SUPPLEMENTAL INFORMATION FOR:

Tunability of transport properties in semi-exfoliated $Ag_xCoO_{2-\delta}$ ($0.4 < x < 1$) crystals

Marc Kamel[a], Hatem M. Titi[b], Mohamad Ataya[b], Antranik Jonderian[b], Kirk H. Bevan[a,c*] and Eric McCalla[b,c*]

[a] Division of Materials Engineering, Faculty of Engineering, McGill University, Montreal, Canada.

[b] Department of Chemistry, McGill University, Montreal, Canada.

[c] Centre for the physics of materials.

*Corresponding author: eric.mccalla@mcgill.ca and kirk.bevan@mcgill.ca

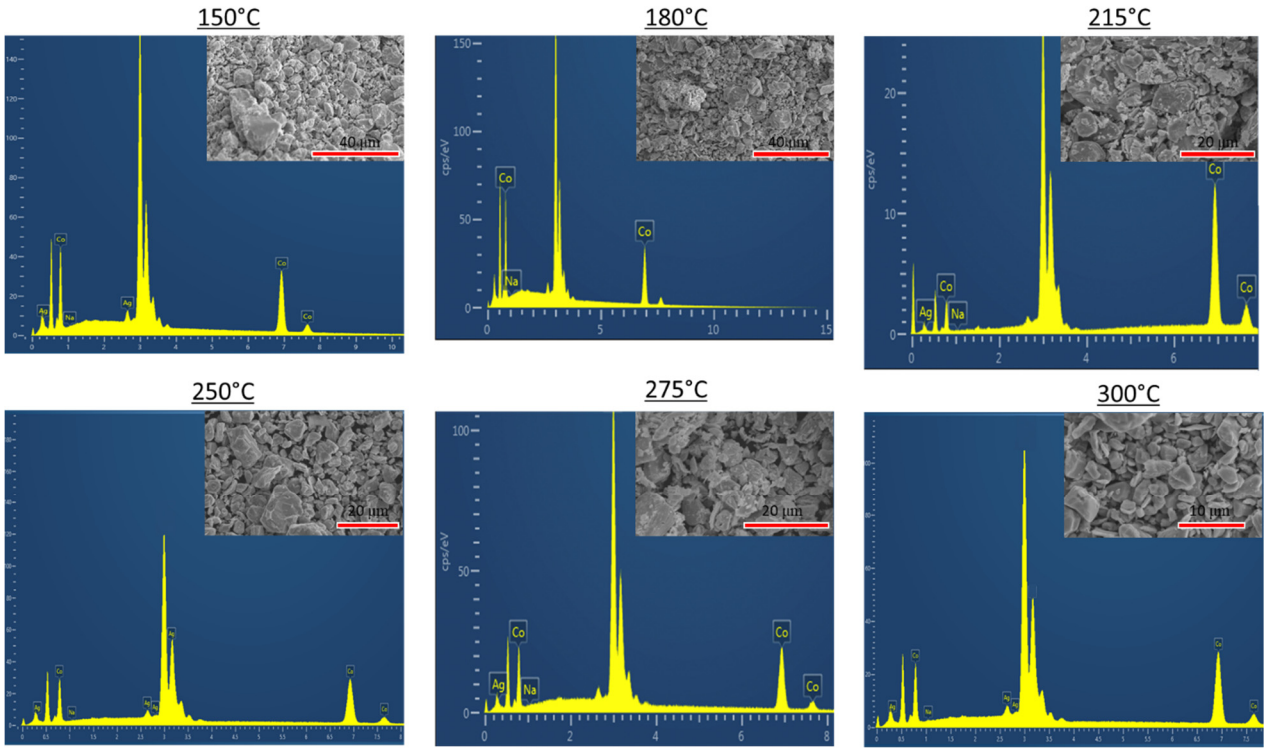

Figure S1: SEM images (insets) and one EDX scan from each sample (note: 6 were collected from each and averaged to obtain Table S1). All samples are made from the powder precursor, the temperature shown is T_{IE}.

