

Communication

Plasma-Deposited Ru-Based Thin Films for Photoelectrochemical Water Splitting

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Abstract: Plasma-enhanced chemical vapor deposition (PECVD) was used to produce new Ru-based thin catalytic films. The surface molecular structure of the films was examined by X-ray photoelectron spectroscopy (XPS). To determine the electro- and photoelectrochemical properties, the oxygen evolution reaction (OER) process was investigated by linear sweep voltammetry (LSV) at pH = 13.6. It was found that Ru atoms were mainly in the metallic state (Ru^0) in the as-deposited films, whereas after the electrochemical stabilization, higher oxidation states, mainly Ru^{+4} (RuO_2), were formed. The stabilized films exhibited high catalytic activity in OER—for the electrochemical process, the onset and η_{10} overpotentials were approx. 220 and 350 mV, respectively, while for the photoelectrochemical process, the pure photocurrent density of about 160 mA/cm² mg was achieved at 1.6 V (vs. reversible hydrogen electrode (RHE)). The plasma-deposited RuO_x catalyst appears to be an interesting candidate for photoanode material for photoelectrochemical (PEC) water splitting.

Keywords: thin-film catalyst; plasma deposition; ruthenium oxide; water splitting; oxygen evolution reaction

1. Introduction

Ruthenium (Ru)—in both its oxidized, especially RuO_2 (Ru^{+4}), and metallic (Ru^0) forms—has been widely studied and applied as a heterogeneous catalyst and electrocatalyst [1,2]. A lot of attention has been paid to the use of such catalysts in the reactions occurring in fuel cells [3,4] as well as in the photo- [5,6], electro- [7–10], and photoelectro-splitting of water [11,12]. In the water splitting processes, Ru-based materials have proven to be one of the most efficient catalysts in the oxygen evolution reaction (OER) [13].

The Ru-based catalytic materials have been prepared in many different ways and various forms. For instance, Reier et al. [14] reported Ru nanoparticles (average size approx. 5 nm) synthesized by an incipient wetness method and then electrochemically oxidized. Although the OER performance of these nanoparticles was outstanding, stability problems prevent their utilization as a practical nanoscaled OER catalyst. Jirkovský et al. [15] also showed that nanocrystalline RuO_2 particles prepared by the sol-gel method exhibited increasing activity towards water oxidation with decreasing particle size (from 40 to 15 nm). The high activity of RuO_2 nanoparticles (~6 nm) for OER was confirmed by Lee et al. [16]. In this case, the study showed high stability of this catalytic form, which can serve as a benchmark in the development of active OER catalysts for electrolyzers, metal-air batteries, and photoelectrochemical (PEC) water splitting applications. The influence of preparation conditions on the catalytic activity of RuO_2 for OER was described by Ma et al. [17]. The RuO_2 catalyst was prepared by a pyrolysis process in a nitrate melt at 300 °C, and then calcined at different temperatures, from 350 to 550 °C. It was found that the electrocatalytic activity of the RuO_2 layer decreased with

increasing calcination temperature. At the same time, the resistance of this layer decreased. More detailed studies regarding the dependence of the activity and stability of the Ru-based catalyst on its preparation procedure were presented by Kim et al. [18]. The catalytic films were prepared by Ru electrodeposition and then thermally oxidized at various temperatures (300–600 °C) under atmospheric conditions. It was concluded that the OER activity and stability were strongly related to the surface composition—specifically, the quantities of anhydrous RuO₂ and hydrous RuO₂ on the surface—which, in turn, was associated with the annealing temperature. Recently, to control the mesoporous structure of RuO₂ and thus create improved electrocatalytic properties over commercial RuO₂ nanoparticles for the oxygen evolution reaction, Han et al. [19] successfully used a nanocasting technique. Interesting results were also obtained by Tsuji et al. [20], who prepared thin films by the RF magnetron sputtering technique and showed that the films in amorphous form are more active in the OER than those containing the rutile crystalline RuO₂ form.

