Control over Electrochemical Water Oxidation Catalysis by Preorganization of Molecular Ruthenium Catalysts in Self-Assembled Nanospheres


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Abstract: Oxygen formation through water oxidation catalysis is a key reaction in the context of fuel generation from renewable energies. The number of homogeneous catalysts that catalyze water oxidation at high rate with low overpotential is limited. Ruthenium complexes can be particularly active, especially if they facilitate a dinuclear pathway for oxygen bond formation step. A supramolecular encapsulation strategy is reported that involves preorganization of dilute solutions (10^{-3} M) of ruthenium complexes to yield high local catalyst concentrations (up to 0.54 M). The preorganization strategy enhances the water oxidation rate by two-orders of magnitude to 125 s^{-1}, as it facilitates the diffusion-controlled rate-limiting dinuclear coupling step. Moreover, it modulates reaction rates, enabling comprehensive elucidation of electrocatalytic reaction mechanisms.

Renewable fuel generation is of crucial importance for the energy transition required for a sustainable society.[1] In that context, water splitting is considered a “holy grail” for the production of hydrogen as a useful fuel.[1,2] As water oxidation involves two water molecules and multiple proton/electron transfers steps (2H_2O→O_2 + 4H^+ + 4e^-), it is a mechanistically complex half-reaction.[2] Finding suitable catalysts that engender rapid catalysis at low overpotentials is indeed challenging.[3] In the past decades, molecular water oxidation catalysts (WOCs) based on various transition metals (Ru, Ir, Cu, Fe, and Ni) have been reported.[2–4] These catalysts operate via the water nucleophilic attack (WNA) mechanism, or coupling of two metal–oxyl radicals (I2M).[5,6] A survey of the WOCs reported to date reveals those that proceed via the I2M mechanism are usually capable of reaching high rates at lower overpotential,[5,6] although the highest rate has been reported for WOCs that follow WNA.[7] The I2M mechanism requires sufficient concentration of the radical-oxo intermediate to allow the coupling step to proceed in a binuclear fashion.[3] Ruthenium-based WOCs are excellent in terms of activity, overpotential, and stability.[6] In particular, RuL^2H^2 type complexes (L = 2,2'-bipyridine-6,6'-dicarboxylate, Het = aromatic N-heterocycles) reported by Sun and co-workers demonstrate exceptional performance.[4] The complex catalyzes water oxidation at low overpotentials and a turnover frequency comparable to the natural photosystem II (100–400 s^{-1}) through the I2M mechanism has been reported when driven by a chemical oxidant (CeIV).[8b,c] The ligand effect is subtle, an analogous complex Ru(phenad)- (pic)_2 (phenad = [1,10] phenanthroline-2,9-dicarboxylic acid, pic = 4-picoline) based on the rigid phenanthroline ligand catalyzes water oxidation via the WNA mechanism (Scheme 1), and higher overpotentials are required to drive the reaction.[6] Also, anchoring of RuL^2H^2 type catalysts on glassy carbon or indium tin oxide surfaces leads to site isolation of the complexes, prohibiting catalysis via the I2M mechanism, and the same complex catalyzes water oxidation via WNA with lower reaction rates.[11]
Ru(bda)Het$_2$ complexes lose their excellent performance under strongly diluted conditions as the rate-determining step (RDS) of diffusion-limited collision of two metal–oxyl radicals becomes slow (Scheme 1, Step IIa), which has been demonstrated by Concepcion and co-workers. Furthermore, the electrochemical reaction mechanism becomes unintelligible under dilute conditions. Meyer and co-workers have demonstrated that the Ru(bda)Het$_2$ catalyst is first-order in catalyst with kinetic isotope effects (KIE) around 2 implying a WNA mechanism. However, they could not exclude that the catalytic process proceeds via an I2M mechanism with a rate determining proton coupled electron transfer (PCET) step to form the ruthenium–oxo intermediate (Scheme 1, Step I), followed by a fast O–O coupling (Scheme 1, Step IIa).

