Effects of synthesis parameters on the properties and photocatalytic activity of the magnetic catalyst TiO2/CoFe2O4 applied to selenium photoreduction

Supplementary Material

EFFECTS OF SYNTHESIS PARAMETERS ON THE PROPERTIES AND PHOTOCATALYTIC ACTIVITY OF THE MAGNETIC CATALYST $TiO_2/CoFe_2O_4$ APPLIED TO SELENIUM PHOTOREDUCTION

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1. MATERIALS AND METHODS

1.1. Experimental Design

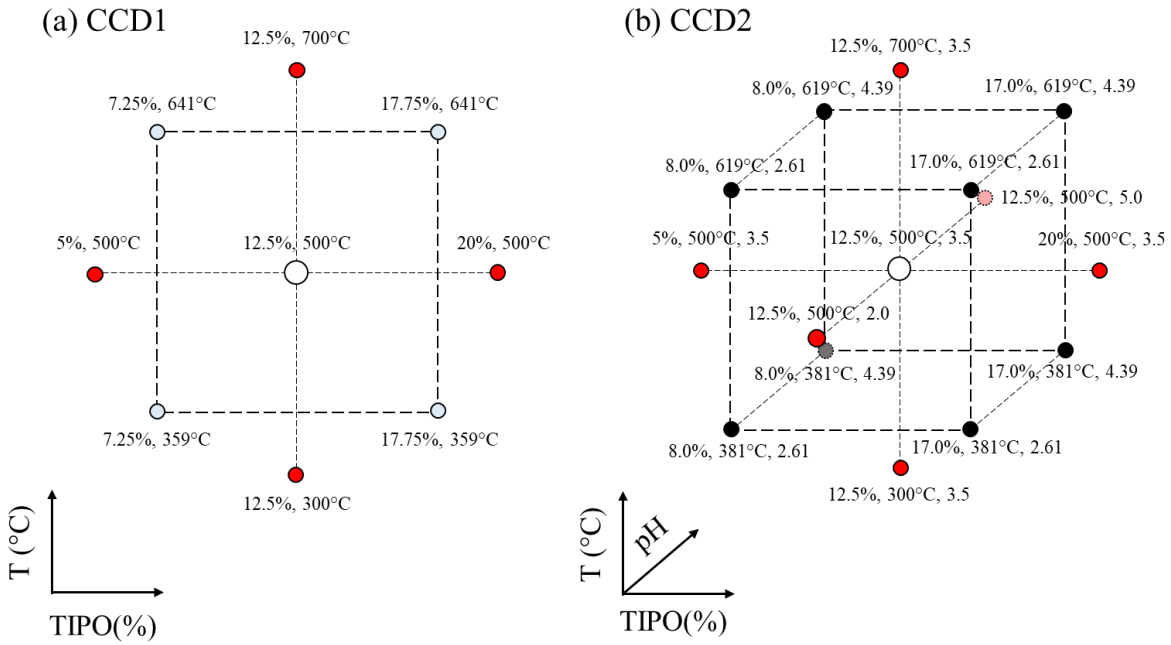


Figure S 1 - Graphical representation of the two experimental designs, two factors (a – CCD1) and three factors (b – CCD2).

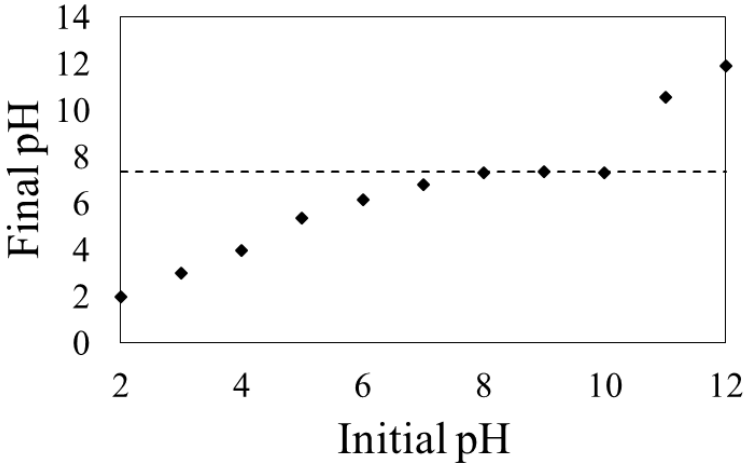
Table S 1 - Correspondence between percentage of TIPO in ethanol and TIPO/$CoFe_2O_4$ mass ratio.

TIPO (%,v/v) in ethanol	5.0	7.25	8.0	12.5	17.0	17.75	20
TIPO/$CoFe_2O_4$ mass ratio	19.2	27.8	30.7	48.0	65.3	68.2	76.8

1.2. Photocatalysts Point of Zero Charge Determination (PZC)

A batch equilibration technique was applied in order to determine the point of zero charge (PZC) of the photocatalysts. The method consisted of adding 50 mg of photocatalyst to 50 ml of distilled water, whose pH had previously been adjusted to a given value (initial pH), leaving them in contact for 24 hours until the equilibrium was reached, and then measuring the pH of suspensions after that time (final pH). For each photocatalyst, this process was repeated 11 times for different initial pH values (2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12). The suspensions were kept in an orbital shaker at 25 ºC and 150 rpm for 24 hours. Through a graph of final pH versus initial pH, it was possible to determine the PCZ as the average of the final pH values that tend to the same value, regardless of the initial pH value

[1]. The Figures S2 a and b present, as examples, the initial pH versus final pH graphs obtained for samples S-300-46.9 and S-500-46.9, respectively.



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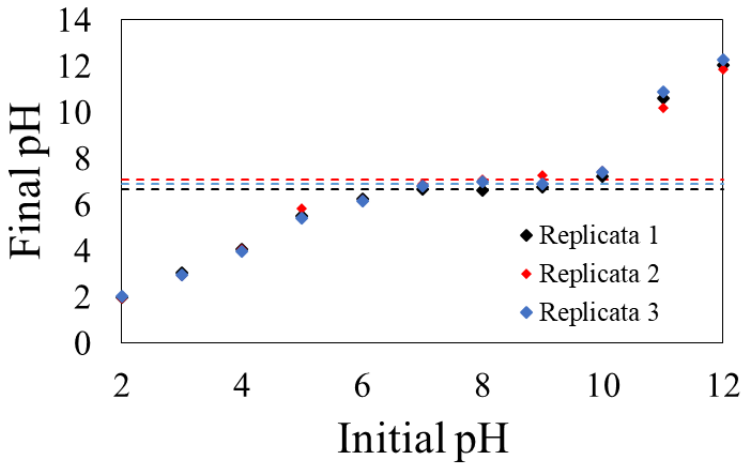


(b)

Figure S 2 – Initial versus Final pH graphs for samples (a) S-300-46.9 and (b) S-500-46.9.

2. RESULTS

2.1. Supplementary SEM and EDS results

Cobalt Ferrite

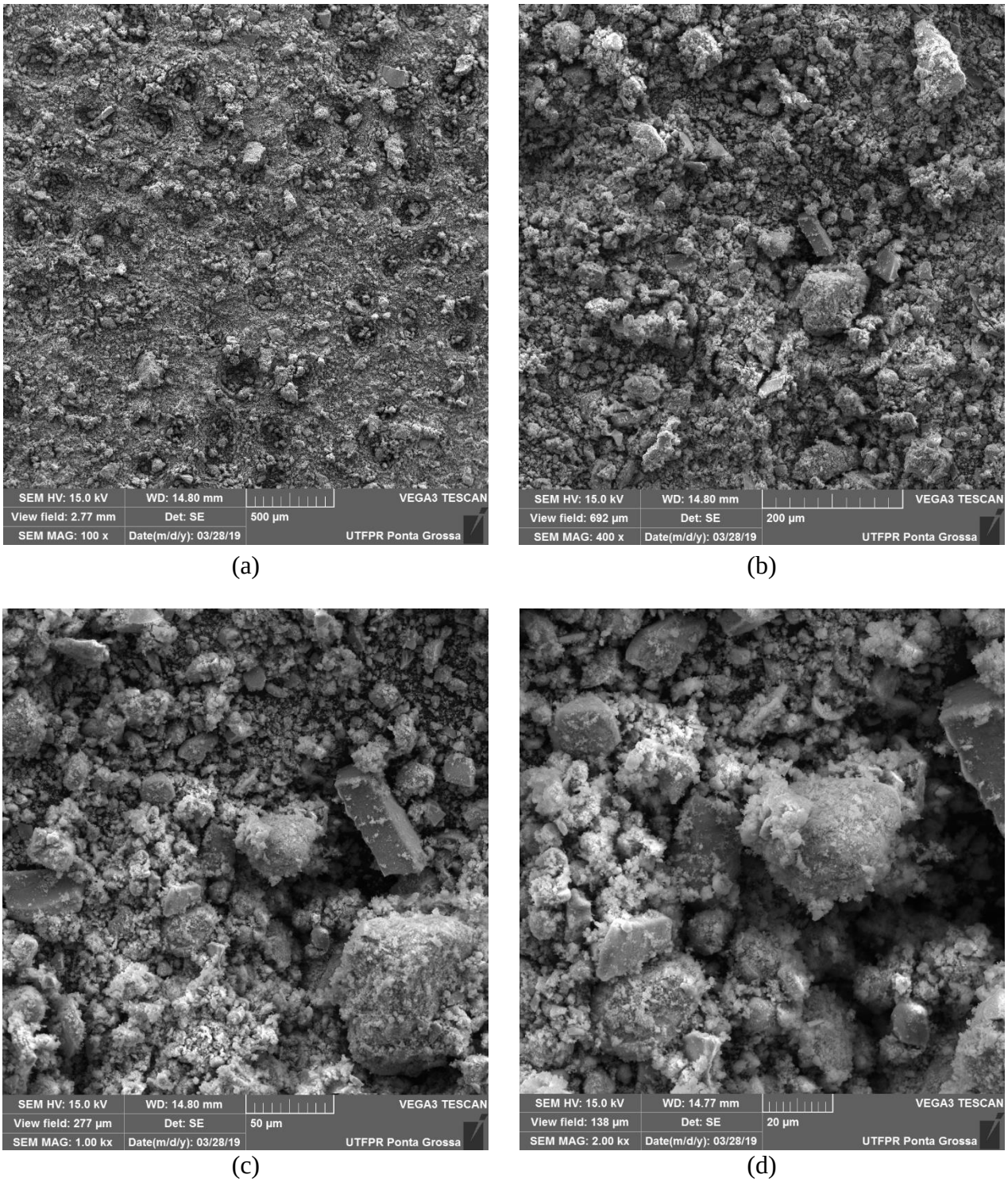
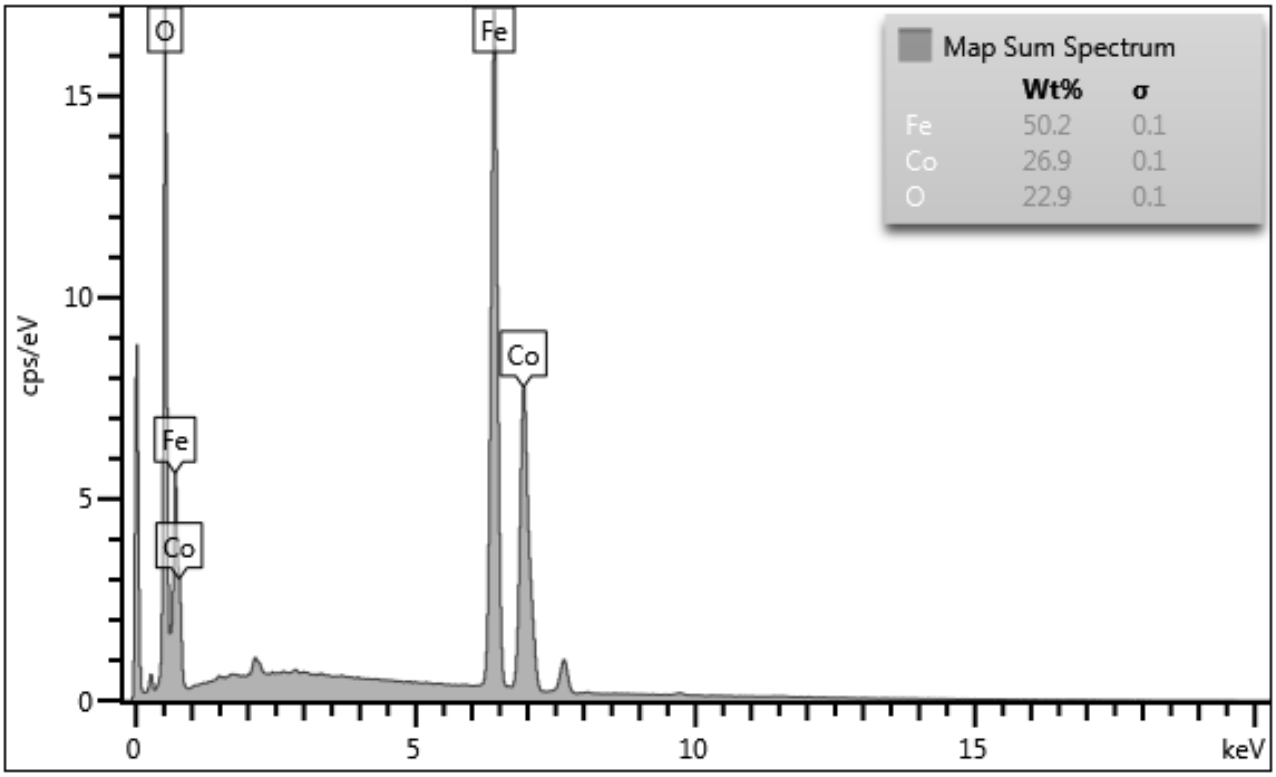


Figure S 3 – Cobalt ferrite ($CoFe_2O_4$) SEM images (a) 50 X, (b) 200 X, (c) 500 X and (d) 1000 X.



