

Improving the Photo-oxidative Performance of Bi_2MoO_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_2MoO_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_2MoO_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_2MoO_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_2MoO_6 compared to Bi_2MoO_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_2MoO_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_2MoO_6 can promote its photocatalytic activity.

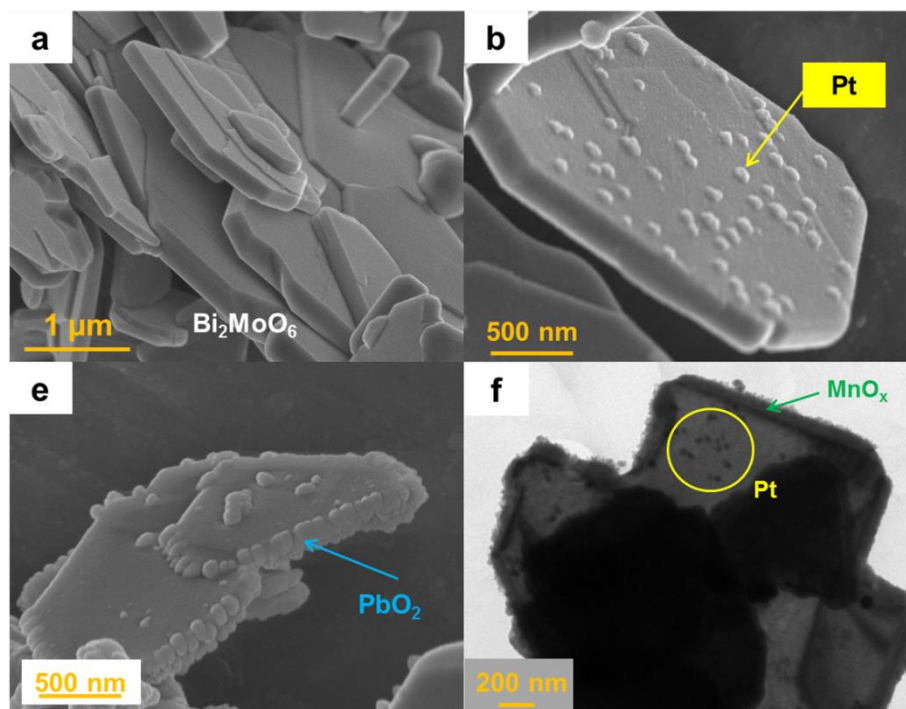


Figure 1. SEM images of (a) plate-like Bi_2MoO_6 , (b) photo-reduced Pt on Bi_2MoO_6 , (c) photo-oxidised PbO_2 on Bi_2MoO_6 , and (d) TEM image of Bi_2MoO_6 with dual photo-deposited MnO_x and Pt co-catalysts

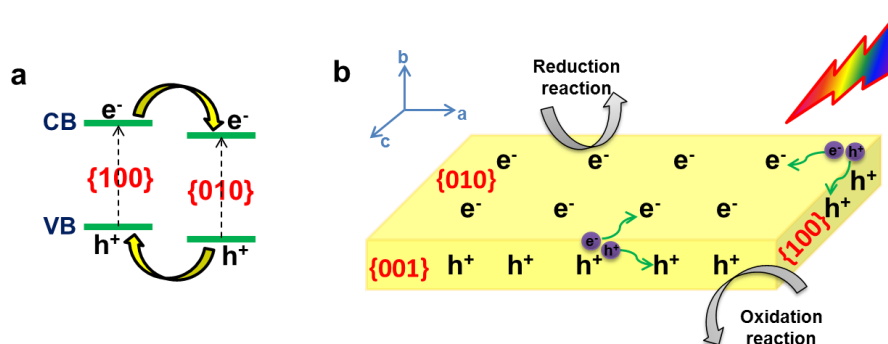


Figure 2. Schematic diagram of proposed charge separation process among $\{010\}$ and $\{001\}/\{100\}$ facets within plate-like Bi_2MoO_6

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References:

- [1] T. Ohno, K. Sarukawa, M. Matsumura, *New J. Chem*, **2002**, 26, 1167-1170
- [2] Q. Zhang, R. Li, Z. Li, A. Li, S. Wang, Z. Liang, S. Liao, C. Li, *Journal of Catalysis*, **2016**, 337, 36-44
- [3] L. Mu, Y. Zhao, A. Li, S. Wang, Z. Wang, J. Yang, T. Liu, R. Chen, J. Zhu, *Energy & Environmental Science*, **2016**, 9, 2463-2469
- [4] R. Li, F. Zhang, D. Wang, J. Yang, M. Li, J. Zhu, X. Zhou, H. Han, C. Li, *Nature Communications*, **2013**, 4, 1432