Exclusive Hydrogen Generation by Electrocatalysts Coated with an Amorphous Chromium-Based Layer Achieving Efficient Overall Water Splitting

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ABSTRACT: Successful conversion of renewable energy to useful chemicals requires efficient devices that can electrocatalyze or photocatalyze redox reactions. To electrocatalyze the hydrogen evolution reaction (HER), such as Pt, can also cause other side-reactions, including the water-forming back-reaction from H₂ and O₂ products. A Cr-based amorphous layer coated on catalysts can work as a successful surface modifier that avoids the back-reaction, but its capabilities and limitations toward other species have not been studied. Herein, we investigated the Cr-based layer on Pt from perspectives of both electrocatalysis and photocatalysis using redox-active molecules/ions (O₂, ferricyanide, IO₃⁻, S₂O₈²⁻, H₂O₂, and CO gas). Our systematic study revealed that utilization of the Cr-based layer realized an exclusive cathodic reaction only to HER, even in the presence of the aforementioned reactive species, suggesting that Cr-based layers work as membranes, as well as corrosion and poison inhibition layers. However, the Cr-based layer experienced self-oxidation and dissolved into the aqueous phase when a strong oxidizing agent or low pH was present. Presented herein are fundamental and critical aspects of the Cr-based modifier, which is essential for the successful and practical development of solar fuel production systems.

KEYWORDS: Photocatalysis, Electrocatalysis, Membrane, Ferricyanide, Iodate, Persulfate, Peroxide, Carbon monoxide

INTRODUCTION

Changing from fossil fuels to solar fuels, e.g., generating H₂ using sunlight, has been pursued for many decades. One option is to use photocatalyst powders that are capable of converting solar energy into usable chemical energy, e.g., photocatalytic water splitting. Successful photocatalytic water splitting requires a suitable band gap in a photon-absorbing semiconductor that is wider than the Gibbs free energy change of the water-splitting reaction (ΔG° = 237 kJ mol⁻¹ ≈ 1.23 eV). In addition, its conduction/valence band position has to be more negative/positive than that of the surface reduction/oxidation reactions, respectively, to drive surface redox reactions and/or drive surface redox reactions (functioning as electrocatalysts). Noble metals, especially Pt, are typically used as cocatalysts that are known for their high activity toward HER because they possess the optimal binding energy for the reaction intermediates. However, most noble metal cocatalysts also actively reduce oxygen back into water, i.e., the oxygen reduction reaction (ORR), which leads to a decrease in the overall efficiency of water splitting. Due to these complexities and difficulties, the reported best solar-to-hydrogen efficiency for photocatalytic overall water splitting so far is merely 1%, which is still greatly inferior to the benchmarking efficiency of 10%.

Core–shell structured cocatalysts have been reported to be successful in photocatalytic overall water splitting and selectively suppress the undesired back-reaction. The first successful core–shell material was reported by Maeda et al., who decorated rhodium nanoparticles with a chromium shell. Some other successful core–shell structures have been reported, for example, a NiO core,10 Ti, Nb, and Ta oxhydroxide shells;21 and a Mo shell.22 Although the core–shell structured materials have been their success, there have been few studies reported on the functionalities of shell materials in detail. The surface electrochemical phenomena occurring on the surface during photocatalytic reactions can be separately studied by electrochemical methods. One such study was reported by Yoshida et al. and explicitly revealed that the CrO₃ layer around noble metals indeed electrochemically enabled selective HER in the presence of oxygen. Such a...
mechanistic study on the photocatalysis from the viewpoint of electrochemistry helps us understand and rationalize the complicated photocatalysis phenomena.24,25

In this context, we examined the CrO3 layer on Pt in both electrocatalytic and photocatalytic hydrogen evolution systems in detail to reveal its capabilities, function, and limitations by using a variety of probe species ([Fe(CN)6]3−, NaIO3, Na2S2O8, H2O2, and CO). H2O2 was considered in this study because it can be the product of water splitting via anodic reactions, which can be reduced on the cathodic side instead of HER taking place, leading to a decrease in efficiency.26 Probe species such as Fe3+/Fe2+ and I3−/I− were tested as they are the most commonly used redox mediators in Z-scheme photocatalytic reactions. However, current Z-scheme systems suffer from low efficiencies because the selectivity is not well-controlled and the reduction/oxidation reactions of these redox mediators prevail over the desired hydrogen/oxidation evolution reactions, leading to an internal short circuit.27 Selectivity toward HER in the presence of Fe3+ and I3− is of great significance to achieve efficient Z-scheme type systems. Persulfate was tested because it is a common sacrificial reagent in photocatalytic systems to examine the anodic reaction of OER and also has a highly positive standard potential of 2.01 V vs standard hydrogen electrode (SHE), meaning it functions as a strong oxidizing agent from the viewpoint of thermodynamics. The investigation of the CrO3 layer in the presence of a stronger oxidizing agent than O2 allows the study of the layer in harsher conditions. Finally, CO gas was tested as it is known to poison noble metal catalysts and would help determine the universality of the CrO3 layer. Our systematic study revealed that, in both electrocatalytic and photocatalytic systems, the CrO3 shell universally achieves selective cathodic hydrogen production in the presence of the aforementioned species. Nevertheless, a critical drawback was also identified: when oxidizing agents that can locally oxidize Cr3+ are present, the CrO3 shell undergoes oxidative dissolution, leading to apparent loss in its performance. The present work provides fundamental details on the CrO3 modifier in both electrocatalytic and photocatalytic systems that shed light on the further development of solar fuel production systems.

