

## A Robust Molecular Catalyst Generated In-Situ for Photo- and Electrochemical Water Oxidation; A Step Towards Artificial Photosynthesis

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Water splitting is the key step towards artificial photosystems for solar energy conversion and storage in the form of chemical bonding. The oxidation of water is the bottle-neck of this process that hampers its practical utility and hence efficient, robust, and also easy to make catalytic systems based on earth abundant materials are of exceptional importance. Here, we present an *in-situ* generated cobalt catalyst  $[\text{Co(II)(TCA)}_2(\text{H}_2\text{O})_2]$  (where TCA = 1-Mesityl-1,2,3-1H-triazole-4-carboxylate) that efficiently conducts photochemical water oxidation at near-neutral conditions. The catalyst showed high stability under photolytic conditions for more than 3 h of photoirradiation. During electrochemical water oxidation, the catalytic system assembled a catalyst film, which proved not to be cobalt oxide/hydroxide as normally expected, but instead and for the first time, generated a molecular cobalt complex incorporating the organic ligand bound to cobalt ions. The catalyst film exhibited low overpotential for electrocatalytic water oxidation (360 mV) and high oxygen evolution peak current density of  $9 \text{ mA cm}^{-2}$  and  $2.7 \text{ mA cm}^{-2}$  on GC and ITO electrodes at only 1.49 and 1.39 V (vs. NHE), respectively, under neutral conditions. Furthermore, DFT calculations predict a mono-nuclear oxidation mechanism and show that this  $\text{Co(TCA)}_2 \cdot 2\text{H}_2\text{O}$  catalyst lies very close to the top of the theoretical volcano plot. Based on these computational results, a small modifications of this type of catalyst can lead to a superb –easily synthesized – industrial water oxidation catalyst. Our finding, exemplified on the *in-situ* generated cobalt complex, might be applicable to other molecular systems and suggests that the formation of catalytic film in electrochemical water oxidation experiments is not always indication of the catalyst decomposition and formation of nanoparticles.