A simple, novel method for preparing an effective water oxidation catalyst

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A novel oxygen catalyst is prepared *via* the photodeposition of ruthenium(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 $RuO_2{\cdot}xH_2O$.[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 ($RuO_2{\cdot}xH_2O$, where x is *ca.* 1.6) at 150 °C for 2 h to produce $RuO_2{\cdot}yH_2O$ (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 photodeposition method using the higher oxides of ruthenium as precursors. Thus, in a one-pot reaction, powdered TiO_2 (Degussa P25) was stirred in an 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 Fig. 1 and show that the green RuO_4^- (λ_{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.

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

After photodeposition, all TiO_2/RuO_2 catalysts were thermally activated (2 h at 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 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)).

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

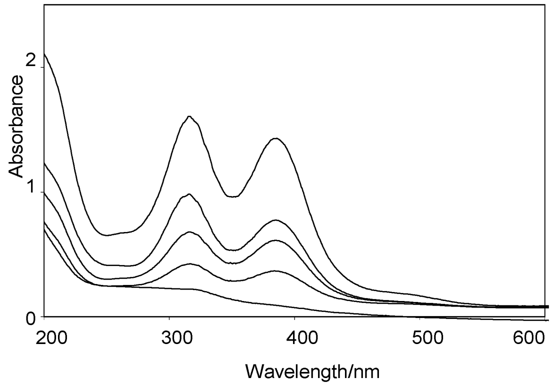

Fig. 1 UV spectra of an irradiated mixture of $KRuO_4$ solution and suspended TiO_2 powder. Spectra acquired (top to bottom) 0, 10, 40, 80 and 120 min.

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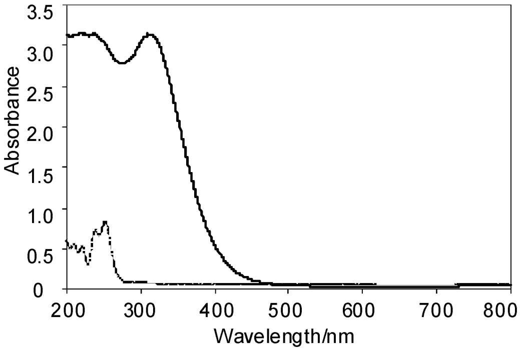

Fig. 2 UV spectrum of a solution of Ce(IV) (10^{-3} M) in 1 M $HClO_4$ before (solid line) and after (broken line) 1 min of mixing with the TiO_2/RuO_2 (1 wt%) catalyst.

During the reaction (eqn (2)) it is possible to monitor the consumption of Ce(IV) both visually and with UV spectrophotometry (Fig. 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.

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 Fig. 3 and show that after the initial catalytic reaction and the associated increase in dissolved oxygen, this concentration decreases with a concomitant increase in oxygen in the gas phase. Near stoichiometric 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) inoculation with Ce(IV). Thus, in this experiment 2.26×10^{-6} moles of RuO_2 were able to catalyse the oxidation of water by 1.5×10^{-4} moles of Ce(IV) without showing any loss of activity, *i.e.* the turn-over number of the RuO_2–TiO_2 catalyst with respect to Ce(IV) is $\gg 66$. 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.

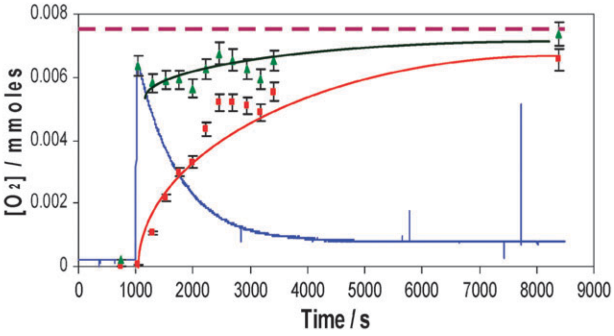

Fig. 3 Solution (line), gas phase (■) and total-system (▲) oxygen concentrations for the addition of 300 μL 0.1 M $Ce(SO_4)_2$ into a suspension of 1% loaded RuO_2 on TiO_2, heat treated at 150 °C (30 mg) in 30 mL 1 M $HClO_4$ (30 mL). Expected oxygen level if 100% stoichiometric is 7.5 μmol (dashed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

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 $RuCl_3{\cdot}2H_2O$ 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 photocatalytic activity. Once loaded with "RuO_2", however, a marked ability for water photo-oxidation is observed in what are otherwise identical test conditions.

In summary, photodeposition of $RuO_2{\cdot}xH_2O$ 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. A commercially 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

1 H. Kato, K. Asakura and A. Kudo, *J. Am. Chem. Soc.*, 2003, **125**, 3082–3089; J. Kim, D. W. Hwang, H. G. Kim, S. W. Bae, J. S. Lee, W. Li and S. H. Oh, *Top. Catal.*, 2005, **35**, 295–303; H. Kato and A. Kudo, *J. Phys. Chem. B*, 2001, **105**, 4285–4292; H. G. Kim, D. W. Hwang, J. Kim, Y. G. Kim and J. S. Lee, *Chem. Commun.*, 1999, 1077–1078; H. Kato and A. Kudo, *Chem. Phys. Lett.*, 1998, **295**, 487–492.
2 A. Mills, C. Lawrence and R. Enos, *J. Chem. Soc., Chem. Commun.*, 1984, 1436–1438; A. Mills and N. McMurray, *J. Chem. Soc., Faraday Trans. 1*, 1988, **84**, 379–390.
3 A. Mills and S. Giddings, *Inorg. Chim. Acta*, 1989, **158**, 49–57.
4 Y. Yamashita, M. Tada, M. Kakihana, M. Osada and K. Yoshida, *J. Mater. Chem.*, 2002, **12**, 1782–1786; T. Kawai and T. Sakata, *J. Chem. Soc., Chem. Commun.*, 1979, 1047–1048; D. Duonghong, E. Borgarello and M. Grätzel, *J. Am. Chem. Soc.*, 1981, **103**, 4685–4690; K. Tanaka, S. Murata and K. Harada, *Sol. Energy*, 1985, **34**, 303–308; K. Sayama and H. Arakawa, *Chem. Lett.*, 1992, 253–256; J. Sato, N. Saito, H. Nishiyama and Y. Inoue, *J. Phys. Chem. B*, 2001, **105**, 6061–6063; P. B. Amama, K. Itoh and M. Murabayashi, *J. Mater. Sci.*, 2004, **39**, 4349–4351.
5 J. W. M. Jacobs, F. W. H. Kampers, J. M. G. Rikken, C. W. T. Bulle-Lieuwma and D. C. Koningsberger, *J. Electrochem. Soc.*, 1989, **136**, 2914–2923; W.-Y. Lin, C. Wei and K. Rajeshwar, *J. Electrochem. Soc.*, 1993, **140**, 2477–2482; Y. Tak and K. Yong, *J. Phys. Chem. C*, 2008, **112**, 74–79.
6 N. Nishimura, J. Taniwaka, M. Fujii, T. Kawahara, J. Ino, T. Akita, T. Fujino and H. Tada, *Chem. Commun.*, 2008, 3564–3566.
7 C. Minero, E. Lorezi, E. Paramauro and E. Pelizzetti, *Inorg. Chim. Acta*, 1984, **91**, 301–305.
8 A. Mills and S. Giddings, *Inorg. Chim. Acta*, 1989, **158**, 49–57; H. N. McMurray, *J. Mater. Chem.*, 1994, **4**, 1283–1287.