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COMMUNICATION

Immobilization of molecular cobalt electrocatalyst by hydrophobic interaction with hematite photoanode for highly stable oxygen evolution

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A unique modification of a hematite photoanode with perfluorinated Co-phthalocyanine (CoFPc) by strong binding associated with hydrophobic interaction is demonstrated. The resultant molecular electrocatalyst – hematite photoanode hybrid material showed significant onset shift and high stability for photoelectrochemical oxidation evolution reaction (OER).

Solar water splitting using light-responsive semiconducting materials and catalytic modules offers an attractive and clean route for producing renewable energy carriers using water and sunlight.¹ To create a solar to fuel conversion device, efficient and stable OER electrocatalysts must be implemented on the surfaces of photo-responsive materials.² Among various semiconductor photoanodes, hematite ($\alpha\text{-Fe}_2\text{O}_3$) is an inexpensive and attractive photoanode material with a band gap of 2.1 eV and an excellent light absorption depth of up to 150 nm.³ However, the minority carrier (hole) mobility of hematite limits (~ 5 nm) its use because it requires effective charge separation at the interfaces.^{4,5}

Light-induced OER activity can be improved using heterogeneous catalysts, such as IrO_2 ,⁶ NiO_x ,⁷ NiFeO_x ,⁸ or CoO_x ,^{9,10} on top of the hematite. This modification is considered to improve the charge separation, hole delivery and its effective consumption at the catalytic site. The measured low OER rates are often impeded by poor contact of the catalyst and the $\alpha\text{-Fe}_2\text{O}_3$ phase.³ In this scenario, hematite performance can be further improved by introducing an efficient OER electrocatalyst that can take up the holes rapidly. However, limiting photocurrents are also observed at higher potential regimes, coinciding with photocurrents of unmodified hematite at about 1.4 V vs RHE.^{4,5}

Several surface-functionalized molecular electrochemical systems have shown high OER rates relative to heterogeneous catalysts.¹¹ Mallouk and coworkers demonstrated the use of molecular–

inorganic heterojunctions to improve photoelectrochemical OER.¹² The catalytic molecular–semiconductor interface comprises unique electronic structures due to the distinct molecular orbitals of the catalyst that can overlap the electronic bands of the semiconductor.¹³ This combination could further overcome the kinetic barriers for catalytic OER at semiconductor surfaces without losing light absorption efficiency due to the low required quantum yield. Easily accessible homogeneous cobalt porphyrins and corroles,¹⁴ and cobalt phthalocyanine (Pc) immobilized on fluorine-doped tin-oxide (FTO) substrates (CoPc/FTO) have shown excellent performance for electrocatalytic OER even at neutral pH.¹⁵ In this study, we investigated the surface modification of an FTO-coated hematite (hematite/FTO) with CoHPc and CoFPc catalysts (Figure 1) for improved photoelectrochemical OER. Static contact angle measurement (Figure 1) clearly demonstrates the hydrophobic nature of the Pc (5×10^{-10} mol cm^{-2}), extent of which is higher for CoFPc (86°) than for CoHPc (53°) and hematite (34°). Because of the high robustness and insoluble/hydrophobic nature of the CoPc catalysts, simple drop casting on a (photo)electrode makes a surface-functionalized assembly sufficiently stable for extended periods of electrocatalysis.¹⁵ As the hydrophobic interactions are driven by entropy, the molecules of Pc will be held at the surface due to water's strong preference to exclude them from the solution.

Figure 1. Structures of the molecular CoPc catalysts used in this study for photoelectrochemical OER and contact angle measurement of hematite and unmodified and CoPc-modified FTO.

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The hematite thin films on FTO-coated glass substrates were fabricated by atmospheric pressure CVD (APCVD). The SEM image of the hematite/FTO shows the nanoparticulate type surface texture of the semiconductor on top of the FTO (Figure S1; ESI). The small particles (100-150 nm) are distributed homogeneously on the FTO substrate. This nanoparticulate surface structure is responsible for the blue and UV light scattering, leading to increased light-harvesting.¹⁶ Absorbance and absorption coefficient were estimated from transmittance and reflectance UV-Vis measurements and the results are shown in Figure S2; ESI). The absorption coefficient is consistent with the literature.¹⁷ The Raman spectrum of the hematite sample shows characteristic Raman features of the presence of α -Fe₂O₃ as a major phase in the film.¹⁸ The Raman band at about 658 cm⁻¹ is associated with the minor magnetite phase (Fe₃O₄) in the sample (Figure 2).¹⁶ The UV-Vis spectrum of the hematite/FTO sample showed an absorption edge in the red region up to 600 nm (Figure 2).

