Nb Additive Incorporation for Enhanced Z-Scheme Photocatalytic Activity in $BiVO_4$

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Photocatalysis is a promising pathway to direct utilization of solar energy for chemical fuel production. A major challenge is development of low cost, stable active materials that utilize a large fraction of the solar spectrum. $BiVO_4$ is a promising candidate material that acts as oxidizing species in a Z-scheme water splitting reaction, capable of utilizing visible light (band gap 2.4 eV). In this work we demonstrate enhanced water-splitting performance of $BiVO_4$ by incorporation of Zr additive and compare the physical mechanism to that of Mo additive that is known to enhance performance of $BiVO_4$.

$BiVO_4$ powder was synthesized via a reaction of NH_4VO_4 and $Bi(NO_3)_3$ in an acidic solution, with precipitate annealed at 500°C. Doped $BiVO_4$ was produced by incorporating 1% molar fraction of Zr or Mo during synthesis. Water splitting reaction was conducted in 10mM $AgNO_3$ aqueous solution and 2x increase of photocatalytically produced oxygen was observed for both Mo an Zr-doped $BiVO_4$ vs. pure $BiVO_4$.

A key question in the initial investigation is whether Zr additive acts to change bulk properties or surface properties of $BiVO_4$. Raman scattering measurements indicated (Figure 1) that effect of 1% Zr additive is qualitatively similar to 1% Mo additive, but Zr-doping results in stronger shifts of the peaks characteristic of monoclinic $BiVO_4$ (826, 365, and 333 cm^{-1}). The shift of VO_4 symmetric stretching mode (826 cm^{-1}) is interpreted as substitution by Zr or Mo on V site.

Time resolved photoluminescence (TRPL) measurements showed a decrease of photoexcited carrier lifetime in Mo- and Zr-doped samples, indicating change in bulk electrical properties.

In summary, we report observation of improved water-splitting photocatalytic activity in $BiVO_4$ via Zr additive incorporation. Raman and TRPL measurements indicate that Zr is likely incorporated into the lattice rather than confined to the surface of $BiVO_4$ grains.

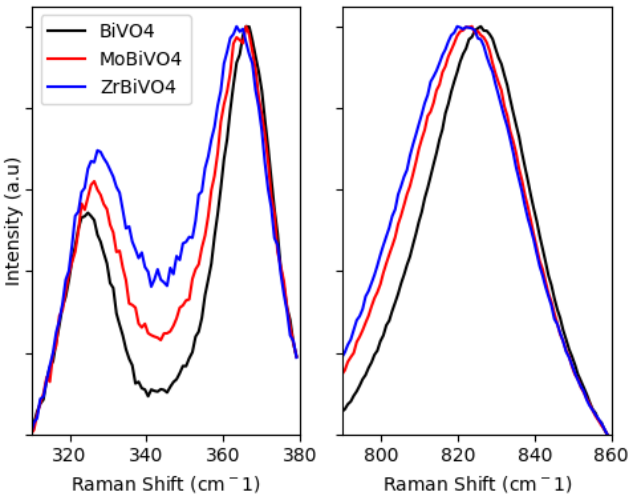

Figure 1 Normalized Raman peaks for $BiVO_4$ (black), Mo-doped $BiVO_4$ (red), and Zr doped $BiVO_4$ (blue).