## ChemComm





**View Article Online** 

Cite this: Chem. Commun., 2014, 50, 13948

Received 3rd September 2014, Accepted 11th September 2014

DOI: 10.1039/c4cc06959e

www.rsc.org/chemcomm

## Immobilization of a molecular catalyst on carbon nanotubes for highly efficient electro-catalytic water oxidation<sup>†</sup>

able approaches are urgently needed.

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Electrochemically driven water oxidation has been performed using a molecular water oxidation catalyst immobilized on hybrid carbon nanotubes and nano-material electrodes. A high turnover frequency (TOF) of 7.6 s<sup>-1</sup> together with a high catalytic current density of 2.2 mA cm<sup>-2</sup> was successfully obtained at an overpotential of 480 mV after 1 h of bulk electrolysis.

The world today is eagerly demanding a renewable energy source as a replacement for fossil fuels that cause environmental and climate concerns. Artificial photosynthesis, which captures and stores solar energy, may provide a sustainable choice.<sup>1,2</sup> Most research efforts in this field have been focused on the development of efficient water oxidation catalysts (WOCs) and proton reduction catalysts to reduce the energy barrier of water splitting reactions.<sup>3–5</sup> Several other aspects, however, have to be considered before the construction of a practical water splitting device. One of the most challenging tasks is to employ these catalysts in functional devices without affecting their performance evaluated under homogeneous system.

For implementation of any WOC in electrocatalytic or photoelectrocatalytic devices for water splitting, the catalysts have to be immobilized on the surface of a conductive electrode or semiconductor.<sup>6,7</sup> One widely applied approach is to ligate molecular catalysts on the surface of the electrode through carboxylic or phosphoric ester linkage.<sup>8–10</sup> Other approaches, reported by our groups recently, include the immobilization of catalysts [**Ru**(**pdc**)(**pic**)<sub>3</sub> pdc = 2, 6-pyridine dicarboxylic acid] on a conductive carbon surface through click chemistry<sup>11</sup> and attachment of complex [**Ru**(**bda**)(Py-pyrene)<sub>2</sub>, **bda** = 2,2'-bipyridine-6,6'-dicarboxylic acid]

<sup>†</sup> Electronic supplementary information (ESI) available. See DOI: 10.1039/c4cc06959e



onto multi-walled carbon nanotubes (MWCNTs) through electrostatic  $\pi$ - $\pi$  stacking interactions.<sup>12</sup> However, difficulties in modifying

the substrate catalyst and fabricating the device hindered further

application of these methods. Therefore, novel and widely applic-

alized CNTs, i.e., covalent and non-covalent functionalization. The

former approach disrupts the  $\pi$ -networks of CNTs, which creates

possible losses in their mechanical and electrical properties. The

latter approach is based on the adsorption of appropriate molecules

on the CNTs surface, which preserves their desired properties, and this approach is widely used.<sup>13–15</sup> Cao *et al.* modified CNTs with

surfactants such as sodium dodecyl sulfate (SDS),<sup>16</sup> in their method,

the hydrophobic aliphatic chain can interact with the surface of the

CNTs, which inspired us. Herein, we report a carbon nanotubes

based nano-material that was functionalized by molecular WOC

**Ru-C12** (Scheme 1) for highly efficient electrocatalytic water oxidation. The catalyst core is the well-defined mononuclear

WOC Ru(pdc)(pic)<sub>3</sub>. The dodecyloxy group was used here in

order to attach the catalyst to the MWCNT. A benefit of this

design is that the long hydrophobic aliphatic chain group can

provide a linkage to the MWCNTs, resulting in an electro-

catalytic nanomaterial. In addition, this dodecyloxy group will

decrease the solubility of Ru-C12 in water, which is an impor-

tant consideration for the application of the self-assembled

oxidation, cyclic voltammetry (CV) measurements were conducted

To measure the electro-catalytic activity of Ru-C12 for water

system between the Ru-C12 and MWCNTs.

