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Chirality enhances oxygen reduction

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Abstract: Controlled reduction of oxygen is important for developing clean energy technologies, such as fuel cells, and is vital to the existence of aerobic organisms. The process starts with oxygen in a triplet ground state and ends with products that are all in singlet states. Hence, spin constraints in the oxygen reduction must be considered. Here we show that electron transfer from chiral electrodes to oxygen (oxygen reduction reaction) is enhanced over that from achiral electrodes. We demonstrate lower overpotentials and higher current densities for chiral catalysts versus achiral ones. This finding holds even for electrodes composed of heavy metals with large spin orbit coupling. The effect results from the spin selectivity conferred on the electron current by the chiral assemblies, the chiral induced spin selectivity effect.

Main Text:

Controlled oxygen reduction reaction (ORR) is central for aerobic life¹ and for developing clean energy technologies like fuel cells^{2, 3}. Understanding the detailed mechanism of the ORR is challenging because one must consider spin selection rules; ground state of diatomic oxygen is in a triplet electronic state ($^3\Sigma_g^-$) while the reaction products are in closed shell singlet states. Indeed, current fuel cell technologies use rare metal catalysts, which possess significant spin-orbit coupling. In contrast, aerobic organisms perform the ORR without the need for precious metals. For example, one might ask: how does the transformation from glucose to water and CO₂, which involves six O₂ molecules, occur so efficiently? Indeed, this question has been investigated and detailed mechanisms have been proposed⁴. While some enzymes possess metal co-factors with significant spin-orbit couplings that may relax spin constraints in the reaction⁵, enzymes without metal cofactors are known to facilitate the efficient reduction of oxygen^{6, 7}. It seems clear that important subtleties of the biochemical mechanism remain elusive.

In spite of a very substantial effort, the intrinsic activity of ORR catalysts has not improved significantly over the past decade and there has been limited success in developing catalysts with lower overpotential⁸. The best ORR catalysts are platinum-based and the adsorption of oxygen on the catalyst is very efficient at low reduction potentials so that the proton and electron transfer are inefficient. Only at high reduction potentials can the reaction proceed due to the decreased stability of the adsorbed oxygen^{9, 10}. This has been considered as the origin of the observed ORR overpotential, and a crucial bottleneck in catalyst development.

We hypothesize that the multielectron reduction of diatomic oxygen (ORR) is enhanced by the use of spin polarized electrons and that chiral biomolecules, which are known to spin polarize electrons via the chiral induced spin selectivity (CISS) effect¹¹, can be used to enhance the ORR efficiency. Previous work demonstrates that electron transport through proteins is spin

dependent¹², including proteins involved in respiration¹³. In part, this hypothesis is substantiated by recent reports that the efficiency and selectivity of the oxygen evolution reaction (i.e., anodic oxidation of water to O₂) is enhanced by using chiral anodes or anodes modified with chiral molecules^{14, 15}.

5 To test this hypothesis, we examined the electrochemical ORR at electrodes modified with chiral organic monolayers. To further relate our findings to fuel cells technology, in the second part of the work, we tested the effect of chirality on metallic thin films and on platinum and gold nanoparticles. In each case, we compare the ORR performance of the chiral modified electrodes, particularly the onset potential and the current densities to their achiral analogues. Platinum
10 nanoparticles were specifically chosen because they are the preferred catalyst in fuel cells¹⁶.

We used an electrochemical assay in which O₂ was bubbled into an electrochemical cell and the reductive current was monitored (Fig. 1a). The electrochemical cell was assembled with a Pt counter electrode, an Ag/AgCl reference electrode, and a working electrode that could be either chiral or achiral. In the first stage of the work we utilized a 100 nm thick gold film that was coated
15 with a self-assembled monolayer (SAM) of chiral cysteine and oligopeptides, SH-(CH₂)₂-NH-(Ala-Aib)_n-COOH (n = 3, 5, 7, 8, 11 referred to as L-ala3, L-ala5, L-ala7, L-ala8, and L-ala11, respectively), or with a monolayer of achiral molecules, 3-mercaptopropionic acid and SH-(CH₂)_n-CH₃ (n = 3, 7, 9, 13, 17) (Supplementary Table 1). The monolayer formation was characterized by infrared spectroscopy, using a polarization modulation-infrared reflectance-
20 absorption spectrometer (Supplementary Figs. 1–3). The electrochemical reduction was performed at pH = 13 with 0.1 M KOH in aqueous solution. Oxygen was bubbled for at least 30 min before starting the measurements, to ensure saturation. All applied potentials were converted to the standard reversible hydrogen electrode (RHE) reference scale.

