

Swiss Roll Nanomembranes with Controlled Proton Diffusion as Redox Micro-Supercapacitors

Hengxing Ji^{*a}, Yongfeng Mei^{*a}, and Oliver G. Schmidt^a

^a*Institute for Integrative Nanosciences, IFW Dresden, Helmholtzstrasse 20, D-01069 Dresden, Germany*

E-mail: h.ji@ifw-dresden.de; y.mei@ifw.dresden;

Supplementary Information

Fig. S1. Fabrication process and structure of Rolled-up Micro-supercapacitor.

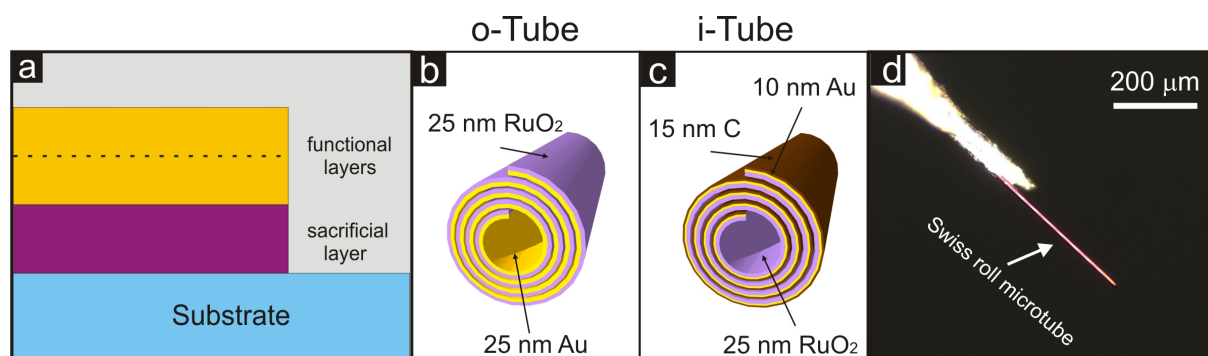


Fig. S1: The redox micro-supercapacitor was fabricated via a rolled-up technology.^{1,2} First, 2 μm photoresist (ARP 3510) was spin-coated onto a Si/SiO₂ substrate at 3500 rpm and patterned by photolithographic processing. Second, 25 nm of Au was deposited onto the photoresist (serving as a current collector) followed by 25 nm of RuO₂ (serving as an electrochemical active layer) for the functional layers of the o-Tube with RuO₂ localized at the outside (Fig. S1(b)). We have also deposited 25 nm RuO₂ on the photoresist layer, and then 10 nm Au and 15 nm Carbon for the functional layers of the i-Tube with RuO₂ at the inside surface (Fig. S1(c)). Here, the carbon layer is used to help the functional layers rolling downward. After the deposition of the functional layers, the sample was immersed into acetone, in which the photoresist layer was dissolved. The functional layers were freed from the substrate and roll downward automatically in the area where the photoresist was removed, due to the film stress gradient. After washing in isopropanol and drying in air, a microtube, hundreds of micrometer in length and several micrometers in diameter, can be achieved. Finally, a single microtube can be picked out and bonded to a gold coated capillary for electrochemical characterization (Fig. S1(d)).

Fig. S2. Chemical composition and structure of RuO₂ film.

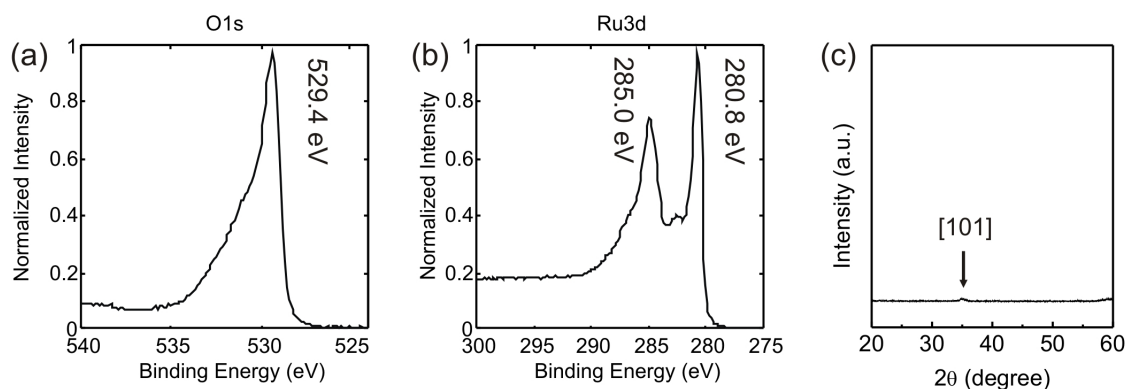


Fig. S2: The chemical composition and structure of a ruthenium oxide layer was characterized by X-ray photoelectron spectroscopy and X-ray diffraction. The O1s peak at 529.4 eV in Fig. S2(a) and the Ru3d peaks at 285.0 eV and 280.8 eV in Fig. S2(b) point to a chemical composition of RuO₂.³ In Fig. S2(c), a weak peak corresponding to the plane [101] in the XRD pattern suggests amorphous structure of RuO₂. These results agree well with literature, namely that a RuO₂ film deposited by RF sputtering at room temperature is amorphous.

Fig. S3 Complex-plane plot of o-Tube in the high frequency range from 5 MHz to 1 kHz.

