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Laser-scribed Ru organometallic complex for the preparation of RuO₂ micro-supercapacitor electrodes on flexible substrate

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ABSTRACT

Flexible and miniaturized energy storage devices are necessary for the development of wearable applications. Hence, micro-supercapacitors, which offer good compromise between energy densities, high power capabilities and long cycle life, have to be integrated on flexible substrates. Laser-writing techniques are suitable for engineering multiple materials within short times. The integration of RuO₂ onto flexible substrates usually relies on the irradiation of ruthenium salts displaying an oxidation state of the metal varying from +II to +IV, and for which additives are necessary in the electrode to compensate the lack of adherence of the resulting large ruthenium grains. Here, we report a facile and scalable preparation of RuO₂ flexible electrodes from direct laser-writing of a spin-coated solution of ruthenium molecular precursor, the Ru(COD)(COT) (COD = 1,5-cyclooctadiene, COT = 1,3,5-cyclooctatriene) and cellulose acetate, without the addition of any other capacitive material in the electrode. The obtained Ru/RuO₂ deposit showed good adherence on a Au thin film deposited on either silicon or polyimide (Kapton™) substrates, and delivered up to 16 mF cm⁻² at 100 mV s⁻¹ in 1 M H₂SO₄. Furthermore, the flexible electrodes exhibited good capacitance retention, with more than 60% of the initial capacitance recorded at high scan rate of 10 V s⁻¹. Laser-writing using this original ruthenium metallic precursor offers an easy and scalable fabrication method for preparing additive-free RuO₂-based micro-supercapacitor electrodes.

1. Introduction

The current technological development towards miniaturized and flexible electronics for wearable applications requires new designs for energy storage devices [1]. While energy delivery is mainly ensured by batteries and supercapacitors, these are actually assembled in a sandwich configuration with metallic current collectors, thus making impossible their integration in roll-up displays, electronic papers, smart cloth, sensors and biomedical devices. To tackle the need for flexible, lightweight, high power and

long cycle life systems, carbon-based micro-supercapacitors (MSCs) have been integrated onto flexible substrates. Therefore, carbon nanotubes (CNT) [2], graphene [3–6], reduced graphite oxide (r-GO) [7] and porous carbon [8] have been explored in the past five years. Another strategy to improve the electrochemical performance of flexible devices consists in the use of pseudocapacitive materials, which store energy via fast and reversible redox reactions occurring mainly at their surface. Metal oxides, such as MnO₂ [9,10], RuO₂ [11], or MXenes [12], as well as conductive polymers [13], have been integrated on flexible substrates via many fabrication processes.

Laser-writing has attracted particular research interest as it provides a facile and scalable one-step process under ambient conditions to manufacture bendable MSCs [14–16]. Based on the pioneer work from Arnold's and Kaner's groups [14,15], direct laser-writing was used to embed pseudocapacitive materials in polyimide [17]. Ruthenium oxide is a good candidate for the preparation of MSCs thanks to its extremely high theoretical pseudocapacitance

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(>1300 F g⁻¹), its acceptable electronic conductivity and long-term cyclability [18]. Besides, the low RuO₂ loadings used in micro-supercapacitor electrodes do not make the cost of RuO₂ precursors a major issue [19]. Recently, Kaner's group prepared laser-scribed graphene (LSG)/RuO₂ based MSCs from a graphene oxide (GO)/RuCl₃ mixture drop-casted on PET [20]. Laser irradiation allowed both GO conversion into graphene and RuCl₃ oxidation into RuO₂. However, RuCl₃·3H₂O, used as a soluble precursor, is an ill-defined compound displaying Ru centers adopting the +II and +IV oxidation states, which can further leave chloride contaminants in the material. Aside, GO is needed to ensure a good adherence of the laser-scribed RuO₂. In search for precursors able at providing a proof of concept of the deposition of thin RuO₂ layers on a flexible substrate by laser writing technology, we turned to ruthenium 1,5-cyclooctadiene 1,3,5-cyclooctatriene (Ru(COD)(COT)) known to decompose in mild conditions without leaving any residues [21].

In this communication, we describe, as a proof of concept, the preparation of adherent pseudocapacitive electrodes for micro-supercapacitor applications starting from the above mentioned organometallic complex in which ruthenium is zerovalent (Ru(0)), using a simple laser-writing process. Thus, RuO₂-based electrodes were obtained from direct laser-writing of a Ru(COD)(COT)/cellulose acetate mixture, supported on a flexible Kapton™/Ti/Au substrate, without using any additional capacitive material or nanostructuring step. Different from Atomic Layer Deposit (ALD) or sputtering techniques, the laser-writing of this original ruthenium metallic precursor provided a facile and scalable fabrication of thin-films RuO₂-based electrodes for designing flexible MSCs.

2. Experimental

2.1. Electrodes preparation

The Ru(COD)(COT)/cellulose acetate mixture was obtained according to previous work [21]. Briefly, in a glove box (O₂ and H₂O contents lower than 0.1 ppm), 67.4 mg of cellulose acetate were dissolved in 3 mL of tetrahydrofuran (THF, Sigma Aldrich). In a different recipient, 125 mg of Ru(COD)(COT) (NanoMePS, France) were dissolved in 1 mL of THF. Then, the Ru(COD)(COT) solution was added into the cellulose acetate solution, resulting in a yellow solution (Ru/polymer 60% wt).

Prior to Ru(COD)(COT)/cellulose acetate mixture deposition, Ti/Au(50 nm/200 nm) was evaporated onto a Kapton™ foil (75 μm, RadioSpare, UK) to insure the current collection during the electrochemical characterizations. Polyimide was chosen for its thermal stability [22]. The as-prepared Ru(COD)(COT)/cellulose acetate mixture was then spin-coated on the flexible substrate (500 rpm, 30 s) to achieve a homogeneous deposit of the ruthenium precursor (thickness of 1.50 ± 0.25 μm). The use of cellulose acetate allows the smooth and homogeneous deposition of the Ru(COD)(COT) precursor during spin-coating, which is not the case when spin-coating is performed without cellulose acetate. Finally, the Kapton™/Ti/Au/Ru(COD)(COT)/cellulose acetate mixture was irradiated with a UV laser (405 nm, power up to 285 mW on the sample, DILASE 250, KLOÉ, France, designed for direct laser-writing), converting the Ru precursor into RuO₂ through combustion of the organic parts of the precursor and the cellulose acetate, and oxidation of the Ru(0). The best results were obtained with the irradiation parameters: 40% of the full power (116 mW), a spot size of 1 μm, a distance between two adjacent lines of 1 μm and a writing speed of 2 mm s⁻¹. The area that was not irradiated by the laser was easily removed by washing the non-laser-scribed Ru(COD)(COT)/cellulose acetate with acetone and ethanol. The procedure could be repeated several times to increase the amount

of coated RuO₂, with a short 20 min annealing at 250 °C after each deposition step.

2.2. Structural and electrochemical characterizations

The chemical composition and morphology of the electrochemically active deposit were investigated by X-ray photoelectron spectroscopy (XPS). The analyses were carried out with a Kalpha XPS ThermoScientific (Thermo fisher scientific, USA) using a monochromatic AlKα source (1486.6 eV). The pressure in the analysis chamber was close to 10⁻⁹ mbar. Constant passed energy was kept at 30 eV with 0.1 eV energy steps for the high resolution scans. All the binding energies refer to a C (1s) peak binding energy of 284.5 eV.

The structure of the laser-scribed RuO₂ was observed through Scanning Electron Microscopy (SEM) with a JSM 7100 F (JEOL, Japan), and the thickness of the coating was estimated from the cross-sectional view of the layered Kapton™/Ti/Au/laser-scribed Ru(COD)(COT).

The electrochemical characterizations of the as-prepared electrodes were carried out using a Biologic VMP3 Potentiostat in 1 M H₂SO₄ in a three-electrode configuration. A Hg/Hg₂SO₄ electrode was used as reference electrode and a 0.64 cm² Pt foil as counter electrode. Cyclic voltammetry was performed at several scan rates and the areal capacitance (C, in F cm⁻²) was calculated from equation (1):

$$C = \frac{\int IdV}{A \cdot v \cdot \Delta V} \quad (1)$$

where I stands for the discharge current (A), v the scan rate (V s⁻¹), ΔV the potential window (V) and A the footprint area of the active material (cm²).

3. Results and discussion

3.1. Laser-scribed ruthenium oxide

An optical view of a 0.25 cm² laser-scribed Ru(COD)(COT) film (center) deposited onto a Kapton™ foil covered with a conducting Ti/Au thin layer (border) is presented in Fig. 1A. The RuO₂ layer grown on the gold layer looks homogeneous and exhibits a granular structure (magnification Fig. 1A). In addition, the material resulting from Ru(COD)(COT) after laser-writing remained onto the flexible substrate even after a scotch scratch test. A thickness of 100 nm was first estimated with an optical profiler (SENSOFAR, Spain) (Fig. S1).