METHODS

Materials. The following chemicals were used: Na2PtCl6·6H2O (>98%, Sigma-Aldrich), NaIO3 (>99.5%, Sigma-Aldrich), Na2S2O8 (>99.0%, Sigma-Aldrich), SrCl2 (>99.95%, Sigma-Aldrich), Na2SO4 (>99.99%, Sigma-Aldrich), KH2PO4 (>99.995%, Sigma-Aldrich), K2HPO4 (>99.95%, Sigma-Aldrich), K2CrO7 (>99.9%, Fisher Scientific), NaOH (>99.9%, Sigma-Aldrich), K2[Fe(CN)6] (>99.9, Sigma-Aldrich), K3[Fe(CN)6] (>99.9, Sigma-Aldrich), SrTiO3 (>99.9%, Wako Pure Chemical Industries), and H2O2 (30% with H2O, Sigma-Aldrich). The water used in all experiments was obtained from a Milli-Q Academic system from Millipore with a resistivity of 18.2 MΩ cm. The pH was determined using a pH electrode from Fisher Scientific. All reagents were provided by commercial suppliers and used without further modification.

Electrochemistry. A research-grade BioLogic VMP3 potentiostat was used for all electrochemical measurements. A conventional single-compartment, three-electrode system was used for electrochemical protocols. Rotating disk electrodes (RDEs) of polycrystalline Pt (3.0 mm diameter, 0.071 cm2 geometric surface area) were used as working electrodes. Before each measurement, the disk electrode was polished first with 1 µm of diamond and then with 0.05 µm of alumina (both purchased from BAS, Inc.). The disk rotation speed was controlled to be 900–4900 rpm. CrO3 was deposited on the Pt RDE by chronopotentiometry (CP) at −20 µA for 10 min in 0.5 M K2CrO4 solution at pH = 9.7.25 (See Figure S1 for details.) A Pt wire was used as the counter electrode in most experiments, unless otherwise stated. Ag/AgCl (saturated KCl) was used as the reference electrode for most experiments, and a Hg/HgO electrode was used at alkaline pH (>13). Before and during the measurements, Ar (99.999%), H2 (99.9999%), or O2 (99.9995%) was continuously supplied through the electrolyte. Cyclic and linear sweep voltammograms were recorded at a scan rate of 50 mV s−1 at room temperature. All reported potentials have been iR corrected (i.e., ohmic drop) and are referenced to either the reversible hydrogen electrode (RHE) or the standard hydrogen electrode (SHE), as specified in each figure.

Photocatalysis. As-prepared SrTiO3 and SrCl2 (mole ratio of 1:5) were ground with a mortar and pestle followed by a flux treatment at 1273 K for 10 h to make highly crystalline SrTiO3.29 Once the powder cooled to room temperature, it was washed with water until no more chloride salt was detected by the AgNO3 test. Pt was deposited on the surface of SrTiO3 via wet impregnation for a calculated 0.5 wt % loading using 25 µL of Na2PtCl6 (0.1 M solution), 5 mL of water, and 100 mg (0.54 mmol) of SrTiO3 that were mixed over a water bath until all the water evaporated. The powder underwent heat treatment at 573 K for 1 h. The Pt/SrTiO3 was collected and used for the photocatalytic reaction. CrO3 was deposited on Pt/SrTiO3 via photodeposition. Typically, 50 mg of Pt/SrTiO3 was dispersed by sonication in 100 mL of 2 mM K2CrO4 solution (see Figure S2 for details). The photocatalytic powder was placed in a photoreactor and irradiated for 6 h. The photocatalytic reactions were conducted at 100 Torr Ar gas in a circulating batch reactor equipped with an online gas chromatograph (GC; Bruker 450 GC, TCD, Ar carrier gas, molecular sieve 13X) that was connected to a vacuum line. A Xe lamp (CERMAPEX300-BF, 300 W) was used as the light source, and the irradiation wavelength was controlled with a combination of a cold mirror and a water filter (300 < λ < 800 nm).

