Supporting Information

Graphene-Supported $[\{Ru_4O_4(OH)_2(H_2O)_4\}(\gamma\text{-}SiW_{10}O_{36})_2]^{10-}$ for Highly Efficient Electrocatalytic Water Oxidation

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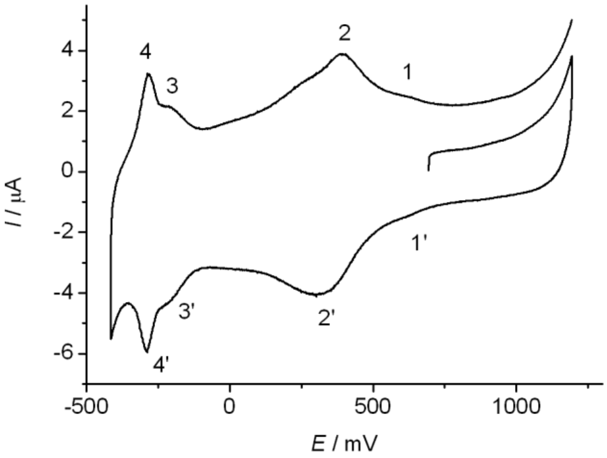

Figure S1. Cyclic voltammogram obtained in 0.5 M H_2SO_4 with a wet graphene modified electrode (details given in text). Scan rate: 50 mV s^{-1}.