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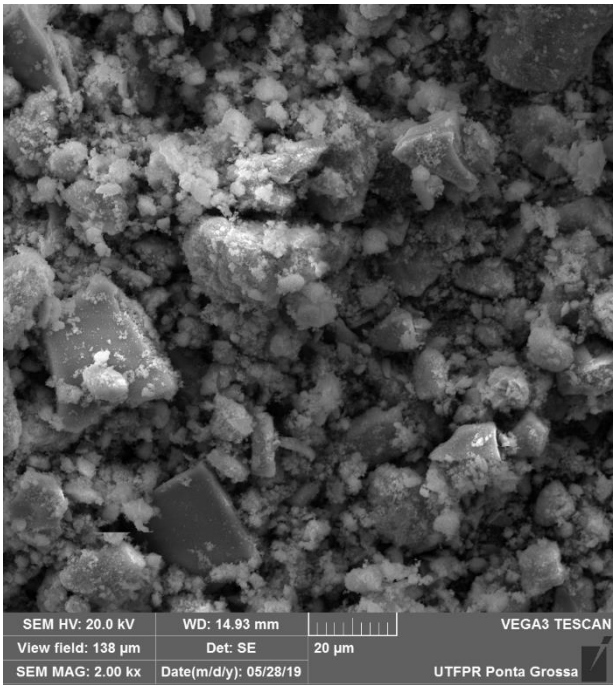

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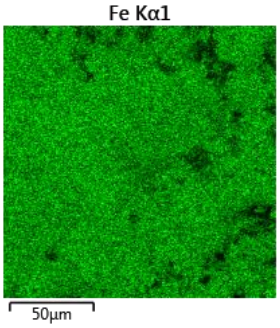

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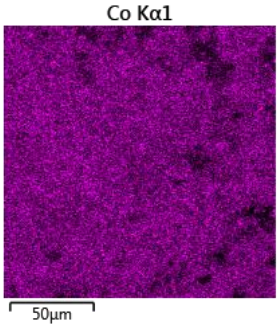

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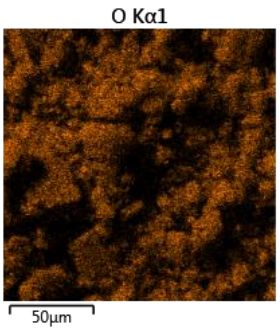
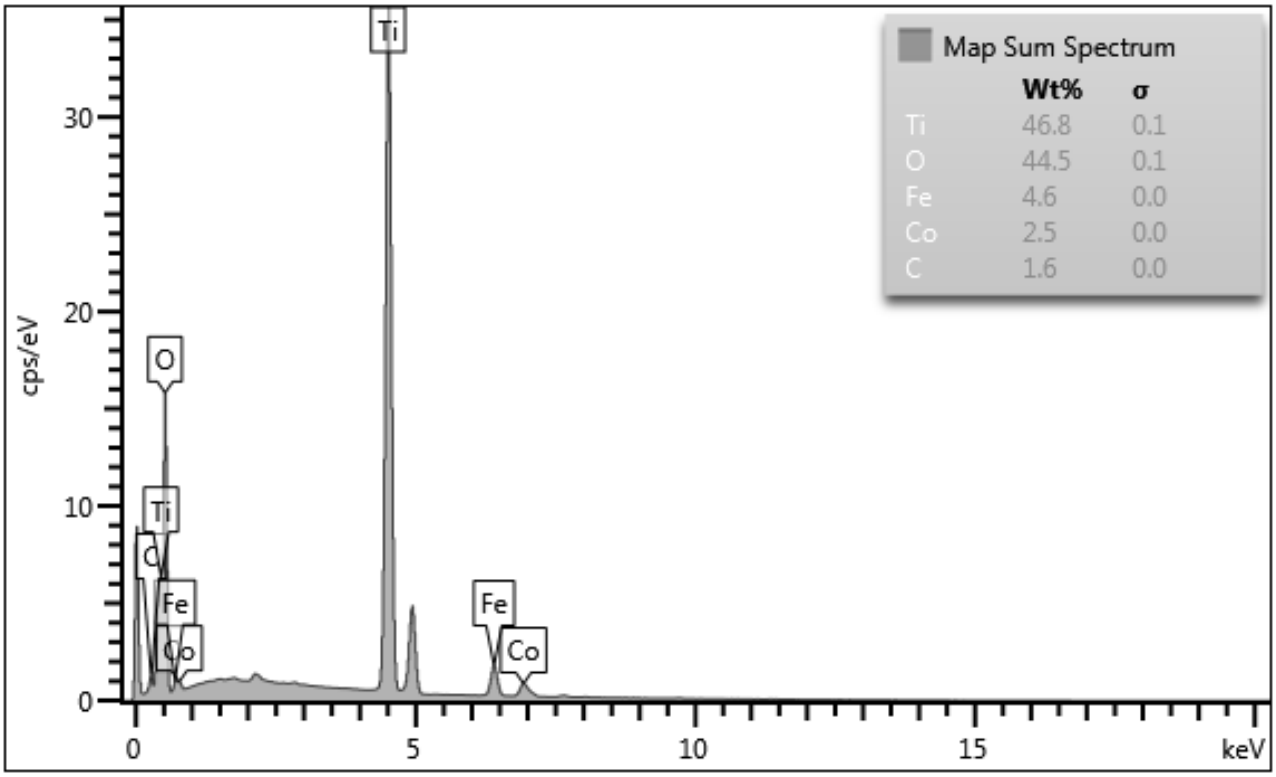


(e)

Figure S 4 – $CoFe_2O_4$ SEM-EDS results: (a) EDS spectrum, (b) $CoFe_2O_4$ SEM image (1000 X) and (c-e) Fe, Co and O surface distribution.



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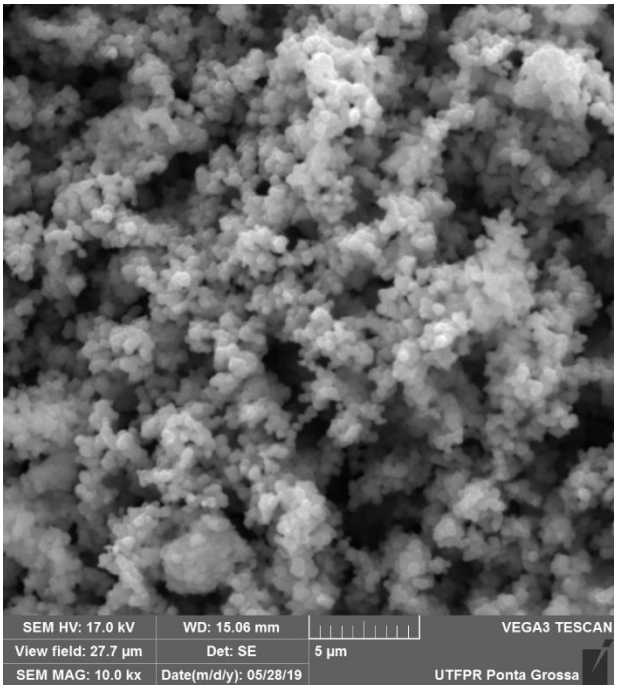

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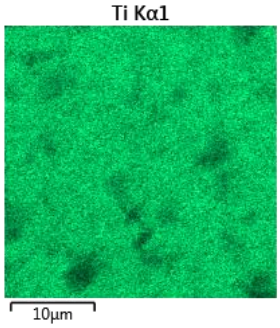

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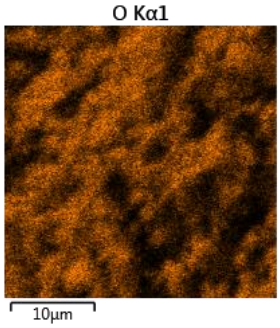

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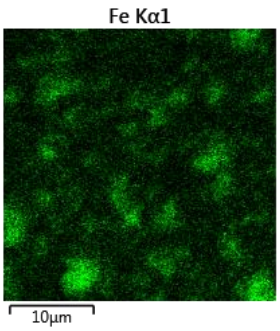

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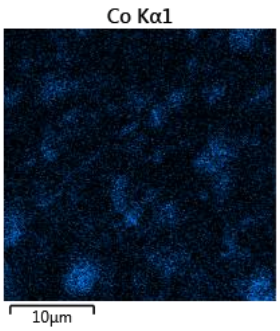
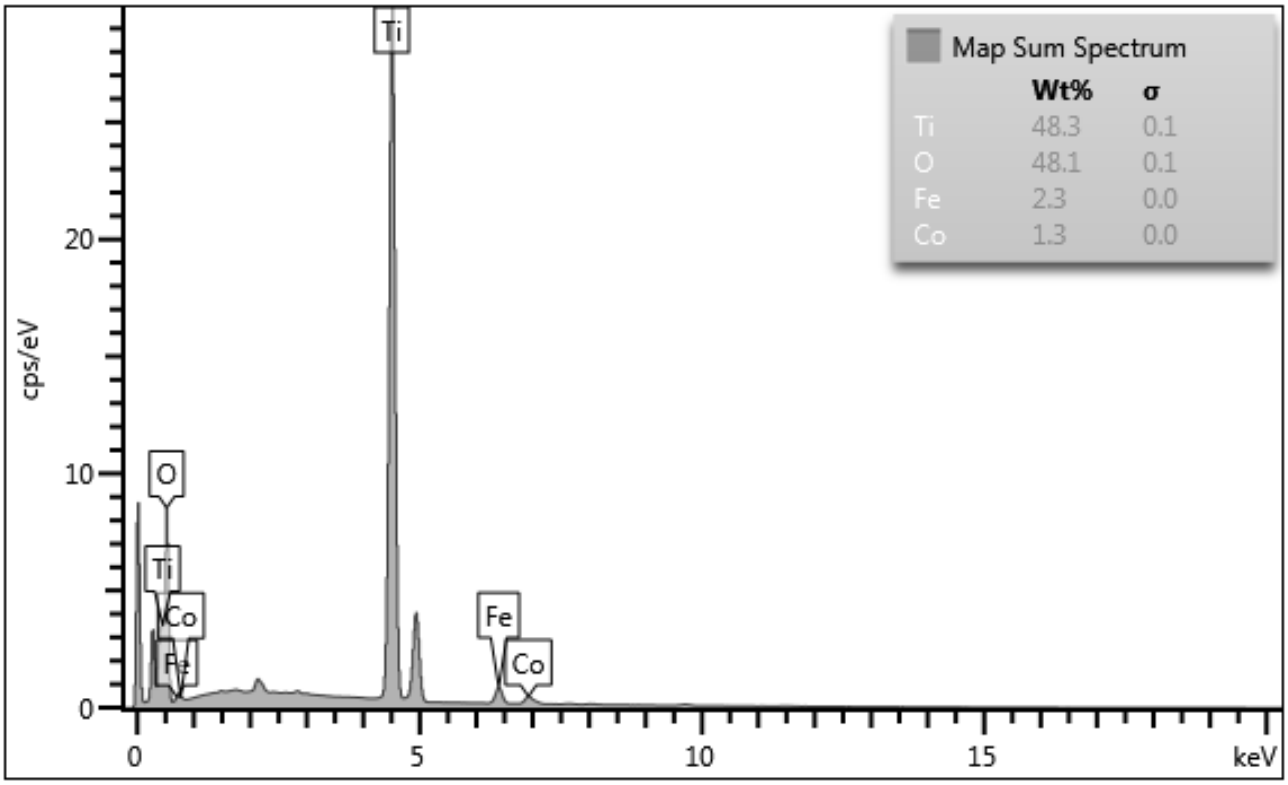


(f)

Figure S 5 – $TiO_2/CoFe_2O_4$ – sample S-500-19.2 SEM-EDS results: (a) EDS spectrum, (b) SEM image (5000 X) and (c-f) Fe, Co, Ti and O surface distribution.



