Electronic Supplementary Information

Lignin coating to quench photocatalytic activity of titanium dioxide nanoparticles for potential skincare applications

*By Michela Morsella, Maria Giammatteo, Lorenzo Arrizza, Lucia Tonucci, Mario Bressan and Nicola d'Alessandro**

a) b)

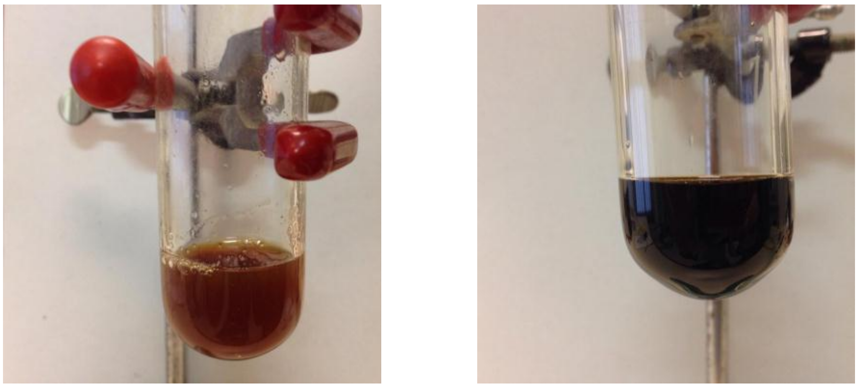


Figure S1: Solution of alkali lignin in a) ethylene glycol and in b) alkaline water.

a) b)

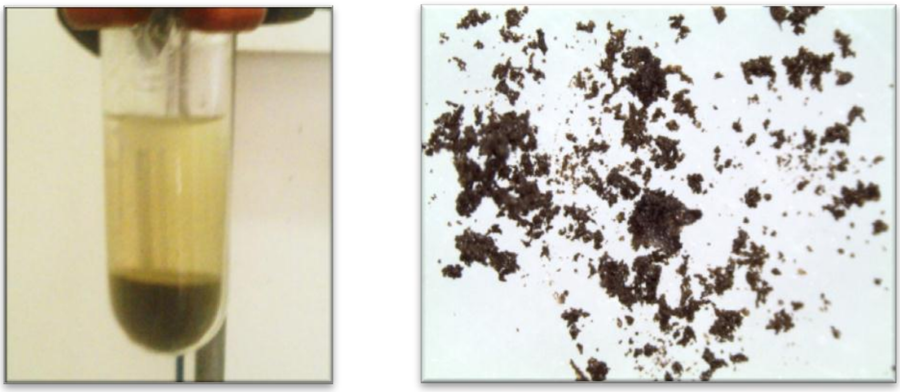


Figure S2: (a) Suspension of clusters 1-A (with rutile) in glass tube; (b) light microscope picture of clusters 1-A powder made with rutile (2x of magnification)

a) b)

Figure S3: (a) Suspension of clusters 1-B (with rutile) in glass tube; (b) light microscope picture of clusters 1-B powder made with rutile (2x of magnification)

a) b)

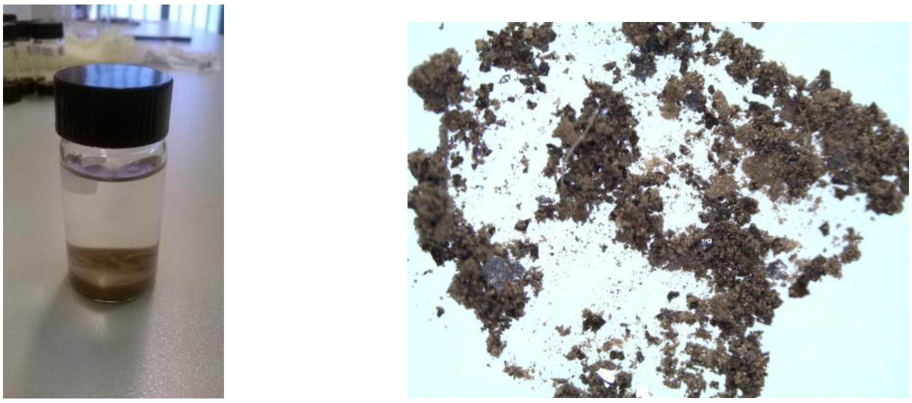


Figure S4: (a) Suspension of clusters 1-A (with anatase) in glass tube; (b) light microscope picture of clusters 1-A powder made with anatase (2x of magnification)

Figure S5: (a) Suspension of clusters 1-B (with anatase) in glass tube; (b) light microscope picture of clusters 1-B powder made with anatase (2x of magnification)

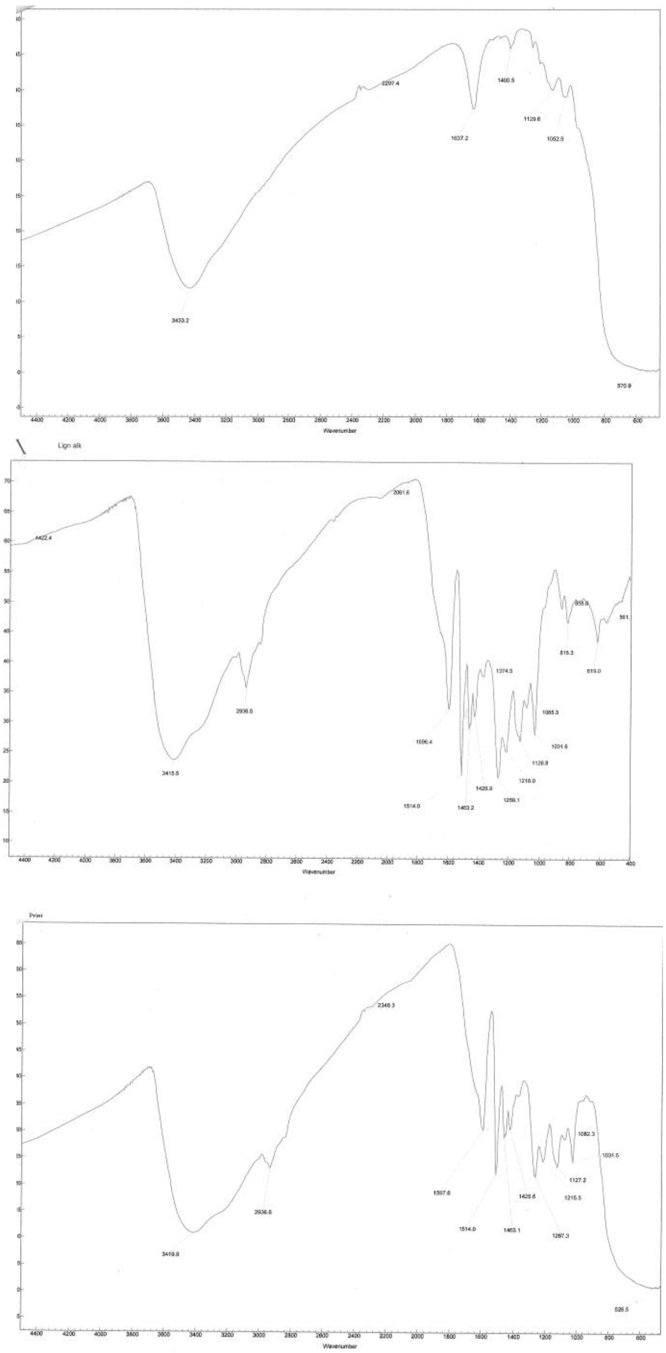


Figure S6: Representative IR spectra of TiO_2 alone (top), lignin alone (middle) and the TiO_2-lignin mixture(bottom).

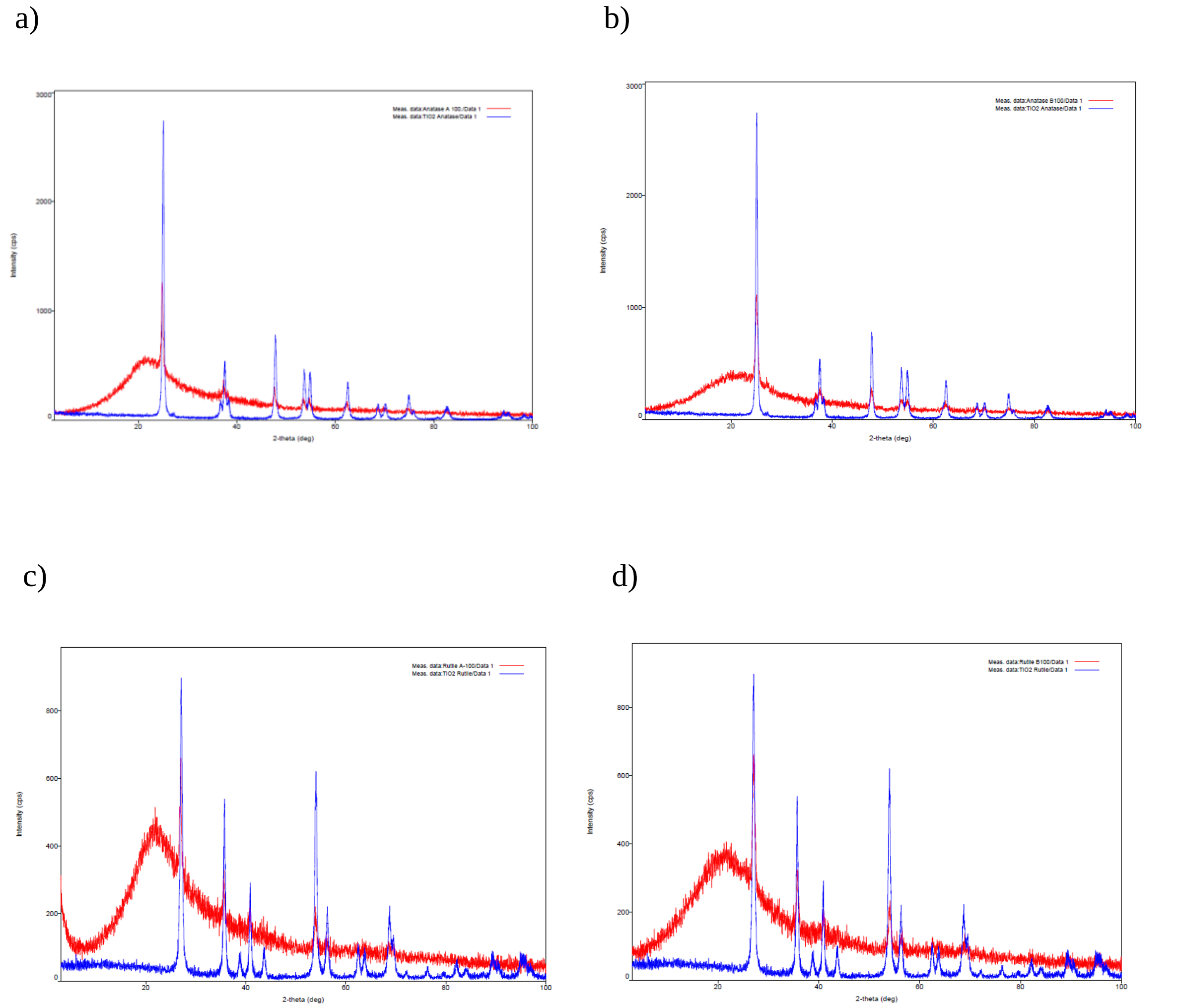


Figure S7: XRD overlap between a) A clusters (red)/TiO_2 anatase (blue) b) B clusters (red)/TiO_2 anatase (blue) c) A clusters (red)/TiO_2 rutile (blue) d) B clusters (red)/TiO_2 rutile (blue)

a)