Fig. 1 | The experimental setup and the effect of chiral monolayers on oxygen reduction. Panel (a) shows a schematic layout of the electrochemical setup, which includes a gold working electrode coated with a self-assembled monolayer of either chiral or achiral molecules. The potentials reported here were converted to the standard reversible hydrogen electrode (RHE) reference scale. Note that the working electrode was static during all the measurements. Panel (b) shows the current versus potential that was measured when the electrode was coated with a monolayer of achiral molecules (the achiral 3-mercaptopropionic acid, blue curves), or the chiral molecules (L-cysteine, red curves) in N₂ (dotted curves) and O₂ (solid curves)-saturated 0.1 M KOH solution. The onset potential is defined as the potential at which the current reaches a value of 0.1 mA/cm², as noted by the dashed line in (b). Current densities were normalized in reference to the geometric area of the working electrode.

Under the alkaline conditions of these studies, two reduction pathways are commonly considered to be possible¹⁷:

Figure 1b presents current versus voltage plots for electrodes that are coated with a SAM of achiral 3-mercaptopropionic acid (blue) or with chiral L-cysteine (red). The significant difference of current density in O₂ and N₂ saturated solutions indicates that both chiral- and achiral-

functionalized electrodes show activity for oxygen reduction. (Fig. 1b and Supplementary Fig. 4). Despite the two molecules being of the same length and of very similar structure (Fig. 1b), a shift of about 0.25 V in the onset potential for the reduction is clearly evident. The onset potential is defined as the potential at which the current reaches a value of 0.1 mA/cm² (dashed line in Figs. 1b, 2a and 2b). Please note that a more positive potential implies a lower barrier for the ORR and that the coverage of organic molecules on the Au surface leads to onset potentials that are smaller than that found for the bare Au¹⁸ (Supplementary Fig. 5).

Figure 2 presents the current vs voltage curves for the ORR when the electrode is coated with achiral (Fig. 2a) and chiral molecules (Fig. 2b) of different length. As seen in Fig. 2c, the onset potential decreases with increasing molecular length for the achiral molecules, indicating an increase in the reaction barrier with increasing SAM thickness. In stark contrast, the onset potential increases with increasing molecular length for the chiral molecules (Fig. 2d), indicating a decrease in the reaction barrier with increasing SAM thickness. The higher barrier that is observed for the achiral molecules is consistent with the increase in electrical resistance of the molecules with increasing length and the decrease in O₂ solubility with the increasing molecular length of alkanes¹⁹. Hence one expects that a lower potential (higher overpotential) will be required to achieve the same current density for a thick film as that observed for a thin film. Surprisingly though, for the SAMs comprising chiral molecules, the potential increases with the length, even though the molecules resistance is known to increase with length and the diffusion of O₂ through the layer to the electrode is expected to decrease with the molecular length. The unusual decrease of the ORR reaction barrier with increasing oligopeptide length correlates with the improved spin filtering of oligopeptides with increasing length (*vide infra*).

Fig. 2 | The molecular length-dependent oxygen reduction. The current-voltage curves were obtained in O₂ saturated solutions of 0.1 M KOH at room temperature and a sweep rate of 50 mV/s. (a) The current vs potential curves are plotted for monolayers of achiral molecules of various lengths. The onset potential becomes more negative as the molecular length increases, indicating a higher barrier for reduction. (b) The current versus potential curves are plotted for monolayers of chiral molecules of various length. The onset potential becomes more positive as the length increases, indicating a lower barrier for reduction. (c, d) The onset potentials versus molecular length for working electrodes modified with achiral and chiral monolayers of different length, respectively. Current densities were normalized in reference to the geometric area of the working electrode.

To confirm that the different behavior does not arise from significant length differences or SAM qualities between the two type of molecules, the current vs potential curves were measured for the ferri/ferrocyanide (Fe(CN)₆^{3-/4-}, 10 mM) redox couple in 0.1 M KCl aqueous electrolyte solution, instead of oxygen (Supplementary Fig. 6). Given that the achiral ferricyanide is a low spin d⁵ complex and ferrocyanide is a low-spin d⁶ coordination complex, no effect from spin

polarization is expected for electron exchange with this redox couple. In this case, the surfaces coated with shorter molecules show a much higher redox peak current than that of longer molecules, independent of whether the molecules are chiral or achiral. These findings are corroborated by impedance measurements which show that the impedance increases with length
5 for both type of molecules (Supplementary Table 2 and Supplementary Fig. 7).

