Water Splitting

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Highly Efficient Oxidation of Water by a Molecular Catalyst Immobilized on Carbon Nanotubes**

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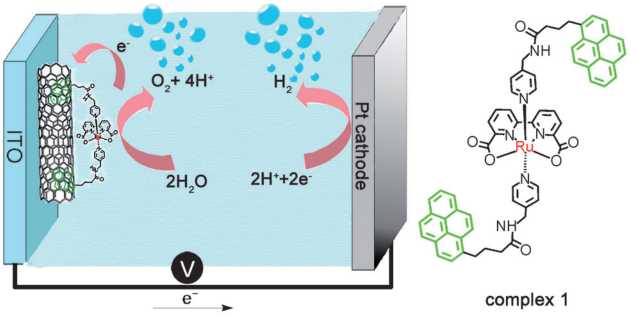
The oxidation of water is of great importance for artificial photosynthetic systems that capture and store solar energy as renewable and sustainable fuel.[1,2] To closely mimic the function of the Mn_4CaO_5 cluster, which is at the heart of photosystem II,[3] intensive research effort has been devoted to the development of catalysts for the oxidation of water.[4,5] In addition to metal oxides, homogeneous molecular catalysts have attracted considerable attention in recent years, mainly because of their tunable structures and rapid oxygen evolution reletive to that observed for heterogeneous catalysts. Among these catalysts, ruthenium complexes have been most successfully used. A few monomeric and polymeric ruthenium catalysts have shown remarkable activities up to thousands of turnover numbers (TONs) for the chemically driven oxidation of water by $Ce(NH_4)_2(NO_3)_6$ (Ce^{IV}) as sacrificial oxidant.[6–9] However, in view of their application as devices for water splitting it is essential to immobilize homogeneous catalysts on surfaces of heterogeneous electrodes without losing their reactivity and stability.[10–17] Therefore, proper methods for combining solid conductors/semiconductors and suitable transition-metal complexes should be developed to efficiently drive the oxidation of water at a minimum overpotential and under ambient conditions.

Along these lines, polypyridyl ruthenium catalysts[10–13] as well as inorganic molecular catalysts[14–16] have been anchored on metal oxide electrode surfaces, which successfully supports the solution reactivity of the catalysts at the solid–solution hybrid interface. Nevertheless, a large-scale implementation of catalyst-modified electrodes is impeded by high overpotentials and low catalytic current densities for water splitting.[18]

The novel monomeric Ru(bpa)(pic)$_2$ (2,2-bipyridine-6,6-dicarboxylic acid, H$_2$bpa; 4-picoline, pic) has been confirmed to be a highly active catalyst and show favorable electrochemical properties with an overpotential as low as 160 mV at neutral pH.[19,20] These observations let to the idea of using this catalyst in artificial photosynthesis systems which are independent of sacrificial chemical oxidants. In this regard, we have shown that the reactivity of this complex can be extended to visible light-driven water oxidation in solution[20] and even at a Nafion-coated photoanode.[21] To improve the surface reactivity of this robust catalyst, we show here that a derivative of Ru(bpa)(pic)$_2$, complex **1** shows a remarkable electrocatalytic performance for the oxidation of water at an electrode (Scheme 1). Multiwalled carbon nanotubes (MWCNTs) were coated on an ITO glass electrode as a solid support possessing excellent chemical stability and outstanding electronic and mechanical properties. The integration of monomeric ruthenium catalyst with MWCNTs was realized by noncovalent π–π stacking interactions. This method has been shown to be a highly convenient approach to molecular engineered hybrid materials.[22] Our research results indicate remarkable properties of the new anodes as advanced electrocatalytic nanomaterials.



Scheme 1. Electrochemical cell for water splitting and structure of the molecular catalyst **1**.

The MWCNT-modified ITO electrode was prepared by electrophoretic deposition of acid-treated MWCNTs onto ITO glass according to a reported procedure.[23] The electrode fabrication proceeded in the presence of magnesium salt so that a compact CNT film on the substrate was obtained. To facilitate the adsorption of the catalyst on the CNT sidewalls,