No.	2-theta	d	Height	FWHM	Int. I(cal)	Int. I(obs	Asym. factor	Decay rate factor		Size	Phase data name
	(deg)	(ang.)	(counts)	(deg)	(counts deg)			eta L/mL	eta H/m	(ang.)	
1	25.077(4	3.5481(5	862(29)	0.386(3)	432(2)	432(2)	1.21(5)	0.528(18	0.60(2)	220,436	Anatase
2	36.74(3)	2.444(2)	42(6)	0.51(4)	27.0(16)	27.0(16)	1.2(3)	0.56(10)	0.47(10)	171,888	Anatase
3	37.552(1	2.3932(9	169(13)	0.422(15	91(3)	91(3)	0.96(15)	0.56(10)	0.47(10)	207,905	Anatase
4	38.34(3)	2.3459(1	48(7)	0.51(5)	32(3)	32(3)	1.5(4)	0.56(10)	0.47(10)	172,306	Anatase
5	47.820(1	1.9005(4	250(16)	0.431(8)	142.3(13	142.3(13	1.11(10)	0.65(5)	0.56(5)	210,796	Anatase
6	53.679(1	1.7061(4	135(12)	0.529(13	98.0(15)	98.0(15)	0.95(10)	0.59(5)	0.78(7)	175,688	Anatase
7	54.873(1	1.6717(4	139(12)	0.468(14	88.3(15)	88.3(15)	1.30(15)	0.59(5)	0.78(7)	199,659	Anatase
8	62.444(7	1.48601(	116(11)	0.491(13	96.2(11)	96.2(11)	0.70(3)	1.55(4)	0.72(4)	197,594	Anatase
9	68.54(2)	1.3679(4	42(6)	0.53(3)	29.2(9)	29.2(9)	0.60(11)	1.10(18)	0.08(8)	188,507	Anatase
10	70.08(3)	1.3416(5	43(7)	0.60(3)	34.5(9)	34.5(9)	0.75(16)	1.10(18)	0.08(8)	169,78	Anatase
11	74.85(3)	1.2675(5	69(8)	0.57(6)	72.5(14)	72.5(14)	0.8(2)	1.1(2)	1.43(14)	182,667	Anatase
12	82.60(4)	1.1671(5	31(6)	1.06(3)	37.3(10)	37.3(10)	1.01(14)	0.32(11)	0.00(10)	104,432	Anatase
13	94.18(6)	1.0517(6	15(4)	0.48(8)	9.0(17)	9.0(17)	3.0(14)	0.59(16)	0.0(3)	254,975	Anatase
14	95.10(4)	1.0439(4	14(4)	1.04(17)	17.8(18)	17.8(18)	2.1(16)	0.59(16)	0.0(3)	118,294	Anatase
15	98.26(13	1.0186(1	9(3)	0.59(11)	5.4(8)	5.4(8)	1.5(14)	0.0(6)	0.0(10)	214,857	Anatase

b)

No.	2-theta	d	Height	FWHM	Int. I(cal)	Int. I(obs	Asym. factor	Decay rate factor		Size	Phase data name
	(deg)	(ang.)	(counts)	(deg)	(counts deg)			eta L/mL	eta H/m	(ang.)	
1	27.060(9	3.2924(1	282(17)	0.487(7)	185.2(15	185.2(15	0.89(6)	0.75(5)	0.57(4)	175,216	Rutile
2	35.679(1	2.5143(1	168(13)	0.392(13	90.0(14)	90.0(14)	0.76(13)	0.93(12)	0.45(6)	222,212	Rutile
3	38.80(5)	2.319(3)	16(4)	0.56(4)	9.3(8)	9.3(8)	1.1(4)	0.0(4)	0.0(4)	156,689	Rutile
4	40.85(2)	2.2072(1	81(9)	0.412(17	43.5(10)	43.5(10)	0.84(17)	0.63(14)	0.54(11)	215,114	Rutile
5	43.586(1	2.0748(8	22(5)	0.53(3)	13.5(6)	13.5(6)	0.59(8)	0.52(19)	0.00(15)	169,876	Rutile
6	54.014(1	1.6963(4	197(14)	0.482(12	130.3(13	130.3(13	1.4(2)	0.57(5)	0.85(10)	193,041	Rutile
7	56.195(1	1.6355(3	64(8)	0.416(15	37.8(9)	37.8(9)	0.40(3)	1.54(17)	0.26(8)	226,116	Rutile
8	62.40(6)	1.4869(1	22(5)	0.78(8)	31.3(15)	31.3(15)	0.53(18)	0.3(3)	1.55(16)	124,028	Rutile
9	68.792(1	1.3635(3	51(7)	0.54(3)	33(8)	33(8)	5(4)	0.02(7)	1.3(3)	185,162	Rutile
10	69.604(1	1.3496(3	33(6)	0.8(2)	32(7)	32(7)	4.9(15)	0.02(7)	1.3(3)	125,399	Rutile
11	82.04(2)	1.1736(2	15(4)	0.38(8)	9.8(7)	9.8(7)	0.5(3)	1.5(3)	0.9(3)	291,952	Rutile
12	89.26(8)	1.0964(7	19(4)	0.82(10)	16.3(18)	16.3(18)	0.7(3)	0.0(2)	0.0(2)	141,882	Rutile
13	90.50(7)	1.0846(6	10(3)	0.71(15)	7.2(15)	7.2(15)	1.1(13)	0.0(2)	0.0(2)	166,75	Rutile
14	94.95(4)	1.0451(4	15(4)	1.71(6)	28.2(11)	28.2(11)	0.26(4)	0.0(3)	0.00(13)	71,7198	Rutile

Figure S8: XRD list peaks of TiO_2 anatase, a) and TiO_2 rutile, b)

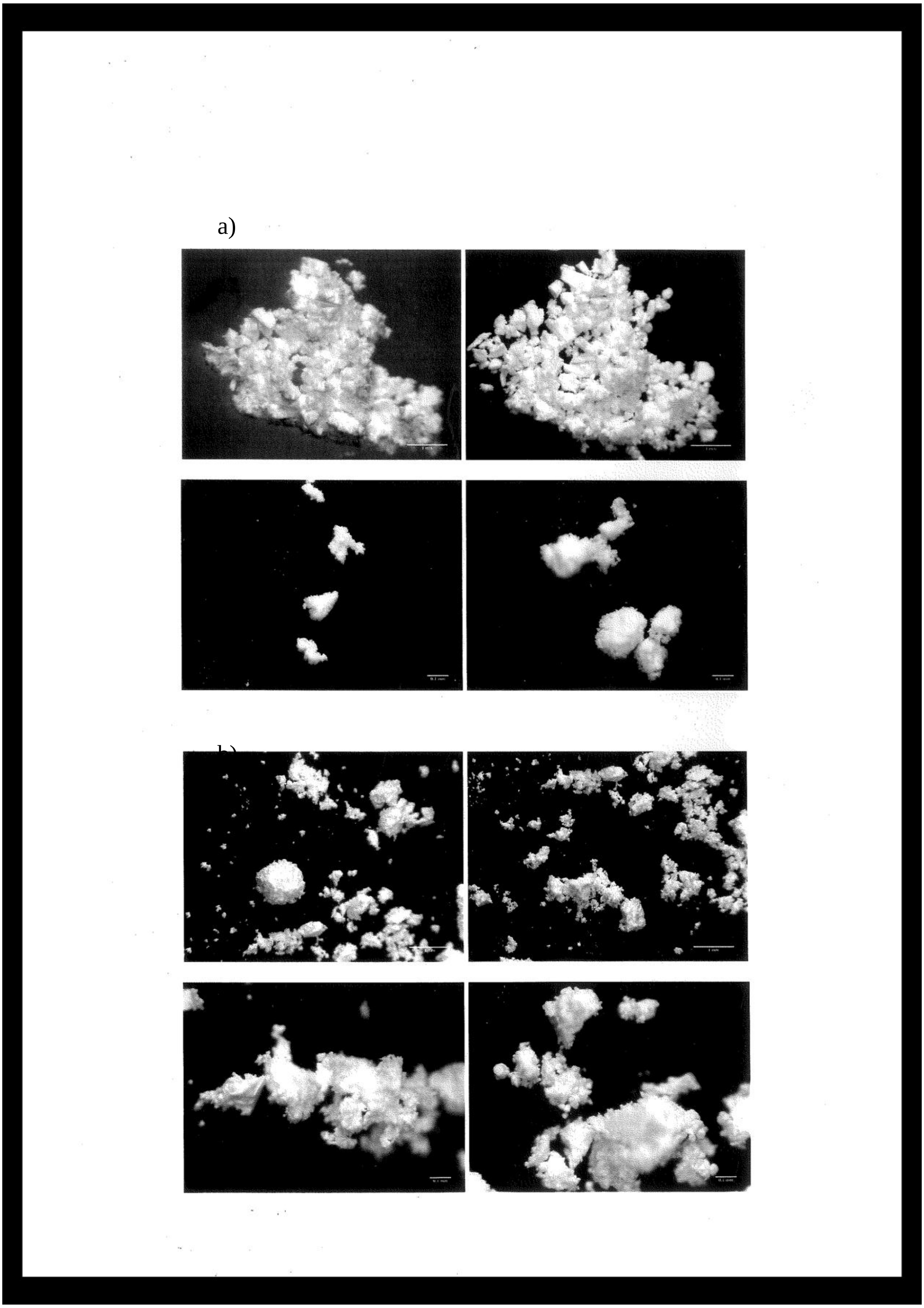


Figure S9: Light microscope images of TiO_2 powder: a) anatase and b) rutile.

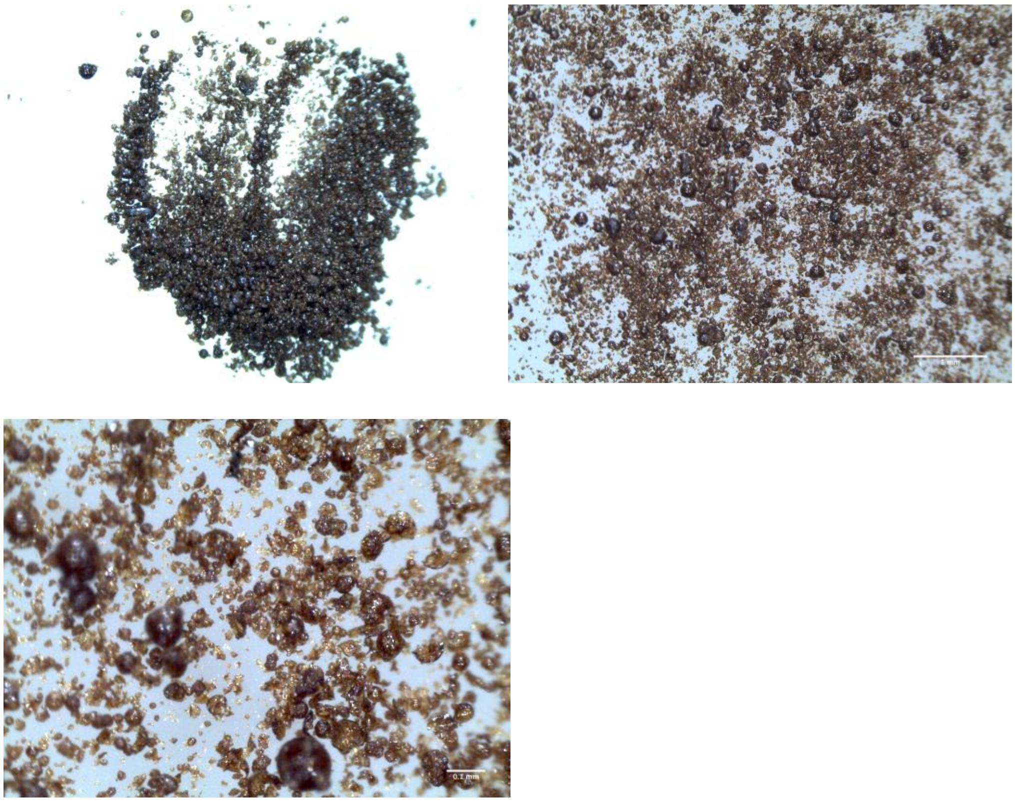


Figure S10: Light microscope image of alkali lignin powder.