In the second part of this work we examine whether the chiral enhancement takes place also when the electrode is made with materials with inherently large spin orbit coupling. We produced thin Au films through electrodeposition, in the presence of tartrate ions in the deposition solution (see the Methods for more details). The handedness of the deposited chiral film was
10 determined by the chiral tartrate ions (Supplementary Fig. 8). The onset potential obtained with the ‘chiral gold film’ was improved compared with that of chiral monolayer coated Au electrodes (Supplementary Fig. 9 and Fig. 1a). Moreover, the ORR onset potential of the chiral metallic Au film was 90 mV higher than that of the film made with a racemic mixture of tartaric acid. A similar enhancement due to chirality was also found in Au nanoparticles with L- or D-cysteine (Fig. 3a
15 and Supplementary Fig. 10). Considering the large spin orbit coupling of Au, the increased ORR onset potential confirms the additional contribution of the spin polarized electrons, induced by the chiral molecules. As will be shown below, this contribution must go beyond only relaxing the spin selection rules. To probe the effect of chirality on materials used in fuel cells, we synthesized platinum nanoparticles (Pt NPs) using the L- and D-enantiomers of cysteine as the ligands
20 (Supplementary Fig. 11). When a racemic mixture of L and D cysteine was used, we refer to it as achiral NPs. L-cysteine modified NPs show clear CD signals in the spectral region of the absorption of the NPs, while the racemic cysteine modified NPs were CD silent (Supplementary Fig. 12). Again, the onset potential of chiral Pt NPs far exceeds that of the achiral one (Supplementary Fig. 13). Measurements on commercial Pt/C catalyst (nominally 20% Pt on carbon

black) was also conducted as the benchmark for comparison. The electrochemically active surface area (ECSA) was calculated²⁰ (see Methods and Supplementary Fig. 14 for more details). After normalization of the oxygen reduction current by the ECSA of each catalyst, the chiral Pt NPs show a higher onset potential on the basis of equivalent Pt mass for the ORR than the state-of-the-art Pt/C catalyst (Fig. 3b), indicating a promising route to the development of fuel cell catalysts.

Fig. 3 | Oxygen reduction of chiral and achiral gold and platinum nanoparticles. The current vs potential measured with (a) gold nanoparticles (Au NPs) and (b) platinum nanoparticles (Pt NPs) of different chirality. Commercial Pt/C catalyst was added for comparison. The loading amount of metal Pt was kept at 42 μg per cm^2 geometric area. Curves were recorded at room temperature, in O_2 saturated 0.1 M KOH solution at a sweep rate of 50 mV/s. Current densities were normalized in reference to the geometric area of GCE (a) and specific electrochemically active surface area (b), respectively.

Previous studies have shown that the coupling of the electron spin direction to the molecule's chiral axis exceeds significantly the thermal energy at room temperature²¹ and that the chiral molecules serve as spin filters²². A measure for the spin dependent filtering is provided by the spin polarization P , which is defined as

$$P = \frac{I_\alpha - I_\beta}{I_\alpha + I_\beta} \quad (3)$$

where I_α is the electron current with the electron spins pointing parallel to their velocity and I_β is the electron current with their spin pointing antiparallel to their velocity. The effect of chiral

molecules on the ORR efficiency can be revealed by probing the correlation between the length of the chiral molecules and the spin polarization of the electrons transmitted through them. As reported earlier for the L-oligopeptides used here (Fig. 4a), the conduction is higher for electrons with their spins aligned parallel to their velocity and the magnitude of the spin polarization increases from 30% to 45% as the oligopeptide length increases²³. Based on the spin polarization results, it is possible to calculate the dependence of the current in the reduction process on the spin polarization (see Methods). This calculation implies that 2.9 ± 1.5 electrons are involved in the rate determining step of the reduction (Supplementary Fig. 15); a similar number of electrons was obtained by the evaluation of current density between a platinum surface and a chiral monolayer (Supplementary Fig. 5). This finding suggests that the oxygen reduction occurs through a two-electron mechanism when monolayer modified Au surface serves as the working electrode, as described above (equation 2).

How does the spin polarization of the electron current affect the reduction of oxygen? Independent of the exact mechanism of the oxygen reduction, it requires at least two electrons in the first stage to generate either O_2^{2-} or HO_2^- ¹⁷. In considering the spin statistics, it is the projection of the O_2 molecule's spin onto the chiral axis emanating from the molecular layer that is important as an O_2 molecule approaches the SAM. For O_2 , with its unpaired electrons, 1 and 2, three possible spin states, $\alpha(1)\alpha(2)$, $\beta(1)\beta(2)$, and $[\alpha(1)\beta(2) + \beta(1)\alpha(2)]/\sqrt{2}$ are possible. In the case of chiral oligopeptides, the two electrons injected from the monolayer have the same spin projection on the molecular axis, namely their state will be $\alpha\alpha$ (Fig. 4b). Thus, the reaction barrier is affected by an entropic factor (related to the spin statistics) and an enthalpic factor arising from the stabilization of the $\beta(1)\beta(2)$ state of the O_2 by the spin exchange interaction with the polarized electrons on the chiral molecules.

Fig. 4 | The effect of chiral molecules. (a) The dependence of the spin polarization on the length of the chiral oligopeptides, adapted with permission from ref. ²³. (b) The splitting in the spin states of the triplet oxygen upon interaction with the spin polarized electrons residing on the chiral molecules. (c and d) The possible spin states in the case of a chiral system (c) and in the case of an achiral one (d). In the case of an achiral system the two electrons can have four possible configurations from which only one of them leads to reaction. In the chiral system there is only one possible configuration and the electrons are strongly coupled to the molecular frame, as a result this is the only configuration that can lead to reaction. (e) The calculated triplet energy levels on the oxygen presented as a function of distance between the chiral molecule and the oxygen.

