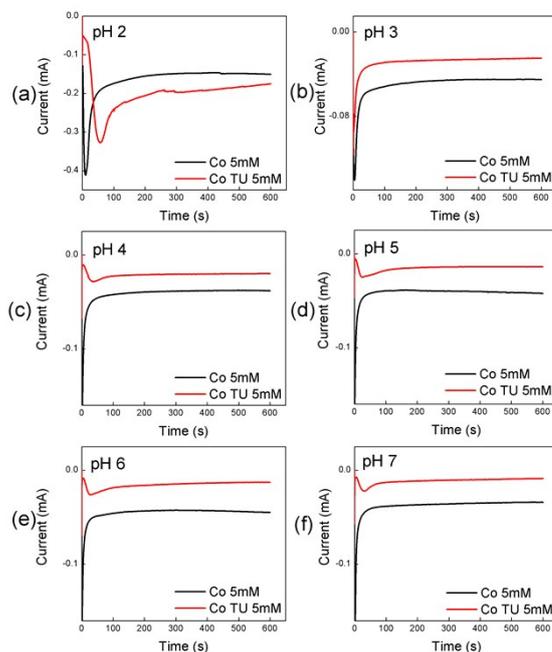
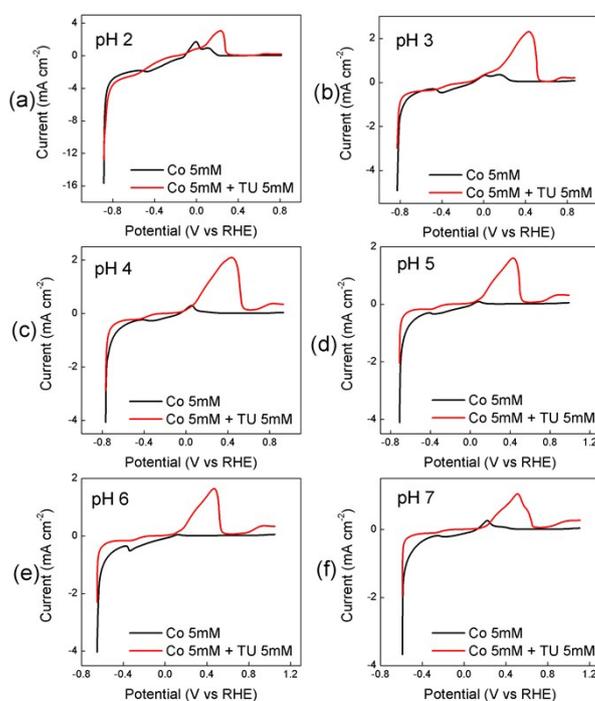


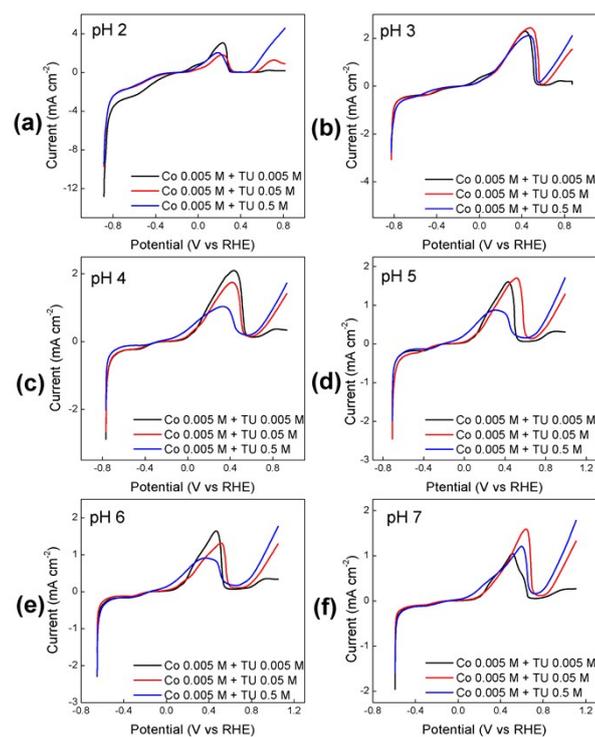
### Supplementary information



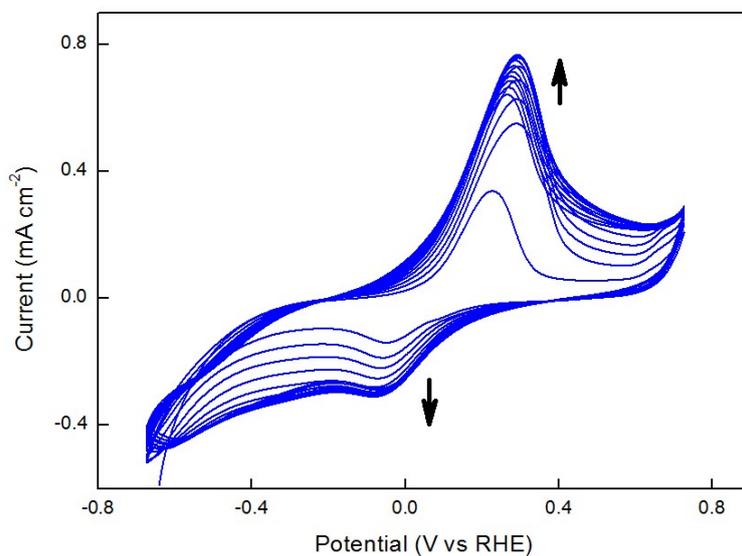
**Figure S1:** Current-time transients recorded at a GC electrode in an electrolyte containing 0.005M of Co (II) and 0.005M of Co (II) + 0.005M of Thiourea at -1.1 V vs Ag|AgCl at different pH values.



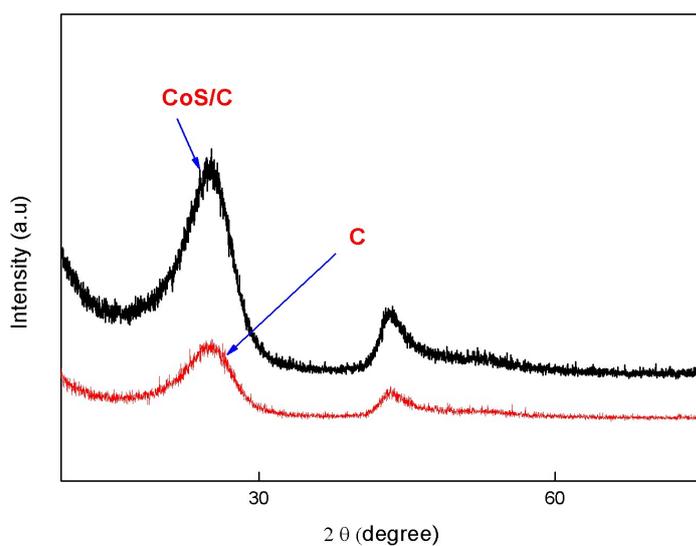
**Figure S2:** Anodic stripping voltammograms after potentiostatic deposition at -1.1 V vs Ag|AgCl for 10 minutes in solutions containing 0.005M of Co (II) and 0.005M of Co (II) + 0.005M of Thiourea at different pH values.



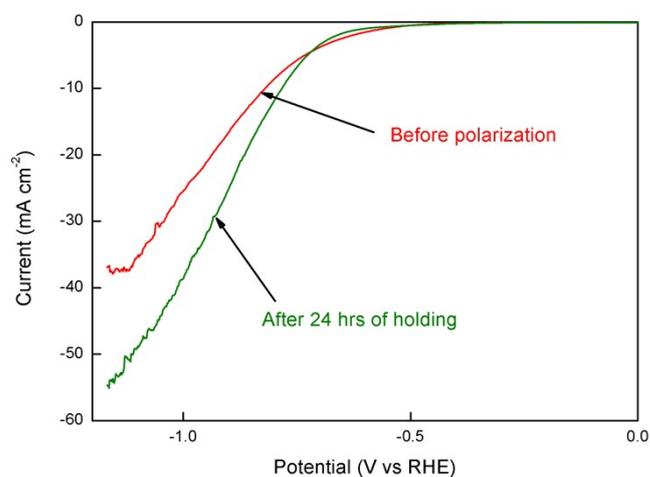
**Figure S3:** Anodic stripping voltammograms after potentiostatic deposition at -1.1 V vs Ag|AgCl for 10 minutes in the solutions containing 0.005 M of Co(II) and 0.005 M of TU, 0.05 M of TU and 0.5 M of TU at different pH values.



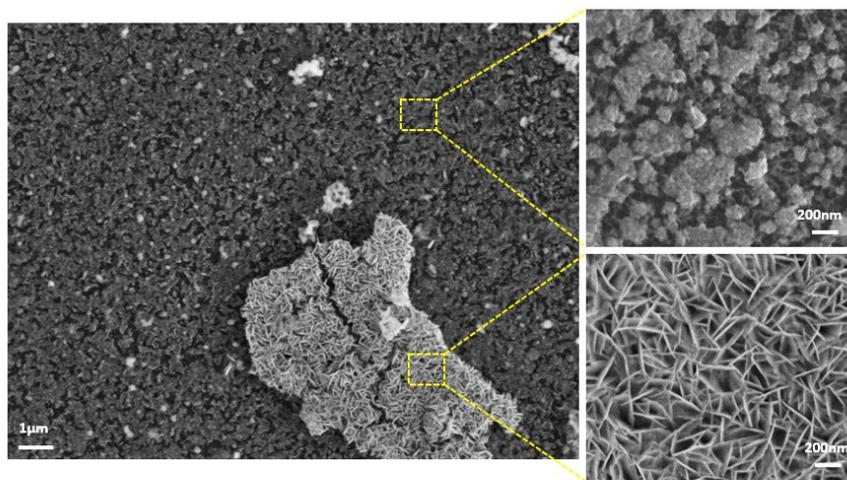
**Figure S4:** Cyclic voltammetry recorded at a glassy carbon electrode performed from -0.67 to 0.72 vs RHE at a scan rate of 15 mV s<sup>-1</sup> in a solution containing 0.005 M Co(II) and 0.005 M TU.



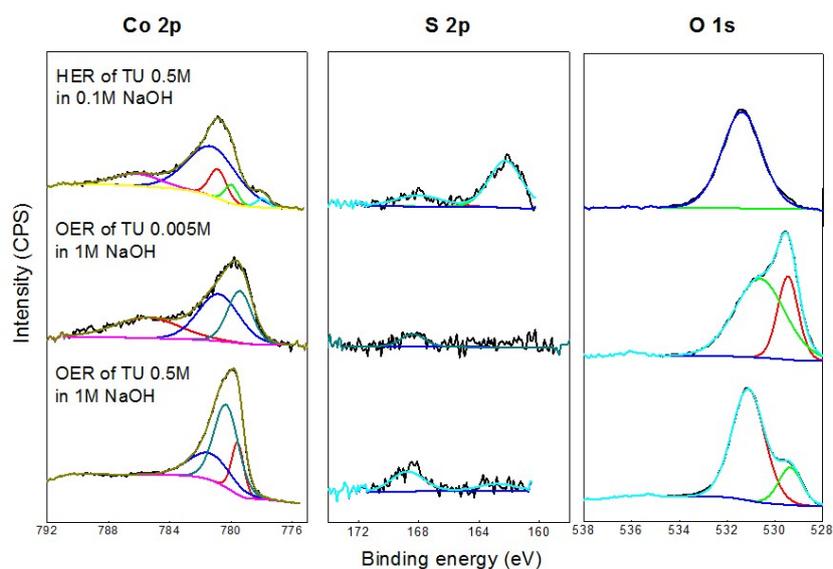
**Figure S5:** XRD of  $\text{CoS}_x$  film electrodeposited on a glassy carbon substrate fabricated by cyclic voltammetry at a scan rate of  $15 \text{ mV s}^{-1}$  for 15 cycles in a solution containing  $0.005 \text{ M}$  of  $\text{Co (II)}$  and  $0.5 \text{ M}$  of thiourea and the blank carbon substrate.



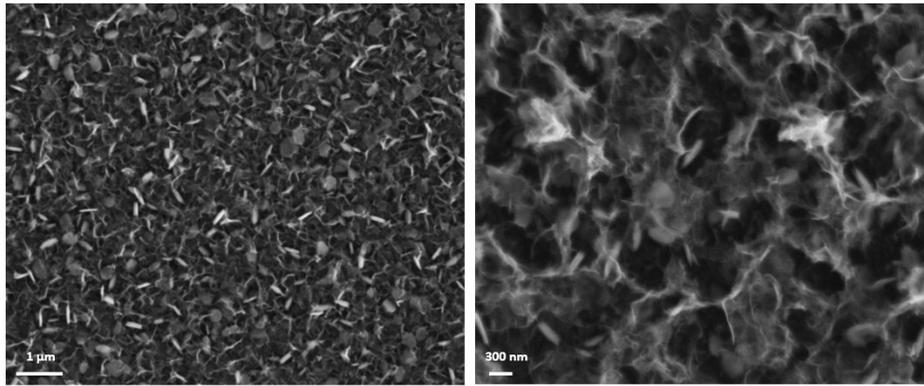
**Figure S6:** Linear sweep voltammograms recorded at a GC electrode modified with  $\text{CoS}_x$  films in phosphate buffer solution (pH 7.4) at a sweep rate of  $5 \text{ mV s}^{-1}$  before and after 24 h of HER at an applied current density of  $-10 \text{ mA cm}^{-2}$ .



**Figure S7:** SEM images of a  $\text{CoS}_x$  film deposited on a glassy carbon electrode via cyclic voltammetry at a scan rate of  $15 \text{ mV s}^{-1}$  for 15 cycles in a solution containing  $0.005 \text{ M}$  of  $\text{Co (II)}$  and (a)  $0.005 \text{ M}$  of thiourea after the OER in  $1.0 \text{ M NaOH}$ .



**Figure S8:** Co 2p, S 2p and O 1s XPS spectra of  $\text{CoS}_x$  deposited films obtained through cyclic voltammetry at a scan rate of  $15 \text{ mV s}^{-1}$  for 15 cycles in solutions of  $0.005 \text{ M Co(II)}$  containing either  $0.005 \text{ M TU}$  or  $0.5 \text{ TU}$  after HER and OER experiments.



**Figure S9:** SEM images of CoS<sub>x</sub> deposited film obtained through cyclic voltammetry at a scan rate of 15 mV s<sup>-1</sup> for 15 cycles in a solutions of 0.005 M Co(II) containing 0.5 TU after the HER in 1.0 M NaOH.