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complex **1** was designed and prepared by attaching pendant pyrene moieties to axial pyridine ligands (Scheme 1). At the first step, pyridine-bearing pyrene was synthesized by condensation of pyerenbutyric acid with aminomethylpyridine (see Scheme S1 in the Supporting Information). Second, this ligand was heated at reflux with a solvent-ligated complex Ru(bpa)(DMSO)$_2$ to yield the crude product of complex **1**, which was purified by column chromatography on silica gel. This two-step synthetic route was found to be a much cleaner and simpler approach relative to a previous method by which Ru(DMSO)$_4$Cl$_2$ directly reacts with the equatorial ligand and the axial ligand in an one-pot reaction.[19] Complex **1** was fully characterized by NMR spectroscopy and high-resolution mass spectrometry (see Figure S2–S5 in the Supporting Information). The UV/Vis spectrum of complex **1** in methanol shows metal-to-ligand charge transfer (MLCT) transition bands at 400 (shoulder) and 500 nm (shoulder) and strong π–π* transition absorptions originated from pyrene moieties between 200 to 350 nm (see Figure S6 in the Supporting Information). The immobilization of the catalyst was achieved by soaking the MWCNT-modified electrode in a stock solution of complex **1** in methanol overnight. The surface coverage of the electroactive catalyst molecules on the electrode was about $(2\pm0.5)\times10^{-9}$ mol cm^{-2} as estimated from cyclic voltammograms (CVs) according to Faraday's law.[10–12]

Scanning electron microscopy (SEM) images (Figure 1 and Figure S7 in the Supporting Information) reveal the disordered porous feature of CNT films composed of intertwined and stacked nanotubes. The large surface area of the CNTs was thus expected to enhance the adsorption of the catalyst moelcules on the electrode. As expected, energy dispersive X-ray spectroscopy (EDX) as a tool for elemental distribution verified the presence of ruthenium on this hybrid electrode (see Figure S8 in the Supporting Information). Except for ruthenium, a certain amount of magnesium was also detected as a consequence of the electrodeposition of magnesium-adsorbed MWCNTs.

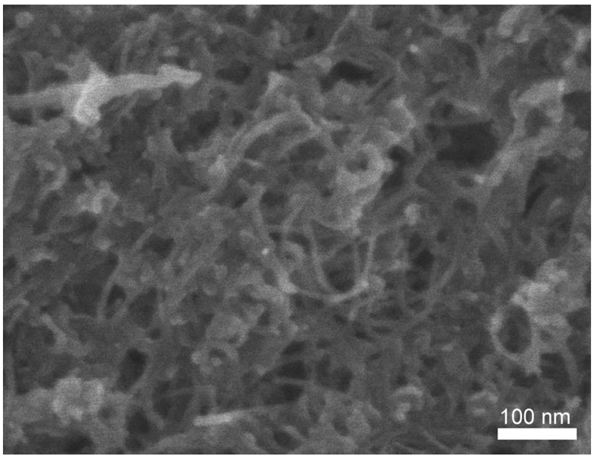

Figure 1. SEM image of the MWCNTs/ITO electrode functionalized by complex **1**.

The surface electronic behavior of **1** on the MWCNT-modified electrode was investigated by cyclic voltammetry. As shown in Figure 2a, at pH 7, two quasi-reversible redox couples of Ru^{II}/Ru^{III} and Ru^{III}/Ru^{IV} are observed at 0.59 and 0.91 V, respectively (all potentials are reported versus the normal hydrogen electrode = NHE). By contrast, only one pair of cyclic voltammetric waves ascribed to Ru^{II}/Ru^{III} was observed in an homogeneous aqueous methanol solution of **1** (see Figure S9 in the Supporting Information, a methanol-containing solution was used due to the poor solubility of **1** in water). The onset of a prominent water oxidation wave occurs at 1.15 V at an overpotential of only 300 mV which reflects the solution behavior for which the catalytic wave was found at 1.2 V (see Figure S9 in the Supporting Information). This onset value agrees well with that of the polyoxometalate ruthenium (0.3 V)[14] catalyst and is lower than those of cobalt