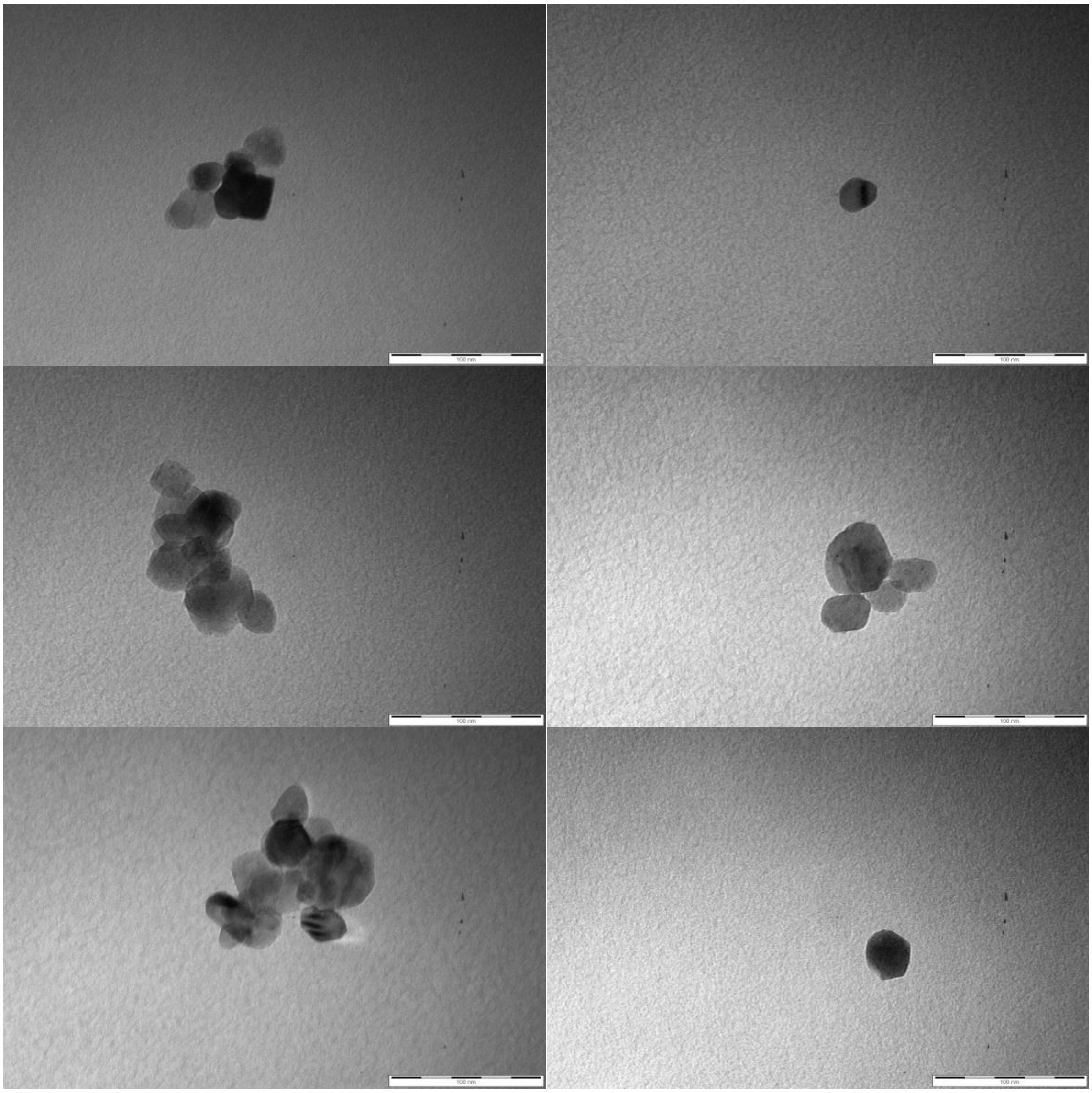


Figure S11: TEM images of TiO_2 anatase nanoparticles.

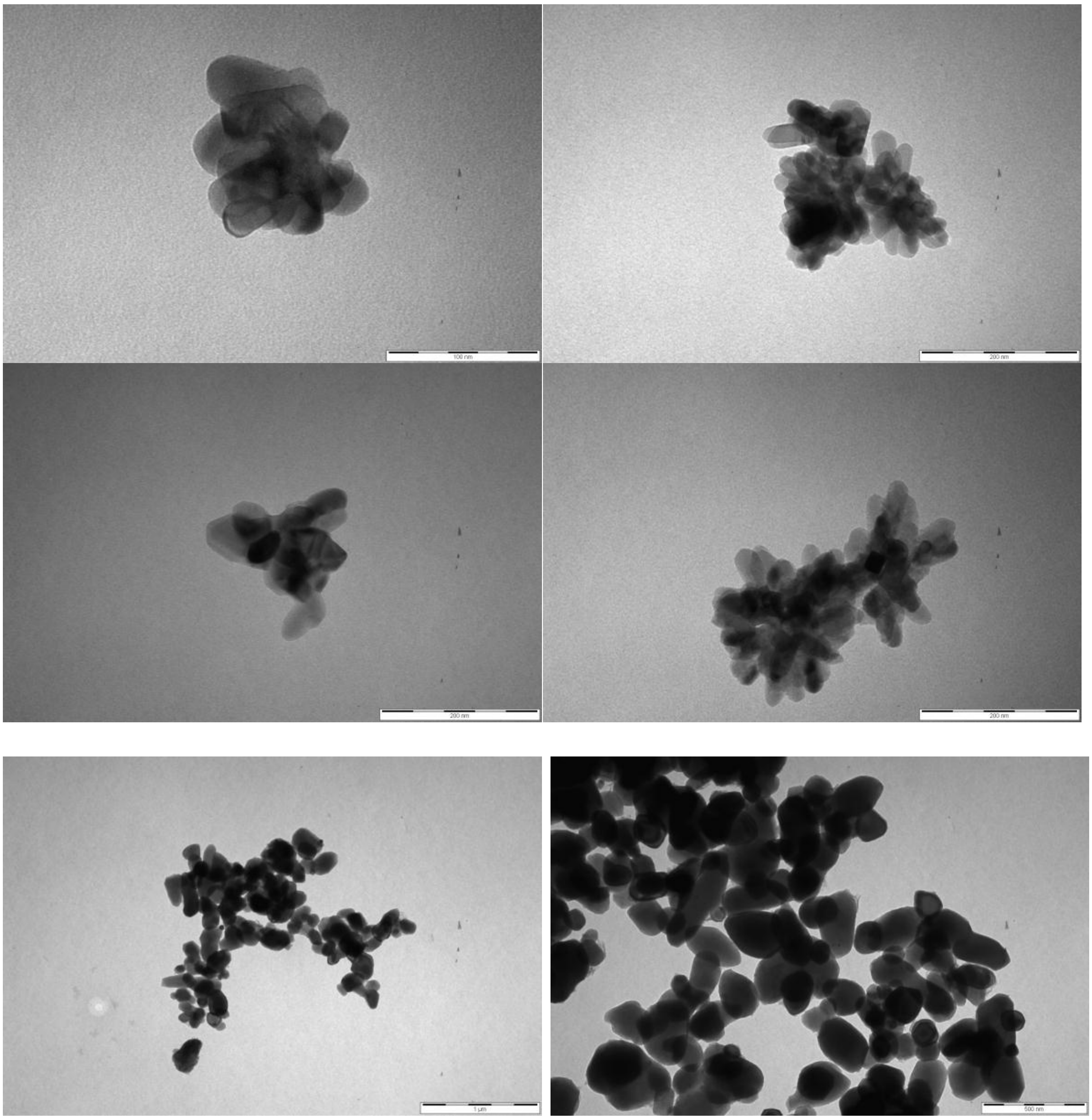


Figure S12: TEM images of TiO_2 rutile nanoparticles.

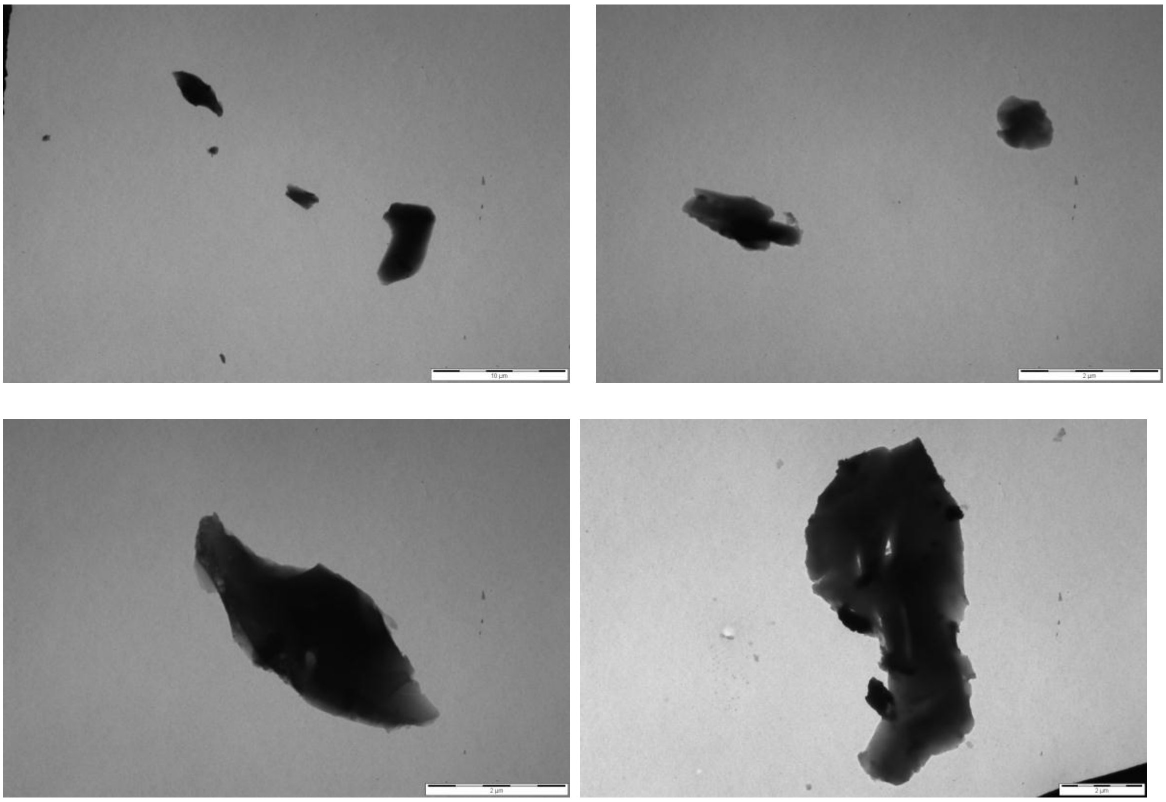


Figure S13: TEM images of alkali lignin.

