Improving the Photo-oxidative Performance of Bi$_2$MoO$_6$ by Harnessing the Synergy between Spatial Charge Separation and Rational Co-catalyst Deposition

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It has been reported that photogenerated electrons and holes can be driven to specific crystal facets within a semiconductor, which is believed to arise from differences in their surface electronic structures, indicating different facets can act as either photo-reduction or photo-oxidation sites.$^{[1,2,3]}$ For instance, the intrinsic nature of charge separation between the {010} and {110} facets of BiVO$_4$ has been demonstrated via the selective photo-deposition of metals and metal oxides.$^{[4]}$ With this in mind, this work examined the electron-hole separation capabilities within faceted plate-like bismuth molybdate (Bi$_2$MoO$_6$), which is an efficient photocatalyst for water oxidation. Herein, we demonstrate that the photo-excited electrons and holes can be spatially separated to the {010} and {001}/{100} facets, respectively, within Bi$_2$MoO$_6$ as evidenced by the facet-dependant photo-deposition of noble metals (e.g. Pt, Au and Ag) or/and metal oxides (e.g. PbO$_2$, MnO$_x$, CoO$_x$), as shown in Fig. 1. Theoretical calculations revealed that differences in energy levels between the conduction band (CB) and valence band (VB) of the {010} and {001}/{100} facets can contribute to electrons and holes being driven to different surfaces of the plate-like Bi$_2$MoO$_6$ (Fig. 2). Utilising this knowledge, the photo-oxidative capability was then improved by adding an efficient water oxidation co-catalyst, CoO$_x$, to the system. Interestingly, we found that the degree of enhancement is highly dependent on the co-catalyst location. A greater amount of oxygen was evolved when CoO$_x$ was selectively deposited on the oxidation (hole-rich) facets of Bi$_2$MoO$_6$ compared to Bi$_2$MoO$_6$ where the CoO$_x$ was randomly distributed on the surface. The elevated performance exhibited when the CoO$_x$ is selectively deposited on the Bi$_2$MoO$_6$ {001}/{100} facets is ascribed to the benefit of hole trapping by the co-catalyst being accentuated over other potentially detrimental co-catalyst effects such as them acting as recombination centres and/or covering reactive sites. These results indicate that the synergy between spatial charge separation and co-catalyst location on the appropriate facets of plate-like Bi$_2$MoO$_6$ can promote its photocatalytic activity.
Figure 1. SEM images of (a) plate-like Bi$_2$MoO$_6$, (b) photo-reduced Pt on Bi$_2$MoO$_6$, (c) photo-oxidised PbO$_2$ on Bi$_2$MoO$_6$, and (d) TEM image of Bi$_2$MoO$_6$ with dual photo-deposited MnO$_x$ and Pt co-catalysts.

Figure 2. Schematic diagram of proposed charge separation process among {010} and {001}/100 facets within plate-like Bi$_2$MoO$_6$.

Funding: Australian Research Council Discovery Project (DP140102581)

Acknowledgement: This work was financially supported by Australian Research Council Discovery Project (DP140102581) programme. We thank the UNSW Mark Wainwright Analytical Centre for providing access to all analytical facilities.

References: