

Electronic Supplementary Information (ESI)

Molecular Cluster Complex of High Valence Chromium Selenide Carbonyl as Effective Electrocatalyst for Water Oxidation

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The thermogravimetric analysis (TGA) of the Cr-Se red and Cr-Se green clusters describes the stepwise decomposition of each sample (Figure S1). The TGA of Cr-Se red in argon showed a gradual decrease in weight in three steps; at the first step between 0°C and 180 °C, 13.3 % weight loss was observed, due to the loss of lattice water.[1] The second weight loss from 180–240 °C corresponds to 38.7% (calcd. 30.5%) which can be attributed to the decomposition of tetraethyl amine.[2] Finally, in the range of 240–900 °C a weight loss of 21.52% (calcd. 22.9%) is attributable to the loss of seven coordinated CO molecules. Similarly, Cr-Se green showed three weight loss steps; where 10.7 % weight loss was observed between 0°C and 180 °C at the first step, confined to loss of lattice water. A to 34.4% (calcd. 30.5%) weight loss from 180–240 °C corresponds to the decomposition of tetraethyl amine. And a weight loss of 16.0% (calcd. 16.7%) in the range of 240–600 °C, attributed to the loss of seven coordinated water molecules. The percentage weight loss in the complexes is in agreement with the calculated values.

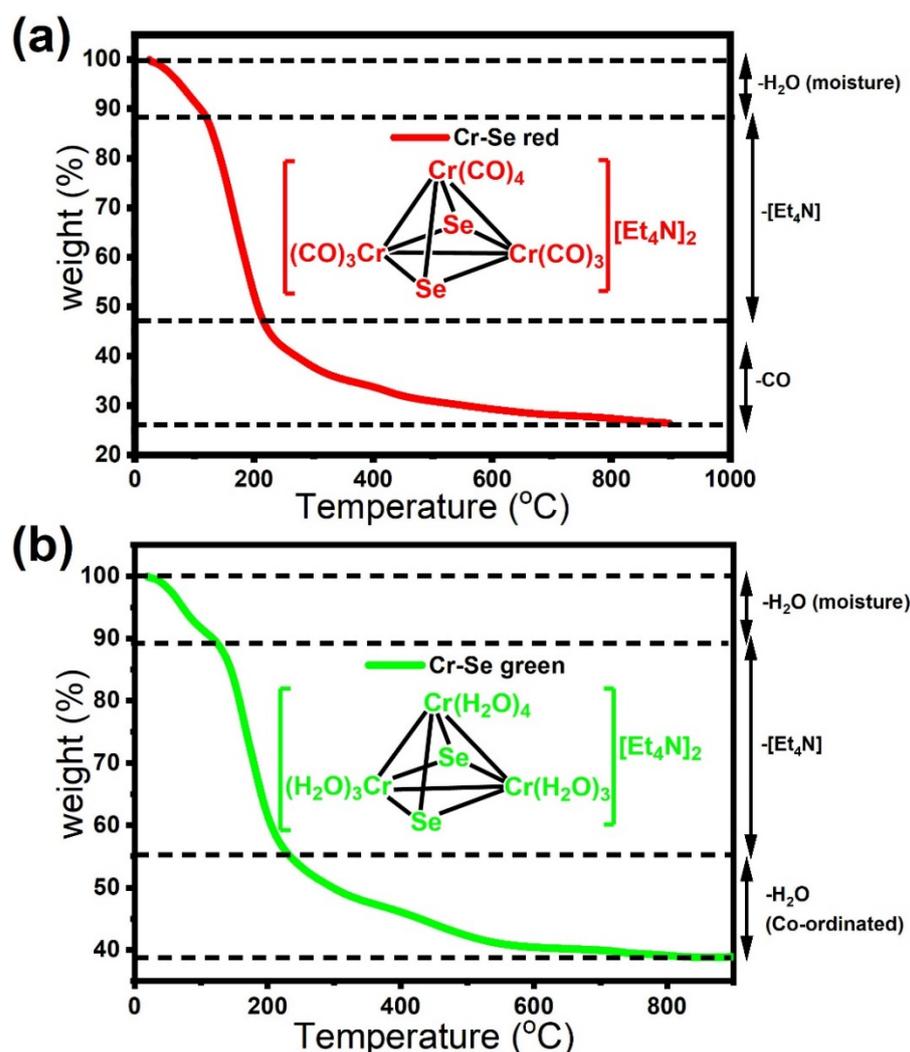


Figure S1. The thermogravimetric (TGA) analysis of (a) Cr-Se red; (b) Cr-Se green.

Table S1. Parameters of Equivalent Circuit Obtained from Fitting of EIS Experimental Data.

Parameters	Cr-Se red	Cr-Se green
R1/ohm	1.38	2.0
R2/ohm	10.10	12.02
R3/ohm	19.84	16.65
C1/F	2.24×10^{-2}	3.9×10^{-3}
W/s ^(1/2) /ohm	6.61×10^{-2}	2.36×10^{-2}

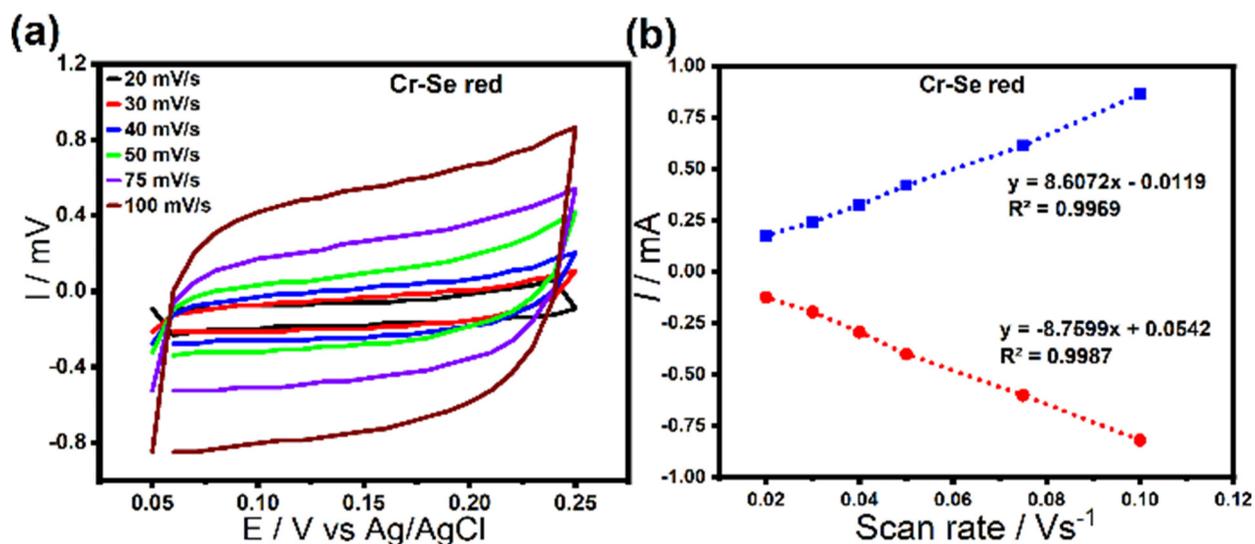


Figure S2. Electrochemical characterization of Cr-Se red catalyst; (a) Cyclic voltammograms measured at different scan rates. (b) The plots of anodic and cathodic currents measured as a function of scan rate.

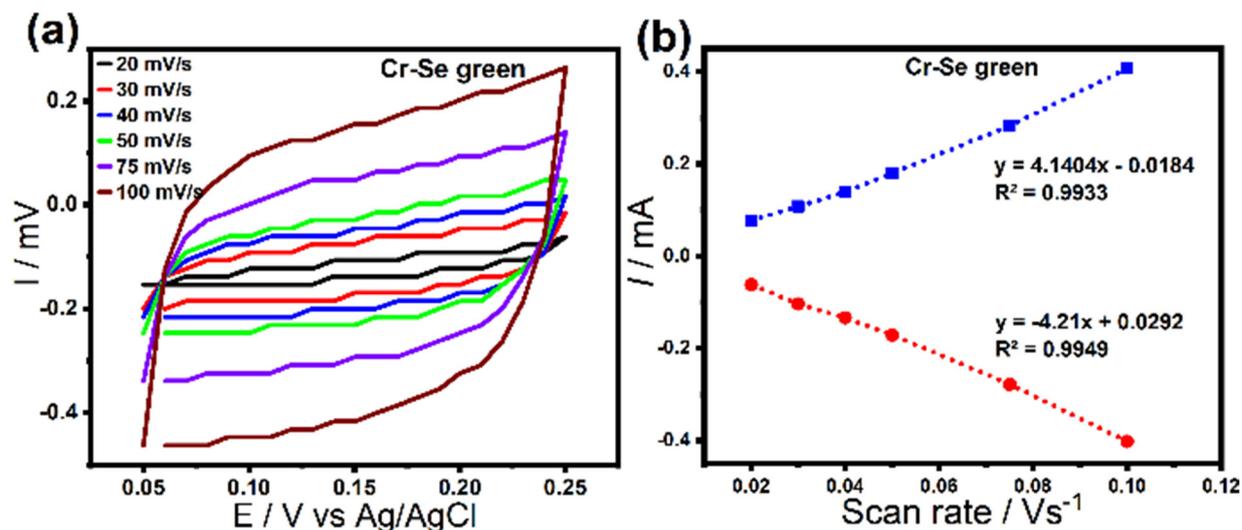


Figure S3. Electrochemical characterization of Cr-Se green catalyst; (a) Cyclic voltammograms measured at different scan rates. (b) The plots of anodic and cathodic currents measured as a function of scan rate.

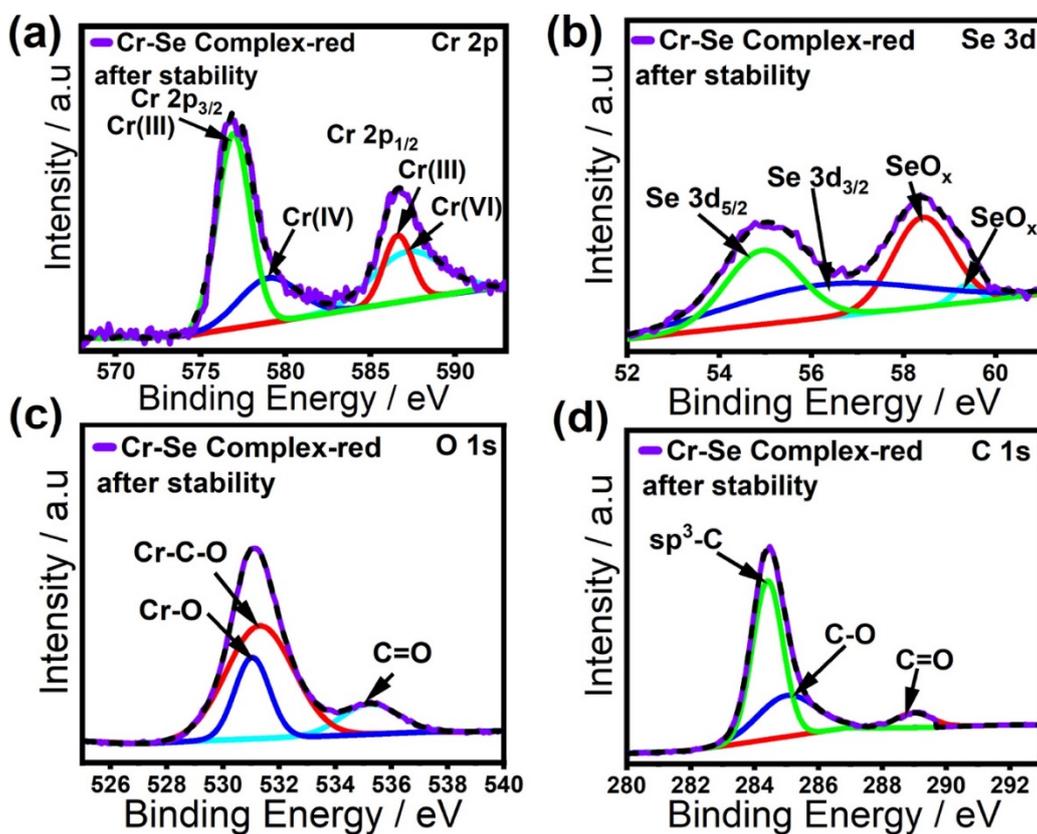


Figure S4. The high-resolution XPS spectra of the Cr-Se red complex after long term chronoamperometry showing (a) Cr 2p peak; (b) Se 3d peak; (c) surface O 1s peak; (d) C 1s peak.