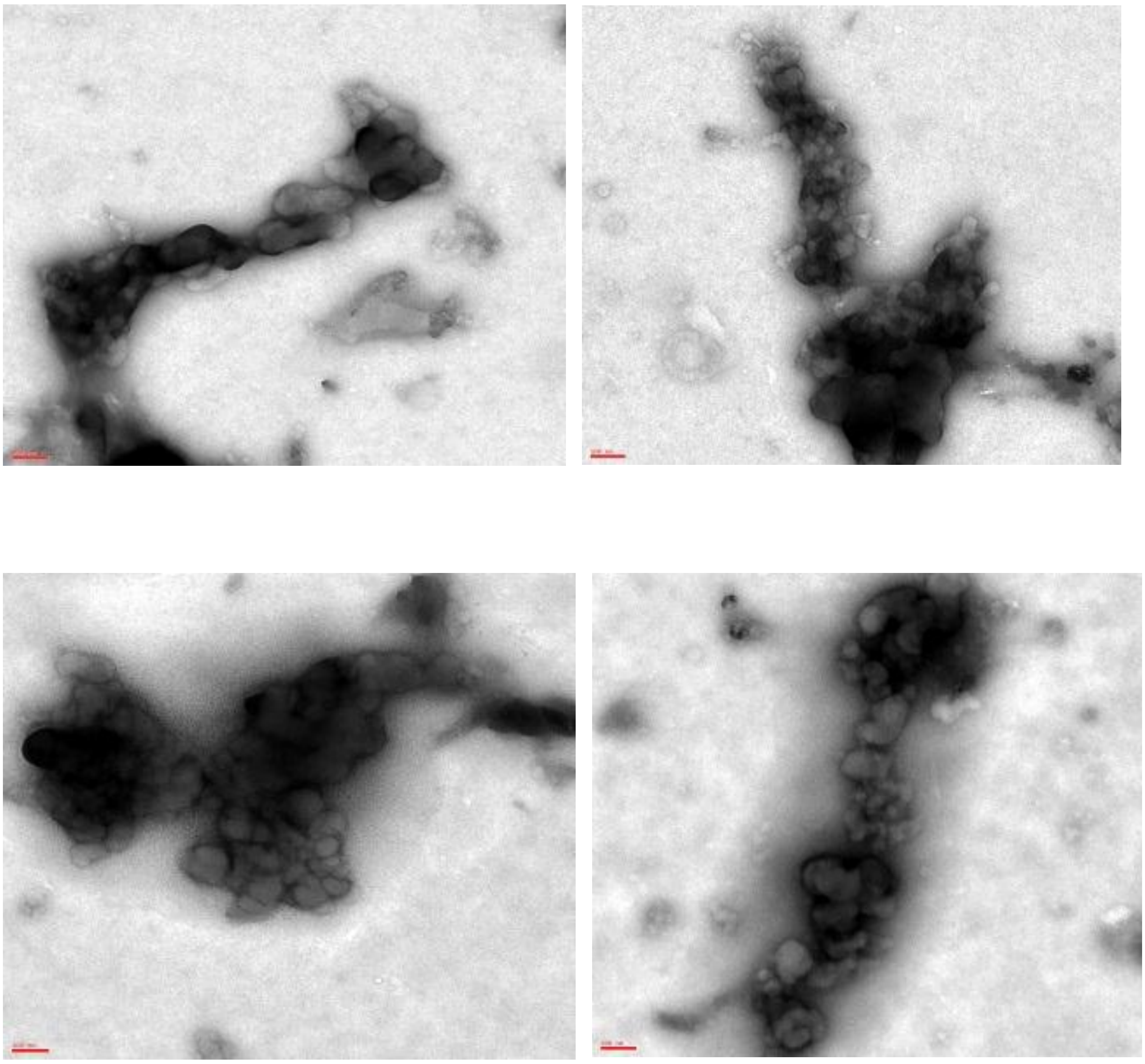


Figure S14: TEM images of clusters 1-A with TiO_2 rutile (bar 100 nm).

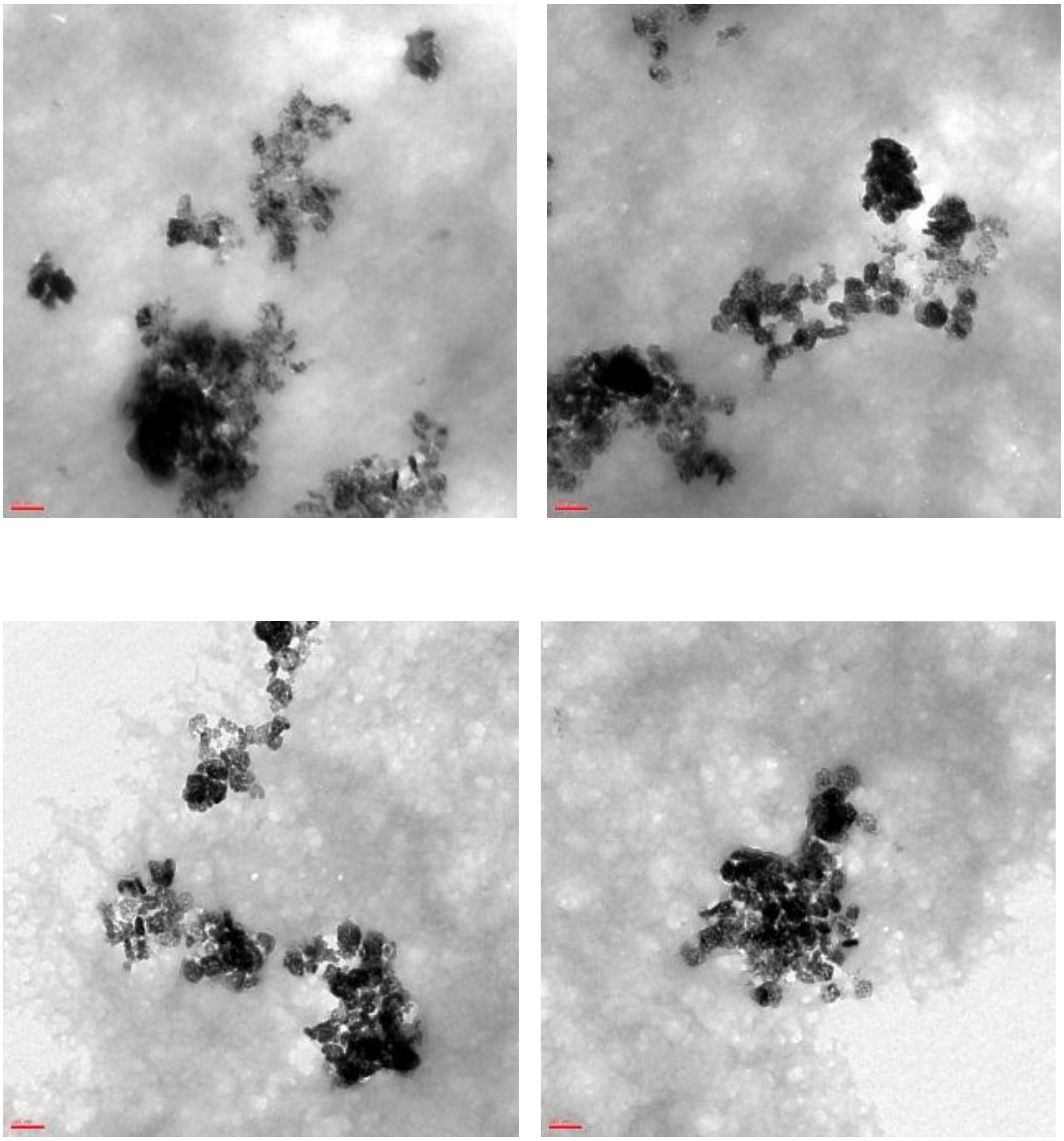
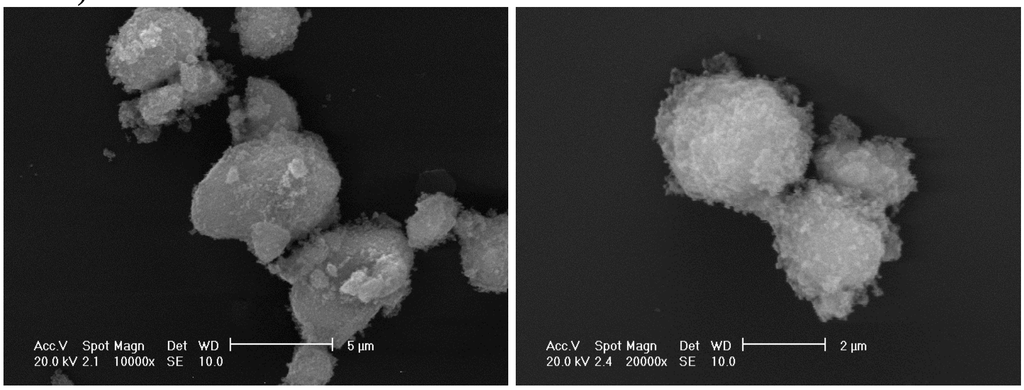


Figure S15: TEM images of clusters 1-B with TiO_2 rutile (bar 100 nm).

a)



b)

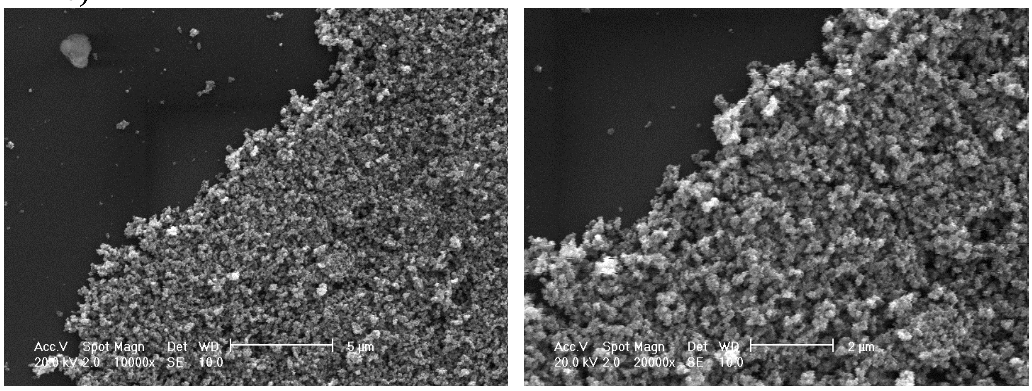


Figure S16: Representative SEM images of the anatase (a) and rutile (b) at different magnification

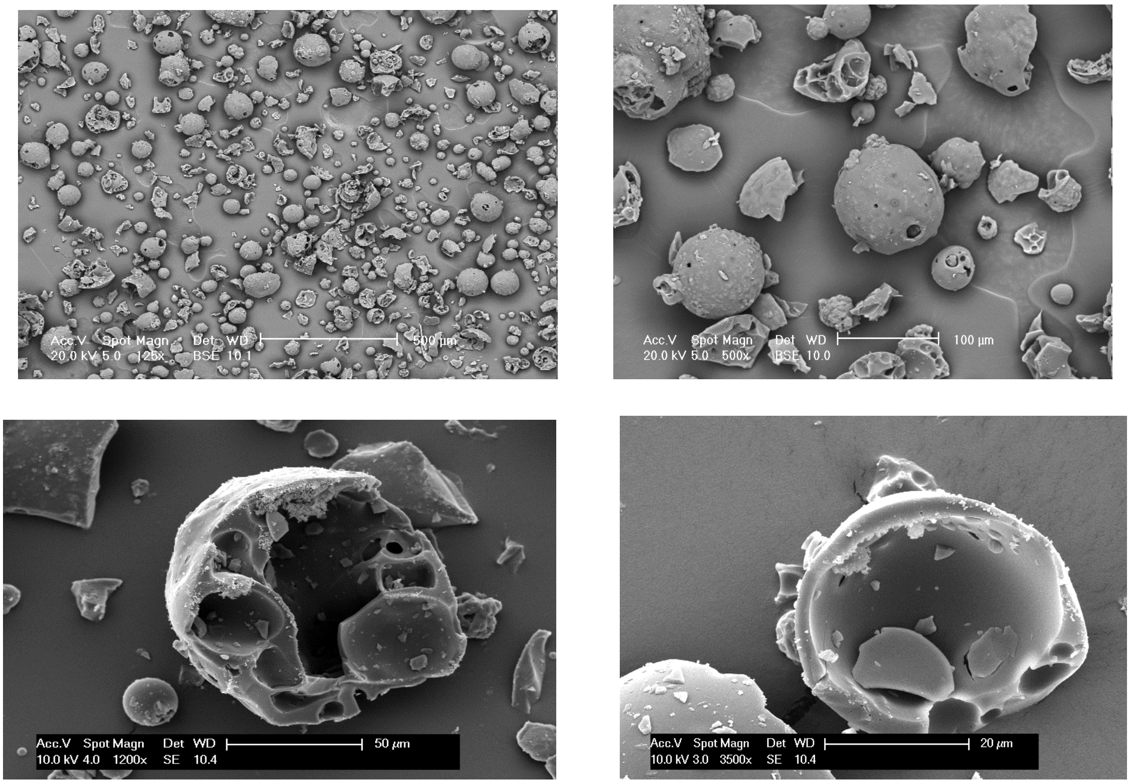


Figure S17: Representative SEM images of lignin acquired at different magnification, as indicated

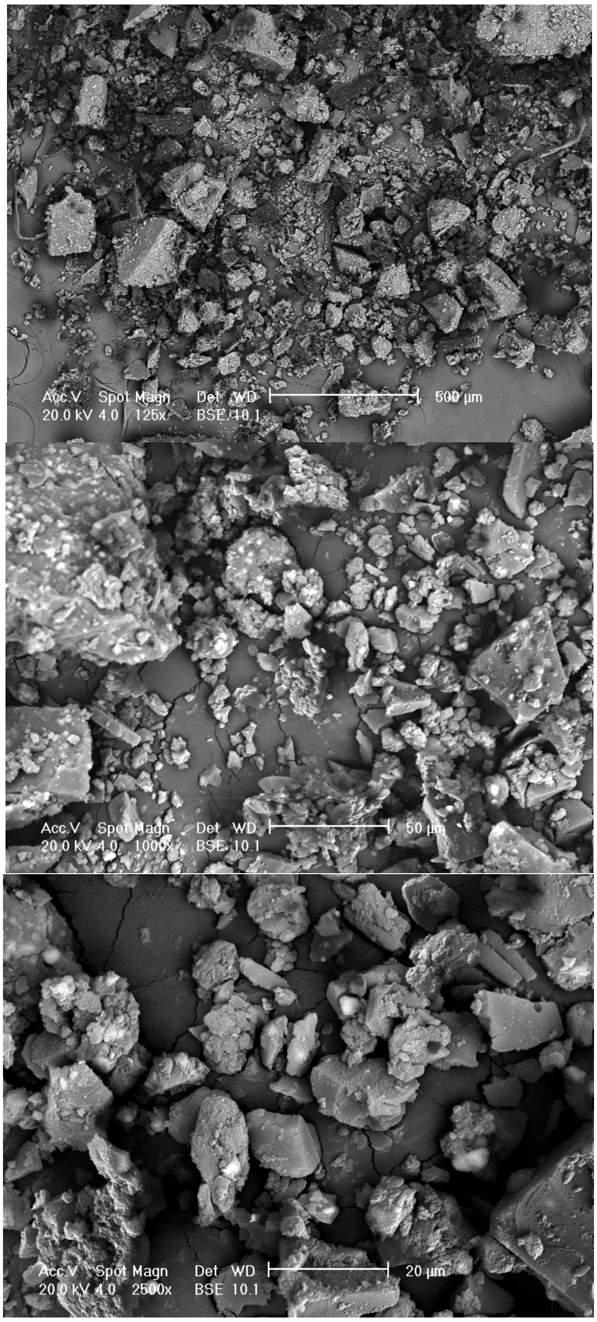


Figure S18: SEM images of cluster A containing anatase, acquired at different magnification

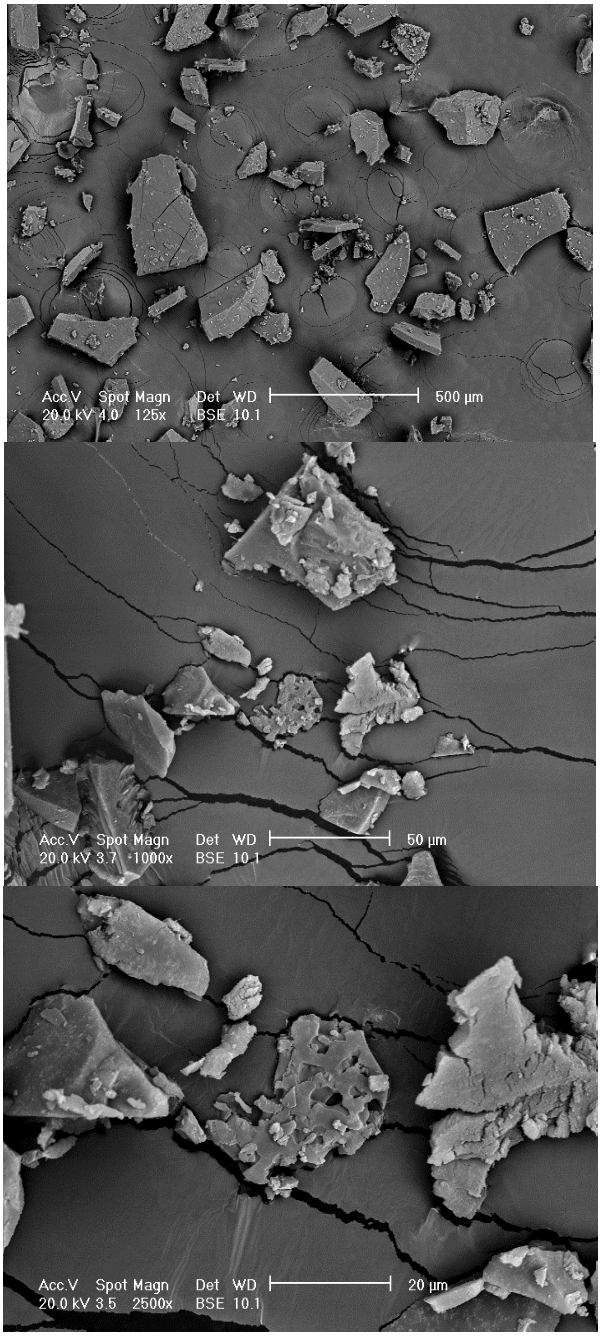


Figure S19: SEM images of cluster A containing rutile, acquired at different magnification

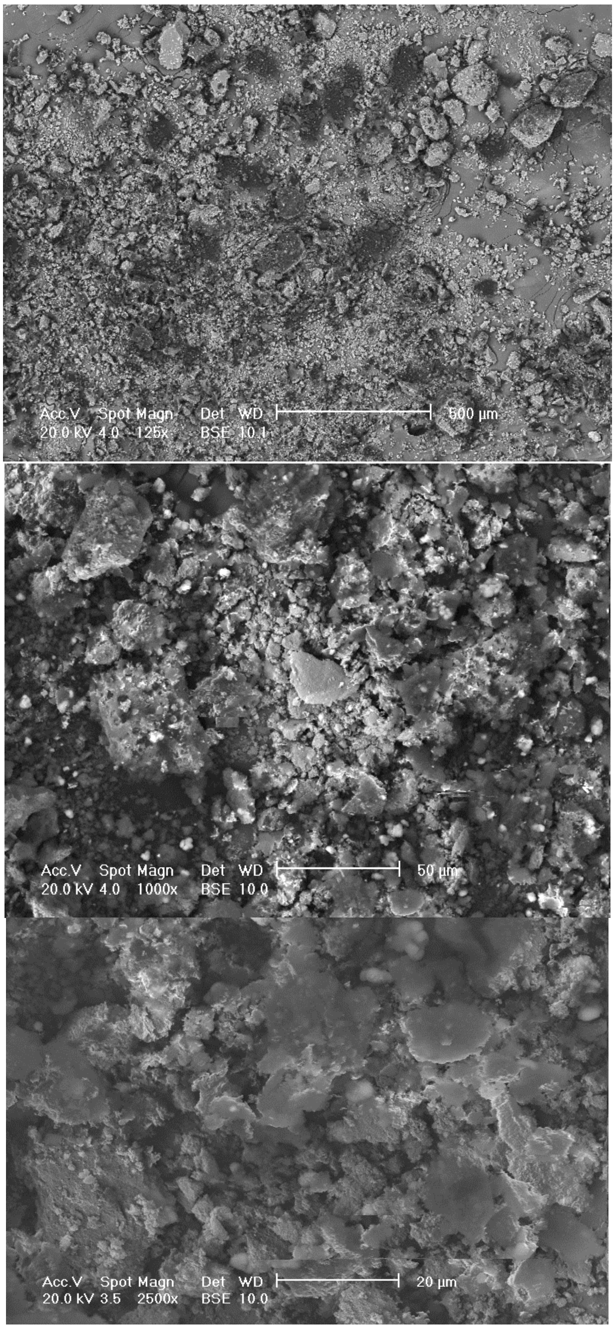


Figure S20: SEM images of cluster B containing anatase, acquired at different magnification

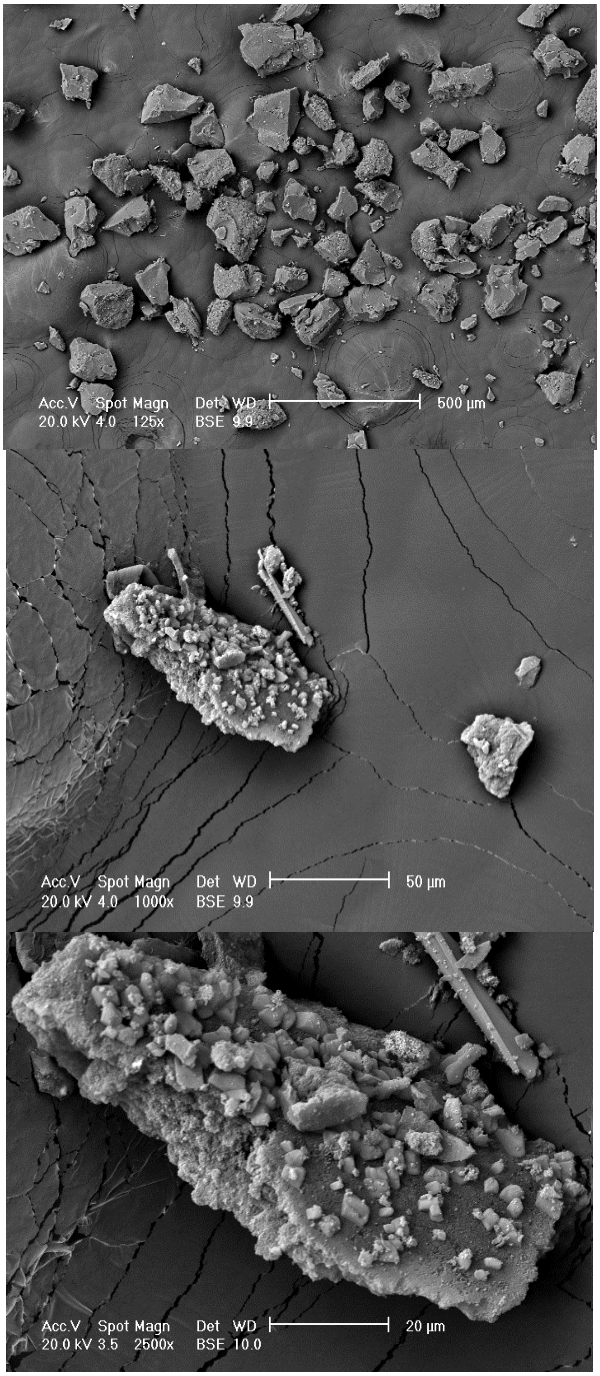


Figure S21: SEM images of cluster B containing rutile, acquired at different magnification

