

Supporting Information

Chemical stability of mesoporous oxide thin film electrodes under electrochemical cycling: from dissolution to stabilization

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Table S1 Film thicknesses as a function of time, obtained by ellipsometry, for the systems immersed in different solutions under and without electrochemical cycling.

Thickness (nm)	0	Fe(CN) ₆ ³⁻ 10 h	Fe(CN) ₆ ³⁻ 24 h	Fe(CN) ₆ ³⁻ 48 h	Ru(NH ₃) ₆ ³⁺ 10 h	Ru(NH ₃) ₆ ³⁺ 24 h	Ru(NH ₃) ₆ ³⁺ 48 h	KCl 10 h	KCl 24h
without cycling									
SiO ₂	135 ± 7	146 ± 7	150 ± 8	53 ± 3	136 ± 7	152	40 ± 2	150 ± 8	99 ± 5
TiO ₂	251 ± 13	-----	-----	-----	----	----	261 ± 13	----	----
Thickness (nm) under cycling	0	Fe(CN) ₆ ³⁻ 1 h	Fe(CN) ₆ ³⁻ 3 h	Ru(NH ₃) ₆ ³⁺ 0.5 h	Ru(NH ₃) ₆ ³⁺ 1 h	Ru(NH ₃) ₆ ³⁺ 7 h			
SiO ₂	165 ± 8	140 ± 7	-----	60 ± 3	20 ± 1	----			
TiO ₂	226 ± 11	-----	197 ± 10	----	----	211 ± 11			
Si _{0.9} Zr _{0.1} O ₂	248								

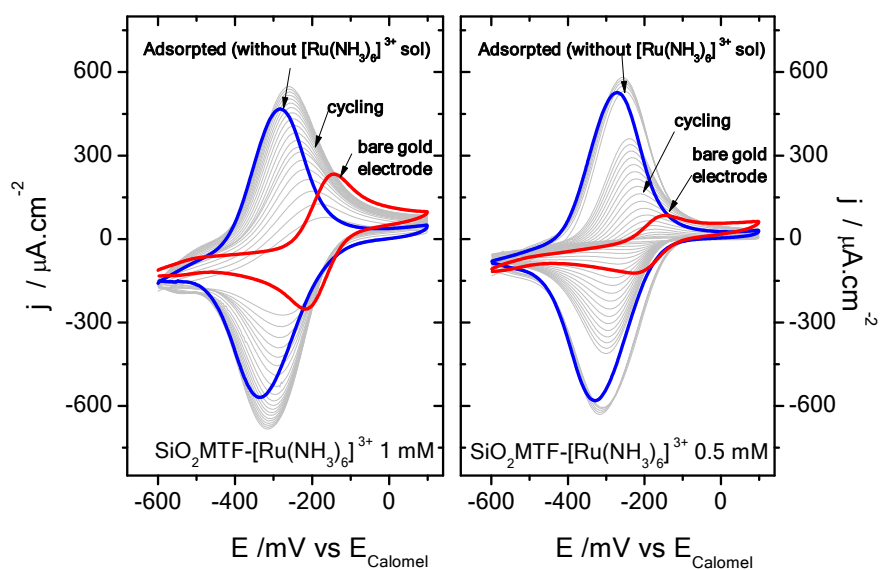


Figure S1 Voltamograms of $\text{Ru}(\text{NH}_3)_6^{3+}$ adsorbed onto SiO_2 MTF measured in KCl solution without $\text{Ru}(\text{NH}_3)_6^{3+}$.

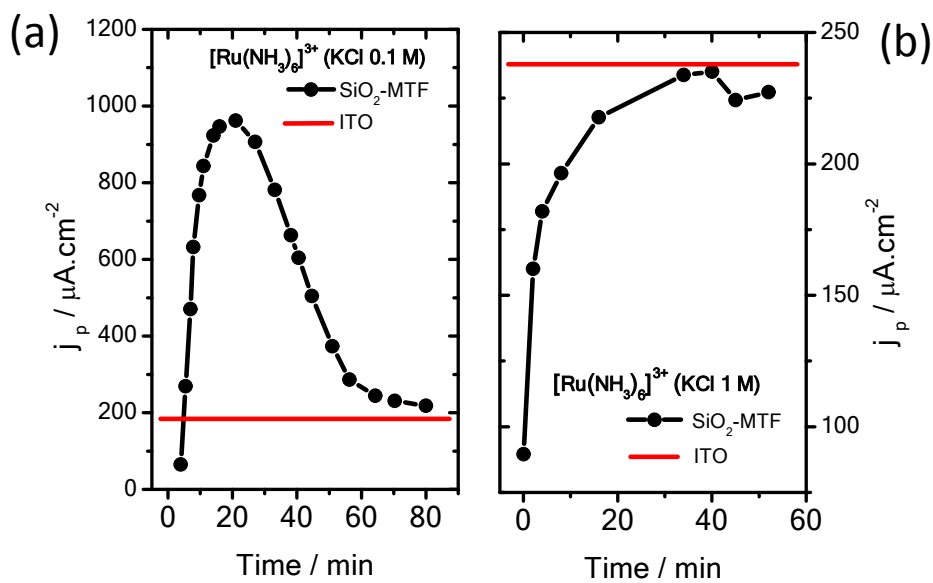


Figure S2 Peak current as a function of time for SiO_2 MTF obtained at 300 mV s^{-1} in the presence of 1 mM $\text{Ru}(\text{NH}_3)_6^{3+}$ and 0.1 M (a) and 1 M (b).

