View Article Online View Journal

NJC Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: T. Zheng and L. Li, *New J. Chem.*, 2018, DOI: 10.1039/C7NJ04330A.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/njc

{[Ru(bda)]_xL_y}_n Cross-linked Coordination Polymers: Toward Efficient Heterogeneous Catalysis for Water Oxidation in Organic Solvent-free System

Tao Zheng and Lianwei Li*

Hefei National Laboratory for Physical Sciences at the Microscale, Department of Chemical Physics, University of Science and Technology of China, Hefei, Anhui 230026, China

Abstract: Development of polymeric catalysts for water splitting has receiving increasing attentions recently. In this work, we successively developed few novel cross-linked coordination polymers (CCPs) with a formula $\{[Ru(bda)]_xL_y\}_n$ as efficient heterogeneous catalysts for water oxidation in organic solvent-free system, where Ru(bda) represents the catalytic center. Detailed water oxidation catalytic kinetics studies suggested that the single-site water nucleophilic attack (WNA) is a general mechanism applied to these polymeric catalysts, different with the small-molecular reference $[Ru(bda)(pic)_2]$ (pic = 4-picoline). The experimental evidence also indicated the importance of interfacial wettability and the existence of Ru(bda)-macrocyclic fragments of polymer network in determining the overall catalytic activity. More interestingly, the end-capping modification via pyridine/dmso exchange reaction further removed the residual $Ru(dmso)_x$ moieties on the surfaces of polymer network, which led to improved performance with impressive TOF $\sim 4.6 \text{ s}^{-1}$ and TON ~ 750 in organic solvent-free system, even superior to $[Ru(bda)(pic)_2]$. The rate of catalysis is among the highest heterogeneous systems reported so far. Electrochemical study showed these polymeric catalysts were also promising electrode materials for electrocatalytic water oxidation, and the electrode based on CCP/Nafion/ITO maintained ~ 73% of its initial activity after 27 cycles under optimal condition.

* To whom corresponding should be addressed. <u>llw@mail.ustc.edu.cn</u>

New Journal of Chemistry Accepted Manuscript

Introduction

The catalytic water oxidation to molecular oxygen involves four-electron-transfer process and is the bottleneck of the half reaction for water splitting.¹⁻³ One of the most extensively studied homogeneous water oxidation catalysts (**WOCs**) are based on ruthenium complexes, which have been shown to exhibit high turnover numbers (TONs) and turnover frequencies (TOFs).² An important development is the discovery of highly active family [Ru(bda)(L)₂] (bda= 2,2'-Bipyridine-6,6'-dicarboxylate, and L: donor ligand) by Sun and co-workers, which was shown to be among the first to reach activities (TON > 8000 and TOF > 300 s⁻¹) comparable to that of the natural oxygen-evolving cluster (TOF ~ 100-400 s⁻¹).⁴

In spite of excellent performance for $[Ru(bda)(L)_2]$ catalyst family, large amounts of organic solvents such like acetonitrile or dimethylformamide were normally needed as cosolvent to increase the solubility of catalyst in water, especially when the axial ligand is composed of large π -extended aromatic ring such like isoquinoline.^{4, 5} From a green chemistry perspective, the utilization of noneco-friendly solvent is highly undesired. Thus, ligand modification is generally adopted to solve the solubility issue and lower the volume ratio of organic solvent used in catalysis. For instance, Würthner et al. recently reported a highly efficient homogeneous system based on metallosupramolecular macrocycle [Ru(bda)(bpb)]₃ (TON ~ 7400, TOF ~ 150 s⁻¹), where triethylene glycol and protonable tertiary amines were incorporated into the bridging ligands to increase the solubility.^{6, 7} However, sophisticated synthesis, time-costing purification and low yield are generally unavoidable.

Heterogeneous catalysts show advantages over homogenous ones for practical applications due to their low cost, facile preparation and ease in separation/recovery. Moreover, the solubility issue is no longer a key consideration. Recently, the metal–organic frameworks

(MOFs) have been applied as the heterogeneous hosts for encapsulating molecular **WOCs**, such as $[(terpy)Mn(\mu-O)_2Mn(terpy)]^{3+}$ and $[Cp*Ir(bpy)Cl]^{+.8-10}$ Meanwhile, the linear coordination polymers were reported as heterogeneous **WOCs**.^{11, 12} Unfortunately, most of these **WOCs**, though very promising in their approaches, showed only limited catalytic activities (TOF < 0.1 s⁻¹ and TON < 100). There is still an urgent demand for the development of highly efficient heterogeneous **WOCs**.

In contrast, metal-containing porous polymer catalytic systems are much less explored for water oxidation application, but they are intriguing because of their diverse synthetic modularity, which allows their structural properties to be tailored systematically for catalytic water splitting.¹³ In our previous work, we have shown that, with proper structural design and manipulation, cross-linked porous conjugated polymer materials can act as efficient heterogeneous photocatalysts for hydrogen evolution reaction.^{14, 15} We also established the structure-activity correlation and clarified the critical role of residual palladium for efficient catalysis.

Here we report the first example of using cross-linked coordination polymers (**CCPs**) with a formula $\{[Ru(bda)]_xL_y\}_n$ as heterogeneous catalysts for water oxidation in eco-friendly water system (**Fig. 1**). These Ru(bda)-based polymeric catalysts are designed based on the following rationales: 1) the 3D polymeric network suppresses the self-oxidation and ligand dissociation, and further improves the storage- and reaction-stability of catalysts; 2) the network porosity and protonable triazine core (**CCP3**) prompt the preorganization and diffusion of water and oxidant molecules; 3) the semiconducting ligand facilitates the electron-transfer during the redox process; 4) the polymeric framework ensures the isolation of individual Ru-sites for mechanistic study; 5) the insolubility of polymeric catalysts in water



renders CCPs viable electrode materials for aqueous electrochemical oxidation.

Fig. 1 (a) Chemical structures of ligands L0-L3 and [Ru(bda)(dmso)₂]. (b) Chemical structures of **LCP** and **CCPs**.

Published on 08 January 2018. Downloaded by Fudan University on 19/01/2018 09:32:37

We carried out detailed kinetics studies on these polymeric catalysts in organic solvent-free aqueous solution by using cerium(IV) ammonium nitrate (CAN) as chemical oxidant. The experimental results supported the water nucleophilic attack (**WNA**) mechanism for these **CCP** catalysts, which was attributed to the local confinement effect. Structure-property correlation study indicated that the hydrophilic nature/interface wettability, existence of Ru(bda)-macrocyclic fragments, and good pre-dispersion of **CCP** catalysts are dominant factors affecting their catalysis performance. It's also found that the 3D cross-linked network is beneficial for the storage- and reaction-stability of catalysts. More interestingly, the post-modification of polymeric catalyst via pyridine/dmso exchange reaction could remove the residual dmso moieties and further led to ~ 6 times of enhancement in catalytic activity with impressive TOF ~ 4.6 s⁻¹ and TON ~ 750 in organic solvent-free aqueous solution. The present study also demonstrated that these polymeric catalysts are promising electrode materials for electrochemical water oxidation due to their insolubility in water.



Fig. 2 (a) FTIR spectra of LCP, CCPs and the ligand precursors. (b) Solid-state ${}^{1}\text{H}-{}^{13}\text{C}$ CP/MAS NMR spectra of CCP1 and CCP3.

Results and Discussion

Synthesis and Characterization of the CCP Heterogeneous WOCs. Three **CCPs** were synthesized by ligand-exchange polycondensation reaction between [Ru(bda)(dmso)₂] and various multi-pyridyl monomers (L0-L3) (**Fig. 1**). Ligands L1 and L3 own the same plane-triangle configuration but different core structure (benzene and triazine). The incorporation of spiro-linkage into L2 is in order to increase the porosity of resultant **CCP** network due to its superior network-supporting effect.¹⁶ Ligands L0-L2 were synthesized through typical Suzuki-coupling procedure (**Fig. S1** and **S2**, see experimental part). During the polycondensation process, the **CCP** products typically started to precipitate out from solution phase after ~ 2 h of reaction (**Fig. S3**). After 24 h of polymerization, the insoluble

products were collected by ultracentrifugation and further purified by successive solvent extraction (methanol, acetone, THF and dichloromethane). It is worth noting that these **CCPs** are highly insoluble in water and various organic solvents, which is the basic premise for their heterogeneous application. Meanwhile, one linear coordination polymer (**LCP**) was prepared as non-porous analogue for comparison.

The resultant CCP powders typically exhibited dark-brown color. FTIR spectra (Fig. 2a) show the skeleton stretching vibration bands of benzene and pyridine rings (1450 \sim 1580 cm⁻¹), accompanied with the feature vibration bands of carboxylic ester (1560 \sim 1720 cm⁻¹) for all these CCPs and LCP. The unique bands of triazine ring (~ 1370 and ~ 1520 cm⁻¹) were observed for CCP3. The vibration peaks of S=O (dmso) located at ~ 1080 cm⁻¹ and ~ 1410 cm⁻¹ show great reduction after polycondensation, indicating the high conversion of reaction. The solid state ¹³C-NMR spectroscopic results further confirmed the structure as proposed (Fig. 2b), namely, the broad peaks ranging from 110 to 160 ppm correspond to signals of aromatic carbons of benzene and pyridine; the carbon signal located at ~ 170 ppm (e) is attributed to carbons of triazine ring from CCP3; the signals ranging from 180 to 240 ppm are attributed from bda units. ICP-MS results quantitatively demonstrate the successful incorporation of Ru(bda) units into these CCPs (Fig. 3a). The measured Ru contents were found to be slightly lower than the theoretical values, probably due to the incompletion of the polymerization. TGA measurements indicate that all these **CCPs** are thermally stable up to 150 °C (Fig. 3b).

Published on 08 January 2018. Downloaded by Fudan University on 19/01/2018 09:32:37

(a) 25

 $Wt\%_{Ru}$

b)

 W/W_0

20

15

10

5

Δ

1.0

0.9

0.8

0.7



Fig. 3 (a) Measured (ICP-MS) and calculated mass fractions ($Wt\%_{Ru}$) of ruthenium element in LCP and CCPs. (b) TGA spectra of the LCP and CCPs in nitrogen.

250 300

T / °C

350

400 450

150 200

Morphology Study of the CCP Catalyst Particles. Morphology study combines SEM, powder-XRD, DSC and gas adsorption measurements. The SEM images show the irregular nanoparticle morphologies with primary particle sizes in the range from 50 to 200 nm for all these **CCPs (Fig. 4a)**, while **CCP2** and **CCP3** catalyst particles show much stronger trend in inter-particle aggregation. The nanoscaled morphology is supposed to be beneficial to heterogeneous catalysis. Powder-XRD measurements (**Fig. 4b**) indicate the semi-crystalline feature for **CCP1** (multiple sharp diffraction peaks, $10^{\circ} \sim 35^{\circ}$), whereas the introduction of spiro-linkages renders **CCP2** amorphous. The observed broad diffraction peaks for **CCP3** indicate some degree of ordered structure. However, no phase transition was observed in the DSC scans for all these **CCPs (Fig. 5)** from -50 °C to 120 °C. The nitrogen adsorption measurements (**Fig. 4c**) show moderate BET surface areas (SA_{BET}) of 24, 55 and 12 m²/g for

CCP1, CCP2 and CCP3, respectively (Figure 2c). As expected, LCP shows non-porous feature.



Fig. 4 (a) SEM images, (b) powder XRD patterns and (c) nitrogen sorption isotherms of **CCP** particles in solid-state.



Fig. 5 DSC scans of LCP and CCPs from -50 °C to 120 °C.



Fig. 6 (a) Schematic illustration of chemically driven water oxidation by using **CCP3** as catalyst and Ce^{IV} as oxidant. (b)-(e) Reaction time (*t*) dependence of oxygen concentration ([O₂]) by using **LCP** and **CCPs** as **WOCs** ([Ce^{IV}] = 100 mM, pH = 1.0). (f) Catalyst concentration (C_{Ru}) dependence of initial oxygen evolution rate (v_i) in log-scale coordinate.

Chemical Water Oxidation Using CCPs as Heterogeneous Catalysts: Kinetics Study. The

catalytic water oxidation in pure water was performed by using cerium(IV) ammonium nitrate (CAN) as sacrificial electron acceptor (**Fig. 6a and Fig. S4**). The reaction kinetics was in-situ monitored with an oxygen-sensor, and the evolved amount of O_2 in gas space was analyzed by GC (**Fig. S5**). In a typical experiment, 0.5 mL of **CCP** water suspension was degassed and injected into O_2 -free HNO₃ solution (9.5 mL, pH 1.0, Ce^{IV} 100 mM) in a sealed vial with rubber septum under constant stirring. Each **CCP** suspension was prepared by diluting a mother suspension (1.0 mg/mL, **Fig. S4**) which was previously stirred vigorously for 24 h to

maximize the specific surface area of catalyst particles (**Table S1**). **Fig. 6b-e** show the reaction time- and catalyst concentration-dependent oxygen evolution curves for LCP and **CCPs**. Obviously, the oxygen evolution rate increases with the molar concentration of Ru (C_{Ru}) , where C_{Ru} represents the total molar concentration of Ru in the final water suspension (10 mL) used for catalysis. Control experiment by using the filtrate of **CCP3** suspension as catalyst solution showed no oxygen evolution (**Fig. S6**), indicating no dissolution of ruthenium complex from polymer backbones into solution phase.

According to Henry's law, the produced molecular oxygen in solution phase is supposed to nucleate, fuse and further diffuse into gas phase to reach the thermodynamic equilibrium. Thus, the observed turning points from increase to decrease in the evolution curves reflect that the O₂ diffusion rate starts to exceed the O₂ evolution rate (**Fig. 6b-e**). To obtain reliable kinetics results, the initial oxygen evolution rates (v_i) were calculated only based on the data within the first few seconds of catalysis, and the exact values of C_{Ru} were calculated according to the previous ICP-MS results (**Table S1**). A few quasi-linear relationships between v_i and C_{Ru} were observed in log-scale, i.e., $v_i \sim C_{Ru}^{\alpha}$. The fitting scaling exponent α is 0.92, 0.95 and 1.11 for **CCP1**, **CCP2** and **CCP3**, respectively (**Fig. 6f**), whereas the exponent is 1.05 for **LCP** and 1.87 for the rederence [Ru(bda)(pic)₂] (**Fig. S7**).

The quasi-first-order kinetics for **CCPs** was also confirmed by monitoring the decay of Ce^{IV} at 360 nm (**Fig. S8** and **S9**) on the basis of the following fact, i.e., $-d[A]/dt \sim -d[Ce^{IV}]/dt \sim v_i$. Based on the first 10 data points (**Fig. S9**), the scaling exponent α is estimated to be 1.11 and 1.05 for **CCP1** and **CCP3**, respectively (**Fig. S8**), consistent with the values obtained from oxygen-sensor measurements. The above experiments seem to imply that these **CCPs** and **LCP** heterogeneous catalysts oxidize water via direct single-site water nucleophilic attack

Recent electrochemical study on Ru(bad)-supported electrodes by Sun et al. demonstrated the significant influence of Ru-site microenvironment on the kinetic isotope effect (KIE),¹⁷ implicating the possible mechanism switch from **I2M** to **WNA** due to the interface confinement effect; however, no other experimental evidence was provided to further support such a structure-mechanism correlation. Without doubt, directly immobilizing Ru(bda)-sites into these **CCP** rigid polymeric framework can be an alternative to impose spatial confinement on catalytic sites. Our observation implied that the local confinement originated from the network rigidity induces the catalytic mechanism switch from **I2M** to **WNA** for these polymeric catalysts.

