

Towards the development of safer by design mineral photocatalytic paint: influence of the TiO₂ modifications on particle release

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Supplementary Material

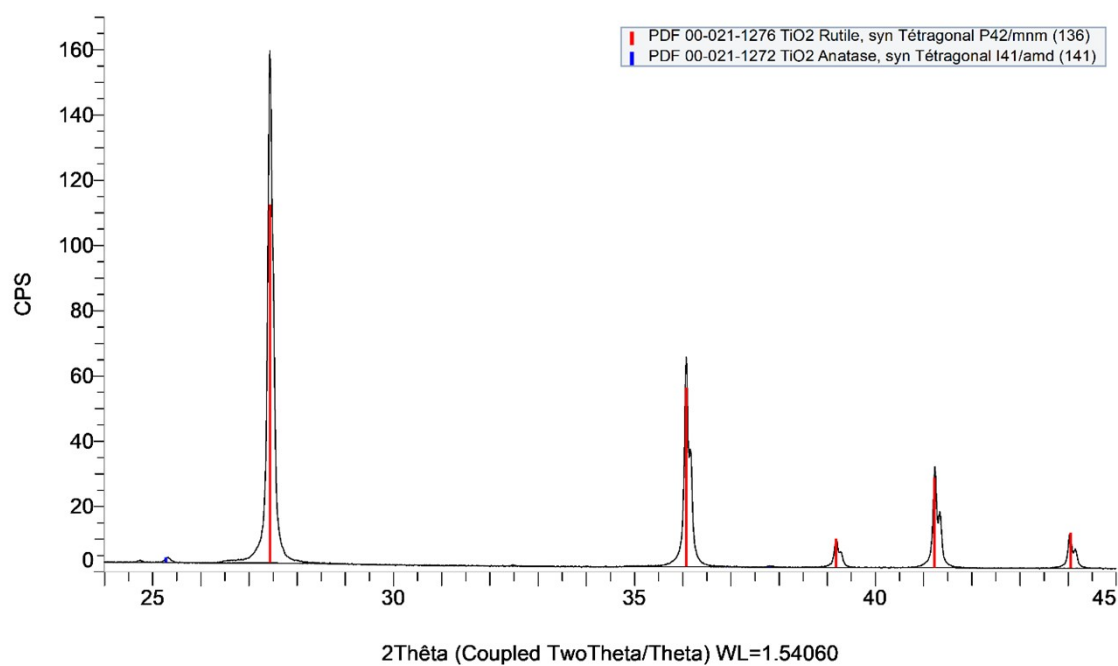


Fig. S1: XRD spectra of TiO₂ microparticles used in paint as a white pigment.

Table S1: Color coordinates for paints before and after 500 hours and 1000 hours exposure to artificial weathering.

Samples	Color coordinates			
	L*	a*	b*	ΔE^*
T 0h	87.57 ± 0.34	0.33 ± 0.08	1.69 ± 0.09	-
T 500h	89.63 ± 0.07	0.53 ± 0.01	0.65 ± 0.02	2.31
T 1000h	89.57 ± 0.04	0.57 ± 0.01	0.64 ± 0.05	2.27
Tn _{TiO2} 0h	90.38 ± 0.33	-0.61 ± 0.03	1.35 ± 0.13	-
Tn _{TiO2} 500h	91.45 ± 0.17	0.45 ± 0.01	0.02 ± 0.00	2.01
Tn _{TiO2} 1000h	89.56 ± 0.37	0.30 ± 0.08	-0.25 ± 0.07	2.01
W 0h	94.58 ± 0.07	-0.34 ± 0.01	3.10 ± 0.05	-
W 500h	94.89 ± 0.16	-0.20 ± 0.05	2.99 ± 0.08	0.36
W 1000h	94.40 ± 0.39	-0.38 ± 0.23	2.85 ± 0.25	0.31
Wn _{TiO2} 0h	95.27 ± 0.12	-0.28 ± 0.01	2.96 ± 0.07	-
Wn _{TiO2} 500h	95.09 ± 0.64	-0.47 ± 0.27	2.55 ± 0.16	0.49
Wn _{TiO2} 1000h	94.49 ± 0.15	-0.27 ± 0.15	3.15 ± 0.03	0.80
W _{PEG1/1} 0h	94.84 ± 0.31	-0.50 ± 0.23	3.08 ± 0.21	-
W _{PEG1/1} 500h	95.29 ± 0.05	-0.24 ± 0.01	3.26 ± 0.04	0.55
W _{PEG1/1} 1000h	94.85 ± 0.46	-0.23 ± 0.10	3.61 ± 0.22	0.59
W _{PEG5/1} 0h	94.90 ± 0.12	-0.35 ± 0.02	3.22 ± 0.09	-
W _{PEG5/1} 500h	95.11 ± 0.19	-0.20 ± 0.02	3.83 ± 0.16	0.66
W _{PEG5/1} 1000h	94.21 ± 0.11	-0.25 ± 0.03	3.99 ± 0.13	1.04
W _{CNC13.7} 0h	94.19 ± 0.49	-0.46 ± 0.25	2.87 ± 0.20	-
W _{CNC13.7} 500h	94.74 ± 0.02	-0.24 ± 0.01	3.07 ± 0.06	0.63
W _{CNC13.7} 1000h	94.83 ± 0.65	-0.18 ± 0.01	2.83 ± 0.03	0.70
W _{CNC21.9} 0h	94.40 ± 0.36	-0.44 ± 0.20	2.96 ± 0.19	-
W _{CNC21.9} 500h	94.69 ± 0.29	-0.18 ± 0.01	3.15 ± 0.17	0.43
W _{CNC21.9} 1000h	94.42 ± 0.08	-0.18 ± 0.01	3.13 ± 0.03	0.31