Figures 4b-d illustrate the spin polarization effect. While in the chiral molecules the spin direction is defined with respect to the molecular axis, on the oxygen the three degenerate spin states split as the molecule approaches the chiral monolayers; i.e., its spin states split, like in the case of a magnetic field, and the state $\beta(1)\beta(2)$ will be stabilized. As the oxygen interacts (electron cloud overlap) with the chiral monolayer film, these interactions grow in strength because of the

spin-exchange effect (Fig. 4b). This effect reduces the enthalpic barrier and a more efficient injection of the spins from the monolayer into the oxygen system results. Moreover, the O₂'s spin state alignment with the chiral film reduces the entropic contributions to the free energy barrier (Fig. 4c and 4d). For the achiral film there are four spin states possible in the monolayer $\alpha\alpha$, $\beta\beta$, $\alpha\beta$ and $\beta\alpha$, from which only one will enable efficient electron transfer to the oxygen (thus the reaction probability is only 1 in 4). Moreover, because the spins on the achiral monolayers are not coupled to the molecular frame, they will not split the spin states of the oxygen and the enthalpic barrier will not be reduced.

Model calculations support the mechanism described above. The theoretical simulations treat the chiral molecule as a chain of nuclear sites, each of which is carrying a single electron level and is coupled to both its nearest neighbours and next-nearest neighbors via both elastic and inelastic spin-orbit interactions^{24, 25} (see Methods for more details). Figure 4e shows the effect of the helix's interaction on the energies of the O₂ molecule's spin substates. Although a simple model, the calculations show a splitting of the triplet state sublevels that can be hundreds of meV (tens of kcal/mole). These findings are consistent with recent works that show enhanced oxygen reduction efficiency with magnetic electrodes^{26, 27}, presumably because of the spin alignment of the injected electrons. The proposed mechanism should be relevant for simultaneous two electron reduction as well as for a sequential process, as long as the second electron is injected on a time scale shorter than the spin depolarization time.

Given that the CISS effect can enhance the rate of multi-electron reaction steps by reducing the number of accessible spin channels, it is interesting to conjecture about its implications for the glucose oxidation process, in which six oxygen molecules and 24 electrons are involved. With the large number of multi-electron transfer steps possible in such a complex redox scheme, the reduction in the entropy of activation by spin filtering could enhance the overall rate by more than

an order of magnitude for chiral biomolecules. Homochirality in biological organisms represents an entropy reduction that increases the organisms Gibbs free energy. It may be that the respiration process and its strong benefit from homochirality, because of the lower number of possible spin states (lower entropic reaction barrier), helps drive this selection. This new mechanism in which spin filtered electrons enhance the overall reaction efficiency may explain, in part, why life has preserved chirality so consistently over evolution.

The present work demonstrates that controlling the spin in multi-electron transfer processes, like the ORR, results in two contributions to the reaction rates. The first is the correspondence with spin selection constraints, allowing for reactions to occur on a triplet potential energy surface. The second is in reducing the number of states available for the reactions, thereby reducing entropic barriers. The present results imply that control over the electron spin is an important attribute for catalysts that are used in important oxygen related reactions and it reduces the overpotential and increases the current density.

Methods

Monolayer formation. The solutions used to prepare the monolayer were firstly bubbled with Ar for more than 30 min. The achiral alkanethiol molecules were dissolved in ethanol to form a 1 mM solution. The chiral oligopeptides were dissolved in 2,2,2-trifluoroethanol ($\geq 99\%$, Sigma-Aldrich) to form a transparent solution of 1 mM. The Au film electrodes were prepared by e-beam evaporation on single-crystal silicon wafers with a combination of Cr (10 nm)/Au (100 nm) layers. Prior to adsorption, the surfaces were cleaned by boiling in acetone and in ethanol for 10 min each, followed by UV/ozone treatment for 15 min, and then immersing in ethanol for 40 min. These surfaces were then dried under nitrogen gas flow and immediately immersed in the solution of thiol molecules for 72 h.

Polarization Modulation-Infrared Reflectance-Absorption Spectroscopy (PM-IRRAS). PMIRRAS was used to characterize the chiral and achiral monolayers on the gold electrodes. The spectra were recorded using a Nicolet 6700 FTIR instrument equipped with a PEM-90 photo-elastic modulator (Hinds Instruments, Hillsboro, OR). Each spectrum was obtained by accumulating 2000 scans with the samples mounted at Brewster angle of 80° . The spectra are shown in Supplementary Figs. 1–3.

