Electronic Supplementary Material (ESI) for Environmental Science: Nano.
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Supporting Information

Environmental release from automotive coatings are similar for different (nano)forms of pigments

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INSTRUMENT DETAILS

Scanning Electron Microscope (SEM)

The white pigment TiO_2 (non nano) was characterized using a a JEOL 7500F high-resolution scanning electron microscope with a cold field effect emitter. All images were obtained at 5kV acceleration voltage.

Transmission Electron Microscopy (TEM)

TEM samples were investigated on a Tecnai G2-F20ST machine (FEI Company, Hillsboro, USA) operated at 200 keV. Energy Dispersive X-ray spectroscopy (EDXS) was applied to determine chemical compositions at distinct spots of the sample using an EDXi-detection system with an energy resolution of 131 eV at Mn-Kα (EDAX, Mahwah, USA). Images and spectroscopy data were evaluated using the Olympus (Tokyo, Japan) iTEM 5.2 (Build 3554) and FEI TIA 4.1.202 software package.

Colorimetry

The colorimetric characterization of the plates was obtained using datacolor spectrophotometer SF 600. The measurements were performed in specular excluded (SPEX) mode with a wavelength range of 400-700 nm. Colorimetric evaluations were made in agreement with the spectral method described in ISO 18314-1 (2015) with d8° geometry. Test features ΔL*, Δa* and ΔC* were evaluated in accordance with ISO 11664-4 (2008) for light source D65 and 10° standard observer from the measurements over a white substrate.

	DPP_nano	**DPP_non-nano**	**DPP_premixed**	**Fe_2O_3**	**Cuphthalocyanine**
Primary particle diameter (TEM, nm)	42	230	233	9	17
Surface area (BET, m^2/g)	94	16	17	107	53
Composition (XPS, at%)	77.1% C; 10.9% O; 5.9% N; 6.1% non metals	79.4% C; 9.9% O; 5.1% N; 0.3% metals; 5.2% non metals	73.5% C; 9.5% O; 8.1% N; 0.4% metals; 8.6% non metals	15.7% C; 54.2% O; 0% N; 28.2% metals; 1.9% non metals	80.5% C; 9% O; 8.5% N; 1.4% metals; 0.7% non metals
Zeta potential (pH 7.4, mV)	-16	-41	-30	-27	- 11
Water contact angle (θ)	135	136	103	10	138

Table S1. Basic physic- chemical characteristics of pigments investigated in this work

Sample	Aging month	dL*
control	0	-
	1	11.92
	2	14.67
	3	18.39
CuPhthalocyanine_matrix-2	0	-
	1	0.80
	2	3.48
	3	2.28

Table S2. Colorimetric properties (dL*) of control and CuPhthalocyanine acrylic plates subjected to NanoRelease protocol.

Weathering			UV-vis		AUC	
Specimen	**Months**	**Sampling method**	**Avg.**	**Std. Dev**	**Avg.**	**Std. Dev**
			OD 350 nm	*OD 350 nm*	*mg/m²*	*mg/m²*
matrix-2	0	shaker	2.20	0.40	201.3	34.7
	1	shaker	3.45	1.85	103.3	102.0
	2	shaker	18.60	0.60	78.7	12.0
	3	shaker	17.50	0.90	156.7	103.3
matrix-2	0	sonication	0.25	0.05	172.7	144.7
	1	sonication	2.65	0.55	289.3	4.0
	2	sonication	9.65	2.95	710.7	162.7
	3	sonication	15.10	0.60	2354.7	312.0
CuPhthalocyanine_matrix-2	0	shaker	0.095	0.025	117.3	65.3
	1	shaker	0.165	0.025	63.3	2.0
	2	shaker	0.205	0.015	74.7	28.0
	3	shaker	0.330	0.010	133.3	16.0
CuPhthalocyanine_matrix-2	0	sonication	0.145	0.035	226.7	40.0
	1	sonication	0.245	0.015	47.3	46.0
	2	sonication	0.370	0.040	72.7	35.3
	3	sonication	0.485	0.005	46.0	11.3

Table S3. UV-vis spectroscopy and analytical ultracentrifuge analysis of leached water from plates weathered for 0, 1, 2 and 3 months.

