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Electrochemical Polymerization Provides a Function-Integrated System for Water Oxidation

Hikaru Iwami,[a,b,c] Masaya Okamura,[b] Mio Kondo,*[a,d,e] and Shigeyuki Masaoka*[a,e]

[a] Mr. H. Iwami, Prof. Dr. M. Kondo, Prof. Dr. S. Masaoka
Division of Applied Chemistry, Graduate School of Engineering
Osaka University
2-1 Yamadaoka, Suita Osaka 565-0871, Japan
E-mail: mio@chem.eng.osaka-u.ac.jp, masaoka@chem.eng.osaka-u.ac.jp
[b] Mr. H. Iwami, Dr. M. Okamura
Department of Life and Coordination-Complex Molecular Science
Institute for Molecular Science (IMS)
5-1 Higashiyama, Myodaiji, Okazaki, Aichi 444-8787, Japan
[c] Mr. H. Iwami
Department of Structural Molecular Sciences
SOKENDAI [The Graduate University for Advanced Studies]
Shonan village, Hayama, Kanagawa 240-0193, Japan
[d] Prof. Dr. M. Kondo
JST, PRESTO, 4-1-8 Honcho, Kawaguchi, 332-0012, Japan
[e] Prof. Dr. M. Kondo, Prof. Dr. S. Masaoka
Innovative Catalysis Science Division,
Institute for Open and Transdisciplinary Research Initiatives (OTRI),
Osaka University, Suita, Osaka 565-0871, Japan

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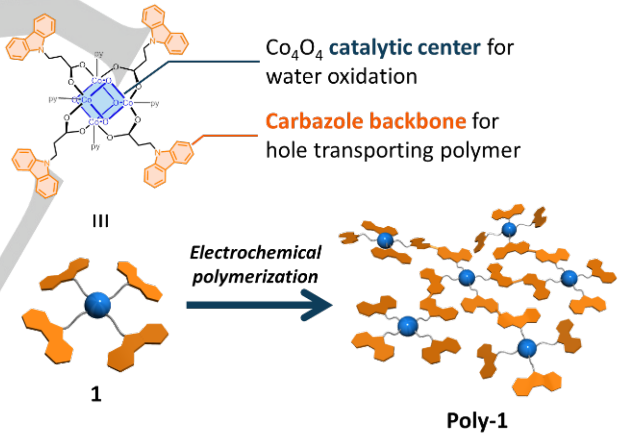
Abstract: Water oxidation is a key reaction in natural and artificial photosynthesis. In nature, the reaction is efficiently catalyzed by a metal-complex-based catalyst surrounded by hole-transporting amino acid residues. However, in artificial systems, there is no example of the water oxidation system which has a catalytic center surrounded by hole transporters. Here, we present a facile strategy to integrate catalytic centers and hole transporters in one system. Electrochemical polymerization of a metal-complex-based precursor afforded the polymer-based material (**Poly-1**). **Poly-1** exhibits excellent hole-transporting ability and catalyzes water oxidation with high performance. It was also revealed that the catalytic activity was almost suppressed in the absence of the hole-transporting moieties. The present study provides a novel strategy for constructing efficient molecule-based systems for water oxidation.



Scheme 1. (Top) Structure of the metal-complex-based precursor (1) developed in this study. (Bottom) Schematic illustration of the preparation of function-integrated catalytic system for water oxidation via the electrochemical polymerization of **1**.

Introduction

Demand for a sustainable society and clean energy production has increased in recent years.[1] Four-electron oxidation of water ($2H_2O \rightarrow O_2 + 4H^+ + 4e^-$) is an important reaction for suppling the protons and electrons required to generate reduced products (i.e., chemical energy) from abundant resources in a clean manner.[2] In nature, the reaction is catalyzed by a metal-complex-based catalyst, the oxygen-evolving complex (OEC), embedded in photosystem II.[3,4] The OEC is known as a highly active and robust catalyst that can drive the reaction under mild condition. In the OEC, a manganese-based multinuclear cluster, which serves as the catalytic center, is surrounded by several amino acid residues, and these residues play an important role in transferring electrons/holes to the catalytic center.[3,4] This fact indicates that the presence of hole transporters close to the metal-complex based catalytic center is a key to efficiently promoting water oxidation reactions. Thus far, there have been many reports on the molecule-based catalytic system for water oxidation. However, the works mainly focus solely on the construction of catalytic centers[2a-g,5,6] or the immobilization of catalytic centers on electrode surfaces[2h,7]. Thus, the literature contains no report on the development of catalytic systems that have a catalytic center surrounded by hole transporting units.

