Efficient Water Oxidation Kinetics and Enhanced Electron Trasport in Li-doped TiO$_2$ Nanotubes Photoanodes

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I. Surface SEM image of TiO$_2$ nanotubes

Figure S1. Surface SEM images of TiO$_2$ nanotubes grown for varying amounts of time. Well-ordered pores with increasing pore diameter are formed until 240 minutes where the top part collapses.

II. Pore size distribution of TiO$_2$ nanotubes anodized for different times

Figure S2. Pore size distribution for TiO$_2$ nanotubes showing an increase in the average pore size as anodization time increases.

Reference Raman signals:

- Anatase TiO$_2$:[1] 144, 196, 400, 517, and 641 cm$^{-1}$
- Co$_3$O$_4$:[2,3] 197, 485, 620, and 691 cm$^{-1}$
- CoOOH:[2,3] 620 and 505 cm$^{-1}$

Figure S3. Raman spectra of TiO$_2$ nanotubes modified by (a) electrodeposited Co oxide, (b) precipitated Co oxide, and (c) photodeposited Co-Pi. Inset: Raman spectra of the precipitate extracted from the solution used to prepare (b). Key: A – anatase TiO$_2$. Inset O – Co$_3$O$_4$. Inset H – CoOOH.
IV. EDS spectra and surface mapping of CoO\textsubscript{x} modified TiO\textsubscript{2} nanotubes

![Figure S4](image_url)

**Figure S4.** (a) EDS spectra of CoO\textsubscript{x} modified TiO\textsubscript{2} nanotubes confirm the presence of elements Co in all three catalysts investigated and the addition of P with Co-Pi. EDS spectra are shown for the highest quantity of catalyst loading. Si originates from the carbon tape used to secure the sample. (b) EDS surface mapping of TiO\textsubscript{2} nanotubes modified by precipitated CoOx catalysts shows a uniform coverage of the nanotube arrays, but no visible deposit.
V. Scanning electron microscopy studies of catalyst modified Li-TiO$_2$ nanotubes.

**Figure S5.** The morphology of electrodeposited Co oxide catalyst prepared by electrodeposition of metallic Co and then electrochemical cycling in an alkaline electrolyte changes from decoration at the mouths of the tubes to the formation of particles on the surface of the nanotube array.
VI. Photocurrent as a function of catalyst deposition amount for Co-Ox based catalysts on TiO$_2$ nanotubes.

**Figure S6.** Photocurrent under two applied potentials for three different Co-based catalysts on TiO$_2$ nanotubes. Under a weak applied potential at 0.5 V$_{RHE}$, a twofold enhancement in the photocurrent is observed. However, at strong applied potential, adding more catalyst results in decreasing photocurrent.
VII. Charge increase for TiO2 nanotubes with various lengths in the process of Li intercalation.

Figure S7. Charge-time curve in the process of Li-intercalation. According to Faraday’s law of electrochemistry, the charge passed is proportional to the mass induced. Apparently, Li amount is increasing with the thickness of the TiO\textsubscript{2} layer, but not proportionally to the tube length, probably due to diffusion limitations. Furthermore, the extent of Li intercalation cannot be precisely determined due to the simultaneous occurrence of hydrogen evolution.
References