Carbon nanotubes have extraordinary electronic, thermal, optical, and mechanical properties. There are two main routes to function-

Scheme 1 Structures of complexes Ru-C12 and Ru(pdc)(pic)<sub>3</sub>.

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Fig. 1 Cyclic voltammograms (CV) of 1 mM **Ru-C12** (red line) and [**Ru(pdc)(pic)**<sub>3</sub>] (blue line) in 0.1 M potassium phosphate buffer (pH 7.0, 10% acetonitrile), with glassy carbon as the working electrode, Ag/AgCl as the reference electrode, and Pt as the counter electrode. Scan rate is 100 mV s<sup>-1</sup>.

both in organic solvent and aqueous solution. Fig. S4 (ESI<sup>†</sup>) shows CV curves of **Ru-C12** and [**Ru(pdc)(pic)**<sub>3</sub>] in dichloromethane. The  $E_{1/2}$  Ru( $\pi/\pi$ ) of **Ru-C12** is dramatically moved to a more negative potential compared to [**Ru(pdc)(pic)**<sub>3</sub>]. This is caused by the electron donating ability of the dodecyloxy group, which enhances the electron density of ruthenium center. Fig. 1 shows CV curves in aqueous pH 7.0 phosphate buffer solution of **Ru-C12** and [**Ru(pdc)(pic)**<sub>3</sub>]. **Ru-C12** exhibits one irreversible Ru( $\pi$ ) to Ru( $\pi$ ) oxidation peak at  $E_{on} = 0.82$  V  $\nu$ s. NHE, indicating the ligand exchange reaction of picoline by water molecule during the redox process as discovered earlier by our group with the core catalyst [**Ru(pdc)(pic)**<sub>3</sub>].

An onset of catalytic water oxidation current by **Ru-C12** was observed at around 1.2 V *vs.* NHE, which is very close to that by  $[\mathbf{Ru}(\mathbf{pdc})(\mathbf{pic})_3]$ . The catalytic current, however, showed more enhancement in the case of **Ru-C12** when potential beyond 1.2 V was applied. Two possible reasons are ascribed to the stronger catalytic current triggered by **Ru-C12** than that by  $[\mathbf{Ru}(\mathbf{pdc})(\mathbf{pic})_3]$ : (1) the electron donating effect of dodecyloxy substituent in **Ru-C12** is beneficial in overcoming the rate-limiting step in the catalytic cycle, assuming that **Ru-C12** and  $[\mathbf{Ru}(\mathbf{pdc})(\mathbf{pic})_3]$  have the same catalytic pathway. (2) The dodecyloxy chain of **Ru-C12** is attracted to the surface of glassy carbon electrode, leading to higher concentration of **Ru-C12** than that of  $[\mathbf{Ru}(\mathbf{pdc})(\mathbf{pic})_3]$  in the interface layer of the working electrode.

**Ru-C12** was successfully immobilized into two types of CNTs: MWCNTs and MWCNTs functionalized with carboxyl group (MWCNTsCOOH). After mixing MWCNTs with **Ru-C12** in water, the resulting solution exhibited a light brown color, indicating that a certain amount of **Ru-C12** still remained in the liquid phase. In contrast, upon mixing MWCNTsCOOH with the same concentration of **Ru-C12**, a colourless solution with precipitation was observed as shown in Fig. S5 (ESI†), which suggests a complete graft of **Ru-C12** onto the surface of MWCNTsCOOH. This is probably because, when the surface of MWCNTsCOOH immobilized by **Ru-C12** becomes more hydrophobic, precipitate could be obtained from the solution. Notably, this precipitation behaviour





Fig. 2 SEM image of the surface of [Ru-C12-MWCNTsCOOH@GDL] electrode.

is promising to prepare an electro-catalytic nanomaterial. In other words, we can easily collect the precipitates and apply them on some conductive substrates for further device making. In the present work, the **Ru-C12**-CNTs precipitates were collected by filtration through a gas diffusion layer (GDL). In such a simple way, GDL-based electrodes were prepared whose size could be tailored.

