

Ruthenium Polyoxometalate as Water Splitting Catalyst: Enhancement of Photochemical Water Oxidation in Presence of CAN

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Solar energy is the only renewable and carbon neutral source of energy to replace the fossil fuels.¹ The conversion of sunlight to other form of energy is a challenging task to the modern age. However nature provides a blue print for storing sunlight in the form of chemical fuels. The primary steps of natural photosynthesis involve the absorption of sunlight and its conversion into spatially separated electron/hole pairs. The holes are then captured by the oxygen evolving complex to oxidize water to oxygen and the electrons are captured by photosystem I to reduce the NADP⁺ to NADPH. Thus overall photosynthesis process store the solar energy by rearranging the chemical bonds of water to form oxygen.²

An approach to mimic the photosynthesis outside the plant cell is to split water molecules to produce oxygen within a photovoltaic cell. The net chemical reactions that occur in the electrodes are capturing of four holes by a catalyst at the anode end and four electrons at the cathode end to produce O₂ and H₂. Breakthroughs are needed in selectivity, speed and stability of the sensitizers that absorb sunlight and the catalysts that split water to O₂ and H₂.³⁻⁵

There are many research groups working on heterogeneous and homogeneous water oxidation catalyst (WOC).⁸ Recently Kanan and Nocera reported a robust heterogeneous WOC based on earth abundant cobalt and phosphate.⁶ Until now, the most promising catalytic systems have been based on Iridium oxide colloids.⁷

Water oxidation driven by a catalyst has been reported in two ways: excess addition of cerium ammonium nitrate (CAN) into the solution of highly acidic solution of catalyst leads to the evolution of oxygen and in other approach, light driven water oxidation by using [Ru(bpy)₃]²⁺ as a photosensitizer and S₂O₈²⁻ as an electron acceptor.

In this report, [Ru(bpy)₃]³⁺ is generated from [Ru(bpy)₃]²⁺ by photooxidation using S₂O₈²⁻ as a sacrificial electron acceptor. CAN is used as an initiator of the oxidation process. In particular one key parameter is the electron transfer rate between the photo generated [Ru(bpy)₃]³⁺ and the catalyst, leading to oxygen evolution. We report herein a di-γ-decatungstosilicate embedding a tetraruthenium(IV)-polyoxo complex as efficient catalyst for water oxidation. In this communication we report the tuning of light-harvesting process by using CAN. In a typical experiment, 40 mL of buffered (Na₂SiF₆-NaHCO₃ buffer) aqueous solution containing 1.5 × 10⁻⁴ M [Ru(bpy)₃]²⁺ with excess amount of

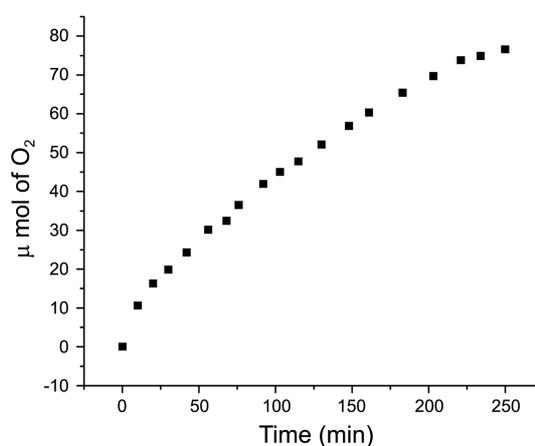
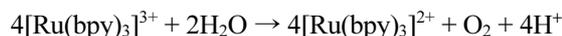


Figure 1. Gas chromatographic detection of oxygen evolved in the headspace of reactions containing Ru-POM and 60 mg of cerium ammonium nitrate.

Na₂S₂O₈ and Na₂SO₄ and variable amount of CAN (varying from 0-7.29 × 10⁻³ M) were excited with xenon lamp light source > 520 nm. 50 μL of gas sample drawn from the headspace was injected into a SRI 310 gas chromatograph equipped with a thermal conductivity detector (TCD) and a 13× packed molecular sieve column. The helium carrier gas flow rate was set at 20 mL/min at 40 psi. The column and TCD temperatures were 80 °C and 100 °C respectively with a hold time of 1 min.

The net reactions occur in the reaction vessel are:



Oxygen evolution in the CAN system was confirmed using gas chromatographic (GC) analyses of gaseous products collected in the headspace of the reaction mixture. There is an excellent observation for catalytic activity which sustain on an average of 300 minutes of photolysis.

UV Visible spectra show a broad absorption band at 451 nm before the photolysis. Red shift of 11 nm with a decrease in absorption coefficient indicates the degradation of the catalyst with time (Figure 2). An increase in fluorescence spectra also indicates the degradation after photolysis. However the catalyst is active up to 300 minutes of photolysis.

