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Hybrid Mesoporous Electrodes Evidence CISS Effect on Water Oxidation

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Abstract

Controlling product selectivity is essential for improving the efficiency of multi-product reactions. Electrochemical water oxidation is a reaction of main importance in different applications, e.g., renewable energy schemes and environmental protection, where H₂O₂ and O₂ are the two principal products. In this communication, the product selectivity of electrochemical water oxidation was controlled by making use of the chiral induced spin selectivity (CISS) effect at mesoporous-TiO₂ on molecule-modified Au substrate. Our results show a decrease in H₂O₂ formation when using chiral hetero-helicene molecules adsorbed on the Au substrate. We propose a mechanism for this kinetic effect based on the onset of CISS-induced spin polarization on the Au-helicene chiral interface. We also present a new tunable substrate to investigate the CISS mechanism.

Main

Product selectivity is a critical performance indicator that holds paramount importance in catalytic systems. The optimization of selectivity towards the desired product is of utmost necessity, particularly in multi-product reactions such as CO₂ reduction and electrochemical

water oxidation.^{1,2} The latter is a reaction of main importance in different renewable energy schemes. In particular, the oxygen evolution reaction (OER, Eq. 1), is a critical process in electrocatalytic water splitting for hydrogen production or artificial photosynthesis³. However, a competing oxidation reaction exists, the production of H₂O₂ (Eq. 2). While this is a valuable chemical with a wide range of industrial applications,^{4,5} its generation is often undesirable in certain practical contexts, e.g., in an electrolyser. This is primarily due to its propensity to adsorb onto the catalyst, reducing the overall reaction rate and potentially diminishing its stability,^{6,7} or to corrode other materials within the electrolytic system. Understanding the reaction pathway to favour one or another product remains essential for optimizing these applications.



The OER has sluggish kinetics, mainly attributed to the need to transfer four electrons. This leads to a high overpotential in water splitting applications. When high potentials are applied to produce oxygen, the formation of H₂O₂ can become a competing reaction. Recently, an additional possible cause of the increased overpotential to achieve the OER related to spin was introduced. The ground state of the oxygen molecule is a triplet state, while that of water is a singlet state. Thus, a spin change needs to occur during the reaction, and these spin-restrictions can increase the overpotential. The formation of H₂O₂, on the other hand, requires the transfer of only two electrons and does not involve a spin conversion, as H₂O₂ is a singlet in its fundamental state.^{2,8}

It was recently reported that a preferred orientation of electron spin can be found in chiral molecules when charges pass through, referred to as chiral induced spin selectivity (CISS) effect.⁹⁻¹¹ This phenomenon can play a paramount role in chemical reactions where spin multiplicity changes are involved.¹¹ Taking into account the different spin states of the products in the water oxidation, the CISS effect can thus have an influence on its product selectivity, favoring the formation of O₂ over H₂O₂ by providing spin-aligned electrons. Hence, using a chiral molecule as a spin polarizer could reduce the amount of H₂O₂ formed, as was already seen in different (photo-) electrochemical reactions.^{6,12}

Along the H₂O₂ hindered formation, the CISS effect has been shown to enhance O₂ production and double the OER activity of state-of-the-art NiFe-based catalysts.^{13,14} However, the latter

predominantly favour the OER and are unable to produce H₂O₂ in great quantities,^{15–18} thus limiting their suitability as a model for investigating CISS-induced changes in the water oxidation pathways. Additionally, the lack of tunability further restricts the possibility for examining such phenomena. Moreover, how a chiral molecule delivers spin-polarized electrons to the catalyst surface (e.g., if the chiral molecule is placed between the catalyst and the substrate, or if it polarizes electrons in its vicinity) requires further investigations.

In this work, we present a new tunable electrode that can be used to quantitatively test the CISS effect in electrochemical water oxidation. To achieve this, we constructed a hybrid electrode comprising an Au substrate coated with a mesoporous TiO₂ thin film. The selection of TiO₂ as our electrode material stems from its ability to generate H₂O₂ in substantial quantities,⁴ as well as its increasing application in H₂O₂ production.^{2,19} Mesoporous TiO₂ thin films can be produced with high surface areas in a controllable manner, and can act as a versatile platform, as pore sizes and wall materials can be easily tuned.^{20–22} The porous structure of the TiO₂ allows uncovered areas at the Au substrate to bond the molecules of interest. Here, we quantitatively compared the selectivity of H₂O₂ formation during the electrochemical water oxidation reaction by using chiral and achiral molecule-modified electrodes. The molecules were added using a near-effortless and non-destructive deposition method on the exposed Au substrate to determine the lower limit of the CISS effect.

