Supporting Information

Investigation of the Fate of Silver and Titanium Dioxide Nanoparticles in Model Wastewater Effluents via Selected Area Electron Diffraction

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23 ASSOCIATED CONTENT



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Preparation of NP stock solutions for artificial wastewater treatment. 8 mL of ultrapure water were added to a glass vial with 2000 mg of NM-300K, resulting in a total Ag concentration of 20 g L⁻¹. The vials were thoroughly shaken by hand for 1 min and sonicated for 15 min in a sonication bath (160 W, Sonorex Super RK 510, Bandelin electronic GmbH & Co. KG, Germany). Subsequently, 15.8 mL of this dispersion were added to polyethylene (PE) containers (Züchner GmbH, Germany) with 6 L of ultrapure water to obtain nominal Ag concentrations of 35 mg L⁻¹.

50 mL of ultrapure water were added to a glass vial with 45.0 mg of NM-105, thoroughly shaken
by hand for 1 min, sonicated for 15 min (160 W, Sonorex Super RK 510, Bandelin electronic
GmbH & Co. KG, Germany) and added directly to the denitrification reactor to reach an average
nominal influent Ti concentration of 5.0 mg L⁻¹.

38 Inductively Coupled Plasma-Mass Spectrometry/ Optical Emission Spectrometry 39 (ICP-MS/OES). Total silver content of wastewater samples before and after cloud point 40 extraction was determined via ICP-MS (iCAP Qc, Thermo Fisher Scientific, Bremen, Germany). Ag-NP-containing effluents were shaken for 30 min and then either used for cloud point 41 42 extraction (see previous paragraph) or directly prepared for analysis. The surfactant-rich phase 43 was diluted to 1.5 mL and sonicated for 10 min. 0.5 mL of both effluent samples were digested 44 for 2 h in 1.5 mL of concentrated nitric acid (70%, analytical reagent grade, Fisher Scientific, 45 Loughborough, UK) and then filtered through a PTFE filter (pore size: 0.45 µm, VWR, 46 Germany) to remove residual sediment particles to prevent clogging of the pneumatic nebulizer. 47 All samples were diluted 100 times with Milli Q water (Resistivity: 18.2 M Ω^* cm). The instrument calibration was performed on the same day with a silver standard solution (Inorganic 48 Ventures, Christiansburg, VA, USA) ranging from 0 μ g L⁻¹ (blank) to 100 μ g L⁻¹. Indium 49 50 (Inorganic Ventures, Christiansburg, VA, USA) was used as an internal standard at a final 51 concentration of 1 µg/L. Preliminary experiments showed that matrix adjusted calibration 52 standards accounting for the presence of the surfactant TX-114 were not necessary (data not shown). The limit of detection (LOD; 3.3 x standard deviation of the blank) and the limit of 53 quantification (LOQ; 10 x standard deviation of the blank) for total silver determination were 54 ranging from 0.3 - 0.4 ng L⁻¹ and 1.0 - 1.3 ng L⁻¹, respectively. Instrumental parameters are 55 56 detailed in the Supporting Information (SI), Table S1.

57 Total Ti content in extracted and wastewater effluents was determined via ICP-OES 58 (ARCOS, SPECTRO Analytical Instruments GmbH, Kleve, Germany) as described by 59 Hartmann et al.¹ In brief, 1.0 mL of the wastewater effluent and blanks as well as the surfactant-60 rich phase of extracted samples were spiked with Sc as an internal standard ($c_{final} = 200 \ \mu g \ L^{-1}$), 61 diluted to 10.0 mL with bidistilled water and evaporated in porcelain crucibles (Carl Roth GmbH & Co. KG, Karlsruhe, Germany). Ammonium persulfate (1.00 g, > 98 % p.a., ACS, Carl Roth 62 63 GmbH & Co. KG, Karlsruhe, Germany) was added to the residue and a Bunsen burner was used 64 to heat the crucible contents to a fume. The high organic content in the extracted samples from 65 the surfactant led to the formation of carbon black within the molten mass and was later removed with a PTFE filter (0.45 µm). The cooled crucibles were subsequently boiled with bidistilled 66 water for 10 min and eventually diluted to a total volume of 15.0 mL in a PP centrifuge vial 67 (VWR International, Langenfeld, Germany). Nitric acid (c_{final} = 2% (w/v)) was added to the 68 69 samples, which were shaken afterwards and analyzed directly. All samples were measured three 70 times and Ti quantification was performed based on the emission line of Ti at 334.187 nm.