Figure 2. (a) Diffuse reflectance UV-Vis spectra for hematite/FTO (red) and CoFPC/hematite/FTO (blue), and transmission UV-Vis spectrum for CoFPC (0.03 mm DMF) in free-standing solution phase. (b) Raman spectra of the nano-structured hematite/FTO, CoFPC/FTO and CoFPC/hematite/FTO (asterisks indicate the α -Fe₂O₃ phase, and the blue arrow refers to the magnetite phase).

CoPc catalyst was introduced by drop casting to achieve a catalyst density of $2-3 \times 10^{-10}$ mol cm⁻² both on FTO directly and on hematite/FTO substrates. Assuming that each Pc unit has an approximately 1.5 nm² area, the catalyst density for a perfectly smooth surface monolayer is approximately 3×10^{-10} mol cm⁻².^{15,19} The CoPc samples were also characterized by Raman and UV-Vis

spectroscopies. The Raman spectra show characteristic vibrational bands at 588 cm⁻¹, associated with deformation of the isoindole ring, and 740-771 cm⁻¹, corresponding to macrocycle deformation (Figure 2b). Additional Raman signals were also observed at 950 cm⁻¹ assigned to phenyl rings, 1135 cm⁻¹ for the stretching vibrations of the pyrrole group, 1360 cm⁻¹ for the C-C stretching vibration of the pyrrole group, and 1470 and 1543 cm⁻¹ for the C-N stretching vibrations in the isoindole.²⁰ These Raman signatures on FTO or hematite/FTO substrates indicate that Pc resides on the top of the Fe₂O₃ photoanode (Figure 2b). The UV-Vis spectrum of the solution phase, free-standing CoFPC exhibits a sharp Q-band at 673 nm, which is characteristic of the monomeric Pc species (Figure 2a).¹⁵ During the UV-Vis measurements on hematite/FTO, the catalytic modification with CoFPC shows no distinct alterations in the light absorption of the photoanodes (Figure 2a). This indicates that no competitive absorption results from the presence of the molecular catalyst species on hematite, which is one of the greatest advantages of using the molecular catalyst. This transparency is in stark contrast to other known overlayer oxides on hematite coated transparent conductive surfaces,³⁻⁸ which significantly block or reflect the relevant photons in the visible light range.

Cyclic voltammograms (CVs) for CoFPC/FTO and CoHPc/FTO at pH 13 show catalytic onset at ~ 1.67 and ~ 1.78 V vs. RHE, respectively (Figure S3a; ESI). This OER onset potential of CoFPC is lower than for most active Co-based molecular catalysts described previously, demonstrating the good catalytic activity of the surface-adsorbed CoPc.¹⁵ The OER current increases sharply after onset, reaching 4.0 and 2.0 mA cm⁻² at 2.0 V vs. RHE for CoFPC/FTO and CoHPc/FTO, respectively. These data show that due to the low overpotential for OER, the CoFPC/FTO sample is more active than CoHPc/FTO. During constant-potential electrolysis (CPE) at 1.85 V vs. RHE (Figure S3b; ESI), the initial catalytic current density is 0.87 mA cm⁻², which drops to 0.75 mA cm⁻², while generating at least 8000 turnovers for OER (measured with an online micro-GC) with a turnover frequency of 4.0 s⁻¹ for the CoFPC/FTO sample. The slight current decrease is ascribed to the generation and accumulation of oxygen bubbles on the CoFPC/FTO surface because the CV after long-term CPE reproduces the current-potential signature (Figure S3c; ESI). These electrocatalytic activities of molecular CoPcs are imperative and provide the basis to pursue photoelectrochemical studies using hematite photoanodes.