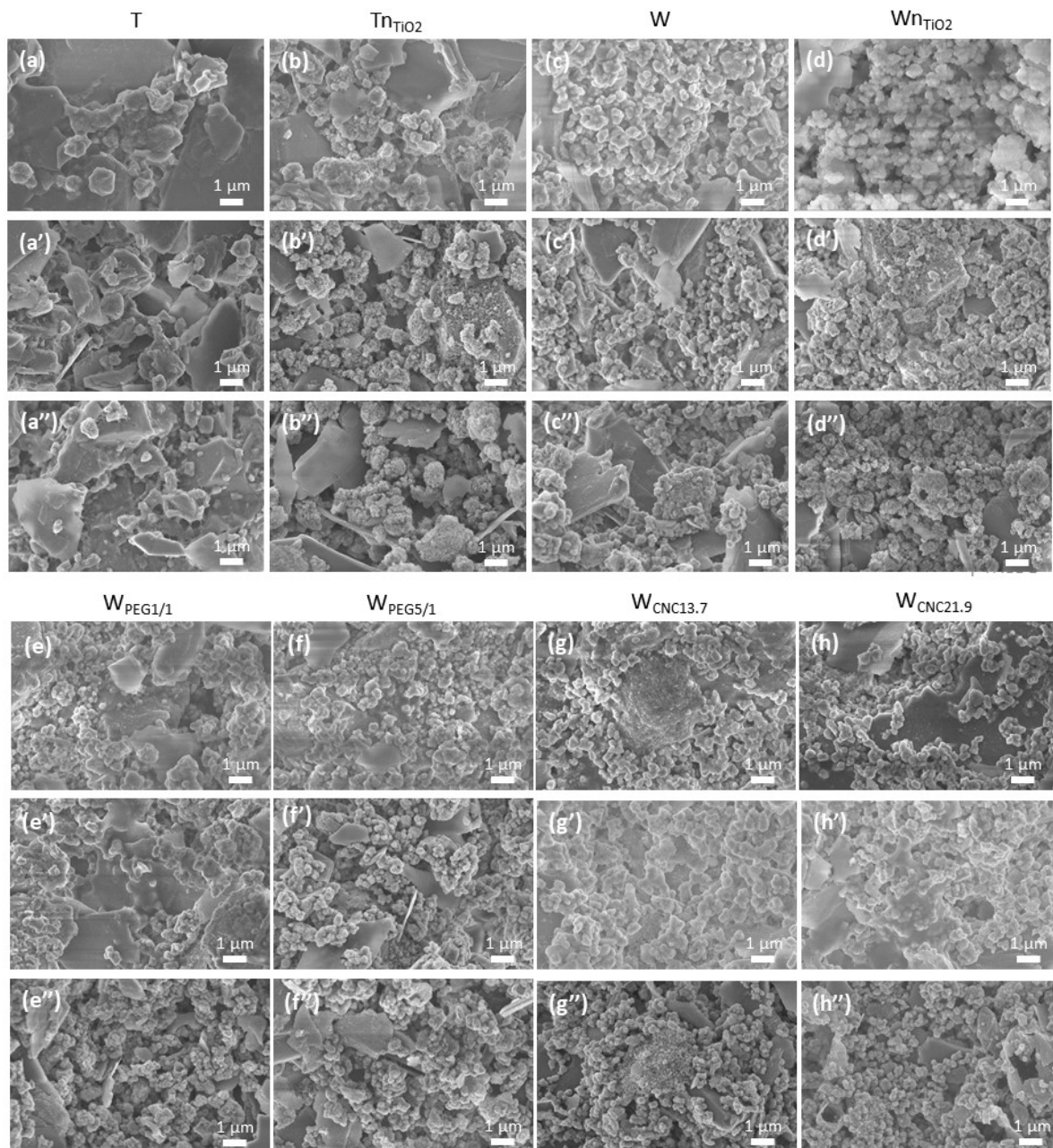


Fig. S2: SEM images of T (a), Tn_{TiO2} (b), W (c), Wn_{TiO2} (d), W_{PEG1/1} (e), W_{PEG5/1} (f), W_{CNC13.7}(g) and W_{CNC13.9} (h) paints before artificial weathering. The paints after 500 hours and 1000 hours exposure to artificial weathering are noted respectively with (') and (''), magnification 50 K

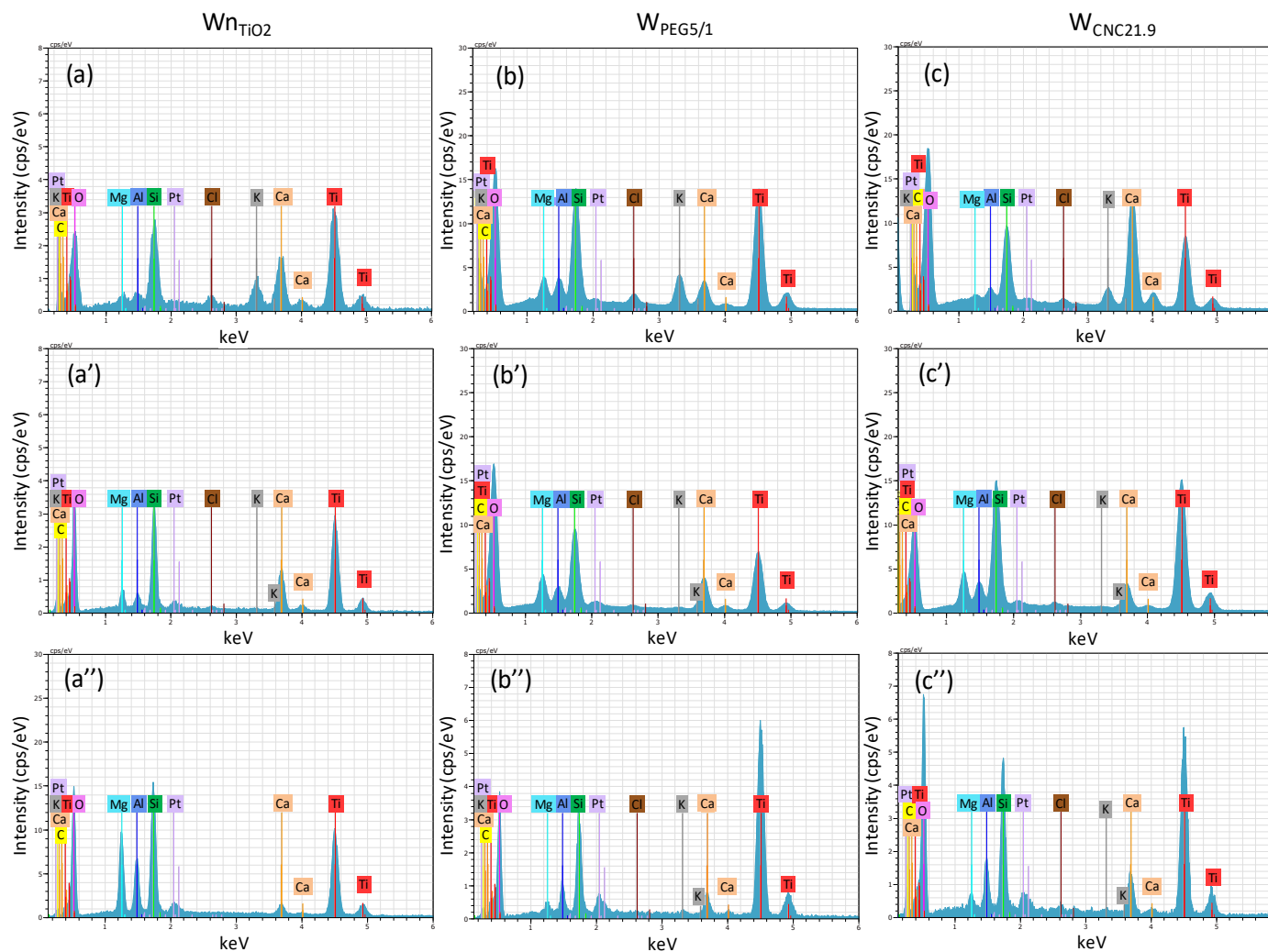


Fig. S3: EDX spectra of Wn_{TiO_2} (a), $W_{PEG5/1}$ (b) and $W_{CNC21.9}$ (c) paints before artificial weathering. The paints after 500 hours and 1000 hours exposure to artificial weathering are noted respectively with (') and ('').

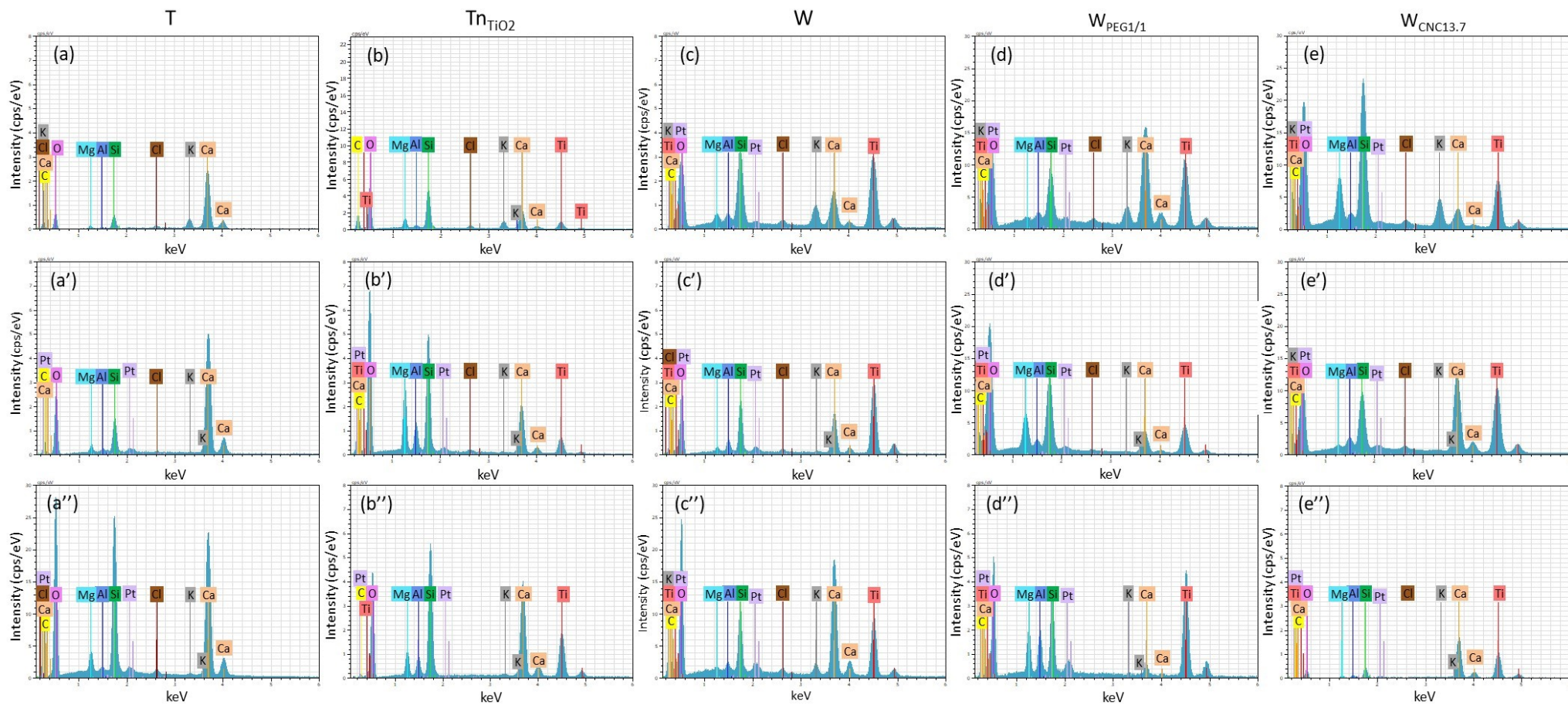


Fig. S4: EDX spectra of T (a), Tn_{TiO_2} (b), W (c), $W_{PEG1/1}$ (d) and $W_{CNC13.7}$ (e) paints before artificial weathering. The paints after 500 hours and 1000 hours exposure to artificial weathering are noted respectively with (') and ('').

Table S2: Chemical composition of paints analyzed by XPS before and after artificial weathering.

Paints	Artificial weathering (hours)	C 1s (%.at)	O 1s (%.at)	Mg 2s (%.at)	Al 2p (%.at)	Si 2p (%.at)	K 2p (%.at)	Ca 2p (%.at)	Ti 2p (%.at)
T	0	64.9	19.9	1.0	0.1	11.3	1.7	0.0	0.0
	500	45.8	31.4	4.5	2.1	12.0	0.3	3.9	0.0
	1000	48.1	30.8	2.2	3.5	12.9	0.5	4.1	0.0
Tn _{TiO₂}	0	67.4	19.4	0.9	0.3	10.3	1.3	0.0	0.1
	500	22.2	42.4	6.6	4.6	16.0	0.7	5.3	2.2
	1000	22.3	47.1	3.2	6.7	16.3	0.7	4.7	2.2
W	0	70.3	17.6	0.1	0.2	10.1	1.2	0.0	0.0
	500	57.5	26.2	2.1	0.9	11.8	0.3	1.4	0.0
	1000	62.3	23.5	3.3	0.7	10.9	0.4	2.1	0.1
Wn _{TiO₂}	0	63.3	22.3	0.8	0.2	9.9	2.5	0.0	0.4
	500	52.6	28.9	2.3	1.3	11.6	0.5	1.7	1.2
	1000	21.1	47.1	8.6	4.9	12.0	0.0	8.3	6.7
W _{PEG1/1}	0	68.6	18.9	0.4	0.2	9.8	1.3	0.3	0.0
	500	15.9	49.7	3.2	6.9	16.5	-	6.1	1.7
	1000	23.1	41.3	3.8	8.2	15.4	0.9	4.7	1.5
W _{PEG5/1}	0	64.9	21.4	0.7	0.3	10.6	1.7	0.5	0.0
	500	53.9	27.4	2.9	1.5	12.2	-	6.1	1.7
	1000	29.4	39.6	3.3	5.1	16.5	0.5	3.9	0.5
W _{CNC13.7}	0	67.0	19.8	0.7	0.0	9.1	2.1	0.5	0.0
	500	36.0	38.3	3.0	3.2	15.3	-	3.7	0.4
	1000	57.6	26.5	1.8	1.2	11.2	0.3	1.2	0.1
W _{CNC21.9}	0	65.3	20.9	0.4	0.2	10.2	2.1	0.4	0.0
	500	38.0	36.2	2.8	4.2	14.9	-	3.6	0.3
	1000	36.6	35.2	3.8	5.0	13.9	0.2	4.4	0.6

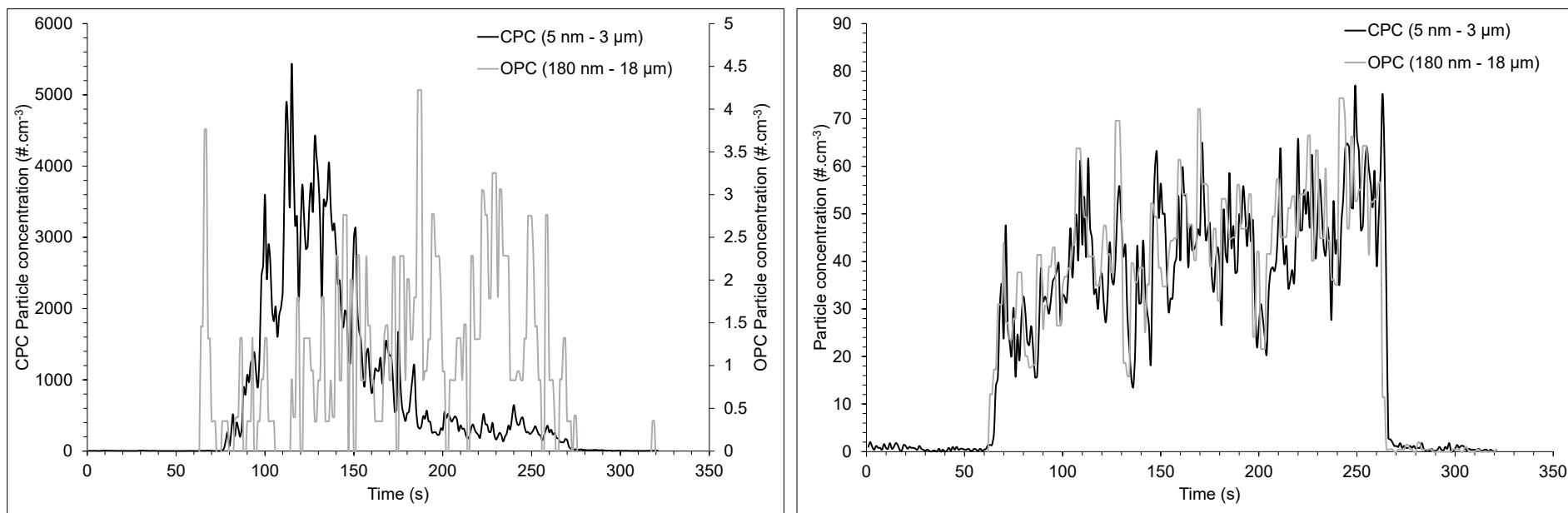


Fig. S5: Concentration of particles released per cm^3 measured by CPC (black) and OPC (grey) during mechanical sollicitation respectively for the first triplicate of W before artificial weathering (left) and Wn_{TiO_2} after 500 hours exposure to artificial weathering.

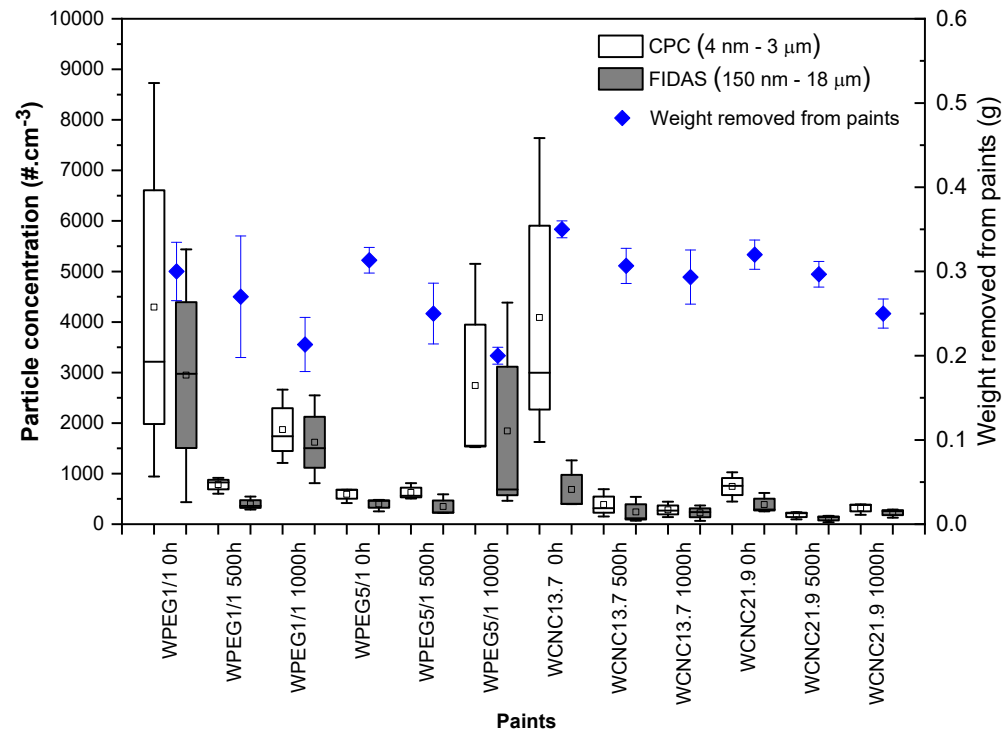


Fig. S6: Concentration of particles released per cm³ measured by CPC in white in the range 4 nm to 3 μm and OPC in grey from 150 nm to 18 μm and weight removed from $W_{\text{PEG1/1}}$, $W_{\text{PEG5/1}}$, $W_{\text{CNC13.7}}$ and $W_{\text{CNC21.9}}$ paints before and after 500 hours and 1000 hours exposure to artificial weathering.

Table S3: Evolution of the mass of Taber samples and loss of mass due to weathering compared to the sample before UV stress. Each value is an average value from triplicate

Paints	Artificial weathering (hours)	Sample weight before abrasion (g)	Sample weight after abrasion (g)	Amount of paint abraded (g)	Δ of weight 0h-Xh (g)
T	0	27.86	27.49	0.37	-
	500	27.61	27.33	0.28	0.09
	1000	27.43	27.15	0.28	0.09
T _{nTiO2}	0	27.83	27.48	0.35	-
	500	27.31	27.09	0.22	0.135
	1000	27.32	27.12	0.20	0.150
W	0	27.66	27.35	0.31	-
	500	27.49	27.21	0.28	0.030
	1000	27.70	27.35	0.35	-0.040
W _{nTiO2}	0	27.60	27.31	0.28	-
	500	27.29	27.07	0.22	0.06
	1000	27.23	27.05	0.18	0.10
W _{PEG1/1}	0	27.52	27.22	0.30	-
	500	27.59	27.32	0.27	0.03
	1000	27.38	27.17	0.21	0.09
W _{PEG5/1}	0	27.60	27.29	0.31	-
	500	27.51	27.26	0.25	0.06
	1000	27.34	27.14	0.20	0.11
W _{CNC13.7}	0	27.83	27.48	0.35	-
	500	27.65	27.35	0.31	0.04
	1000	27.69	27.40	0.29	0.06
W _{CNC21.9}	0	27.72	27.40	0.32	-
	500	27.56	27.27	0.30	0.02
	1000	27.51	27.26	0.25	0.07

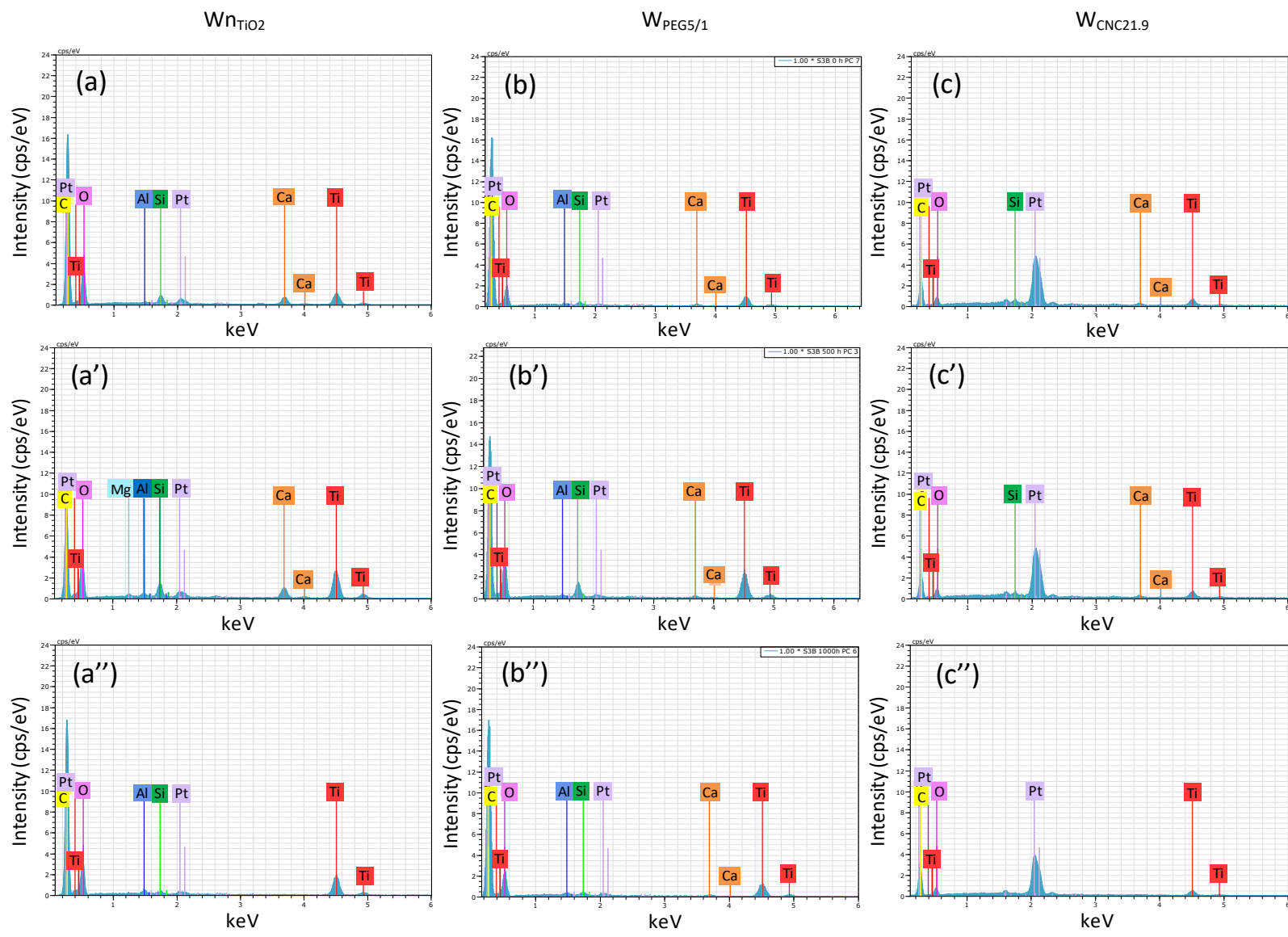


Fig. S7: EDX spectra of particles released from paints W_{TiO_2} (a), $W_{PEG5/1}$ (b) and $W_{CNC21.9}$ (c) paints. The paints after 500 hours and 1000 hours exposure to artificial weathering are noted respectively with (') and (").