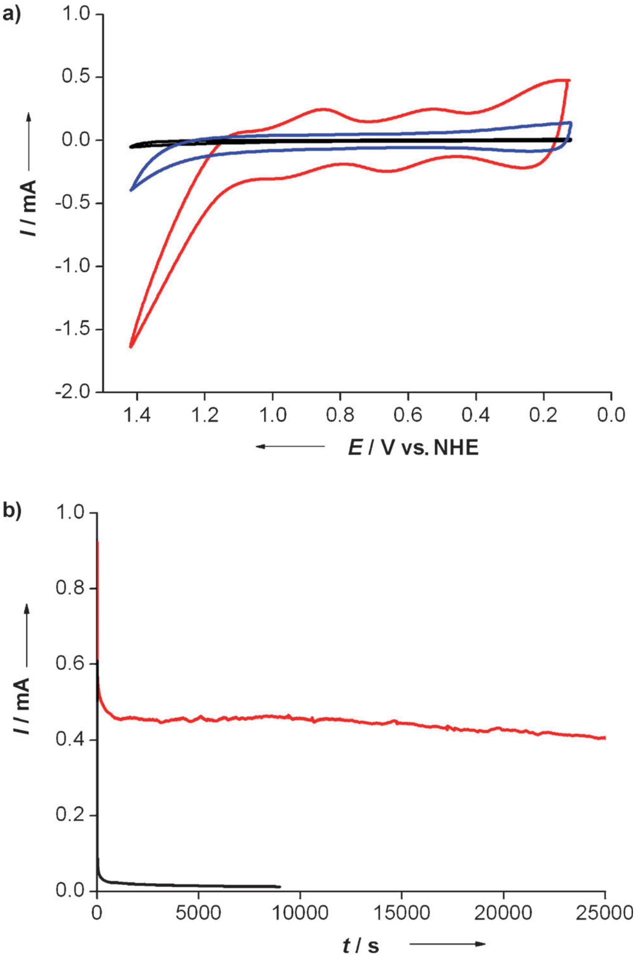

Figure 2. Electrochemical properties of the hybrid electrodes. a) Cyclic voltammograms of the bare ITO substrate (black trace), MWNTs deposited onto an ITO electrode (blue trace) and MWCNT/ITO electrode functionalized by complex **1** (red trace) in 0.1 M aqueous Na$_2$SO$_4$ solutions and at a scan rate of 0.1 V s^{-1}. b) Electrolysis of the bare MWCNT/ITO electrode (black trace) and the MWCNT/ITO electrode functionalized by complex **1** (red trace, density of complex **1**: $\Gamma\approx1.8\times10^{-9}$ mol cm^{-2}, active electrode area: $A\approx2$ cm^2) at 1.4 V (vs. NHE) in 0.1 M Na$_2$SO$_4$ electrolyte at pH 7.

phosphate (Co-Pi, 0.4 V)[24] and cobalt corrole (0.6 V)[25] catalysts, confirming that **1** is one of the most powerful catalysts for the oxidation of water. Under the same conditions, bare ITO or MWCNTs/ITO electrodes without catalyst show no activity for the oxidation of water within the range of CV measurements (Figure 2 a).

The electrolysis was carried out in neutral aqueous solution containing 0.1 M sodium sulfate in a three-electrode cell equipped with a MWCNTs/ITO working electrode functionalized by complex **1**, a Pt mesh as counter electrode, and a Ag/AgCl reference electrode. By gradually elevating the applied potentials, an appreciable catalytic current appears at an overpotential η of 0.28 V. This result agrees with the observations of CV analysis and implicates that relatively low overpotential is needed in bulk electrolysis. The activity of this functionalized electrode was further investigated by setting a constant applied potential at 1.4 V. Under these conditions, both oxygen and hydrogen bubbles were immediately released from the working electrode and the counter electrode, respectively. Meanwhile, a sustained current as high as 450 μA was obtained, corresponding to a current density of 220 $\mu A\,cm^{-2}$ (Figure 2 b). By contrast, the MWCNTs/ITO electrode without catalyst decoration is essentially inert under identical conditions (Figure 2 b). The long-term electrolysis over 10 h gave a total TON of 11 000 cycles accounting for an average turnover frequency (TOF) of about 0.3 s^{-1} (see Figure S10 in the Supporting Information). During this process, the catalytic current slightly dropped to 350 μA, which was assumed to be caused by partial desorption of CNTs from ITO glass substrate.

The molecular nature of the catalytically active species were identified by CVs, which show an identical redox behavior before and after different periods of electrolysis (see Figure S11 in the Supporting Information). Loss of catalyst from the electrode surface was quantified by integration of redox waves and was found to be in accordance with the decrease of catalytic current over the same period of time.

