

Figure S1 Set-up for the DC-plasma assisted anodic oxidation of Co foil. The initial electrolyte is pure ethanol, which turns yellow after the electrochemical reaction.

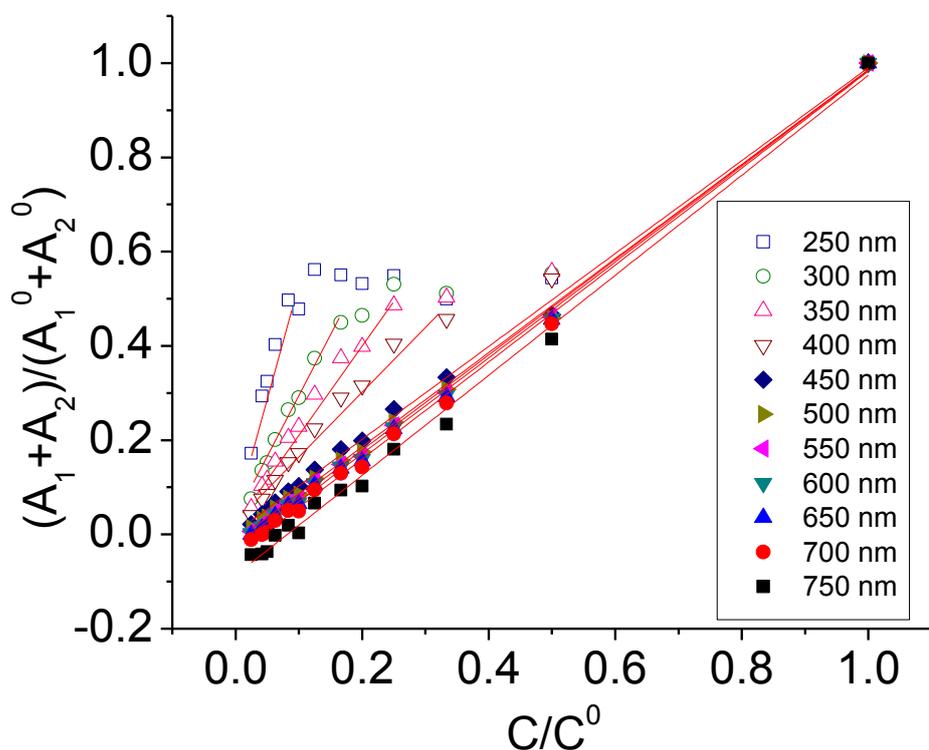


Figure S2 Dependence of absorbance (normalised by the undiluted solution) on the dilution coefficient (C/C^0 , where C and C^0 are the concentration of quantum dots in diluted and undiluted solution) at different wavelength. The limiting current of the sample is 4.58 mA and the red lines are fitting of the linear region.

According to Lambert-Beer's law:

$$A_1 = \varepsilon_1 b C$$

$$A_2 = \varepsilon_2 b k C$$

$$A_1 + A_2 = (\varepsilon_2 k + \varepsilon_1) b C$$

Where A_1 and A_2 are the respective absorbance, b is the path length, and C is the concentration of the cobalt oxide quantum dots, ε_1 and ε_2 are the respective wavelength (λ)-dependent molar absorptivity coefficients with units of $M^{-1} \text{ cm}^{-1}$, k is the concentration ratio between the by-product and Co_3O_4 quantum dots. If we normalize the total absorbance by that of the undiluted solution, $A_1^0 + A_2^0$, at each wavelength

$$\frac{A_1 + A_2}{A_1^0 + A_2^0} = \frac{(\varepsilon_2 k + \varepsilon_1) b C}{A_1^0 + A_2^0} = \frac{(\varepsilon_2 k + \varepsilon_1) b C^0}{A_1^0 + A_2^0} (C/C^0)$$

The slope S of the plotting between the total absorbance $(A_1+A_2)/(A_1^0+A_2^0)$ versus dilution coefficients (C/C^0) will be:

$$S = \frac{(\varepsilon_2 k + \varepsilon_1) b C^0}{A_1^0 + A_2^0}$$

If the absorption from the by-product can be neglected under certain wavelength λ , then:

$$S = \frac{\varepsilon_1 b C^0}{A_1^0}$$

Since $\varepsilon_1=A_1^0/C^0$ for the product of low concentration (*ca.* 1.0 g solid product/L),