In parallel to water oxidation catalysis development, the field of supramolecular catalysis has progressed significantly, providing new ways to position catalysts in confined spaces. In this context we generated M$_2$L$_{24}$ nanospheres (M = corners Pt$^{2+}$ or Pd$^{2+}$, L = bispyridyl building block), initially developed by Fujita and co-workers endohedrally functionalized with guanidinium groups to which sulfonate-bearing catalysts can be strongly bound by complementary hydrogen bonds and carboxylate functionalized substrates can be preorganized to these catalysts resulting in a 40-fold rate enhancement for the Au$^+$-catalyzed cyclization of acetylenic acid. We anticipate that these supramolecular nanospheres are ideal to preorganize Ru(bda)Het$_2$ type WOCs, as these should strongly benefit from high local concentration if they follow the preferred I2M mechanism. Hence, we report the application of the guanidinium functionalized M$_2$L$_{24}$ nanospheres (Figure 1a,b) as nanoconcentrators for the supramolecular encapsulation of a homogenous WOC Ru(bda)(PySO$_3$TBA)$_2$ (Figure 1c, PySO$_3$TBA = pyridine-3-sulfonate, TBA = tetra(n-butyl)ammonium) by strong binding (> 10$^3$ M$^{-1}$) between the guanidinium and sulfonate entities. Encapsulation of 12 Ru(bda)(PySO$_3$TBA)$_2$ catalysts within the nanosphere enhanced the solution concentration of 2.5 × 10$^{-5}$ M to a local concentration of 0.54 M, resulting in a two orders of magnitude increase in the rate of electrochemical water oxidation (0.93–125 s$^{-1}$).

The guanidinium functionalized building blocks, the corresponding nanospheres, and the ruthenium complexes were synthesized as previously reported. Endohedral binding of Ru(bda)(PySO$_3$TBA)$_2$ inside the nanosphere (up to 12 equiv) was confirmed by $^1$H NMR (Supporting Information, Figure S3). The addition of more than 12 equiv of guest (ratio sulfonate/guanidinium = 1) results in diffusion-ordered spectroscopy (DOSY) of nanosphere demonstrates a clear single band at log D = −9.6 m$^2$s$^{-1}$, consistent with previously reported M$_2$L$_{24}$ nanospheres of similar size. Signals originating from bound Ru(bda)(PySO$_3$TBA)$_2$ guests display the same log D values as the nanosphere (Supporting Information, Figure S4d), in contrast to the free Ru(bda)$(PySO_3TBA)_2$ complex (log D = −8.8 m$^2$s$^{-1}$), supporting quantitative encapsulation. Catalyst encapsulation is further confirmed by cold-spray-ionization time-of-flight mass spectrometry (CSI-ToF-MS), where peaks attributed to the nanosphere with encapsulated catalyst are detected (Supporting Information, Figures S5–S12 and Table S1).

To gain more detailed insight into catalyst distribution and the effect of local catalyst concentration on catalyst mobility within the sphere, classical molecular dynamics simulations were performed (Supporting Information, Section S3). Up to 12 catalysts they dominantly reside at close distance to the guanidinium for optimal hydrogen bonding. When more than 12 catalysts are present, catalyst population at the edges significantly increases (Supporting Information, Figure S15), which experimentally manifests as precipitation from solution (see above). When the nanosphere is loaded with up to 12 ruthenium catalysts, the diffusion within the sphere is only slightly affected (Supporting Information, Figure S17), so we may safely assume that catalyst mobility in the cage is sufficient to facilitate dinuclear reaction pathways, which is important for the I2M mechanism.

Having established that up to 12 Ru(bda)(PySO$_3$TBA)$_2$ complexes can be bound at the endohedral site of the nanosphere, the effect of such preorganization on the electrocatalytic water oxidation performance was evaluated. Owing to the low solubility of the nanosphere in water, acetonitrile with 10% deionized water was used as solvent with 0.1 M TBAF$_6$ as electrolyte. The stability of the M$_2$L$_{24}$ nanospheres in the presence of 10% D$_2$O and 0.1 M TBAF$_6$ was confirmed by $^1$H NMR and $^1$H DOSY NMR measurements (Supporting Information, Figure S18), consistent with reported data. Catalysis at the metal center of Ru(bda)$(PySO_3TBA)_2$ under standard conditions proceeds through the steps: Ru$^{11}$OH$_2$ $\rightarrow$ Ru$^{11}$−OH $\rightarrow$ Ru$^{9}$−OH $\rightarrow$ Ru$^{8}$−O (or Ru$^{7}$−O) based on the Pourbaix diagram (Supporting Information, Figure S19). The Ru(bda)(PySO$_3$TBA)$_2$ exhibits higher catalytic currents than Ru(bda)(pic)$_2$ with similar onset potential (Supporting Information, Figure S20).