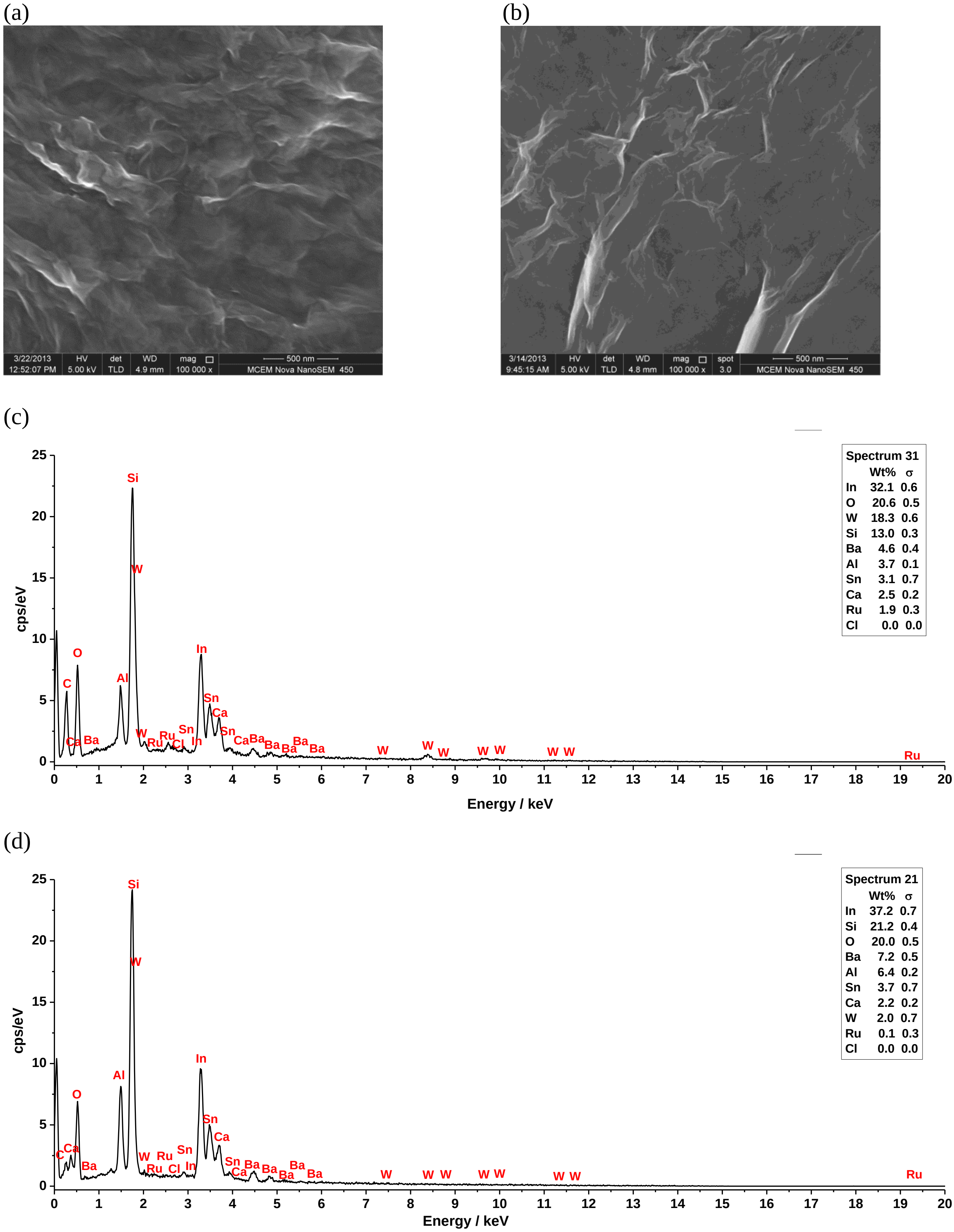

Figure S2. SEM images and EDX spectra obtained from a **1**–graphene modified electrode (a and c) and a **1**–dry graphene modified electrode (b and d).

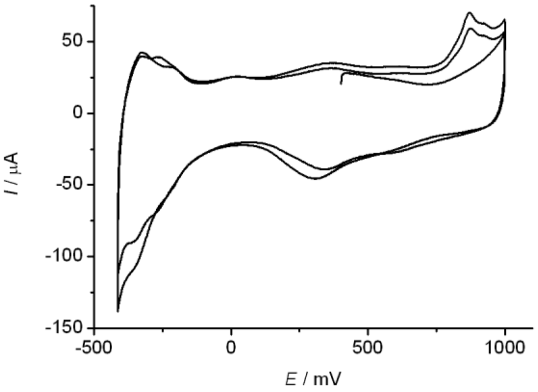

Figure S3. Cyclic voltammograms obtained with a **1**–graphene modified electrode in 0.5 M H_2SO_4. Scan rate: 50 mV s^{-1}. Graphene deposition: 30 cycles of potential between 0 and -1.4 V (vs. Ag/AgCl, 3 M NaCl) in 1 mg ml^{-1} graphene oxide (0.05 M Na_2HPO_4) at a scan rate of 50 mV s^{-1}.

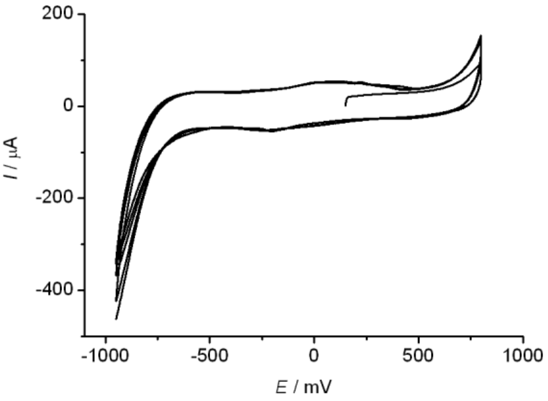

Figure S4. Cyclic voltammograms obtained with a **1**–graphene modified electrode in 0.1 M borate buffer containing 1 M $Ca(NO_3)_2$, pH 7.50. Scan rate: 50 mV s^{-1}. Graphene deposition: 30 cycles of potential between 0 and -1.4 V (vs. Ag/AgCl, 3 M NaCl) in 1 mg ml^{-1} graphene oxide (0.05 M Na_2HPO_4) at a scan rate of 50 mV s^{-1}.