Weathering		UV-Vis		AUC	
Specimen	**Sampling Method**	**Avg.** *OD 350 nm*	**Std. Dev.** *OD 350 nm*	**Avg.** *mg/m²*	**Std. Dev** *mg/m²*
matrix-2	Shaker	18.6	0.60	78.7	12.0
	Sonication	9.70	2.95	710.7	162.7
CuPhthalocyanine_matrix-2	Shaker	0.21	0.015	74.7	28.0
	Sonication	0.37	0.04	72.7	35.3
Fe_2O_3_matrix-2	Shaker	0.21	0.03	195.3	76.6
	Sonication	0.39	0.04	27.3	7.3
DPP_nano_matrix-2	Shaker	0.39	0.05	56.7	20.7
	Sonication	0.64	0.23	104.7	2.0

Table S4. Data of UV-vis spectroscopy and analytical ultracentrifuge for matrix-2 plates aged for 2 months.

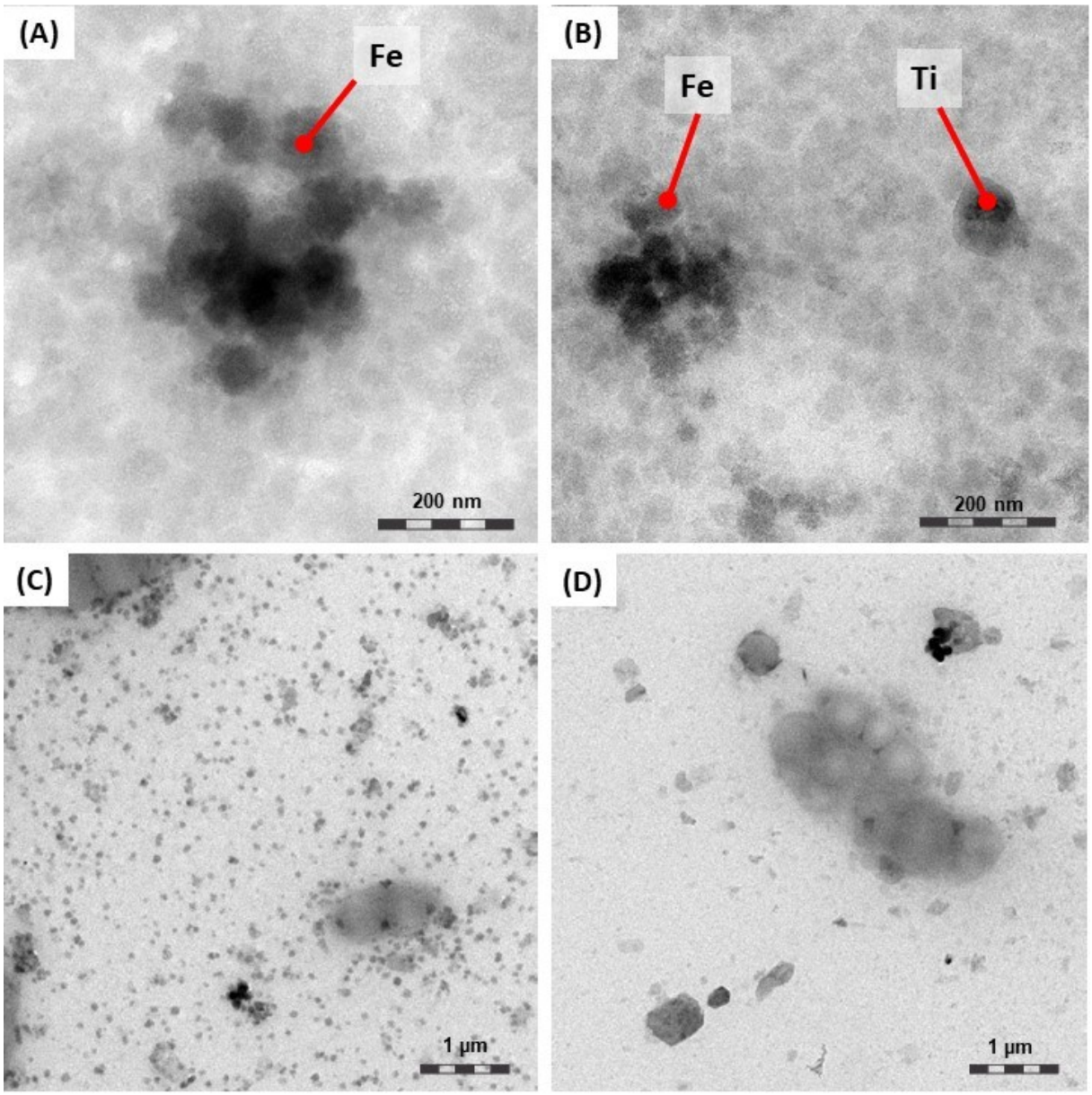

Fig. S1. TEM pictures of the released fragments from Fe_2O_3 (A, B) and DPP (C, D) acrylic plates after 2 month of Kalahari protocol. EXD spectroscopy confirmed the presence of iron and titanium particles in the leached water.

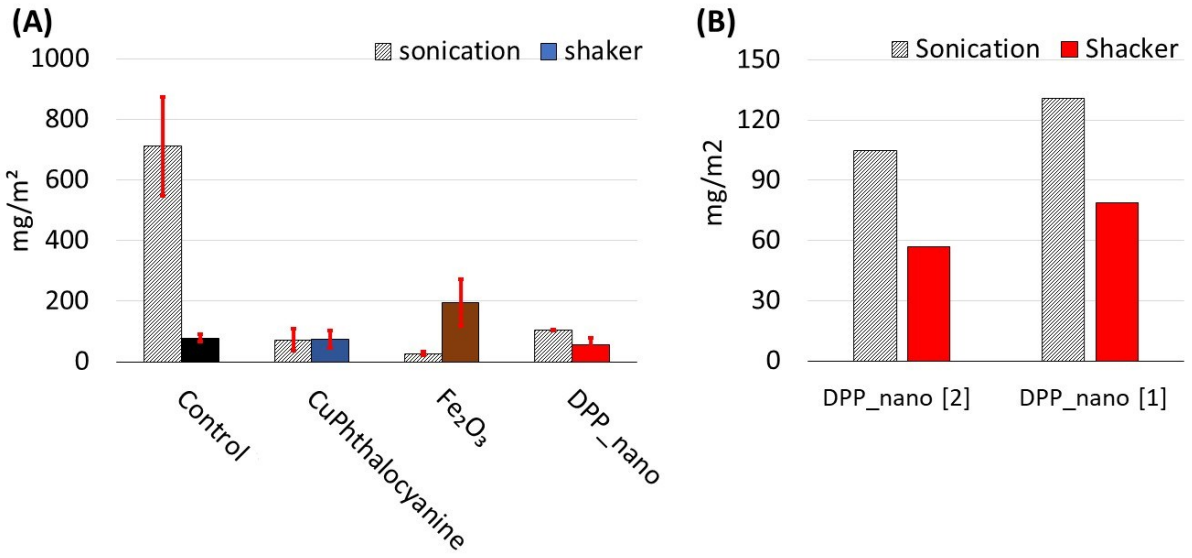

Fig. S2. Analytical ultracentrifuge data of immersion water from (A) matrix-2 and (B) matrix-2 and -1 plates after 2 months of aging. All the drop-off suspensions were subjected to (plotted as shaded bar) sonication or (plotted as filled bar) shaking stimulation.