The platinum nanosphere (Pt$_{12}$L$_{24}$) was chosen over the palladium analogue for the catalyst preorganization experiments as it usually exhibits superior stability. The cyclic voltammetry (CV) measurements on a solution containing 0.02 mM platinum sphere displays voltammograms that overlap with the blank, even after successive scans (Supporting Information, Figures S1–S12).
and local catalyst that is bound in the nanosphere (6 equiv 10)

The dependence of X

The number of Ru(bda)(PySO$_{2}$)$_{2}$ was varied which is cm $s^{-1}$

When the local catalyst concentration (Supporting Information, Figure S26) for Ru(bda)(PySO$_{2}$TBA)$_{2}$ was evaluated in the presence of guanidinium-binding sites (BuGd; Supporting Information, Figure S25), giving similar catalytic currents, showing that this hydrogen-bonding binding alone does not lead to enhanced catalytic rates. The catalytic current varies linearly with the local catalyst concentration (Supporting Information, Figure S26) for Ru(bda)(PySO$_{2}$TBA)$_{2}$, bound in the nanosphere (constant Ru(bda)(PySO$_{2}$TBA)$_{2}$/nanosphere ratio), indicating that also the encapsulated catalyst behaves as a soluble catalyst. To confirm the stability of the nanosphere system, electrolysis was conducted at 1.3 V. The current declined by about 10% during 8000 s electrolysis, which is similar to the decline in absence of nanosphere, and throughout the experiment the current is about 3 times higher than in absence of nanosphere (Supporting Information, Figure S27a). The $^1$H NMR and $^1$H DOSY NMR spectra after electrolysis are similar to that taken before the experiment (Supporting Information, Figure S27b,c). To confirm oxygen was formed, the Faradic efficiency was determined to be 96.3 % using a rotating ring-disk electrode in standard conditions (Supporting Information, Figure S29). [19]

To demonstrate the effect of high local concentration on water oxidation catalysis, the dependence of catalytic current and rate (k$_{cat}$) on the amount of catalyst per nanosphere was determined. The overall concentration of Ru(bda)-(PySO$_{2}$TBA)$_{2}$ was kept constant (2.5 $\times$ 10$^{-3}$ M), whereas the number of Ru(bda)(PySO$_{2}$)$_{2}$ per nanosphere was varied from 1 to 12, which translates to estimated local catalyst concentration from 0.04 to 0.54 M. [20] The current densities increase considerably with the increased local catalyst concentration (Supporting Information, Figure S30), and the highest current density was achieved by the encapsulation of 12 Ru(bda)(PySO$_{2}$)$_{2}$ on average per nanosphere. The k$_{cat}$ was determined by combining Randles–Sevcik equation with kinetics plots (k$_{cat}$/p vs. $\sqrt{v}$) (Supporting Information, Section S4.3). The clear increase of k$_{cat}$ was achieved by just changing the local catalyst concentration within the nanosphere (Figure 2a), with a maximum rate of 125 s$^{-1}$ which is more than 130 times higher than that observed for the non-encapsulated system (0.93 s$^{-1}$). The large enhancements in k$_{cat}$ suggest that this reaction proceeds via the I2M mechanism where the RDS of O–O coupling (Scheme 1, Step Iia) is promoted by catalyst preorganization in the nanosphere. Even for an average of one catalyst per nanosphere the calculated k$_{cat}$ is still higher than in absence of the nanosphere. These statistical mixtures contain enough nanospheres with at least two catalysts to facilitate the reaction to proceed via the favorable I2M mechanism. To further confirm this, experiments were performed in which excess nanosphere was used, indeed leading to lower catalytic currents (Supporting Information, Figure S35). When the ratio of catalyst to nanosphere was 1:8, the catalytic current and thus the rate dropped to 20% (0.18 s$^{-1}$) compared to that of the molecular catalyst in absence of nanosphere. Under these conditions, site isolation of the Ru(bda)(PySO$_{2}$)$_{2}$ in the nanosphere prevents the I2M mechanism to occur.

To further find evidence for the mechanism by which Ru(bda)(PySO$_{2}$TBA)$_{2}$ converts water into oxygen when located in the nanosphere, we performed KIE studies (Supporting Information, Equation (5)) and looked more carefully at the reaction rate as function of the local catalyst concentration. In the range of local catalyst concentration between 0 and 0.27 M, a second order in local catalyst is found based on a linear relationship between $\sqrt{k_{cat}}$ and local catalyst concentration (Supporting Information, Figure S36). This suggests that in this concentration regime the catalyst operates via the I2M reaction mechanism with the O–O coupling as the RDS. In line with this, a low secondary isotope effect (KIE < 1.5) is observed (Figure 2b). [21] When the local...
The rate-limiting type complexes also (red) and Ru(phenda)(PySO\textsuperscript{oxo}Angew. Chem. 2018 c Proc. Natl. Acad. Sci. USA 42 2009 57 www.angewandte.de Energy difficult 115 121 Chem. (blue) by 2018 48 Tcatalyst find 2009 Comparison of the reaction rate improvement observed for in the huge effect is observed. (Figure-103 Acc. Chem. Res. 2018 Therefore, 130 114 electrochemical catalysis ·ruthenium complexes ·intermediate the proper for 2018 130,2009 276 1993 ·chemistry, ·catalysis ·reduction of the rate