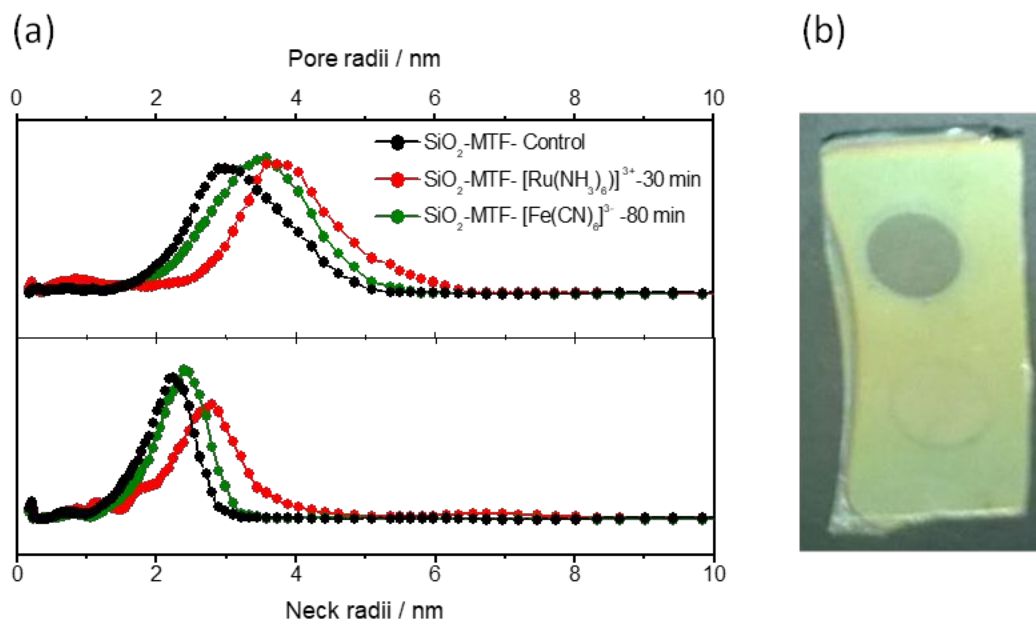


Figure S3 (a) Pore and neck size distributions obtained by means of EEP for SiO₂ MTF as prepared (black) and after applying electrochemical cycling for 30 min in the presence of 1 mM Ru(NH₃)₆³⁺ (0.1 M KCl) (red), and for 80 min in the presence of 1 mM Fe(CN)₆³⁻ (0.1 M KCl) (green). (b) Appearance of the film after the experiments: the upper circle was the zone exposed to Ru(NH₃)₆³⁺ and the lower circle was the zone exposed to Fe(CN)₆³⁻.

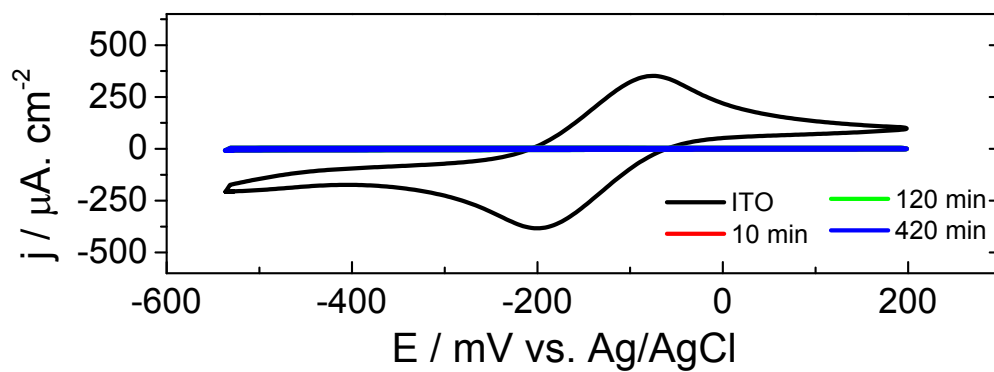


Figure S4 Voltammograms obtained at a scan rate of 300 mV s⁻¹ for bare ITO and for non-mesoporous SiO₂, at different times in the presence of Ru(NH₃)₆³⁺.

