Enhanced catalytic activity of Fe phthalocyanines linked to Au(111) via conjugated self-assembled monolayers of aromatic thiols for O_2 reduction

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ABSTRACT

We have obtained and characterized self assembled monolayers (SAMs) of 4-aminothiophenol (4-ATP) and 1-(4-mercaptophenyl)-2,6-diphenyl-4-(4-pyridyl)pyridinium tetrafluoroborate (MDPP) functionalized with iron phthalocyanine (FePc) adsorbed on gold (111) electrodes. The catalytic activity of these SAMs/FePc was examined for the reduction of O_2 in aqueous media (pH = 4) and compared with that of bare gold and of gold coated directly with FePc molecules. Scanning tunneling microscopy (STM) studies confirm the functionalization of the 4-ATP by FePc. The electrocatalytic studies carried out with Au/FePc, Au/4-ATP/FePc and Au/MDPP/FePc electrodes show that the O_2 reduction takes place by a 4-electron transfer to give water in contrast to a 2-electron-transfer process observed on the bare gold. The activity of the electrodes increases as follows: Au<Au/FePc<Au/4-ATP/FePc<Au/MDPP/FePc.

1. Introduction

Metallophthalocyanines are well known electrocatalysts for the reduction of O_2 (ORR) [1–5]. Fe phthalocyanines catalyze the reduction of O_2 directly to water via 4-electrons, with rupture of the O—O bond in contrast to Co phthalocyanines [1–5]. Metal macrocyclics can be confined to electrode surfaces by simple adsorption [1–5]. More recently, preformed self-assembled thiol monolayers (SAMs) have been used as molecular anchors for these metal complexes [6–10]. When using SAMs, the macrocyclic complex can be immobilized onto a gold substrate by two methods: i) by using the thiol functionality (—SH), incorporated on the macrocyclic ligand that serves as anchor to form the SAM [11] and ii) by preforming a SAM with a thiol group and then binding to it macrocyclic molecules via a nitrogen functionality present on the other end of the thiol molecule [7–10]. The second approach has some advantages because it avoids the time-consuming preparation of macrocyclic molecules with thiol functionalities. There are several reports in the literature that use a preformed SAMs to immobilize Co porphyrins [6,7] and Fe phthalocyanines [8–10,12]. In this work we have investigated the catalytic activity of Fe-phthalocyanine for ORR adsorbed directly on Au (111) and also anchored on SAMs pre-formed on Au (111).

2. Experimental

Electrochemical measurements were performed using water purified with a MilliporeMilli-QBiocel Ultrapurewater system. Solutions were purged with ultrapure nitrogen or ultrapure O_2 for 45 min prior to each electrochemical measurement. 4-Aminothiophenol (4-ATP, 97%) and Fe phthalocyanine were from Aldrich. 1-(4-Mercaptophenyl)-2,6-diphenyl-4-(4-pyridyl)pyridinium tetrafluoroborate (MDPP) was synthesized according to ref. [13]. Tetrahydrofuran (THF) was from JT Baker. All other reagents were analytical grade and used as received. Gold slides were annealed using a H_2 flame, in order to obtain preferential Au(111) orientation. To obtain Au/FePc electrodes, the Au(111) electrodes were placed for 5 min in a 1.0 mM FePc solution, under nitrogen and then rinsed with the solvent to eliminate any excess of FePc. The preparation of Au (111)/ 4-ATP/FePc and Au (111)/MDPP/FePc was achieved as follows: after annealing, the Au slides were dipped into a 50-μM ethanolic solution of 4-ATP or MDPP for 24 h. After this, the electrodes were further rinsed with ethanol for 20 min and dried under N_2. The SAMs/Au (111) electrodes were further modified with FePc by incubating them for 4 hours in a 1×10^{-3} mM solution of FePc in THF. The Au samples were then placed for 5 min in THF under N_2. Surface characterization was achieved by STM with an ECM-2 microscope (Veeco, USA) using commercial cut Pt-Ir tips. The cyclic voltammetry experiments were performed with a Bio-Analytical Systems, BasI-Epsilon potentiostat, using a conventional three-electrode electrochemical cell. The working electrode was a thin vapor deposited Au film on glass (12×12 mm slides from Arrandee®). The reference electrode was Ag/AgCl$_{sat}$ and platinum wire of 5 cm^2 was the counter electrode.

