Title:	Synthesis of manganse and cobalt based oxide nanomaterials for water oxidation
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Abstract:	Artificial photosynthesis is a promising method that directly transforms solar energy into chemical energy. To achieve artificial photosynthesis, efficient water oxidation catalysts (WOCs) are essential. RuO2 and IrO2 are known to be efficient catalysts for water oxidation. But they are very expensive and scarce. Hence, it is necessary to find an efficieient, inexpensive catalyst for this process. In nature, the manganese-oxo-calcium cluster (Mn4CaO5) in the oxygen-evolving center (OEC) of Photosystem II, catalyzes water oxidation. Inspired by this process, abundant and inexpensive manganese, cobalt oxides have been recognized for their high potential as effective and reliable materials for water oxidation reaction. However, these oxides catalysts still exhibit less water oxidation efficiency. In this thesis, we have developed two simple approaches to improve the water oxidation activity of manganese and cobalt based oxides. i) Tuning the valence of the active catalytic site and (ii) developing high surface area porous catalysts using a selective dissolution approach. The oxidation state of Mn has been tuned between +3 and +4 by synthesizing solid solutions of La1-xCaxMnO3 (x = 0, 0.1, 0.3, 0.5,0.7,0.9, 1). It has been observed that the gradual substitution of La+3 by Ca+2 leads to the significant enhancement of photochemical and electrochemical water oxidation activity of these solid solutions up to x= 0.5 and therefter the activity started decreasing. Substitution of trivalent La+3 with divalent Ca+2 introduces mixed-valence of Mn in the material and the ratio of Mn+3/Mn+4 playing a vital role in enhancing the water oxidation activity. Further, the CaMnO3 was treated with dilute HNO3 solution for selective dissolution of calcium ions from the structure to generate porous MnO2 nanomaterials. These nanomaterials were heated at different temperatures to get porous manganes oxide nanostructures with different crystal structure. They have surface area in the range of 106-272 m2/g and exhibit remarkable photochemical water oxidation activity with a maximum turnover frequency (TOF) of 3.29 x 10-3 s-1 and electrochemical activity showing 430mV overpotential at 10 mA/cm2 with the Tafel slope value of 133mV/dec. The porous MnO2 nanomaterials exhibit better current density compare to commercial RuO2. Further, NaCoO2 layered materials were synthesized by simple citrate-gel method. Sodium ions are extracted from this material by treating it with dilute HNO3 solution to get HCoO2 nanostructures. By extracting sodium ions from NaCoO2, the photochemical water oxidation turnover frequency has been improved from 0.9 x 10-3 s-1 to 2.90 x 10-3 s-1 and the electrochemical overpotential, Tafel slope for water oxidation decreases from 600 mV to 370 mV and 93 mV/dec to 47 mV/dec, respectively. These sodium ions extracted catalyst shown higher water oxidation activity than the commercial RuO2, which is frequently used as a benchmark for water oxidation. Our findings in this thesis demonstrate the development of inexpensive promising substitutes for the noble metal-based catalysts for the water oxidation reaction.
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