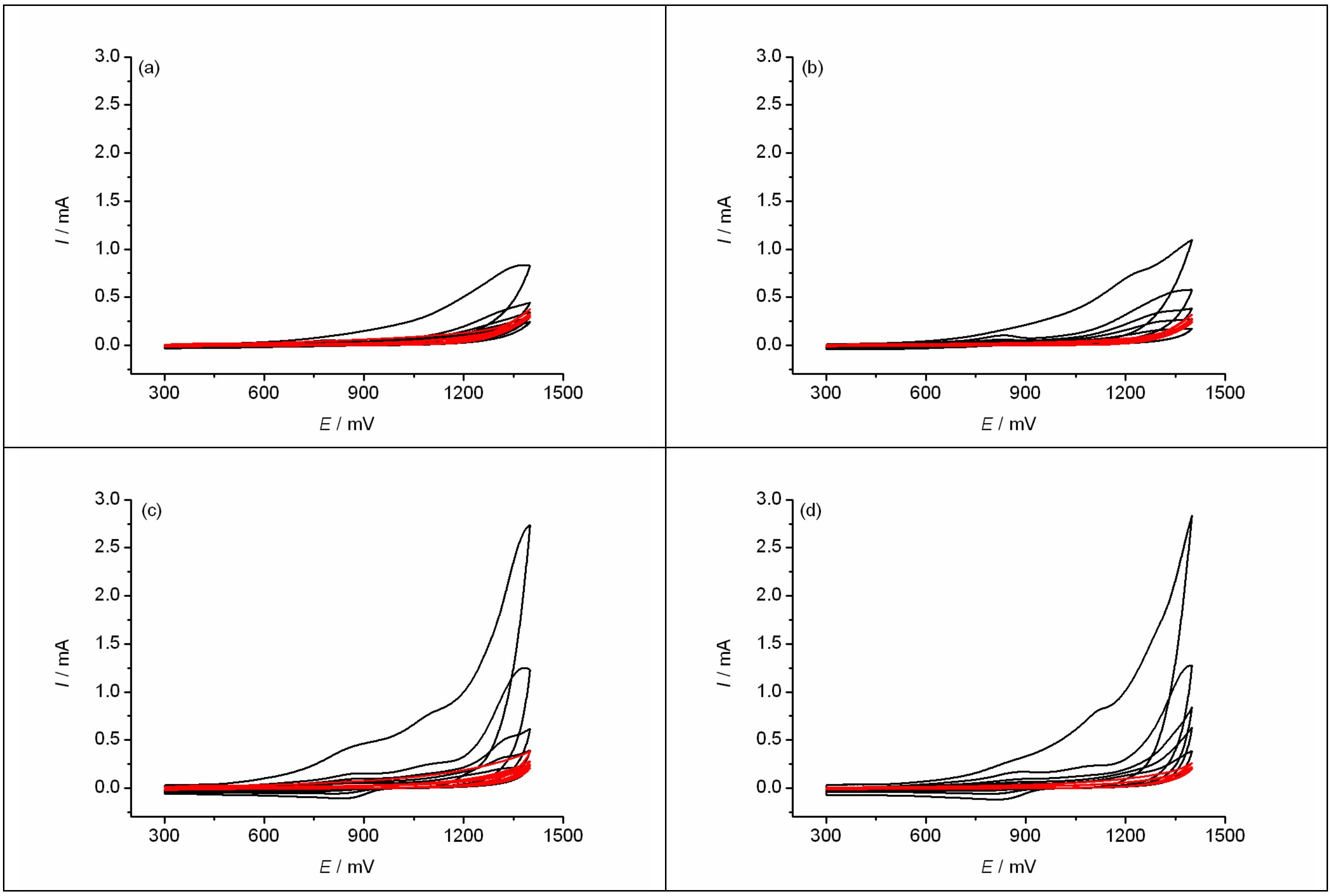

Figure S5. Electrocatalytic water oxidation using a **1**–graphene modified electrode (—) or a graphene modified electrode (—) in 0.1 M sodium phosphate buffer, pH 7.50, in the absence (a) and presence of additional supporting electrolyte (b) 0.1 M $LiClO_4$, (c) 1 M $NaNO_3$ and (d) 1 M KNO_3.

