Facile assembly of an efficient CoO$_x$ water oxidation electrocatalyst from Co-containing polyoxotitanate nanocages†‡

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Cobalt-containing polyoxotitanates (TiCo) are excellent precursors for the simple and scalable preparation of Nocera-type CoO$_x$ water-oxidation electrocatalysts. The TiCo cages serve as a reservoir for cobalt ions in a titania matrix on fluoride-doped tin oxide electrodes, and form, in situ, the active CoO$_x$ catalyst for O$_2$ evolution with high stability in phosphate buffer in pH neutral water.

The production of H$_2$ through electro- or photochemical water splitting is a promising approach to provide renewable energy.$^1$ Efficient and stable water oxidation is generally considered as the major challenge in water splitting, because it requires finely tuned proton-coupled four-electron chemistry$^2$ and continued exposure to highly anodic conditions.$^3$ Research into effective oxygen evolution catalysts is, therefore, indispensable if water splitting is to become a viable technology.

Recent examples for water oxidation systems include electrodes modified with nature’s catalyst photosystem II,$^4$ molecular synthetic catalysts,$^5$ and metal oxides.$^6$ Cobalt-containing catalysts have emerged as a particularly efficient and affordable candidate for water splitting.$^7$ In water oxidation, various cobalt(iii) salts (e.g. Co(NO$_3$)$_2$, CoSO$_4$, CoCl$_2$, etc.$^8$) form CoO$_x$ in phosphate buffer (Co-P) in situ during electro-deposition on an indium-tin oxide substrate at high potential for several hours.$^9$ Co-P shows high electroactivity toward water oxidation and self-healing features via a series of linked equilibria.$^9$ Recently, a cobalt polyoxometalate (Co-POM) complex$^{10}$ was reported to form active CoO$_x$ films after decomposition of the Co-POM during electrocatalysis.$^{11}$

We are interested in the application of mixed-metal nanocages as precursors for water oxidation catalysts and our current attention focuses on heterobimetallic polyoxotitanate nanocages [Ti$_i$O$_j$(OR)$_m$$_n$] (where M is a transition metal)$^{12}$ Such doped titania cages can act as readily-hydrolysable single-source precursors for the preparation of metal-doped TiO$_2$ films with tunable nanostructures and electro- and photochemical properties.$^{13}$ To the best of our knowledge, however, there is no report on the use of heterometallic polyoxotitanate nanocages as pre-electrocatalysts for electrochemical water oxidation.

In this communication, we report the preparation of efficient CoO$_x$ water oxidation electrocatalysts from the nanosized TiCo cages [Ti$_i$O$_j$(OPr)$_m$$_n$ ($[(CoBr)$_6$Ti$_{15}$O$_{24}$(O$_x$)$_{16}$]) (1) and [$(Co$)Ti$_i$O$_j$(OPr)$_m$$_n$ (2). Cages 1 and 2 were prepared in one step by heating Ti(OPr)$_4$ and CoX$_2$ (where X is Br or I) in an approximately 9 to 1 ratio.$^6$ The solid-state structures of the previously reported bromide cage (1)$^{14}$ and the novel neutral heterometalllic Ti$_{12}$Co cage (2) are shown in Fig. 1.$^1$.

The ion-separated cage pair in 1 shows the notable encapsulation of a ‘naked’ Br$^-$ anion at the centre of the spherical shell of the [$(Co$)Br$_6$Ti$_{15}$O$_{24}$(OPr)$_{18}$Br]]$^+$ anion.$^{14}$ The solid-state structure