Helicenes are organic molecules with axial chirality, high racemization barriers and a rigid structure.^{23,24} These make them ideal molecules for electrode modification especially when incorporating heteroatoms in the helicene framework, to provide heterohelicenes,^{25,26} or when attaching functional groups that preserve the chirality of the molecule and stably bind to metal surfaces.²⁵

Mesoporous TiO₂ thin films were prepared on Au (111) substrates by evaporation-induced self-assembly. Figure 1 shows the mesoporous structure obtained, with a highly porous and well-ordered hexagonal structure with a pore diameter of ca. 8 nm. This allowed the deposition of small molecules within the pores. Enantiopure (*M*)-bis(thiadiazole)-[8]helicene (helicene hereafter)¹³, a chiral molecule capable of binding to the gold substrate, was used. Indeed, in a previous recent study,¹³ some of us chirally functionalized gold electrodes, coated with NiO_x catalysts, with bis(thiadiazole)-[8]helicene and its shorter analogue thiadiazole-[7]helicene.²⁷

Their achiral analogue, 2,1,3-benzothiadiazole has the same interaction with the surface but lacks the chiral helicene structure (Figure 2).

Based on scanning tunnelling microscopy (STM) measurements of ultra-thin mesoporous TiO_2 thin films after helicene deposition (Suppl. Figure 1), it appears that most of the molecules are located in the pores, and the TiO_2 surface is uncovered. This observation is consistent with the high affinity of the thiadiazole group to the gold substrate,¹³ and its low affinity to the TiO_2 walls. It is likely that helicene molecules can only be stably adsorbed on the Au substrate. Considering the self-assembled packing structure that we have reported for (*M*)-bis(thiadiazole)-[8]helicene on gold surfaces¹³, and that the pore has a diameter of 8 nm and a height of ca. 5-7 nm, we estimate that there are approximately 25 molecules per pore.

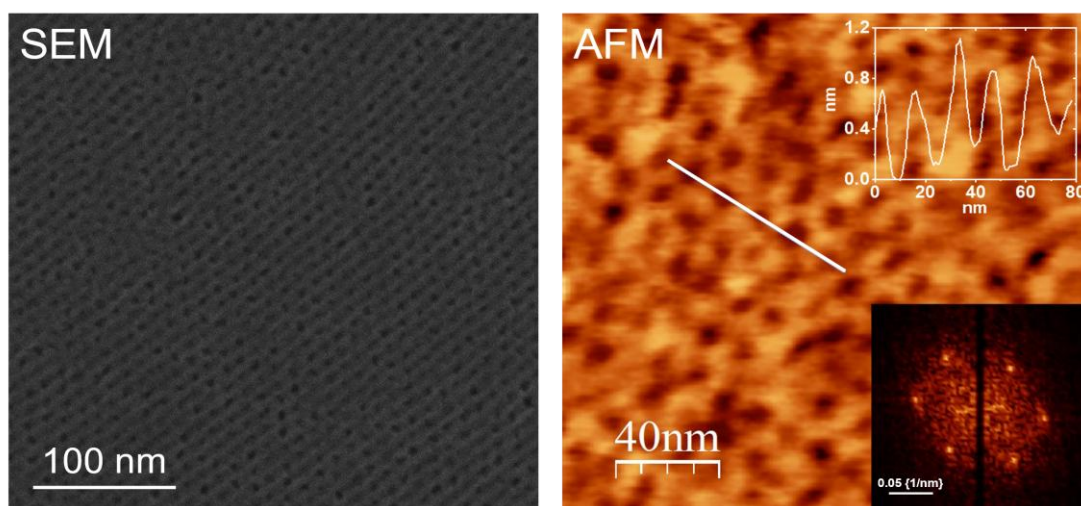


Figure 1. Highly ordered mesoporous TiO_2 film on Au(111): Top-view SEM and AFM images. Insets in the AFM image show the height profile and the fast Fourier transform.