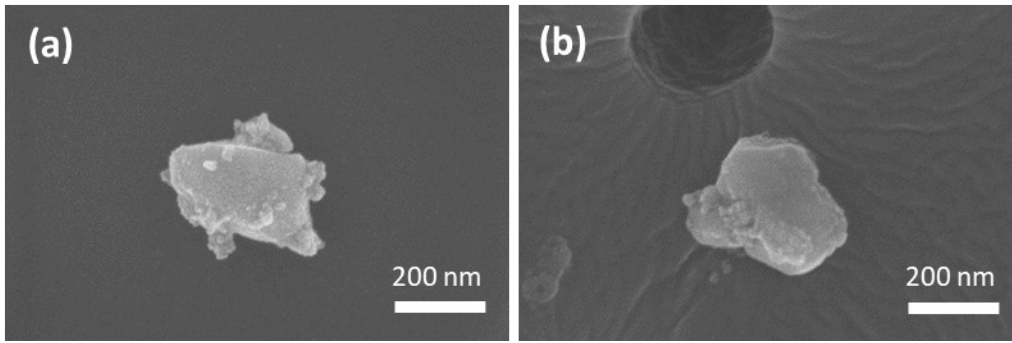


Fig. S8: SEM images of individual particles released from $WnTiO_2$ after 500 hours (a) and 1000 hours (b) exposure to artificial weathering, magnification 100 K.

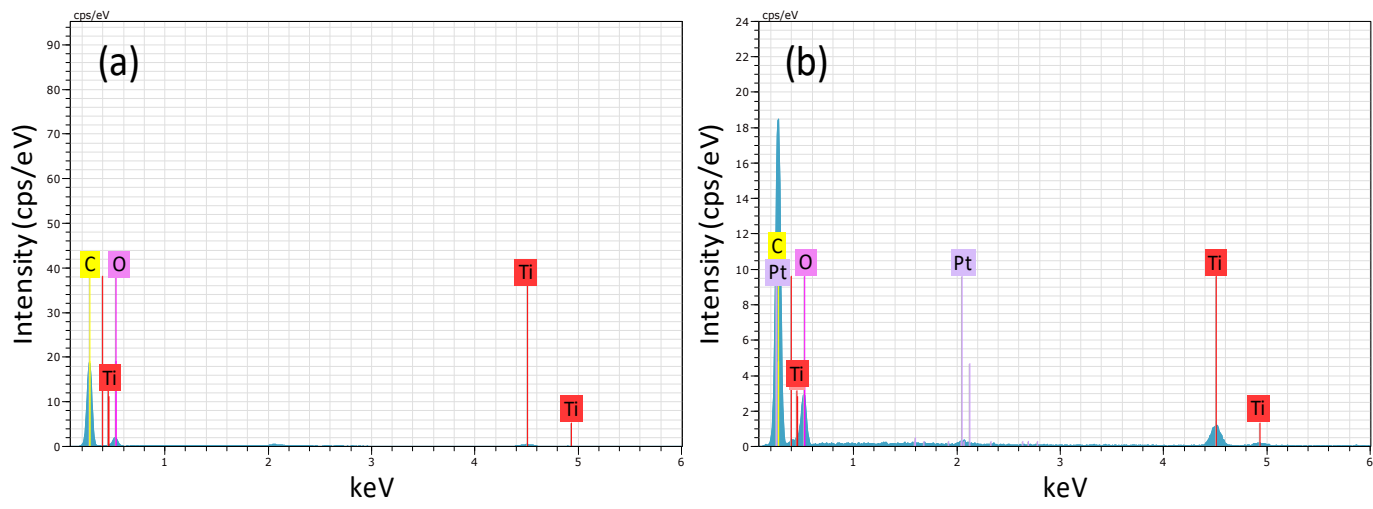


Fig. S9: EDX spectra of individual particles released from $WnTiO_2$ after 500 hours (a) and 1000 hours (b) exposure to artificial weathering.