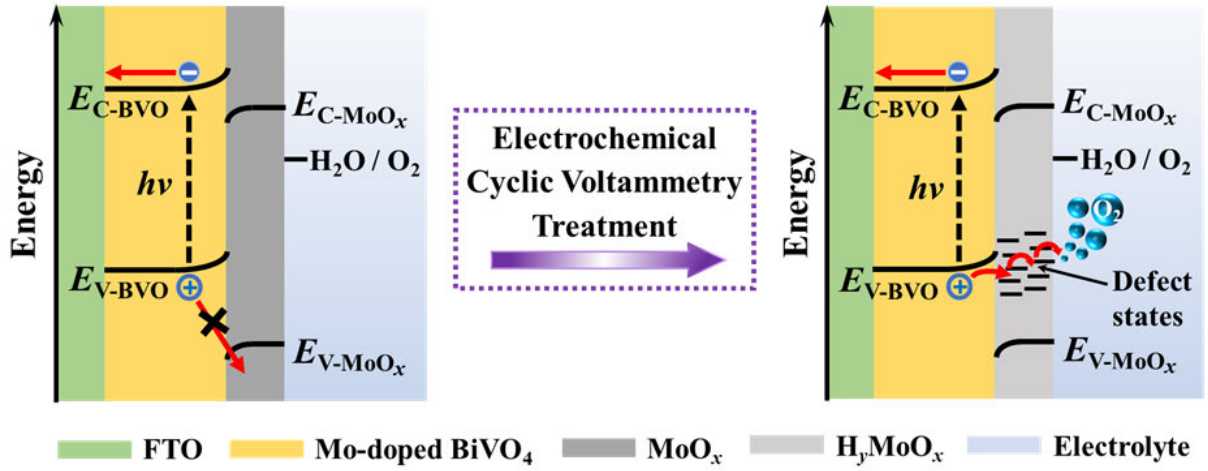
Constructing charge transfer channels on a photoanode surface by electrochemical treatment

October 28 2022



Electrochemical cyclic voltammetry treatment initiates the formation of HyMoOx surface defects, which act as charge transfer channels for photogenerated holes. Via these charge transfer channels, the charge separation and photoelectrochemical performance of Mo-doped BiVO4 electrode are significantly enhanced. Credit: *Chinese Journal of Catalysis* (2022). DOI: 10.1016/S1872-2067(21)63986-4

Photoelectrochemical (PEC) water splitting presents a promising way to convert solar energy into storable and transportable hydrogen energy. Among investigated semiconducting materials, $BiVO_4$ is considered as

an intriguing photoanode candidate, due to its low theoretical onset potential and relatively high photocurrent. Regarding its poor electronic conductivity, Mo doping is demonstrated as an effective strategy for enhancing carrier concentration and n-type conductivity.

However, MoO_x is found to segregate at the surface of Mo-doped $BiVO_4$ photoanodes, which serves as recombination centers and degrades the PEC performance. A previous study has proposed an electrochemical treatment to etch these surface MoO_x segregations, thus realizing the activation of Mo-doped $BiVO_4$ electrodes.

Yet it is difficult to explain the phenomenon that electrochemically activated Mo-doped $BiVO_4$ electrodes gradually loss their activity when exposed to air at room temperature, because MoO_x segregations cannot re-form under this condition. The underlying mechanism for electrochemical activation of Mo-doped $BiVO_4$ needs further clarification.

Recently, a research team led by Prof. Zhaosheng Li from Nanjing University, China offered a new insight into the electrochemical activation of Mo-doped $BiVO_4$ photoanodes: electrochemical treatment not only removes partial MoO_x segregations, but also initiates the formation of H_yMoO_x surface defects which provide charge transfer channels for photogenerated holes. The results were published in *Chinese Journal of Catalysis*.

Using XPS, Raman and XRD measurements, it is revealed that simultaneous reduction and proton insertion in the MoO_x species occur during electrochemical treatment via a faradaic reaction: $MoO_x + yH^+ + ye^- = H_yMoO_x$. The formed H_yMoO_x surface defects are sensitive to oxidative environment under which they would be slowly transformed back to MoO_x via a deprotonation process: $H_yMoO_x + (y/4)O_2 = MoO_x + (y/2)H_2O$.

Electrochemical oxidation of one-electron, highly reversible redox couple ferricyanide/ferrocyanide, $[Fe^{III}(CN)_6]^{3-}/[Fe^{II}(CN)_6]^{4-}$, confirms that MoO_x species blocks holes while H_yMoO_x surface defects act as efficient hole-transfer channels. The energy-diagram change of Mo-doped $BiVO_4$, MoO_x and electrolyte system before and after electrochemical treatment suggests that H_yMoO_x surface defects introduce defect energy levels thereby allow photogenerated holes to transport through.

Based on these experimental results, an explanation to photoactivity variation of electrochemically treated Mo-doped $BiVO_4$ exposing to air is proposed. Upon electrochemical treatment, freshly formed H_yMoO_x surface defects behave as efficient hole transfer channels thereby increase the photocurrent greatly.

When exposing to air, these H_yMoO_x surface defects would be oxidized and transformed into MoO_x, the photoactivity decline depends greatly on environmental temperature and exposure time. Once sufficient oxidation of H_yMoO_x defects completes, hole-blocking MoO_x will dominate at Mo-doped $BiVO_4$ surface and largely suppress the photoactivity.

The introduced concept of surface charge transfer channel is well worth further understanding and optimization, which would offer new opportunities for future development of various fields including energy storage, sensor, and surface/interface science.

More information: Zhiwei Li et al, Electrochemical creation of surface charge transfer channels on photoanodes for efficient solar water splitting, *Chinese Journal of Catalysis* (2022). DOI: 10.1016/S1872-2067(21)63986-4