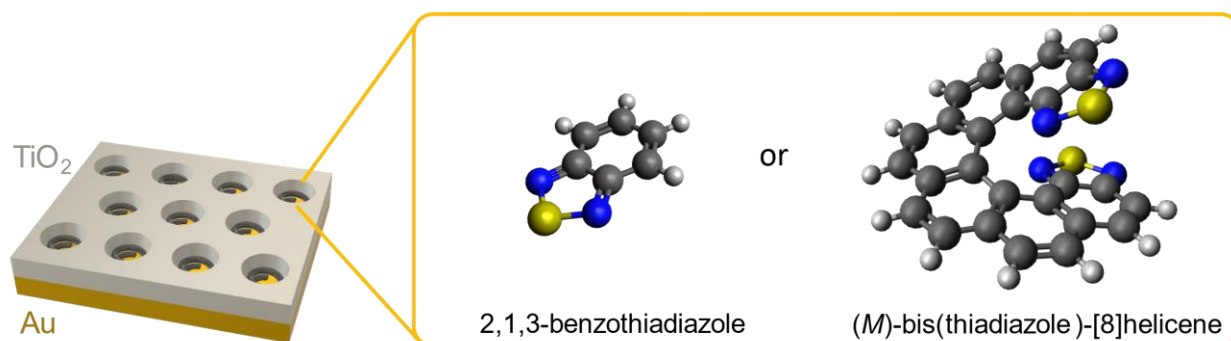


Figure 2. Scheme of the TiO₂/Au electrodes and molecules used in this work: 2,1,3-benzothiadiazole (achiral) and (*M*)-bis(thiadiazole)-[8]helicene (chiral).

Figure 3 displays the measured current during a 40-minute electrochemical reaction at a potential of 3.0 V vs. RHE. The current obtained in bare electrodes and those modified with helicene or benzothiadiazole is similar, which could be an indication that the active surface area does not change significantly. The total current accounts for the water oxidation reactions (OER and H₂O₂ formation) and possibly some Au oxidation. CVs of the different studied samples also show a similar behaviour (Suppl. Fig. 2). Nonetheless, the amount of H₂O₂ produced differs significantly, with a decrease of approximately 33% in the number of moles formed in helicene-modified electrodes compared to benzothiadiazole-modified ones. The same trend was observed in thicker TiO₂ samples (ca. 60 and 200 nm thickness, Suppl. Fig. 3). The effect of the chiral molecules is stronger when the film thickness is lower. See Methods and Suppl. Fig. 4 for further information on H₂O₂ quantification. Even if we could not quantify the oxidation state of the molecules after OER for this system, according to our previous work, the helicene molecules are stable on the Au surface after electrolysis.¹³ Moreover, if oxidation of the helicene molecules by highly oxidant intermediates²⁸ generated on TiO₂ were to occur, it is reasonable to expect a similar situation with the control benzothiadiazole molecule. The use of this control molecule allows us to assign the observed reduction on the H₂O₂ production to the presence of the chiral molecules.

