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# High chlorine evolution performance of electrochemically reduced TiO<sub>2</sub> nanotube array coated with a thin RuO<sub>2</sub> layer by the self-synthetic method†

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Recently, reduced TiO<sub>2</sub> nanotube arrays *via* electrochemical self-doping (r-TiO<sub>2</sub>) are emerging as a good alternative to conventional dimensionally stable anodes (DSAs) due to their comparable performance and low-cost. However, compared with conventional DSAs, they suffer from poor stability, low current efficiency, and high energy consumption. Therefore, this study aims to advance the electrochemical performances in the chlorine evolution of r-TiO<sub>2</sub> with a thin RuO<sub>2</sub> layer coating on the nanotube structure (RuO<sub>2</sub>@r-TiO<sub>2</sub>). The RuO<sub>2</sub> thin layer was successfully coated on the surface of r-TiO<sub>2</sub>. This was accomplished with a self-synthesized layer of ruthenium precursor originating from a spontaneous redox reaction between Ti<sup>3+</sup> and metal ions on the r-TiO<sub>2</sub> surface and thermal treatment. The thickness of the thin RuO<sub>2</sub> layer was approximately 30 nm on the nanotube surface of RuO<sub>2</sub>@r-TiO<sub>2</sub> without severe pore blocking. In chlorine production, RuO<sub>2</sub>@r-TiO<sub>2</sub> exhibited higher current efficiency (~81.0%) and lower energy consumption (~3.0 W h g<sup>-1</sup>) than the r-TiO<sub>2</sub> (current efficiency of ~64.7% and energy consumption of ~5.2 W h g<sup>-1</sup>). In addition, the stability (ca. 22 h) was around 20-fold enhancement in RuO<sub>2</sub>@r-TiO<sub>2</sub> compared with r-TiO<sub>2</sub> (ca. 1.2 h). The results suggest a new route to provide a thin layer coating on r-TiO<sub>2</sub> and to synthesize a high performance oxidant-generating anode.

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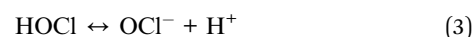
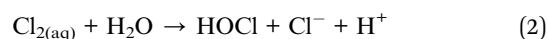
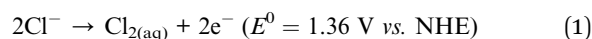
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## 1. Introduction

The electrochemical oxidation process (EOP) has emerged as an alternative to the conventional oxidation process because of its relatively simple facilities, maintenance, and accessibility.<sup>1–8</sup> In addition, as the need for a decentralized water treatment system has increased, the spectrum of EOP's application is broadening from urban to rural areas and developing countries.<sup>2,4,9–11</sup> The process controls contaminants by generating oxidants on-site. In particular, chlorine (Cl<sub>2</sub>) has been widely used to remove microorganisms, organic matters, and ammonia effectively along with other oxidants such as ozone, hydroxyl, and sulphate radicals.<sup>1,4,5,10,12–16</sup> The generated Cl<sub>2</sub> diffuses to the bulk

solution (below eqn (1)–(3)), and they exist three major species including Cl<sub>2</sub> (pH < 3), HOCl (pH 3–8), and OCl<sup>–</sup> (pH > 8).<sup>1</sup>



Moreover, Cl<sub>2</sub> is considered as a disinfectant to protect from the infectious COVID-19 in the water, sanitation, and hygiene (WASH) field by World Health Organization (WHO),<sup>17</sup> and several researchers suggested using it for treating the wastewater from hospital or household against potentially dangerous coronavirus.<sup>18,19</sup> Thus, practically, the Cl<sub>2</sub> generation system by EOP has a lot of attention with the advantages and is thought to be a suitable technology for small communities to overcome the disease.

For the high efficiency of EOP, the anode material is a pivotal factor governing oxidant species, energy consumption, and cost-effectiveness. A dimensionally stable anode (DSA; RuO<sub>2</sub>, IrO<sub>2</sub>, etc.) has an excellent electrochemical property for chlorine evolution reaction (CIER),<sup>5,14,20–27</sup> but, one obstacle in the effective use of DSA is the high manufacturing cost based on the inclusion of expensive noble metals.

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In this regard, recently, a reduced TiO<sub>2</sub> nanotube array (r-TiO<sub>2</sub>), which can be simply fabricated by electrochemical self-doping of an anatase TiO<sub>2</sub> nanotube array (a-TiO<sub>2</sub>), has attracted much attentions as a promising electrode in electrochemical ClER.<sup>11,28–30</sup> The self-doping simply converts Ti<sup>4+</sup> in a-TiO<sub>2</sub> to Ti<sup>3+</sup> *via* the intercalation of protons as self-dopants, potentially leading to high electrocatalytic activity in the generation of oxidants with high surface area and low-cost.<sup>28,31</sup> In spite of its advantages, r-TiO<sub>2</sub> has unfortunately suffered from a poor long-term service time, low current efficiency and high energy consumption in chlorine production.

Therefore, this study aimed to enhance the chlorine generation performance of r-TiO<sub>2</sub> with a simple thin layer coating of RuO<sub>2</sub> as an excellent anode material (RuO<sub>2</sub>@r-TiO<sub>2</sub>). This RuO<sub>2</sub> thin layer was coated on the surface of r-TiO<sub>2</sub> *via* the spontaneous reduction of ruthenium precursor resulting from a partial conversion reaction of Ti<sup>3+</sup> to Ti<sup>4+</sup> (ref. 32 and 33) in r-TiO<sub>2</sub> and the followed thermal treatment, successfully leading to the improvement of electrocatalyst for chlorine evolution. To fully understand its surface properties, we used field emission scanning electron microscopy (FE-SEM), field emission transmission electron microscopy (FE-TEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The electrocatalytic activity for ClER was investigated with cyclic voltammetry (CV) measurement and the *N,N*-diethyl-*p*-phenylenediamine (DPD) method. Furthermore, scanning electrochemical microscopy (SECM) was employed as an *in situ* analysis to investigate the enhanced ClER from the uniformly coated RuO<sub>2</sub> on the r-TiO<sub>2</sub>.

## 2. Materials and methods

### 2.1 Preparation of r-TiO<sub>2</sub> and RuO<sub>2</sub>@TiO<sub>2</sub>

r-TiO<sub>2</sub> was prepared by a typical two-step anodization method and electrochemical self-doping. First, the Ti foil was anodized at 60 V for 2 h in an ethylene-glycol-based electrolyte containing DI water (2.5 wt%) and NH<sub>4</sub>F (0.2 wt%). The formed nanotube film was peeled off by a compressed air stream, and then a second-anodization was conducted at 40 V for 7 h under the same electrolyte condition. By annealing the as-prepared TiO<sub>2</sub> NTA at 450 °C for 1 h in air, the crystal structure was converted into an anatase-dominant phase (a-TiO<sub>2</sub>).<sup>34</sup> Then, electrochemical doping was performed on the a-TiO<sub>2</sub> under cathodic polarization with constant current (16.7 mA cm<sup>-2</sup>) for 90 s in a phosphate buffer solution ([KH<sub>2</sub>PO<sub>4</sub>]<sub>0</sub> = 0.1 M with KOH, pH = 7.02).<sup>28–30</sup> The prepared r-TiO<sub>2</sub> had a thickness of approximately 13.8 μm and the width of the nanotubes was 130 ± 30 nm (Fig. S1†).

Prior to the RuO<sub>2</sub> coating process, the r-TiO<sub>2</sub> was fully dried at room temperature, then immersed in an aqueous ruthenium precursor solution (5 mM RuCl<sub>3</sub>·H<sub>2</sub>O in deionized (DI) water) under the dark condition for 24 h to produce the self-synthesized coating (Ru@r-TiO<sub>2</sub>). After that, the treated r-TiO<sub>2</sub> was fully washed with DI water to remove the remained ruthenium precursor in the nanotubes, then annealed in 450 °C (air) for 1 h to be oxidized (RuO<sub>2</sub>@r-TiO<sub>2</sub>). The process is presented briefly in Fig. 1.

### 2.2 Characterization of RuO<sub>2</sub>@r-TiO<sub>2</sub>

The morphologies of r-TiO<sub>2</sub> and RuO<sub>2</sub>@r-TiO<sub>2</sub> were observed with field emission scanning electron microscopy (FE-SEM, JSM-6701F, JEOL, Japan) at 20 kV, and field emission transmission electron microscopy (FE-TEM, JEM-F200, JEOL, Japan) was employed to confirm the deposited RuO<sub>2</sub> layer on the wall of r-TiO<sub>2</sub> including energy-dispersive X-ray spectroscopy (EDS). An X-ray diffractometer (XRD, Bruker D8 DISCOVER, Germany) and X-ray photoelectron spectroscope (XPS, Sigma Probe, ThermoVG, UK) were used to examine the material species of the TiO<sub>2</sub> NTA-based electrodes.

### 2.3 Evaluation of electrochemical properties of RuO<sub>2</sub>@TiO<sub>2</sub>

The electrochemical properties of RuO<sub>2</sub>@r-TiO<sub>2</sub> were investigated by cyclic voltammetry (CV) measurement with a three-electrodes system (reference electrode: Ag/AgCl in sat. KCl, counter electrode: Pt mesh) at a scan rate of 5 mV s<sup>-1</sup>. To understand the electrocatalytic activity of RuO<sub>2</sub>@r-TiO<sub>2</sub>, chlorine was electrochemically produced in a two-electrodes system that consisted of RuO<sub>2</sub>@r-TiO<sub>2</sub> as an anode and Pt mesh as a cathode with a constant current density of 16.7 mA cm<sup>-2</sup> in 0.1 M NaCl. The produced chlorine concentration was monitored by the *N,N*-diethyl-*p*-phenylenediamine (DPD) method with a spectrophotometer (DR 900, Hach Co., USA, 530 nm). The current efficiency (%) and the energy consumption (W h g<sup>-1</sup>) of chlorine generation were calculated by eqn (4) and (5).

$$\text{Current efficiency (\%)} = \frac{c \times V \times n \times F}{M(\text{Cl}_2) \times I \times t} \times 100 \quad (4)$$

$$\text{Energy consumption (W h g}^{-1}\text{)} = \frac{I \times \int edt}{c \times V} \quad (5)$$

where  $c$  is the concentration of generated chlorine (g L<sup>-1</sup>),  $V$  is the electrolyte volume (L),  $n$  is the electrons' number (1 eq. mol<sup>-1</sup>),  $F$  is the faradaic constant (96 485 C eq.<sup>-1</sup>),  $M(\text{Cl}_2)$  is the molecular

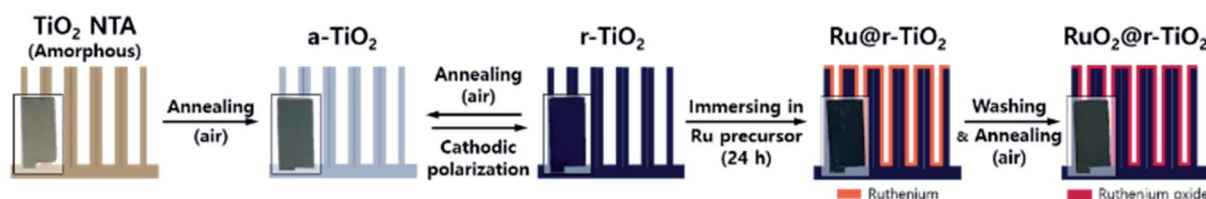


Fig. 1 Scheme of thin RuO<sub>2</sub> layer coating process on reduced TiO<sub>2</sub> nanotube array *via* electrochemical self-doping.



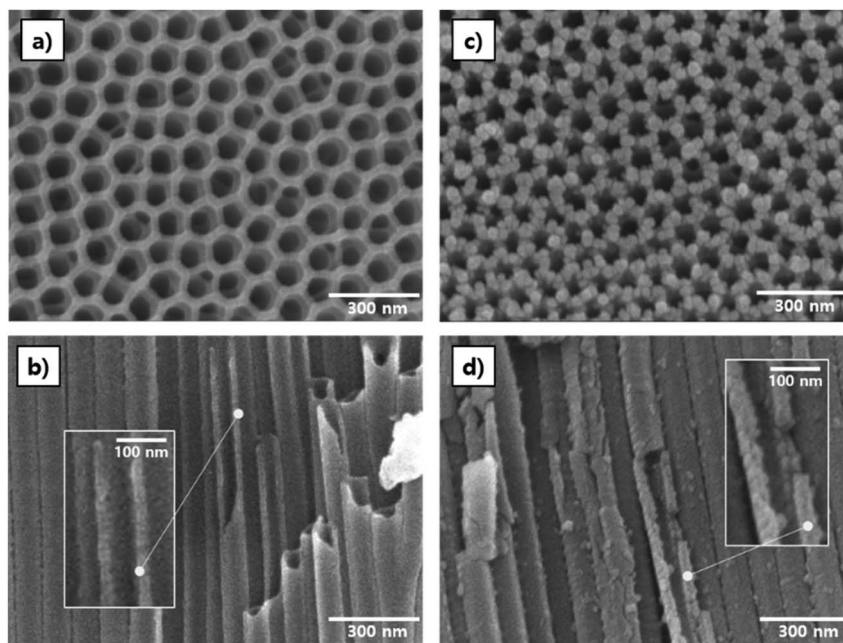


Fig. 2 Morphologies of (a) top- (b) cross sectional view of r-TiO<sub>2</sub> and (c) top- (d) cross sectional view of RuO<sub>2</sub>@r-TiO<sub>2</sub> with a field emission scanning electron microscope (FE-SEM).

weight of chlorine ( $71 \text{ g mol}^{-1}$ ),  $I$  is the applied constant current ( $\text{C s}^{-1}$ ),  $t$  is the operation time (s), and  $e$  is the cell voltage (V).

To confirm the chlorine evolution mechanism of RuO<sub>2</sub>@r-TiO<sub>2</sub>, the hydroxyl radical production was investigated with a degradation of terephthalic acid (TA) as a probe compound. In addition, the effect of hydroxyl radical on chlorine evolution was examined by adding 1 M *t*-BuOH. The TA degradation was measured by high-performance liquid chromatography (HPLC; Ultimate 3000, Dionex, Sunnyvale, CA, USA) in the methanol and formic acid (0.1%) mixture eluent (v/v, 60 : 40).<sup>35</sup> Furthermore, scanning electrochemical microscopy [SECM; SP-300 (bipotentiostat), M470 (SECM Workstation, Bio-Logics SAS), France] was performed to scrutinize the activities for CLER on samples as an *in situ* measurement. This

visualized the scanned area ( $500 \mu\text{m} \times 500 \mu\text{m}$  of the electrodes) with a colour gradation from blue to red.

### 3. Results and discussion

#### 3.1 Morphology of RuO<sub>2</sub>@r-TiO<sub>2</sub>

Fig. 2 shows FE-SEM images (top and cross sectional view) of r-TiO<sub>2</sub> and RuO<sub>2</sub>@r-TiO<sub>2</sub>. As can be seen in Fig. 2, significant differences on the nanotube edge and sidewall of RuO<sub>2</sub>@r-TiO<sub>2</sub> were found. The RuO<sub>2</sub>@r-TiO<sub>2</sub> revealed that a large number of nano-grains were formed on the verges of the nanopore entrances compared to the r-TiO<sub>2</sub> in Fig. 2a and c. In addition, the sidewall of RuO<sub>2</sub>@r-TiO<sub>2</sub> was thicker after deposition on r-

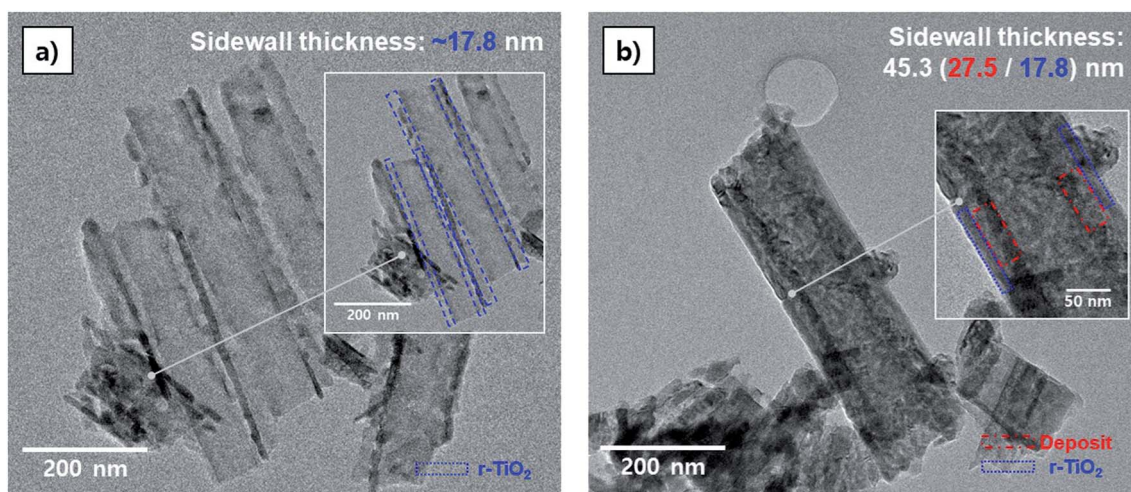


Fig. 3 Nanotube structure characterization of (a) r-TiO<sub>2</sub> and (b) RuO<sub>2</sub>@r-TiO<sub>2</sub> using field emission transmission electron microscope (FE-TEM).



TiO<sub>2</sub> (Fig. 2b and d). It seems that the assemblies of nano-grains on the sidewall of the inner pore were formed to a thin layer (see inset image of Fig. 2d).