The Tafel plot (see Figure 3 and Figure S12 in the Supporting Information) displays a linear dependence of the logarithm of current density (based on the first 300 s of electrolysis) as well as of the TOF value on the overpotential up to 0.45 V at pH 7. The Tafel slope is 160 mV per decade, which is between those shown by Co-Pi (59 mV per decade)[24] and polyoxometalate-ruthenium-modified electrodes (280 mV per decade).[14] When the overpotential varied from 0.3 to 0.8 V, the corresponding TOFs were 0.03–0.84 s^{-1}. Comparisons with previously described anodes that incorporated catalysts by acidic binding to metal oxide nanoparticles,[10–12] Nafion film doping[15,21] or electrostatic interactions with CNTs decorated by polyamidoamine ammonium dendrimers,[14] evidenced the superior electrocatalytic capability of the new materials. For example, TOF values of 0.01–0.09 s^{-1} have been reported for inorganic polyoxometalate ruthenium complex at CNT-based electrodes in neutral electrolytes at $\eta = 0.35$–0.6 V.[14] At the same overpotential scale, TOF values in the range 0.07–0.48 s^{-1} equal to a five- to seven-fold enhancement on the efficiency of the catalysts were observed when MWCNTs/ITO electrodes functionalized by **1** were used. Recently, a high TOF of 0.6 s^{-1} was reported for a supramolecular ruthenium assembly bound electrode in acidic solution at 1.8 V.[12] In comparison, as our electrodes work under neutral conditions, only an applied potential of 1.5 V was required to oxidize water with a similar TOF. In a separate experiment, the oxygen evolved by electrolysis at 1.4 V was monitored online by a fluorescence-based oxygen sensor fixed in the headspace of a gas-tight cell and calibrated by gas chromatography (see Figure S13 in the Supporting Information). The amount of produced oxygen was detected to be 46.9 μmol, which matched well the charge of 18.8 C passed during electrolysis, corresponding to a nearly quantitative Faradaic efficiency of 96 % (see Figure S14 in the Supporting Information).

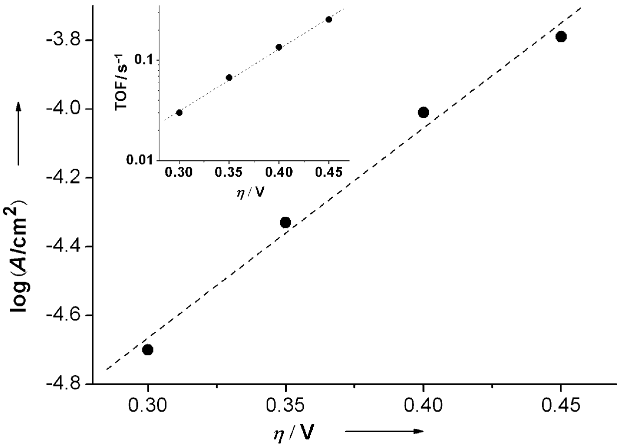

Figure 3. Dependence of the current density on the overpotential in an aqueous 0.1 M Na_2SO_4 solution at pH 7. The inset shows the dependence of the turnover frequency (TOF) on the overpotential under the same conditions.

Electrolysis by using NaCl as the electrolyte was also investigated to get insight into the adaptability of the functionalized electrodes. A sustained high current up to 600 μA was attained at 1.4 V (see Figure S15 in the Supporting Information), which is even better than that obtained using Na_2SO_4 electrolyte (450 μA). Hypochlorite titration[26] confirmed that there was no chlorine produced during electrolysis at 1.4 V and the electrode worked well at a potential (1.3 V) lower than the standard oxidation potential for chloride ions (see Figure S15 in the Supporting Information). Thus, the new electrodes possess the merit of using sea water as fuel similar to the Co-Pi electrode reported by Nocera and co-workers,[24,26] but in our case, a buffered electrolyte is not necessary to maintain the high activity.

In summary, we have successfully immobilized a molecular catalyst for the oxidation of water (complex **1**) on an ITO electrode by taking advantage of MWCNTs as an ideal platform for loading the catalyst and a medium for fast electron and hole transfer. We also created a molecular device for water splitting with low overpotential. Through this strategy, the molecular nature of the catalyst was retained at a heterogeneous surface, leading to a remarkable efficiency of water oxidation at a relatively low applied potential in non-buffered neutral aqueous solution. To the best of our knowledge, complex **1** is the most efficient molecular catalyst that has been used for the electrocatalytic oxidation of water. The highly convenient π–π stacking approach for functionalization of the electrode and the high tunability of the molecular catalyst are of considerable importance for the development of optimized nanomaterial-based oxygen-evolving anodes that meet the requests of operating electrochemical and photoelectrochemical cells for water splitting.