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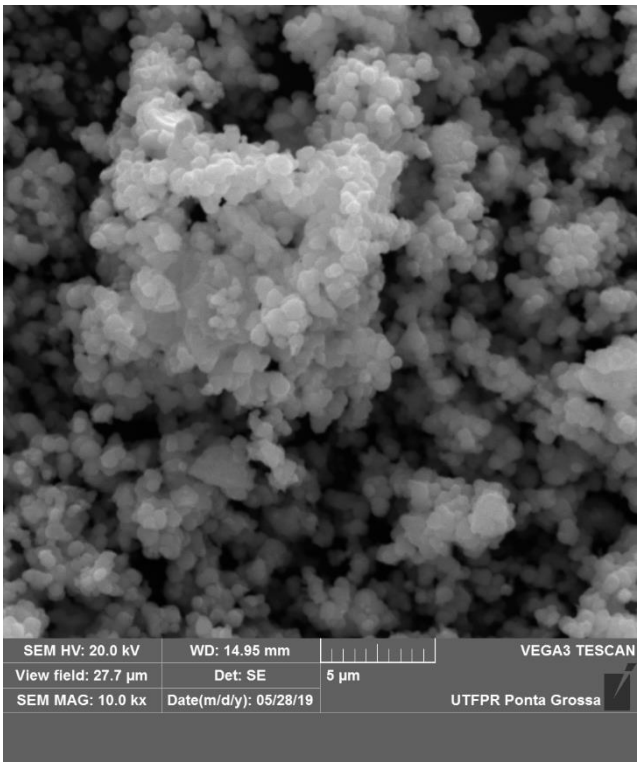

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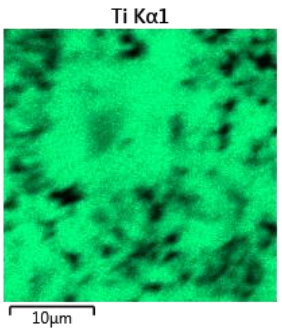

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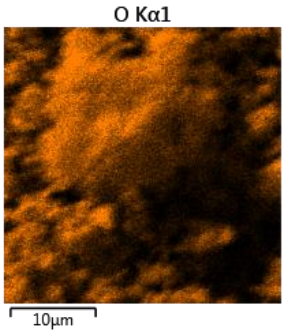

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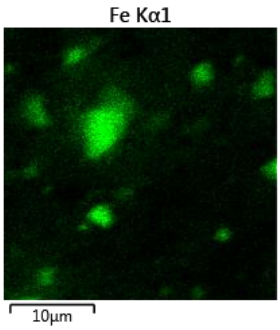

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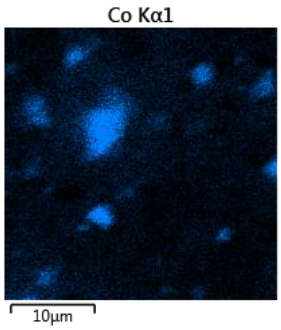

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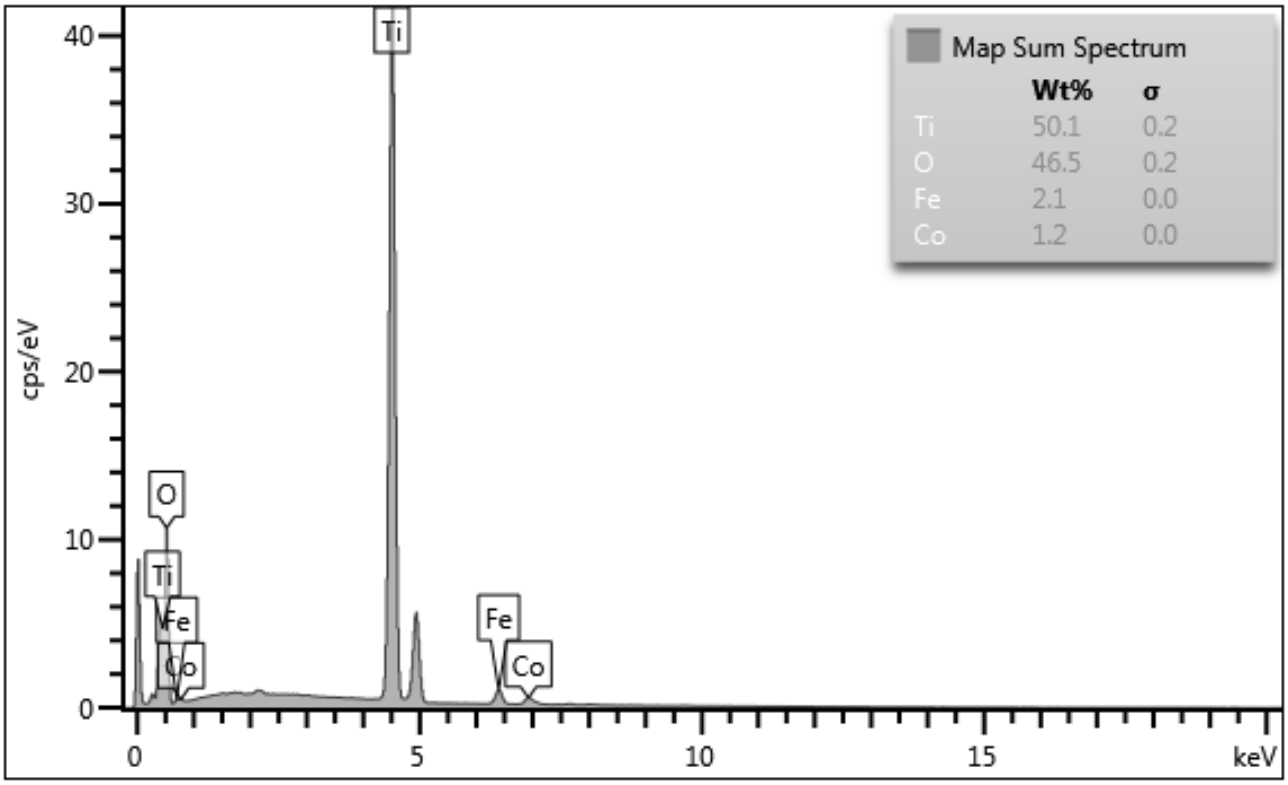
Figure S 6 – $TiO_2/CoFe_2O_4$ – sample S-359-27.8 SEM-EDS results: (a) EDS spectrum, (b) SEM image (5000 X) and (c-f) Fe, Co, Ti and O surface distribution.



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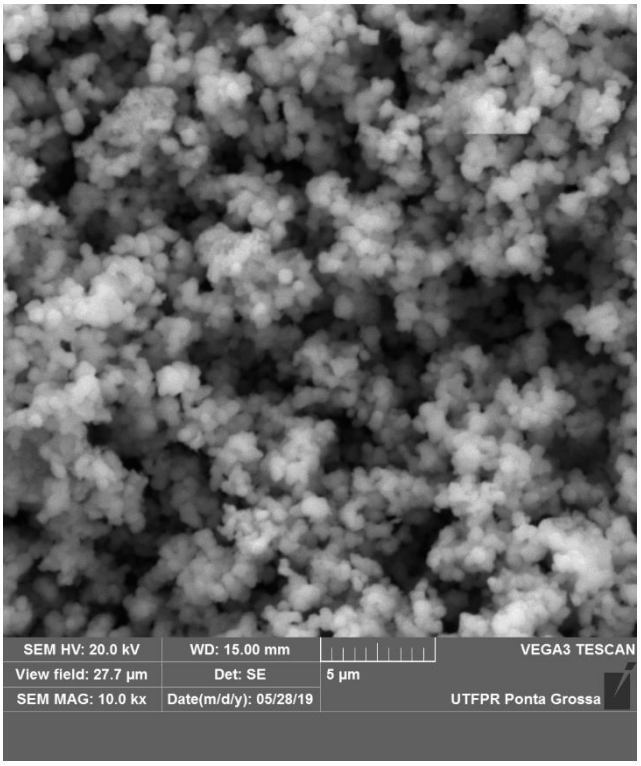

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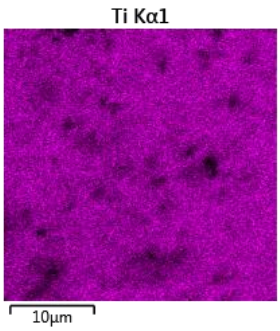

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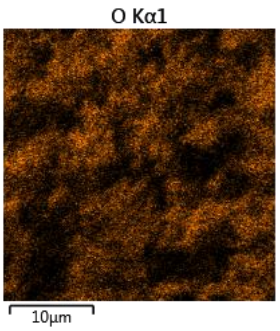

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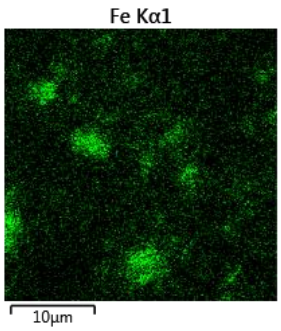

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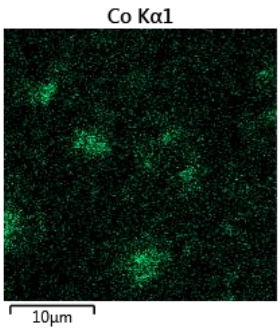
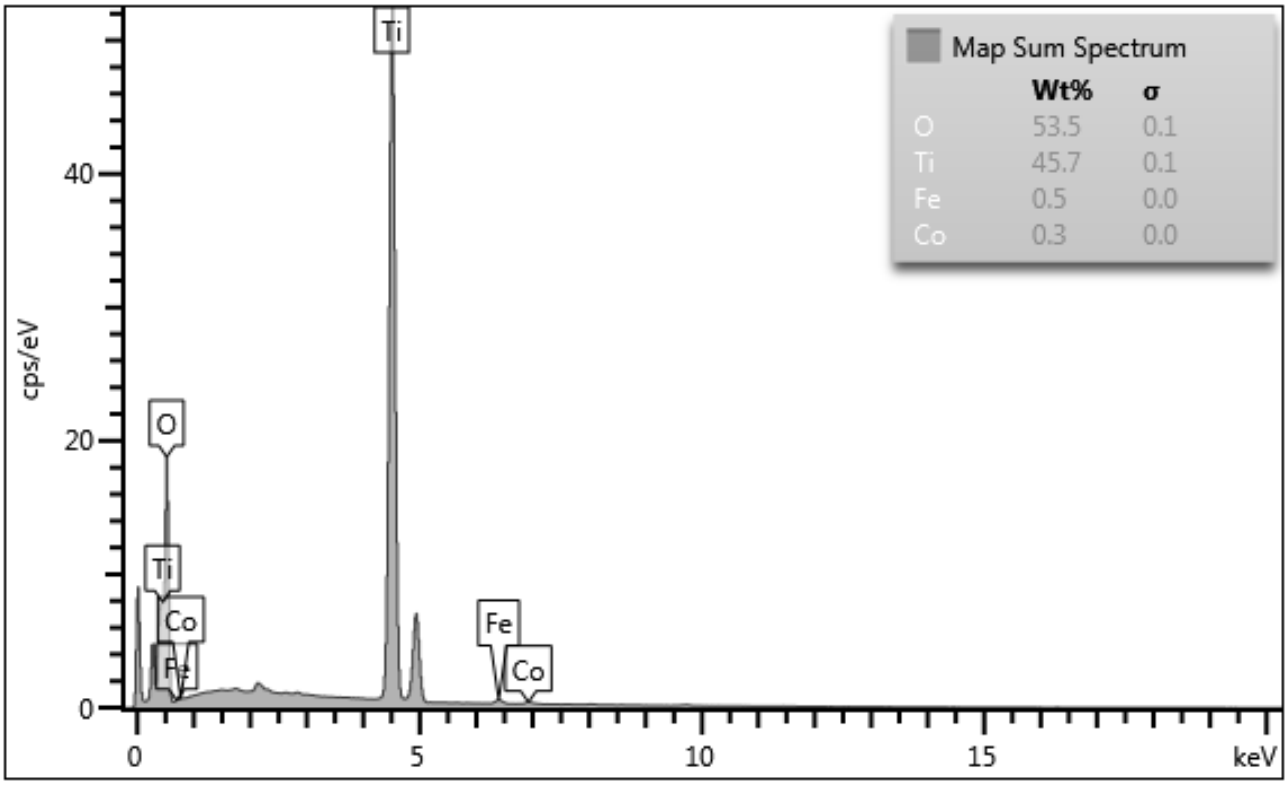


(f)

Figure S 7 – $TiO_2/CoFe_2O_4$ – sample S-641-27.8 SEM-EDS results: (a) EDS spectrum, (b) SEM image (5000 X) and (c-f) Fe, Co, Ti and O surface distribution.



