Supporting Information

Exclusive hydrogen generation by electrocatalysts coated with an amorphous chromium-based layer achieving efficient overall water splitting

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Supporting information includes 17 pages and 16 figures.
Figure S1. (a) Potential profile during deposition of Cr on the Pt disk in 0.5 M K$_2$CrO$_4$ (pH=9.7) with Ar or H$_2$. (b) CrO$_x$/Pt testing in 0.5 M Na$_2$SO$_4$ with O$_2$ bubbling (pH=4.5, 50 mV s$^{-1}$, 3600 rpm).
The deposition of CrO$_x$ onto Pt is shown in Figure S1a in both Ar and H$_2$ gas. The deposition in the presence of Ar showed an almost constant open-circuit potential (OCP) at 0.6 V vs. SHE. When a constant current was applied, the potential was substantially negatively shifted (to −0.5 V vs. SHE). In H$_2$ gas, a negative shift in the open-circuit potential was observed. The resulting OCP was around −0.5 V vs. SHE, which was similar to that observed during chronopotentiometry (CP) in Ar for the electrodeposition of chromium. This result indicated that CrO$_4^{2−}$ was capable of electroless deposition onto Pt RDE using only H$_2$ bubbling under the open-circuit potential. Figure S1b shows cyclic voltammograms (CV) from samples using different CP times (from 0 to 1 min). The CVs demonstrated that changing the CP time led to a similar amount of O$_2$ blocking, as there was negligible change from 0 to 1 min CP time.

Note: The onset potentials for HER in Figures 1, 3-7 are slightly different which may be due to the local redox between the CrO$_x$ layer and any oxidizing agent. The electrode was kept in the solution prior to each experiment for 30 min with either Ar or O$_2$ bubbling, during which CrO$_x$ could slightly undergo local redox which may alter the surface exposing a different number of active sites.
Figure S2. (a) Photocatalytic activity time course of Cr photodeposition on Pt/SrTiO$_3$ (100 mL of 2 mM K$_2$CrO$_4$ solution, UV light irradiation (300 < $\lambda$ < 800 nm), and 50 mg of catalyst).
**Figure S3:** TEM of CrO$_x$/Pt/SrTiO$_3$ (on Cu grid) with corresponding EDS analysis. Red circle in TEM images indicate the spot where EDS analysis was performed.
Figure S4. X-ray photoelectron spectra of (a) Cr 2p, (b) Pt 4f, (c) Sr 3d, and (d) Ti 2p.
Figure S5. (a) XRD pattern and (b) UV-Vis absorption spectra of bare SrTiO$_3$, Pt/SrTiO$_3$, and CrO$_x$/Pt/SrTiO$_3$.

Figure S6. Photocatalytic time course of CrO$_x$/Pt/SrTiO$_3$ with evacuation of gases every 5 h (100 mL of 0.1 M NaOH solution, UV light irradiation (300 < $\lambda$ < 800 nm), 50 mg of catalyst, and volume of reactor=512 mL).
Figure S7. Cyclic voltammograms of pristine Pt and Cr-modified Pt (CrO\textsubscript{x}/Pt) disk electrodes in 1.5 M K-phosphate (KH\textsubscript{2}PO\textsubscript{4}/K\textsubscript{2}HPO\textsubscript{4}=80/20, pH 5.8) with (a) O\textsubscript{2} and (b) H\textsubscript{2} bubbling at disk rotation speeds of 1600, 2500, 3600 and 4900 rpm (50 mV s\textsuperscript{-1} and 298 K).

Figure S8. Photocatalytic activity time courses in unbuffered and buffered 0.5 M K-phosphate (KH\textsubscript{2}PO\textsubscript{4}/K\textsubscript{2}HPO\textsubscript{4}=60/40) of (a) Pt/SrTiO\textsubscript{3} and (b) CrO\textsubscript{x}/Pt/SrTiO\textsubscript{3} (100 mL of solution, UV light irradiation (300 < \lambda < 800 nm), and 50 mg of catalyst).
Discussion for Figure 3a:

For the Fe redox reactions, the electrons were incapable of tunneling from the Pt through the CrOx layer to reduce Fe. The formula that describes electron tunneling is shown in Equation 5:

\[
\text{Probability of tunneling } \propto e^{-\beta x} \quad (5)
\]

where \(x\) is the distance that the electron will tunnel and \(\beta\) is a factor that depends on the height of the energy barrier and the nature of the medium between the states. Although the exact distance that an electron tunnels in this situation is unknown, the tunneling rate decreases exponentially with distance, and theoretically, in electrochemical solutions, electrons do not tunnel more than \(~1.5\) nm. To reduce CrO\(_x\) onto the surface of Pt, the Cr\(^{6+}\) in the electric double layer would be reduced onto the Pt, and
furthermore, to grow the CrO$_x$ to be 2 nm in thickness, as previously reported, electrons would have to tunnel from the Pt to continue depositing CrO$_x$. The self-limiting growth of CrO$_x$ may be because electrons cannot tunnel through more than 2 nm and are therefore unable to reduce Fe.