Ru-based catalytic materials were also obtained in more complex forms. Das et al. [21], for example, prepared ruthenium oxide on zeolite Y by thermal decomposition of ruthenium carbonyl, resulting in RuO₂ fibers with the approximate dimensions of lengths of 50 nm and widths of 5 nm. This material proved to be a very effective catalyst for water oxidation to O₂. Another important solution proposed by Park et al. [13] was the fabrication of three-dimensional RuO₂ branched Au-TiO₂ nanowire arrays for the photostable electrodes in PEC water oxidation. These nanowire arrays have shown a remarkable enhancement in the photocurrent density by approximately 60% and 200% in the UV-visible and Visible region respectively, compared with pristine TiO₂ nanowires at the same potential. Recently, some progress in the construction of Ru-based catalysts for the OER has been made by producing their composites, e.g., with iridium oxide [22], or alloys, e.g., with platinum [23]. Much attention is also paid to co-catalysts with RuO₂ participation [12,24,25].

One particularly interesting method that could be used to prepare Ru-based catalysts is plasma-enhancement chemical vapor deposition (PECVD). This method is very useful and efficient in the production of completely new materials with a controlled molecular structure and, as a consequence, with the desired properties. The great advantage of this method is the ability to easily realize molecular projects through the selection of appropriate plasma process parameters, as well as the selection of precursors and their mixtures. In addition, the PECVD enables the synthesis of uniform and very thin films (with thicknesses much lower than 1 µm) on virtually any support (e.g., fine meshes) without changing their geometry. This is especially important when designing sophisticated systems for structured reactors. The PECVD method has already been widely used to produce various thin films from metalorganic precursors, which have been studied as catalysts in chemical and electrochemical processes [26,27]. Among them, plasma-deposited Ru-based films were also tested in the CO₂ hydrogenation process [28]. However, these films have not been studied in electrochemical and photoelectrochemical water splitting processes.

Considering the above, in the present paper, we have focused our attention on the possibilities of applying these new catalytic systems, which are plasma-deposited Ru-based films, in the oxygen evolution reaction, both in the electrochemical and photoelectrochemical processes. Positive results would pave the way for progress in using the PECVD method to produce nanocatalysts for water splitting.

2. Results and Discussion

The first step in examining the possibility of utilizing plasma-deposited Ru-based thin films as catalysts in the OER was to determine their activity and stability in this process. Figure 1 presents the measurements of linear sweep voltammetry (LSV) in successive cycles for the film (approx. 200 nm), deposited on carbon paper and used as the working anode. As one can see, after five cycles the sample is practically stable. The first measurement cycle of the dependence of current density on the applied potential, strongly different from the others, should undoubtedly be associated with changes in the molecular structure of the Ru-based film. Then, the film surface stabilizes and shows good electrocatalytic activity towards OER, with an onset potential of about 1.45 V vs reversible hydrogen

electrode (RHE), which gives an overpotential $\eta = 220$ mV. The overpotential required for the current density of 10 mA/cm^2 , as a commonly used OER reference is, in this case, $\eta_{10} = 350$ mV. Further measurement for 5 h at a constant current of 10 mA did not practically change this value, indicating good stability of the tested catalytic film. For a typical RuO_2 catalyst measured in similar alkaline conditions, the onset and η_{10} overpotentials were approx. 280 and 420 mV, respectively [29]. For more sophisticated systems, namely Ru- RuO_2 /CNT hybrids, $\eta_{10} = 210$ mV [10]. In turn, electrodeposited Ru films were characterized by $\eta_{10} = 320$ mV [30]. As one can see, our plasma-deposited films can be classified as catalysts with high OER performance.