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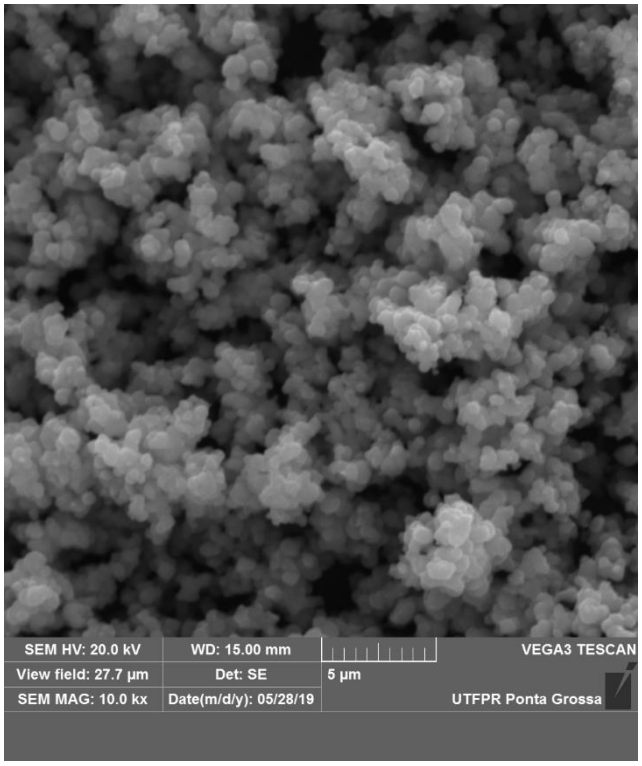

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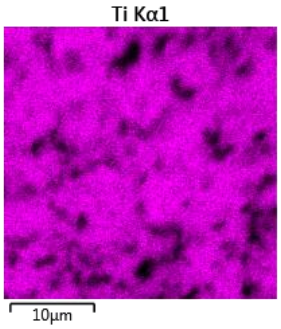

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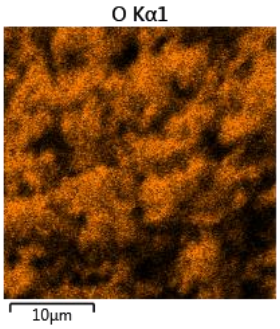

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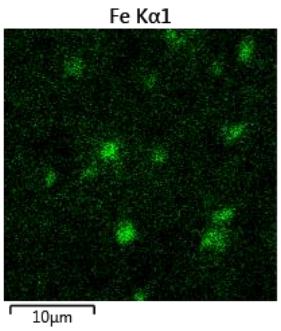

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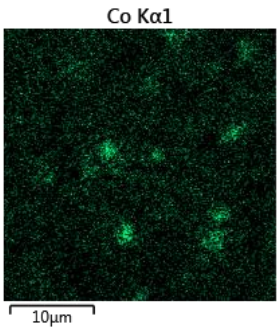

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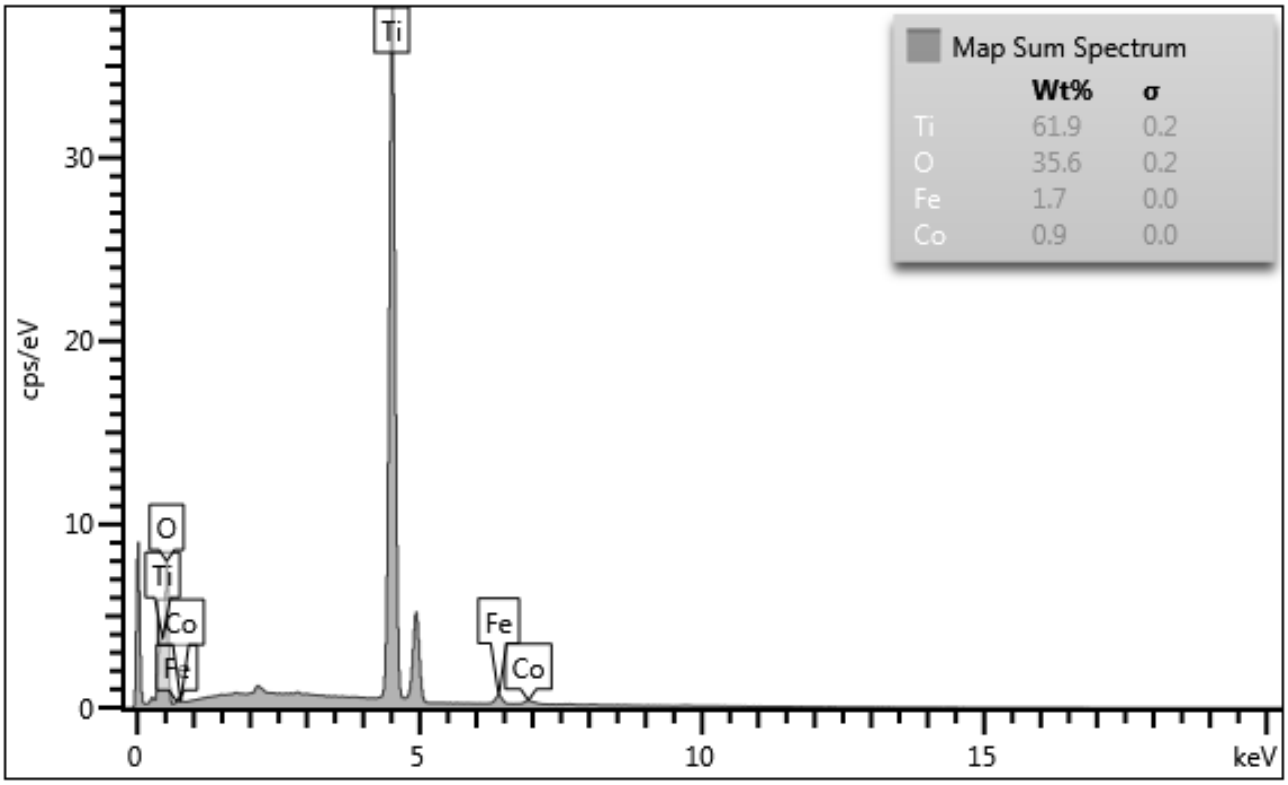
Figure S 8 – $TiO_2/CoFe_2O_4$ – sample S-300-48.0 SEM-EDS results: (a) EDS spectrum, (b) SEM image (5000 X) and (c-f) Fe, Co, Ti and O surface distribution.



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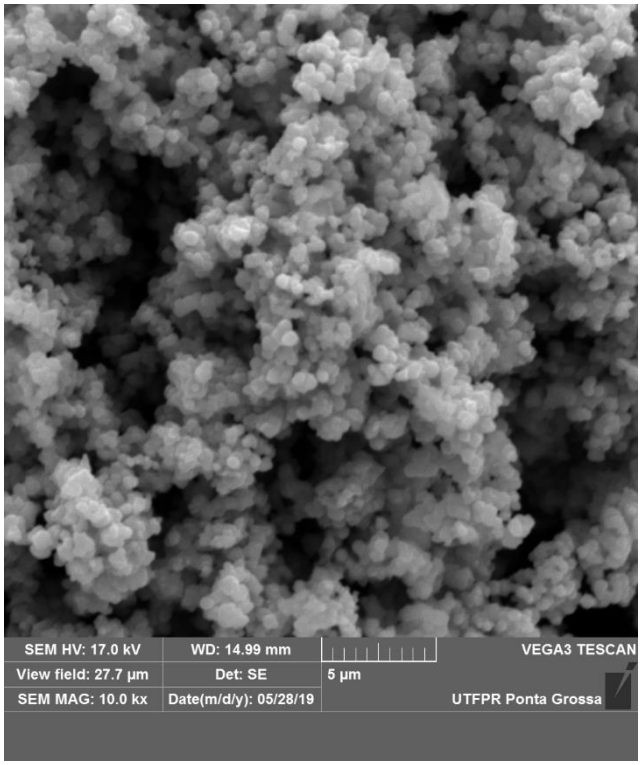

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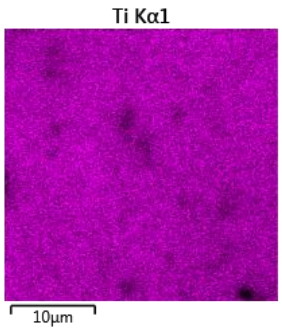

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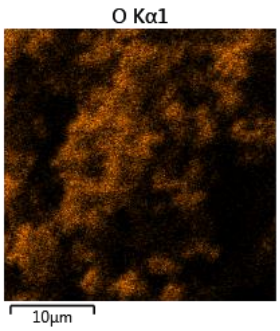

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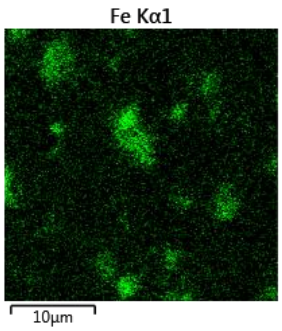

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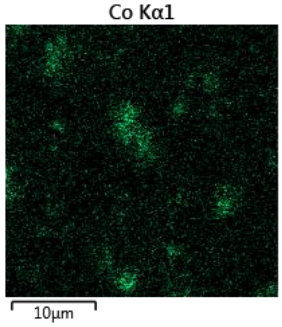

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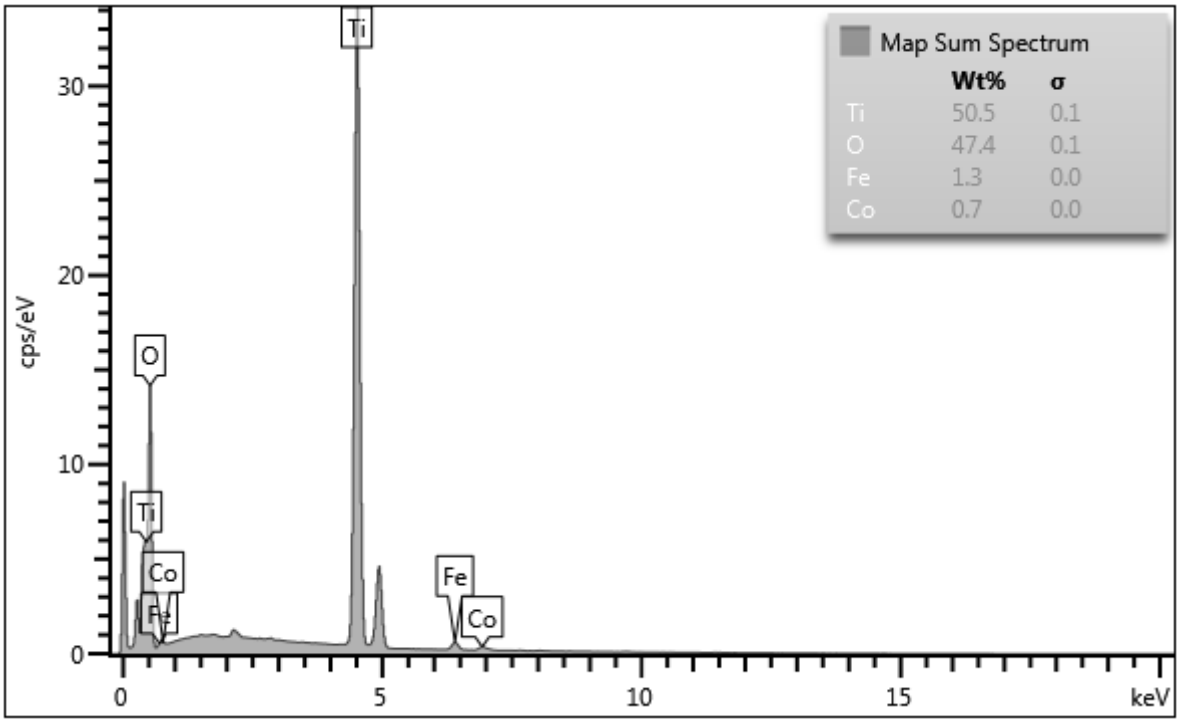
Figure S 9 – $TiO_2/CoFe_2O_4$ – sample S-500-48.0 SEM-EDS results: (a) EDS spectrum, (b) SEM image (5000 X) and (c-f) Fe, Co, Ti and O surface distribution.