Here, we disclose a novel approach for developing an artificial catalytic system for water oxidation. Inspired by the natural water oxidation system, we hypothesized that the integration of catalytic centers and hole transporters into one material could be a promising strategy. Based on this strategy, a

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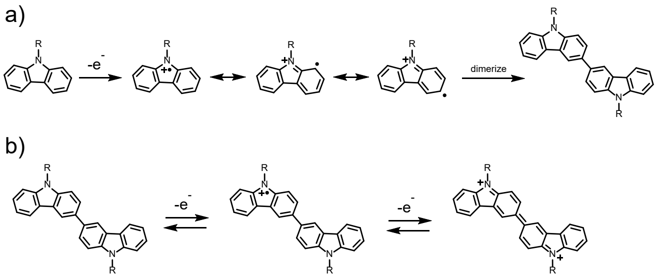
polymer-based catalytic system was constructed by assembling catalytic center and hole transporter units. The several spectroscopic measurements clearly demonstrated that these functional units are successfully incorporated in the assembled system (**Poly-1**). It was also revealed that **Poly-1** exhibited high hole transporting ability. Moreover, **Poly-1** can promote electrocatalytic water oxidation with a high faradaic efficiency (>90%) and a low overpotential (η = 413 mV) in aqueous media. This performance of **Poly-1** is of the highest class compared to the relevant systems.



Scheme 2. (a) Oxidative dimerization of carbazole derivatives to form biscarbazole derivatives. (b) Redox properties of biscarbazole derivatives.

Results and Discussion

The key to our success is the utilization of a newly designed metal-complex-based precursor, **1**, shown in Scheme 1. **1** is comprised of two distinct functional units: a tetranuclear cobalt complex and carbazole moieties (Scheme 1, top). The tetranuclear cobalt complex has a cubane-shaped structure, which is also observed in the OEC, and it serves as an artificial catalyst for water oxidation.[8] Carbazole derivatives are known to dimerize under oxidative conditions (Scheme 2a).[9] In addition, the formed biscarbazole exhibits hole-transfer ability (Scheme 2b),[10] which should favor the oxidative catalytic reaction. Therefore, materials with catalytic centers and hole transporters should be accessible (**Poly-1**, Scheme 1, bottom) by the electrochemical polymerization of **1**.

The metal-complex-based precursor, **1**, was synthesized by following Scheme S1 in the Supporting Information (SI). Initially, carbazole-9-propionic acid (Hczp) was synthesized by modifying a previously reported procedure[11] (yield: 57%) and was characterized by ^1H NMR spectroscopy. Subsequently, Hczp was reacted with $Co_4O_4(OAc)_4(py)_4$ (^-OAc = acetate anion, py = pyridine)[12] in MeCN at 60 °C for 1 h. The reaction was monitored by thin-layer chromatography and quenched after the consumption of $Co_4O_4(OAc)_4(py)_4$. Notably, the ligand substitution reaction at 90 °C led to the decomposition of the starting materials, and thus, the reaction was conducted at a moderate temperature (60 °C). The crude product was further purified by silica-gel column chromatography, and the desired complex **1** was obtained in 66% yield. The complex was characterized by ^1H NMR spectroscopy, single-crystal X-ray structural analysis and elemental analysis.

Single crystals of **1** suitable for X-ray diffraction measurements were obtained by vapor diffusion of Et_2O into a CH_2Cl_2 solution of **1** at room temperature. An ORTEP diagram of **1** is shown in Figure S1. **1** crystallized in $P\overline{1}$, and the asymmetric unit contains one complex and 2.5 CH_2Cl_2 molecules as solvents of crystallization. In **1**, all the acetate ligands were exchanged for czp^- ligands. The average bond distances between the Co ions and the oxygen atoms in the μ-oxo bridging ligand (Co-O_{oxo}) and between the Co ions and the oxygen atoms of czp^- ligands (Co-O_{cpz}) are 1.855(3)-1.867(2) and 1.947(3)-1.995(3) Å, respectively. These values are comparable to those reported previously.[13]