SEM and EDX experiments show that the nano-structure is well retained and presents a large specific surface area after **Ru-C12–** MWCNTsCOOH is adsorbed on GDL (Fig. 2). The Ru content is 3.26 wt% on the [**Ru-C12–**MWCNTsCOOH@GDL] electrode (Table S1, ESI†), while there is no Ru on [MWCNTsCOOH@GDL] electrode (Table S2, ESI†). Fig. S9 and S11 (ESI†) show that the distribution of [**Ru-C12–**MWCNTsCOOH@GDL] is more uniform than that of bare [MWCNTsCOOH@GDL]. These observations confirmed that the electrodes were successfully prepared with the achievement of a **Ru-C12–**MWCNTsCOOH@GDL] composition electro-active nanomaterial.

Catalytic activities of water oxidation for the functionalized catalyst-CNTs@GDL electrodes were investigated in a 50 mM potassium phosphate buffer solution. Both the functionalized electrodes and the pristine electrode (control) were examined as working electrodes. Because the surfaces of CNTs are highly hydrophobic, a rotating disk electrode was employed to get rid of bubbles (generated oxygen) on the surface and to ensure an effective contact between the surface of the working electrode and water during bulk electrolysis.

When [MWCNTsCOOH@GDL] was used as a blank, no significant catalytic current could be observed below the applied potential until 1.6 V (vs. NHE) in CVs (Fig. 3), which indicates that MWCNTsCOOH is inactive for water oxidation. Furthermore, the performance of [MWCNTs@GDL] is similar to that of [MWCNTsCOOH@GDL], where almost no catalytic current can be observed. When [**Ru(pdc)(pic)**<sub>3</sub>] was employed on CNTs electrodes, the formed [**Ru(pdc)(pic)**<sub>3</sub>-MWCNTsCOOH@GDL] electrode shows only a slight enhancement in the catalytic current in comparison to the blank electrode [MWCNTsCOOH@GDL]. In contrast, when **Ru-C12** was employed, significant enhancement of catalytic current was observed for the formed [**Ru-C12**-MWCNTsCOOH@GDL] electrode.

The significant enhancement in catalytic current is ascribed to the large amount of catalyst loading on the electrode and to



Fig. 3 CVs of [**Ru-C12**–MWCNTsCOOH@GDL] electrode (blue), [**Ru-C12**–MWCNTs@GDL] electrode (green), [**Ru(pdc)(pic)**<sub>3</sub>–MWCNTsCOOH@GDL] electrode (red), without catalyst only [MWCNTsCOOH@GDL] (light blue), without catalyst only [MWCNTs@GDL] (pink), only GDL (black). All CV curves were obtained by using rotating disk electrode (1000 rpm, 0.2 cm<sup>2</sup>) as working electrode, Ag/AgCl as the reference electrode, and Pt as the counter electrode in aqueous solution (phosphate buffer, pH 7.0, ionic strength = 0.1), with scan rate of 100 mV s<sup>-1</sup>.

the long hydrophobic aliphatic chain assisted immobilization of Ru-C12 on MWCNTsCOOH. [Ru-C12-MWCNTs@GDL] was used as a reference in comparison to the [Ru-C12-MWCNTsCOOH@GDL] electrode, whereas both of them exhibit an identical redox waves for the Ru(II) to Ru(III) and an onset potential of uprising current at around 1.15 V. These potentials are consistent with our observation of the electrochemical analysis of WOC Ru-C12 in homogeneous conditions. However, the catalytic current of [Ru-C12-MWCNTsCOOH@GDL] is much higher than that of [Ru-C12-MWCNTs@GDL] electrode. This might be due to the larger loading amount of catalyst on the surface of MWCNTsCOOH than MWCNTs, as discussed above. Another reason could be attributed to the carboxyl group, -COOH, in MWCNTsCOOH, which might form a hydrogen bonding network with water molecules, making the electrode surfaces have better contact with water in the buffer solution.