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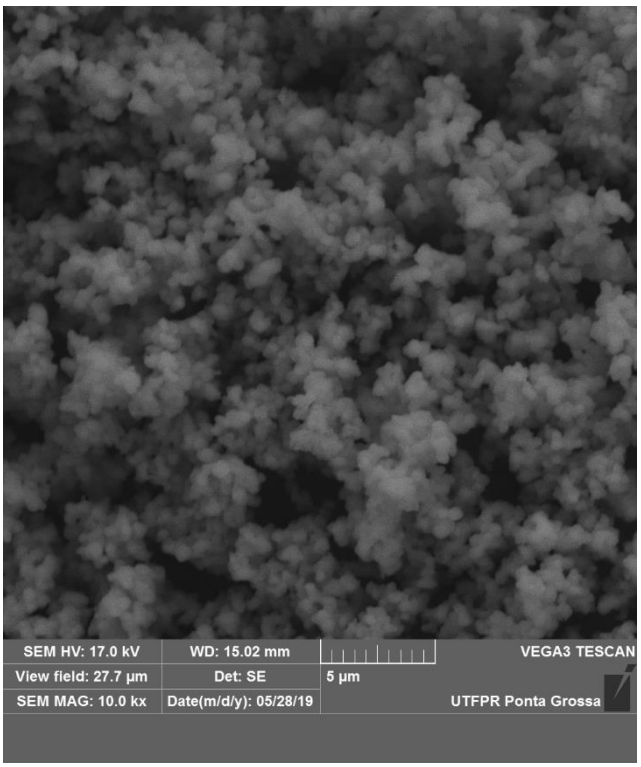

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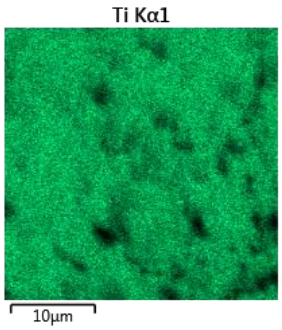

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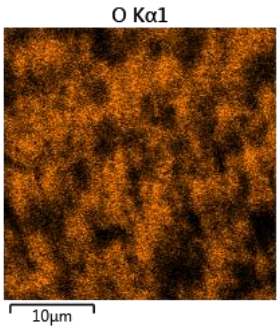

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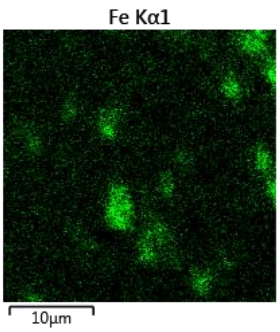

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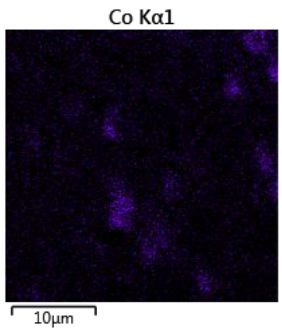

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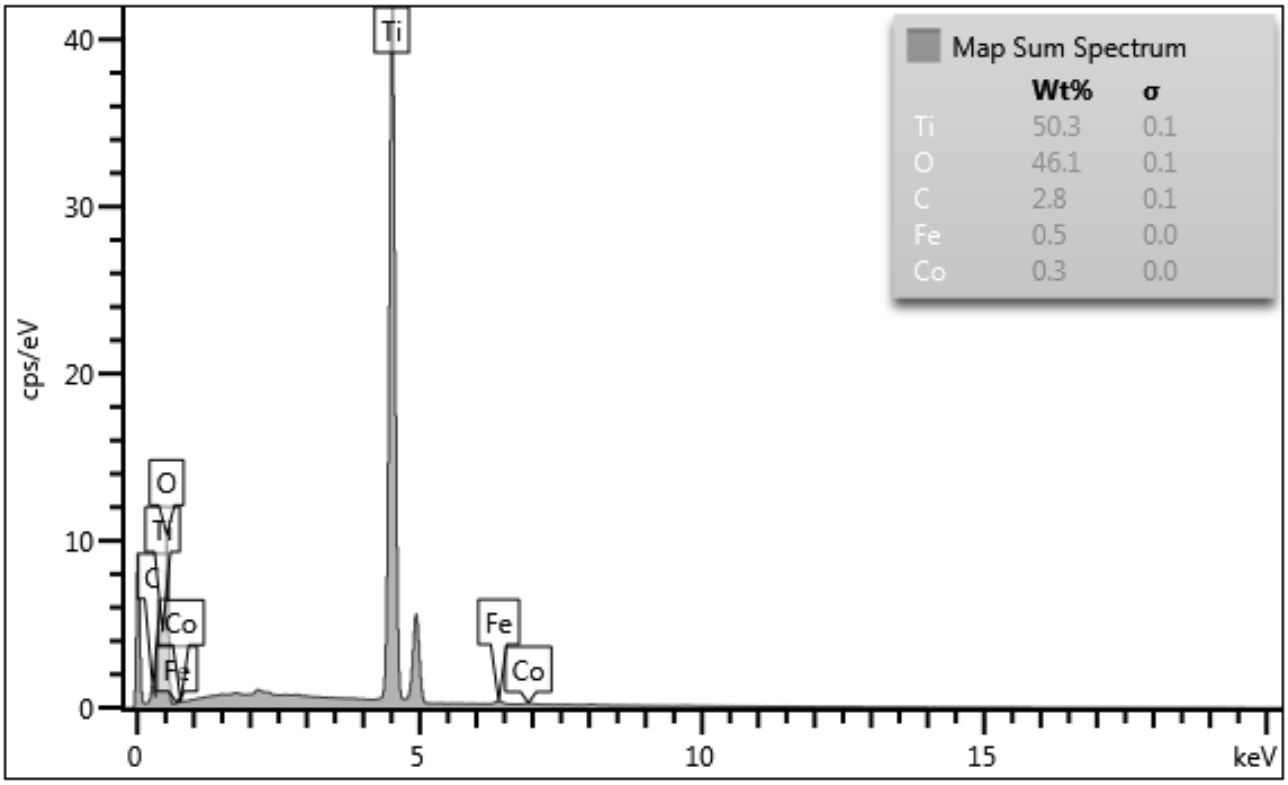
Figure S 10 – $TiO_2/CoFe_2O_4$ – sample S-700-48.0 SEM-EDS results: (a) EDS spectrum, (b) SEM image (5000 X) and (c-f) Fe, Co, Ti and O surface distribution.



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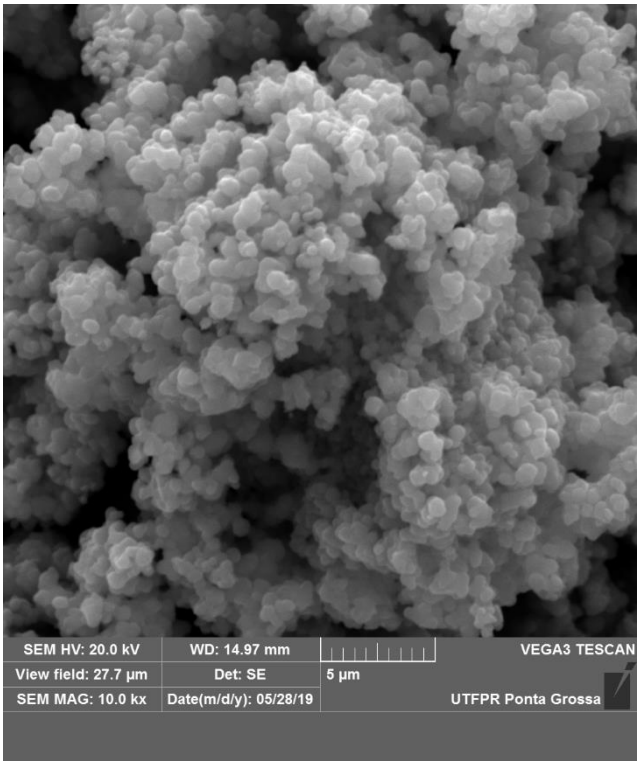

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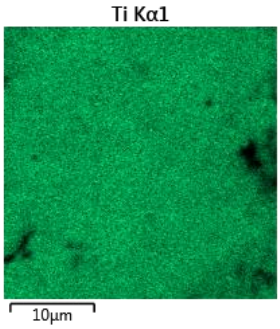

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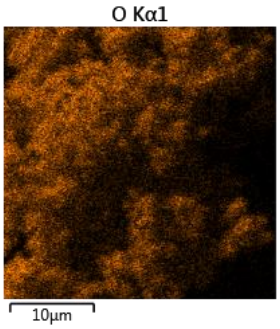

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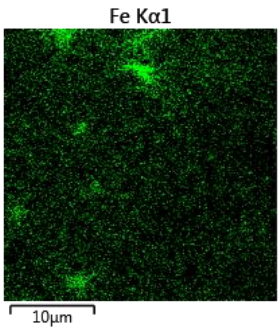

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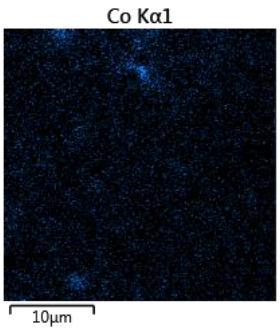
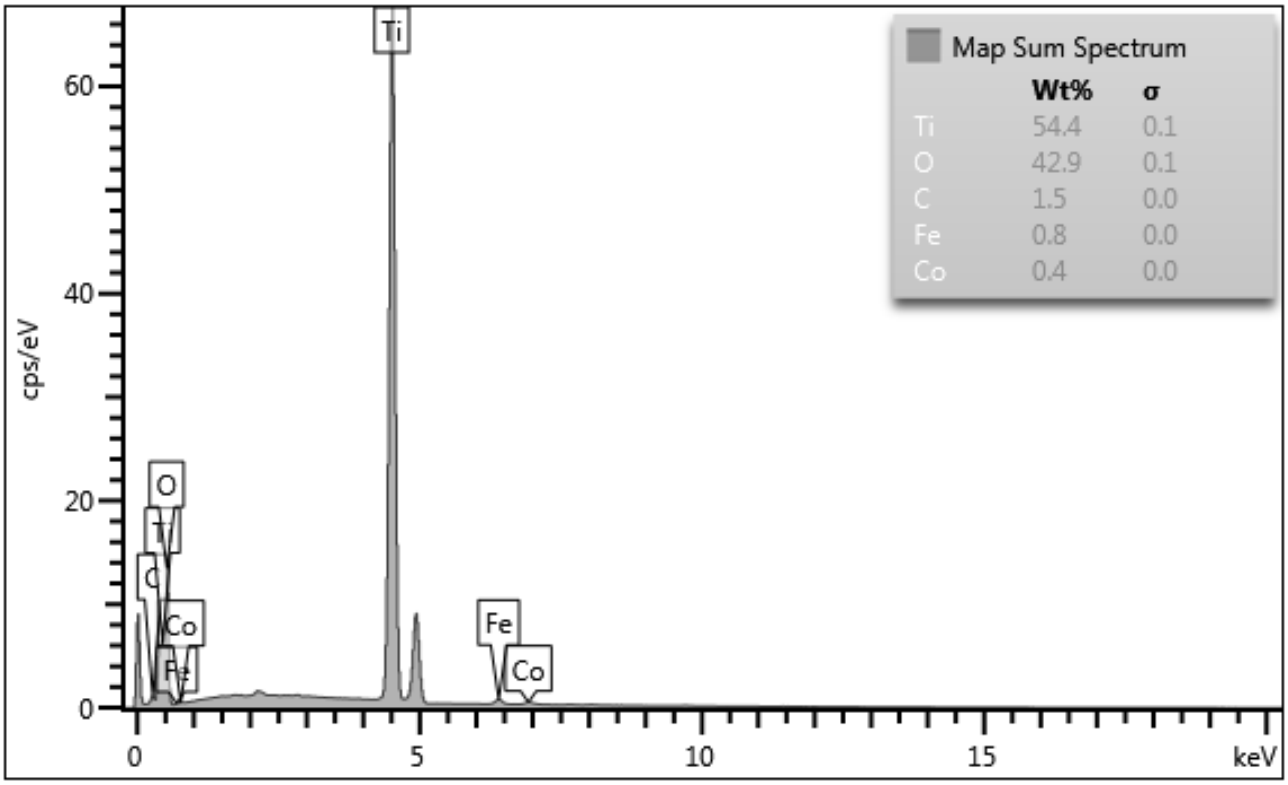


(f)

Figure S 11 – $TiO_2/CoFe_2O_4$ – sample S-359-68.2 SEM-EDS results: (a) EDS spectrum, (b) SEM image (5000 X) and (c-f) Fe, Co, Ti and O surface distribution.