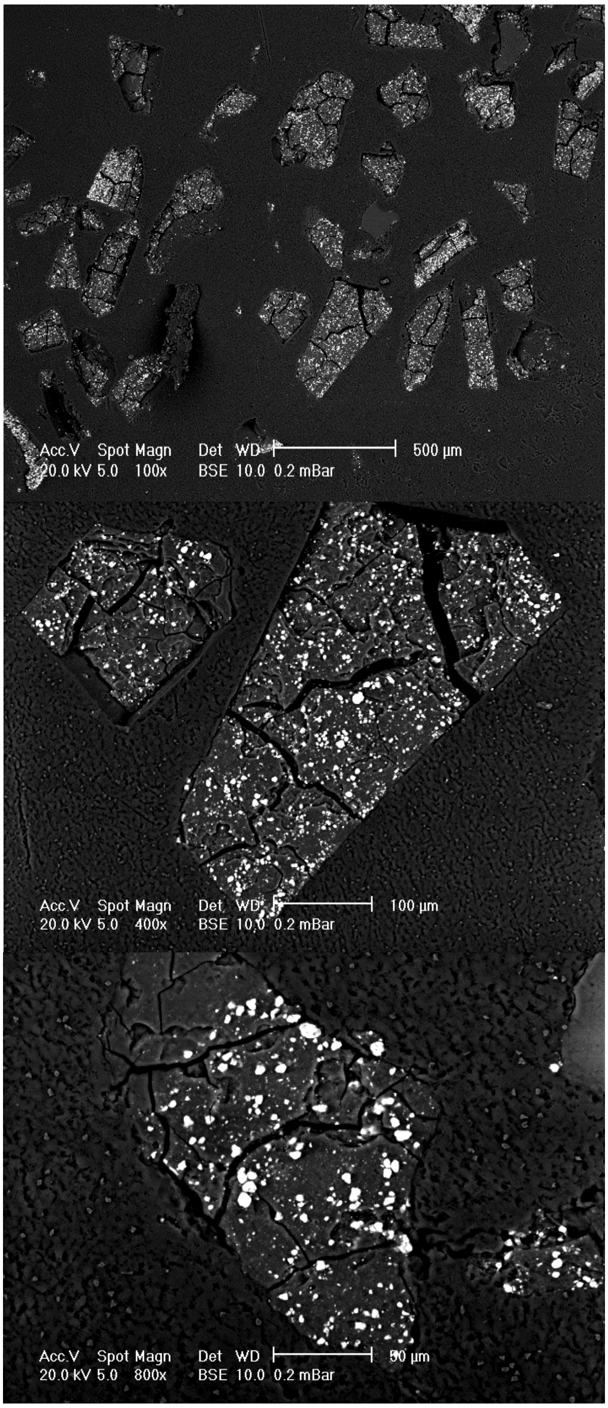


Figure S22: Polished sample, cluster A with anatase

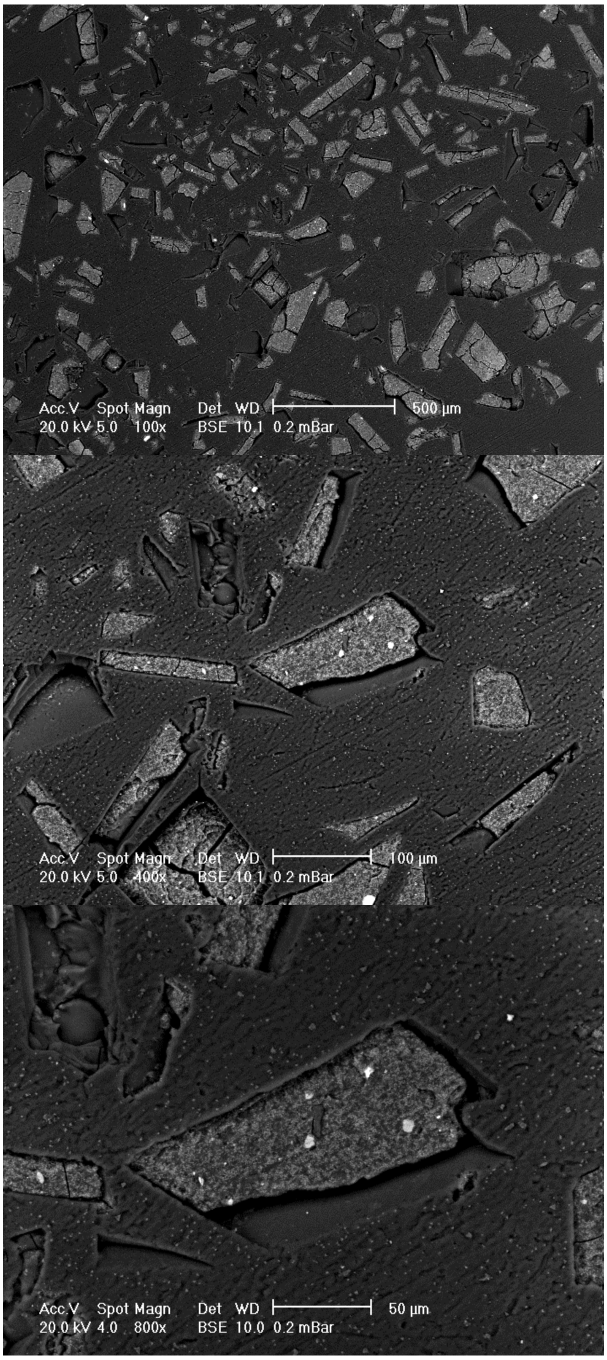


Figure S23: Polished sample, cluster A with rutile

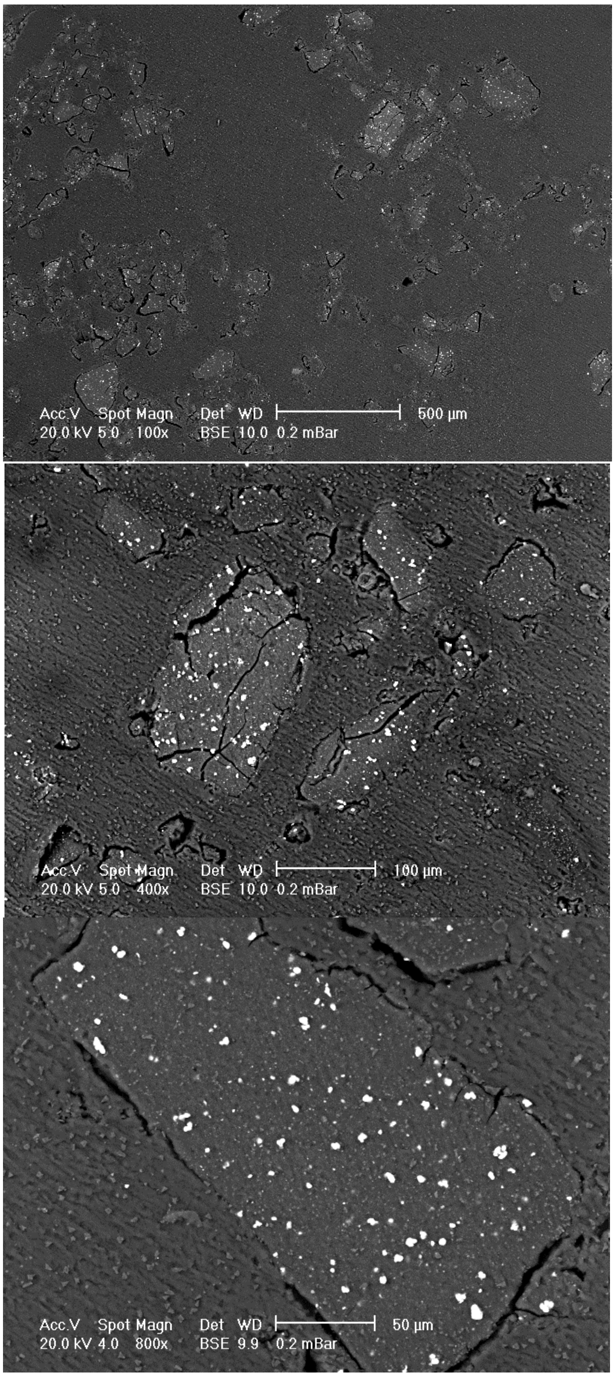


Figure S24: Polished sample, cluster B with anatase

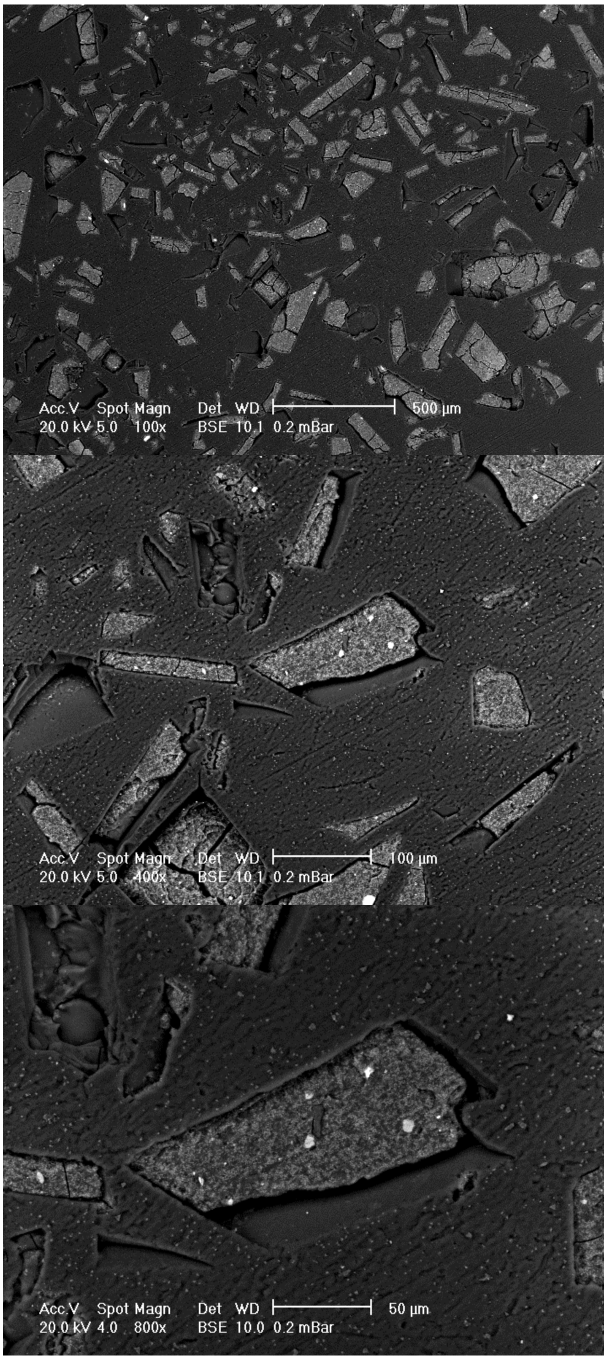


Figure S25: Polished sample, cluster A with rutile

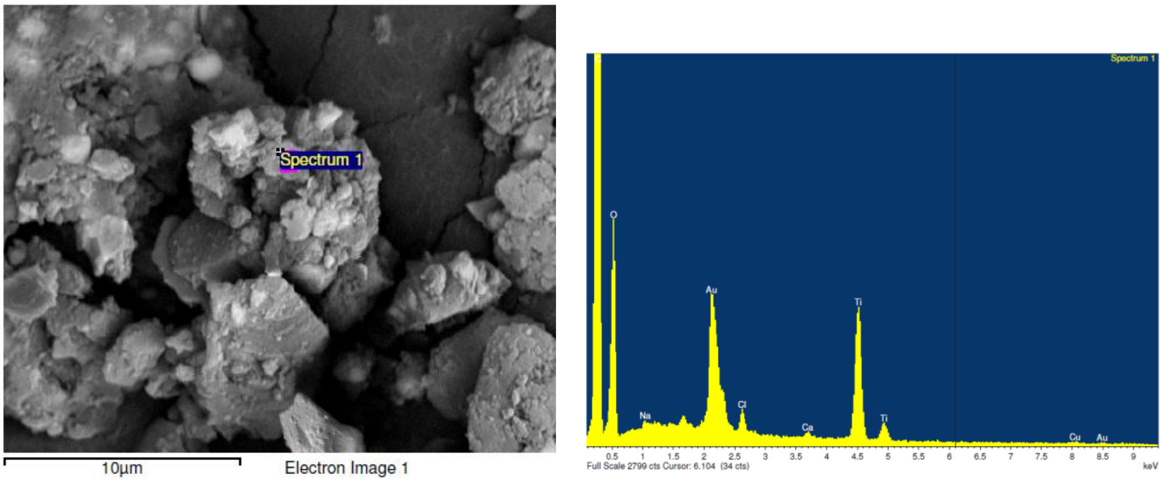


Figure S26: Microanalysis of clusters A containing anatase

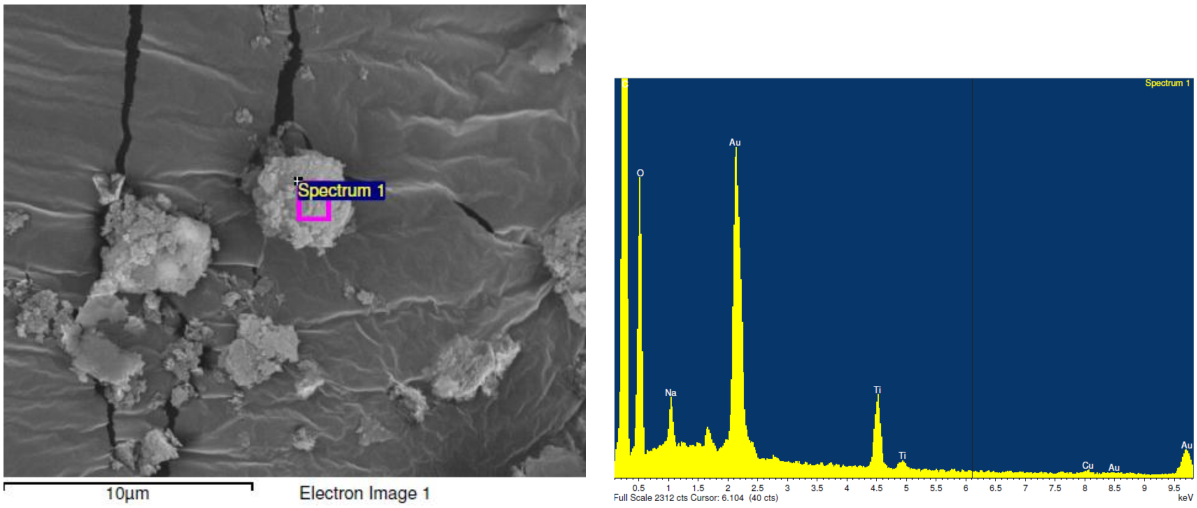


Figure S27: Microanalysis of clusters B containing anatase

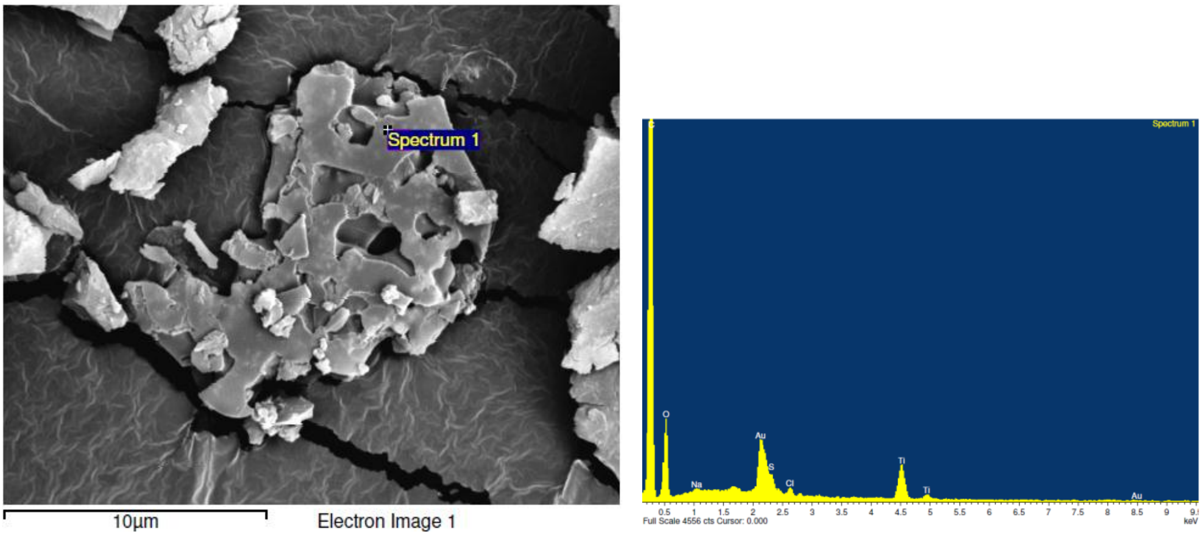