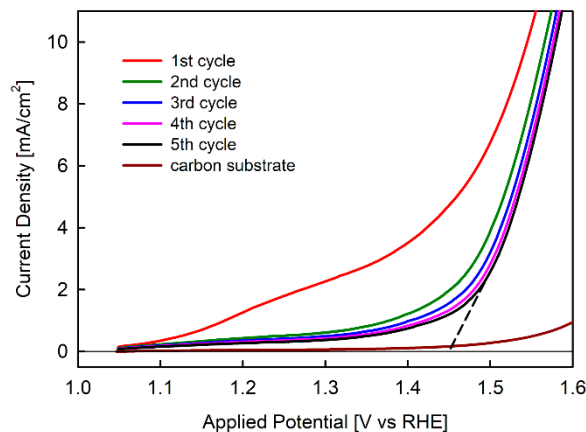


Figure 1. Linear sweep voltammetry (LSV) for the plasma-deposited Ru-based film. Current density as a function of applied potential (V vs reversible hydrogen electrode (RHE)) for five successive measurement cycles. The LSV for the carbon substrate is also shown.

For comparison, the polarization curve for a pure carbon substrate is also shown in Figure 1. Almost no current signal is recorded in the potential range used, which confirms the catalytic activity of the plasma-deposited Ru-based films.

To accurately determine the presumed changes in the molecular structure of the Ru-based film surface, which occur during LSV measurements, investigations by X-ray photoelectron spectrometry (XPS) were performed. The most intense XPS Ru 3d band is composed of doublet Ru 3d_{5/2} and Ru 3d_{3/2}. Due to the fact that the latter peak was overlapping with a very intense C 1s band originating from the carbon substrate, the analysis was carried out only for the 3d_{5/2} peak. By eliminating C 1s and Ru 3d_{3/2} signals from the spectrum envelope, the remaining Ru 3d_{5/2} peak was deconvoluted into four symmetrical, Gaussian:Lorentzian (70:30) shaped components, for both the as-deposited film and the film with stabilized structure after five LSV cycles (Figure 2). The component located at a binding energy of 280.0–280.1 eV is undoubtedly assigned to metallic Ru⁰ atoms. The three remaining components situated in the higher binding energy region represent oxidized Ru states: Ru⁺⁴ (at 280.5–280.6 eV), Ru⁺³ (281.4–281.5 eV) and finally Ru⁺⁶ (at 282.3–282.4 eV) [31].

The XPS results indicate a significant surface oxidation of the film during the electrochemical process. As-deposited Ru-based films contain about 58.0 at % of Ru⁰ (in relation the total Ru content), whereas, after electrochemical stabilization, it decreases to 14.4 at %. In fact, the Ru-based film is transformed into an active and stable catalyst composed mainly of the Ru⁺⁴ oxidation state (RuO_2). Its content increases from 29.3 at % up to 46.3 at %. It should also be noticed that the concentration of Ru⁺³ and Ru⁺⁶ oxidation states clearly increase in the film surface after stabilization via LSV measurements, from 8.1 at % to 25.8 at % and from 4.6 at % to 13.4 at %, respectively.

Although there is no doubt that the plasma-deposited Ru-based film used as the anode in the OER is oxidized, especially in the first LSV measurement cycle, it is difficult to determine at this moment which oxidation forms of ruthenium present on the stable film surface are mainly responsible for catalyzing the oxygen evolution process.

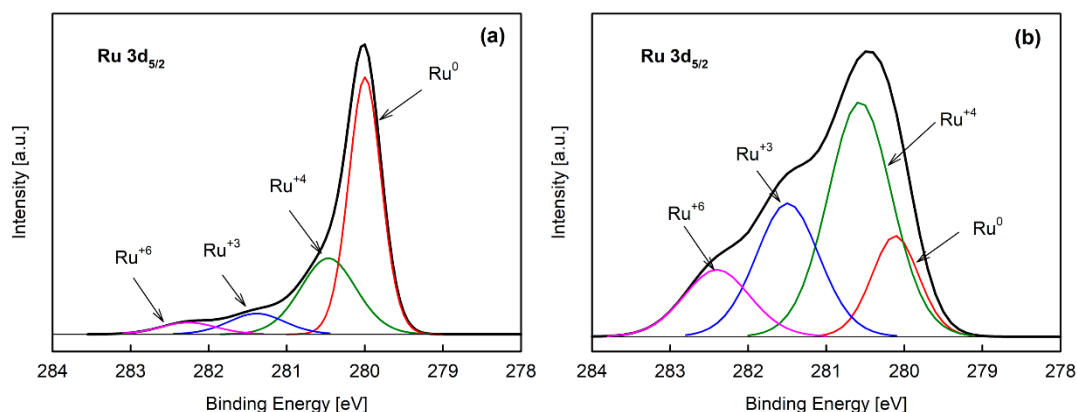


Figure 2. X-ray photoelectron spectrometry (XPS) Ru 3d_{5/2} spectra of the plasma-deposited Ru-based film: (a) as-deposited; (b) after five LSV cycles.