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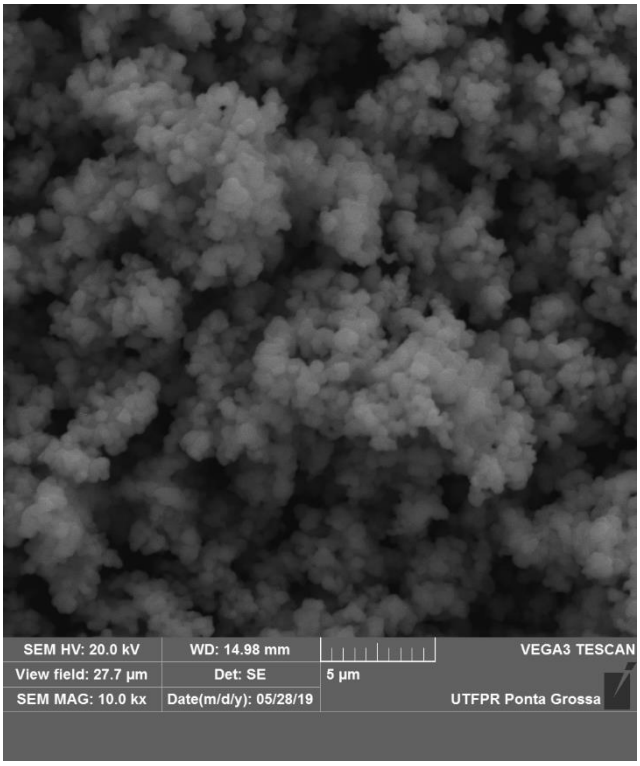

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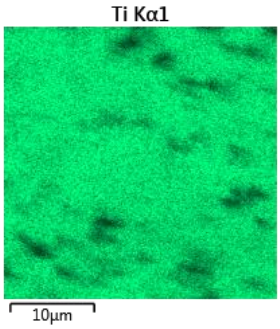

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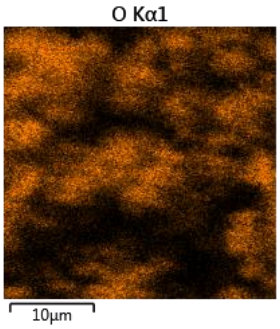

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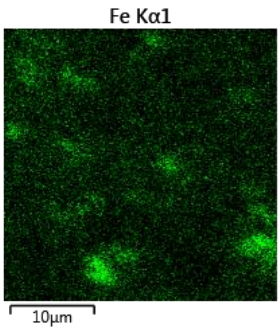

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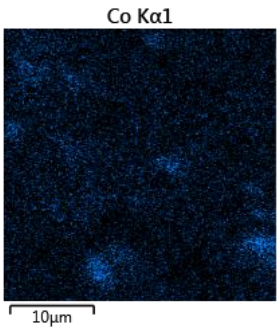
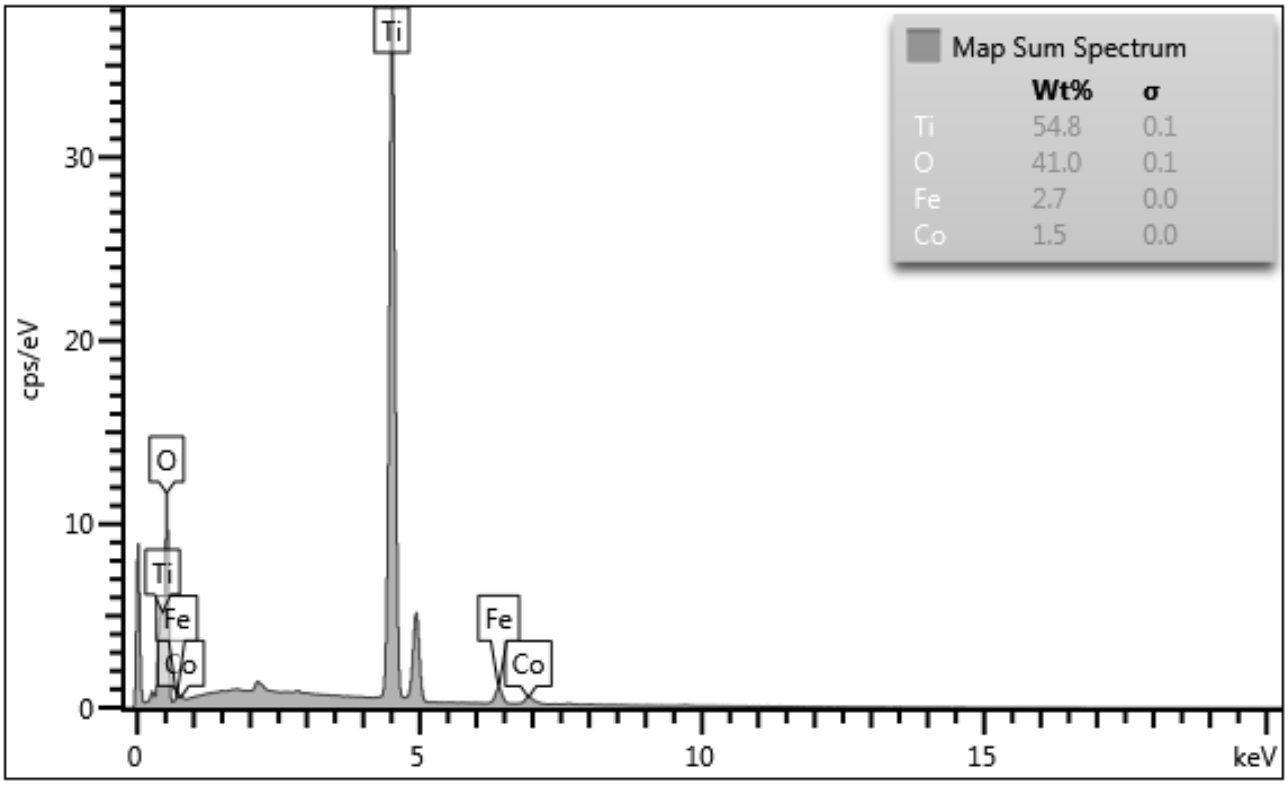
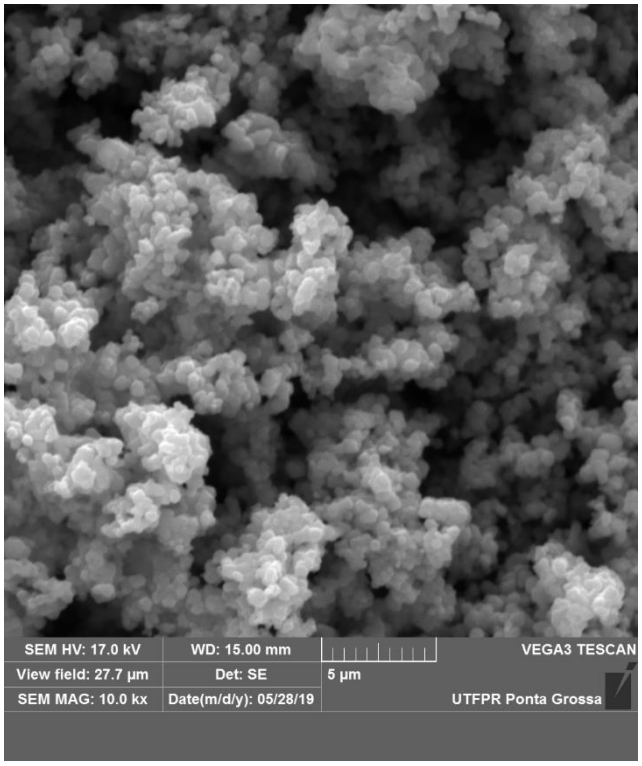


(f)

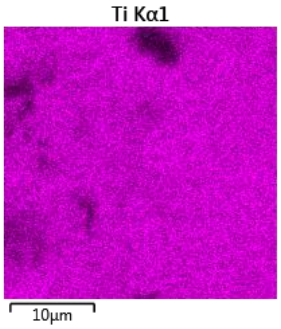
Figure S 12 – $TiO_2/CoFe_2O_4$ – sample S-641-68.2 SEM-EDS results: (a) EDS spectrum, (b) SEM image (5000 X) and (c-f) Fe, Co, Ti and O surface distribution.



(a)



(b)



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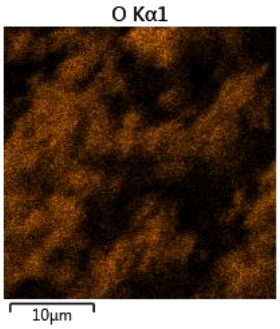

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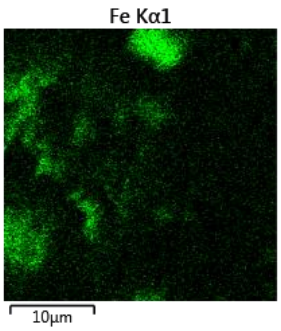
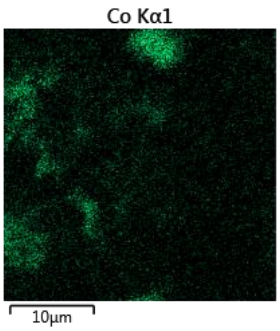


(e)



(f)

Figure S 13 – $TiO_2/CoFe_2O_4$ – sample S-500-76.8 SEM-EDS results: (a) EDS spectrum, (b) SEM image (5000 X) and (c-f) Fe, Co, Ti and O surface distribution.

2.2. Rietveld refinement

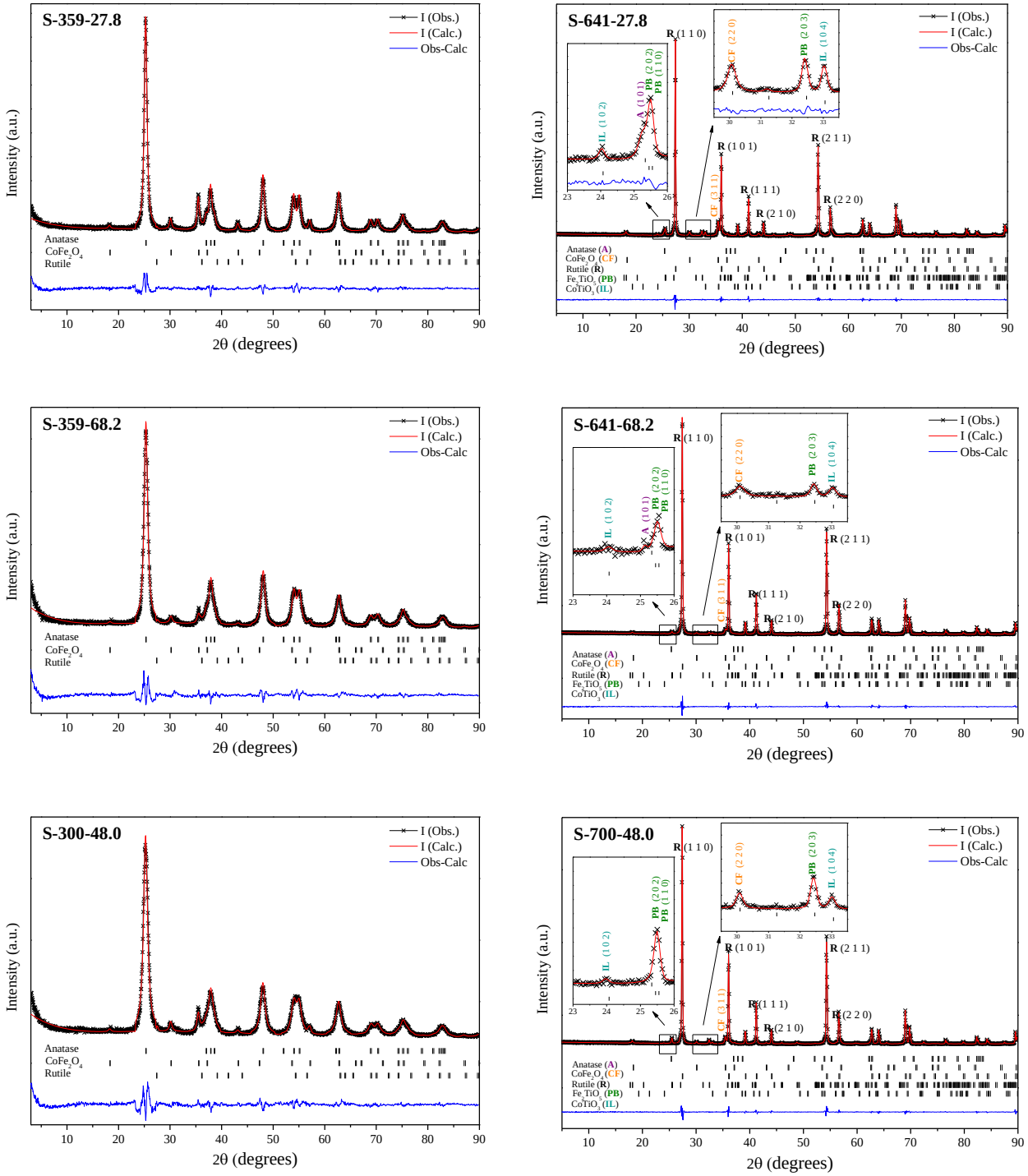


Figure S 14 – Rietveld refinement plots.