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[1] L. Hammarström, S. Hammes-Schiffer, *Acc. Chem. Res.* **2009**, *42*, 1859–1860.
[2] N. S. Lewis, D. G. Nocera, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 15729–15735.
[3] Y. Umena, K. Kawakami, J.-R. Shen, N. Kamiya, *Nature* **2011**, *473*, 55–60.
[4] P. D. Tran, V. Artero, M. Fontecave, *Energy Environ. Sci.* **2010**, *3*, 727–747.
[5] H. Dau, C. Limberg, T. Reie, M. Risch, S. Roggan, P. Strasser, *ChemCatChem* **2010**, *2*, 724–761.
[6] X. Sala, I. Romero, M. Rodriguez, L. Escriche, A. Llobet, *Angew. Chem.* **2009**, *121*, 2882–2893; *Angew. Chem. Int. Ed.* **2009**, *48*, 2842–2852.
[7] S. Romain, L. Vigara, A. Llobet, *Acc. Chem. Res.* **2009**, *42*, 1944–1953.
[8] J. J. Concepcion, J. W. Jurss, M. K. Brennaman, P. G. Hoertz, A. O. T. Patrocinio, N. Y. M. Iha, J. L. Templeton, T. J. Meyer, *Acc. Chem. Res.* **2009**, *42*, 1954–1965.
[9] I. Romero, M. Rodríguez, C. Sens, J. Mola, M. R. Kollipara, L. Francàs, E. Mas-Marza, L. Escriche, A. Llobet, *Inorg. Chem.* **2008**, *47*, 1824–1834.
[10] F. Liu, T. Cardolaccia, B. J. Hornstein, J. R. Schoonover, T. J. Meyer, *J. Am. Chem. Soc.* **2007**, *129*, 2446–2447.
[11] Z. Chen, J. J. Concepcion, J. W. Jurss, T. J. Meyer, *J. Am. Chem. Soc.* **2009**, *131*, 15580–15581.
[12] J. J. Concepcion, J. W. Jurss, P. G. Hoertz, T. J. Meyer, *Angew. Chem.* **2009**, *121*, 9637–9640; *Angew. Chem. Int. Ed.* **2009**, *48*, 9473–9476.
[13] J. Mola, E. Mas-Marza, X. Sala, I. Romero, M. Rodríguez, C. Viñas, T. Parella, A. Llobet, *Angew. Chem.* **2008**, *120*, 5914–5916; *Angew. Chem. Int. Ed.* **2008**, *47*, 5830–5832.
[14] F. M. Toma, A. Sartorel, M. Iurlo, M. Carraro, P. Parisse, C. Maccato, S. Rapino, B. R. Gonzalez, H. Amenitsch, T. D. Ros, L. Casalis, A. Goldoni, M. Marcaccio, G. Scorrano, G. Scoles, F. Paolucci, M. Prato, M. Bonchio, *Nat. Chem.* **2010**, *2*, 826–831.
[15] R. Brimblecombe, G. F. Swiegers, G. C. Dismukes, L. Spiccia, *Angew. Chem.* **2008**, *120*, 7445–7448; *Angew. Chem. Int. Ed.* **2008**, *47*, 7335–7338.
[16] R. Brimblecombe, A. Koo, G. C. Dismukes, G. F. Swiegers, L. Spiccia, *J. Am. Chem. Soc.* **2010**, *132*, 2892–2894.
[17] C. Herrero, A. Quaranta, W. Leibl, A. W. Rutherford, A. Aukauloo, *Energy Environ. Sci.* **2011**, *4*, 2353–2365.
[18] D. G. Nocera, *ChemSusChem* **2009**, *2*, 387–390.
[19] L. Duan, A. Fischer, Y. Xu, L. Sun, *J. Am. Chem. Soc.* **2009**, *131*, 10397–10399.
[20] L. Duan, Y. Xu, P. Zhang, M. Wang, L. Sun, *Inorg. Chem.* **2010**, *49*, 209–215.
[21] L. Li, L. Duan, Y. Xu, M. Gorlov, A. Hagfelt, L. Sun, *Chem. Commun.* **2010**, *46*, 7303–7309.
[22] P. D. Tran, A. Le Goff, J. Heidkamp, B. Jousselme, N. Guillet, S. Palacin, H. Dau, M. Fontecave, V. Artero, *Angew. Chem.* **2011**, *123*, 1407–1410; *Angew. Chem. Int. Ed.* **2011**, *50*, 1371–1374.
[23] Z. S. Wu, S. F. Pei, W. C. Ren, D. M. Tang, L. B. Gao, B. L. Liu, C. Liu, H. M. Cheng, *Adv. Mater.* **2009**, *21*, 1756–1760.
[24] M. W. Kanan, D. G. Norcera, *Science* **2008**, *321*, 1072–1075.
[25] D. K. Dogutan, R. McGuire, Jr., D. J. Nocera, *J. Am. Chem. Soc.* **2011**, *133*, 9178–9180.
[26] Y. Surendranath, M. Dincă, D. G. Nocera, *J. Am. Chem. Soc.* **2009**, *131*, 2615–2620.