Nanofabrication and Electrochemical Characterization of Self-assembled Monolayers sandwiched between Metal Nanoparticles and Electrode Surfaces

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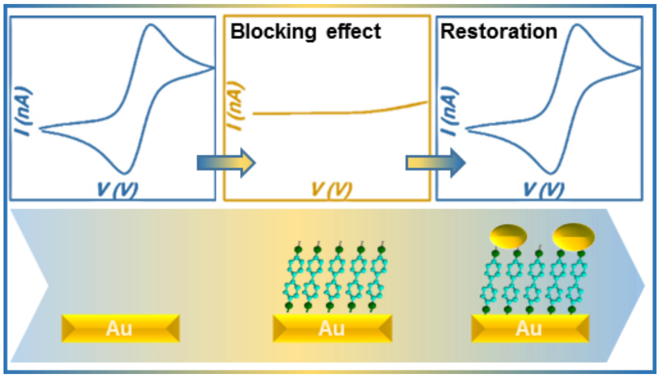
ABSTRACT

Nanoscience and nanotechnology have reached the syllabi of many upper-division undergraduate and master-level courses all over the world. There is therefore a growing need for practical exercises that illustrate the fabrication, characterization, properties and applications of nanomaterials. Here we describe an advanced-level laboratory experiment in which students had the opportunity to fabricate surfaces modified by ordered monolayers and nanostructured materials. The surface modification was quantified by means of a quartz crystal microbalance, whilst the electrochemical properties of the nanoarchitectures were assessed using cyclic voltammetry experiments. Electron transfer across self-assembled monolayers mediated by gold nanoparticles was presented as a topic for discussion, and consideration of potential practical applications of the observed phenomena (catalytic and electrocatalytic processes as well as development of optical, (opto)electronic and photovoltaic devices with enhanced properties) was proposed as a further reading exercise.

ABSTRACT GRAPHIC



KEYWORDS

Upper-Division Undergraduate, Graduate Education/Research, Multidisciplinary, Hands on learning, Materials Science

PEDAGOGICAL GOALS

Nanoscience and nanomaterials have found, or been proposed for, applications in many important fields including health, electronics, energy production and storage, purification and environmental cleanup applications, as well as industrial uses (foods, textiles, cosmetics, sports, coatings aerospace and vehicle technologies, catalysis, construction materials, military technology, etc.). This opens the need for designing new laboratory demonstrations[1] that can illustrate the phenomena occurring at the nanoscale.[2-7] In this practical exercise, students were guided through several aspects of nanoscience, illustrated through a variety of surface modifications and manipulations. Specifically, the experiment exposed students to the following concepts and skills:

(i) The key concept of 'bottom-up' assembly, illustrated through the formation of a monolayer by means of the self-assembly method.

(ii) Determination of the surface coverage using a quartz crystal microbalance.

(iii) Synthesis of gold nanoparticles by reduction of a metal precursor.

(iv) Immobilize gold nanoparticles onto a thiol terminated monolayer.

(v) The effects of surface coverage illustrated through the cyclic voltammetry response of a redox probe in a bare gold electrode, a gold electrode covered by a tightly-packed monolayer and a gold nanoparticle/organic monolayer/gold sandwich structure.

(vi) The potential applications of the fabricated devices.

EXPERIMENTAL OVERVIEW

A detailed student handout and the instructor notes for this laboratory experiment are provided in the Supporting Information. Scheme II in the Supporting Information summarizes the set of experiments of this practical. The practical was designed to be completed over three laboratory sessions (three hours each), in groups of four or five individuals. A chronogram of the activities carried out is presented in the Supporting Information. The students prepared self-assembled monolayers (SAMs) of a dithiol compound, whose surface coverage was determined by means of a Quartz Crystal Microbalance (QCM). Cyclic voltammetry (CV) experiments demonstrated that the SAM blocked the electron transfer at the electrode. Subsequently, gold nanoparticles (GNPs) were synthetized and deposited onto the SAM surface, which was also quantified by QCM. CV experiments demonstrated that the electron transfer was restored in the GNPs/SAM/gold devices.

HAZARDS

This practical required the use of ethanol which is a volatile and flammable solvent. Gold(III) chloride hydrate may cause irritation to the skin, eyes, and respiratory tract, and may be harmful if swallowed or inhaled. Sodium borohydride is a toxic, flammable compound and is also a source of basic borate salt, which can be corrosive. There is a flammability hazard associated with the production of hydrogen from the reaction between gold(III) and sodium borohydride. The reaction was performed in a fume hood. Appropriate personal protection equipment (PPE) (gloves, safety glasses or goggles, laboratory coats, covered shoes, etc.) was worn when handling chemical reagents.