Because the geometries of the sample inside the integrating sphere are identical:

$$S = b = \text{constant}$$

The plot $(A_1+A_2)/(A_1^0+A_2^0)$ versus dilution coefficients (C/C^0) using the data from integration sphere to exclude the effect of scattering was shown in Figure S2. For the absorbance measured under light of wavelengths between 450 nm and 750 nm, the S values are in between 0.985 to 1.06 cm, indicating that the absorbance from the impurity is actually insignificant. For the absorbance measured under light of 400 nm or shorter, there is an obvious increase of S under low concentration, showing the additional absorbance due to the by-product.

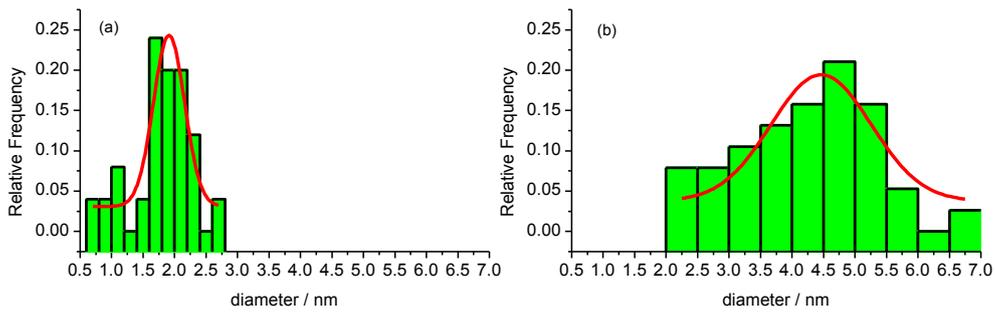


Figure S3. Particle size distribution for the Co_3O_4 particles synthesised using 4.58 mA (a) or 0.72 mA (b) limiting currents.

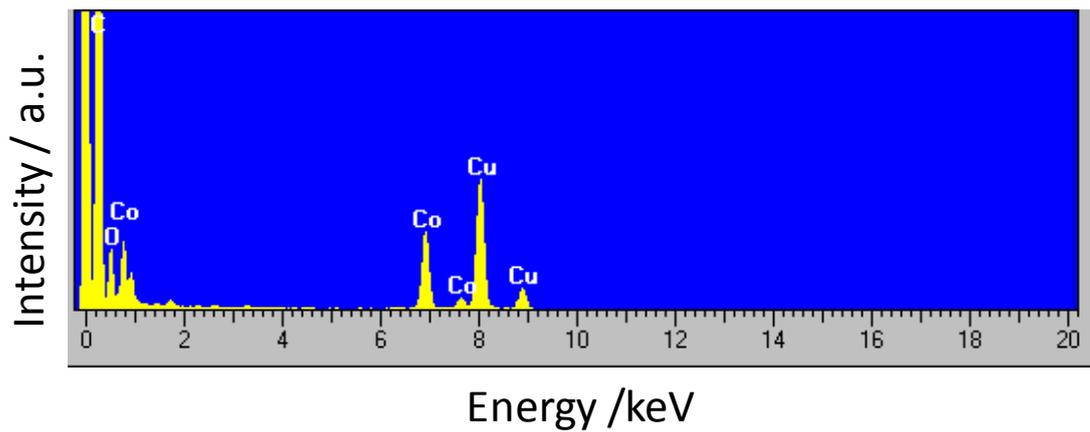


Figure S4. EDS of the sample with a limiting current of 4.58 mA. The copper is from the grid.