Synthesis of chiral gold films. Chiral gold (Au) films were synthesized by using an electrodeposition method²⁸. Briefly, 0.2 M L- or DL-tartaric acid, 0.02 M $\text{Na}_3\text{Au}(\text{S}_2\text{O}_3)_2$, 0.42 M $\text{Na}_2\text{S}_2\text{O}_3$, 0.42 M Na_2SO_3 were added in 10 mL of water and the pH was adjusted to 8. A three-electrode electrochemical cell was employed for the deposition in which a 15 nm of Au coated quartz substrate was used as the working electrode. A saturated calomel electrode (SCE) and a Pt wire were used as the reference and counter electrode respectively. For the deposition, a constant potential of -0.63 V was applied for 5 minutes. After the electrodeposition, the electrode was washed with water and used for the ORR experiment.

Synthesis of chiral gold nanoparticles. The synthesis of chiral gold nanoparticles was done by following procedure that reported in ref.²⁹. Typically, cubic Au seeds were firstly synthesized and dispersed in aqueous CTAB (1 mM) solution. 0.8 ml of 100 mM CTAB and 0.2 ml of 10 mM gold chloride trihydrate were added into 3.95 ml of deionized water to use as the growth solution. Cubic seed solution was then added to the growth solution, and 100 μM cysteine was added after 20 min. The sample was placed in a 30°C bath for 2 h, and the pink solution gradually became blue with large scattering. The solution was centrifuged twice to remove unreacted reagents.

Synthesis of chiral platinum nanoparticles. Platinum nanoparticles (Pt NPs) were synthesized using chloroplatinic acid hydrate and L- or DL-cysteine as ligands with water as a reaction media. In 718 μL of E-pure water, 82 μL of 122 mM chloroplatinic acid, 200 μL of 7.5 mM L- or DL-cysteine, and 200 μL of 200 mM NaBH_4 were added. For the circular dichroism measurements, the concentration of cysteine was increased to 50 mM. After two hours of magnetic stirring in N_2 atmosphere at room temperature, brownish transparent nanoparticle dispersions were obtained. The synthesized nanoparticles were analyzed after sufficient purifications by rinsing NPs with E-pure water. The precipitation was done by precipitation with addition of a larger volume of isopropanol followed by centrifugation for 20 min at 10,000 rpm.

Circular Dichroism (CD) measurements. The Circular Dichroism measurements were carried out using a Chirascan spectrometer, Applied Photo Physics, England. The measurement conditions for all spectra were done at a scan range of 185 to 700 nm; 0.5 sec time per point; 1 nm step size; and a 1 nm bandwidth. For the solution sample, a quartz cuvette with an optical pathway of 2 mm was used. The CD spectra of Au films with L or DL-tartaric acid were measured on quartz substrate with a thickness of 0.5 mm.

Electrochemical tests. Electrochemical measurements were performed using a three-electrode electrochemical cell, equipped with an Ag/AgCl (3M NaCl) reference electrode and a platinum wire as the counter electrode. The working electrode was an Au film modified with different molecules (*vide supra*). Electrochemical data were recorded at room temperature on a potentiostat (PalmSens4) electrochemical workstation. The potential was measured versus an Ag/AgCl reference electrode, and then calibrated with reference to a standard reversible hydrogen electrode (RHE). Note that the working electrode was static during all the measurements.

The electrolyte for oxygen reduction reaction was 0.1 M aqueous KOH (pH 13). Before each measurement, the electrolyte was purged with O₂ for 30 min and subjected to O₂ flow during the tests. For the control experiments, operation procedures were the same except the O₂ was replaced with N₂. The oxygen reduction properties of molecules coated surfaces were studied at room temperature by using linear sweep voltammetry (LSV) at a scan rate of 50 mV/s. Cyclic voltammetry (Supplementary Fig. 5) and electrochemical impedance spectra (Supplementary Fig. 6) were collected in aqueous solution with 0.1 M KCl and 10 mM Fe(CN)₆^{3-/4-}. Electrochemical impedance spectra were conducted with a frequency range of 50 kHz–5 Hz.

For the chiral Au film, the synthesized thin film on quartz substrates were directly used as the working electrode for oxygen reduction reaction. For the Au and Pt NPs, same amount of chiral or achiral NPs was dispersed in water by vigorous stirring and sonication. 8 µL of the NPs solution was dropped onto a glassy carbon electrode (GCE; 3 mm in diameter from ALS Co., Ltd., Japan). The loading amount of metal Pt were kept as 42 µg per cm² geometric area (confirmed by ICP-MS). After water evaporation under room temperature for 3 h, 4 µL of 0.05 wt% Nafion solution was dropped on the electrode surface to cover and stabilize the NP assembly on the electrode surface. Such NPs loaded GCE was immersed into the solution as a working electrode. ORR activities were measured under oxygen purging in O₂-saturated 0.1 M KOH at room temperature.