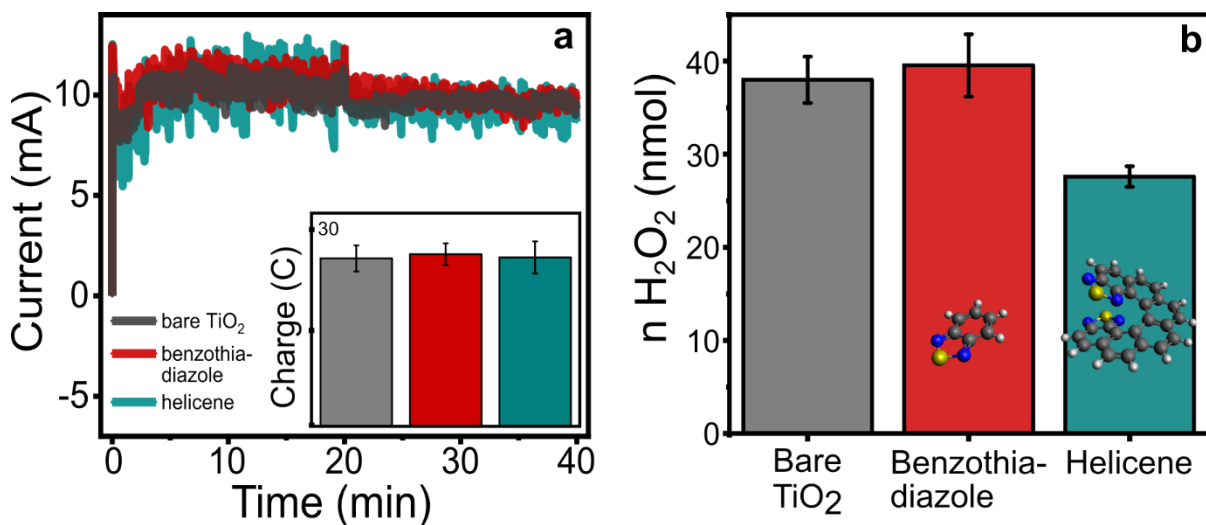


Figure 3. a) Chronoamperometry of bare TiO₂ and helicene or benzothiadiazole-modified electrodes. The noise is caused by bubble formation and release during the measurement. Inset shows the charge transferred after 40 min. b) Amount of H₂O₂ produced for each type of electrode.

The reduction in H₂O₂ formation with the chiral molecules was not observed in TiO₂ samples deposited on FTO, or in bare Au substrates (Suppl. Table 1 and 2). Thus, it is likely that the molecules are not directly affecting the active sites at the TiO₂ surface (i.e., where the reaction occurs), but their presence at the Au substrate affects the reaction happening on the TiO₂.

It is also interesting to note that although the molecules are not located between the substrate and the catalyst, or at the active sites on the catalyst, the CISS effect is anyway observed. This is evidence of CISS in a totally new and different configuration from previous studies, leading to new insights into the mechanism of the CISS effect.

It has been suggested that the chiral molecules act as spin filters when electrons pass through them.¹⁰ Some other works indicated that a chiral molecule polarizes the spin of electrons in its vicinity.^{11,29-31} In this work, we used a molecule-catalyst configuration that differs from the catalyst-chiral molecule-substrate sandwich configuration where the current goes through the chiral molecules. Here, the helicene molecules are adsorbed on the areas of Au surface that are not covered by TiO₂. The catalytic activity is still predominant at TiO₂ surface sites, regardless of the fact that the spin polarization interfacial activity seems to take place at the gold surface. Our results suggest that the spin polarization is somehow transmitted to the TiO₂ surface.

Although the mechanism is not totally clear, it has been demonstrated both theoretically and experimentally that spin polarization occurs as a consequence of electron transfer, electron transport and bond polarization through chiral centers. Based on this result we suggest that the formation of the bond between the chiral molecule and the gold surface leads to spin polarization^{32,33} in the Au substrate surrounding the molecules, subsequently affecting the kinetics of the reaction taking place at the catalysts supported by the same Au substrate (Figure 4), or that the spin-polarized electrons are transmitted through the molecules in close proximity to the TiO₂ walls, effectively acting as a bridge between the Au and TiO₂.

To explain the spin polarization around the molecules, we could assume that the nanoscale Au surface exposed to the electrolyte becomes ferromagnetic, as was observed for small Au nanoparticles.^{34–36} This would lead to a generation of spin polarization at the interface of chiral molecules and gold. In the context of understanding the magnetic behaviour of gold nanoparticles coated with organic molecules linked through N or S atoms, the transition from diamagnetism to ferro- and ferri-magnetism was mediated by precursor states called spin-polarized singlets (SPS), that is singlet states corresponding to systems with an even number of electrons where both the total spin and the total sum of local spin densities around atomic centres vanish, but the individual local spin densities were not zero. The TiO₂ cavities in the nanoscale could have the right order of magnitude to provoke similar effects in our system.

