Evolving O_2 (OER) Cleans Waste Water

It was evident that a CoO_x/Co-black composite electrode can accumulate reactive oxygen species (ROS) and other oxidants for the treatment of latrine wastewater that was collected on the Caltech campus….

X-ray absorption spectra (XAS), X-ray photoelectron spectra (XPS) and electron paramagnetic resonance (EPR) spectra of Co-black indicate that bulk oxygen vacancies (O_v) are the primary source of an enhanced conductivity. A CoO_x/Co-black composite electrode was found to be active for the electrochemical production of reactive oxygen species (ROS) and other oxidants (*i.e.*, reactive chlorine species (RCS)) for the treatment of waste water.

TiO_2 has long been recognized as a stable and reusable photo-catalyst for water splitting and pollution control, but it is an inefficient anode material in the absence of photo-activation because of its poor electron conductivity. To overcome this limitation, conductive TiO_2 nanotube array electrodes in a series have been developed.

Conductive TiO_2 nanotube arrays (NTA) either blue or black in appearance have been reported. Both electrochemical and thermal reduction promote the formation of Ti^{3+} sites and adjacent oxygen vacancies (O_v) in TiO_2. The idea essentially is to fill the O_v by oxidizing Ti^{3+} *via* adsorbed oxygen species. Conductive NTA electrodes are known to have satisfactory electrochemical oxidation activity.[1,2] The concentration of oxygen vacancies (O_v) decreases in the order black (22%) > blue (17%) > pristine NTA (12%). XPS analyses also found that Co doping results in a significantly decreased Ti oxidation state in Co-black NTA and creates more surficial Ov (25%) (**Fig. 1 and 2(a)**).

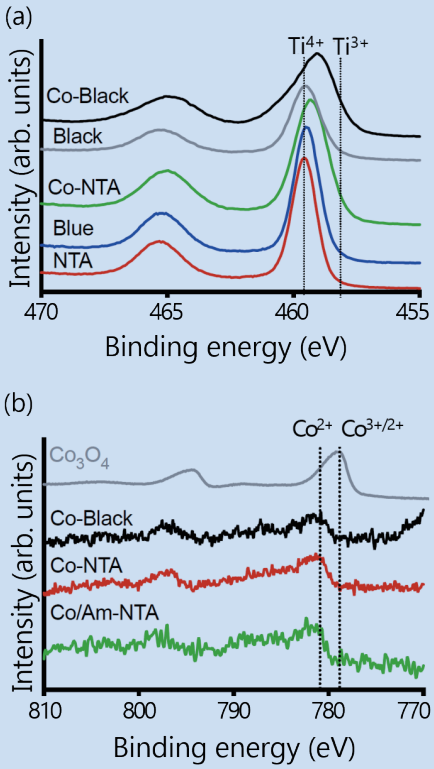

Fig. 1: X-ray photoelectron spectra of (a) Ti 2p and (b) Co 2p orbitals [Reproduced from Ref. 3]

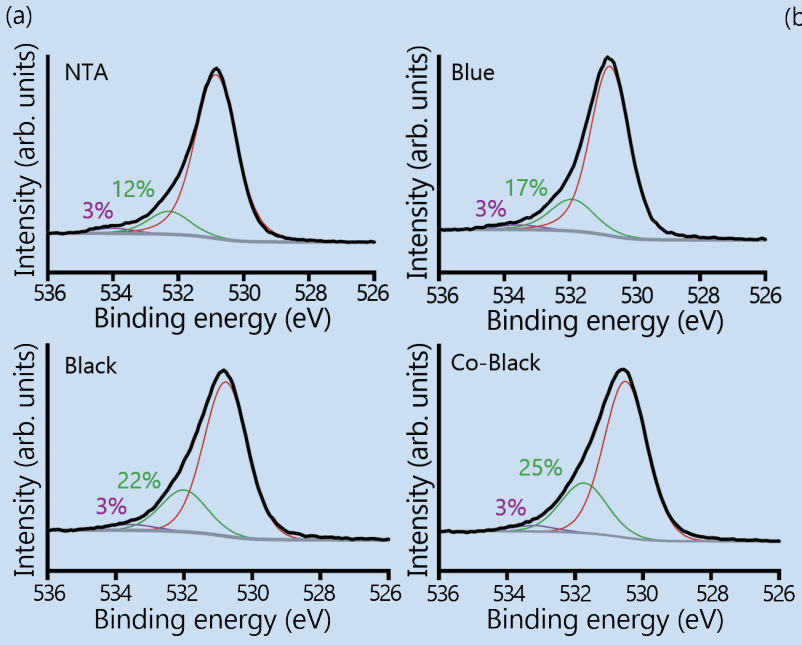

Fig. 2: (a) Deconvolution analyses of O 1s X-ray photoelectron spectra; (b) Co K-edge XAS (insert: enlarged view of pre-edge structure). [Reproduced from Ref. 3]