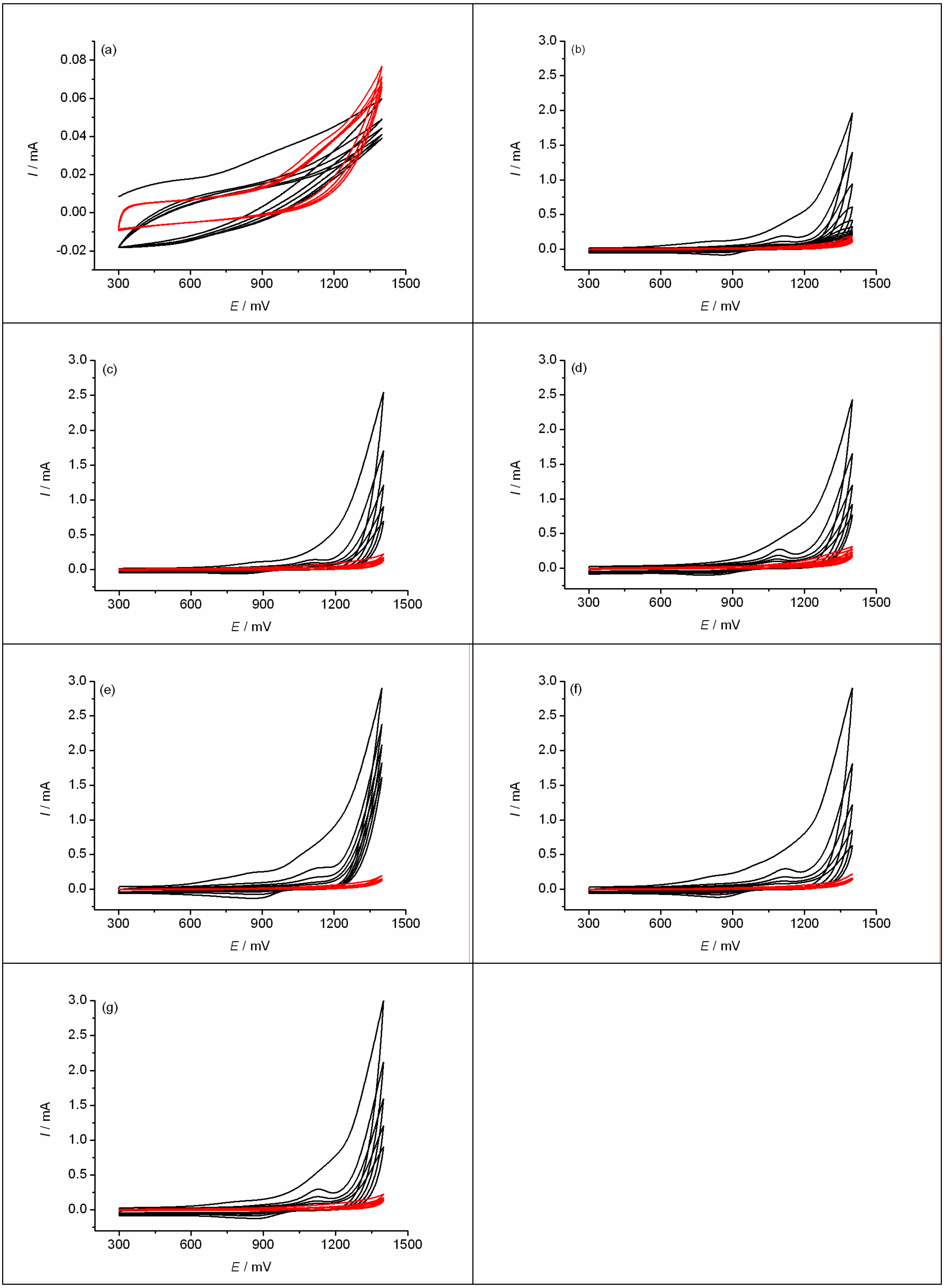

Figure S6. Electrocatalytic water oxidation using a **1**–graphene modified electrode (—) or a graphene modified electrode (—) in 0.1 M sodium borate buffer, pH 7.50 in the absence (a) and presence of additional supporting electrolyte (b) 1 M $LiNO_3$, (c) 1 M $NaNO_3$, (d) 1 M KNO_3, (e) 1 M $Ca(NO_3)_2$, (f) 1 M $Mg(NO_3)_2$ and (g) 2 M $NaNO_3$.

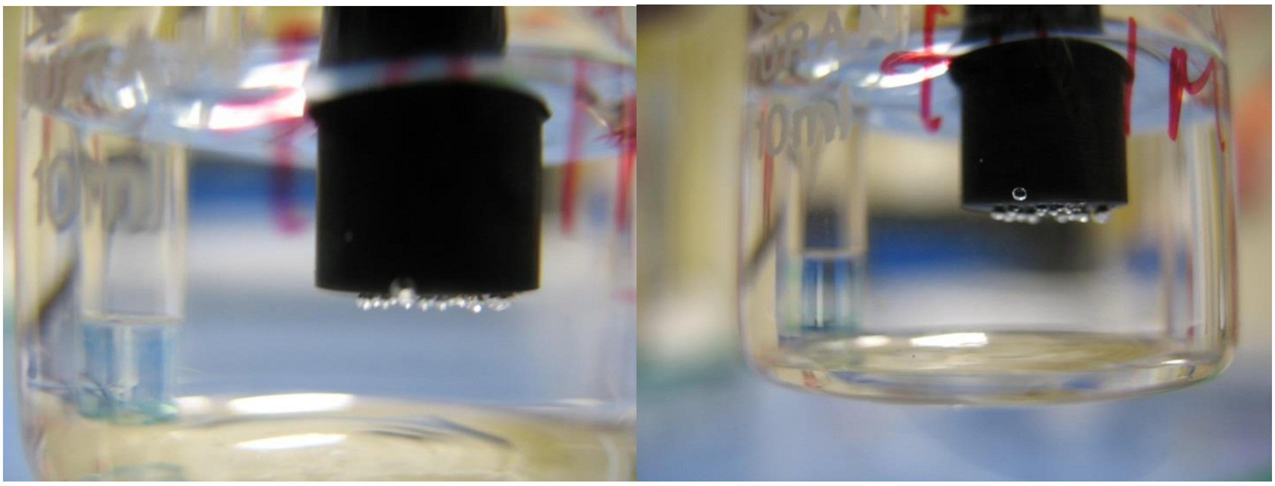

Figure S7. Photographs showing oxygen gas bubbles formed after the potential was cycled 5 times between +300 and +1400 mV vs. Ag/AgCl at a scan rate of 50 mV s^{-1} when using a **1**–graphene modified GC electrode with 0.1 M sodium borate buffer (pH 7.50) containing 0.1 M $LiClO_4$ as the aqueous supporting electrolyte.

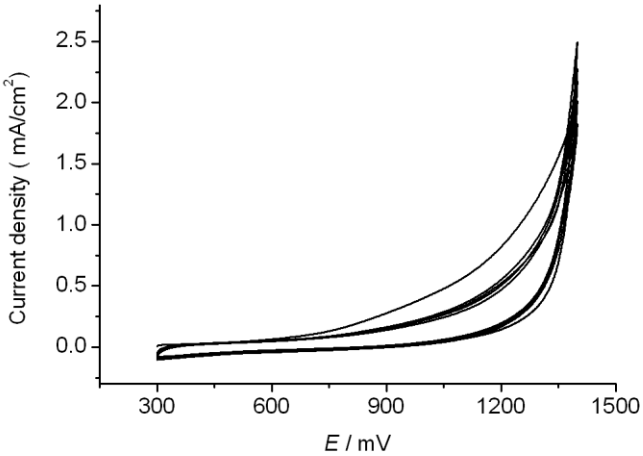

Figure S8. Electrocatalytic water oxidation using a **1**–dry graphene modified electrode in 0.1 M sodium borate buffer, pH 7.50 with 1 M $Ca(NO_3)_2$ as the additional supporting electrolyte (5 cycles of potential). Scan rate: 50 mV s^{-1}.

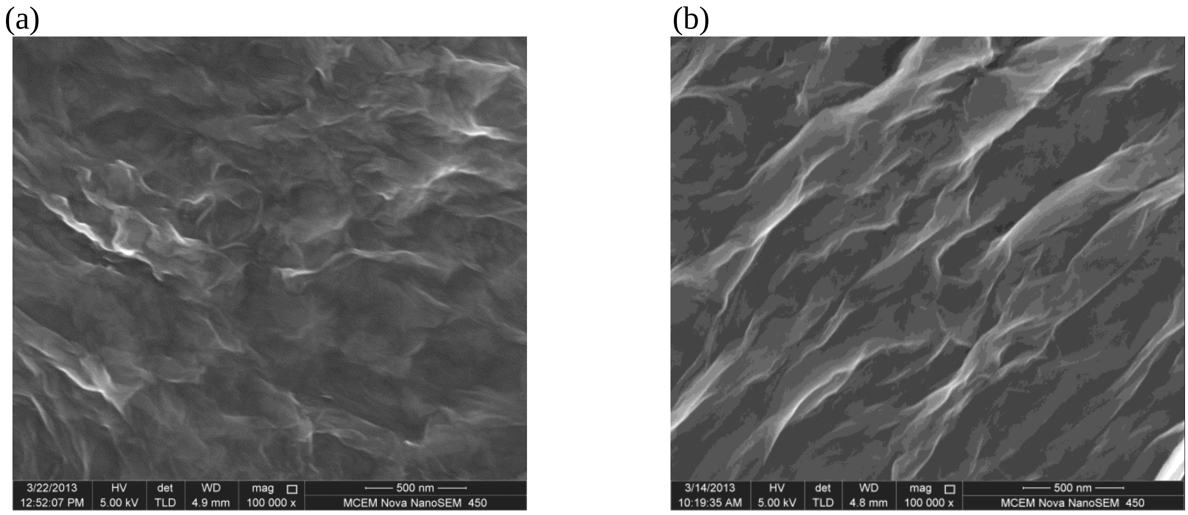

Figure S9. SEM images of a **1**-graphene modified ITO electrode taken before (a) and after (b) a constant potential electrolysis at 1.3 V for 500 s. For better comparison, only half of the **1**-graphene modified ITO electrode was in contact with the electrolyte solution during electrolysis. SEM images were taken at both electrolyzed and un-electrolyzed parts of the modified electrode.