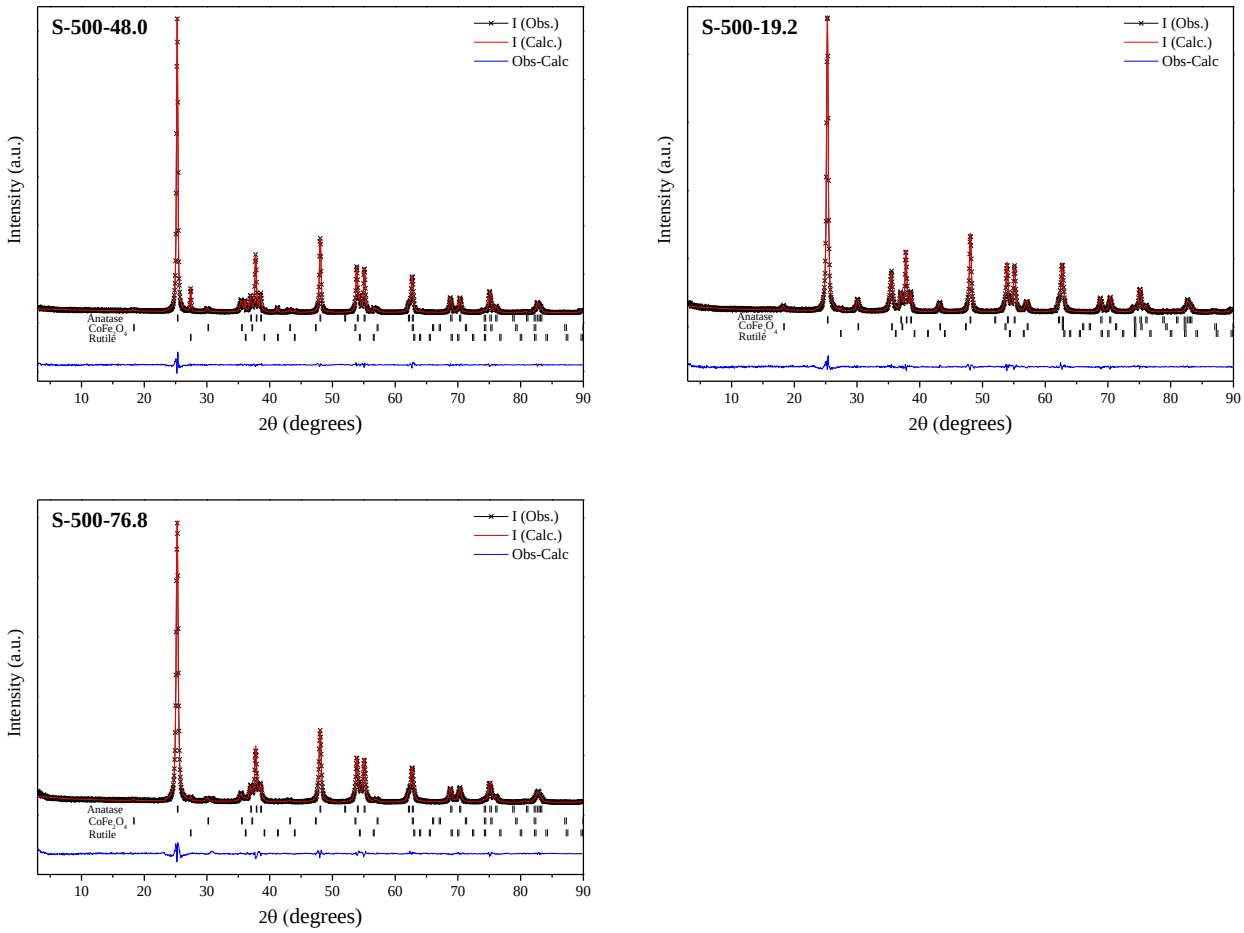


Figure S 15 - Rietveld refinement plots.

2.3. Band gap results (Photoacoustic Spectroscopy)

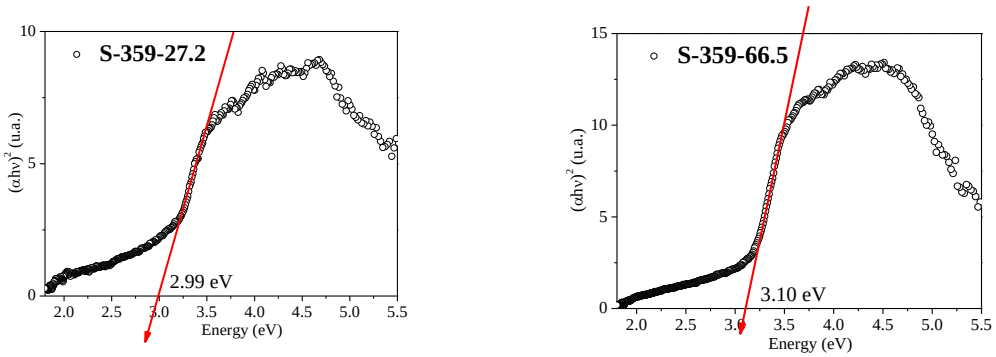


Figure S 16 – Band gap determination through PAS signal

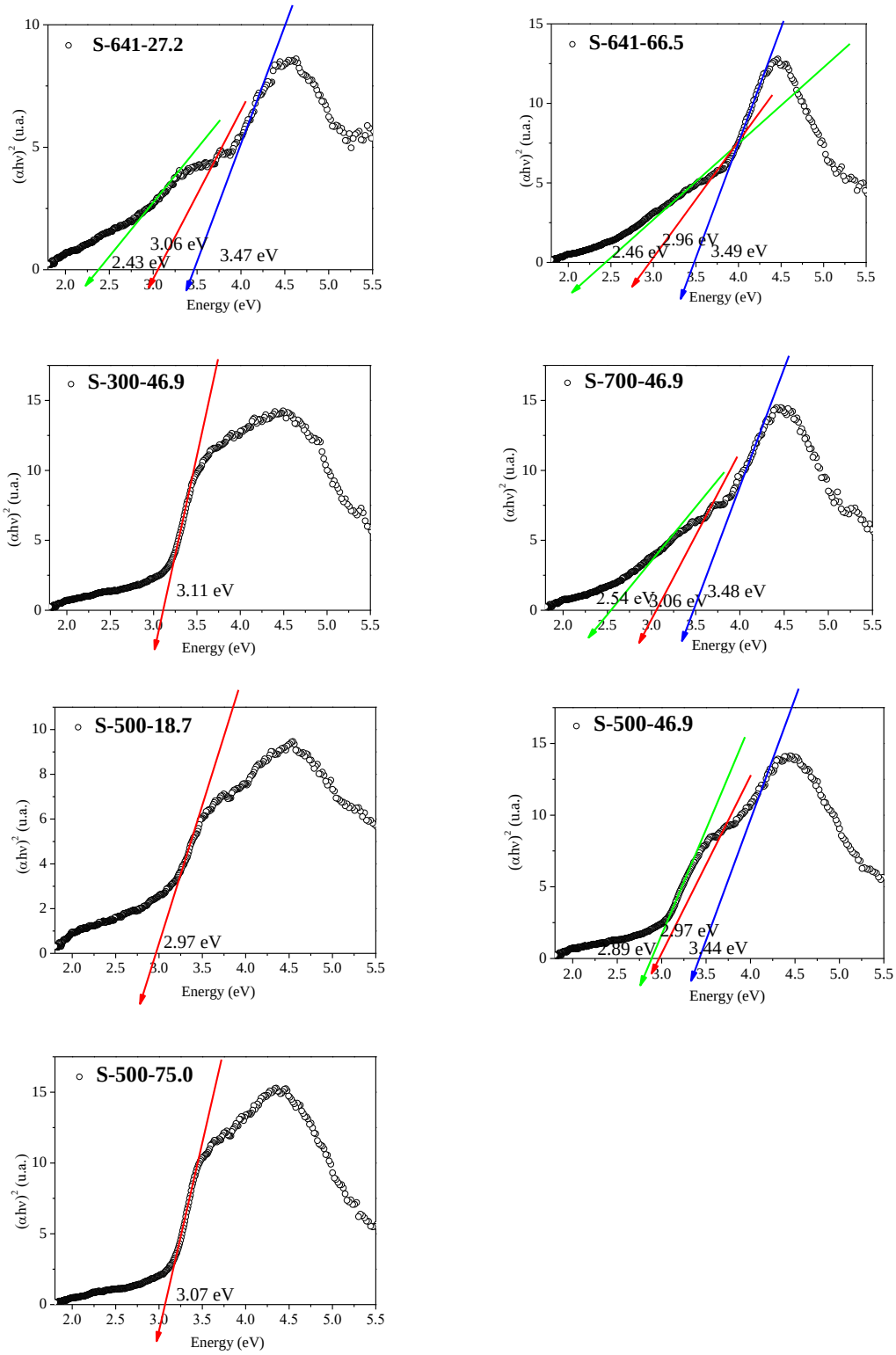


Figure S 17 - Band gap determination through PAS signal.

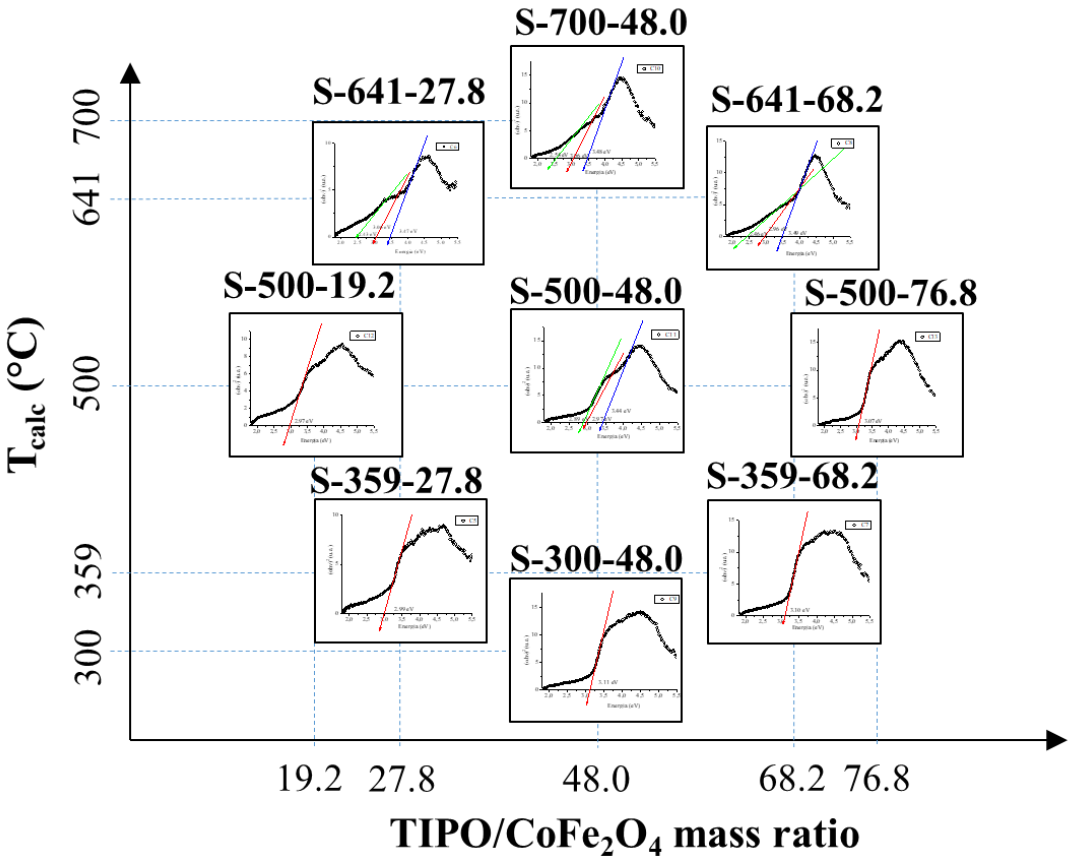


Figure S 18 - Band gap determination through PAS signal, organized according to de CCD1