RESULTS AND DISCUSSION

In this study, the functionality of CrO3 shells is studied in both electrocatalytic and photocatalytic systems in detail. For the electrochemical experiments, a polycrystalline Pt RDE with a geometric surface area of 0.071 cm2 was used as the working electrode. Figure 1a shows a cyclic voltammogram (CV) of the Pt RDE in 0.5 M Na2SO4 solution at pH 13 as a representative case with O2 bubbling at 3600 rpm. In the figure, below 0.9 V on the RHE scale, an increasing cathodic current density was observed; this current density reached a constant value at ~0.5 V vs RHE. The constant current density of ~5 mA cm−2 at ~0–0.5 V vs RHE indicates limitation by mass transport that is ascribable to oxygen diffusion-limited ORR (water-forming reaction).32 Further increases in the cathodic current below 0 V vs RHE are assigned to HER, as we have previously reported.33,34 CrO3 was electrochemically deposited on the Pt RDE by chronopotentiometry following literature procedures (−20 µA for 10 min in 0.5 M K2CrO4 solution; see Figure S1 for a discussion on the deposition conditions) and was tested under the same conditions as the bare Pt RDE. The CrO3/Pt RDE showed negligible current at 0–0.7 V vs RHE, and increasing cathodic current below 0 V vs RHE was ascribable to HER. The absence of limiting diffusion currents clearly suggests nearly complete selective suppression of ORR by the CrO3 layer. These observations demonstrated that the CrO3 layer selectively suppressed ORR without significantly losing HER activity of the substrate (Pt), consistent with literature reports.35

For the investigation of photocatalytic reactions, UV-responsive SrTiO3 was chosen as a model photocatalyst because its conduction band edge is more negative than the HER equilibrium potential and its valence band edge is more positive than the OER equilibrium potential, indicating that this
A semiconductor is thermodynamically capable of overall water splitting under UV light irradiation. To facilitate the surface redox reactions, the surface of SrTiO3 was decorated with an optimized loading of 0.4 wt % of Pt via the wet impregnation method. Figure 2a shows the transmission electron microscopy (TEM) image, and Figure 2b shows the corresponding energy-dispersive spectroscopy (EDS) analysis for Pt/SrTiO3, revealing that the Pt nanoparticles on the surface ranged from 0.5 to 4 nm in size. The EDS analysis shows clear signals of Sr and Ti from SrTiO3 and Pt from the nanoparticles (and Cu from the TEM grid). CrOx was photodeposited on the surface of Pt/SrTiO3 from a 2 mM K2CrO4 solution. In the sample after deposition, EDS (Figure 2d; also see Figure S3) showed an additional peak at 5.4 keV that is ascribable to Cr, and X-ray photoelectron spectroscopy (XPS) spectra (Figure S4) exhibited peaks at approximately 576 and 586 eV that correspond to a Cr 2p orbital (Cr3+), indicating that Cr6+ in the solution was successfully reduced onto Pt/SrTiO3. Notably, X-ray diffraction (XRD) profiles (Figure S5a) did not exhibit any changes in the bulk structure before/after the deposition, and UV–vis spectra (Figure S5b) indicated negligible influence of Pt and CrOx on the absorption edge.

The photocatalytic gas evolution time course for Pt/SrTiO3 in 0.1 M NaOH solution with UV light irradiation is presented in Figure 1b. Initial gas evolution rates at 0.5 h were approximately 60 (H2) and 30 (O2) μmol h−1. The observed H2/O2 ratio of 2 was consistent with the stoichiometry of water splitting, showing that the prepared Pt/SrTiO3 was capable of photocatalytically splitting water into H2 and O2. The gas evolution rates decreased over time to ~0 after 8 h. In addition, when the light was turned off after 10 h of irradiation, negative rates (approximately ~50 and ~25 μmol h−1 for H2 and O2, respectively) were observed, which indicates that the water formation reaction from H2 and O2 occurred. The observed back-reaction rates were almost comparable to the initial rate, which unambiguously accounts for the observed negligible gas evolution rate at ~8−10 h in the figure: Pt/SrTiO3 is not only capable of splitting water molecules but also even catalyzes the back-reaction of water formation in the dark, which results in no apparent gas evolution in the steady state. For a successful water-splitting reaction, therefore, a strategy to selectively suppress the back-reaction is essential.

The photocatalytic gas evolution rates for CrOx/Pt/SrTiO3 are shown in Figure 1b. The initial gas evolution rates were 120 (H2) and 60 (O2) μmol h−1. The rates then dropped to a steady rate of 90 (H2) and 45 (O2) μmol h−1 after 4 h, presumably because of any surface contaminants that were used as a sacrificial reagent, which was also the case for Pt/SrTiO3. Indeed, the powder exhibited the rate of 90 μmol h−1 when it was reused multiple times for a total of 20 h (Figure S6). The evolved H2/O2 ratio was continuously 2 for the full duration of the experiment, consistent with the stoichiometry of water splitting. When the light was turned off after 10 h, the rate dropped to almost zero, indicating no apparent back-reaction, which contrasted with the observation for Pt/SrTiO3. These observations clearly show that the CrOx/Pt/SrTiO3 successfully achieved overall water splitting.