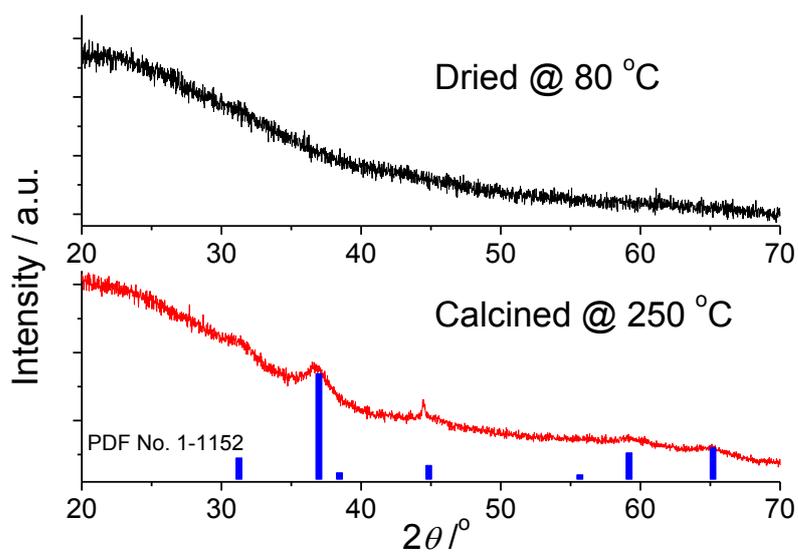


Figure S5. XRD of the sample dried at 80 °C on glass and calcined at 250 °C.

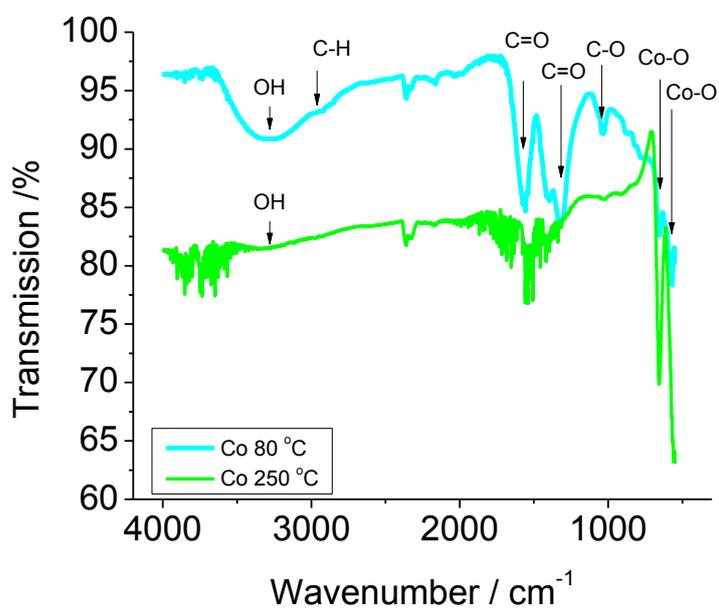


Figure S6. FTIR for powder samples from the electrolysis under a limiting current of 4.58 mA calcined at 80 °C and 250 °C.

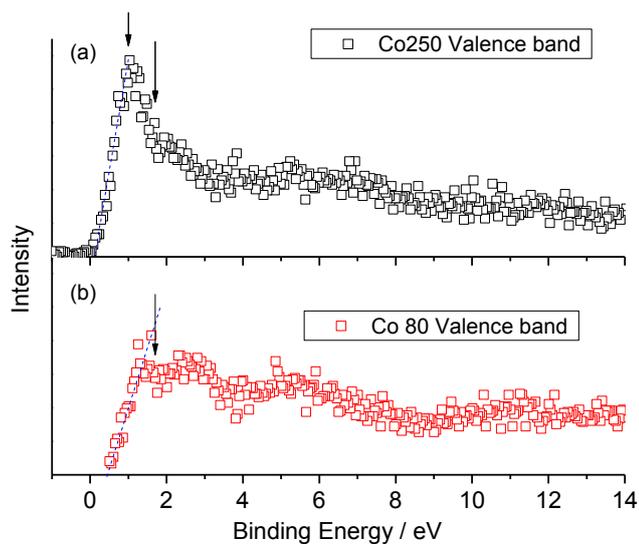


Figure S7. Valence band XPS of solid product dried at 80 °C (a) and 250 °C (b). The arrows in (a) indicate the energy position at 1.0 eV and 1.7 eV and the one in (b) represents 1.7 eV.