Michael R. Hoffmann (California Institute of Technology) collaborating with Sofia Ya Hsuan Liou (National Taiwan University), synthesized cobalt-doped black-TiO_2 nanotube array (Co-black NTA) electrodes and showed that this electrochemical system exhibits a smaller OER (oxygen evolution reaction) over-potential (352 mV) than a dimensionally stable IrO_2 anode (DSA) (434 mV) electrode, and was stable for more than 200 h of continuous operation in a $NaClO_4$ electrolyte at 10 mA cm^{-2}.[3]

The oxidation state and coordination environment of the Co dopant were further investigated with XAS. The Co K-edge XAS were recorded at **TLS 17C1**. The absorption edge of Co-black overlaps with that of CoO, indicating that the surficial Co ions of Co-black are identified as Co^{2+} (**Fig. 2(b)**). The overall Co K-edge profile of Co-black also clearly revealed differences in the coordination structure from that of oxide particles. In particular, the pre-edge signals of Co-black corresponding to 1s–3d electronic transitions are present in an O_h configuration, unlike CoO and Co_3O_4.[4] Given that no CoO_x particulates were found with both SEM and TEM, Co^{2+} in Co-black is hence atomically doped into the lattice of TiO_2, adopting the same O_h configuration.

Furthermore, the coordination structure of Co^{2+} remains intact after electrolysis for 100 h, as indicated by the unchanged Co K-edge profiles of Co-black before and after use (**Fig. 2(b)**). With all these observations combined, the authors suggest that Co^{2+} is effectively immobilized on NTA and its reduced valence state results not from H_2 reduction but from a strong Co–TiO_2 interaction.

The Co–TiO_2 interaction is strong enough to prevent Co leaching at circum-neutral pH. Co-black was hence further applied to treat latrine wastewater that was collected on the Caltech campus in a prototype solar-toilet system.[5,6] The results indicate that Co-black outperforms the IrO_2 DSA through its greater CER activity (**Fig. 3(a)**). As expected, the chemical-oxygen-demand (COD) removal capability of Co-black is superior to that of IrO_2 DSA and C-DSA (commercialized IrO_2 DSA) (**Fig. 3(b)**). The effluent after 8 h of treatment appears clear and suitable for non-potable water reuse (**Fig. 3(c)**). In conclusion, this work demonstrated that cobalt-doped black TiO_2 nanotubes serving as a stable anode for oxygen evolution can be effective for electrochemical treatment of waste water. (Reported by Steve S.-F. Yu, Academia Sinica)

This report features the work of Michael R. Hoffmann, Ya Hsuan Liou and their collaborators published in ACS Catal. ***8****, 4278 (2018).*

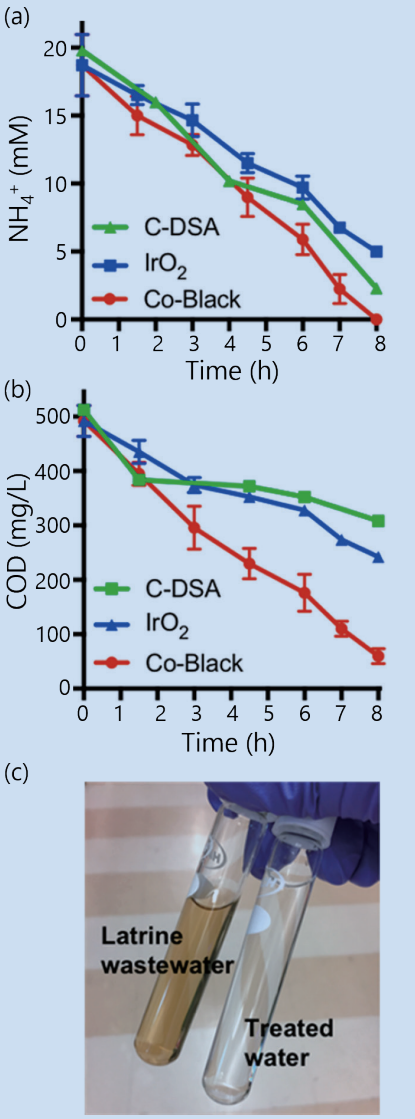

Fig. 3: Decay of (a) COD and (b) NH_4^+ as a function of duration of electrolysis. (c) Photograph of waste water before and after electrolysis. [Reproduced from Ref. 3]

TLS 17C1 W200 – EXAFS

- XANES
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