The sidewall condition of RuO<sub>2</sub>@r-TiO<sub>2</sub> is inspected meticulously by FE-TEM in Fig. 3. Considering the thickness of the r-TiO<sub>2</sub> sidewall (*ca.* 14–22 nm), the sidewall thickness of RuO<sub>2</sub>@r-TiO<sub>2</sub> (*ca.* ~45.3 nm) was approximately three times thicker. With the distinguished interface layer at RuO<sub>2</sub>@r-TiO<sub>2</sub> (red dashed square in inset image of Fig. 3b) and the results of EDS in Fig. S2,† we see that RuO<sub>2</sub> was successfully deposited on the sidewall of RuO<sub>2</sub>@r-TiO<sub>2</sub>. It is plausible that the RuO<sub>2</sub>@r-TiO<sub>2</sub> revealed a fine coating on the overall surface of r-TiO<sub>2</sub> with open-top and hollow nanotube structure *via* the self-synthesized coating method.

### 3.2 Characteristics of the deposits on RuO<sub>2</sub>@r-TiO<sub>2</sub>

To better understand the deposits on RuO<sub>2</sub>@r-TiO<sub>2</sub>, the XRD patterns and XPS spectra of as-prepared r-TiO<sub>2</sub> and RuO<sub>2</sub>@r-TiO<sub>2</sub> are further analysed in Fig. 4. From the results of the XRD patterns in Fig. 4a, an elusive peak appears at 28° with regard to RuO<sub>2</sub> at RuO<sub>2</sub>@r-TiO<sub>2</sub>.<sup>36–38</sup> Hence, the coated RuO<sub>2</sub> is examined in detail through the XPS results of Ru 3d, O 1s, and Ti 2p in Fig. 4b–d. As shown in Fig. 4b, the RuO<sub>2</sub>@r-TiO<sub>2</sub> exhibited a clear RuO<sub>2</sub> peak at 280.4 eV in the XPS spectra of Ru 3d<sub>5/2</sub>.<sup>38–43</sup> From the shoulder peak (529.4 eV) in XPS spectra of O 1s (red line in Fig. 4c), the deposition of RuO<sub>2</sub> was further confirmed.<sup>38,39,44–46</sup> Moreover, this is clearly supported by the peak shift (1.2 eV) from 458.9 to 457.7 eV in Fig. 4d of Ti 2p<sub>3/2</sub> indicating a heterojunction of RuO<sub>2</sub> and TiO<sub>2</sub>.<sup>40,42,47</sup>

These results suggest that the RuO<sub>2</sub> thin layer was well-formed on the overall surface of RuO<sub>2</sub>@r-TiO<sub>2</sub> *via* the self-synthesized coating method. Note that the self-synthesis

method has been reported in the nanoparticles of noble metals on a TiO<sub>2</sub> sphere with the spontaneous redox reaction between metal ions and the reduced TiO<sub>2</sub>.<sup>32,33</sup> To the best of our knowledge, this is the first report to prepare a thin RuO<sub>2</sub> layer coating on electrochemically reduced TiO<sub>2</sub> NTA *via* the previous phenomenon including the following thermal treatment, without severe pore blockage and toxic chemicals when compared to other methods for treating active materials on the TiO<sub>2</sub> NTAs.<sup>37,48–53</sup>

### 3.3 Electrocatalytic activities of RuO<sub>2</sub>@r-TiO<sub>2</sub>

Fig. 5 shows the improved electrochemical properties of RuO<sub>2</sub>@r-TiO<sub>2</sub>. From the result in Fig. 5a, where the RuO<sub>2</sub>@r-TiO<sub>2</sub> initiated an oxygen evolution reaction (OER) at a potential of approximately 1.1 V vs. Ag/AgCl, the over-potential of which decreased significantly by up to 1.0 V compared to the r-TiO<sub>2</sub>. This means that the surface of RuO<sub>2</sub>@r-TiO<sub>2</sub> had a higher electrocatalytic activity for OER when assisted by the thin RuO<sub>2</sub> layer. In the cathodic biased potential regime ranging from 0 to –1.5 V vs. Ag/AgCl on the RuO<sub>2</sub>@r-TiO<sub>2</sub>, there were no reactions regarding proton inter/deintercalation (–0.6/–0.9 V vs. Ag/AgCl) which was obviously found on r-TiO<sub>2</sub> (blue dash line in the inset image of Fig. 5a) as a unique electrochemical feature of r-TiO<sub>2</sub>.<sup>28,54–57</sup> Additionally, as shown in Fig. S3,† in contrast to RuO<sub>2</sub>@r-TiO<sub>2</sub>, the r-TiO<sub>2</sub> lost its electrochemical property after the thermal treatment. This implies that the self-synthesized coating covered the entire surface of the r-TiO<sub>2</sub> and that the r-TiO<sub>2</sub> under the deposit of RuO<sub>2</sub>@r-TiO<sub>2</sub> was prevented from oxidizing during the thermal treatment. Accordingly, its electrochemical property did not vanish even when it was annealed in the air condition; rather, this property was improved by the formed RuO<sub>2</sub>.