Note that the intramolecular dimerization of two neighboring Ru^V=O species could also lead to an apparent first-order kinetics process accompanied with a radical coupling mechanism.^{18, 19} To clarify this point, we further investigated how the initial reaction rate depends on the oxidant concentration. The results show that the value of v_i for **CCP1** and **CCP3** increases almost linearly with [Ce^{IV}] under stoichiometric amounts of CAN (**Fig. S11** and **S12**). The reaction kinetics is quasi-first-order on Ce^{IV} concentration based on quantitatively fitting results (**Fig. S11**), which is consistent with the observation by Würthner et al. in their macrocycle-systems.^{6,7} To further address whether O–H bond cleavage is involved in the rate-determining step, the kinetic isotope effect (KIE) of **CCP3** was tested by using D₂O as reaction solvent. The KIE_{H/D} value is expected to be > 2.0 if the proton-coupled process is involved; while it is generally between 0.7 ~ 1.5 if the catalytic mechanism is through the dimerization of two metal oxide.²⁰ The measured KIE_{H/D} value for **CCP3** is 2.4

New Journal of Chemistry Accepted Manuscript

(Fig. S13), which is much higher than the reported value (0.9) for $[Ru(bda)(pic)_2]$ homogeneous catalyst,^{6,7} further supporting the WNA mechanism.

All the above evidences ambiguously confirm that these polymeric catalysts catalyze water oxidation through the single-site **WNA** mechanism. For non-porous **LCP** catalyst, the observed **WNA** mechanism is reasonable because the mobility of active Ru sites of catalyst particles is greatly hindered due to the insoluble characteristics and compact interchain stacking (nonporous feature). Whereas for **CCP WOCs**, the features of porosity and 3D cross-linking are more likely to promote the thermal fluctuation and dimerization of neighboring Ru centers, resulting in **CCP** catalysts going through **I2M** mechanism. This is exactly what observed by Sun and his coworkers in their recent study on Ru(bad)-based cross-linked polymer film.¹⁷ The film was prepared by radical polymerization of [Ru(bda)(4-vinylpyridine)₂] monomers on electrode, and the KIE study revealed that the **I2M** mechanism was applied to the Ru(bad)-based polymer catalyst, which was attributed to the close spatial distance and flexibility of carbon-carbon linkage between Ru centers. Therefore, our results clear clarify that it is the space confinement effect imposed by network rigidity that ensures the isolation of individual Ru sites and dominates the **WNA** catalytic mechanism.

Correlation between Catalytic Performance and Catalyst Structure. In addition to mechanism study, we also tried to understand how the polymer network parameter affects the catalytic performance. **Fig. 7a** summarizes the experimental values of initial TOF (v_i/C_{Ru}) and TON for these polymer catalysts. As shown, the overall catalytic performance follows the order as: **CCP3** > **CCP1** > **LCP** ≥ **CCP2**. The highest activity was achieved for **CCP3** with TOF ~ 0.85 s⁻¹ (C_{Ru} = 70.5 µM) and TON ~ 290 (C_{Ru} = 70.5 µM), but it is kind of poorer than

13

the performance of reference [Ru(bda)(pic)₂] with TOF ~ 3.5 s⁻¹ ($C_{Ru} = 76.0 \mu M$) and TON ~ 670 ($C_{Ru} = 19.0 \mu M$) in water. However, it has to be noted that the higher performance of [Ru(bda)(pic)₂] was achieved by the usually much faster **I2M** mechanism, whereas the **CCPs** reported here work via **WNA** mechanism.



Fig. 7 (a) Plot of experimental TOF and TON values for LCP and CCPs, where $[Ce^{IV}] = 100$ mM, pH = 1.0 (HNO₃), and $C_{Ru} = 62.6$, 68.1, 63.8, and 70.5 μ M for LCP, CCP1, CCP2 and CCP3, respectively. (b) BET surface area (SA_{BET}) dependence of TOF and TON values for LCP and CCPs. (c) Experimental contact angles for LCP and CCPs. (d) Contact angle dependence of TOF and TON values for LCP and CCPs.

In addition, no correlation between the catalytic activity and SA_{BET} was observed (**Fig. 7b**), namely, **CCP2** with the highest SA_{BET} (55 m²/g) presented the lowest activity, which goes against our original conjecture. It is noted that when catalysis is performed inside porous materials, there is always a question as to whether the catalysis is only limited to the outermost surface of catalyst particles.⁸⁻¹⁰ Thus, we carried out contact angle measurement on these insoluble **CCP** materials to explore the **CCP**/water interfacial property (**Fig. 7c**). The results demonstrate that **LCP**, **CCP1** and **CCP2** are highly hydrophobic, reflected in the large

14

contact angles ($103^{\circ} \sim 110^{\circ}$), whereas **CCP3** is much less hydrophobic (83°). The replacement of pure water by HNO₃ (aq, pH ~ 1.0) further led to increased interfacial wettability. Especially for **CCP3**, the great difference in contact angles between pure water (83°) and HNO₃ (69°) can be rationalized by the fact that the protonation of triazine units can significantly enhance the hydrophilicity. Apparently, the catalytic activity negatively correlates with the contact agnle/interfacial energy (**Fig. 7d**). The above evidences imply that the diffusion process of reactant molecules (CAN and water), inside the porous network, might suffer great hindrance due to the large **CCP**/water interfacial energy. Thus, the catalysis is supposed to be limited only on the macroscopic surface of catalyst particles for **CCP1** and **CCP2**, whereas the catalysis is even probably allowed to occur in the outermost few porous layers near the surface for **CCP3**. Construction of fully hydrophilic cross-linked network is probably a good solution for the further enhancement of **CCP**/water interfacial wettability.