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Different tests of the electrocatalytic activity for O_2 were performed in freshly prepared buffer solutions (pH 4.0) at 25 °C.

3. Results and discussion

Fig. 1a shows the STM image of the Au(111) surface modified with a Fe-phthalocyanine anchored via a 4-ATP SAM. Bright spots stand out showing evident regular structures on the SAM surface. These local bright regions, with diameters between 2 and 3 nm and about 0.5 nm height, are associated with the presence of the FePc molecules anchored to the 4-ATP layer (see Fig. 1b). The sectional analysis of surface shown in Fig. 1b, passing through the top of bright regions, reveals sub-nanometric height structures with a very similar pattern to that reported on previous STM-UHV publications on FePc layers adsorbed directly on Au(111) [14,15]. Despite the fact that our STM measurements were collected in air, our results clearly show that the FePc molecules are present and anchored on the 4-ATP SAM surface.

Fig. 1c compares the potentiodynamic response of the Au(111) electrode in the presence of oxygen before and after modification using different molecular configurations containing SAMs with and without FePc. The current intensity for all systems varies linearly with the square root of the potential scan rate, a result that typically corroborates that the ORR is under mass-transport control. The dashed line shows the response of the bare Au(111). ORR on gold proceeds only via 2-electrons to give peroxide [16,17] so the voltammetric response corresponds to a total transfer of 2-electrons. After modification of the Au(111) with a SAM of MDDP, the ORR currents are severely suppressed, indicating that most of the surface of Au(111) is coated with these SAMs, probably leaving very few open spots for the direct reduction of O_2 on the Au sites (see purple line). When the Au(111) is modified with a SAM of 4-ATP, the O_2 reduction currents are suppressed to even much lower values compared to those obtained with MDDP (see green line), showing that in this case the SAM layers are probably more compact hindering the access of O_2 molecules to Au sites. So, in both cases, as expected, the SAMs of both thiols act as inhibitors of the reduction of molecular oxygen, showing no catalytic activity for the reaction. The blue line shows the response of the Au (111) surface when it is modified by direct adsorption of FePc on its surface. The results for the Au surface coated directly with FePc are interesting: in spite of the fact that the bare Au(111) is active for ORR, after adding FePc to its surface, an enhancement of the currents is observed. FePc probably covers more Au active sites compared to the new Fe active sites existing in the FePc molecules but this is surpassed by the superior catalytic activity of FePc. If one assumes that the FePc is flatly adsorbed on the Au(111) surface, forming a monolayer, each FePc molecule covers from 18 to 24 Au active sites [14]. This estimation is based on STM high-resolution images obtained in high vacuum of monolayers of FePc on Au (111), that show that FePc can adopt a flat conformation covering 18–24 Au atoms [14]. The FePc monolayer leaves at least 15% of the Au surfaces uncoated so it can be argued that when the Au (111) surface is modified with FePc some Au sites might still be active for O_2 reduction. On the other hand, in spite of some surface loss of the electrode by FePc coating, new active sites for O_2 reduction are generated, due to the Fe center present in the phthalocyanine. So, although the gold surface loses about 85% of its active sites by the effect of FePc coating, the net result is a much higher activity. Fe sites are then very effective for promoting the O_2 reduction in spite of being diluted by a ratio of at least 20:1, compared to the number of coated Au atoms. It has been discussed by Scherson [18] for O_2 reduction on Fe porphyrins confined on graphite, from earlier data published by Shigehara and Anson [19], that very few Fe active sites are sufficient to sustain catalytic currents. It is important to point out that, as shown in many publications, FePc