The electrochemical behaviors of **1** were investigated by cyclic voltammetry (CV) in an organic medium (0.1 M tetra-*n*-butyl ammonium hexafluorophosphate ($TBAPF_6$) in CH_2Cl_2), and the results are shown in Figure 1. In the first cycle (Figure 1a), the oxidation peak was observed at approximately 0.278 V (*vs.* Fc/Fc^+), and the peak was assigned to the oxidation of the cobalt center, $Co^{III}_3Co^{IV}/Co^{III}_4$[13]. Upon further sweeping of the potential to the positive region, a large peak attributed to the oxidation of the carbazole moieties was observed at approximately 0.7 V. In the reverse scan, two new redox waves were observed at 0.323 and 0.601 V. These redox waves were due to the formation of a biscarbazole structure.[10] In the second and subsequent cycles (Figure 1b), the intensity of the current attributed to the redox couple of biscarbazole ($E_{½}$ = 0.432 and 0.755 V) was increased, indicating the formation of further biscarbazole moieties upon electrochemical oxidation. Note that the similar trend was also observed when an ITO was used as a working electrode (Figure S2). These results indicate that **1** is electrochemically polymerized via the dimerization of czp^- ligands.

To elucidate the polymerization behavior of **1**, electrochemical measurements were also conducted using a transparent electrode (ITO plate) as the working electrode. In this experiment, a constant potential (1.3 V vs. Ag/Ag^+) was applied to the ITO electrode in a 0.1 M $TBAPF_6$-CH_2Cl_2 solution containing

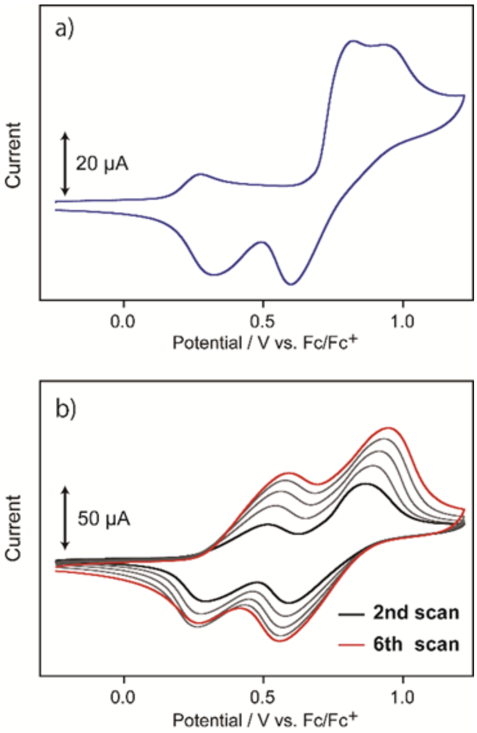


Figure 1. Cyclic voltammograms of a 0.19 mM solution of **1**. (a) 1st scan and (b) 2nd to 6th scans. Measurements were performed in a CH_2Cl_2 solution containing 0.1 M $TBAPF_6$ under Ar at a scan rate of 100 mV s^{-1}. Working electrode, glassy carbon; counter electrode, Pt wire; reference electrode, Ag/Ag^+. CV scans were initiated from the open-circuit potential.

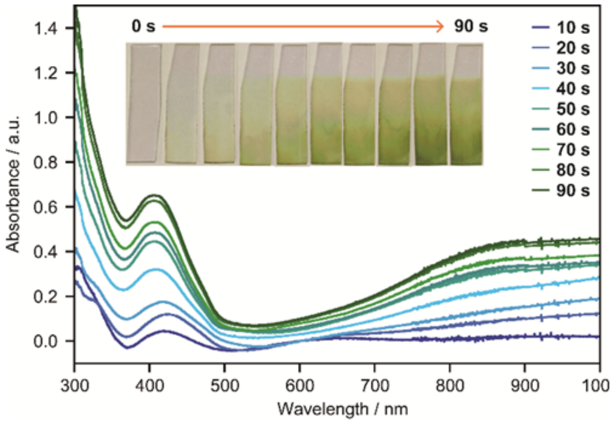


Figure 2. UV-vis absorption spectra of the ITO electrodes electrolyzed at 1.3 V vs. Ag/Ag$^+$ for 10-90 s using a 0.1 M TBAPF$_6$-CH$_2$Cl$_2$ solution containing 0.19 mM of **1**. (Inset) Photographs of the ITO electrodes after the electrolysis.