The electrochemically active surface area (ECSA) was measured by using the hydrogen adsorption/desorption method on platinum in alkaline conditions²⁰. 0.1 M KOH aqueous solution was firstly purged with O₂, and a continuous stream of argon was introduced into the cell to maintain an inert atmosphere. The CV curves were recorded between 0.0 V and 1.2 V versus the RHE with a scan rate of 50 mV/s. The ECSA was determined by integrating the hydrogen adsorption charge on the CVs (Supplementary Fig. 14), and calculated as: $ECSA = Q_{des} / (m \times Q_{ref})$, where Q_{des} is the overall charge of the H desorption, Q_{ref} is the charge density associated with a monolayer adsorption of H₂ on platinum with unit weight and m is the loading amount of platinum on electrode.

Calculation for the number of electrons transferred. The electron transfer number for the oxygen reduction process can be estimated by comparison of the spin polarization (Fig. 4a) and the current-voltage profiles shown in Supplementary Fig. 6. Consider the case for the ORR through L-ala3 versus the ORR through L-ala7. If the rate

limiting ORR step involves transfer of a single electron, then the ratio of the spin polarizations through the two peptide films should be equal to the ratio of the observed currents through the films. If however, there is a multiple electron process (n electrons transferred in the reaction step) then the ratio should be a multiplication of each spin effect. This logic suggests that we can use the equation:

$$\frac{SP_{ala7} \times I_{ala7}}{SP_{ala3} \times I_{ala3}} = \left(\frac{I_{ala7}}{I_{ala3}} \right)^n \quad \text{Eq. 3}$$

to estimate n . On the left, the product of the spin polarization for L-ala7 ($SP_{ala7} = 45 \pm 3\%$) and $SP_{ala3} = \text{L-ala3}$ ($31 \pm 3\%$) and the current densities, I_{ala7} and I_{ala3} , represent the spin polarized current through each film. The current densities, I_{ala7} and I_{ala3} , are estimated in the manner illustrated by Supplementary Fig. 7. In order to obtain two current densities at the same overpotential, we first took the tangent at maximum slope of the reduction current and extrapolated it to current density of zero, obtaining the intersections (a and a'). From the intersection, we then moved to the negative potential with 0.1 V (b and b'). The current density at this potential was regarded as I_{ala7} or I_{ala3} (the point marked with arrows); i.e., $I_{ala7} = -0.16 \text{ mA/cm}^2$ and $I_{ala3} = -0.13 \text{ mA/cm}^2$. Using these values in Eq. 3, we find that $n = 2.8$. Therefore, based on the spin polarization from Fig. 4a and the above-mentioned equation, we conclude that 2.9 ± 1.5 electrons are involved in the rate determined step of the reduction process.

We also compared the reduction current versus potential curves of a bare Au surface, platinum (Pt) surface, and a monolayer of L-ala11 (Supplementary Fig. 8) by shifting them to the same overpotential, as described in Supplementary Fig. 7. If we assume that the oxygen reduction reaction proceeds via a four-electron ($4e^-$) pathway on Pt³⁰, the electron transfer number is about 2.35 based on the current densities of L-ala11 and Pt surface. In addition, two-electron ($2e^-$) reduction of oxygen has been reported for polycrystalline Au surfaces^{31,32}, so that the similar current density of Au and L-ala11 indicate that a mainly two-electron process occurs in the chiral oligopeptides coated surfaces. This number is consistent with our results calculated from spin polarization.

Model calculations. The inelastic component in this model is composed of nuclear vibrations that couple to the electronic structure, through both spin-independent and spin-dependent electron-vibration coupling. These two components originate from nuclear motion that changes the nuclear confinement potential and, hence, pertain to both the overlap matrix elements included in the tunneling rates between nuclei as well as to the spin-orbit interaction in the structure. The theoretical simulations are performed using a model for the chiral molecule based on a chain of nuclear sites, each of which is carrying a single electron level (ϵ_m) and is coupled to its nearest neighbours via both elastic (t_0) and inelastic (t_1) hopping and to its next-nearest neighbours via both elastic (λ_0) and inelastic (λ_1) spin-orbit interactions, see refs. ²⁴ and ²⁵. The inelastic component in this model is composed of nuclear vibrations, modes ω_m , that couple to the electronic structure, through both spin-independent (t_1) and spin-dependent (λ_1) electron-vibration coupling. These two components originate from nuclear motion that changes the nuclear confinement potential $V(\mathbf{r})$ and, hence, pertain to both the overlap matrix elements included in the tunnelling rates between nuclei as well as to the spin-orbit interaction in the structure, see ref. ²⁴ for more details. The chiral molecule is attached on one end to a metallic reservoir ($\mathcal{H}_{res} = \sum_k \epsilon_k \psi_k^\dagger \psi_k$), see refs. ²⁴ and ²⁵, whereas the opposite end is connected to the O₂ molecule by way of a direct via direct exchange interaction v of the form

