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# A Simple, Novel Method for Preparing an Effective Water Oxidation Catalyst

**Andrew Mills,* Paul A. Duckmanton and John Reglinski**

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**A novel oxygen catalyst is prepared via the photodeposition of ruthnium (IV) oxide on a titania photocatalyst derived from a perruthenate precursor.**

The splitting of water into hydrogen and oxygen has long been an attractive prospect as a route to generating a useful fuel. The ability to achieve this using sunlight is of particular interest as it is viewed as a truly renewable source of energy. A number of photocatalysts have been reported for UV driven water splitting[1]. However, for efficient solar energy to chemical energy conversion, *visible-light* photocatalysts need to be developed and these usually require the presence of effective $H_2$ and $O_2$ catalysts. One of the most promising catalysts for water oxidation is a partially dehydrated form of commercially available $RuO_2.xH_2O$.[2] Its degree of hydration has been found to be crucial for high catalyst activities, with optimal levels being ~14 wt%. This is achieved by thermally activating the commercial material ($RuO_2.xH_2O$, where $x$ is *ca.* 1.6) at 150°C for 2 h to produce $RuO_2.yH_2O$ (where $y$ is *ca.* 1.2; hereafter referred to as "$RuO_2$").[3] Higher levels of hydration produce catalysts that are susceptible to oxidative corrosion to $RuO_4$, whilst total dehydration to crystalline $RuO_2$ halts catalytic activity due to sintering and the associated significant drop in surface area.

A number of methods exist for the loading of "$RuO_2$" onto substrate surfaces. All involve either difficult to produce and handle starting materials (such as $RuO_4$), high temperature oxidations (which can completely dehydrate the $RuO_2$), or both.[4] As a result, these methods can introduce inconsistencies between loadings and give rise to poor quality and low activity catalysts.

Reductive or oxidative photodeposition is an ideal method for the loading of catalytic materials onto the surfaces of photocatalysts. To date, the range of metal oxides deposited in this way has been limited.[5] Recently the photodeposition of $MnO_2$ (from $MnO_4^-$) onto $TiO_2$ produced a material suitable for the catalytic decomposition of hydrogen peroxide.[6] Unfortunately, we have found this material exhibits little or no activity as a water oxidation catalyst. This study prompted us to investigate a simple photo-deposition method using the higher oxides of ruthenium as precursors. Thus, in a one-pot reaction, powdered $TiO_2$ (Degussa P25) was stirred in a aqueous solution of $KRuO_4$ and irradiated with a Xe or Hg arc lamp. $KRuO_4$ consumption was monitored via centrifugation of the sample followed by UV spectrophotometry of the supernatant solution. The results of this work are illustrated in figure 1 and show that the green $RuO_4^-$ ($\lambda_{max}$ = 315 and 385 nm) disappears with irradiation time. Concurrent with this change the titania becomes grey in colour, indicating the formation of $TiO_2/RuO_2$. The overall process is summarised in eqn (1). Similarly ruthenate, $RuO_4^{2-}$, is photoreduced by a titania photocatalyst to $RuO_2$. Finally, in the absence of the titania photocatalyst the reagents remain unchanged.

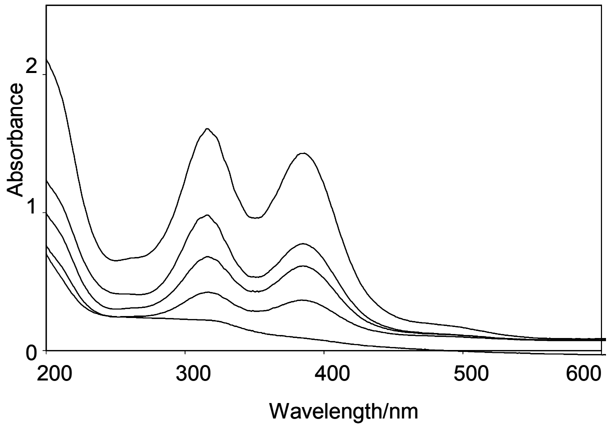

Figure 1: UV Spectra of an irradiated mixture of $KRuO_4$ solution and suspended $TiO_2$ powder. Spectra acquired (top to bottom) 0, 10, 40, 80 and 120 min.