To determine the strength of the interaction between **Ru-C12** and the surfaces of the CNTs and stability, the [**Ru-C12–**MWCNTsCOOH@GDL] electrode was rotated (1000 rpm) for 2 h without applying any potential. CV measurements (Fig. S6, ESI†) were carried out before and after rotation, and they show almost identical CVs, which suggests that both the catalysts and the CNTs are strongly attached to the GDL, demonstrating a steady and stable combination among the three components in [**Ru-C12–**MWCNTsCOOH@GDL].

The effective coverage of functional WOCs ( $\Gamma_0$ , mol cm<sup>-2</sup>) on the [**Ru-C12–**MWCNTsCOOH@GDL] electrode surface was estimated according to an established method.<sup>17</sup> According to eqn (S1) (ESI†), the peaks currents of Ru(II) to Ru(III) redox couple and the scan rate were supposed to follow a linear relationship. When the scan rates were increased from 25 to 300 mV per second, the peak currents of Ru(II) to Ru(III) to Ru(III) to Ru(III) to the scan rate (Fig. S8, ESI†). An average catalyst coverage of 8.5 ± 0.4 (10<sup>-10</sup> mol cm<sup>-2</sup>) was obtained from three independent measurements. This average

catalyst coverage is far less than the amount of **Ru-C12** loading (0.24 mg cm<sup>-2</sup>, see ESI†), because only the outside superficial layer of the hybrid material contacts with the aqueous electrolyte and responds to the CV sweep.

In comparison to our previous study, where  $[\mathbf{Ru}(\mathbf{pdc})(\mathbf{pic})_3]$ was immobilized on conductive carbon surface *via* covalent bonding with an effective loading of  $1.2 \pm 0.4(10^{-10} \text{ mol cm}^{-2})$ ,<sup>11</sup> the effective loading of catalyst in the present study was significantly improved. More importantly,  $\Gamma_0$  in the present work was estimated by CV performed under aqueous conditions, same as where catalytic O<sub>2</sub> evolution was carried out, whereas the loading amount of catalyst in our previous work was estimated in organic solvent. Therefore, we believe that the catalyst loading  $\Gamma_0$  represents the realistic amount of catalysts involved in electro-catalytic water oxidation. Moreover, the value of  $\Gamma_0$  was expected to be significantly enhanced if a conducting supporting material with larger specific surface was used instead of GDL.

The electro-catalytic activity of **[Ru-C12–**MWCNTsCOOH@GDL] was further evaluated by chronoamperometric experiments in a pH 7.0 phosphate buffer. In a typical experiment, the current density was monitored continuously under a sequence of applied potential steps in the range from 1.12 to 1.32 V (Fig. 4). TOFs were calculated according to eqn (S2) (ESI<sup>+</sup>).

The catalytic current density measured on [**Ru-C12–**MWCNTs-COOH@GDL] electrode as a function of  $\eta$  followed a Tafel behaviour (the inset in Fig. 5). The logarithm of yielded TOFs varies linearly on the applied overpotentials from 300 to 500 mV. A TOF of 5.1 s<sup>-1</sup> was achieved at  $\eta$  = 350 mV, while it reaches 13.7 s<sup>-1</sup> at  $\eta$  = 500 mV. At 1.3 V, the calculated TOF is 12.4 s<sup>-1</sup>, which is the initial TOF for bulk electrolysis. Bulk electrolysis experiments (which will be discussed later) show that the faradaic efficiency is nearly 100%; hence, the initial TOF obtained here is credible.

The overpotential  $\eta$  refers to the additional voltage to the thermodynamically required oxidation potential of water at pH 7.0 (*E* = 0.82 vs. NHE). Under an applied overpotential  $\eta$  beyond 350 mV,



Fig. 4 Chronoamperometric current densities measured in phosphate buffer (pH 7.0, IS = 0.1 M) at [**Ru-C12**–MWCNTsCOOH@GDL] (red) and [MWCNTsCOOH@GDL] (black) under the application of sequential potential steps.