On the other hand, we noticed the the importance of incorporation of Ru(bda)-macrocyclic fragments into the **CCP** network for efficient catalysis. Namely, the best two polymeric catalysts are **CCP1** and **CCP3**, and both of them are constructed by ligands with plane-triangle configuration. Recent studies by Würthner et. al. have already demonstrated the cooperative effect of multi-Ru centers for efficient homogeneous catalysis, where a few metallosupramolecular macrocycle [Ru(bda)(bpb)]₃ **WOCs** were prepared by incorporating three Ru(bda) fragments into a cyclic arrangement using bpb (1,4-bis(pyrid-3'-yl)benzene) as the bridging ligand.^{6, 7} It was found that the [Ru(bda)(bpb)]₃ macrocycle could facilitate the preorganization of water molecules in the cavity and decrease the reaction activation energy, which was beneficial for the proton-coupled process. Similarly, such a preorganizationeffect is also supposed to exist for **CCP WOCs** containing Ru(bda)-macrocyclic fragments on

15

surface, which helps partially explain why CCP1 and CCP3 presented higher activities than CCP2 and LCP.



Fig. 8 (a)-(b) Long-term oxygen evolution curves by using different amounts of **CCP3** as **WOCs**. (c) Oxygen evolution curves by using [Ru(bda)(pic)₂] **WOC** under different storage time. (d) Oxygen evolution curves by using **CCP3 WOC** under different storage time.

Stability of CCP WOCs during Storage and Catalysis. To further examine the stability of CCP catalysts under reaction condition, we attempted to monitor the long-term oxygen evolution by using CCP3 as catalyst. As shown in Fig. 8a and 8b, after bubbling nitrogen gas into the solution phase, oxygen evolution was clearly observed within 2000 s, and the presented activity showed no obvious catalyst concentration dependence. In addition to reaction stability, the storage stability is also important to catalyst activity. It is known that the self-oxidation and ligand dissociation are considered to be the main degradation pathways for $[Ru(bda)L_2]$ catalyst family. Therefore, $[Ru(bda)L_2]$ catalyst solution is normally sensitive to air and needed to be used immediately after its preparation. Fig. 8c shows that, after the $[Ru(bda)(pic)_2]$ stock solution was stirred for 24 h, the solution color changed from brown to

green, which was also reflected in the shift in UV-vis spectra (**Fig. S14**). Accordingly, the catalytic rate dramatically decreased from 48.0 to 20.8 μ M/s. Whereas for **CCP3** (**Fig. 8d**), 20% of enhancement in activity was even observed when the stirring time was prolonged to 48 h. This can be rationalized that the prolonged strong shearing could further break the **CCP** particles into smaller sizes and expose more active Ru-centers. More importantly, the diffusion reflectance UV-vis spectra showed no obvious spectrum shift (**Fig. S14**), indicating that the structure of **CCP3** was intact after prolonged mechanical stirring.

All in all, the good stability in catalysis and storage is attributed to the 3D cross-linked structure, which prevents the self-oxidation and ligand dissociation. The best activity of **CCP3** is mainly attributed to the optimal balance between various factors, such as the high interfacial wettability, the moderate porosity and the existence of water-molecule preorganization effect.

Published on 08 January 2018. Downloaded by Fudan University on 19/01/2018 09:32:37

Though the apparent reactivity of small-molecule reference $[Ru(bda)(pic)_2]$ appears slightly higher than **CCP3**, such comparison must be viewed with caution because not all of the catalytic centers in polymeric catalyst are accessible during the catalysis in present system (as stated above). Thus, model calculation was further carried out to estimate the percentage (x%) of active Ru-sites in the total number of Ru-sites in heterogeneous catalysis, by assuming only the Ru-sites on the surface of the nanoscaled catalyst particles are account for the catalytic activity (**Fig. S15**, and calculation details in Supporting Information). One specific case was considered, i.e., the particle surface is totally occupied by well-defined Ru(bda)-macrocyclic fragments. By assuming the packing density of **CCP** particles (0.6 g/mL) and the average particle size (50 nm), the estimated x% is ~ 2.0%, indicating that only a small portion of Ru-sites is able to take part in the catalysis. This qualitative estimation is further consistent

with the following observation.



Fig. 9 (a) Schematic illustration of post-modification of CCP3 via pyridine/dmso exchange reaction. (b) Reaction time (*t*) dependence of oxygen concentration ([O₂]) by using CCP3_M as WOCs. (c) Experimental TOF and TON values for CCP3 and CCP3_M, where $C_{Ru} = 70.5 \mu M$ (CCP3) and $C_{Ru} = 17.63 \mu M$ (CCP3_M) were used in experiments. (d) Experimental contact angles for CCP3 and CCP3_M.

Post-modification of CCP Network via Pyridine/dmso Exchange Reaction. For heterogeneous catalysis, the number of catalytic centers located at the most surficial structure of network has been proven to be crucial.^{8, 21, 22} After polycondensation reaction, there is still a trace amount of inactive Ru(dmso)_x moieties remain on the network surface. To activate these potential Ru-sites, **CCP3** was further treated with pyridine/methanol solution to end-cap the dmso sites (**Fig. 9a**). Surprisingly, the post-modified **CCP3** catalysts (**CCP3**_M) showed dramatically enhancement in activity with impressive TOF ~ 4.6 s⁻¹ and TON ~ 750 in pure water (**Fig. 9b and 9c**), which is even superior to the performance of reference [Ru(bda)(pic)₂]. Preliminary kinetics study implies that the catalytic mechanism for the

modified CCP3 WOC is still based on the single-site WNA (Fig. S16).