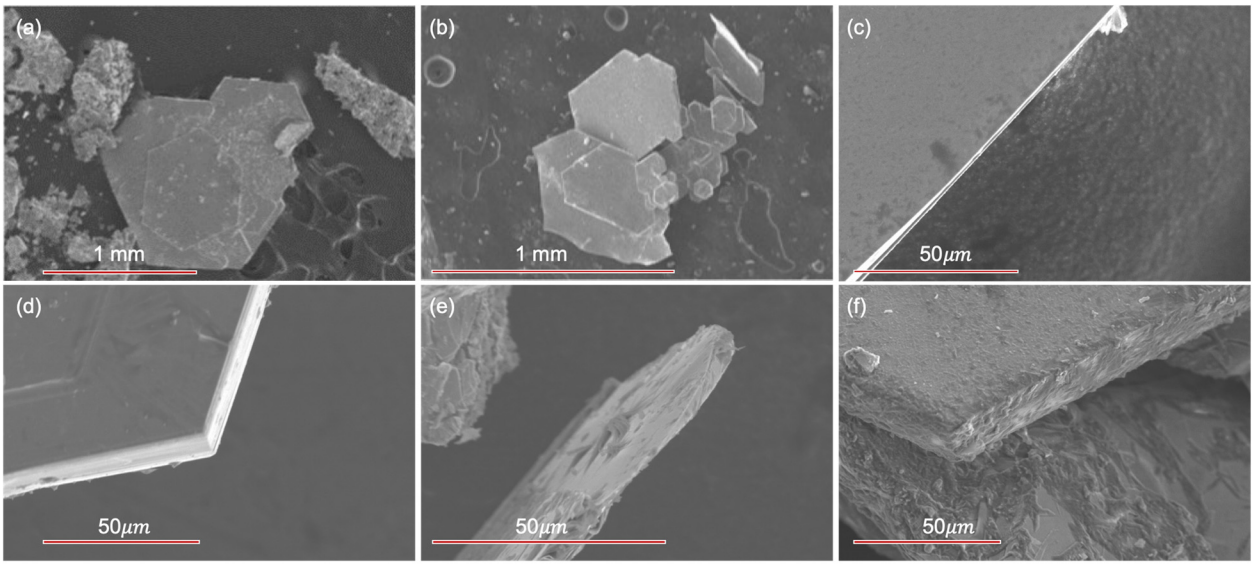

Figure S2: SEM pictures showing $NaCoO_2$ single crystal precursors.