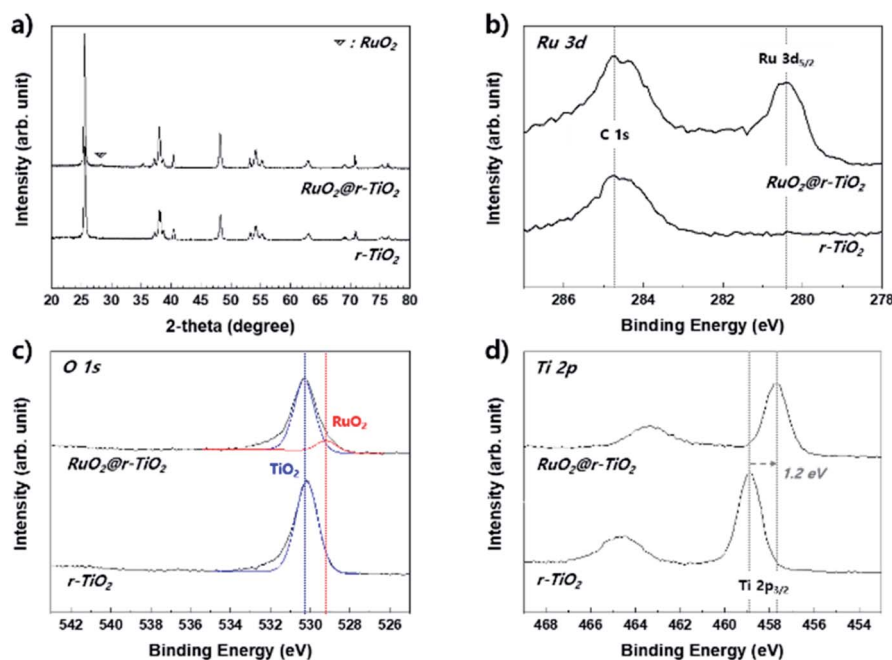


Fig. 4 (a) XRD patterns and XPS spectra (b) Ru 3d, (c) O 1s, and (d) Ti 2p of r-TiO<sub>2</sub> and RuO<sub>2</sub>@r-TiO<sub>2</sub>.



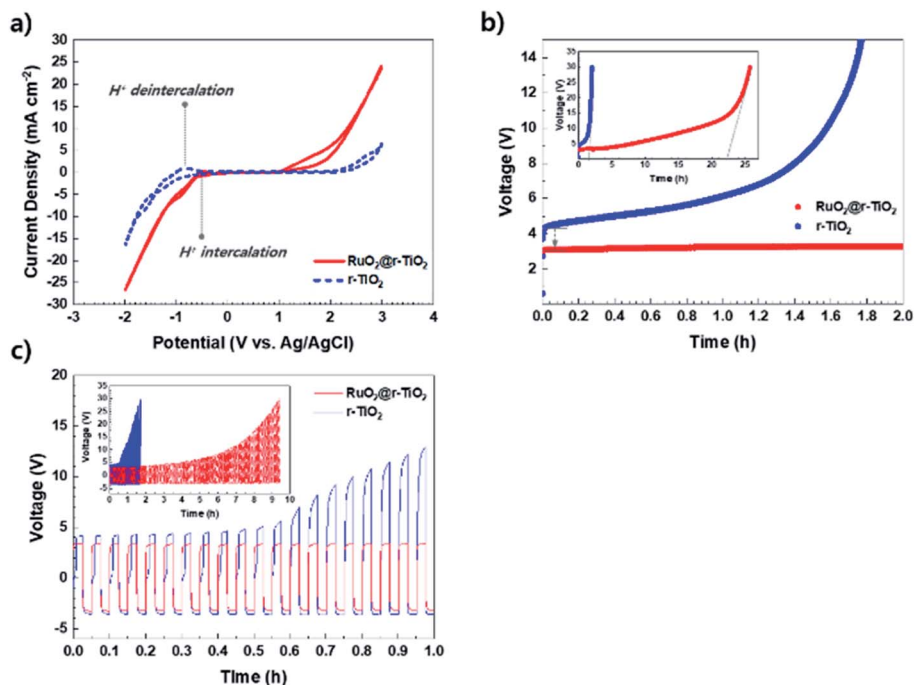


Fig. 5 (a) Cyclic voltammograms (CV) (scan rate: 5 mV s<sup>-1</sup>), the stability test with (b) applied constant current density (16.7 mA cm<sup>-2</sup>), and (c) polarity reversal operation (±16.7 mA cm<sup>-2</sup>, switching time 90 s) of r-TiO<sub>2</sub> and RuO<sub>2</sub>@r-TiO<sub>2</sub> in 0.1 M phosphate buffer solution (PBS).

For oxygen evolution under a constant current condition (Fig. 5b), RuO<sub>2</sub>@r-TiO<sub>2</sub> led to a lower initial operational cell voltage (~3.0 V) than r-TiO<sub>2</sub> (~4.2 V), and it showed significantly enhanced stability with a value that was approximately 20 times higher (~22 h) than that of r-TiO<sub>2</sub> (~1.2 h). This can be evaluated based on the drastic increase in cell voltage. In addition,

under a polarity reversal operation (switching constant current for +16.7 mA cm<sup>-2</sup> vs. -16.7 mA cm<sup>-2</sup>), the RuO<sub>2</sub>@r-TiO<sub>2</sub> was highly stable on the stress from the harsh reversal condition compared to r-TiO<sub>2</sub>. This indicates that RuO<sub>2</sub>@r-TiO<sub>2</sub> is a more reliable material than r-TiO<sub>2</sub> in various environmental and industrial applications. Nevertheless, for the further success of