Published on 08 January 2018. Downloaded by Fudan University on 19/01/2018 09:32:37

The successful insertion of pyridine into network is reflected in the enhanced vibration peak located at 1150 cm⁻¹ in FTIR spectra (**Fig. S17**). Diffusion reflectance UV-vis spectra also show slight red-shift (**Fig. S18**) for **CCP3**_M, probably due to the enhanced metal-to-ligand charge transfer interaction. Meanwhile, the interfacial wettability of **CCP3**/water seems to be unchanged after modification (**Fig. 9d**).

In addition to the end-capping effect, the possibility of dynamic ligand-exchange between free pyridine and L3 ligand cannot be excluded at present stage, which will disrupt the polymer network and expose more active centers for catalysis (**Fig. 9a**). The structural evolution during the ligand exchange process needs to be further investigated. On the other hand, the substituted pyridine-derivatives, such as 4-pyridine carboxylate and hydroxypyridine, might act as better modification reagents to regulate the interfacial wettability and enhance the activity of the resultant **CCP**. Further investigation of the post-modification of **CCP** catalysts is undergoing in our lab.

Electrochemical Study of CCP/nafion/ITO Film. The insolubility of **CCPs** in water makes these polymeric catalysts viable electrode materials for electrocatalytic water oxidation studies. Electrochemical activities of working electrodes based on **CCP**/nafion/ITO film were further investigated (**Fig. S19**). Working electrode was typically made by drop-casting 100 μ L of suspension containing 0.4 mg of **CCP** catalyst and 4 ~ 64 μ L of nafion solution (5%wt) onto an ITO electrode. The mass ratio of nafion and **CCP** (wt_{nafion}/wt_{CCP}) varied from 0.5 to 8.0. The electroactive area (1.5 cm²) was controlled with Kapton tape mask.



Fig. 10 (a) and (b) Repetitive cyclic voltammograms (CVs) for CCP1/nafion/ITO and CCP3/nafion/ITO electrodes at pH = 8.0 up to 1.50 V (100 mV/s). (c) Mass ratio of nafion and CCP (wt_{nafion}/wt_{CCP}) dependence of catalytic current at 1.50 V. (d) Repetitive cyclic voltammograms for CCP1/nafion/ITO electrode at pH = 8.0 up to 1.00 V (100 mV/s).

Fig. 10a and 10b show the typical cyclic voltammograms using CCP1 and CCP3 as active materials. Weak redox waves for Ru-species between 0.4 to 1.0 V (vs Ag/AgCl) were first observed, and followed by a large catalytic water oxidation wave with the onset potential $E_{onset} = \sim 1.0$ V. Control experiment by using bare nafion/ITO as electrode shows much higher overpotential and weaker electrocatalytic waves at 1.5 V (black curve, Fig. 10b). Under optimal nafion loading, catalytic currents as high as 0.55 and 0.53 mA/cm² can be achieved for CCP1 and CCP3, respectively (Fig. 10c and S19). Excess loading of nafion binder leads to thicker films and prevents the mass transport of water molecules.

In recent work reported by Antoni Llobet et al.,²³ they observed a decrease by ~ 20% in the intensity of electrocatalytic wave (Ru^{III/II} couple) and an increase by ~ 40% in the intensity at 0.9 V after 20 scan cycles for [Ru(bda)(pyridine)₂]-modified glass carbon electrode, which implies the depletion of the Ru–OH₂ active species from the surface of electrode and the

formation of more active RuO₂ species. When scan was carried out from 0.0 to 1.0 V for CCP1/nafion/ITO (Fig. 10d), the Ru^{III/II} couple at ~ 0.50 V can be more clearly seen as well as the electrocatalytic waves associated with the Ru^{IV/III} (0.7 V) and Ru^{V/IV} (0.9 V) couples. The weak signals for Ru^{IV/III} and Ru^{V/IV} couples are due to the slow proton-coupled electron transfer process in heterogeneous film.¹⁰ But most of all, the intensities at different potentials are almost constant after 5 cycles, indicating the good stability of CCP catalysts.

The durability of the hybrid electrode at high potential (1.5 V) was also evaluated. The catalytic current at 1.5 V decreases by 11% and 6% for **CCP1** and **CCP3** after 5 cycles (**Fig. 10a** and **10b**), respectively. **CCP3**/nafion/ITO maintains ~ 73% of initial intensity after 27 cycles (**Fig. S20**) under optimal condition. It is known that the main degradation pathway of [Ru(bda)L₂] catalyst family is through the dissociation of axial pyridyl ligands and diffusion of the cleaved fragments into the solution;²⁴ thus, the design idea of incorporating the catalytic site into cross-linked polymeric network helps impart a better stability through the cooperative chelate effect.

Conclusions

Published on 08 January 2018. Downloaded by Fudan University on 19/01/2018 09:32:37.

In summary, as a proof of concept, we demonstrated the feasibility of utilizing cross-linked coordination polymers (**CCPs**) with [Ru(bda)] complex for heterogeneous water oxidation. These porous polymeric catalysts oxidize water via the single-site water nucleophilic attack. Post-modification via pyridine ligand exchange reaction allows **CCP** catalyst to reach high TON and TOF values of > 750 and > 4.6 s⁻¹. Meanwhile, these **CCP** catalysts also present good electrochemical activities on ITO electrodes, and the durability of electrode was greatly improved due to their unique network structure. The results clearly indicate that cross-linked

coordination polymers could preserve catalytic Ru sites under harsh oxidative conditions, among other benefits of the heterogeneous catalysis. Our investigation also reveals the potential for further improving the catalyst efficiency and active site utilization through rational design of polymeric catalyst at both molecular and morphological levels.