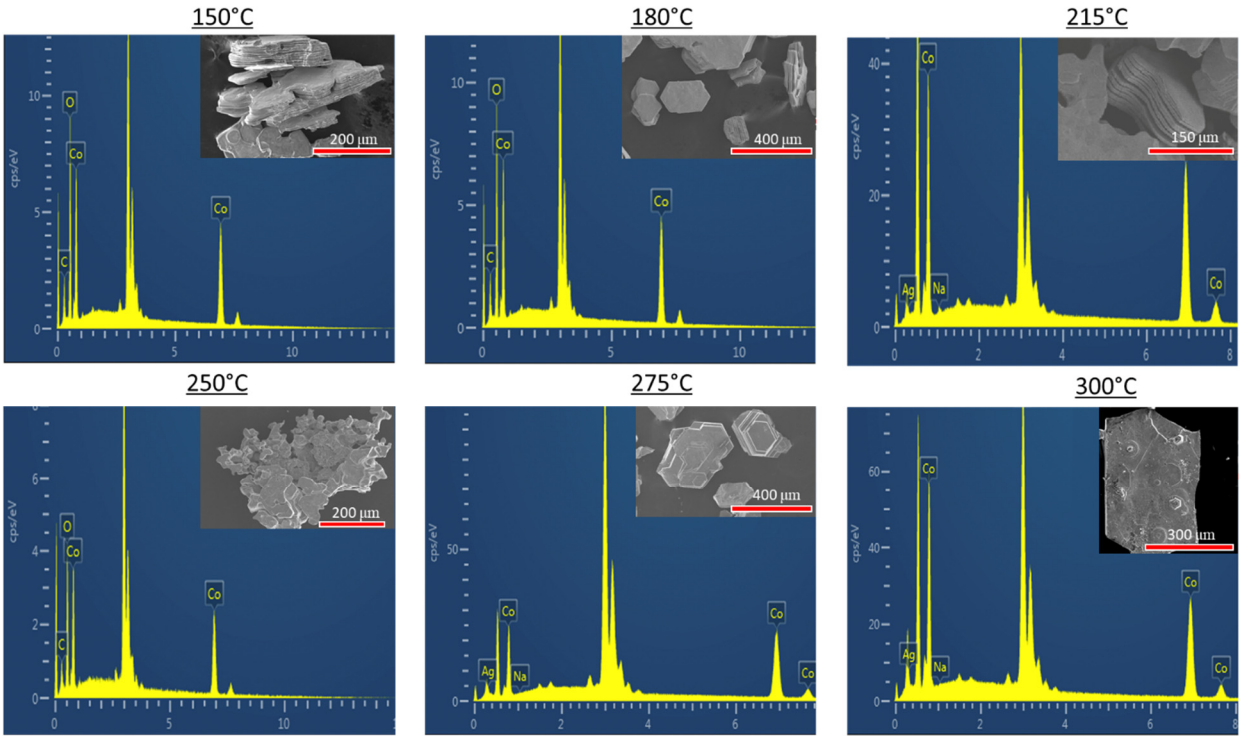

Figure S3: SEM images (insets) and one EDX scan from each sample (note: 6 were collected from each and averaged to obtain Table S1). All samples are made from the single-crystal precursors, the temperature shown is T_{IE}.

Table S1: EDX results for both the polycrystalline and crystal samples after ion exchange.

T_{IE} (°C), sample	Na/Co	Ag/Co
150, crystal	0.04	0.42
180, crystal	0.03	0.56
215, crystal	0.04	0.57
250, crystal	0	0.70
275, crystal	0	0.81
300, crystal	0.03	0.98
150, polycrystalline	0	0.80
180, polycrystalline	0	0.85
215, polycrystalline	0	0.82
250, polycrystalline	0	0.84
275, polycrystalline	0	0.78
300, polycrystalline	0	0.84
300,Crystal (No silver nitrate)	0.085	0

Table S2: Extracted parameters for the powder samples: particle size obtained from at least 15 measurements from each SEM image with the standard deviation in brackets, crystallite size extracted from XRD, and the weight percent of the delafossite phase based on XRD (the remainder is metallic silver).

	T_{IE} (°C)	Particle size (μm)	Crystallite size (nm)*	D3-$AgCoO_2$ phase (μm)
Polycrystalline samples	150	1.95 (0.35)	87	92%
	180	2.3 (0.39)	75	94%
	215	2.25 (0.44)	88	94%
	250	2.25 (0.45)	105	94%
	275	1.9 (0.4)	74	94%
	300	2.12 (0.4)	113	95 %

*The crystallite size was obtained from the full width at half maximum of the largest XRD peak at a scattering angle of about 37°. The peak width was first corrected for machine broadening using a Lorentzian correction and then the crystallite size was calculated using the Scherrer equation.

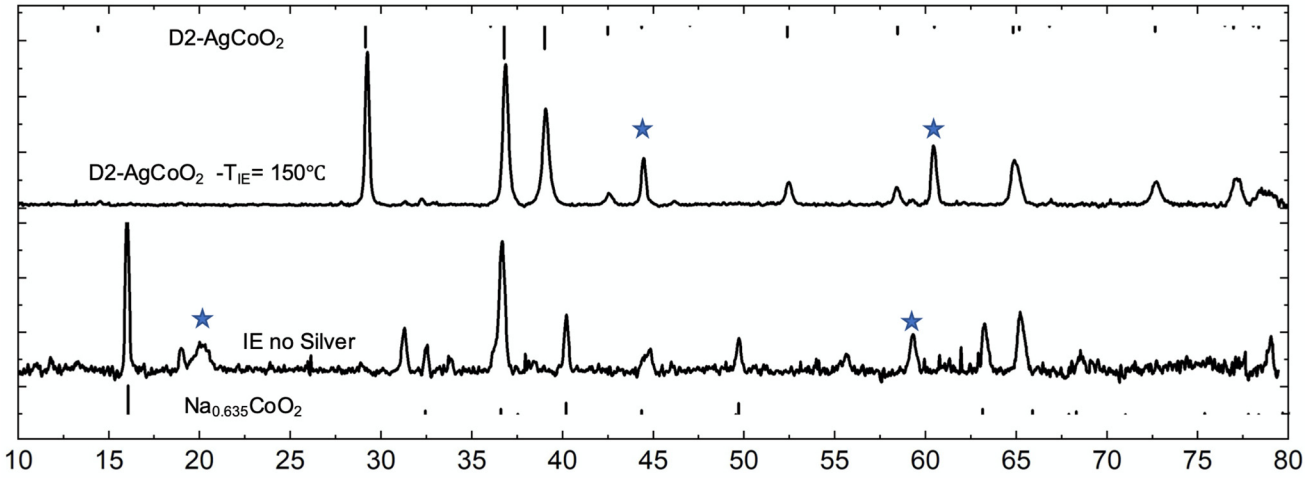

Figure S4: XRD patterns of $Ag_xCoO_{2-\delta}$ crystals synthesized at 150°C and crystals made without silver during ion exchange step.

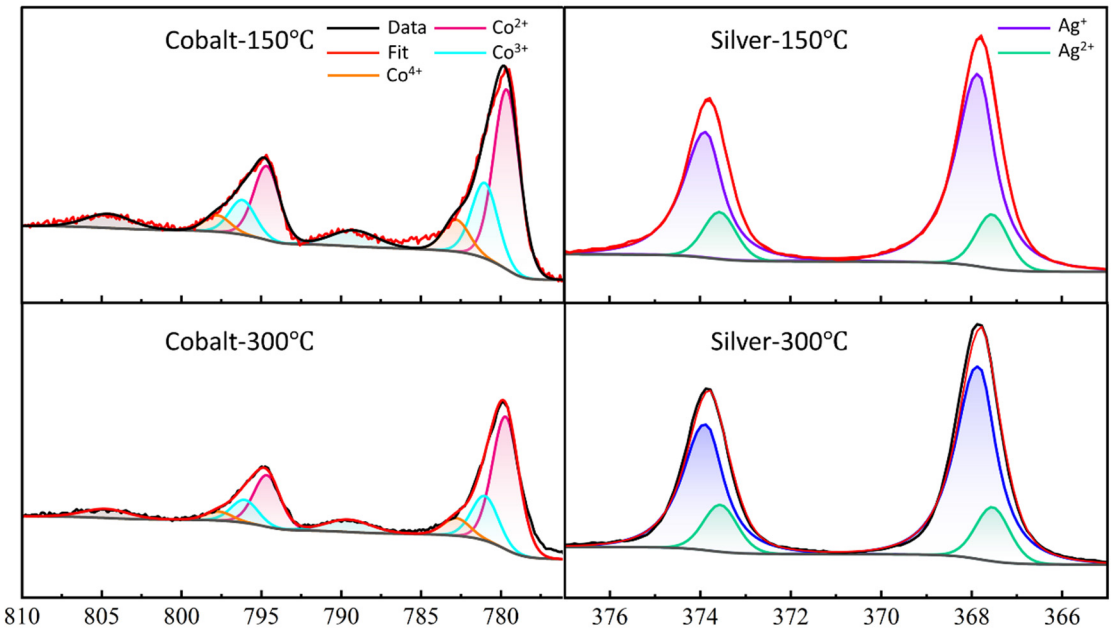

Figure S5: XPS patterns of Silver and cobalt from D3-$AgCoO_{2-\delta}$ polycrystalline made at 150°C (a and b) and 300°C (c and d).

Table S3: Parameters obtained from fitting the polycrystalline and crystals XPS patterns (Figs. 5 and S3). Binding energy (BE) and full width at half maximum (FWHM) are both in eV, while at. % denotes the atomic percent of each oxidation state. Based on refs. [36],[37][38][39], the expected positions of Ag^{+}, Ag^{2+}, Co^{2+}, and Co^{3+} are 367.9, 367.6, 780.0, and 781.3 eV, respectively.

Polycrystalline

T_{IE}= 150 °C

State	B.E	FWHM	At%
Ag^{+}	367.84	0.88	84.47
Ag^{2+}	367.54	0.88	15.53

State	B.E	FWHM	At%
Co^{2+}	779.70	1.97	68.07
Co^{3+}	781.00	1.97	22.92
Co^{4+}	782.78	1.97	9.01

T_{IE}= 300 °C

State	B.E	FWHM	At%
Ag^{+}	367.84	0.91	83.68
Ag^{2+}	367.54	0.91	16.32

State	B.E	FWHM	At%
Co^{2+}	779.63	1.92	67.40
Co^{3+}	781.00	1.92	24.58
Co^{4+}	782.78	1.92	8.02

Cystals

T_{IE}= 150 °C

State	B.E	FWHM	At%
Ag^{+}	368	0.91	31.15
Ag^{2+}	367.54	0.93	68.85

State	B.E	FWHM	At%
Co^{2+}	779.70	1.64	57.38
Co^{3+}	781.00	1.64	31.77
Co^{4+}	782.78	1.64	10.86

T_{IE}= 300 °C

State	B.E	FWHM	At%
Ag^{+}	368.2	0.97	89.87
Ag^{2+}	367.54	0.97	10.13

State	B.E	FWHM	At%
Co^{2+}	779.62	1.34	66.35
Co^{3+}	781.00	1.34	26.81
Co^{4+}	782.62	1.34	6.85

Table S4: Experimental and computational (DFT) lattice parameters of D2 and D3-$Ag_xCoO_{2-\delta}$. For D2, *c* = c/2*, for D3, *c* = c/3.*

Sample	*a*	*b*	*c*	*c**
D2-$AgCoO_{2-\delta}$ (X)	2.8738 (2)	2.8738 (2)	12.240 (1)	6.120
D3-$AgCoO_{2-\delta}$ (PC)	2.8703 (2)	2.8703 (2)	18.3276 (1)	6.1092
D2-$Ag_0CoO_{2-\delta}$ (X)	2.8526 (3)	2.8526 (3)	12.108 (1)	6.054
D2-$Ag_{0.42}CoO_{2-\delta}$ (X)	2.8373 (2)	2.8372 (2)	12.0897 (9)	6.0449
D2-$Ag_{0.42}CoO_{2-\delta}$ (X) #2	2.8447 (1)	2.8447 (1)	12.0217 (6)	6.0109
D2-$Ag_{0.56}CoO_{2-\delta}$ (X)	2.8564 (1)	2.8564 (1)	12.1911 (8)	6.0956
D2-$Ag_{0.57}CoO_{2-\delta}$ (X)	2.8522 (1)	2.8522 (1)	12.1517 (6)	6.0759
D2-$Ag_{0.57}CoO_{2-\delta}$ (X) #2	2.8526 (2)	2.8526 (2)	12.108(1)	6.054
D2-$Ag_{0.7}CoO_{2-\delta}$ (X)	2.8670 (3)	2.8670 (3)	12.225 (1)	6.113
D2-$Ag_{0.81}CoO_{2-\delta}$ (X)	2.8666 (2)	2.8666 (2)	12.197 (1)	6.098
DFT - D2-$AgCoO_2$	2.891	2.891	12.435	6.217
DFT - D2-$Ag_{0.5}CoO_2$	2.842	2.859	12.327	6.163
DFT - D2-$AgCoO_{1.5}$	2.886	2.870	11.785	5.893
DFT - D3-$AgCoO_2$	2.891	2.891	18.642	6.214

Table S5: DFT lattice parameters both before and after relaxation.