![Fig. 1](image-url) (a) The cage anion of [Ti$_{12}$O$_{14}$(OPr)$_{17}$]$^+$[$(Co$)Br$_6$Ti$_{15}$O$_{24}$(OPr)$_{18}$Br]]$^+$ (1). A full structural description and data can be found in ref. 14. (b) Crystallographic structure of the Ti$_{12}$Co cage [$(Co$)Ti$_{15}$O$_{24}$(OPr)$_{18}$Br]$^+$ as ball and stick representation for all non-H atoms. Selected bond lengths (Å) and angles (°): Co–O$_{oxo}$ range 1.859(14)–2.082(15), Co–I 2.589(4), Co–O 1.970(14)–2.228(16), O–Co–O range 76.2(6)–101.3(6), O–Co–I range 107.6(4)–116.4(5). Ti (red), O (blue), C (grey), Co (green), Br (brown), I (magenta).
of 2 is similar to the cationic cage in 1, but one of the [TiO]$_2$$^+$ moieties is replaced by a [CoI]$^+$ unit. The Co$^+$ centre of 2 adopts a highly distorted square-based pyramidal coordination geometry, with the Co–O bond lengths [1.970(14)–2.228(16) Å] and O–Co–O angles [107.6(4)–116.4(5)º] varying over a broad range. Unlike 1, in which one of the bromide anions is located at the centre of the spherical shell, the iodide anion in 2 has a more conventional exo-bonding mode [Co–I 2.589(4) Å]. The reason for this difference is unclear but is most likely the result of the much greater ionic radius of I$^-$ compared to Br$^-$. It can be noted in this regard that the Ti$_4$I$_4$O$_8$ shell of 2 measures approximately 3.7 to 5.8 Å and is too small to accommodate an iodide ion. The optical and electrochemical properties of 2 are shown in Fig. S1 and S2 (ESI†).

Electrodes for water oxidation were prepared by drop-casting fresh solutions of the TiCo nanocages 1 or 2 (40 μL of 0.01 M in dichloromethane) on fluoride-doped tin oxide (FTO, exposed area of 0.5 cm$^2$) coated glass. The FTO|TiCo electrodes, i.e., FTO|1 and FTO|2, were dried for 20 min in air at room temperature, whereupon the electrodes were rinsed with water. For comparison, FTO|Co(NO$_3$)$_2$ was also prepared by drop-casting Co(NO$_3$)$_2$·6H$_2$O (40 μL of 0.01 M in water) on FTO by the same method. The electrodes were then immersed into an electrochemical cell containing phosphate (Pi) electrolyte solution (0.1 M, pH 7). All electrochemical experiments were performed using a conventional three-electrode system with the (un)modified FTO working electrode, a Pt foil counter electrode and a Ag/AgCl/saturated KCl reference electrode at 25 °C. A stable electrode film was obtained in 5 min by cycling the electrochemical potential five times between 0.2 and 1.7 V vs. NHE with a scan rate of 50 mV s$^{-1}$.

Cyclic voltamograms (CVs) for FTO|1, FTO|2, FTO|Co(NO$_3$)$_2$ and unmodified FTO electrodes in Pi solution (0.1 M and pH 7) at a scan rate of 50 mV s$^{-1}$ are shown in Fig. 2. FTO|1 and FTO|2 exhibit comparable electrochemical responses with a Co$^{III}$/Co$^{II}$ oxidation wave at approximately $E_p = 1.20$ V, followed by catalytic oxidation of water at an onset potential of approximately 1.27 V vs. NHE. FTO|Co(NO$_3$)$_2$ and unmodified FTO electrodes show less favorable electrochemical responses and high anodic currents are only observed at more positive potentials. The poor performance of FTO|Co(NO$_3$)$_2$ can, at least in part, be attributed to the weak attachment of the cobalt ions on the FTO surface and its removal during the rinsing procedure (Fig. 2a). In contrast, Co ions in FTO|1 and FTO|2 are entrapped in the Ti–O–Ti network, resulting from hydrolysis and polycondensation of the polyoxotitanate nanocages after the drop-casting procedure by moisture in air.$^{15}$

The FTO|TiCo electrodes not only exhibited high electrocatalytic activity, but also showed high stability in a pH neutral Pi solution (Fig. 2b). An initial current density of 0.8 mA cm$^{-2}$ at an applied potential of 1.35 V vs. NHE was obtained, which retained approximately 80% of the initial density after 1 h. The FTO|Co(NO$_3$)$_2$ electrode exhibited an initial current density of 0.52 mA cm$^{-2}$ and approximately 80% of electroactivity was lost after 1 h. Employing the FTO|TiCo electrodes in a Na$_2$SO$_4$ (0.1 M) solution resulted in a reduced initial current response (0.55 mA cm$^{-2}$) with a decrease in current density of approximately 92% after 1 h operation at 1.35 V vs. NHE.$^{16}$

Controlled potential electrolysis with FTO|1 in a pH neutral Pi solution (0.1 M) allowed us to determine the Faradaic yield of electrocatalytic O$_2$ evolution. After 1 h and at a potential of 1.35 V vs. NHE, a charge of 4.07 C was passed through FTO|1 and 9.4 μmol of O$_2$ were detected with a fluorescence oxygen probe (Fig. S3, ESI†). The O$_2$ measurement confirms that the anodic catalytic current arises from O$_2$ evolution with a Faradic efficiency of approximately 90%.

