Abstract

Water oxidation is the bottleneck in artificial photosynthetic systems that aim to split water into hydrogen and oxygen. However, water oxidation occurs readily in plants, catalyzed by the Mn_4O_4Ca manganese cluster. In addition to this, manganese minerals are ubiquitous in nature displaying layered and tunnel structures. In this study, mixed valent porous amorphous manganese oxides (AMO), along with cryptomelane type tunnel manganese oxides (OMS-2) and layered birnessite (OL-1) have been used as water oxidation catalysts. Significantly higher turnovers were obtained with AMO (290 mmol O_2/mol Mn) compared to tunnel structure OMS-2 (110 mmol O_2/mol Mn) and layered structure OL-1 (27 mmol O_2/mol Mn) in water oxidation tests with Ce^{4+}. Oxygen evolution was also confirmed under photochemical conditions using $Ru(bpy)_3^{2+}$ as a photosensitizer and persulfate as a sacrificial agent. The differences in catalytic activity among these catalysts have been probed using X-ray diffraction, transmission electron microscopy, Raman and Fourier transform infrared (FTIR) spectroscopy, average oxidation state, and compositional analyses. Comparison of AMO against prominent manganese catalysts described in literature shows AMO provided the highest turnover numbers. AMO catalyst was also reusable after regeneration. O-18 labeling studies proved that water was the source of dioxygen and IR proved the structural stability of AMO after reaction. AMO is related to hexagonal birnessites such as layered biogenic manganese oxides or H^+-birnessite that have cation vacancies in the MnO_2 sheets rather than completely filled Mn^{3+}/Mn^{4+} sheets, and this is influential in catalytic activity.