Figure S28: Microanalysis of clusters A containing rutile

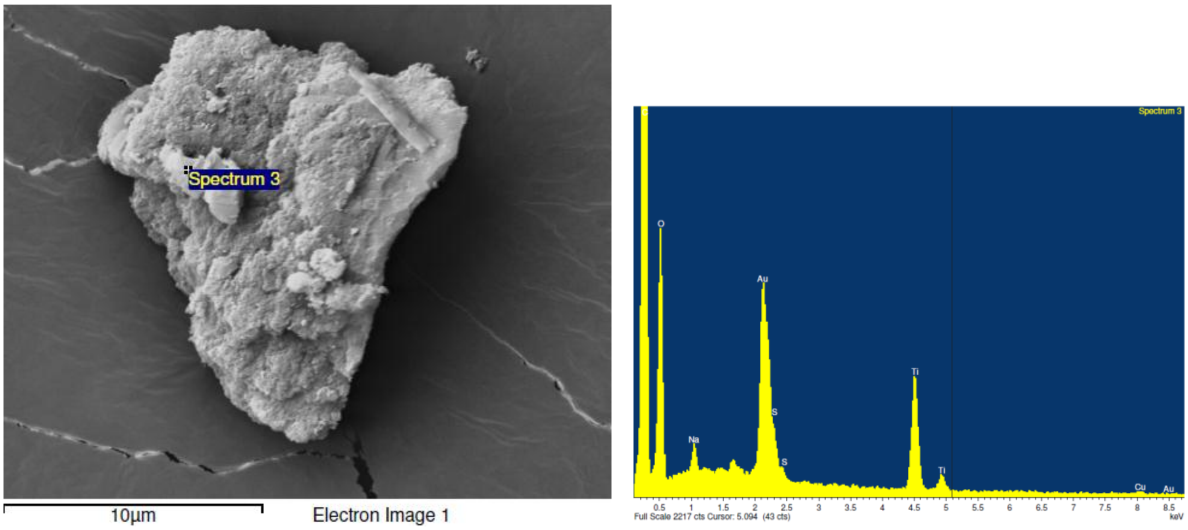


Figure 29: Microanalysis of clusters B containing rutile

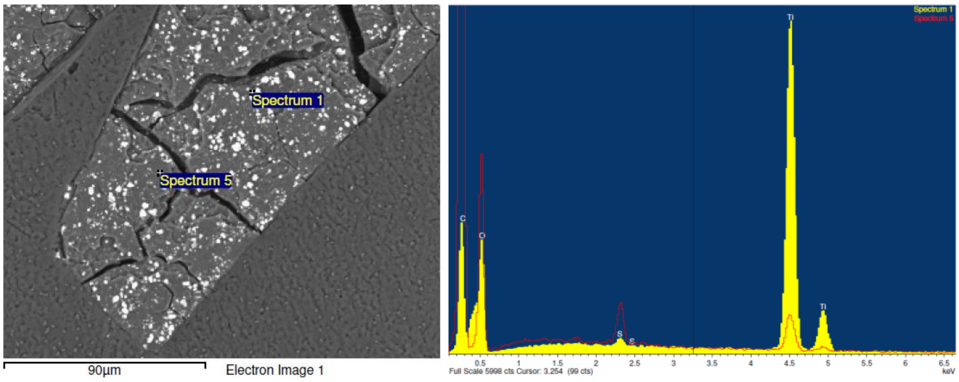


Figure S30: Microanalysis of section of clusters A with anatase

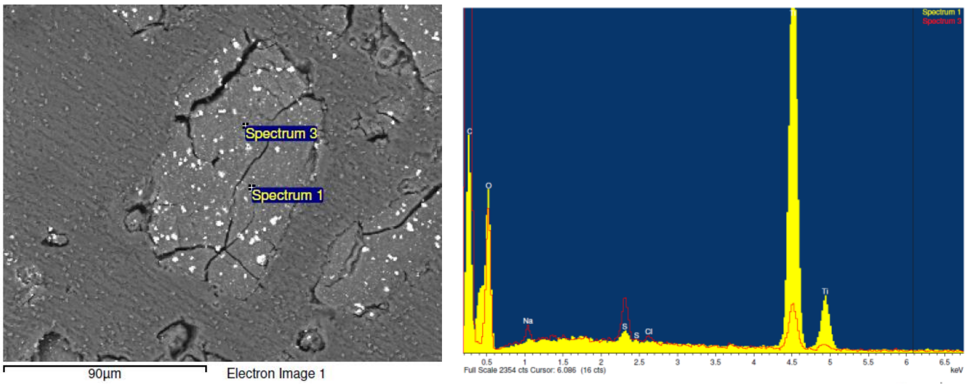


Figure S31: Microanalysis of section of clusters B with anatase

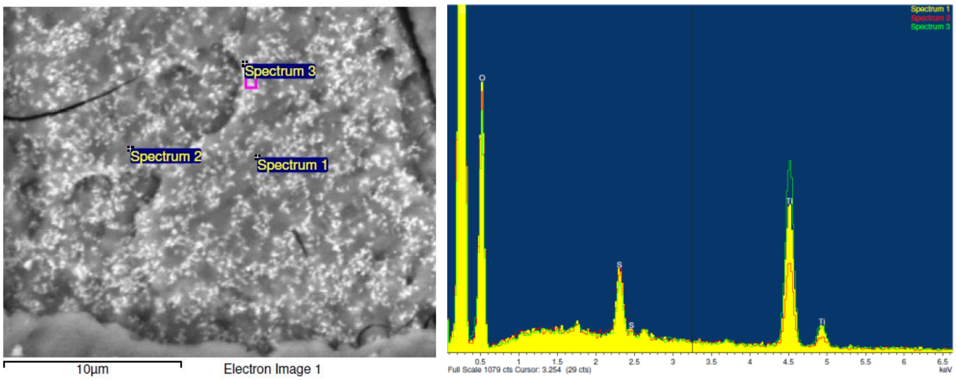


Figure S32: Microanalysis of section of clusters A with rutile

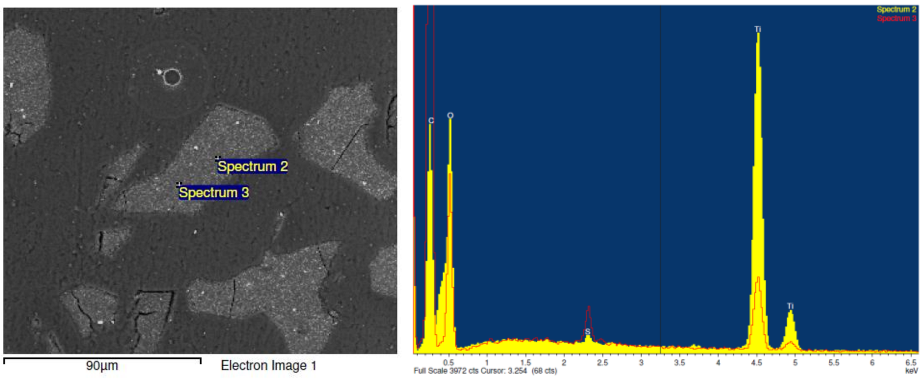


Figure S33: Microanalysis of section of clusters B with rutile

a) b)

