

## Structural and bandgap modification of KLaTiO<sub>4</sub> hydrogen evolution catalyst

Junwei Li, Brendan J. Kennedy, Chris D. Ling, Thomas Maschmeyer

School of Chemistry, The University of Sydney, Sydney, NSW Australia

Juli0440@uni.sydney.edu.au

Alternative fuel sources are needed to replace fossil fuels to reduce the emission of greenhouse gases contributing to global warming. Hydrogen gas is one popular choice to replace fossil fuels [1] as an energy storage medium, due to its high energy density per unit weight. Hydrogen can be generated renewably by sunlight driven, photocatalytic water-splitting. Metal oxides, including those with a Ruddlesden-Popper layered perovskite structures are being studied as potential photocatalysts [2]. The structure contains multiple cationic sites, which allows for different combinations of metal cations for tuning the bandgap. The layered structuring also allows for the intercalation of different cations within the structure that allows for modifications post synthesis, therefore further optimising the photocatalyst [3].

KLaTiO<sub>4</sub> is a n=1 Ruddlesden-Popper that can be used as a Hydrogen Evolution Catalyst (HEC), producing 9.540 μmol of H<sub>2</sub> gas per hour from 20 mg of catalyst, when using methanol as sacrificial electron donor and platinum co-catalyst, and illuminated by a Hg lamp with a 305 nm cut-off filter. The main disadvantage of KLaTiO<sub>4</sub> is its high bandgap (4.09 eV) that is above the visible light region, which makes it a poor choice for a HEC that uses solar energy. Reduction of the bandgap of KLaTiO<sub>4</sub> for sunlight driven hydrogen evolution was attempted by cationic and anionic doping. The crystal structures, and sample purity, was determined using synchrotron X-ray powder diffraction (PXRD) and Rietveld refinement.

Cationic doping of KLaTiO<sub>4</sub> was achieved by partially replacing lanthanum with praseodymium or ytterbium, yielding two solid solution series: KLa<sub>x</sub>Pr<sub>1-x</sub>TiO<sub>4</sub> and KLa<sub>x</sub>Yb<sub>1-x</sub>TiO<sub>4</sub> (x = 0.005, 0.01 and 0.03). While none of the samples from KLa<sub>x</sub>Pr<sub>1-x</sub>TiO<sub>4</sub> series produced hydrogen, all the KLa<sub>x</sub>Yb<sub>1-x</sub>TiO<sub>4</sub> were able to produce H<sub>2</sub>. In comparison to KLaTiO<sub>4</sub>, ytterbium-doped samples have reduced catalytic activity compared to KLaTiO<sub>4</sub>, as seen in figure 1.

Anionic doping of KLaTiO<sub>4</sub> was attempted with nitrogen. Attempts to synthesise KLaTiO<sub>3</sub>N were done by using TiN as a reagent in place of TiO<sub>2</sub> with annealing the sample under N<sub>2</sub> flow at 800 °C. PXRD patterns of initial samples show good crystallinity, and no observable structural difference to KLaTiO<sub>4</sub>. When tested as HEC in identical testing condition stated above all nitrogenated samples had similar rates of hydrogen evolution.

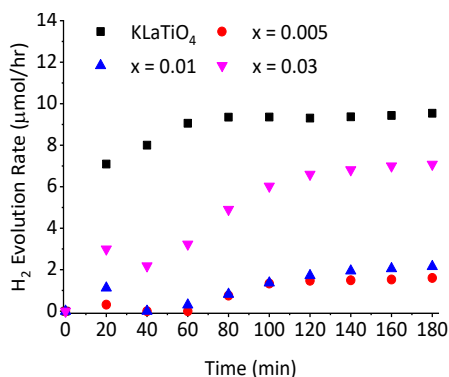


Figure 1. Hydrogen evolution rate of KLa<sub>x</sub>Yb<sub>1-x</sub>TiO<sub>4</sub> samples.

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