Experimental Section

Unless otherwise stated, all chemicals obtained from commercial suppliers were used without further purification. $[Ru(bda)(dmso)_2]$ and $[Ru(bda)(pic)_2]$ were prepared according to literatures.^{25, 26} Ligands L0-L2 were synthesized through typical Suzuki-coupling procedure,¹⁴ and the synthesis detailed can be found in the Supporting Information. FTIR spectra were recorded on Nicolet[™] iS[™]10 FTIR Spectrometer as KBr pellets. UV-vis absorption spectra were measured on a Shimadzu UV-3600 device. Diffuse reflectance accessory was used for the measurement of solid samples. Solid-state ¹³C-NMR spectra were recorded on a Bruker DRX-500 spectrometer. TGA measurement of the polymers was performed using a TA O600 instrument under nitrogen with a heating rate of 15 °C/min. DSC was performed on a Q2000 differential scanning calorimetry from TA Instruments under a nitrogen flow rate of 100 mL/min with a scanning rate of 10 °C/min. The contact angle measurements were performed using a KSV (Helsinki, Finland) CAM 200 contact angle goniometer, and the CCP powders were compressed in to thin discs for measurement. SEM images were recorded on FEI NanoSEM. Wide angle powder X-ray diffraction (XRD) patterns were collected using a Bruker D8 diffractometer with a Cu K α X-ray source ($\lambda = 0.154$ nm) operating at 40 kV and 40 mA by depositing fine-powder on glass substrate. Nitrogen BET surface areas were measured using a Micromeritics ASAP 2010 system.

Synthesis of LCP and CCPs through Ligand Exchange Reaction. The synthesis procedure for **CCP3** is as follows: [Ru(bda)(dmso)₂] (625 mg, 1.25 mmol) and L3 ligand monomer (261 mg, 0.835 mmol) were dissolved in a degassed mixture of chloroform and methanol (60 mL + 30 mL) and heated for 24 h at 65 °C under N₂. The mixture was cooled to room temperature, separated by centrifugation, and extracted successively with methanol, acetone, THF and dichloromethane. The final product was dried in vacuum for 12 h at 45 °C to give **CCP3** (yield 95%). The synthesis procedures for **LCP** (yield 75%), **CCP1** (yield 85%) and **CCP2** (yield 93%) are identical with that of **CCP3**.

Post-modification of CCP3 Network via Pyridine/dmso Exchange Reaction. In a glove box, the as-prepared **CCP3** (100 mg) was suspended in anhydrous methanol (20 mL), and an excess of distilled pyridine (500 uL) was further added. The vial was sealed and the mixture was stirred at 50 °C for 12 hrs. The insoluble polymer was recycled by centrifugation, and further washed with methanol, acetone and dichloromethane. The product was dried in vacuum for 12 h at 45 °C to give **CCP3_M** (80 mg).

Published on 08 January 2018. Downloaded by Fudan University on 19/01/2018 09:32:37

Kinetics Study on the Chemically Driven Water Oxidation Reaction Monitored by an Oxygen Sensor. The Ce^{IV} driven water oxidation reactions were performed under ambient conditions in a 25 mL glass vial with a rubber stopper. Before measurement, the degassed water suspension of CCP (1.0 mg/mL) was stirred vigorously for 24 h in a sealed vial. Water suspension with different C_{Ru} was prepared by diluting the mother suspension. In each experiment, 548 mg of cerium(IV) ammonium nitrate (CAN) was dissolved in 9.5 mL of a HNO₃ solution (pH 1.0) in a 25 mL glass vial capped with a rubber stopper. The CAN solution was bubbling with N₂ for 10 min. Then, 0.5 mL of air-free CCP water suspension

New Journal of Chemistry Accepted Manuscript

was injected into the reaction vial through a septum via an air-tight syringe under vigorous stirring. The produced O_2 in solution phase was recorded in-situ by an oxygen sensor (Unisense, OX-N). Calibration of oxygen sensor was carried out before each measurement. For turnover number (TON) measurement, the reaction was stopped after 6 h, and 300 µL of the gas in head space were taken out with a gas-tight syringe and injected into the gas chromatograph with a thermal conductivity detector using argon as carrying gas. A few injections of known amount of O_2 were used as calibration standards. The O_2 concentration was obtained based on 2 injections.

Kinetics Study on the Chemically Driven Water Oxidation Reaction Monitored by UV-vis Spectrometer. The water oxidation kinetics with respect of the concentrations of Ce^{IV} and CCP catalyst was also studied by monitoring the loss of Ce^{IV} under pH 1.0 using UV-vis. The reaction kinetics depending on the concentration of CCP catalyst was measured under the condition as follows: the concentration of Ce^{IV} was kept 1.12 mM for each run, but the concentration of CCPs was changed from $2.5 \sim 20.0 \mu$ M. The reaction kinetics depending on the concentration of Ce^{IV} was measured under the condition as follows: the concentration of CCP catalyst was kept at 20.0 μ M (CCP1) and 10 μ M (CCP3) for each run, but the concentration of Ce^{IV} was changed from 1.12 mM, 1.96 μ M, 2.80 mM, to 3.60 mM. Typically, the CCP water suspension was rapidly injected into the quartz cell containing 3 mL of Ce^{IV} under vigorous stirring. The UV-vis spectrum was recorded after the solution was vigorously stirred for ~ 3 s.