On the basis of the observations for Pt/SrTiO3 and CrOx/Pt/SrTiO3, we attempted the following quantitative rationalization of the reaction rate. The overall water splitting,
The redox reaction with ferro-/ferricyanide species was tested because it is an outer-sphere reaction, which is fundamentally different from the other reactions discussed, i.e., HER or ORR. Figure 3a shows CVs using pristine Pt and CrO\textsubscript{x}/Pt RDEs in 10 mM K\textsubscript{3}Fe(CN)\textsubscript{6} with 1.5 mol L\textsuperscript{−1} K-phosphate solution with Ar bubbling (KH\textsubscript{2}PO\textsubscript{4}/K\textsubscript{2}HPO\textsubscript{4} = 80/20, pH 5.8; see Figure S7 for CVs in the absence of $K_x$Fe(CN)\textsubscript{6} under buffered conditions). Buffered solution was used to prevent pH changes in the system, and the near-neutral pH was chosen to avoid oxidation of CrO\textsubscript{y} by Fe\textsuperscript{2+} (see Pourbaix diagram in Figure 9; see also the final section for discussion on the oxidative loss of CrO\textsubscript{x}). The Pt disk showed a constant current density of $\sim-6$ mA cm\textsuperscript{−2} at 0−0.7 V vs RHE, indicative of the diffusion-limited reduction of Fe\textsuperscript{3+} to Fe\textsuperscript{2+}. The increase in the cathodic current when the potential was below 0 V vs RHE originated from HER. In contrast, when the surface of Pt was decorated with CrO\textsubscript{y}, no constant current was observed when the potential was above 0 V vs RHE, indicating that CrO\textsubscript{x}/Pt was not capable of reducing Fe\textsuperscript{3+} in the solution. Nevertheless, an increase in the cathodic current was observed below 0 V vs RHE and was ascribable to HER, demonstrating that CrO\textsubscript{x} can electrochemically realize selective HER without parasitic reduction of Fe\textsuperscript{3+}. These results clearly indicate that the outer-sphere-type reaction of Fe\textsuperscript{3+} reduction cannot occur even on the surface of the CrO\textsubscript{x} shell. According to theoretical predictions, the tunneling of electrons can occur at distances less than $\sim$1.5 nm,\textsuperscript{37} which is shorter than the thickness of the prepared Cr shell (2 nm). For Fe\textsuperscript{3+} to be reduced, the Fe\textsuperscript{3+} species thus must penetrate the CrO\textsubscript{x} layer, which was most likely not allowed due to its membrane-like function. These rationales suggest that the CrO\textsubscript{x} shell functions as a selective membrane through which hydronium ions, but not Fe\textsuperscript{3+}, can penetrate, leading to selective hydrogen production.

![Figure 3](https://example.com/figure3.png)

**Figure 3.** (a) Cyclic voltammograms over pristine Pt and Cr-modified Pt (CrO\textsubscript{x}/Pt) disk electrodes, recorded at a scan rate of 50 mV s\textsuperscript{−1}, at a disk rotation speed of 3600 rpm and at 298 K in 10 mM K\textsubscript{3}Fe(CN)\textsubscript{6} + 1.5 M K-phosphate (KH\textsubscript{2}PO\textsubscript{4}/K\textsubscript{2}HPO\textsubscript{4} = 80/20, pH 5.8), with Ar bubbling. (b) Photocatalytic activity time courses of Pt/SrTiO\textsubscript{3} and CrO\textsubscript{x}/Pt/SrTiO\textsubscript{3} in 1 mM K\textsubscript{3}Fe(CN)\textsubscript{6} + 1 mM K\textsubscript{4}Fe(CN)\textsubscript{6} + 0.5 M K-phosphate (KH\textsubscript{2}PO\textsubscript{4}/K\textsubscript{2}HPO\textsubscript{4} = 60/40) (under UV light irradiation (300 < $\lambda$ < 800 nm), 50 mg of catalyst).
of the Fe couple that was 10-fold lower than that in the electrochemical study, as the presence of 10 mM Fe couple led to no gas evolution due to parasitic photon absorption by the Fe complex in the UV range (for UV-vis spectra of the iron species, see Figure S9). For Pt/SrTiO₃, no gas evolution was detected, presumably because the generated holes and electrons from the photocatalyst were used to cycle the redox couple between Fe²⁺ and Fe³⁺ (short circuit), which is thermodynamically more favored than water splitting. In the CrOₓ/Pt/SrTiO₃ system, the rate of H₂ evolution started at 200 μmol h⁻¹, while the O₂ evolution rate started at 50 μmol h⁻¹. The gas evolution using a CrOₓ shell was well-aligned with the electrochemical observation that was discussed in Figure 3a. However, the H₂/O₂ ratio here was not 2:1, indicating that overall water splitting was not the case. The increase in H₂ production is probably due to the Fe²⁺ ions acting as a sacrificial reagent by consuming a hole generated from the SrTiO₃. A sharp decrease in the H₂ evolution rate was observed between 2 and 6 h, when it stabilized at 100 μmol h⁻¹, and the oxygen evolution rate decreased to 25 μmol h⁻¹, which was lower than the hydrogen evolution rate in the absence of the Fe redox couple (140 μmol h⁻¹; see Figure S8). Because ~550 μmol of Fe²⁺ was calculated to be remaining in solution after the whole reaction, the decrease in the rate could not be ascribed to the full consumption of the Fe complex. The lower activity is most likely due to competitive light absorption, as both iron species absorb especially close to 390 nm in the UV range, which is where the absorption edge of SrTiO₃ is located. In addition, photocatalytic reactions were examined in the presence of only K₄Fe(CN)₆ which exhibited stochiometric water splitting (H₂/O₂ ratio of 2; data not shown), which is consistent with our analysis.

