Relationship between synthesis temperature and the photocatalytic activity of $BiVO_4$

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Bismuth vanadate ($BiVO_4$) is a promising photocatalyst for visible-light-driven water splitting thanks to its direct band gap ～2.4eV, favorably positioned band edges and its good chemical stability. However, $BiVO_4$ practically exhibits poor photocatalytic activity because of low conductivity and fast recombination of photogenerated electron-hole pairs. Moreover, the photocatalytic property of $BiVO_4$ strongly depends on its crystal form. The monoclinic form (ms-$BiVO_4$) is the most photocatalytically active due to the weak hole localization ascribed to the distinct overlap of O 2p and Bi 6s orbitals in the valence band (VB) [1]. Therefore, it is important to retain the monoclinic structure. In this work, we attempt to fine-tune the photocatalytic property of $BiVO_4$ by varying the synthesis temperature. $BiVO_4$ crystals were prepared at different temperatures 30, 60, 80 and 100°C. An increase of photocatalytically produced oxygen was observed with the increase of synthesis temperature of $BiVO_4$. Rietveld refinement for XRD diffractograms of synthesized samples indicates that relatively high synthesis temperatures are favorable to form ms-$BiVO_4$. Interestingly, the [VO_4] tetrahedron chains are not affected by the increase of synthesis temperature of $BiVO_4$, as suggested by Raman scattering. Steady state photoluminescence study reveals strong sub-gap emission at wavelengths between 600 and 1000 nm in all samples. These emission lines could be assigned to intrinsic defects, possibly the oxygen vacancies (OVs). Time resolved photoluminescence (TRPL) measurements show increase of photoexcited carrier lifetime with the increase of synthesis temperature, indicating low recombination rates (Fig.1). The OVs act as n-dopants and hence they contribute to polaronic conduction in $BiVO_4$ [2]. In our assumption, the increase of synthesis temperature might lead to an increase of OVs concentration in the $BiVO_4$ crystal, which improves the electrical properties at the bulk and /or the surface.

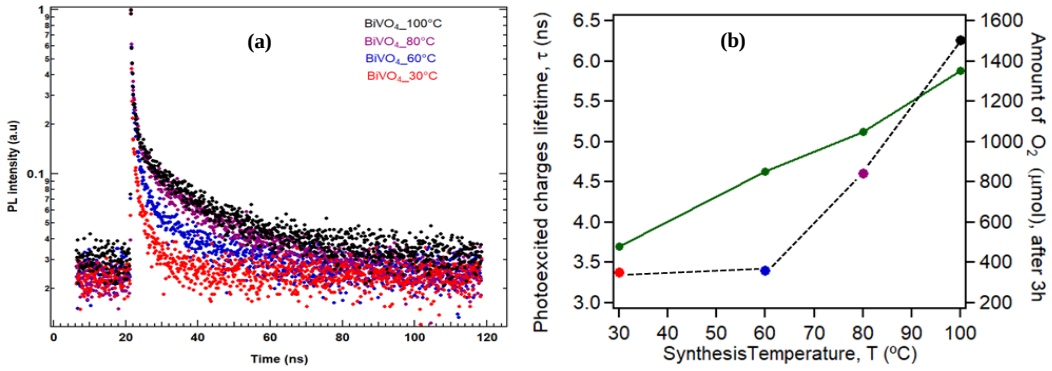

Fig.1 (a) TRPL signal from $BiVO_4$ samples synthesized at different temperatures 30, 60, 80 and 100°C, monitored at 750nm. (b) photoexcited charges lifetime, τ obtained by biexponential fitting of TRPL signals vs. synthesis temperatures (left) and amount of photocatalytically produced O_2 vs. synthesis temperatures (right)

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[2] Hosung Seo, Yuan Ping, and Giulia Galli, Chem. Mater. 2018, **30**, 7793