The plasma-deposited Ru-based films were also tested as a photo-electrocatalyst for the OER process. These investigations were carried out as follows: firstly, five LSV cycles in the dark were performed to obtain the stable form of the film deposited on the carbon paper and used as the anode. In Figure 3a, the course of the last cycle is shown as curve (a). Then, the anode was irradiated by a 150 W xenon lamp (full spectral range from 230 to 750 nm) for 1 h, after which time the LSV relationship (curve (b)) was recorded without interrupting the lighting. Finally, one more LSV measurement (curve (c)) was made in the dark. The sample showed almost identical electrocatalytic activity as before irradiation.

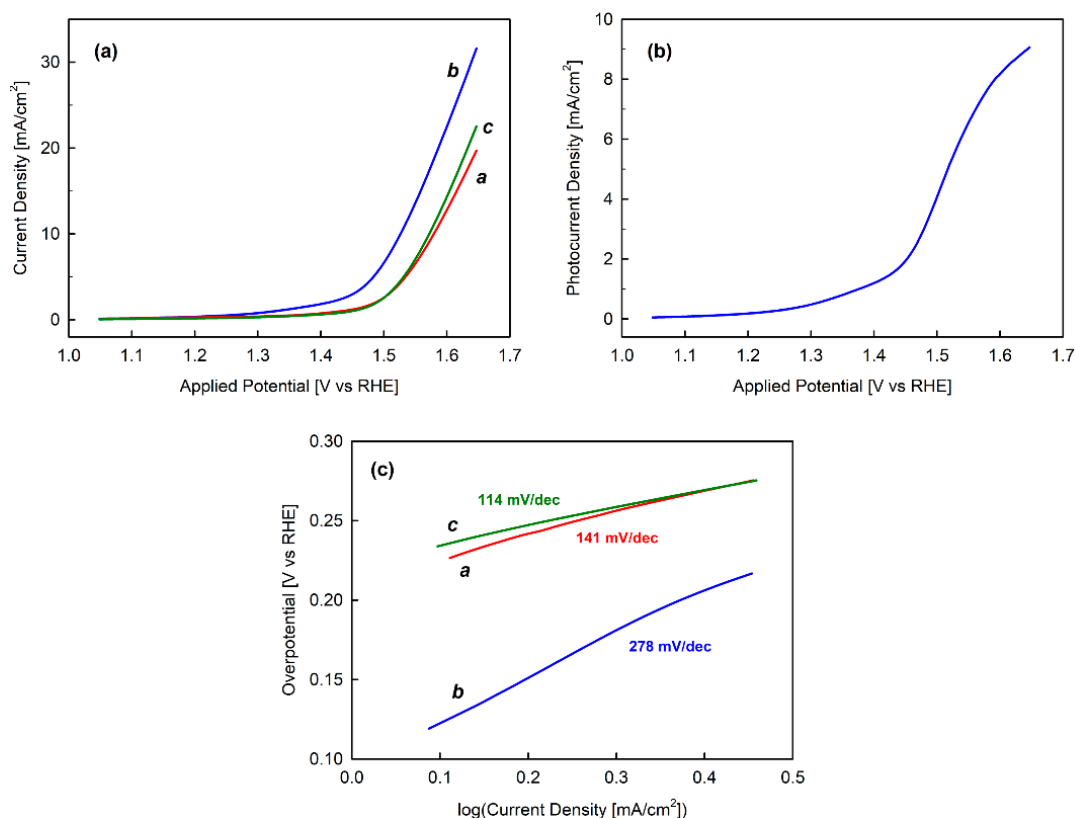


Figure 3. Photoelectrochemical response of the plasma-deposited Ru-based film in the oxygen evolution reaction (OER) process: (a) LSV measurements: a—in the dark, b—under illumination, c—in the dark after illumination; (b) photocurrent dependence; (c) Tafel plots.