The conversion of the Ru(COD)(COT) precursor into RuO₂ was monitored by XPS, since the diffraction peaks related to RuO₂ were not clearly visible from X-Ray diffraction analyses (Figs. S2 and S3). As important information can be missed on the Ru(3p) spectra, the Ru(3d) core level was first studied. A deconvolution was necessary as the Ru(3d) core level overlaps the C(1s) core level. The presence of carbon (detailed in Supplementary Materials) is assumed to be a surface contamination layer formed on the electrode surface during storage, since the C-bindings are no longer visible after a 30s Ar⁺ erosion of the surface (Figs. S4A and S4B). Also, the possible presence of carbon coming from the laser-writing of cellulose acetate was definitely excluded by performing cyclic voltammetry on laser-scribed cellulose acetate, where no additional capacitive current was evidenced (Fig. S5). Fig. 1B (left) shows the Ru(3d) core level recorded for the laser-scribed Ru(COD)(COT). The Ru(3d) peaks are resolved as two 3d_{5/2} and 3d_{3/2} doublets, with a spin-orbit splitting of 4.2 eV. The Ru 3d_{5/2} binding energy is determined as 280.9 eV,

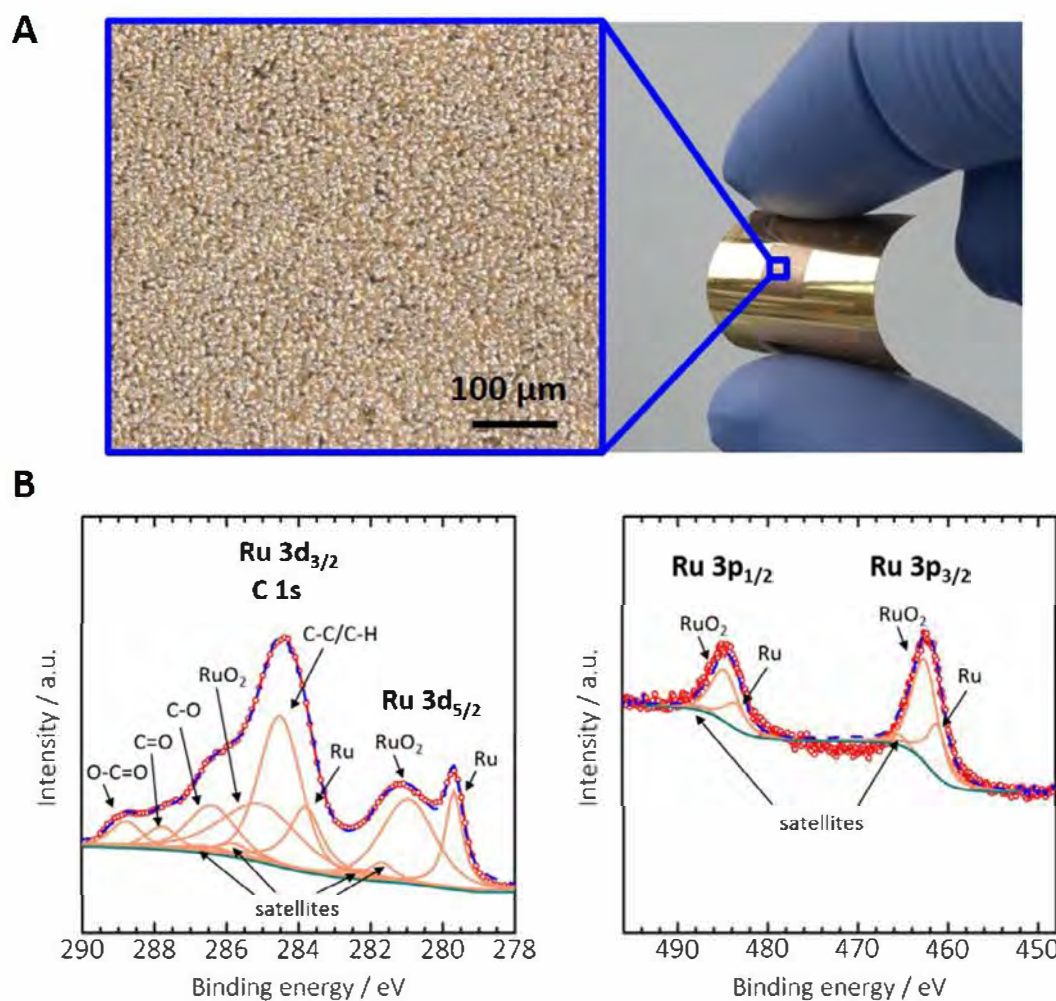


Fig. 1. Chemical composition of the as-prepared electrode material. (A) Optical view of the as-prepared Kapton™/Ti/Au/laser-scribed Ru(COD)(COT) electrode (right) and microscope observation of the laser-scribed Ru(COD)(COT) (left). (B) Corresponding high resolution XPS spectra of the Ru(3d) and Ru(3p) regions.

which is characteristic for Ru(IV) [23]. The presence of a second lower binding energy spin-orbit doublet, with a Ru 3d_{5/2} component located at 279.7 eV, shows that the electrode contains zerovalent Ru [24]. The corresponding satellites were added accordingly. Hence, the laser-writing of Ru(COD)(COT) leads to a mixture of metallic ruthenium and ruthenium oxide, arising either from a spontaneous oxidation or induced by the temperature reached upon laser irradiation. This supports the assumption that the laser irradiation removes the organic chains of the Ru precursor under ambient atmosphere. Then, the Ru(3p) core level spectrum shown Fig. 1B (right) was deconvoluted accordingly [23]. The atomic ratio between metallic Ru(0) and Ru(IV) is calculated to be 1:2 from both Ru(3d) and Ru(3p) core level analysis.