$$4RuO_4^- + 4H^+ + 4TiO_2 \xrightarrow{h\nu} 4TiO_2/RuO_2 + 3O_2 + 2H_2O \quad (1)$$

After photodeposition, all $TiO_2/RuO_2$ catalysts were thermally activated (2h @ 150°C) to ensure high activity and oxidative corrosion stability. High resolution TEM images of the $TiO_2/RuO_2$ powder particles reveal the presence of small deposits (2-3 nm diameter) that are most likely ruthenium (IV) oxide particles very finely distributed over the surface of the titania. SEM-EDX indicates a level of ruthenium loading at ca. 0.5%/w for all samples.

Whilst much of the literature has focussed on the testing of such loaded semiconductor photocatalysts for the UV driven splitting of water, few have independently tested the oxygen catalyst activities of these materials.[7] Ce(IV) is an excellent benchmark test reagent of water oxidation catalyst materials, as it is sufficiently oxidising for the reaction to proceed readily and yet kinetically inert. In the presence of an oxygen catalyst Ce(IV) is able to facilitate the oxidation of water by acting as a sacrificial electron acceptor (eqn 2).

$$4Ce^{4+} + 2H_2O \xrightarrow{O_2\,\text{catalyst}} 4Ce^{3+} + 4H^+ + O_2 \qquad (2)$$

During the reaction (eqn 2) it is possible to monitor the

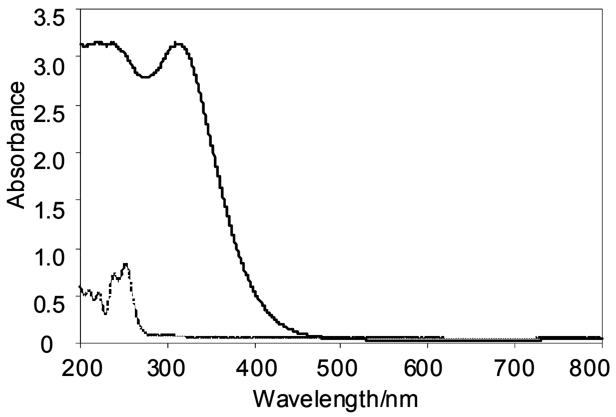

**Figure 2**: UV Spectrum of solution of Ce(IV) ($10^{-3}$ M) in 1 M $HClO_4$ before (solid line) and after (broken line) 1 min of mixing with the $TiO_2/RuO_2$ (1 wt%) catalyst

consumption of Ce(IV) both visually and with UV spectrophotometry (figure 2). Thus, when used to test the photodeposited $TiO_2/RuO_2$ catalyst, the yellow solution produced upon injection of the Ce(IV) decolourises as the Ce(IV) is reduced to Ce(III). Whilst this demonstrates the consumption of Ce(IV), it gives no direct information regarding the generation of oxygen, although bubbles can be seen.

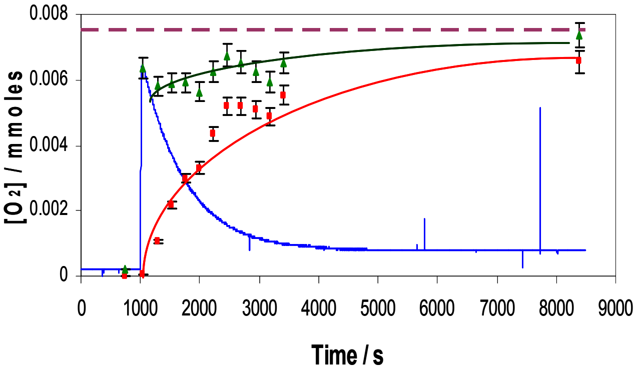

**Figure 3**: Solution (line), gas phase (●) and total-system (▲) oxygen concentrations for addition of 300 μL 0.1 M $Ce(SO_4)_2$ into a suspension of 1% loaded $RuO_2$ on $TiO_2$, heat treated at 150°C (30 mg) in 30 mL 1 M $HClO_4$ (30 mL). Expected oxygen level if 100% stoichiometric is 7.5 μmol (dashed line).