Linear sweep voltammograms (LSV) during chopped light irradiation for the hematite/FTO, CoFPC/hematite and CoHPc/hematite are shown in Figure 3. First, the bare hematite was investigated in the presence of sacrificial reagents (pH 13, 0.5 M H₂O₂ or 0.5 M Na₂S, Figure S4 ESI). The onset potential for photoanodic current was identified to be ~ 0.65 V vs. RHE, consistent with the literature.⁵ The photoanodic current monotonically increased with increasing applied potential. Dense nature of the studied hematite leads to a reasonable and reproducible photoresponse, adequate to investigate the effects of catalysts. It is worth mentioning that each bare hematite substrate was separately evaluated before loading each Co catalyst, yet high reproducibility of our hematite synthesis has been confirmed as shown in Figure 3a-c.

For comparison, we also prepared a Co-Pi/hematite system and studied it under the same conditions. The anodic currents were measured in the dark during potential sweep at approximately 1.69

V vs. RHE, irrespective of the presence of catalysts on the hematite surface. Under illumination, photocurrent is generated at approximately 1.03 V vs. RHE on the unmodified hematite sample. The current linearly increases with increasing potential up to ~ 1.35 V and begins to decline before sharply increasing at 1.65 V vs. RHE, consistent with the behavior reported for hematite photoanodes.²¹ On the Co-Pi/hematite, the photocurrent onset occurs at ~ 0.8 V vs. RHE. In addition, the current increases along with a positive sweep and begins to decline once a higher potential regime is reached (Figure 3a). This photoanodic behavior is very common for CoO_x type catalyst modified hematite/FTO and is attributed to the lower rate of holes transport and lower consumption by heterogeneous catalysts at a high driving energy.⁹ At 1.23 V vs. RHE, the photoanodic current density for Co-Pi/hematite increases to 0.45 mA cm^{-2} . This was the highest photocurrent within our optimization using the Co-Pi/hematite system because an increased Co-Pi amount inhibits light penetration, thus drastically reducing the performance of the system (see also ESI).

Figure 3. Chopped-light AM 1.5G illumination anodic linear sweep voltammetry (LSV) data for (a) Co-Pi/hematite, (b) CoHPc/hematite, and (c) CoFPc/hematite, all compared with respective hematite/FTO before introducing Co catalyst (5 sec interval, scan rate 10 mV sec^{-1}) and (d) long-term controlled potential electrolysis at 1.37 V vs. RHE in 0.1 M NaOH on hematite/FTO and CoFPc/hematite with and without AM 1.5G illumination (pH 13, 0.1 M NaOH, CoPc catalyst densities $\sim 2.70 \times 10^{-10} \text{ mol cm}^{-2}$).

The catalytic effects of CoFPc on the hematite photoanode can be seen during chopped-light LSV, as represented in Figure 3c. A cathodic shift of ~ 200 mV was observed in the onset potential compared to the bare hematite, and the current density increased to $\sim 1.0 \text{ mA cm}^{-2}$ at 1.23 V vs. RHE, more than twice as high as that of the Co-Pi/hematite sample. The current improvement on CoFPc/hematite is observed at all potentials during the LSV under light. This response of molecular CoFPc on hematite is unique and is in contrast with that observed for Co-Pi/hematite (Figure 3a) and reported hematite modified with heterogeneous catalysts, such as IrO_2 , NiO_x , or CoO_x . In those systems, photocurrent saturation appeared at ≥ 1.20 V vs. RHE. The superior photocatalytic activity of CoFPc/hematite relative to Co-Pi/hematite is ascribed to the lack of

inhibition of photon absorption due to the monolayer nature of molecular catalysts on the surface of hematite (Figure 3) and to the maintenance of effective charge separation at the catalyst/semiconductor interface over a wide potential range.

For the CoHPc on the hematite photoanode, the onset of electrochemical current under illumination was initiated at 1.0 V vs. RHE (Figure 3b) due to the higher overpotential required to initiate OER on the CoHPc/hematite system relative to the CoFPc/hematite photoanodic combination, as observed during electrochemical studies (Figure S3; ESI). Moreover, a lower photocurrent density is observed for CoHPc/hematite during a forward sweep from 1.2 to 1.6 V, which is approximately half of the photocurrent observed for the CoFPc/hematite sample but is still greater than the photocurrent in the Co-Pi/hematite system. Compared to the unmodified hematite, an increase in the photocurrent of approximately 35% was observed for the CoHPc/hematite photoanodic system.