	Pre-relaxation (Å)	Post-relaxation (Å)
D2-$AgCoO_2$	a = 2.862 b = 2.862 c = 12.286	a = 2.891 b = 2.891 c = 12.435
D3-$AgCoO_2$	a = 3.023 b = 3.023 c = 18.760	a = 2.891 b = 2.891 c = 18.642
D2-$Ag_{0.5}$CoO2	a = 2.862 b = 2.862 c = 12.286	a = 2.842 b = 2.859 c = 12.327
D2-$AgCoO_{1.5}$	a = 2.862 b = 2.862 c = 12.286	a = 2.886 b = 2.870 c = 11.785

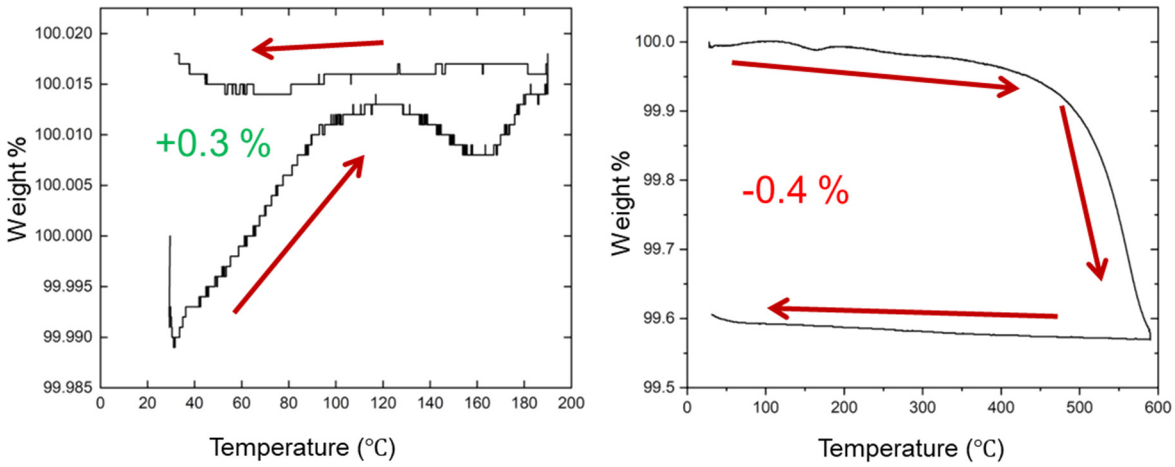

Figure S6: TGA graphs from polycrystalline D3- $Ag_xCoO_{2-\delta}$ heated to 190 °C (left) and 590 °C (right).

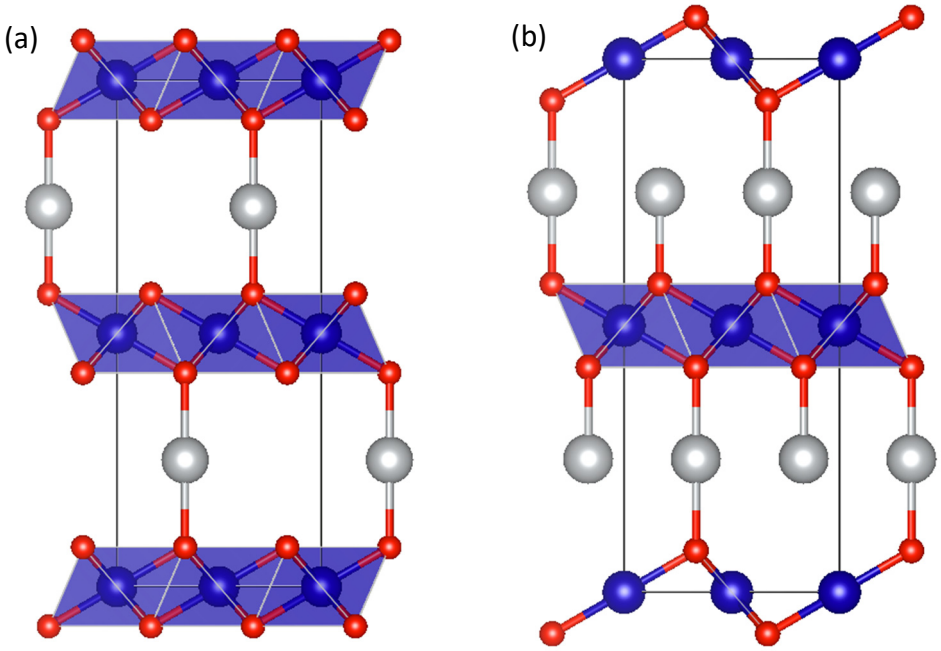

Figure S7: Crystal structures used in the DFT calculations: D2-$Ag_{0.5}CoO_2$ (a) and D2-$AgCoO_{1.5}$ (b).