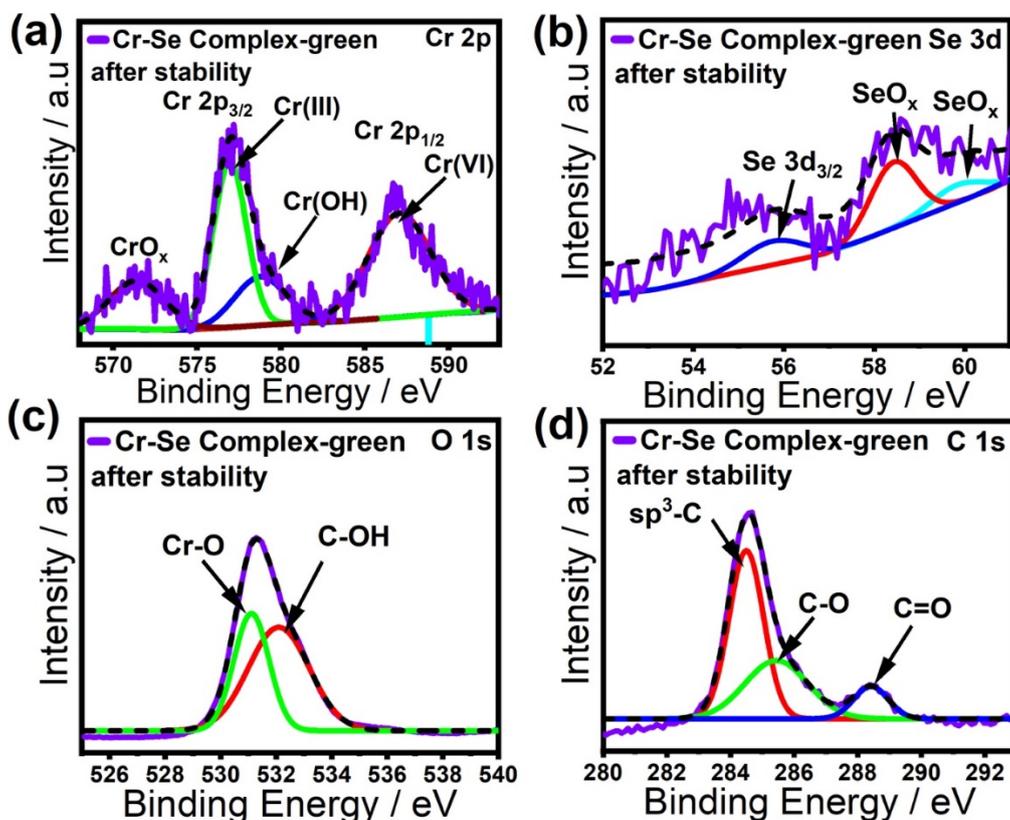


Figure S5. The high-resolution XPS spectra of the Cr-Se green complex after chronoamperometry showing (a) Cr 2p peak; (b) Se 3d peak; (c) surface O 1s peak; (d) C 1s peak.

Table S2. Comparison of the OER performances in an alkaline electrolyte (overpotential at 10 mA cm⁻² current density, and Tafel slope) of published recently chromium-based catalysts with our work.

Catalysts	Electrolyte	Overpotential (η @ 10 mA.cm ⁻²)	Tafel slope (mV dec ⁻¹)	Substrate	References
*CoCr ₂ O ₄	1.0 M NaOH	400 mV	87 mV dec ⁻¹	Glassy carbon	[3]
*CoFeCr	1.0 M KOH	330 mV	61 mV dec ⁻¹	Ni foam	[4]
*NiCrFeO ₄	1.0 M KOH	298 mV	44.47mV dec ⁻¹	PAN	[5]
*Cr ₂ S ₃	1.0 M KOH	230 mV	162 mV dec ⁻¹	Carbon Fibre	[6]
*Cr(salen)Cl	3.0 M NaOH	426 mV	-	Glassy carbon	[7]
#\$Cr(H-byp)(bis-bpymd)	OH	390 mV	-	-	[8]
#\$Cr(tpy)(py)(isoquin)	OH	380 mV	-	-	[8]
#\$Cr(DPA)(2,2'-bpymd)	OH	320 mV	-	-	[8]
* γ -CrOOH	1.0 KOH	334 mV	41.4 mV dec ⁻¹	NF	[9]
*CrON	1.0 KOH	409 mV	157 mV dec ⁻¹	Carbon paper	[10]
Cr-Se red	1.0 M KOH	310.0 mV	82 mV dec ⁻¹	Carbon paper	This work
Cr-Se green	1.0 M KOH	350.0 mV	107 mV dec ⁻¹	Carbon paper	This work

* Bulk solid samples, # Complexes, \$ Computational study.

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