$v = \langle \psi_N^\dagger | \boldsymbol{\sigma} \cdot \mathbf{S}_{O_2} | \psi_N \rangle$, where $\psi_N^\dagger$ (ψ_N) denotes the creation (annihilation) spinor at the molecular site N , whereas $\boldsymbol{\sigma}$ is the vector of Pauli matrices, and $\mathbf{S}_{O_2} = \mathbf{S}_1 + \mathbf{S}_2$ is the spin operator for the O_2 molecule, where $\mathbf{S}_{1,2}$ denotes the spin 1/2 operator for the two unpaired electrons. The exchange integral v is calculated as function of the distance R between the chiral and O_2 molecules by using the expression for the exchange between the electrons in an H_2 molecule, see, e.g., ref. ³³,

$$v = j_0 \frac{\mathcal{A}-\mathcal{B}}{5a_0},$$

$$\mathcal{A} = \frac{6}{s} (S^2(\gamma + \ln s) - S'^2 E_1(4s) + 2SS' E_1(2s)),$$

$$\mathcal{B} = \left(-\frac{25}{8} + \frac{23s}{4} + 3s^2 + \frac{s^3}{3}\right)e^{-s}, \quad S = \left(1 + s + \frac{s^2}{3}\right)e^{-s},$$

where $j_0 = e^2/4\pi\epsilon_0$, e is the electron charge, ϵ_0 is the vacuum permittivity, $S'(s) = -S(s)$, $s = R/a_0$, a_0 is the Bohr radius, γ is the Euler constant, and $E_1(x)$ is the exponential integral.

For the simulations presented in the main text, we have modelled a chiral molecule with six turns of eight ions per turn, and the parameters (in units of $t_0 = 40$ meV)

t_1	λ_0	λ_1	$\epsilon_m - \mu$	ω_m	Γ_0
1/10	$t_0/40$	1/100	-2	1/10,000	$t_0/1,000$

where μ is the overall chemical potential for the system, whereas Γ_0 denotes the coupling strength between the metallic reservoir and the chiral molecule. All simulations are done at $T = 300$ K.

One end of the chiral molecule is attached to a metallic reservoir, and the opposite end interacts with the O_2 molecule by a direct exchange interaction v which is calculated as function of the distance R between the chiral and O_2 molecules (see Fig. 4e) by using the expression for the exchange between the electrons in an H_2 molecule²⁴. The exchange interaction is $v = \langle \psi_N^\dagger | \boldsymbol{\sigma} \cdot \mathbf{S}_{O_2} | \psi_N \rangle$, where $\psi_N^\dagger$ (ψ_N) denotes the creation (annihilation) spinor at the molecular site N , $\boldsymbol{\sigma}$ is the vector of Pauli matrices, and $\mathbf{S}_{O_2}$ is the spin operator for the O_2 molecule. The assembly of the metal, chiral molecule, and O_2 molecule constitutes an open system in which the charge distribution and accompanied spin polarization of the chiral molecule, and the magnetic moment of the O_2 molecule are determined in a self-consistent computation, using non-equilibrium Green functions.

References

1. Babcock, G. T. How oxygen is activated and reduced in respiration. *Proc. Natl. Acad. Sci. U. S. A.* **96**, 12971–12973 (1999).
2. Ehteshami, S. M. M. & Chan, S. H. The role of hydrogen and fuel cells to store renewable energy in the future energy network–potentials and challenges. *Energy Policy* **73**, 103–109 (2014).
3. Bauen, A., Foradini, F. & Hart, D. “Fuel cell-based renewable energy supply: sustainable energy for isolated and island communities” in *New and Renewable Technologies for Sustainable Development*, N. H. Afgan, M. da Graça Carvalho, Eds. (Springer, Boston, 2002), pp. 421–428.
4. Babcock, G. T. & Wikström, M. Oxygen activation and the conservation of energy in cell respiration. *Nature* **356**, 301–309 (1992).
5. Ferguson-Miller, S. & Babcock, G. T. Heme/copper terminal oxidases. *Chem. Rev.* **96**, 2889–2908 (1996).
6. Silva, P. J. Refining the reaction mechanism of O₂ towards its co-substrate in cofactor-free dioxygenases. *PeerJ* **4**, e2805 (2016).
7. Gabison, L. et al. X-ray, ESR, and quantum mechanics studies unravel a spin well in the cofactor-less urate oxidase. *Proteins* **79**, 1964–1976 (2011).
8. Kulkarni, A., Siahrostami, S. Patel, A. & Nørskov, J. K. Understanding catalytic activity trends in the oxygen reduction reaction. *Chem. Rev.* **118**, 2302–2312 (2018).
9. Nørskov, J. K., Rossmeisl, J., Logadottir, A. & Lindqvist, L. Origin of the overpotential for oxygen reduction at a fuel-cell cathode. *J. Phys. Chem. B* **108**, 17886–17892 (2004).