To further characterize the as-prepared electrode material, SEM observations were carried out. Fig. 2A is a top view SEM image of the RuO₂ coating (left) deposited onto a Kapton™/Ti/Au substrate (right). While focusing on the laser-scribed area (Fig. S6A), it is seen that the deposited material grown on the Kapton™/Ti/Au (Fig. 2B) consists in 5 μm-length Ru containing elongated islands (evidenced by EDX as shown Fig. S6B) presenting a flake-like open porous structure for the coating. Cross-sectional observations of the layered Kapton™/Ti/Au/RuO₂ electrode (Fig. 2C) were used to estimate an average thickness of 210 ± 50 nm for the RuO₂ deposit (Fig. 2D).

3.2. Electrochemical characterization

To investigate the electrochemical performance of the as-prepared RuO₂, laser writing was performed on both Si/Ti/Au and Kapton™/Ti/Au. Electrochemical characterizations were carried out in 1 M H₂SO₄ from cyclic voltammetry at different scan rates. Fig. 3A shows the cyclic voltammogram recorded at 100 mV s⁻¹ for a Si/Ti/Au/RuO₂ electrode. The current was normalized to the RuO₂ area. The electrode exhibits the electrochemical signature expected for RuO₂ [25] and delivers 24.5 mF cm⁻², which is comparable to the values reported for planar design [26,27]; however, a deviation from the ideal response is observed at low potentials. This deviation has already been observed for hydrated RuO₂ · xH₂O [25]. The current arising from reversible ion adsorption on the bare Si/Ti/Au substrate is negligible (dashed line).

A pseudocapacitive signature is still observed with the flexible Kapton™/Ti/Au/RuO₂ electrode, although only 6.5 mF cm⁻² are delivered. This difference is assumed to originate from the heat diffusion, which depends on the nature of the substrate used, thus influencing the growth of the deposit during laser-writing. Since such a low areal capacitance is likely due to a low mass of active material, five successive Ru(COD)(COT)/cellulose acetate spin-coating and laser writing cycles were performed on Kapton™/Ti/Au, leading to a labeled 5-Kapton™/Ti/Au/RuO₂ electrode. The