The electrochemical study clearly revealed that the CrOₓ shell achieved selective HER in the presence of Fe³⁺ ions, which was indeed the case for the photocatalytic system. The observed decrease in the performance during photocatalysis was thus rationalized as being most likely due to photon absorption rather than electrochemical phenomena. Therefore, was thus rationalized as being most likely due to photon absorption rather than electrochemical phenomena. Therefore, surface redox reactions, even for outer-sphere-type reactions.

NaiO₃. The reduction of iodate, which is known as an electron acceptor and a redox mediator in Z-scheme systems, was investigated. Figure 4a presents CVs of Pt and CrOₓ/Pt RDEs in 0.1 M NaOH with 1 mM NaIO₃ and Ar bubbling. When the pristine Pt RDE was used, a cathodic current arose at ~0.6 V vs RHE and then plateaued when the potential reached ~0.3 V vs RHE, which was ascribable to diffusion-limited reduction of IO₃⁻. Below ~0 V vs RHE, the cathodic current further increased, which was attributed to HER. In contrast, CrOₓ/Pt exhibited a substantial cathodic current only below 0 V vs RHE. The lack of any clear fingerprint of IO₃⁻ reduction when CrOₓ was present clearly indicated that CrOₓ enables the selective HER even in the presence of iodate; this behavior likely occurs because CrOₓ prohibits the access of iodate to the reduction active sites.

Figure 4b shows the photocatalytic time course for Pt/SrTiO₃ and CrOₓ/Pt/SrTiO₃ in 0.1 M NaOH and 10 mM NaIO₃. For bare Pt/SrTiO₃, the H₂ evolution rate was close to 0 μmol h⁻¹, indicating that IO₃⁻ was preferentially reduced, as observed in the electrochemical study. Interestingly, however, the corresponding O₂ evolution rate was 25 μmol h⁻¹, which was lower than that of CrOₓ/Pt/SrTiO₃ in the absence of any sacrificial reagent (Figure 1). This apparent contradiction could be rationalized by the competitive oxidation of I⁻ produced by the IO₃⁻ reduction, consistent with the previous reports on Z-scheme systems. CrOₓ/Pt/SrTiO₃ on the other hand, maintained steady performance throughout the duration of the experiment at a 2:1 ratio of H₂ to O₂ at a rate of 80 and 40 μmol h⁻¹, respectively, indicating overall water splitting without unwanted side-reactions, consistent with the observation in the electrochemical study.

In summary, in both electrocatalysis and photocatalysis systems, the CrOₓ shell was found to successfully suppress the reduction of iodate, leading to selective hydrogen production. In addition, our photocatalysis study demonstrated that the SrTiO₃ surface is capable of oxidizing I⁻, which led to lower water splitting efficiency. Therefore, when the practical application of CrOₓ shell was considered for redox-mediated photocatalytic reactions, additional strategies are required to regulate the side-reaction on the anodic side.

Na₂S₂O₈. Persulfate is one of the most commonly used sacrificial reagents (electron scavenger) in photocatalysis; however, electrochemical study of the reduction of persulfate in relevant conditions has rarely been reported. In this section, we extend our study to the reduction of persulfate in both
electrocatalytic and photocatalytic systems. Figure 5a shows CVs of Pt and CrOx/Pt RDEs in 0.1 M NaOH with 1 mM Na2S2O8 and Ar bubbling. The Pt RDE exhibited an increasing negative current density at applied potentials starting at 0.4 V vs RHE. At potentials less than ~0 V vs RHE, the cathodic current became more apparent, which could be ascribable to HER. Interestingly, this result showed that the reduction of persulfate in the electrochemical system is not particularly kinetically facile, even using Pt, although persulfate is one of the most commonly used electron scavengers in photocatalytic systems.