10. Seh, Z. W. et al. Combining theory and experiment in electrocatalysis: Insights into materials design. *Science* **355**, eaad4998 (2017).
11. Naaman, R., Paltiel, Y., & Waldeck, D. Chiral molecules and the electron's spin. *Nat. Rev. Chem.* **3**, 250–260 (2019).
12. Mishra, D. et al. Spin-dependent electron transmission through bacteriorhodopsin embedded in purple membrane. *Proc. Natl. Acad. Sci. U. S. A.* **110**, 14872–14876 (2013).
13. Mishra, S., Pirbadian, S., Mondal, A. K., El-Naggar, M. Y. & Naaman, R. Spin-dependent electron transport through bacterial cell surface multiheme electron conduits. *J. Am. Chem. Soc.* **141**, 19198–19202 (2019).
14. Mtangi, W., Kiran, V., Fontanesi, C. & Naaman, R. The role of the electron spin polarization in water splitting. *J. Phys. Chem. Lett.* **6**, 4916–4922 (2015).
15. Mtangi, W. et al. Control of electrons' spin eliminates hydrogen peroxide formation during water splitting. *J. Am. Chem. Soc.* **139**, 2794–2798 (2017).
16. Nie, Y. Li, L. & Wei, Z. Recent advancements in Pt and Pt-free catalysts for oxygen reduction reaction. *Chem. Soc. Rev.* **44**, 2168–2201 (2015).
17. Wang, D. et al. Transition metal and nitrogen Co-doped carbon-based electrocatalysts for the oxygen reduction reaction: from active site insights to the rational design of precursors and structures. *ChemSusChem* **14**, 33–55 (2021).
18. Ge, X. et al. Oxygen reduction in alkaline media: from mechanisms to recent advances of catalysts. *ACS Catal.* **5**, 4643–4667 (2015).
19. Murov, S. L., Carmichael, I. & Hug, G. L. *Handbook of Photochemistry*, 2nd ed. (Marcel Dekker, New York, 1993).

20. Yang, X., Nash, J., Oliveira, N., Yan, Y. & Xu, B. Understanding the pH dependence of underpotential deposited hydrogen on platinum. *Angew. Chem. Int. Ed.* **58**, 17718–17723 (2019).
21. Meirzada, I. et al., Long-timescale magnetization ordering induced by an adsorbed chiral monolayer on ferromagnets. *ACS Nano* **15**, 5574–5579 (2021).
22. Waldeck, D. H., Naaman, R. & Paltiel, Y. The spin selectivity effect in chiral materials. *APL Mater.* **9**, 040902 (2021).
23. Mishra, S. et al. Length-dependent electron spin polarization in oligopeptides and DNA. *J. Phys. Chem. C* **124**, 10776–10782 (2020).
24. Fransson, J. Vibrational origin of exchange splitting and chiral-induced spin selectivity. *Phys. Rev. B* **102**, 235416 (2020).
25. Fransson, J. Charge redistribution and spin polarization driven by correlation induced electron exchange in chiral molecules. *Nano Lett.* **21**, 3026–3032 (2021).
26. Zeng, Z. et al. Magnetic field-enhanced 4-electron pathway for well-aligned Co₃O₄/electrospun carbon nanofibers in the oxygen reduction reaction, *ChemSusChem* **11**, 580–588 (2018).
27. Minaev, B. F. Spin effects in reductive activation of O₂ by oxydase enzymes. *RIKEN Rev.* **44**, 147–149 (2002).
28. Estrine, E. C., Riemer, S., Venkatasamy, V., Stadler, B. J. H., & Tabakovica, I. Mechanism and stability study of gold electrodeposition from thiosulfate-sulfite solution. *J. Electrochem. Soc.* **161**, D687–D696 (2014).
29. Lee, H. E. et al. Amino-acid- and peptide-directed synthesis of chiral plasmonic gold nanoparticles. *Nature* **556**, 360–365 (2018).

30. Shao, M., Chang, Q., Dodelet, J. P. & Chenitz, R. Recent advances in electrocatalysts for oxygen reduction reaction. *Chem. Rev.* **116**, 3594–3657 (2016).
31. Kim, J. & Gewirth, A. A. Mechanism of oxygen electroreduction on gold surfaces in basic media. *J. Phy. Chem. B* **110**, 2565–2571 (2006).
32. Wroblowa, H. S. & Razumney, G. Electroreduction of oxygen: a new mechanistic criterion. *J. Electroanal. Chem.* **69**, 195–201 (1976).
33. Atkins, P. W. *Molecular Quantum Mechanics*, 2nd ed. (Oxford University Press, 1983).

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Author contributions

R.N. conceived and guided the whole project. Y.S. fabricated the monolayer modified electrodes and conducted the measurements. F.T. and Y.S. performed the electrochemical impedance measurements. W.Z. performed part measurements of oligopeptides modified electrodes. F.T. and K.S. conducted the measurements of Au nanoparticles. K.S. performed the measurements of Au thin film. Y.S. conducted the measurements of Pt nanoparticles. J.F. performed the calculations. J.F., D.H.W and R.N. coordinated the writing of the paper, and all authors contributed to revising the paper.

Competing interests

Authors declare no competing interests.

Supplementary information

Supplementary Figures 1 to 15

Supplementary Tables 1 to 2

References

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