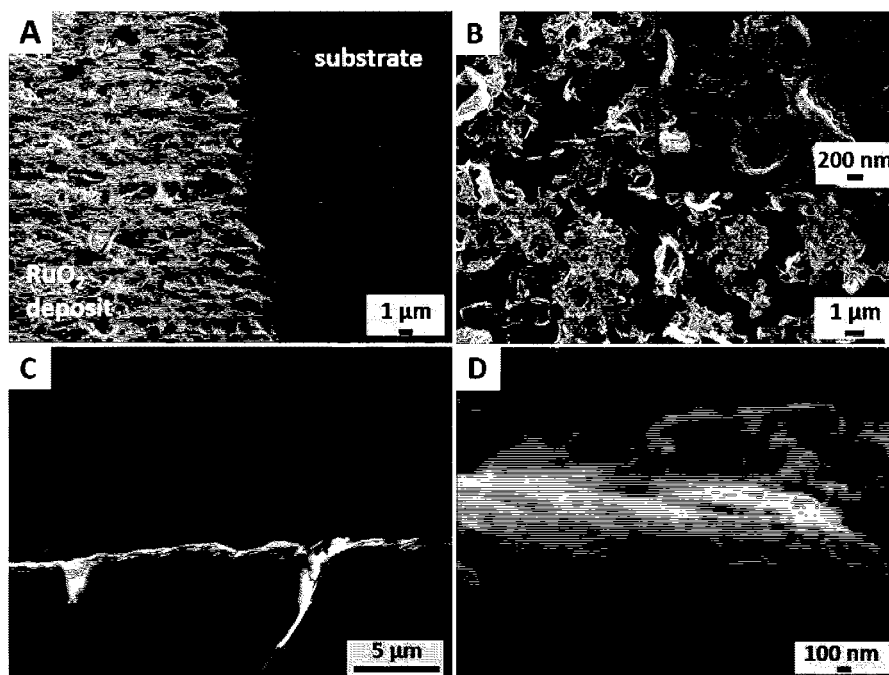


Fig. 2. SEM observation of the Kapton™/Ti/Au/RuO₂ electrode. (A) Tilted view of the RuO₂/substrate interface. (B) Observation of flake-like RuO₂ (inset) present within the 5 μm-long islands. (C) Cross-sectional view of the flexible electrode with (D) a 210 nm-thick RuO₂ deposit.