Oxygen evolution study was carried out with different

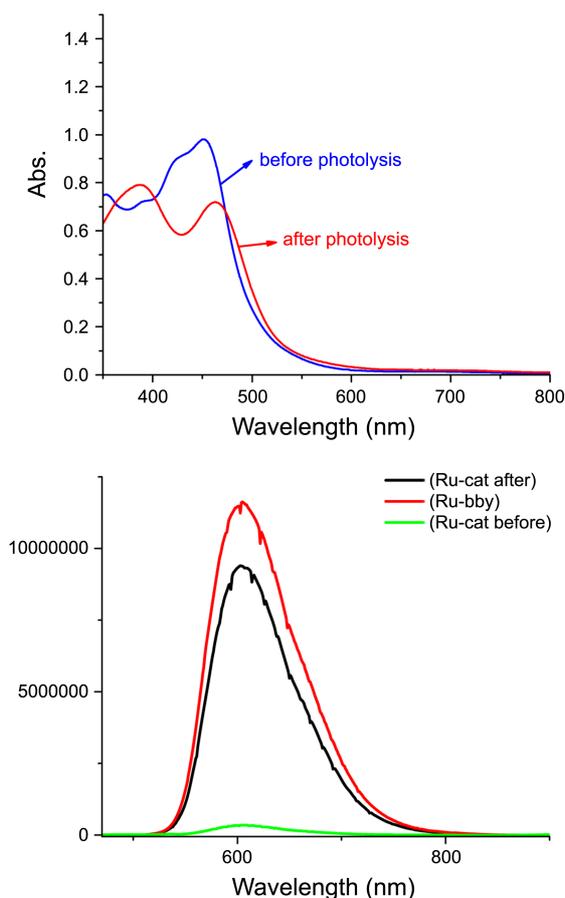


Figure 2. Absorption and emission spectra of Ru-POM before and after photolysis.

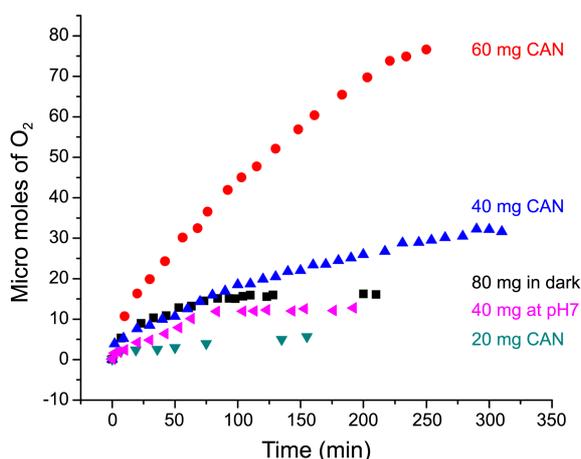


Figure 3. Gas chromatographic detection of oxygen evolved in the headspace of reactions containing Ru-POM with different amount of cerium ammonium nitrate.

concentration of CAN and it is revealed that using 9×10^{-4} M concentration of CAN no oxygen evolution can be identified whereas the maximum moles of oxygen can be collected using a 1.8×10^{-3} M of CAN. With increasing CAN concentration the rate of oxygen evolution increases as shown in Figure 3. After a certain concentration of CAN the dark reaction starts and little amount of oxygen can be observed

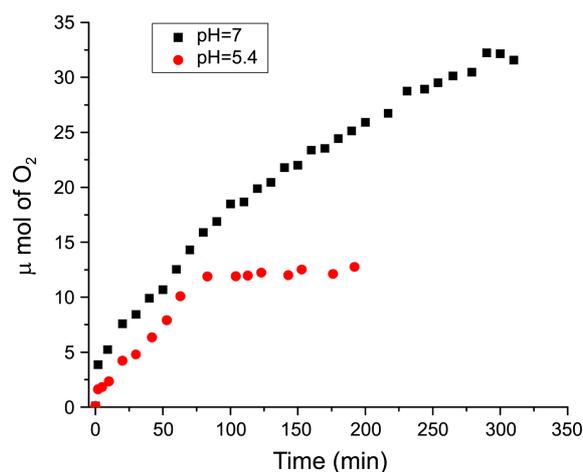


Figure 4. Gas chromatographic detection of oxygen evolved in the headspace of reactions containing Ru-POM at pH 5.4 and pH 6.7.

in the GC analysis.

Oxygen evolution experiment was carried out in different pH. Figure 4 shows that use of phosphate buffer which lowers pH of the system (pH 5.4) is relatively less efficient to that of the use of silicate buffer. The hydrogen, produced by the water splitting, is present in the solution as H^+ ion. That may decrease the pH of the solution. On the other hand the oxygen evolution process highly depends on the pH of the medium. At lower pH this process is hindered.

So we demonstrate that although there is an increase of H^+ ion concentration in the medium, silicate/phosphate buffer helps to maintain the pH constant which ultimately favours the oxygen evolution.

In conclusion, Ru-POM was studied as water oxidation catalysts. This catalyst was found to be highly active under chemical and photochemical water oxidation conditions in presence of cerium ammonium nitrate. Ru-POM catalyst could be regenerated after reaction. Most interestingly, this catalyst is active under light illumination for a time period over five hours. GC studies showed oxygen evolution is standardized at a considerable low acidic condition with a particular CAN concentration.

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