Subtracting curve (c) from curve (b), the pure photocurrent response of the film in the OER process is obtained (Figure 3b). The rapid increase in the photocurrent above 1.4 V indicates strong photocatalytic activity of the plasma-deposited Ru-based films. With an applied potential of 1.6 V (vs RHE), the photocurrent density reaches about 9.0 mA/cm², which is a very high performance in the OER process compared to other Ru-based [13], as well as other thin-film types of photocatalysts tested in this process [32]. It should also be emphasized that the films we study represent a very small amount of material. Taking the active surface of the anode equal to 0.8 cm², the film thickness of about 200 nm and its density about 3–4 g/cm³, we can determine the photocurrent density per unit mass of the catalyst, which for the potential of 1.6 V (vs RHE) is about 160 mA/cm²mg.

The electro- and photoelectro-catalytic OER kinetics of the plasma-deposited Ru-based films were analyzed using the appropriate Tafel plots (Figure 3c) derived from the polarization curves shown in Figure 3a. The linear regions of the Tafel plots are fitted to the Equation:

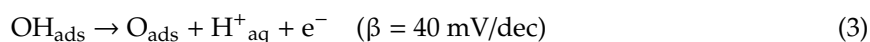
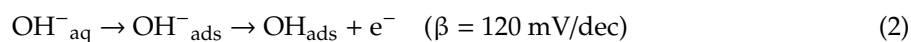
$$\eta = \alpha + \beta \log(j), \quad (1)$$

where η is overpotential, j is the current density, and β is the Tafel slope).

The resulting Tafel slopes are found to be ~141, ~278, and ~114 mV/dec for the sample measured in the dark, under illumination, and in the dark after lighting, respectively. The Tafel slopes for the film in the dark, before and after lighting, are almost the same, but the slope for the illuminated sample is clearly higher, although in this case the same current density as for the sample in the dark is obtained at lower overpotential values. This indicates a more complex mechanism of the oxygen evolution process during UV-visible irradiation.

Despite notable experimental and theoretical work on Ru-based catalysts for the electrocatalytic OER process, let alone its photoelectro-catalytic studies, the mechanism of this process is still unclear [33–35]. This problem is further complicated by the fact that the OER process is significantly influenced by the structure and nanostructure of ruthenium-based catalysts, which largely depends on the preparation conditions of these materials [15,20]. From the electronic structure point of view, catalysts based on RuO₂, depending on the production procedure and the post-deposition treatment, can behave as a semiconductor [36] that exhibits both p-type and n-type electrical conductivity [37,38], and also, especially after calcination at high temperature (above 523 K), can reveal metallic-like properties [39].

In our case, the structure of the films is very complex and, as is shown by XPS studies (Figure 2), consists of different types of ruthenium oxides, but with a significant predominance of RuO₂ in electrochemically stabilized films. Since the films are prepared only at a slightly elevated temperature, it can be assumed that they have the nature of a semiconductor. However, despite the lack of precise knowledge about the molecular structure of the films under discussion, the basic reactions in the OER process that occur on the film surface in an alkaline solution can be proposed according to [40]:



where the symbols aq, ads, and g denote molecules in solution, adsorbed on the catalytic film surface and in the gas phase, respectively.

Reactions (2) and (3) are sequential steps associated with electron transfer, which drives the OER process and generates the measured current (Figure 3). The theoretical calculation of the Tafel slope (β) showed that, depending on which step is rate-determining, the values of these slopes differ significantly (as given for reactions (2) and (3)) [33]. As one can see, in our case the estimated Tafel

slope value for the electrocatalytic (in dark) process (Figure 3c) is largely consistent with the value provided for step (2). It follows that the bottleneck of the OER process is the adsorption of OH^- ions on the catalytic film surface and the electron transfer.