0.19 mM **1** for 10 – 90 s, and after electrolysis, the electrodes were analyzed by UV-vis absorption spectroscopy. The UV-vis absorption spectra of the electrodes are shown in Figures 2 and S3. A band center at approximately 420 nm and a broad band at approximately 800 nm were observed in all cases, and the intensities of the bands gradually increased as the electrolysis time increased. The band at 800 nm can mainly be attributed to the intervalence charge transfer (IVCT) transitions of mixed-valent biscarbazole units or charge-resonance bands in the case of Robin-Day class III systems.[10,14] These results clearly demonstrate that the carbazole moieties of **1** were dimerized upon oxidation to afford a polymer with a biscarbazole backbone. To further verify the structure of the polymer, the infrared spectra of **1** before and after polymerization were measured (Figure S4). Both spectra showed several common vibration peaks, COO$^-$ asymmetric vibration (1550 cm^{-1}), pyridine ring vibration (760 cm^{-1}) and Co-O$_{oxo}$ stretching vibration (630 cm^{-1}).[13] The data strongly indicates that the cobalt-cubane structure is preserved in the polymer. We also analyzed the obtained polymer by scanning electron microscopy (SEM). The SEM image of the polymer shows a flat surface structure, indicating the formation of a homogeneous film on the electrode (Figure S5, top). It should be noted that the morphology of the film is completely distinct from that of oxidized Co phosphate inorganic materials (Figure S8, top), which indicates that the oxidized Co phosphate inorganic materials are not formed during the polymerization of **1**. The energy dispersive X-ray (EDX) elemental map of the film showed a uniform distribution of cobalt, which also suggests the homogeneity of the polymer (Figure S5, bottom). In the EDX spectrum (Figure S6), peaks attributable to fluorine and phosphorus were also detected, suggesting that PF$_6^-$ was doped into the polymer. The control experiments using the oxidized Co phosphate inorganic materials revealed stronger peak intensities of Co and P (Figure S8, bottom) than **Poly-1** (Figure S6), supporting that the film has different composition from oxidized Co phosphate inorganic materials. These observations indicate that **1** is electrochemically polymerized to uniform polymer, **Poly-1**, which has both biscarbazole and cobalt cubane moieties.

To clarify charge transfer ability of **Poly-1**, electrochemical impedance spectra (EIS) were measured. EIS were measured for a bare glassy carbon (GC) electrode, the GC electrode modified with the cobalt cubane complex without biscarbazole moieties, Co$_4$O$_4$(PhCOO)$_4$(py)$_4$ (Co$_4$O$_4$(PhCOO)$_4$(py)$_4$@GC, PhCOOH = benzoic acid, for the details of the sample preparation, see the Supporting Information (P.S14)), and the GC electrode modified with **Poly-1** (**Poly-1**@GC). Figure 3a shows the EIS measured at 1.30 V vs. Ag/AgCl of the bias potential. The diameters of semicircles in Nyquist plots were decreased in the order of a bare GC, Co$_4$O$_4$(PhCOO)$_4$(py)$_4$@GC and **Poly-1**@GC. Fitted charge