EXPERIMENTAL SECTION

Reagents and Equipment

All materials are commercially available and were used as received: biphenyl-4,4′-dithiol (95%) and gold(III) chloride hydrate(~52% Au basis) were purchased from Aldrich; hexaammineruthenium(III) chloride (ACS reagent, 98%) and potassium chloride (puriss. p.a. ≥ 99.5%) were provided by Sigma and Fluka, respectively. Gold electrodes on glass for the CV studies were purchased from Arrandee™. Substrates for the QCM experiments were purchased from Stanford Research (AT-cut, α-quartz crystals with a resonant frequency of 5 MHz having circular gold electrodes patterned on both sides).

QCM measurements were carried out using a Stanford Research system instrument. CV experiments were done using a potentiostat from Eco Chemie and a standard three electrode cell.

EXPERIMENTS AND RESULTS

Self-assembled films are spontaneously formed on surfaces by chemisorption of the head group of an organic compound onto a substrate.[8] Typical examples include thiols on gold and trichlorosilanes on glass. The ease of preparation and the fact that it is possible to fabricate SAMs on a variety of substrates using different terminal functional groups have made the self-assembly technique a widely used ‘bottom-up’ method of surface modification. For further details about SAMs see reference[8] and the Supporting Information. Quartz crystal microbalances determine the mass variation per unit area by measuring the change in frequency of a quartz crystal resonator. The QCM can be used under vacuum, in gas phase and in liquid environments. Therefore, it represents a useful tool for the determination of the surface coverage of SAMs onto gold substrates. More information about QCM fundamentals and experiments can be found in reference[9] and in the Supporting Information.

Prior to the SAM formation the resonant frequency of a clean QCM substrate, f_0, was determined. Afterwards, a gold electrode from Arrandee™ for the electrochemical experiments and a gold substrate from Standford Research for the QCM studies were immersed in a 1 mM solution of biphenyl-4,4′-dithiol (Figure 1) in absolute ethanol, and incubated at 20 °C for 24 hours in the absence of light.

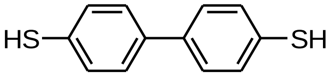


Figure 1. Chemical structure of biphenyl-4,4′-dithiol.

Immersion of the gold electrodes in a biphenyl-4,4′-dithiol solution resulted in the formation of a gold-thiolate monolayer according to:[10]

$$\mathrm{Au + HS\text{-}R\text{-}SH \rightarrow Au\text{-}S\text{-}R\text{-}SH + \tfrac{1}{2}\, H_2}$$

The modified gold electrodes were rinsed thoroughly with absolute ethanol to remove any physisorbed material and dried in nitrogen. Afterwards, the resonant frequency of the modified QCM substrate was determined, f_1 (see Scheme I.b in the Supporting Information).The change in the frequency of oscillation ($\Delta f = f_0 - f_1 = 20$ Hz) was introduced in the Sauerbrey equation:[11]

$$\Delta f = -\frac{2\cdot f_0^2\cdot \Delta m}{A\cdot \rho_q^{1/2}\cdot \mu_q^{1/2}} \qquad (1)$$

where f_0 is the fundamental resonant frequency, Δm is the mass change, A is the electrode area, ρ_q is the density of the quartz (2.65 $g\cdot cm^{-3}$) and μ_q is the shear module ($2.95\cdot 10^{11}$ $dyn\cdot cm^{-2}$). Figure 2 shows the QCM values at different incubation times. The formation of the monolayer was completed after ca. 24 hours of incubation. The resulting surface coverage for the biphenyl-4,4′-dithiol monolayer on gold was $6.1\cdot 10^{-10}$ $mol\cdot cm^{-2}$, which is in good agreement with the theoretical value, $6.2\cdot 10^{-10}$ $mol\cdot cm^{-2}$, determined from a molecular model (Spartan®08 V1.0.0).

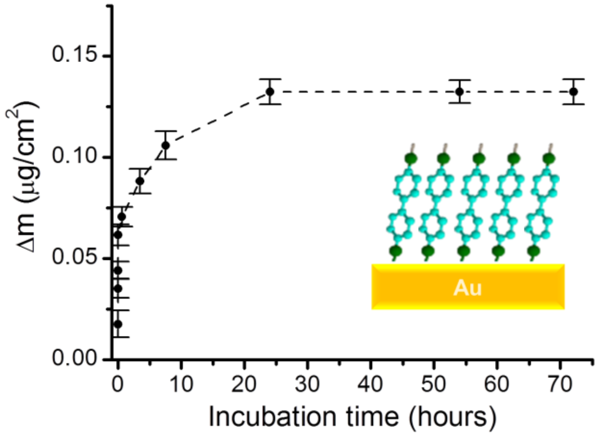


Figure 2. Surface coverage of a gold substrate upon incubation time in a biphenyl-4,4′-dithiol solution.