When the film is illuminated, assuming, as discussed above, its semiconductor nature, we can expect the generation of electron–hole pairs. The measured energy gap for RuO_2 -based semiconductive catalysts is 2.6–2.9 eV [36,41], which indicates that the light used in our studies (230–750 nm, 5.4–1.7 eV) can generate electron–hole pairs in the bulk of the film. However, the possibility of a photoinjection of current carriers at the contact between the semiconducting film and the metal-like substrate, which is carbon (graphite) paper, cannot be overlooked [42]. The thickness of the film (approx. 200 nm) allows light to reach the contact. The graphite with an energy gap close to 0 eV and a work function of about 4.2–5.2 eV [43] can form with RuO_2 , with an energy gap equal to 2.6–2.9 eV, as mentioned above, and the work function of about 5.2 eV [44], a junction similar to the neutral contact with a barrier height not higher than 2.9 eV. The barrier can be easily overcome by the photon energy of the light used. Although in our case we do not know the details of the electronic structure of the plasma-deposited Ru-based catalytic film, the observed photoconductivity and the discussion presented above authorize us to assume that photogenerated or photoinjected holes (these carriers are of interest due to the positive polarization of the catalytic electrode) are transported by the electric field to the film surface contacting with the solution. Such holes (h^+) play the role of additional active centers that enhance the performance of step (2) by recombining with the negative charge on OH^- ions:



In this case, the rate-determining process in the OER is photogeneration (photoinjection) of holes and their transport through the semiconductor film to its surface in contact with the solution.

3. Materials and Methods

The Ru-based films were deposited in a parallel-plate radio frequency (RF 13.56 MHz) plasma reactor (self-constructed), schematically presented in Figure 4a. The carrier gas (argon with a purity of 99.99%, Linde Gaz Polska Ltd., Cracow, Poland) was introduced through a mass flow controller (Model 5850, Brooks Instrument LLC, Hatfield, PA, USA) into the gas system of the reactor, with a flow rate of 0.71 sccm. Bis(ethylcyclopentadienyl)ruthenium(II) (98%, Sigma-Aldrich, St. Louis, MO, USA, with the chemical formula shown in Figure 4b) liquid in the standard state, was used as a ruthenium precursor. The reservoir for the precursor was heated to 413 K to ensure adequate vapor pressure. The mixture of the precursor vapor and the carrier gas was fed to the plasma reactor chamber by means of a perforated grounded electrode. All the gas lines and both the electrodes were heated to 433 K to prevent precursor condensation. The glow discharge power was 40 W, and the total pressure maintained in the plasma chamber was approx. 4.0 Pa. The films (about 200 nm thick) were deposited on the carbon paper (SpectraCarb, The Fuel Cell Store, College Station, TX, USA) used as a substrate.

The electrochemical and photoelectrochemical experiments were carried out at room temperature in a 1M NaOH (p.a., P.H. Stanlab Ltd., Lublin, Poland) electrolyte (pH = 13.6) in a three-electrode electrochemical cell (Photon Institute Ltd., Cracow, Poland) adopted for photoconductivity measurements. The Ru-based films plasma-deposited on the carbon substrate constituted the working photoanode. In turn, a saturated calomel electrode (SCE, Eurosensor, Gliwice, Poland) and a Pt electrode (Photon Institute Ltd., Cracow, Poland) were used as the reference and counter electrodes, respectively. The electrodes were coupled to a potentiostat (Metrohm, Model: Autolab PGSTAT 302N, Metrohm AG, Herisau, Switzerland). The electrochemical properties of the films were characterized using the linear sweep voltammetry method (LSV) under dark conditions and illumination with an Xe illuminator (Photon Institute Ltd., Cracow, Poland) equipped with a 150 W xenon short arc lamp (Model UXL 151-H, Ushio Inc., Tokyo, Japan) and a hot mirror (Edmunds Optics, Barrington, NJ, USA) to decrease the heat caused by infrared radiation. The illuminator's light spectrum corresponded

to the full emission spectrum of the Xe lamp in the range of 230–750 nm. The area of samples was approx. 0.8 cm². The working electrode was scanned at 25 mV/s between 0 and 600 mV versus SCE. All potentials measured with respect to SCE were recalculated against a reversible hydrogen electrode (RHE), according to the following equation:

$$E_{RHE} = E_{SCE} + E^0_{SCE} + 0.059 \text{ pH} \quad [\text{V}], \quad (7)$$

where E^0_{SCE} is the standard potential of SCE equal to 0.244 V at 298 K.