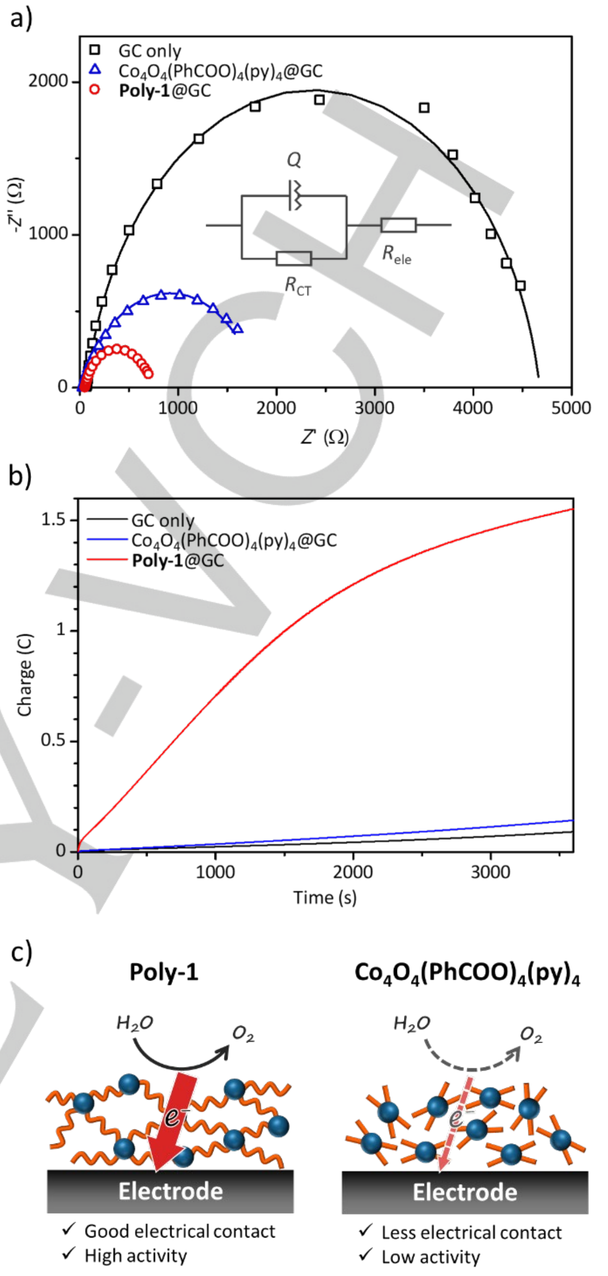


Figure 3. (a) Nyquist plots of a bare GC (black), Co$_4$O$_4$(PhCOO)$_4$(py)$_4$@GC (blue) and **Poly-1**@GC (red). Measurements were performed in 0.2 M phosphate buffer (pH = 7.06) under an argon atmosphere. (Inset) the equivalent circuit for fitting data. Applied potential: 1.30 V vs. Ag/AgCl, measurement range: 0.1 Hz -100 kHz. 20 nmol of Co$_4$O$_4$(PhCOO)$_4$(py)$_4$ was mounted from a CH$_2$Cl$_2$ solution of Co$_4$O$_4$(PhCOO)$_4$(py)$_4$ by drop-cast method to prepare Co$_4$O$_4$(PhCOO)$_4$(py)$_4$@GC. (b) Controlled potential electrolysis data of **Poly-1**@GC (red line), Co$_4$O$_4$(PhCOO)$_4$(py)$_4$@GC (blue line) and a bare GC (black line) in phosphate buffer solutions (pH = 7.06) under an argon atmosphere. Applied potential: 1.30 V vs. Ag/AgCl. (c) Schematics of the comparison of properties between **Poly-1**@GC, Co$_4$O$_4$(PhCOO)$_4$(py)$_4$@GC.

transfer resistance (R_{CT}) values with the equivalent circuit (Figure 3a inset) of a bare GC, $Co_4O_4(PhCOO)_4(py)_4$@GC, and **Poly-1**@GC were 4606, 1706 and 679 Ω respectively (Table S2). R_{CT} of **Poly-1**@GC was reduced to 15% of bare GC and 40% of $Co_4O_4(PhCOO)_4(py)_4$@GC. These results clearly demonstrate that charge transfer ability is largely enhanced due to the biscarbazole moieties embedded in **Poly-1**.