Cyclic voltammetry is a potential sweep method where the potential is changed at a certain scan rate and the current at the working electrode is measured. The plot of current *vs.* potential is a cyclic voltammogram. CV is widely used to measure the redox potential of electroactive materials, to determine the electrode reaction mechanisms, and it is also used as an indirect measurement of defect densities in thin films. In this practical, CV was used to study the blocking effect of a tightly-packed monolayer on gold and the electron transfer after deposition of gold nanoparticles onto the monolayer. For ease of understanding and operating the electrochemical section, consult references[12-15] as well as the Supporting Information. In this practical, a bare gold electrode (working electrode) of 1 cm^2 was introduced in an electrochemical cell containing a 1 mM $[Ru(NH_3)_6]Cl_3$ and 0.1 M KCl aqueous solution. The reference electrode was Ag/AgCl, KCl (3M) and the counter electrode was a Pt sheet. The solution was purged with nitrogen for 30 minutes to remove oxygen, which is electroactive at negative potentials. The scan rate was 0.1 $V \cdot s^{-1}$. The electrochemical process that took place during the first half cycle was:

$$[Ru(NH_3)_6]^{3+} + 1e^- \rightarrow [Ru(NH_3)_6]^{2+}$$

The experiment was repeated using the SAM/gold electrode as the working electrode. It is well-known that the deposition of a SAM of an organic material onto an electrode leads to a diminution of the electron transfer to redox species in solution.[2,16] This phenomenon was clearly observed in the practical (Figure 3). Thus, the lack of Faradaic current confirmed that the SAM was tightly-packed, essentially pinhole free[2] and effectively blocked electron transfer between the redox probe and the electrode surface.

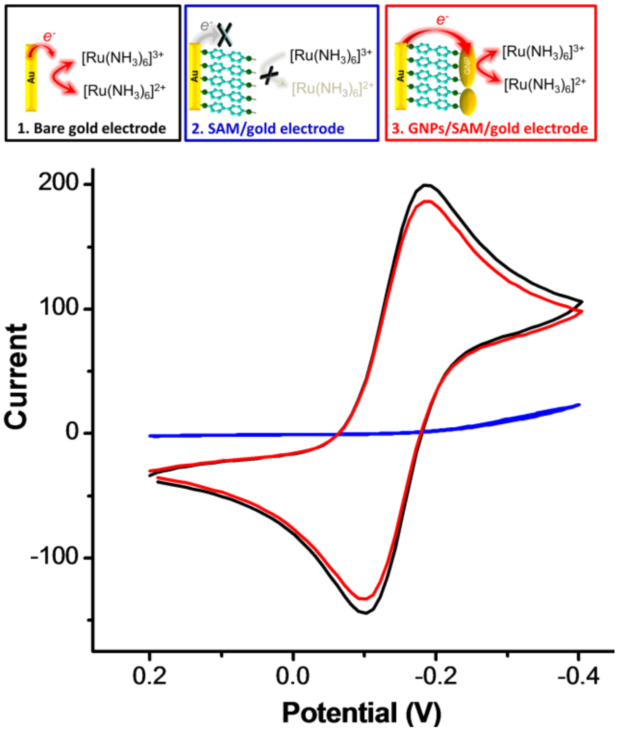


Figure 3. Cyclic voltammograms obtained using a bare gold electrode (black), a gold electrode covered by a biphenyl-4,4′-dithiol SAM (blue), and the SAM covered by GNPs (red) as working electrodes.

A dispersion of gold nanoparticles (GNPs) was prepared by adding rapidly dropwise 0.5 mL of a 10^{-3} M $NaBH_4$ (freshly prepared) aqueous solution to 30 mL of a 10^{-5} M $HAuCl_4$ aqueous solution with vigorous stirring at 2 °C using an ice-water bath. The hydrodynamic diameter of these GNPs was in the 7-28 nm range.[17] Incubation of the

SAM/gold substrate in the dispersion of GNPs (at 2 °C) started 15 min after the mixture of the reactants. Figure 4 shows the mass change obtained with the QCM versus the incubation time (each point was determined after the substrate was withdrawn from the incubation solution, rinsed with water and dried with nitrogen). An incubation time of 100 min into the GNPs dispersion led to a maximum surface coverage (Figure 4).

