}^{-2}$. Moreover, increasing the time of exposure of the surface to the Pb^{II} solution did not increase the quantity of the metal that was trapped, which suggests that the system reached equilibrium in 10 min.

Conclusions

The electrostatic layer-by-layer assembly of cationic G4-PAMAM and anionic mixed-ligand monolayer protected gold nanoclusters with 15-crown-5 functionality was successful on both indium tin oxide and on gold. In the former case, the surface was treated with 3-aminopropyl triethoxysilane, and in the latter, 4-amino-

thiophenol. Up to 16 bilayers were formed with a constant quantity of the MPC in each. The assembly yielded a 1.1 monolayer of the MPC per cycle, the trapping capacity of which was $2.8 \times 10^{-10} \text{ mol Pb}^{\text{II}} \text{ cm}^{-2}$ per monolayer. Facile diffusion of a neutral compound, ferrocene, through an assembly comprising 4 bilayers was demonstrated.

These LBL assemblies are not only useful for fundamental studies but also have promise for electrochemical stripping analysis. In this regard, functionalities other than crown ethers can be used as trapping agents, thereby extending the scope of possible analytes. In addition, in the manner reported by Wagner et al. [24], the complexing agent may enhance the analytical utility of the LBL assembly by blocking the transport of an interfering species to the electrode surface.

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