

**Adjusting Metal Oxide Photocatalysis using Organic-Inorganic Hybrid Films Obtained by
Molecular Layer Deposition
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Metal Oxides (MOs) are used for numerous applications including catalysis, sensing, photonics, optoelectronic devices, renewable energy, electrochemistry and more. MOs exhibit a unique combination of properties including their high chemical and physical stability, durability, rich surface reactivity, catalytic and photocatalytic functions. MO photocatalytic properties and performance is typically optimized by control over the crystalline phases, incorporation of impurities in the MO lattice, also commonly termed doping, formation of noble metal-MOs hybrids, and more. In particular, the photocatalytic performance of TiO₂ thin films is widely studied with well established understanding of the roles of grain size, phase composition (anatase vs. rutile), supporting substrate, and deposition conditions.

Recent studies highlight the importance of non-stoichiometric oxides for tuning and optimizing the reactivity and performances of MO catalysts. Specifically for MOs, oxygen vacancies (OVs) are important structural defect that alter the reactivity of MOs by introduction of new electronic states within the band gap (BG). In addition, OV often function as adsorption sites for Lewis acids and bases making them surface active sites for heterogeneous catalysis. OV design offers additional valuable handles for optimizing MO electronic structure further to control over the crystalline phase and impurity doping. One of the most widely studied MOs in the context of OV is non-stoichiometric Titania, with deviation from ideal oxide stoichiometry. The electronic structure, charge transport, and surface properties of TiO_{2-x} are closely related to the details of the defects and OV.

Here we demonstrate the use of hybrid organic-inorganic thin obtained by molecular layer deposition films for attaining oxygen-deficient Titania and tuning of the photocatalytic properties of the films. The decomposition of the organic components and formation of the carbon-rich oxide offers control over the resulting oxide electronic properties. Ti-EG films annealed at 650 °C exhibit superior reactivity for degradation of organic molecules while Ti-EG films annealed at 520 °C yield the direct photocatalytic production of hydrogen peroxide (H₂O₂).^{1,2} Both systems exhibit activities that are not typically attainable by Titania owing to the adjustable electronic structure of annealed Ti-EG films.

References

[1] Ishchuk et al, ACS Nano, 2012, (8), pp 7263–7269

[2] Kaynan et al, J Mat Chem A, 2014, (2), pp 13822-13826