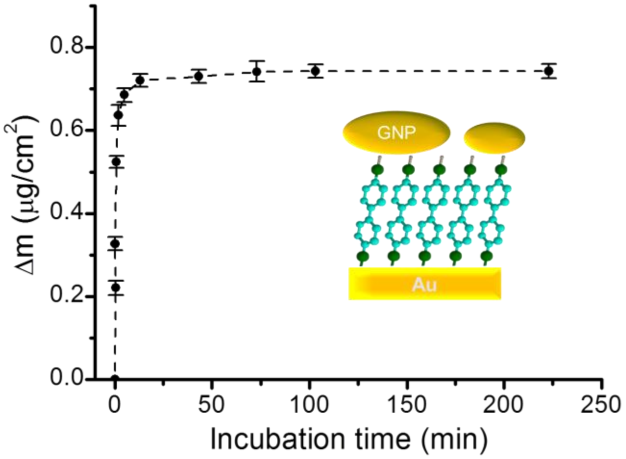


Figure 4. Deposited mass of GNPs *vs.* incubation time.

Incubation of the SAM/gold devices in a GPNs dispersion did not affect the integrity of the SAM as demonstrated through experiments in the Supporting Information. After the deposition of the GNPs on the SAM surface, the cyclic voltammogram (Figure 3) exhibited a quasi-reversible behavior with a cathodic-anodic peak separation of 77 mV as well as a near unity peak current ratio as observed for a bare gold electrode under the same conditions. As previously reported, the deposition of conducting nanostructures onto modified electrodes – made of insulating organic layers that completely block the electron transfer when immersed in a redox probe – results in a restoration of the Faradaic current[18] in systems where disruption of the SAM by penetration of the conducting nanostructures through the layer is ruled out by experimental evidence.[19] This effect has been observed for several types of conducting nanostructures including metal nanoparticles,[19] carbon nanotubes,[20] graphene sheets,[21] quantum dots[22] and even purely molecular objects containing a large number of redox centers.[23] This restoration of the electron transfer has been attributed to a relay station effect of the conducting nanostructures that facilitates the electronic coupling between the underlying electrode and the redox probe.[24] Therefore, when the conducting nanostructure is attached to the SAM-modified electrode, the electron transfer process involves two consecutive steps: (i) electron transfer between the underlying electrode and the conducting nanostructures, mediated by electron tunneling through the organic layer, and (ii) electron transfer between the conducting nanostructures and the redox probe, which is the rate-limiting step with regard to charge transfer within these particular systems.

EVALUATION AND ASSESSMENT

The students were asked to answer specific questions prior to the experiment to ensure their understanding of the fundamentals behind this practical (Supporting Information). Through the anwers to these questions the students were expected to attain and demonstrate a strong understanding of the nanofabrication and nanocharacterization methods involved in this practical. Before the commencement of the laboratory sessions students were invited to undertake further reading (Supporting Information) and after completion of the practical entered into a class debate on the potential applications of these nanostructures. In our classes, the instructor initiated the debate by asking why GNP/SAM/electrode devices could have interest or applications beyond a conventional electrode. The students in our cohort indicated the different properties of nano-sized gold from the bulk counterpart and also noted that GNPs exhibit a high electrocatalytic activity, which may result in electrocatalytical applications. A significant number of students also highlighted the possibility of forming arrays of electrodes in which each electrode is as small as a few nanometers resulting in a higher sensitivity and selectivity, i.e, sensor applications including biosensors and immunosensors. Some students remarked that the passivating organic layer may result in electrodes with a low background capacitance which facilitates low detection limits in electroanalysis. Students also mentioned potential applications in the field of photovoltaics due to the high density of states that can exist on the nanoparticles and also the fact that the energy levels of the nanoparticles are tuneable by altering their size.

Assessment of student understanding of associated concepts was achieved by the laboratory report that students were asked to prepare (Supporting Information). Nearly all students showed a strong grasp on the experiments involved and a good understanding of the practical.

CONCLUSIONS

This demonstration tied together several nanofabrication and characterization techniques and the observation of new phenomena and properties of materials at the nanoscale. Ultimately, we expect that this comprehensive activity, which builds on the excitement of creating conducting nanostructures with important optical, electronic and catalytic applications, will stimulate interest in nanoscience and nanotechnology and contribute to inspire students to pursue careers in these fields.

ASSOCIATED CONTENT

Supporting Information

Experimental handout for the students and notes for the instructor are included in the Supporting Information. This material is available via the Internet at http://pubs.acs.org.

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