2.4. Adsorption and Photocatalysis Results

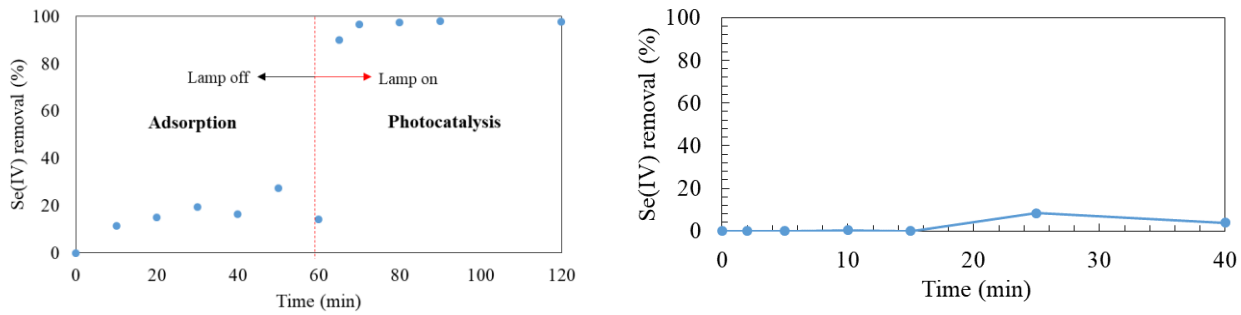


Figure S 19 – (a) Se(IV) removal (%) over time, with 60 min of adsorption in the dark followed by 60 min of photocatalysis. Photocatalyst TiO_2/ $CoFe_2O_4$ produced using a TIPO/$CoFe_2O_4$ mass ratio equal to 46.9 and calcined at 500 ºC. Catalyst concentration = 0.1 g L^{-1}, pH = 3.5; and (b) Se (IV) removal (%) over time by photolysis, without the addition of catalyst and pH = 3.5.

Table S 2- Se(IV) removal results for 19 tests performed under different conditions. Removal (%) after 30 min of adsorption in the dark and after 2 min of exposure to UV radiation are presented for each test.

Test	T_{calc} (ºC)	TIPO/$CoFe_2O_4$ mass ratio	pH	Se(IV) removal (%)	
				30 min of adsorption	2 min photocatalysis
1	381 (-1)	30.7 (-1)	2.61 (-1)	39.7	96.3
2	619 (+1)	30.7 (-1)	2.61 (-1)	-	4.3
3	381 (-1)	65.3 (+1)	2.61 (-1)	3.0	99.1
4	619 (+1)	65.3 (+1)	2.61 (-1)	-	2.9
5	381 (-1)	30.7 (-1)	4.39 (+1)	-	92.4
6	619 (+1)	30.7 (-1)	4.39 (+1)	6.6	4.3
7	381 (-1)	65.3 (+1)	4.39 (+1)	15.8	89.0
8	619 (+1)	65.3 (+1)	4.39 (+1)	5.1	1.1
9	300 (-α)	48.0 (0)	3.50 (0)	86.6	96.1
10	700 (+α)	48.0 (0)	3.50 (0)	1.4	4.2
11	500 (0)	19.2 (-α)	3.50 (0)	23.6	85.7
12	500 (0)	76.8 (+α)	3.50 (0)	29.0	89.4
13	500 (0)	48.0 (0)	2.00 (-α)	17.8	49.2
14	500 (0)	48.0 (0)	5.00 (+α)	30.9	55.7
15	500 (0)	48.0 (0)	3.50 (0)	22.6	76.8
16	500 (0)	48.0 (0)	3.50 (0)	-	78.5
17	500 (0)	48.0 (0)	3.50 (0)	-	84.4
18	500 (0)	48.0 (0)	3.50 (0)	38.65	85.8
19	500 (0)	48.0 (0)	3.50 (0)	13.90	82.7

2.5. Response Surface Analysis (CCD1)

2.5.1. Specific Surface Area (BET)

Table S 3 – Effects estimates for specific surface area.

Factor	Effect	Std. Error Pure Error	t(2)	p	Cnf. Limit, -95, %	Cnf. Limit, +95, %
Mean/ Interaction	26.3333	1.452966	18.1238	0.003031	20.0817	32.5849
(1) T_{calc} (ºC) (L)	-69.4307	1.779513	-39.0167	0.000656	-77.0873	-61.7741
T_{calc} (ºC) (Q)	58.6667	2.118044	27.6985	0.001301	49.5535	67.7799
(2) TIPO mass ratio (L)	14.8891	1.779513	8.3669	0.013986	7.2325	22.5457
TIPO mass ratio (Q)	13.6667	2.118044	6.4525	0.023186	4.5535	22.7799
(1) por (2)	-19.0000	2.516611	-7.5498	0.017095	-29.8281	-8.1719

Table S 4- ANOVA table for specific surface area

Factors	Quadratic Sum	Degrees of freedom	Quadratic Mean	F	P
Model	15324.50	5	3064.90	21.17	0.0022
(1) T_{calc} (ºC) (L)	9641.25	1	9641.25	1522.30	0.0006563
T_{calc} (ºC) (Q)	4858.98	1	4858.98	767.21	0.0013009
(2) TIPO mass ratio (L)	443.37	1	443.37	70.01	0.0139855
TIPO mass ratio (Q)	263.69	1	263.69	41.63	0.0231864
(1) por (2)	361.00	1	361.00	57.00	0.0170953
Residuals	724.05	5	144.81		
Lack of fit	711.380995	3	237.126998	37.441105	0.0261262614
Pure error	12.6666667	2	6.33333333		
Total quadratic sum	16048.5455	10			

2.5.2. Band gap Energy (Eg)

Table S 5- Effects estimates for band-gap

Factor	Effect	Std. Error Pure Error	t(2)	p	Cnf. Limit, -95, %	Cnf. Limit, +95, %
Mean/ Interaction	2.890000	0.111198	25.98968	0.000125	2.536118	3.243882
(1) T_{calc} (ºC) (L)	0.348315	0.078629	4.42986	0.021373	0.098083	0.598547
T_{calc} (ºC) (Q)	0.457500	0.130391	3.50867	0.039235	0.042537	0.872463
(2) TIPO (L)	0.067855	0.078629	0.86298	0.451618	-0.182377	0.318087
TIPO (Q)	0.182500	0.130391	1.39963	0.256106	-0.232463	0.597463
(1) por (2)	-0.045000	0.111198	-0.40468	0.712836	-0.398882	0.308882

Table S 6- ANOVA table for band gap

Factors	Quadratic Sum	Degrees of freedom	Quadratic Mean	F	P
Model	0.4205	5	0.0841	6.80146	0.0727
(1) T_{calc} (ºC) (L)	0.2426	1	0.2426	19.6241	0.02137
T_{calc} (ºC) (Q)	0.1522	1	0.1522	12.3111	0.03923
(2) TIPO mass ratio (L)	0.0092	1	0.0092	0.74476	0.45161
TIPO mass ratio (Q)	0.0242	1	0.0242	1.95904	0.25610
(1) por (2)	0.0020	1	0.0020	0.16377	0.71283
Error	0.0371	3	0.0124		
Total quadratic sum	0.4576	8			

2.5.1. Anatase mass percentage

Table S 7- Effects estimates for anatase percentage

Factor	Effect	Std. Error Pure Error	t(2)	p	Cnf. Limit, -95, %	Cnf. Limit, +95, %
Mean/ Interaction	87.40	20.78	4.206	0.024539	21.27	153.53
(1) T_{calc} (ºC) (L)	-76.75	14.69	-5.223	0.013648	-123.51	-29.99
T_{calc} (ºC) (Q)	-52.80	24.37	-2.167	0.118801	-130.35	24.75
(2) TIPO (L)	3.98	14.69	0.271	0.804003	-42.78	50.74
TIPO (Q)	-9.55	24.37	-0.392	0.721288	-87.10	68.00
(1) por (2)	-1.65	20.78	-0.079	0.941712	-67.78	64.48

Table S 8- ANOVA table for anatase percentage

Factors	Quadratic Sum	Degrees of freedom	Quadratic Mean	F	P
Model	14550.29	5	2910.058	6.7392	0.073612
(1) T_{calc} (ºC) (L)	11781.40	1	11781.40	27.28400	0.013648
T_{calc} (ºC) (Q)	2027.54	1	2027.54	4.69549	0.118801
(2) TIPO mass ratio (L)	31.70	1	31.70	0.07341	0.804003
TIPO mass ratio (Q)	66.33	1	66.33	0.15361	0.721288
(1) por (2)	2.72	1	2.72	0.00630	0.941712
Error	1295.42	3	431.81		
Total quadratic sum	15845.71	8			

2.6. Response Surface Analysis (CCD2)

Table S 9 – Effects estimates for selenium removal after 2 minutes of photocatalysis.

Factor	Effect	Std. Error Pure Error	t(2)	p	Cnf. Limit, -95, %	Cnf. Limit, +95, %
Mean/ Interaction	82.17	1.72	47.76	0.000001	77.39	86.94
(1) pH (L)	-0.71	2.08	-0.34	0.749528	-6.50	5.07
pH (Q)	-26.44	2.08	-12.68	0.000223	-32.23	-20.6520
(2) %TIPO (L)	0.15	2.08	0.07	0.946170	-5.64	5.94
%TIPO. (Q)	-1.62	2.08	-0.78	0.480262	-7.41	4.17
(3) T_{calc} (L)	-75.97	2.08	-36.45	0.000003	-81.76	-70.18
T_{calc} (Q)	-28.07	2.08	-13.46	0.000176	-33.86	-22.28
(1) by (2)	-2.00	2.72	-0.73	0.503436	-9.56	5.56
(1) by (3)	3.05	2.72	1.12	0.325435	-4.51	10.61
(2) by (3)	-1.00	2.723325	-0.37	0.732073	-8.56	6.56

Table S 10- Model coefficients for Se(IV) removal after 2 min of photocatalysis.

Factors	Coefficients	Coefficient Std. Error	Cnf. Limit, -95, %	Cnf. Limit, +95, %
Mean/ Interaction	82.17	1.72	77.39	86.94
(1) pH (L)	-0.36	1.04	-3.25	2.54
pH (Q)	-13.22	1.04	-16.11	-10.33
(2) %TIPO (L)	0.07	1.04	-2.82	2.97
%TIPO. (Q)	-0.81	1.04	-3.70	2.08
(3) T_{calc} (L)	-37.99	1.04	-40.88	-35.09
T_{calc} (Q)	-14.03	1.04	-16.93	-11.14
(1) by (2)	-1.00	1.36	-4.78	2.78
(1) by (3)	1.53	1.36	-2.26	5.31
(2) by (3)	-0.50	1.36	-4.28	3.28

Table S 11- ANOVA table for selenium removal model after 2 min of photocatalysis

Factors	Quadratic Sum	Degrees of freedom	Quadratic Mean	F	P
Model	24263.71	9	2695.97	13.4	0.0003
(1) pH (L)	1.74	1	1.74	0.117	0.749528
pH (Q)	2385.72	1	2385.72	160.838	0.000223
(2) %TIPO (L)	0.08	1	0.08	0.005	0.946170
%TIPO. (Q)	8.97	1	8.97	0.605	0.480262
(3) T_{calc} (L)	19705.02	1	19705.02	1328.458	0.000003
T_{calc} (Q)	2688.23	1	2688.23	181.233	0.000176
(1) by (2)	8.00	1	8.00	0.539	0.503436
(1) by (3)	18.60	1	18.60	1.254	0.325435
(2) by (3)	2.00	1	2.00	0.135	0.732073
Residuals	1810.84	9	201.20		
Lack of fit	1751.71	5	350.34	23.619	0.004543
Pure error	59.33	4	14.83		
Total quadratic sum	26073.87	18			