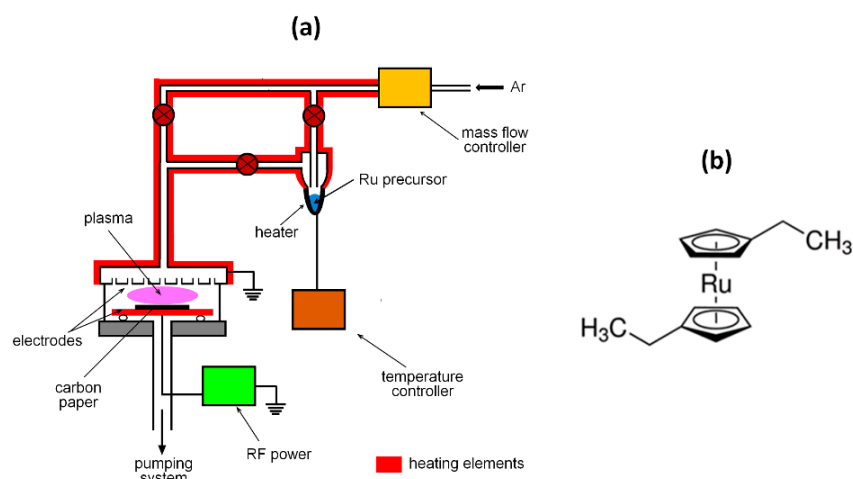


Figure 4. (a) schematic diagram of the RF plasma reactor used for deposition of Ru-based films; (b) chemical formula of the Ru-precursor.

The study of the surface molecular structure of the deposited films was carried out by X-ray photoelectron spectroscopy (XPS), using an AXIS Ultra spectrometer (Kratos Analytical Ltd., Manchester, UK) with monochromatic Al K α X-rays (1486.6 eV). The spectra were collected from at least five analysis areas of 300 μm $\times$ 700 μm , for each sample. The power of the anode was set at 150 W and the hemispherical electron energy analyzer was operated at a pass energy of 20 eV for all the high-resolution measurements. All the measurements were carried out using a charge neutralizer, and the main carbon peak (graphitic C 1s, 284.6 eV) was taken for a final calibration of each spectrum.

4. Conclusions

The main feature of the PECVD method—apart from its wide capabilities and low costs of producing new materials, and also catalytic ones—is the ability to prepare very thin films with a controlled molecular structure, and thus also controlled properties. In our work, we have confirmed the advantages of this method by plasma-depositing new Ru-based films, which have turned out to be a very active electro- and photoelectro-catalyst in the OER process. Generally, the molecular structure of the deposited material is in the form of RuO_x, with a predominance of RuO₂ (about 46 at % in relation to the total Ru atoms in various oxidation states) in electrochemically-stabilized films. The films tested as an anode electrocatalyst in alkaline electrolyte (1M NaOH) reveal the overpotential required for the current density of 10 mA/cm² equals to 350 mV, which classified them as a catalyst with very high OER performance. The photoelectrochemical properties of these films in the OER process are even more promising. For an applied potential of 1.6 V (vs RHE), the pure photocurrent density reaches about 9.0 mA/cm², which, taking into account the amount of catalytic material, gives a photocurrent efficiency of about 160 mA/cm² mg. Plasma-deposited thin Ru-based films fit well into the group of nanocatalysts, with potential applications for photoelectrochemical water splitting. Research on further improvement of the catalytic activity of these films, for example by plasma co-deposition with other metal atoms, which can easily be accomplished by the PECVD technique, should undoubtedly continue.

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Conflicts of Interest: The authors declare no conflict of interest.

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