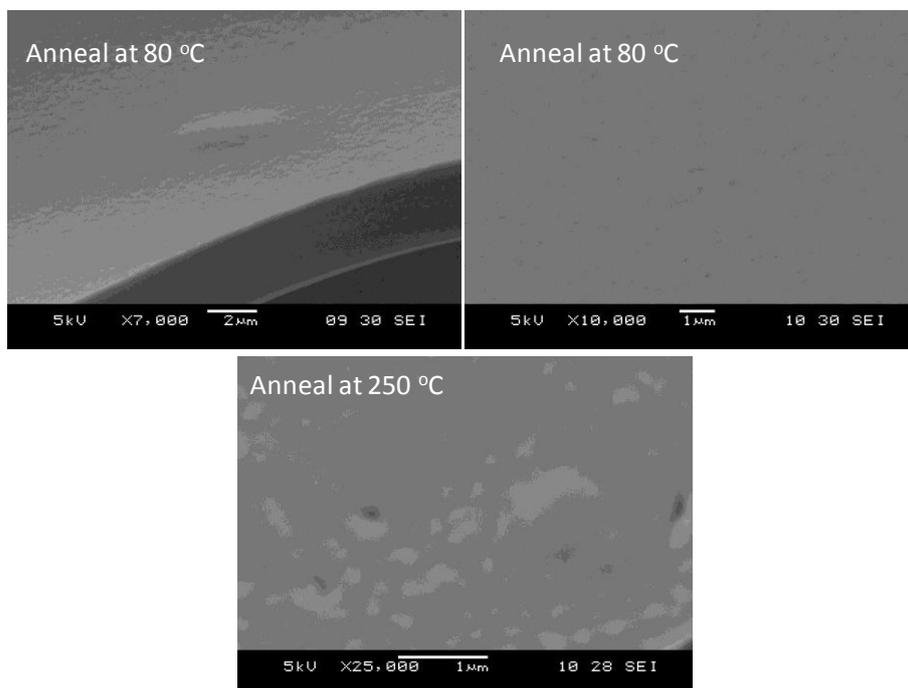


Figure S8. SEM images of drop-cast film from the solution electrolysed under a limiting current of 4.58 mA after drying at 80 °C and 250 °C.

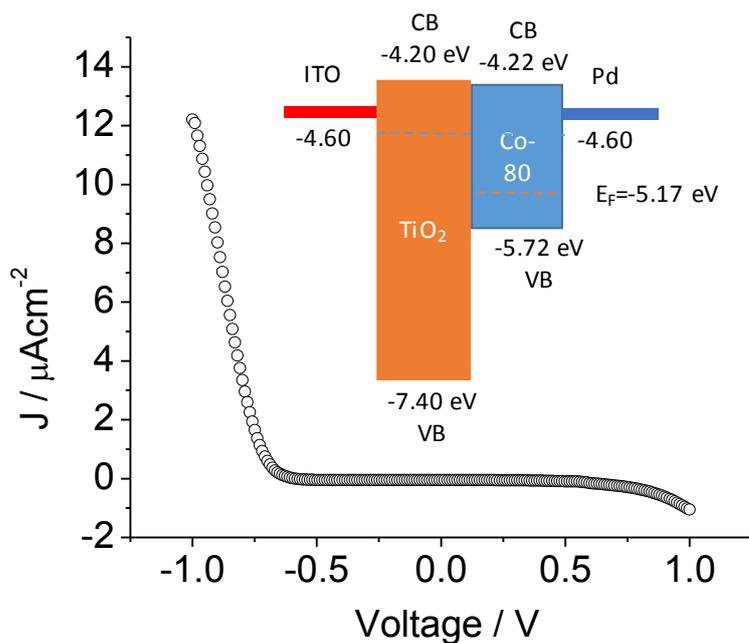


Figure S9. J - V curves of the coating on top of an dense TiO_2 layer. The inset shows the layered structure and energy level of conduction band (CB) and valence band (VB) for TiO_2 sublayer and the coating dried at 80 °C (Co-80). The Fermi level (E_F) of the Co-80 coating is measured using a Kelvin probe in relation to gold film and the separation between the E_F and valence band is deduced from the valence-band XPS in Figure S6, where the E_F sits on the zero point. The energy levels in respect of E_F , conduction band (CB) minimum and valence band (VB) maximum indicated that the spinel with by-product showed a p -type semiconducting behaviour.