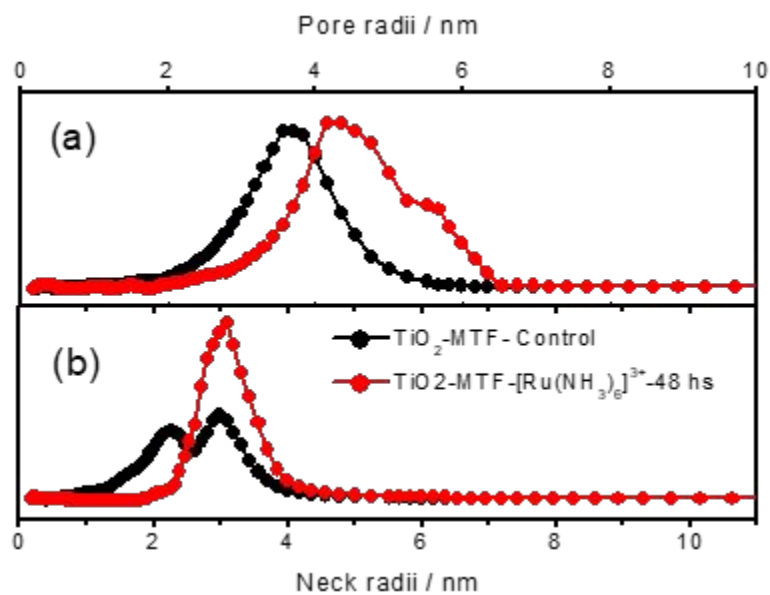


Figure S5 (a) Pore and (b) neck size distributions obtained by means of EEP for TiO₂ MTF before and after 48 h immersion in 1 mM Ru(NH₃)₆³⁺ (0.1 M KCl).

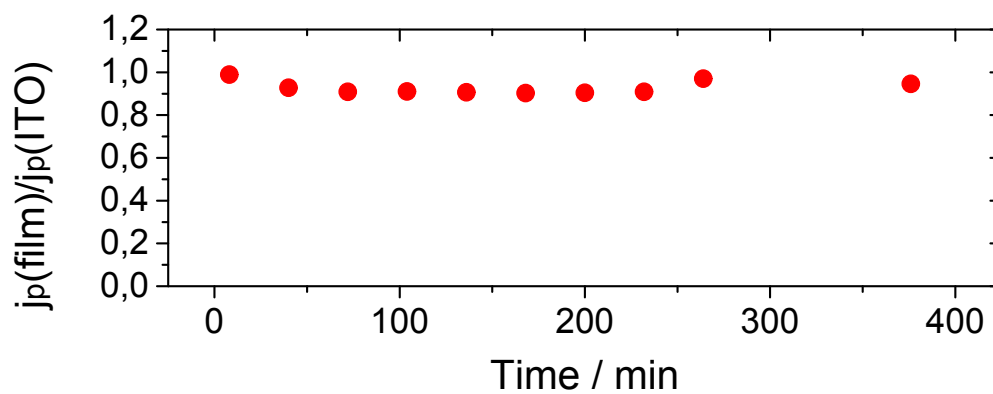


Figure S6 Peak current density as a function of time for TiO₂ MTF, obtained at 50 mV s⁻¹ in the presence of Fe(CN)₆³⁻.

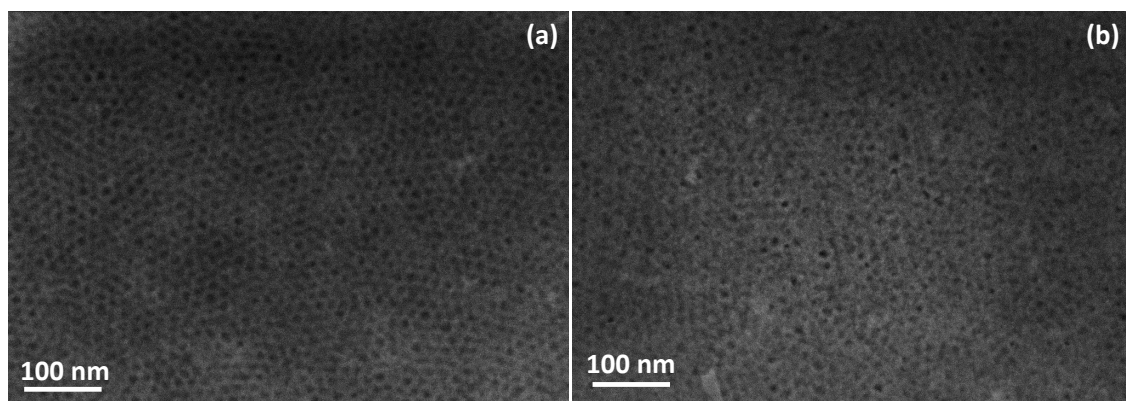


Figure S7 SEM image of $\text{Si}_{0.9}\text{Zr}_{0.1}\text{O}_2$ MOTF surface over gold electrode before **(a)** and after **(b)** electrochemical cycling in $\text{Ru}(\text{NH}_3)_6^{3+}$ (0.1 M KCl) solution.