catalyzes the ORR preferentially via 4 electrons [1–5], so the enhancement of the catalytic currents in the presence of FePc can be attributed in part to a change in the overall mechanism of the reaction. If the reaction on the Au/FePc proceeds via 4 electrons, the current peak should be almost double compared to that obtained with bare Au(111). However, with the Au/FePc electrode, only an increment of ca. 60% occurs, so probably the ORR proceed via two parallel mechanisms: via 2-e to give peroxide and via 4-e to give water, so the peak currents on the Au/Fe will involve a total transfer of an average of 3.3 electrons. This result suggests that a parallel process involving 2-electrons probably takes place on the uncovered Au sites. Similar results are obtained when FePc is anchored to the Au surface via 4-ATP (Au/4-ATP/FePc), since the current intensities are similar (slightly lower) to those obtained on Au/Fe, but they are still higher than those corresponding to bare Au (111). Further, a shift to low overpotentials of almost 0.1 V is observed by the mere presence of the thiol anchor. This effect is surprising since the presence of a spacer should decrease the overall ET rate, in spite of the fact that the aminothiophenol spacer has a π-conjugated system. As shown by several authors [20–22], ET transfer rates via conjugated systems decrease as the length of the chain increases and this effect is more pronounced for aliphatic chains [22]. A more dramatic effect is observed when a bulkier spacer (Au/MDDP/FePc) is used to anchor the FePc to the Au(111) surface. A shift of the ORR currents of more than 0.1 V is observed compared to Au/ATP/FePc, and of more than 0.2 V compared to bare Au. The peak current of ORR with the Au/MDDP/FePc is also the largest of all systems examined and are 2.1 times larger than those obtained with bare Au, so this is a strong indication that for this system the ORR process occurs almost entirely via 4 electrons to give water. The uncovered Au sites probably do not contribute much to the measured currents at those potentials. However, it can be concluded from the data of Fig. 1c that without doubt, the presence of FePc in any conformation increases the amount of electrons per oxygen molecule transferred, and in the case of Au/MDDP/FePc, the process seems to proceed almost entirely via 4 electrons. Further, the SAMs functionalized with MDDP and FePc present the highest activity for O_2 reduction than all the other conformations, both in terms of number of electrons per O_2 molecule transferred and also by the decrease in the overpotential of the reaction by more than 0.2 V compared to bare Au. However, when a spacer is used the rate of ET should not increase, the longer the spacer, the lower the ET rate (assuming the rate-determining step is the transfer of one electron to the dioxygen molecule [23]). The observed rate increase suggests that a new effect is operating, which may be related with the presence of a larger, delocalized π-systems that probably decreases the reorganizational energy of the whole system, decreasing the activation energy. Further, axial ligation to the Fe center by the spacer via a nitrogen atom could also favor the interaction of O_2 with the Fe center. As discussed by Kasai et al. [24] for the ligation of O_2 to Fe in heme, axial ligation can affect the orientation of the O_2 molecule on the Fe center. O_2 reduction can have two possible orientations when interacting with the Fe center: end-on (tilted) and side-on (with O_2 parallel to the plane). The end-on orientation does not favor the splitting of the O—O bond that is required for a 4-electron reduction process so this configuration should lead to a 2-electron reduction mechanism to give peroxide. Further, the side-on interaction involves a transition state that has larger energy (higher activation energy). In contrast, the side-on orientation does promote the splitting of the O—O bond and involves a transition state of lower energy, involving lower activation energy for the process. So if the latter configuration predominates, the overall process for O_2 reduction should proceed via 4-electrons. So in our case, the axial ligation of the bulkier spacer seems to favor the side-on interaction, facilitating the splitting of the O—O bond and the overall ORR via 4 electrons and probably lowering