Our electrochemical study suggests that the Co-containing electrocatalyst formed is comparable with the Co–Pi catalyst reported by Nocera’s group.$^{6a,b}$ The nanocages 1 and 2 show a comparable activity, indicating that the same water oxidation catalyst is formed from these two nanocage precursors on the FTO substrate. Catalytic activity with high stability is only observed in the presence of cobalt ions, and Pi allows for the in situ formation of the catalyst from the decomposed TiCo cages under anodic condition.

However, several differences between FTO|TiCo and Co–Pi exist. Scanning electron microscopy (SEM) images of FTO|1 and FTO|2 are shown in Fig. 3 and Fig. S4 (ESI†), respectively. Both electrodes show a similar surface morphology with porous islands and cracks between these islands. For comparison, electrodeposited Co–Pi forms a thin film coalesced with individual 1–5 μm spherical nodules particles.$^{6c}$ The porous islands and cracks on FTO|TiCo give access to a high surface area and are presumably formed during the rapid evaporation of dichloromethane. No obvious change is observed in the surface morphology of the islands before and after 1 h applied potential at 1.35 V vs. NHE (FTO|1*). However, electrodeposition of a new layer is observed in the crack area in FTO|1* (Fig. 3b).
Detailed examination of the chemical composition of the islands and cracks was carried out by energy dispersive X-ray (EDX) analysis on FTO|1 (Fig. S5 (ESI†) and Table 1). Before electrochemical treatment, the Co/Ti ratio of 0.26 in the islands reflects the ratio of these elements in nanocage 1 of 0.22. Co and P are not detectable in the crack area of the FTO|TiCo electrodes before electrochemical treatment. After applying 1.35 V vs. NHE for 1 h, the Co content on the islands decreased and significant amounts of Co (8.2%) and P (4.8%) were found on the electro-deposited layers in the crack area. EDX analysis therefore confirms that Co ions migrate under anodic conditions from the islands to the crack area; in analogy to the mechanism suggested for self-healing in Co–P.9 The stoichiometric ratio of Co: P of 2:1 in the cracks is also indicative of the formation of a Co–P type species.6a Powder X-ray diffraction (XRD) studies reveal that the deposited CoOx catalyst and the titania matrix are amorphous (Fig. S6, ESI†).

In summary, our study demonstrates that TiCo cages are excellent single-source precursors for the assembly of technologically important materials for water oxidation. By simple drop-casting TiCo cages 1 and 2 on FTO electrodes, we incorporated Co ions in a titania matrix, which form an active CoOx species in situ within minutes by applying a positive potential (>1.2 V vs. NHE). Work is currently in progress to study nanosized cages for different redox reactions.

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Notes and references


Table 1 Summary of the EDX analyses of the as-prepared FTO|1 and the FTO|1*

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<tr>
<th>Electrode (position)</th>
<th>C</th>
<th>O</th>
<th>Sn</th>
<th>Ti</th>
<th>Co</th>
<th>Br</th>
<th>P</th>
<th>K</th>
</tr>
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<tbody>
<tr>
<td>FTO</td>
<td>1 (island)</td>
<td>5.76</td>
<td>56.59</td>
<td>0.00</td>
<td>21.67</td>
<td>5.81</td>
<td>10.18</td>
<td>0.00</td>
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<tr>
<td>FTO</td>
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<td>4.03</td>
<td>71.91</td>
<td>21.82</td>
<td>0.71</td>
<td>0.00</td>
<td>0.38</td>
<td>0.00</td>
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<td>1.15</td>
<td>0.00</td>
<td>9.00</td>
</tr>
<tr>
<td>FTO</td>
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<td>7.07</td>
<td>0.31</td>
<td>8.24</td>
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