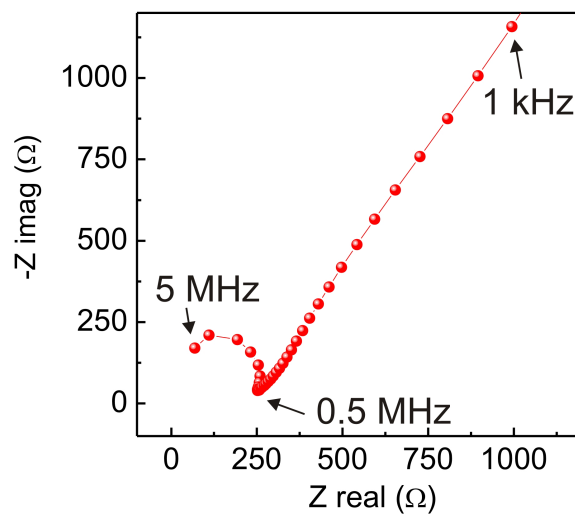
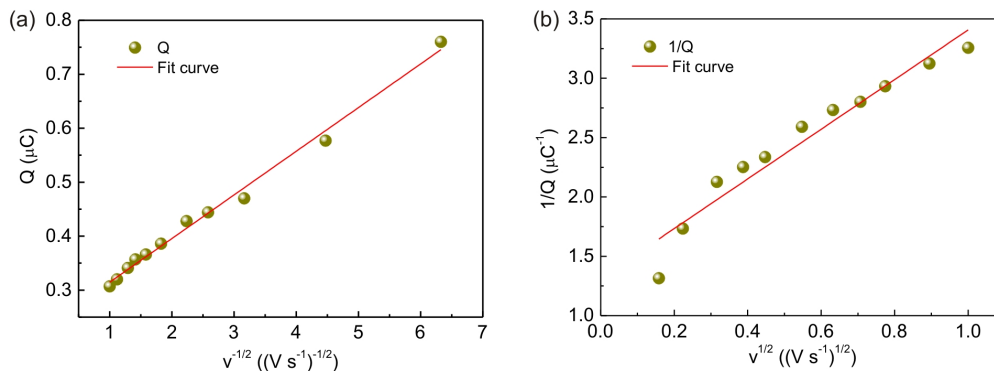


Fig. S3: complex-plane plot of o-Tube in the high frequency shows a semicircle, which is caused by a parallel combination of solution resistance and double layer capacitance.^{4,5}

Fig. S4. Dependence of voltammetric charge on the scan rates of cyclic voltammetry.

o-Tube



i-Tube

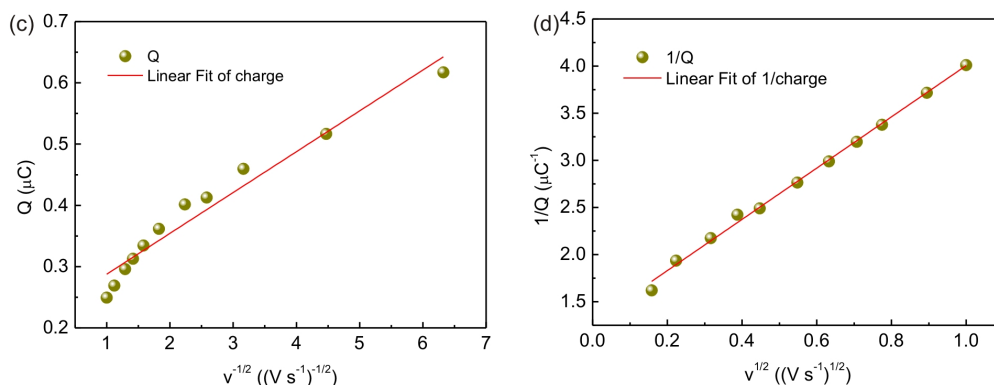


Fig. S4: According to the study by Trasatti et al.,⁶ the voltammetric charge Q_T is composed of an “outer charge” (Q_o) and an “inner charge” (Q_i). Q_o originates from the direct accessible surface, which corresponds to the region touching the electrolyte solution directly. In this case the reactive species diffusion does not control the reaction. Q_i comes from the charge originating from less accessible surface, such as pores, grain boundaries, and cracks; where the reaction is controlled by diffusion processes. Q_o can be derived from an extrapolation of the voltammetry charge Q as $v = \infty$ from the plot of Q vs $v^{-1/2}$, whereas, the total charge Q_T can be calculated from an extrapolation of Q at $v = 0$ from the plot $1/Q$ vs $v^{1/2}$. Thus, the “inner charge” Q_i which comes from the diffusion controlled reaction can be deduced from $Q_T - Q_o$. Fig. 4 presents the Q - v plot of the o-Tube (Fig. S4(a), Fig. S4(b)) and i-Tube (Fig. S4(c), Fig. S4(d)).

Experimental

The photolithography process was carried out by a MA56 mask aligner. Au films were evaporated through E-beam evaporation at a rate of $1 \text{ \AA s}^{-1}$. RuO₂ films were deposited by RF-sputtering at 100 W, 5×10^{-3} mbar O₂/Ar with a concentration ratio of 1:4 from a metallic Ru target. The carbon film was deposited by RF-sputtering at 200 W, 7.5×10^{-4} mbar Ar from a graphite target.

Electrochemical characteristics of the redox micro-supercapacitor were examined by a IM6 (Zahner) at 25 °C in a three-compartment cell with 0.5 M H₂SO₄ electrolyte solution. A Ag/AgCl electrode was used as the reference and a piece of platinum foil was employed as the counter electrode. The cyclic voltammetry curve was recorded at the potential sweep range of 0 ~ 0.8 V vs SHE. The AC impedance was measured at a potential of 0.8 V (vs SHE) and frequency range of 40 mHz ~ 5 MHz

References

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