The photocatalytic activities of the hematite films modified with Co-Pi and CoPc can be explained by the transient photocurrents generated during light chopping at five sec intervals. Illumination of hematite induces the accumulation of photogenerated charges at the interfaces, in particular, hole congregation at the semiconductor/electrolyte junction due to the low mobilities for the charge carriers and the slow kinetics of the oxygen generation reaction.^{21,22} Small transient response with our bare hematite may be due to dense nature of film with low surface area. For the Co-Pi/hematite sample (Figure 3), an anodic current spike is also observed during this charge accumulation phase, which decreases rapidly with time and forward potential sweep because the accumulated holes disorder the charge dissemination in the space charge layer.²³ Ultimately, a steady-state current vs. potential regime is achieved between carrier recombination and OER.³ Conversely, the anodic current spikes for the CoFPc/hematite system are not significant, and they almost completely disappear at potential >1.1 V vs. RHE (Figure 3c).

Furthermore, there is a clear indication of current increase with potential during each light-assisted LSV interval, suggesting the faster OER electrochemical kinetics for the molecular-semiconductor system relative to the Co-Pi/hematite junction. This also demonstrates that the photogenerated holes on hematite rapidly activate the molecular complex for OER on the surface of the semiconductor. We cannot exclude the possibility that modification of hematite with molecular CoPc improve the charge-carrier separation at the Co-hematite interface. McFarland and coworkers ascribed the onset potential shift observed for hematite photoanode to adsorption of fluoride ions which shifts the flat band potential negatively.²⁴ Durrant and coworkers also reported that the surface modification with CoO_x alters the electronic structure to enhance charge separation, rather than electrocatalytic improvement.⁴ From our observation, excellent electrocatalytic performance at least helps to improve photocurrent for the same reaction, as the reaction should proceed through the same elementary steps.

To test the long-term stability, controlled-potential water electrolysis experiments were conducted in the dark and under full light (Figure 3d). For broader applications, it is important to choose a potential that results in a considerable photocurrent density of $\geq 1 \text{ mA cm}^{-2}$. Therefore, CPE for the CoFPc/hematite system was conducted at 1.37 V vs. RHE for all four sets of experiments. In the dark, a photocurrent density of $<0.1 \text{ mA cm}^{-2}$ is observed for the

hematite/FTO and CoFPC/hematite samples, consistent with the data presented in Figure 3a and 3c. Under solar illumination, the photocurrent increases to approximately 1.1 mA cm⁻² for the CoFPC/hematite sample and is stable over time. The unmodified hematite/FTO generates a photocurrent density of ~0.57 mA cm⁻², which is also stable over an hour of oxidative operation. The LSVs after CPE under illumination show no noticeable decrease in the photocurrent performance, which confirms the stability of the photoelectrochemical molecular-inorganic heterojunction for OER (Figure S5; ESI). We further evaluated CoFPC/hematite sample for much longer period of time up to 60,000 s at 1.7 V vs. RHE so as to clearly detect O₂ evolved by in-line micro-GC. The data are shown in Figure S6, ESI. The current as well as O₂ evolution monotonically increased throughout the experiment, consistent with high stability of the CoFPC/hematite under photoanodic O₂ evolution conditions. The mole of electrons that are expected from the measured current ($e^-/4$) is in very good agreement with the amount of detected O₂, confirming that Faradaic efficiency of this process is close to 100%.

The modification of a thin film hematite photoanode with a molecular CoPc improved the photoelectrochemical performance for OER. The cathodic onset shift of OER with the catalyst modification suggested that improved charge separation occurred at the catalyst-semiconductor interface. On the CoFPC/hematite photoanode, the photocurrent is nearly doubled relative to the unmodified hematite, even at higher potentials, indicating that the CoPc on the surface of the hematite enhanced the hole delivery to the catalyst and its subsequent consumption, which minimizes the recombination. During long-term operation of the small molecule-semiconductor combination, a sustained photocurrent density is maintained, without any spectroscopic changes. Unlike heterogeneous catalysts, molecular catalytic species on photoactive semiconductors interfere minimally with the incident light. This robust molecular-inorganic hybrid system utilizing hydrophobic interaction of the molecular catalyst to the inorganic surface is a promising development in the field of solar to fuel conversion.

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