Electrochemical Study. Electrochemical measurements were performed on a commercial instrument with a standard three-electrode configuration: reference electrode: Ag/AgCl (3 M

KCl aqueous solution), working electrode: ITO, auxiliary electrode: Pt slice (~ 2.5 cm²). 150 mL of 0.1 M K₂HPO₄ solution (pH = 8.0) was used as electrolyte solution, and 3 M HNO₃ was used to adjust the pH value. Scan rate was fixed at 100 mV/s. Before measurement, a water suspension of **CCP** (4.0 mg/mL) in H₂O was stirred vigorously for 24 h in a sealed vial. Working electrode was made by drop-casting 100 μ L of suspension containing 0.4 mg of **CCP** catalyst and 4 ~ 64 μ L of nafion solution onto an ITO electrode. Kapton tape functions as mask to control the electroactive area to be 1.5 cm².

Acknowledgements

The National Natural Scientific Foundation of China Projects (21774116 and 51703216) are gratefully acknowledged.

Notes and references

- 1 X. Chen, S. Shen, L. Guo and S. S. Mao, Chem. Rev., 2010, 110, 6503-6570.
- 2 J. D. Blakemore, R. H. Crabtree and G. W. Brudvig, Chem. Rev., 2015, 115, 12974-13005.
- 3 S. J. A. Moniz, S. A. Shevlin, D. J. Martin, Z.-X. Guo and J. Tang, *Energy Environ. Sci.*, 2015, 8, 731-759.
- 4 L. Duan, F. Bozoglian, S. Mandal, B. Stewart, T. Privalov, A. Llobet and L. Sun, *Nat. Chem.*, 2012, **4**, 418-423.
- 5 R. Staehle, L. Tong, L. Wang, L. Duan, A. Fischer, M. S. G. Ahlquist, L. Sun and S. Rau, *Inorg. Chem.*, 2014, **53**, 1307-1319.
- 6 M. Schulze, V. Kunz, P. D. Frischmann and F. Würthner, Nat. Chem., 2016, 8, 576-583.
- 7 V. Kunz, M. Schulze, D. Schmidt and F. Würthner, ACS Energy Letters, 2017, 2, 288-293.

- 25
- 8 C. Wang, J.-L. Wang and W. Lin, J. Am. Chem. Soc., 2012, 134, 19895-19908.
- 9 B. Nepal and S. Das, Angew. Chem. Int. Ed., 2013, 52, 7224-7227.
- 10 R. E. Hansen and S. Das, Energy Environ. Sci., 2014, 7, 317-322.
- 11 D. Liu, Q. Liu, Y. Li, M. Wang, X. Yang, T. Wu, C. Moorefield, P. Wang and G. R. Newkome, *Dalton Trans.*, 2015, **44**, 11269-11273.
- 12 R. Mishra, E. Ülker and F. Karadas, *ChemElectroChem*, 2016, **3**, 1-7.
- 13 G. Zhang, Z.-A. Lan and X. Wang, Angew. Chem. Int. Ed., 2016, 55, 15712-15727.
- 14 L. Li, Z. Cai, Q. Wu, W.-Y. Lo, N. Zhang, L. X. Chen and L. Yu, J. Am. Chem. Soc., 2016, 138, 7681-7686.
- 15 L. Li, W.-y. Lo, Z. Cai, N. Zhang and L. Yu, Macromolecules, 2016, 49, 6903-6909.
- 16 J. Weber and A. Thomas, J. Am. Chem. Soc., 2008, 130, 6334-6335.
- 17 F. Li, K. Fan, L. Wang, Q. Daniel, L. Duan and L. Sun, ACS Catal., 2015, 5, 3786-3790.
- 18 Y. Jiang, F. Li, B. Zhang, X. Li, X. Wang, F. Huang and L. Sun, Angew. Chem. Int. Ed., 2013, 52, 3398-3401.
- 19 L. L. Zhang, Y. Gao, Z. Liu, X. Ding, Z. Yu and L. C. Sun, *Dalton Trans.*, 2016, **45**, 3814-3819.
- 20 H. Yamada, W. F. Siems, T. Koike and J. K. Hurst, J. Am. Chem. Soc., 2004, 126, 9786-9795.
- 21 X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen and M. Antonietti, *Nat. Mater.*, 2009, 8, 76-80.
- 22 V. W.-h. Lau, M. B. Mesch, V. Duppel, V. Blum, J. Senker and B. V. Lotsch, *J. Am. Chem. Soc.*, 2015, **137**, 1064-1072.
- 23 R. Matheu, L. Francàs, P. Chernev, M. Z. Ertem, V. Batista, M. Haumann, X. Sala and A.

New Journal of Chemistry Accepted Manuscript

Llobet, ACS Catal., 2015, 5, 3422-3429.

- 24 L. Duan, C. M. Araujo, M. S. G. Ahlquist and L. Sun, Proc. Natl. Acad. Sci., 2012, 109, 15584-15588.
- 25 F. Li, B. Zhang, X. Li, Y. Jiang, L. Chen, Y. Li and L. Sun, *Angew. Chem. Int. Ed.*, 2011, 50, 12276-12279.
- 26 L. Duan, L. Wang, A. K. Inge, A. Fischer, X. Zou and L. Sun, *Inorg. Chem.*, 2013, 52, 7844-7852.

For table of content used only



Cross-linked coordination polymers (**CCPs**) with a formula $\{[Ru(bda)]_xL_y\}_n$ were developed as heterogeneous catalysts for water oxidation in organic solvent-free system.