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

Yi-Hsuan Lai, a Chia-Yu Lin, a Yaokang Lv, b,c Timothy C. King, b Alexander Steiner, d Nicoleta M. Muresan, a Lihua Gan, d Dominic S. Wright b and Erwin Reisner* a

Cobalt-containing polyoxotitanates (TiCo) are excellent precursors for the simple and scalable preparation of Nocera-type CoOₓ 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 CoOₓ catalyst for O₂ evolution with high stability in phosphate buffer in pH neutral water.

The production of H₂ through electro- or photochemical water splitting is a promising approach to provide renewable energy. 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 and continued exposure to highly anodic conditions. 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, molecular synthetic catalysts, and metal oxides. Cobalt-containing catalysts have emerged as a particularly efficient and affordable candidate for water splitting. In water oxidation, various cobalt(n) salts (e.g. Co(NO₃)₂, CoSO₄, CoCl₂, etc.) form CoOₓ in phosphate buffer (Co-P) in situ during electro-deposition on an indium-tin oxide substrate at high potential for several hours. Co-P shows high electrocatalytic toward water oxidation and self-healing features via a series of linked equilibria. Recently, a cobalt polyoxometalate (Co-POM) complex was reported to form active CoOₓ films after decomposition of the Co-POM during electrocatalysis.

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 [TiₓOᵧ(OR)z] (where M is a transition metal). Such doped titania cages can act as readily-hydrolysable single-source precursors for the preparation of metal-doped TiO₂ films with tunable nanostructures and electro- and photochemical properties. 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 CoOₓ water oxidation electrocatalysts from the nanosized TiCo cages [Ti₁₂O₁₅(Pr)₁₇] [(CoBr)₆Ti₁₅O₂₄(Pr)₁₈(Br)] (1) and [(Co)Ti₁₁O₁₃(Pr)₁₇] (2). Cages 1 and 2 were prepared in one step by heating Ti(Pr)₄ and CoX₂ (where X is Br or I) in an approximately 9 to 1 ratio. The solid-state structures of the previously reported bromide cage (1) and the novel neutral heterometallic Ti₁₂Co cage (2) are shown in Fig. 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 [(CoBr)₆Ti₁₅O₂₄(Pr)₁₈(Br)]⁻ anion. The solid-state structure

Fig. 1 (a) The cage anion of [Ti₁₂O₁₅(Pr)₁₇][(CoBr)₆Ti₁₅O₂₄(Pr)₁₈(Br)]⁻ (1). A full structural description and data can be found in ref. 14. (b) Crystallographic structure of the Ti₁₁-Co cage [(Co)Ti₁₁O₁₃(Pr)₁₇] (2) as ball and stick representation for all non-H atoms. Selected bond lengths (Å) and angles (°): Co-Oₐ, 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).

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of 2 is similar to the cationic cage in 1, but one of the $[\text{TiO}]^{2+}$ moieties is replaced by a $[\text{Co}]^{2+}$ unit. The Co$^6$ 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)]° 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 $\text{I}^−$ compared to Br$^-$. It can be noted in this regard that the Ti$_{11}$O$_{14}$ 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 (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 (Fig. 2). The fluctuations in the electrochemical responses with a Co$^{III}$/Co$^{II}$ oxidation wave at approximately 1.20 V vs. NHE 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%.

Controlled potential electrolysis with FTO|1 in a pH neutral P$_i$ 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.$^{16}$ 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 Pt 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.$^{60}$ 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. The stoichiometric ratio of Co: P of 2:1 in the cracks is also indicative of the formation of a Co–P type species. 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

16. Prevaline OPToTiCo electrodes at 430 °C had an adverse effect on the electrocatalytic activity (Fig. S7, ESI‡).