Nonetheless, CrOx/Pt can selectively evolve hydrogen in both electrocatalytic and photocatalytic systems, even in the presence of a strong electron scavenger. Nonetheless, CrOx was found to likely undergo local redox reactions with a strong oxidizing agent, probably due to the substantial thermodynamic driving force for the local redox reaction, which can be mitigated by keeping CrOx in the reducing environment. Detailed discussion of the limitations of the CrOx shell is in the final section.

This section revealed that CrOx/Pt can selectively evolve hydrogen in both electrocatalytic and photocatalytic systems, even in the presence of a strong electron scavenger. However, Na2S2O8 can serve as a sacrificial reagent to overall water splitting. A material's photocatalytic water-splitting reaction rates were stable during the measurements (10 h), which contrasts with the observed decrease in its performance in the electrochemical study. The discrepancy can be rationalized by the fact that, during photocatalysis, CrOx/Pt/SrTiO3 was continuously irradiated, i.e., the active site that is responsible for the hydrogen production had been likely kept under reducing conditions that can mitigate the local redox reaction between CrOx and S2O82− or avoid the oxidative loss of the CrOx shell from the surface. This rationale implies that, for the CrOx shell to stably function when oxidizing agents are present, substantial cathodic potential is required.

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H2O2. Depending on the nature of the oxidation active site, H2O2 instead of O2 can be generated during electrolysis. This section discusses the impact of the presence of H2O2 on the performance of CrOx shells. Figure 6a shows the CVs of Pt and CrOx/Pt RDEs in 0.1 M NaOH with 1 mM H2O2 and Ar bubbling. The pristine Pt exhibited a decreasing cathodic current with successive cycles (see Figure S10), implying that the CrOx shell could not stably function in the presence of persulfate, likely due to the local redox reaction (S2O82− reduction and CrOx oxidation) while potential cycling. Detailed discussion of the local redox reactions is to be provided in the final section.

Figure 5b shows the photocatalytic time course for Pt/SrTiO3 and CrOx/Pt/SrTiO3 in 0.1 M NaOH and 10 mM Na2S2O8. Pt/SrTiO3 showed minimal H2 evolution (a rate of <5 μmol h−1), while its O2 evolution rate was steady at ~50 μmol h−1. Because the persulfate, which is known to function as a sacrificial reagent, was present, the corresponding reduction reaction here is the reduction of persulfate. The photocatalytic OER rate decreased to almost zero after 7 h, which is most likely due to the consumption of the persulfate that was present in the solution. There was 1.0 mmol of sacrificial reagent present in the solution, as it was 100 mL of a 10 mM Na2S2O8 solution in the reactor. Decomposing each persulfate anion requires 2 electrons; therefore, 1.0 mmol of S2O82− would correspond to 0.5 mmol of O2. From Figure 5b, the amount of O2 that evolved was close to 450 μmol in the first 8 h (before the rate decreased). When the O2 rate decreased, an increase in the H2 evolution rate was observed, corresponding to switching from reducing the sacrificial reagent to overall water splitting. A slight increase in the H2 evolution rate was observed, which coincided with the decrease of the O2 evolution rate and likely corresponded to a switch from the sacrificial reagent-assisted oxygen production to overall water splitting. When the surface of Pt was covered with a CrOx shell, gas evolution rates of approximately 100 (H2) and 50 (O2) μmol h−1 were observed throughout the duration of the experiment, as shown in Figure 5b. The ratio of hydrogen/oxygen evolution rates was 2, clearly revealing that CrOx/Pt/SrTiO3 was capable of evolving H2 and O2 even in the presence of persulfate. Interestingly, this material’s photocatalytic water-splitting reaction rates were stable during the measurements (10 h), which contrasts with the observed decrease in its performance in the electrochemical study. The discrepancy can be rationalized by the fact that, during photocatalysis, CrOx/Pt/SrTiO3 was continuously irradiated, i.e., the active site that is responsible for the hydrogen evolution could not stably function when oxidizing agents are present, substantial cathodic potential is required.
RDE exhibited a constant current when the potential was <0.7 V vs RHE, clearly showing that H2O2 was reduced and was limited by diffusion. Below 0 V vs RHE, a substantial increase in the reduction current was observed that can be assigned to HER. In contrast, CrOx/Pt showed negligible current density from 0 to 0.7 V vs RHE, and the apparent reduction current below 0 V vs RHE is ascribed to HER. The CrOx shell stably functioned in the presence of H2O2 and can notably also prevent molecular species from penetrating toward the Pt surface.