Fig. 5 TOF plot of [**Ru-C12**–MWCNTsCOOH@GDL] electrode as a function of overpotential  $\eta$ . The inset is Tafel plots showing current density of [**Ru-C12**–MWCNTsCOOH@GDL] electrode vs.  $\eta$ .

an appreciable catalytic current was observed for [**Ru-C12**– MWCNTsCOOH@GDL], while a negligible current was seen for the control electrode [MWCNTsCOOH@GDL]. This difference in current densities became quite significant at  $\eta = 500$  mV, indicating a much more effective Faraday process that is attributed to a more efficient catalytic water oxidation occurred on the [**Ru-C12**–MWCNTsCOOH@GDL] surface.

Bulk electrolysis was carried out with a controlled potential of 1.3 V vs. NHE on [**Ru-C12–**MWCNTsCOOH@GDL] in 50 mM potassium phosphate buffer for a time period of 1 h and 15 h. The corresponding current density was recorded and has been shown in Fig. S14a (ESI†). Based on the current, the total charge passed through the cell was calculated. The amount of charge that passed the electrode was divided by 4F to get a theoretical  $O_2$ yield, which was 4.9 and 31.2 µmol for 1 h and 15 h, respectively. The real oxygen evolution was monitored by a fluorescence-based oxygen sensor fixed in the headspace of a gas-tight cell. At the end of experiment, the amount of oxygen was calibrated by injecting 0.5 mL headspace gas sample into GC. Product of 4.7 µmol  $O_2$ after 1 h and 29.0 µmol  $O_2$  after 15 h were confirmed, corresponding to a faradaic efficiency of 96% and 93%, respectively.

The average TOF based on the overall TON is 7.6 s<sup>-1</sup> during 1 h and 3.5 s<sup>-1</sup> during 15 h electrolysis experiments (Fig. S14b, ESI†). This decay of TOF during bulk electrolysis suggests a decrease in the catalytic rate probably due to the decomposition of the catalyst. Although not all catalysts in [**Ru-C12–MWCNTsCOOH@GDL**] are able to remain intact, the stability of the immobilized catalysts is critically improved in comparison to [**Ru(pdc)(pic)**<sub>3</sub>] evaluated under homogeneous catalytic conditions.<sup>18</sup>

After 15 h electrolysis experiments driven by a relatively low potential 1.3 V ( $\nu$ s. NHE), the current density of 0.84 mA cm<sup>-2</sup> retained, a TON of  $1.7 \times 10^5$ , and an average TOF of  $3.5 \text{ s}^{-1}$  were obtained. Table S3 (ESI†) lists the performance of [**Ru-C12**–MWCNTsCOOH@GDL] in the current work and that of previously reported anodes for electrocatalytic water oxidation, including incorporated catalysts by covalent bond to metal

oxide nanoparticles,<sup>8,10</sup> electrostatic interactions with CNTs decorated by polyamidoamine ammonium dendrimers,<sup>19</sup> and our previous study where the complex [Ru(bda)(Py-pyrene)2] was attached to MWCNTs through electrostatic or  $\pi$ - $\pi$  stacking interactions.<sup>12</sup> [**Ru-C12–**MWCNTsCOOH@GDL] is clearly superior to any other system in the table in terms of overpotential, current density, TON and TOF.

In summary, a molecular WOC Ru-C12 with a long alkyl chain has been successfully synthesized and fully characterized. This complex has been immobilized on CNTs through the hydrophobic interaction forming a hybrid nanomaterial, which can be easily deposited onto GDL. This fabricated [Ru-C12-MWCNTsCOOH@GDL] electrode not only preserves the water oxidation activity of the molecular catalyst, but also exhibits an essentially high initial TOF of 12.4 s<sup>-1</sup>. Furthermore, an average current density of 0.84 mA cm<sup>-2</sup>, corresponding to an impressive TOF of 3.5  $s^{-1}$ , was achieved after 15 h bulk electrolysis at overpotential of 480 mV in pH 7.0 buffer. This methodology provides a simple and reliable approach for transformation from a homogeneous catalyst to a functional electrochemical electrode for a total water splitting cell (as shown by the video in ESI<sup>†</sup>). Further research is being carried out to improve the stability of the system towards practical implementation.

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