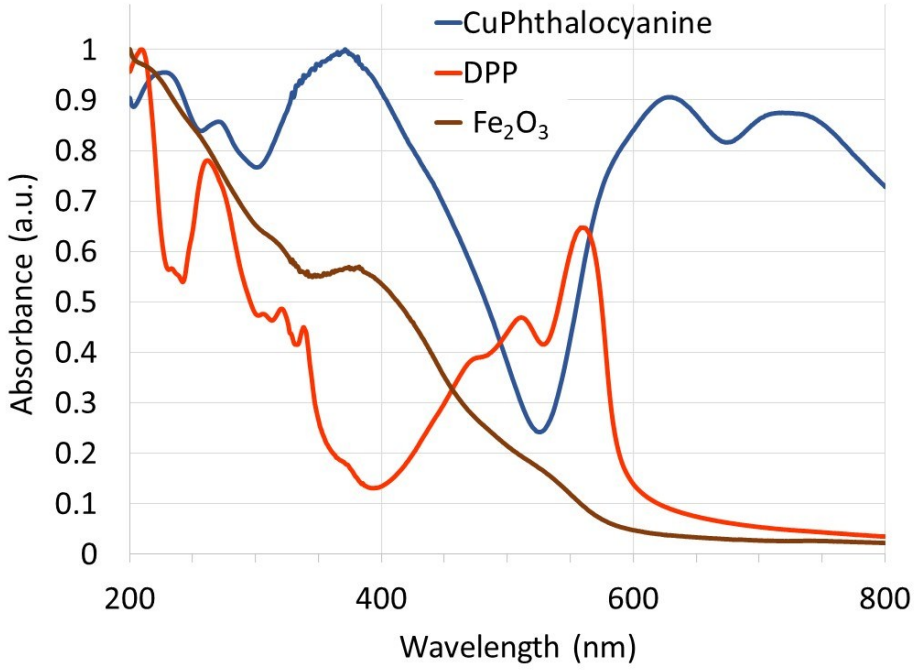

Fig. S3. UV-vis spectra overlap of the three groups of pigments (blue CuPhthalocyanine, red DPP, brown Fe_2O_3) investigated in this work

Sample	Month	Method	UV-vis 280 nm	AUC conc mg/m²
DPP Plate				
Pre-mixed	2	Sonication	0.14	111.4
	2	Shaker	0.01	124.3
Non-Nano	2	Sonication	0.15	94.3
	2	Shaker	0.01	117.9
Nano	2	Sonication	0.16	79.3
	2	Shaker	0.01	130.7
DPP-TiO_2 Plate				
Pre-mixed	2	Sonication	0.47	137.1
	2	Shaker	0.31	199.3
Non-Nano	2	Sonication	0.39	98.6
	2	Shaker	0.37	98.6
Nano	2	Sonication	0.61	87.9
	2	Shaker	0.37	122.1

Table S5. Data of UV-vis spectroscopy and analytical ultracentrifuge for plates aged for 0 and 2 months

Sample	Method	% UV variation	% AUC variation
DPP_premixed	sonication	81	23
	shaker	73	60
DPP_non-nano	sonication	167	5
	shaker	667	-16
DPP_nano	sonication	124	11
	shaker	92	-7

Table S6. Percentage variation of UV abs (at 280 nm) and fragment concentration (mg/m²) values of DPP + TiO_2 plates respect to DPP plates alone. All plates were evaluated after 2 months artificial weathering.