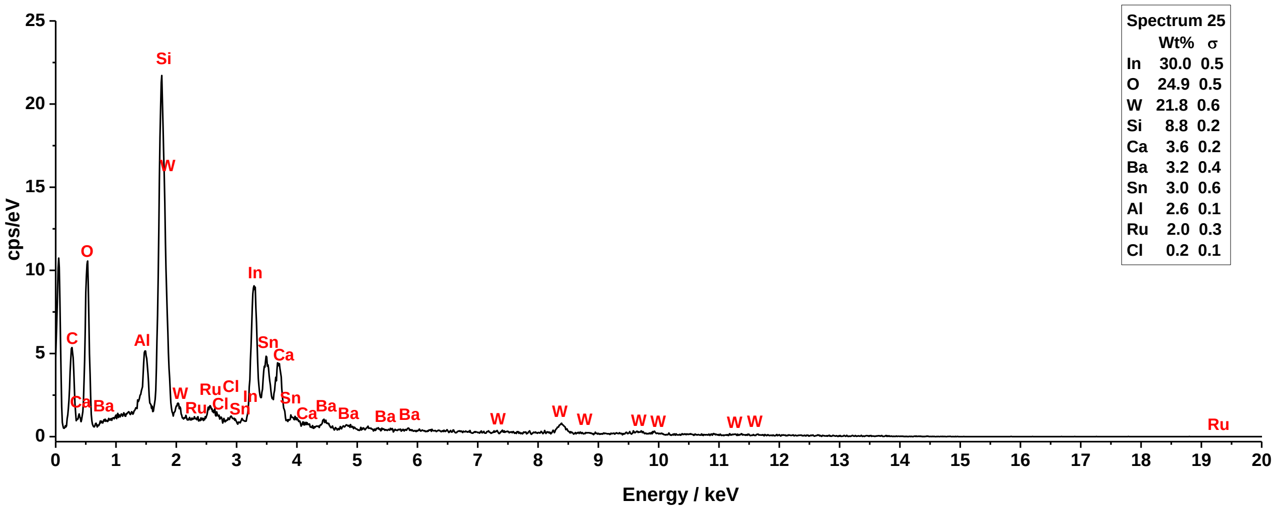

Figure S10. EDX spectrum of a **1**–graphene modified ITO electrode taken after the control potential electrolysis at 1.3 V for 500 s.

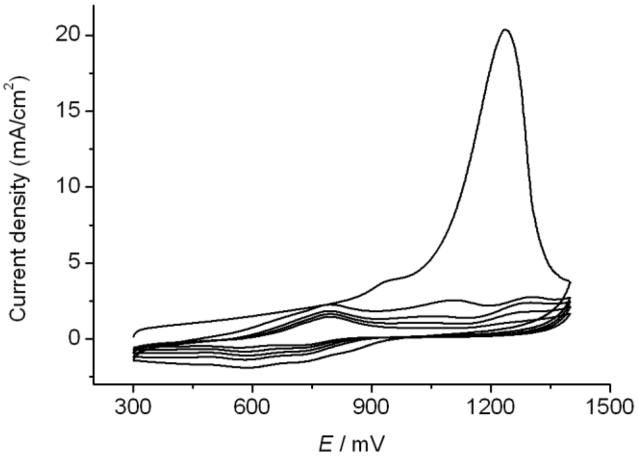

Figure S11. Cyclic voltammogram obtained at a RuO_2–graphene modified glassy carbon electrode (fabricated using drop casting method with 5 μL of 2.7 mg/ml RuO_2). Experimental conditions are the same as Figure 3.

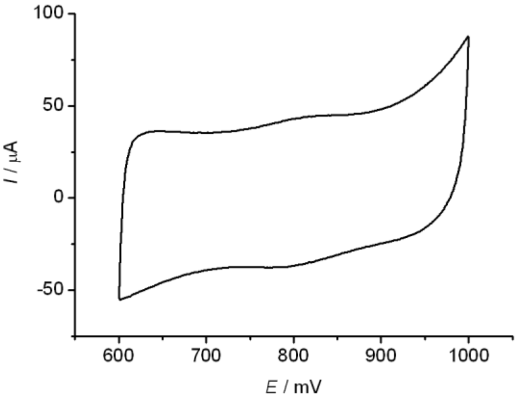

Figure S12. Cyclic voltammogram of **1**–graphene modified RRDE electrode obtained in 0.1 M HCl containing 1 M $Ca(NO_3)_2$, scan rate: 50 mV s^{-1}.