In order to demonstrate the stoichiometric generation of oxygen via eqn (2) by the $TiO_2/RuO_2$ catalyst, $O_2$ evolution in the solution was followed using a Clark-type electrode (Rank Brothers), and simultaneously the variation in oxygen level in the gas phase was monitored by gas chromatography. The results of this work are illustrated in figure 3 and show that after the initial catalytic reaction and the associated increase in dissolved oxygen, this concentration decreases with a concommitant increase in oxygen in the gas phase. Near stoiciometiric amounts (97%) of the expected oxygen level (7.5 μmol) were observed after 2 h.

The stability of the $TiO_2/RuO_2$ catalyst was demonstrated via a series of repeated purge and injection cycles, at a catalyst concentration of 0.1 wt%. It was shown that there was little appreciable decrease in catalytic rate with repeated (5 cycles) innoculation with Ce(IV). This is in contrast to results for non-heat-treated $TiO_2/RuO_2$, where a marked decrease in catalytic activity was observed upon repeated injection.[8] Furthermore, the catalytic rate was found to be proportional to catalyst concentration, as expected for a surface-catalysed reaction.

A comparison of the photodeposited $TiO_2/RuO_2$ catalyst with catalysts prepared by two alternate loading methods (e.g. decomposition of $RuO_4$ onto $TiO_2$ followed by heat treatment at 150°C, and incipient wetness of $RuCl_3.2H_2O$ onto $TiO_2$ followed by thermal oxidation at 500°C in air showed both had inferior activities.

Other semiconductor supports were also found to be suitable for photodeposition. One of note is Kronos VLP 7001 (N-doped titania), which, when used in the UV-light driven oxidation of water alone using 0.01 M $Na_2S_2O_8$ in 0.1 M NaOH as the sacrificial electron acceptor, displays no catalytic activity. Once loaded with "$RuO_2$" however, a marked ability for water-oxidation is observed.

In summary, photodeposition of $RuO_2.xH_2O$ from $KRuO_4$ is a simple method for loading a highly active, finely divided form of ruthenium (IV) oxide onto a semiconductor photocatalyst, such as $TiO_2$. Acommercially available visible light photocatalyst has shown an increase in rate for UV light driven water oxidation upon loading with a photodeposited $RuO_2$ oxygen catalyst. This method should prove useful in preparing further visible light driven water-splitting systems.

## Notes and references

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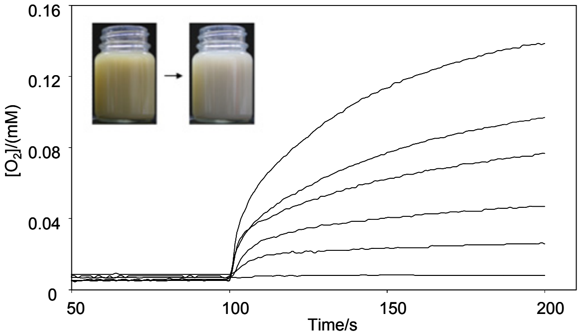

A novel oxygen catalyst ($TiO_2/RuO_2$) is prepared via the photodeposition of ruthnium(IV) oxide on a titania photocatalyst derived from perruthenate. The figure shows the rate of oxygen evolution as a function of catalyst concentrations (0-67 mg/L). The inset shows the colour change (yellow/colourless) which arises from the consumption of the sacrificial oxidant $Ce(SO_4)_2$.