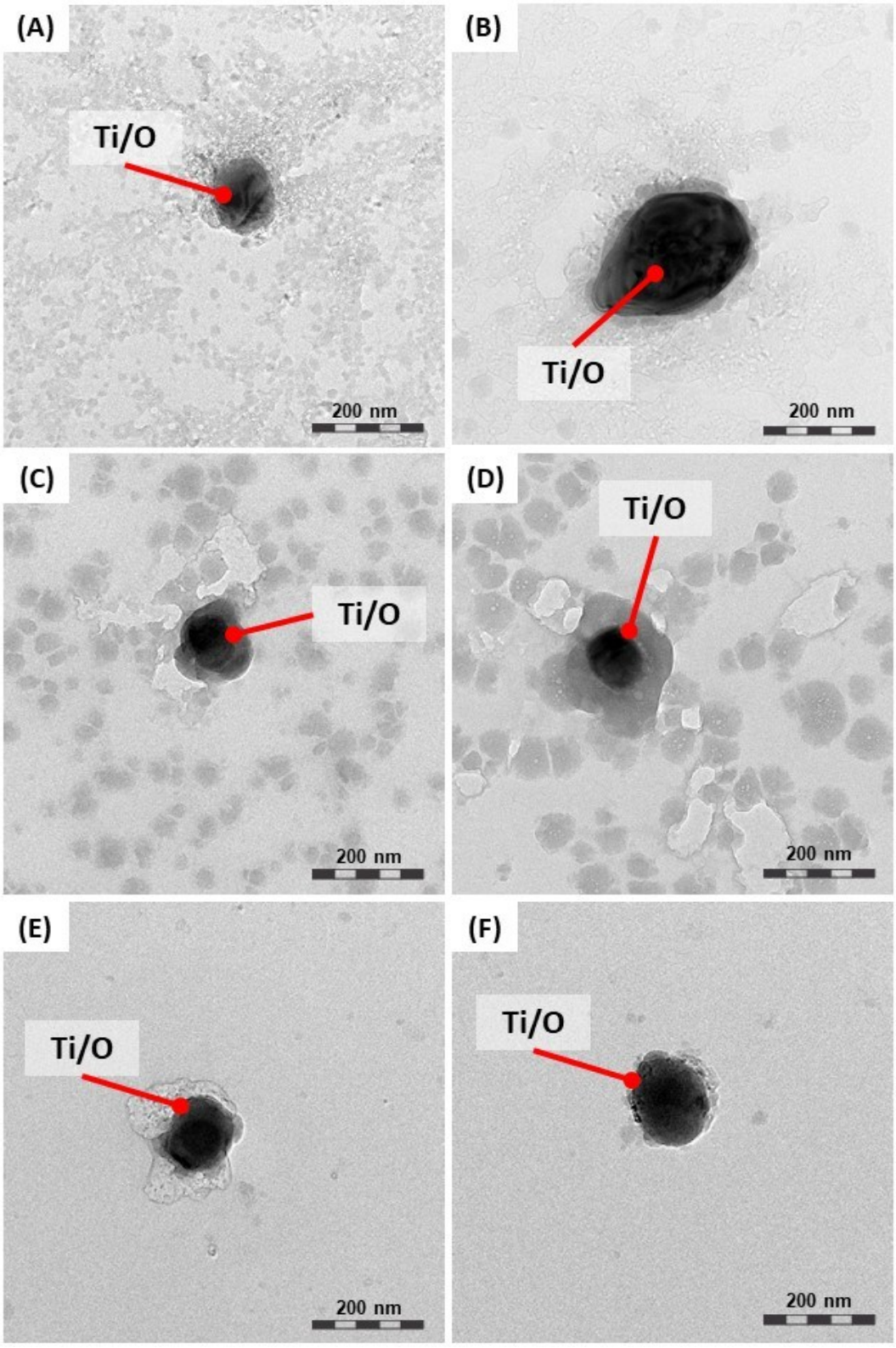

Fig. S4. TEM pictures of the released fragments from (A, B) DPP_premixed + TiO_2, (C, D) DPP_nano + TiO_2 and (E, F) DPP_non nano + TiO_2 plates.

Calculation of Mass Release

AUC data in metrics of mg/MJ was calculated multiplying "mg/m²" values per "surface area/UV energy". The equation employed is the following:

$$Mass\ release\ (\frac{mg}{MJ}) = \frac{fragment\ amount\ (mg)}{plate\ surface\ area\ (m^2)} * \frac{plate\ surface\ area\ (m^2)}{UV\ energy\ (MJ)}$$