The transfer of spin polarization information to the active sites can then occur in the vicinity of the TiO₂/Au/molecules interface, as this type of behaviour has been found in other systems where the spin polarization transfer occurs effectively with a distance of the order of the coherence length.³⁷ Even though this transfer of polarization is essential for the observed kinetic effect, we cannot rule out the possibility that the Au-helicene chiral interface can provide an alternative kinetic path to the predominant one associated with the TiO₂ sites. We are currently advancing further work to elucidate this point.

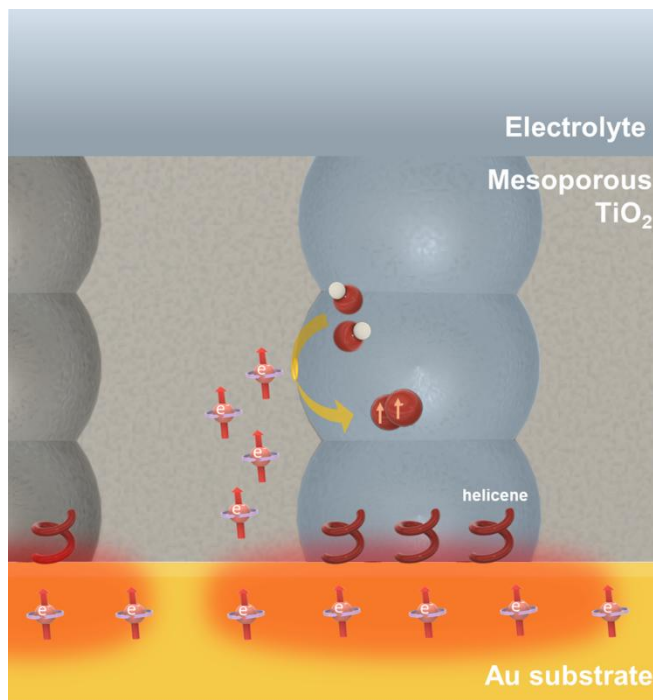


Figure 4. Illustration of the CISS effect on the helicene-modified mesoporous TiO₂ on Au substrate. The chiral molecules could polarize the spin of electrons traveling through the gold (red areas) and turn the TiO₂ into a spin-polarized state, which can then favour the formation of triplet O₂ over H₂O₂ production.

Considering that the accessible Au surface is limited by the pore size of the TiO₂ mesoporous structure, this hybrid substrate offers an intriguing opportunity to serve as a customizable platform for probing the limits of the CISS effect within confined systems. Tuning this model system could provide valuable insights into fundamental inquiries arising from this investigation, such as the optimal pore sizes and distances, the minimal quantity of chiral molecules required for discernible shifts in product selectivity trends. Further studies could assist in the mechanism understanding, as it is not yet clear whether the TiO₂ surface is influenced by Au polarization caused by the chiral molecules, or if the change in selectivity is the result of changing the way reaction intermediates adsorb on TiO₂ because the pores act as a grid of spin-polarized centres.

In summary, these results introduce a new tunable model system to study the CISS effect on the H₂O₂ formation on hybrid nanostructured electrodes. The use of chiral helicene molecules is an exceptionally efficient way to optimize product selectivity and energy efficiency in electron spin-dependent electrocatalysis applications. Moreover, the mesoporous structure can act as a versatile platform, as pore sizes and wall materials can be easily tuned, not only for electrocatalysis but TiO₂ also can be explored as a photoelectrocatalyst for this reaction, allowing for further studies of the CISS effect in nanostructured materials. This work is a first step in the direction of designing tunable substrates for CISS studies in electrocatalytic interfaces.

Supplementary Material

See the supplementary material for Experimental Methods and Supplementary Data.

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Author Declarations

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Priscila Vensaus: Conceptualization, investigation, visualization, writing – original draft. **Yunchang Liang:** Conceptualization, investigation, visualization, writing – original draft. **Nicolas Zigon:** Investigation, review & editing. **Narcis Avarvari:** writing – review & editing, funding acquisition. **Vladimiro Mujica:** writing – review & editing. **Galo J. A. A. Soler-Illia:** Supervision, writing – review & editing. **Magalí Lingenfelder:** Conceptualization, supervision, writing – review & editing, funding acquisition.

Data Availability

The data that support the findings of this study are available within the article and its supplementary material.

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