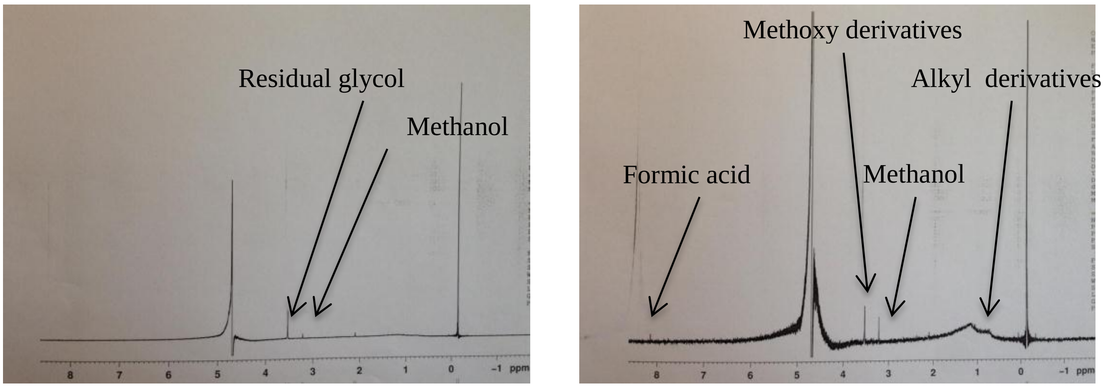
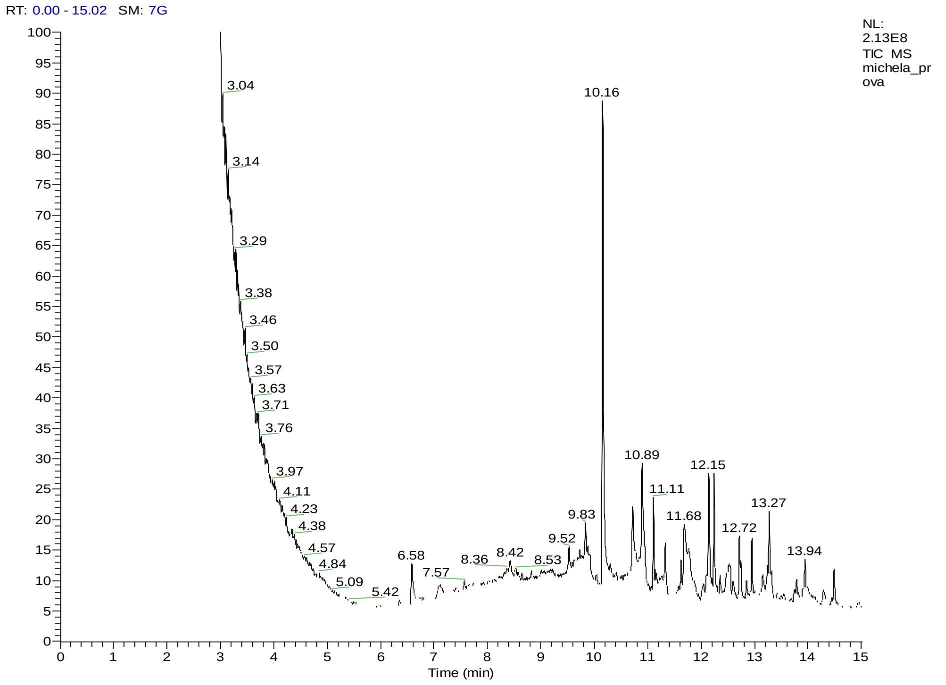


Figure S34: ^{1}H NMR of clusters' supernatant after irradiation (313 nm, 24 h): a) from cluster A and b) from cluster B

a)



b)

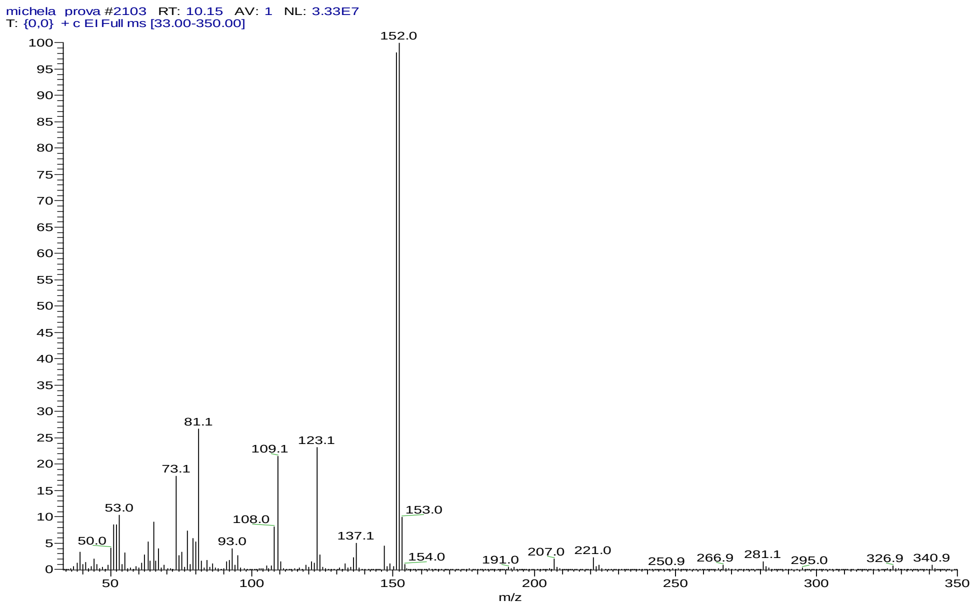
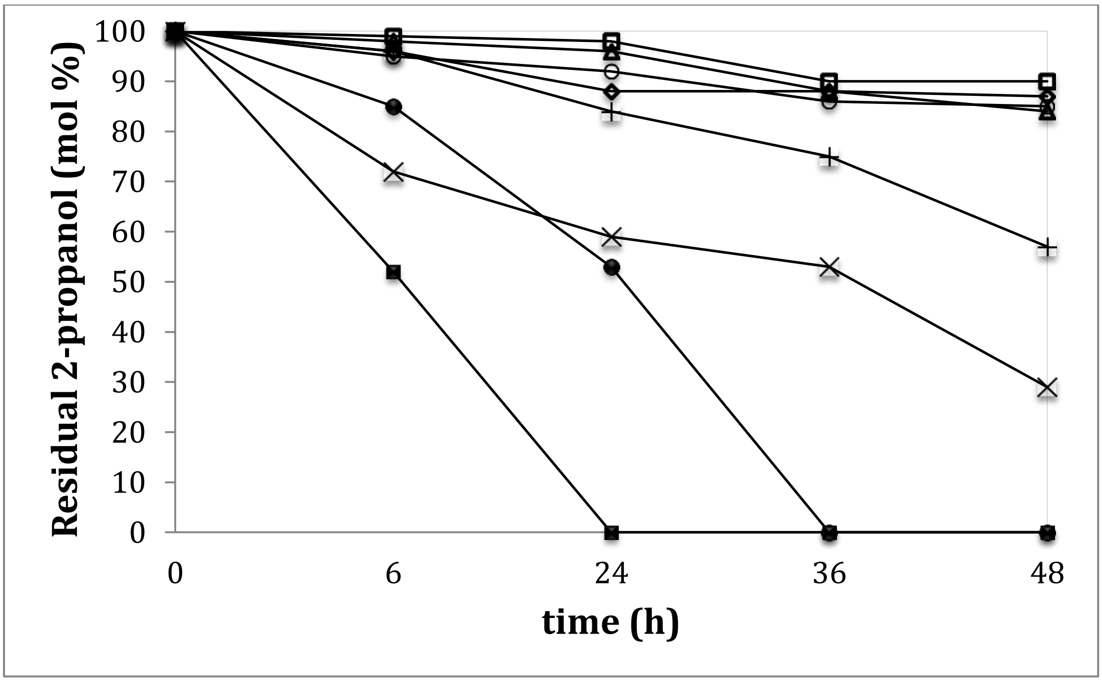
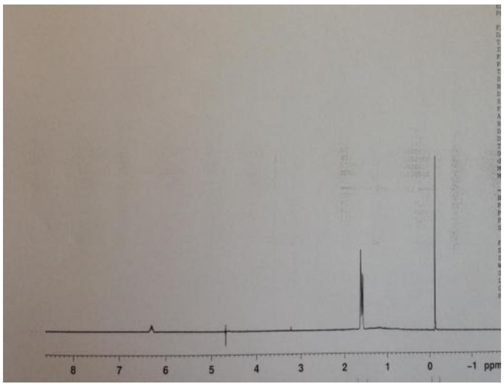


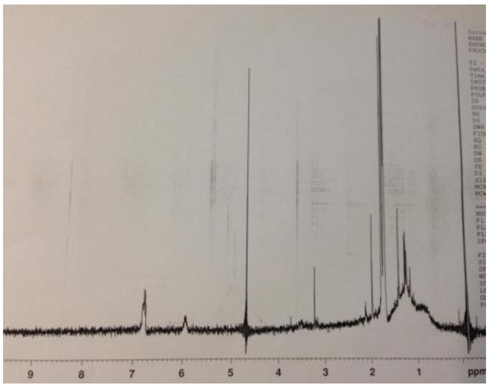
Figure S35: a) GC-MS chromatogram (TIC) of cluster B supernatant (chloroform extract) after irradiation at 313 nm; b) mass spectrum of vanillin appearing at 10.16 sec in the TIC chromatogram.



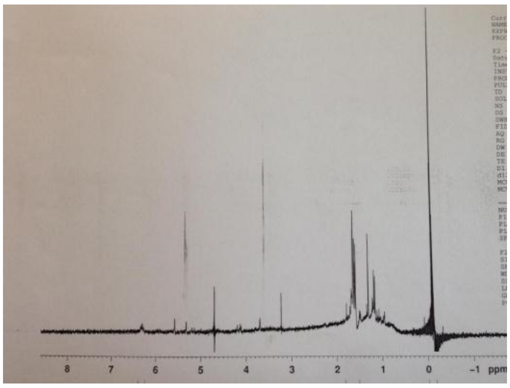
Figure_S36: Time course of transformation of 2-propanol at 310 nm; reactions performed in presence of cluster A containing rutile (empty squares), cluster B containing anatase (empty triangles), cluster B containing rutile (empty circles), cluster A containing anatase (empty rhombs), a simple mixture lignin/TiO_2^-rutile (+), a simple mixture lignin/TiO_2^-anatase (X), rutile (full circles), anatase (full squares).

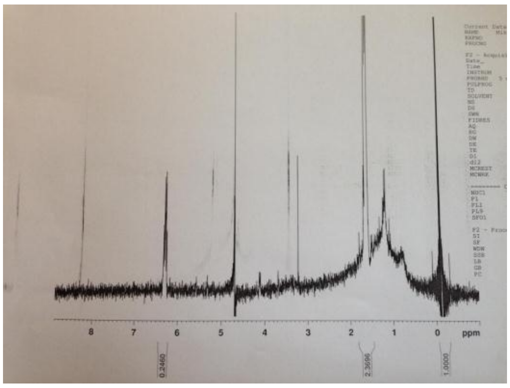
a) b)





c) d)





e)

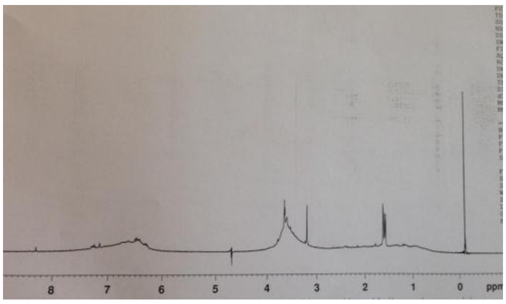


Figure S37: ^{1}H NMR (in D_2O) of: a) tiglic acid; b) tiglic acid irradiated at 313 nm for 6h; c) tiglic acid + anatase irradiated at 313 nm for 6h; d) tiglic acid+ rutile irradiated at 313 nm for 6h; e) tiglic acid+alkali lignin irradiated at 313 nm for 6h

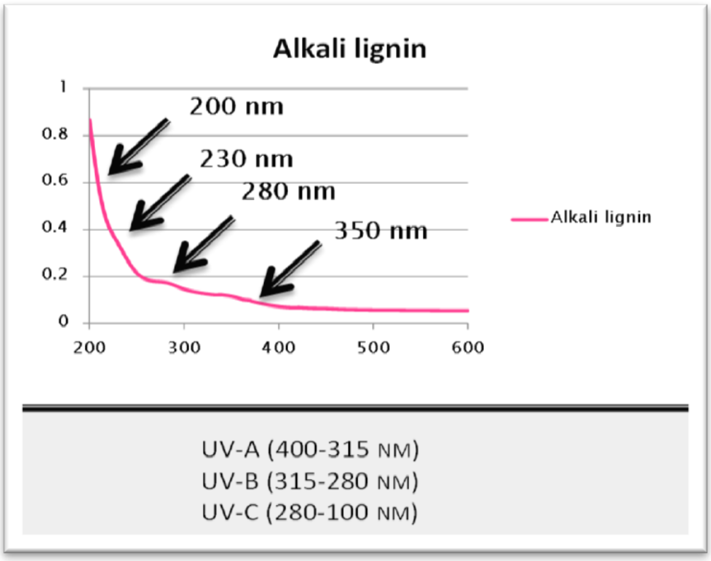


Figure S38: UV-vis spectrum of alkali lignin in aqueous solution at alkaline pH (NaOH).