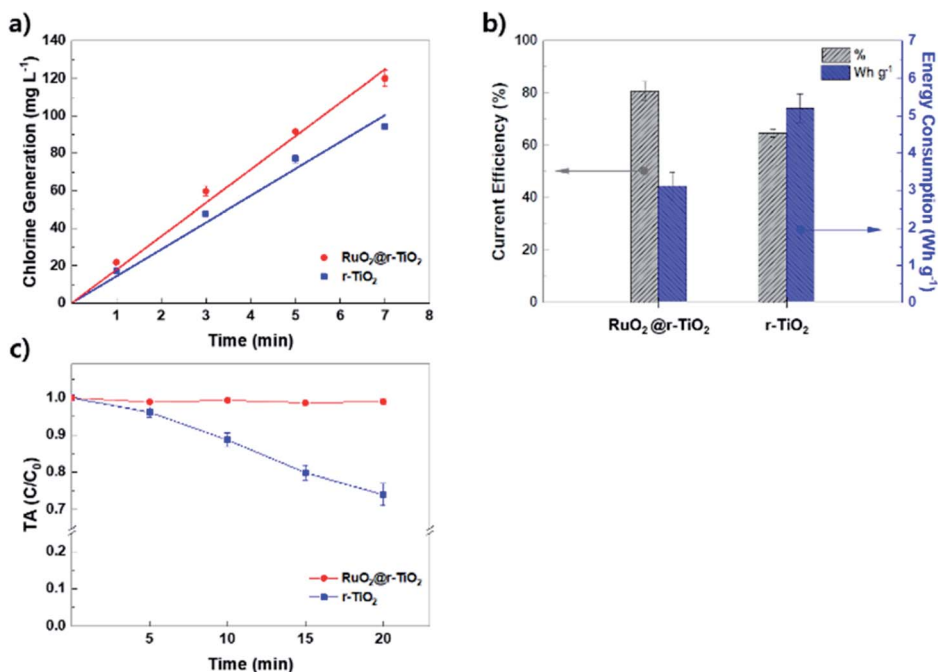


Fig. 6 (a) Evolution of chlorine (16.7 mA cm<sup>-2</sup>, 0.1 M NaCl) and (b) the current efficiency and energy consumption in 3 min, and (c) terephthalic acid (TA) degradation for hydroxyl radical measurement (0.1 mM TA, 16.7 mA cm<sup>-2</sup>) of RuO<sub>2</sub>@r-TiO<sub>2</sub> and r-TiO<sub>2</sub>.



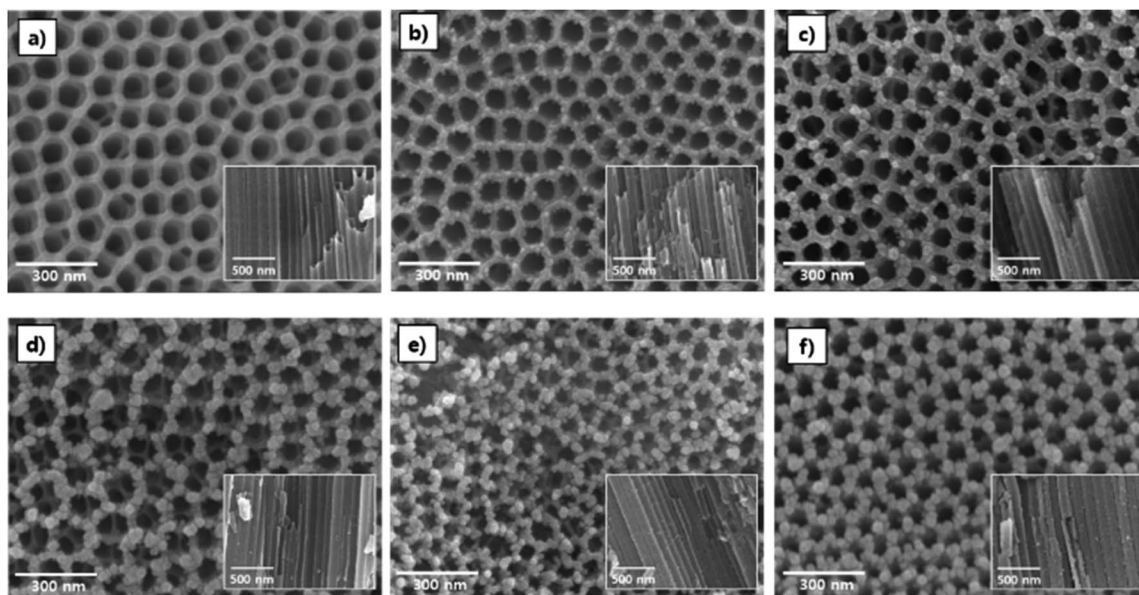


Fig. 7 FE-SEM images (cross sectional view in inset images) of (a) r-TiO<sub>2</sub> and RuO<sub>2</sub> coated electrodes after immersion in 5 mM aqueous ruthenium precursor for (b) 1, (c) 3, (d) 6, (e) 12, and (f) 24 h. Note that FE-SEM images of r-TiO<sub>2</sub> and RuO<sub>2</sub>@r-TiO<sub>2</sub> (24 h) were from the result of Fig. 2 in order to compare the morphologies of each electrode.

RuO<sub>2</sub>@r-TiO<sub>2</sub>, the long-term performance stability must be improved *via* controlling the doping level of r-TiO<sub>2</sub> (Fig. S4 in ESI†). It is required to further study the effect of type of catalyst (*i.e.*, IrO<sub>2</sub>, Pt and carbon, *etc.*) for thin layer coating, coating thickness, and temperature of thermal treatment on CIER.

Fig. 6 shows the enhanced chlorine evolution performance and the pathway for CIER of RuO<sub>2</sub>@r-TiO<sub>2</sub> compared to r-TiO<sub>2</sub>. As shown in Fig. 6a, the chlorine production rate of RuO<sub>2</sub>@r-TiO<sub>2</sub> was estimated to be approximately 17.85 mg L<sup>-1</sup> min<sup>-1</sup>. This is approximately 20% faster than that of r-TiO<sub>2</sub> (14.35 mg L<sup>-1</sup> min<sup>-1</sup>). Correspondingly, RuO<sub>2</sub>@r-TiO<sub>2</sub> exhibited a current efficiency of 81.0% with an energy consumption of 3.0 W h g<sup>-1</sup>, indicating higher electrocatalytic activity for chlorine production compared to r-TiO<sub>2</sub> (current efficiency of 64.7% and

energy consumption of 5.2 W h g<sup>-1</sup> in Fig. 6b). The high chlorine evolution performances can be explained by the uniformly organized nanotube structure with the thin RuO<sub>2</sub> layer.

Furthermore, with the thin RuO<sub>2</sub> layer, the surface of RuO<sub>2</sub>@r-TiO<sub>2</sub> was converted to be more attractive for chlorine than hydroxyl radical (Fig. 6c). This resulted in excellent chlorine production performances, namely the RuO<sub>2</sub>@r-TiO<sub>2</sub> can be defined as an active electrode (high efficiency for chlorine production; RuO<sub>2</sub>, IrO<sub>2</sub>, *etc.*) rather than an inactive electrode (high efficiency for hydroxyl radical; r-TiO<sub>2</sub>, boron doped diamond electrode, SnO<sub>2</sub>, PbO<sub>2</sub>, *etc.*)<sup>5,14,20,28,37</sup>. Note that, in common, the active electrode produces CIER *via* direct electron transfer with chloride ions whereas the inactive electrode leads to CIER by the indirect pathway mediated by hydroxyl radicals.