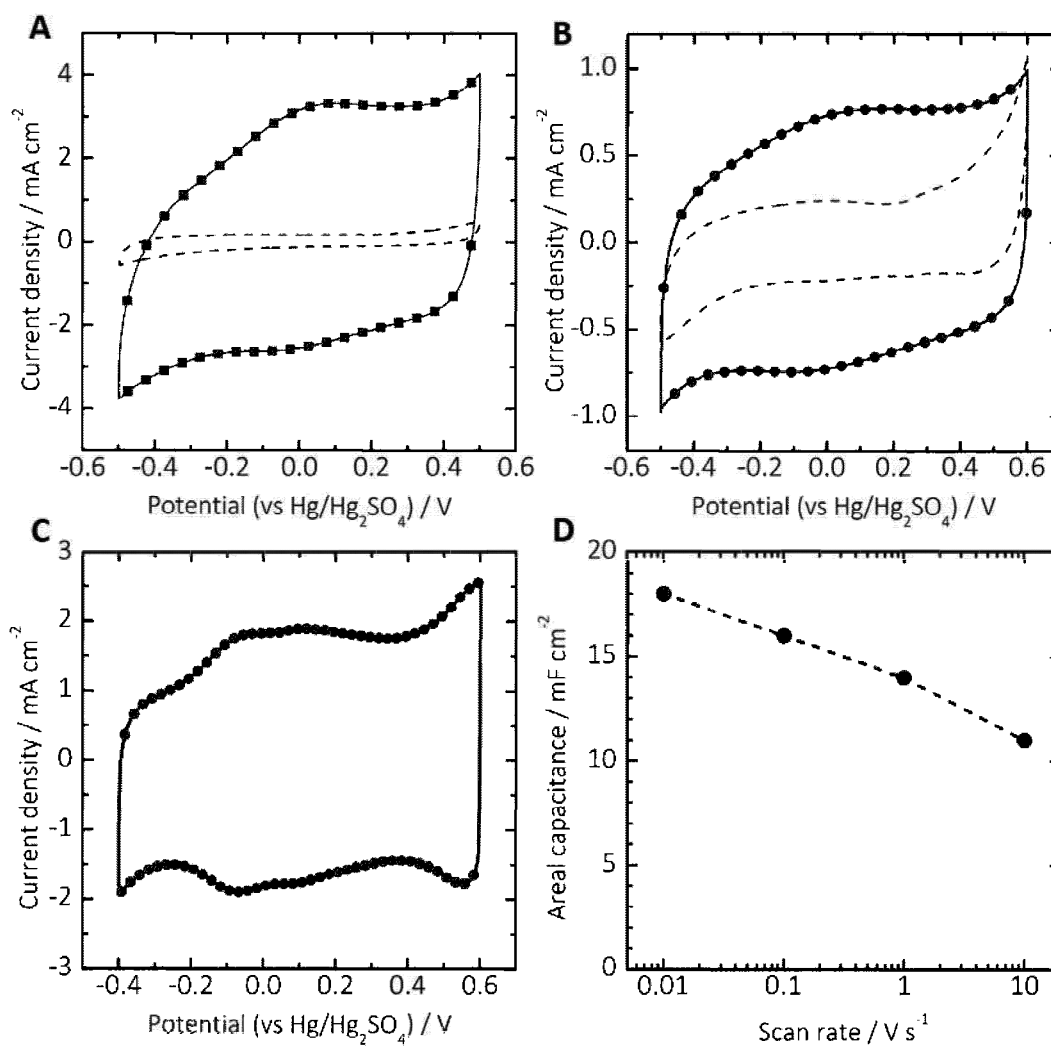


Fig. 3. Electrochemical characterization of the laser-scribed RuO₂. (A) Cyclic voltammograms of a Si/Ti/Au/RuO₂ electrode and (B) Kapton™/Ti/Au/RuO₂ electrode recorded at 100 mV s⁻¹ in 1 M H₂SO₄. The current represented as dashed line is attributed to the substrate. (C) Improvement of the areal capacitance after five successive spin-coating/laser-writing cycles performed on the flexible substrate and (D) performances of the 5-Kapton™/Ti/Au/RuO₂ electrode.

corresponding CV curve recorded at 100 mV s^{-1} in $1 \text{ M H}_2\text{SO}_4$ is presented in Fig. 3C (solid circles). Again, the electrochemical signature of pseudocapacitive RuO_2 is visible, delivering an areal capacitance value of 16 mF cm^{-2} , which is about three times higher than that of the RuO_2 active layer previously obtained. The areal capacitance does not increase linearly with the number of layers; this was ascribed to a change of the hydration number of the RuO_2 during the annealing steps, as confirmed by the shape of the cyclic voltammogram obtained such as previously reported by Zheng et al. [25]. This moderate areal capacitance value is similar to most of the capacitance reported for interdigitated micro-supercapacitor electrodes [2,3,16], although hybrid LSG/ RuO_2 electrodes deliver higher capacitance of 171 mF cm^{-2} [20]. However, this method allows to prepare thin layers of active materials using a wet synthesis route that avoids the use of complex Atomic Layer Deposition (ALD) or sputtering techniques [27]. Besides, a loading of $25 \mu\text{g cm}^{-2}$ was calculated from ICP-MS measurements, thus corresponding to a gravimetric capacitance of 640 F g^{-1} , which is consistent with the values reported in the literature [25].

The rate performances of the laser-scribed RuO_2 electrodes were assessed from the CVs performed at different scan rates. Fig. 3D shows the change of the areal capacitance, calculated from the integration of the CVs during discharge, with the scan rate. At a high scan rate of 10 V s^{-1} , the KaptonTM/Ti/Au/ RuO_2 electrode still delivers 11 mF cm^{-2} , which is more than 60% of the initial capacitance at the low scan rate of 10 mV s^{-1} . Thus, the thin RuO_2 coating ensures high rate performances, as well as its binder-free structure.

4. Conclusion

Ruthenium oxide was successfully deposited as a thin layer on both gold-coated silicon and KaptonTM substrates with good adherence by UV laser irradiation of an organometallic $\text{Ru}(\text{COD})(\text{COT})$ precursor, dispersed in a cellulose acetate film. Laser-writing led to the release of the $\text{Ru}(\text{O})$ atoms from the organometallic complex, which were partially oxidized under air. Although a modest capacitance value of 6.5 mF cm^{-2} was recorded in sulfuric acid, the KaptonTM/Ti/Au/ RuO_2 electrodes exhibited a pseudocapacitive ruthenium oxide signature, despite the fact that no additional material was used to improve the adherence and the electronic/protonic conductivity of the laser-scribed RuO_2 . The amount of active material could be further increased by repeating the fabrication process several times. Doing so, an areal capacitance of 16 mF cm^{-2} was obtained at 100 mV s^{-1} with a flexible RuO_2 electrode prepared from five repetitions of spin coating/laser scribing cycles. In addition, more than 60% of the initial capacitance was still delivered at a high scan rate of 10 V s^{-1} . Spin-coating and laser writing constitute a facile and scalable route to design thin films RuO_2 electrodes under ambient conditions.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.electacta.2018.05.198>.

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