**Figure S10.** Cyclic voltammograms of a Cr-modified Pt (CrO$_x$/Pt) disk electrode in 0.1 M NaOH + 0.1 mM Na$_2$S$_2$O$_8$ with Ar bubbling, and electrode rotating at 900 rpm (50 mV s$^{-1}$ and 298 K).
Figure S11. Photocatalytic activity time course (control experiments) in (a) 10 mM H₂O₂ in 0.1 M NaOH solution with irradiation and (b) 10 mM H₂O₂ in 0.1 M NaOH with 50 mg of Pt/SrTiO₃ under dark conditions. No gases evolved with NaIO₃, Na₂S₂O₈, or Fe couple control experiments (100 mL of solution and UV light irradiation (300 < λ < 800 nm).

Figure S11a shows that 80 µmol of O₂ evolved in 3 h without catalyst and under UV light irradiation, and Figure S11b shows that 125 µmol of O₂ evolved in 3 h under dark conditions and with Pt/SrTiO₃ catalyst. Therefore, H₂O₂ is not an ideal sacrificial reagent when testing materials, as it is unclear whether the evolved gases truly come from either photocatalytic decomposition, UV light decomposition, or decomposition from dark reactions with catalysts.
Figure S12. Cyclic voltammograms of (a) pristine Pt and (b) Cr-modified Pt (CrO$_x$/Pt) disk electrode in 0.1 M NaOH with 1% CO/Ar or Ar bubbling at a disk rotation speed of 900 rpm (50 mV s$^{-1}$ and 298 K).
Figure S13. (a) First and final CV after 18 h of sequential CV scans. Recorded at a scan rate of 50 mV s\(^{-1}\), at a disk rotation speed of 3600 rpm and at 298 K. (b) OCP measured sequentially for longer times after CV scans in 1.0 M NaOH for the CrO\(_x\)/Pt disk electrode.

These experiments were performed in conjunction with the experiments in Figure 8 from the main text. First, 18 h of sequential CV scans were performed, and the first and final cycles are shown in
Figure S13a, indicating stable performance in 1.0 M NaOH solution with oxygen bubbling. Next, the OCP was measured after sequentially increasing the duration of the OCP. The OCP values are shown in Figure 13b, and the CVs are shown in Figure 8a.

Figure S14. 0.5 M KCl + 0.5 mM $K_3$Fe(CN)$_6$ + 0.5 mM $K_4$Fe(CN)$_6$ at pH=5.8 while sequentially increasing the sweep range after each cycle (disk rotation speed of 3600 rpm, scan rate 50 mV s$^{-1}$, and 298 K).

The CrO$_x$/Pt RDE was tested with Fe redox reactions in which, after each successive CV scan, the potential range was increased in the positive direction. The CrO$_x$/Pt could successfully block the Fe redox couple until the potential was greater than 0.7 V vs. RHE, at which point Fe redox peaks could be observed (black line), indicating the dissolution of the Cr layer into the solution.
The CrO\textsubscript{x} layer was not stable in acidic pH, as predicted by the Pourbaix diagram in Figure 9, because, thermodynamically, CrO\textsubscript{x} is more oxidizing than water at such a low pH and converts from Cr\textsuperscript{3+} to Cr\textsuperscript{6+}. The loss of Cr was observed in the electrocatalytic system in Figure S15, as each successive CV scan shows increasing cathodic current, indicating a loss of CrO\textsubscript{x} layer.
Figure S16. (a) Chronoamperometry (CA) of CrO$_x$/Pt RDE over 10 h in 1.5 M KH$_2$PO$_4$-K$_2$HPO$_4$ (80-20 ratio) solution with Ar or O$_2$ bubbling. The CA potential was changed every hour using the potentials shown in (b) where the potential of the solution with and without iR correction are presented (3600 rpm and 298 K).
References