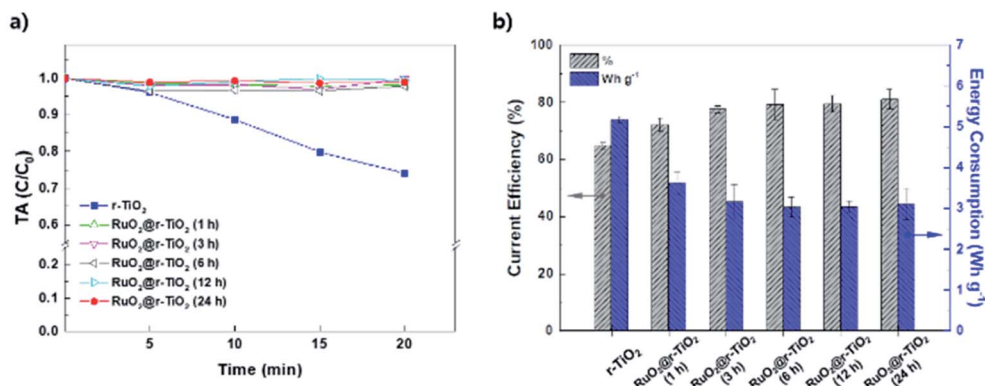


Fig. 8 (a) OH radical generation measurement with TA degradation (0.1 mM TA, 16.7 mA cm<sup>-2</sup>) and (b) chlorine generation efficiency and energy consumption (16.7 mA cm<sup>-2</sup>, 0.1 M NaCl, 3 min) of r-TiO<sub>2</sub> and RuO<sub>2</sub> coated electrodes after immersion in 5 mM aqueous ruthenium precursor for 1, 3, 6, 12, and 24 h. Note that chlorine generation efficiency, energy consumption, and the TA degradation data of r-TiO<sub>2</sub> and RuO<sub>2</sub>@r-TiO<sub>2</sub> (24 h) are from the results of Fig. 6.



This is well supported by the effect of the hydroxyl radical scavenger on the chlorine evolution (Fig. S5†). With the addition of *t*-BuOH as hydroxyl radical scavenger, the chlorine evolution efficiency of RuO<sub>2</sub>@r-TiO<sub>2</sub> did not meaningfully decrease, whereas that of r-TiO<sub>2</sub> was significantly reduced. This means the small effect of hydroxyl radical on the chlorine evolution of RuO<sub>2</sub>@r-TiO<sub>2</sub> instead of r-TiO<sub>2</sub> produced chlorine mediated by hydroxyl radical.<sup>39</sup> Considering the effect of hydroxyl radical on CIER of RuO<sub>2</sub>@r-TiO<sub>2</sub> and r-TiO<sub>2</sub>, the surface of RuO<sub>2</sub>@r-TiO<sub>2</sub> behaves active electrodes. Eventually, we see the surface of RuO<sub>2</sub>@r-TiO<sub>2</sub> was converted to an active electrode from an inactive electrode. It is attributed to that the RuO<sub>2</sub> thin layer was uniformly coated on the surface of nano-pores of r-TiO<sub>2</sub>, and thus, the surface of r-TiO<sub>2</sub> only worked as substrate, not catalytic material.

### 3.4 Effect of the immersion time on chlorine production efficiency of RuO<sub>2</sub>@r-TiO<sub>2</sub>

To optimize the deposition of RuO<sub>2</sub> on RuO<sub>2</sub>@r-TiO<sub>2</sub>, we further investigate the effect of the RuO<sub>2</sub> loading amount controlled *via* Ru precursor dipping time (ranging from 1 to 24 h) on the deposition and chlorine evolution efficiency of RuO<sub>2</sub>@r-TiO<sub>2</sub>. Fig. 7 shows the morphologies of the RuO<sub>2</sub>@r-TiO<sub>2</sub> samples prepared with the time of 1, 3, 6, 12, and 24 h. As shown in

Fig. 7, as the immersion time increased, the size of the nano-grains on the nano-pore edge and the thickness of the side-wall (inset images) gradually increased. In particular, regardless of the time, surfaces of all samples were more attractive for chlorine evolution than hydroxyl radical (Fig. 8a). However, compared to the chlorine evolution performances of RuO<sub>2</sub>@r-TiO<sub>2</sub> prepared with the immersion times of 6, 12 and 24 h (current efficiency of 79.2, 79.4, and 81.0%; and energy consumption of 3.0, 3.0, 3.0 W h g<sup>-1</sup>, respectively), the RuO<sub>2</sub>@r-TiO<sub>2</sub> prepared with immersion times of 1 and 3 h resulted in relatively low chlorine evolution performance with current efficiencies of 72.2, 77.6% and energy consumption of 3.6, 3.2 W h g<sup>-1</sup>, respectively (see Fig. 8b, and refer to all data of chlorine generation in Fig. S6a†). Correspondingly, a similar trend in the long-term stability was found (Fig. S6b†).

Moreover, this is well supported by the results obtained with the sample generation/tip collection (SG/TC) mode of SECM (Fig. 9) which visualized the electrocatalytic activity for chlorine production *via* a chlorine reduction reaction at -0.2 V vs. Ag/AgCl (the detailed experimental condition are shown in Fig. S7 and S8†).<sup>58,59</sup> As shown in Fig. 9, the electrocatalytic activity was evenly enhanced across the entire surface after 12 h according to the condition of deposited RuO<sub>2</sub> confirmed previously in Fig. 7 with FE-SEM. Particularly, compared to the pristine r-TiO<sub>2</sub> (Fig. 9a) which revealed nano-patterns of