The photocatalytic time courses for Pt/SrTiO3 and CrOx/Pt/SrTiO3 in 0.1 M NaOH and 10 mM H2O2 are shown in Figure 6b. Pt/SrTiO3 showed an initial rate of 175 μmol h−1 for O2 evolution, which then rapidly decreased to 0 μmol h−1 after 4 h, while the H2 evolution rate remained close to 0 for the full duration of the experiment. The decrease of O2 production to 0 corresponded to the full consumption of all H2O2 in solution. The same logic that was used in the Na2S2O8 section applies: specifically, 0.5 mmol of O2 is expected, as the decomposition of H2O2 is a 2e− process. After consuming H2O2, no H2 and O2 evolved, presumably because the ORR/OER pair prevailed because the system contained 500 μmol of O2. It should be noted that H2O2 can be decomposed by UV light irradiation as well as the presence of catalysts such as Pt, and thus, the rate observed here was not entirely ascribable to photocatalytic decomposition of H2O2. CrOx/Pt/SrTiO3, on the other hand, evolved H2 at a rate of 110 μmol h−1 and O2 at a rate of 75 μmol h−1. The ratio of hydrogen/oxygen production did not correspond to the stoichiometry of water splitting, most likely because of the decomposition of H2O2 under UV-light irradiation, as shown in Figure S11. Notably, the observed H2 production rate was almost comparable to that in the absence of H2O2, indicating that the CrOx shell prevents the reduction of H2O2, consistent with the electrochemical study. Therefore, even if the oxidation site of the photocatalyst generates partial amounts of H2O2 instead of O2, the CrOx shell can suppress the reduction of molecular H2O2, preventing harm to the catalyst.

CO. One of the most well-known molecules that can poison the catalyst is CO. Herein, we further extend our study to water splitting in the presence of CO to see if CrOx shell can prevent poisoning of the Pt surface. Figure 7 shows CVs using the Pt and CrOx/Pt RDEs in 0.1 M NaOH solution with 1% CO/Ar bubbling. The Pt RDE exhibited almost negligible currents at potentials from −0.1 to 0.7 V vs RHE, and a slight increase in the cathodic current, ascribable to HER, was observed at...
potentials less than −0.2 V vs RHE. The observed HER rate was substantially smaller than those in all other cases and can be accounted for by the CO molecules sticking to the Pt surface. However, when the CrO₃ shell was present, substantially increasing reduction current was observed when the potential was <0 V vs RHE; this current was ascribed to HER and was quantitatively almost the same as the HER activity in the absence of CO (see Figure S12). This observation clearly shows that the CrO₃ shell is capable of preventing Pt poisoning from CO without losing the HER activity of the Pt substrate.

**Figure 7b** shows photocatalytic time courses of Pt/SrTiO₃ and CrO₃/Pt/SrTiO₃ in Milli-Q water with Ar or 40 kPa of 1% CO/Ar. During the first 2 h of the experiment, the H₂ evolution rates in water solution without CO in the system were 20 and 50 μmol h⁻¹ for Pt/SrTiO₃ and CrO₃/Pt/SrTiO₃, respectively. When CO gas was introduced to the system at 2 h, the H₂ evolution rate of Pt/SrTiO₃ dropped to 2 μmol h⁻¹, most likely due to poisoning of Pt by CO, consistent with the electrochemical study (Figure 7a). After 7 h, CO was purged from the system and replaced with Ar; after a 1 h induction period, Pt/SrTiO₃ exhibited almost the same H₂ evolution rate as in the beginning, indicating that the CO had desorbed from the Pt surface. In contrast, CrO₃/Pt/SrTiO₃ exhibited an almost unchanged H₂ evolution rate. Therefore, it is inferred that CO cannot poison the Pt when the CrO₃ shell is present.