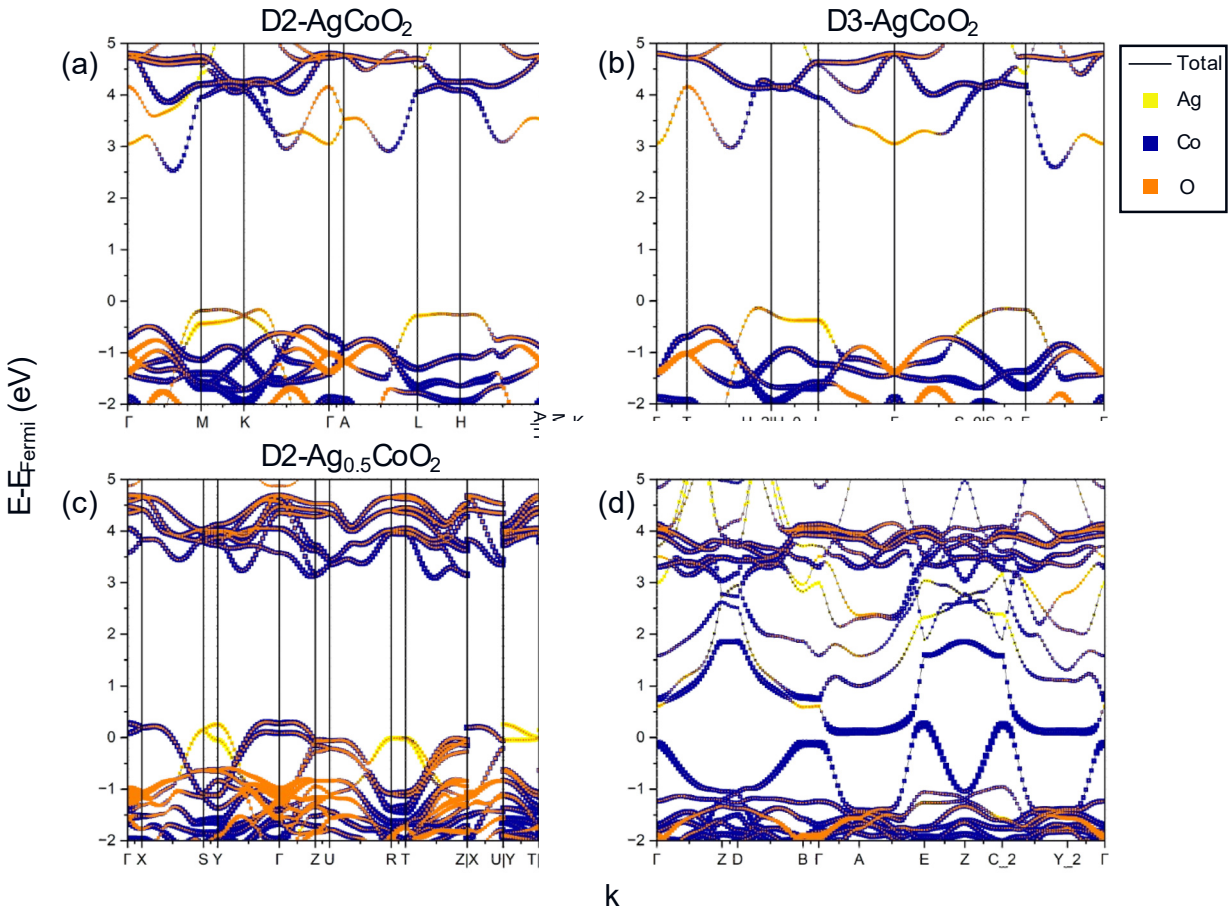

Figure S8: Density of states projected onto each element for (a) D2-$AgCoO_2$, (b) D3-$AgCoO_2$, (c) D2-$Ag_{0.5}CoO_2$ and (d) D2-$AgCoO_{1.5}$.