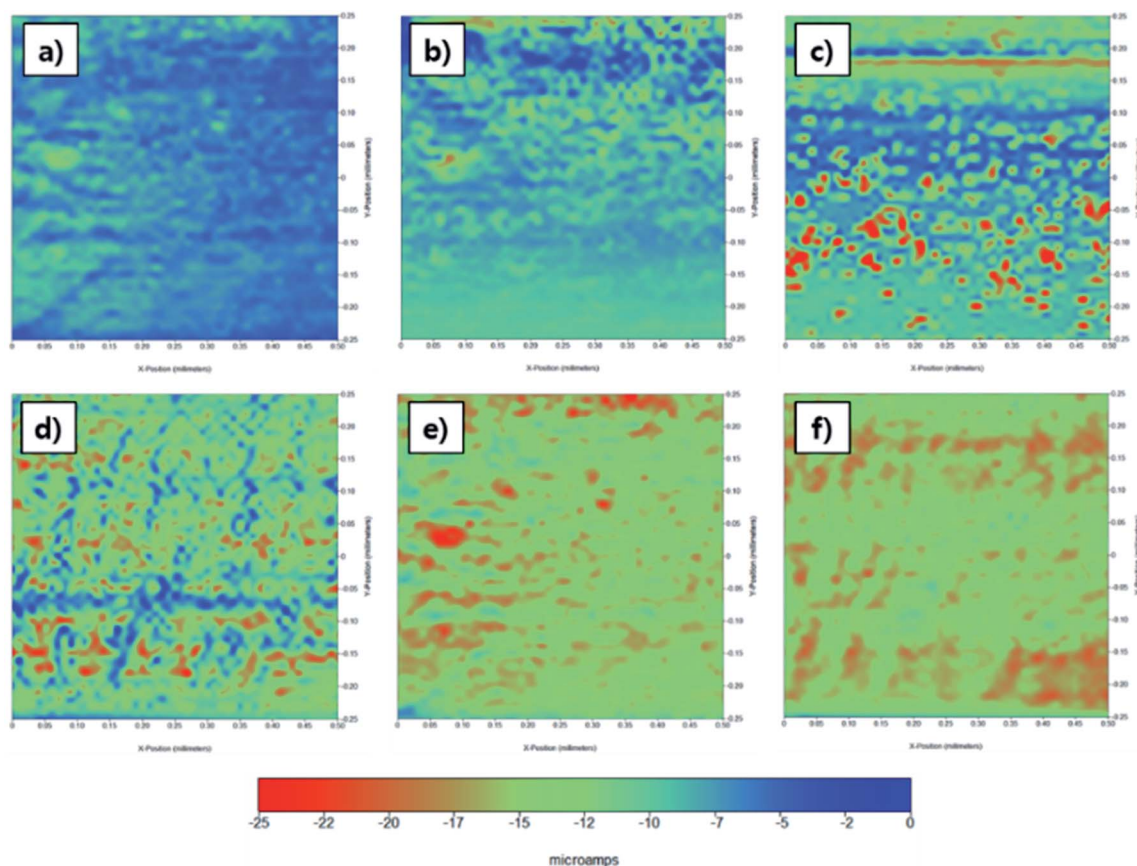


Fig. 9 Area scan of scanning electrochemical microscopy (SECM) in 0.1 M NaCl, 16.7 mA cm<sup>-2</sup>; (a) r-TiO<sub>2</sub>, RuO<sub>2</sub> coated electrodes after immersing in 5 mM aqueous ruthenium precursor for (b) 1, (c) 3, (d) 6, (e) 12, and (f) 24 h.



emerald-colored rings, reddish cores were observed after commencing RuO<sub>2</sub> deposition on r-TiO<sub>2</sub> (Fig. 9b–f). The RuO<sub>2</sub> coated inner pores improved the chlorine generation inside of the nanotubes, so that the higher activity (red) was measured at the center of the patterns than the circular edge. In Fig. 9f, circular nano-patterns on RuO<sub>2</sub>@r-TiO<sub>2</sub> (24 h) were uniformly distributed in red. This color change verifies that the RuO<sub>2</sub> was effectively coated at the top edge of the tubes and even at its inner-pores as previously shown in images of SEM and TEM (Fig. 2 and 3), resulting in the enhanced the electrocatalytic performance for the CIER. As such, the morphological and electrochemical properties of r-TiO<sub>2</sub> are feasible to be facily controlled with the self-synthesis coating method that can be extended to various fields of studies utilizing TiO<sub>2</sub> NTA-based electrocatalysts.

## 4. Conclusions

In this study, we successfully fabricated the RuO<sub>2</sub>@r-TiO<sub>2</sub> with a self-synthesized coating method leading to a RuO<sub>2</sub> thin layer coating on r-TiO<sub>2</sub> and demonstrated considerably enhanced electro-catalytic activity for chlorine production. The fine RuO<sub>2</sub> coating was achieved *via* the self-synthesized coating originating from the conversion of Ti<sup>3+</sup> to Ti<sup>4+</sup> on r-TiO<sub>2</sub> and thermal treatment under the atmospheric condition. Using various surface analysis including FE-SEM, FE-TEM, EDS and XPS, the formation of a RuO<sub>2</sub> thin layer (thickness of ~27.5 nm) on the inner pore sidewall of RuO<sub>2</sub>@r-TiO<sub>2</sub> was clearly proven. The RuO<sub>2</sub>@r-TiO<sub>2</sub> exhibited the highly enhanced electrocatalytic activity for chlorine production with the production rate of 17.85 mg L<sup>-1</sup> min<sup>-1</sup>, the high current efficiency of 81.0%, energy consumption of 3.0 W h g<sup>-1</sup>, and long-term stability of ~22 h compared to r-TiO<sub>2</sub> (production rate of 14.35 mg L<sup>-1</sup> min<sup>-1</sup>, the current efficiency of 64.7%, energy consumption of 5.2 W h g<sup>-1</sup>, and long term service time of 1.2 h). In addition, the performances of RuO<sub>2</sub>@r-TiO<sub>2</sub> was optimized by controlling the immersion time in the precursor. These results provide a new approach to the thin metal oxide coating on r-TiO<sub>2</sub> and provide opportunities for various applications such as electrolysis, photo-catalyst, and energy storage devices.

## Conflicts of interest

There are no conflicts to declare.

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