**Reaction Conditions Suitable for Chromium Layer.**

The previous sections have shown that, in both electrocatalytic and photocatalytic systems, the CrO₃ layer can successfully block outer-sphere reactions as well as reduction of anions, molecular species, and gases. Such a universal function of CrO₃ seems surprising; however, it has some drawbacks. As described in the section on persulfate, CrO₃ likely undergoes local redox reactions with species that are present in the solution; Cr⁴⁺ is oxidized in these reactions, leading to the loss of CrO₃. Such local redox events are studied electrochemically in detail in this section, using O₂ as a model oxidizing agent. CV was carried out using a CrO₃/Pt RDE for 1800 cycles in the potential range of −0.1−0.7 V vs RHE at a scan rate of 50 mV s⁻¹ in 1.0 M NaOH with O₂ bubbling (Figure S13a). No substantial change in the CV was obtained, which indicates the excellent stability of the CrO₃ shell under working conditions. Two obvious conditions under which CrO₃ is unstable were oxidizing conditions above 0.7 V vs RHE in which the CrO₃ was oxidized (Figure S14), and acidic pH (pH 2 and lower, Figure S15), both of which are consistent with the literature.₂³ In addition, the presence of O₂ was found to oxidize the CrO₃ shell in nonworking conditions. **Figure 8a** shows CVs of a CrO₃/Pt RDE in 1.0 M NaOH with O₂ bubbling in between successive scans while the rest time was sequentially increased. The CV after 1 min of resting conditions exhibited almost negligible current from 0 to 0.7 V vs RHE and increasing reduction current when the potential was <0 V vs RHE, which is ascribable to HER; this is consistent with all the other CVs of CrO₃/Pt in this study. While increasing the duration of the resting time to 30 min and 1 h did not lead to any significant changes in the CV, the CV after 2 h of resting conditions with O₂ bubbling exhibited reduction current from 0 to 0.7 V vs RHE. The open-circuit potential (OCP) that was recorded during the resting conditions is presented in Figure S13b and reveals that the OCP shifted to positive values, reaching 1.1 V vs RHE. Such a positive potential was sufficient to oxidize and dissolve the CrO₃ shell. ORR was observed as the reduction current from 0 to 0.7 V vs RHE in Figure 8a and was most likely due to the loss of the CrO₃ shell on the Pt surface. The same experiment was performed with Ar bubbling instead of O₂ and the results are compiled in Figure 8b. Similar CVs were observed after different resting times, indicating that the CrO₃ layer remained stable in the absence of O₂. The stability of CrO₃/Pt RDE with O₂ was further tested by a 10 h chronoamperometry (CA) study (see Figure S16a,b), where the potential was changed every hour to increasingly more cathodic current. Figure S16a showed that HER was stable at each potential and with both Ar and O₂ gas. These results clearly showed that CrO₃ is stable under working conditions, but O₂ and CrO₃ undergo local redox reactions when no current/potential is applied, resulting in the loss of the CrO₃ shell from the catalyst surface.

The primary requirement for such losses of CrO₃ is that the local redox reaction is thermodynamically allowed. The local redox reaction can thermodynamically occur when the equilibrium potential for the reduction of the oxidizing agent is at a more positive potential than the oxidation of Cr³⁺, or in other words, the local redox reaction is exothermic. **Figure 9** compiles a Pourbaix diagram of representative half-reactions from this study. In the figure, cathodic half-reactions that are located at more positive potentials than the oxidation of Cr³⁺...
can undergo local redox events with Cr\(^{3+}\), i.e., the loss of the CrO\(_x\) shell. Among the species tested in this study, the loss of the Cr layer thermodynamically prevails in the presence of persulfate (at all pH levels), hydrogen peroxide (at all pH levels), oxygen (at all pH levels), and Fe\(^{3+}\) (>pH 10). Indeed, as observed in this study, the presence of O\(_2\) in 1.0 M NaOH or persulfate in 0.1 M NaOH resulted in local redox events; however, the presence of hydrogen peroxide did not cause local redox reactions, most likely due to its sluggish kinetics on CrO\(_x\) surfaces. Thus, for the practical application of the CrO\(_x\) layer, consideration of both thermodynamics and kinetics are of great significance; for example, under practical solar fuel production conditions via photocatalytic overall water splitting, the evolved oxygen can accumulate in the system and light does not irradiate all the time. Thus, the CrO\(_x\) shell can be lost. Therefore, to realize more practical solar fuel production systems, additional measures need to be taken.

**CONCLUSION**

The universal functionality of Cr-based layers decorating hydrogen evolution catalysts was explored in both electrocatalytic and photocatalytic systems. Our systematic study disclosed that selective HER was universally possible when decorating Pt electrode with a layer of CrO\(_x\) even in the presence of [Fe(CN)\(_6\)]\(^{3-}\), NaIO\(_4\), Na\(_2\)S\(_2\)O\(_8\), and H\(_2\)O\(_2\). Additionally, the poisoning of Pt surfaces by CO gas was prevented by the CrO\(_x\) shell by regulating the access of CO to the Pt surface. As a result, efficient photocatalytic overall water splitting using the Cr-decorated electrocatalyst was efficiently achieved, even in the presence of such redox species. Nevertheless, it was also found that, in the presence of strong oxidizing agents, whose reduction potentials are located at more positive values than that of the oxidation of Cr\(^{3+}\), local redox events can occur under dark condition, leading to the loss of Cr. The presence of persulfate and O\(_2\) resulted in the gradual loss of the CrO\(_x\) shell due to such local redox events in nonoperating (open-circuit) conditions. Therefore, although CrO\(_x\) layers stably function under HER operating conditions (at negative potential), an additional strategy to mitigate the local redox reactions seems essential for the practical application of photocatalytic systems.

**ASSOCIATED CONTENT**

2 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsusschemeng.7b01704.

CVs, photocatalytic time courses, control experiments, and additional characterization (PDF)

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**Notes**

The authors declare no competing financial interest.

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