Finally, the electrocatalytic activity of **Poly-1** for water oxidation was evaluated. To investigate the catalytic activity, **Poly-1** was immobilized on a glassy carbon electrode (**Poly-1**@GC, for details of the preparation of the film, see the SI). Figure S9 shows the cyclic voltammograms of **Poly-1**@GC in a phosphate buffer solution (pH = 7.06). A large irreversible current was clearly observed at approximately 1.0 V (vs. Ag/AgCl), which confirms the water oxidation ability of **Poly-1**. The overpotential (η) was estimated to be 413 mV. To further verify the water oxidation performance of **Poly-1**, controlled potential electrolysis of **Poly-1** was then performed. After 1 h of electrolysis of **Poly-1**@GC at 1.30 V (vs. Ag/AgCl), 1.55 C of charge was passed, and 3.68 μmol of O_2 as the major product was detected by gas chromatography (Figure 3b and Table S3). The maximum faradaic efficiency of the reaction based on the $4e^-$ process was estimated to be 91.5%. The isotope labelling experiments using ^{18}O-labelled water, $H_2{}^{18}O$ (97%) were also performed. After the 30 min of the electrolysis at 1.30 V (vs. Ag/AgCl), gaseous phase was analyzed by GC-MS. As a result, the formation of $^{18}O_2$ as a major product was confirmed (Figure S11). Moreover, the ratio between $^{18}O_2$ and $^{18}O^{16}O$ was in good agreement with the theoretical values (exp. $^{18}O_2$: $^{18}O^{16}O$ = 100 :7.8, theor. $^{18}O_2$: $^{18}O^{16}O$ = 100 : 6.1). These results clearly demonstrate that the origin of oxygen atoms in evolved dioxygen is water in the catalysis mediated by **Poly-1**. To investigate the stability of **Poly-1**, a long-term electrolysis was carried out. During 6 h of electrolysis at 1.30 V (vs. Ag/AgCl), the current passed continuously (Figure S12), and the formation of dioxygen with 88.6% of Faradaic efficiency was confirmed (Table S4), which suggests that **Poly-1** was stable under the catalytic condition. These results clearly demonstrate that **Poly-1** can promote electrocatalytic water oxidation. It should be noted that the catalytic activity is almost suppressed under identical experimental condition when the electrode modified with the complex without biscarbazole moieties, $Co_4O_4(PhCOO)_4(py)_4$ @GC, was used (Figure 3b, blue line). The result together with the results of the EIS measurements clearly demonstrate that the existence of biscarbazole moieties as hole transporters is essential to achieve the efficient catalysis. In other words, the importance of the integration of hole transporting units close to the catalytic center is successfully confirmed. In addition, the catalytic performance of **Poly-1** was of the highest class among the reported cobalt-complex-based catalytic system for water oxidation in terms of overpotentials and faradaic efficiencies (for the details of the comparisons with other relevant catalysts, see Table S5).[5g, 15-23]

Conclusion

In conclusion, we have developed a facile method to integrate molecule-based catalytic centers and hole transporters into one material. The electrochemical polymerization of the precursor with a cobalt-cubane moiety and carbazole units afforded a film-based material (**Poly-1**). The characterization of **Poly-1** was performed by various experimental techniques, including UV-vis absorption spectroscopy IR spectroscopy, SEM and EDX, and the integration of two functional units were confirmed. The properties of **Poly-1** was analyzed by EIS and the high transporting ability was clarified. Moreover, **Poly-1** can catalyze the water oxidation reaction with a high faradaic efficiency and a low over potential. Notably, the results of control experiments disclosed that the integration of two functional units are essential to achieve excellent activity of **Poly-1** (Figure 3c). Our study is a significant example of a molecule-based catalytic system that mimics the key features of the OEC; the systems with a catalytic center surrounded by hole transporting units. Collectively, the present study offers a novel concept for obtaining efficient catalytic system for water oxidation.

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Conflict of Interest

The authors declare no competing financial interest.

Keywords: cobalt • electro catalysis • heterogeneous catalysis • water oxidation • electrochemical polymerization

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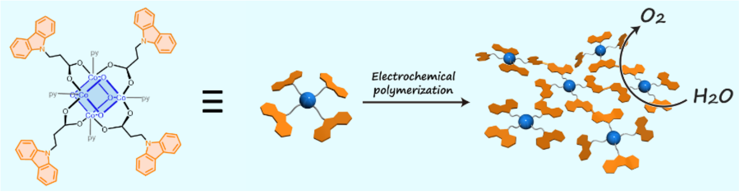

Four-electron oxidation of water with the function-integrated polymer is reported. Electrochemical polymerization provided a material with molecule-based active sites and hole-transporting moieties. Electrochemical impedance analysis revealed that hole transporting polymer reduced charge transfer resistance. The material catalyzed electrochemical water oxidation with a high faradaic efficiency and a low overpotential.