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Parameter	ICP-MS (Ag)	ICP-OES (Ti)
Nebulizer	Pneumatic glass nebulizer	Standard cross-flow nebulizer
Spray chamber	Peltier-cooled cyclonic quartz	Standard Scott type
Radio-frequency power [W]	1550	1200
Torch injector inner diameter	2.5	2.0
[mm]		
Cooling flow [L min ⁻¹]	14.0	13
Auxiliary flow [L min ⁻¹]	0.8	0.8
Nebulizer flow [L min ⁻¹]	1.1	0.9
Sampling position [mm]	5	n/a
Number of measurements	10	3
Measured isotope	$^{107}Ag^{+}$	n/a

72 **Table S1.** ICP-MS and ICP-OES instrumental parameters for total Ag and Ti measurements.

73 n/a = not applicable

75 FFT Analysis of watewater-borne AgNPs. Prior to SAED analysis, the mineral phase of a 76 single wastewater-borne Ag-NP was investigated via high-resolution TEM (HR-TEM) as shown 77 in Figure S2. The nanoparticle is oriented in such a way that one of its crystal plane directions is 78 parallel to the incident electron beam and thus gives rise to two-dimensional lattice fringes. The 79 spacing between those fringes is 7.89 Å, which is close to the d-spacing of the monoclinic α -Ag₂S(100) plane (7.87 Å).² The calculated FFT pattern in panel B is in good agreement with the 80 theoretical pattern of the (100) zone axis of α -Ag₂S (acanthite) with the cell constants a = 4.23 Å, 81 b = 6.91 Å, c = 7.87 Å, and $\beta = 99^{\circ}$ 35'. The space group for this crystal is $P2_1/n$.³ Acanthite is 82 83 the thermodynamically stable crystal structure of Ag₂S below 173 °C. Above this temperature, it 84 converts to the body-centered cubic argentite phase.



Figure S2. Mineral phase analysis of a single wastewater-borne silver nanoparticle: HR-TEM
image (A), obtained FFT pattern (B), theoretical (100) pattern of α-Ag₂S (C).

Z	Element	Family	Atomic fraction [%]	Atomic error [%]	Mass fraction [%]	Mass error [%]
6	C	K	73.8	5.2	52.9	2.3
8	0	K	15.3	3.2	14.6	3.0
14	Si	K	6.7	1.4	11.3	2.2
16	S	K	< 0.1	< 0.1	0.1	0.0
29	Cu	K	1.7	0.3	6.3	0.9
47	Ag	L	2.5	0.3	14.9	1.8

Table S2. Elemental composition of pristine Ag-NPs as determined by EDX.

Table S3. Elemental composition of wastewater-borne Ag-NPs as determined by EDX.

Z	Element	Family	Atomic fraction [%]	Atomic error [%]	Mass fraction [%]	Mass error [%]
6	С	K	58.3	4.6	31.1	1.6
7	N	K	5.7	1.2	3.5	0.7
8	0	K	15.9	3.4	11.3	2.3
11	Na	K	1.2	0.3	1.3	0.3
13	Al	K	0.2	0.1	0.3	0.1
14	Si	K	4.9	1.0	6.1	1.2
15	Р	K	0.1	< 0.1	0.2	0.0
16	S	K	3.6	0.7	5.1	1.0
20	Ca	K	0.1	< 0.1	0.2	< 0.1
29	Cu	K	3.2	0.5	9.1	1.3
47	Ag	L	6.7	0.9	31.9	4.0

Z	Element	Family	Atomic fraction [%]	Atomic error [%]	Mass fraction [%]	Mass error [%]
6	С	K	34.5	5.1	20.7	1.9
7	Ν	K	3.7	1.0	2.6	0.6
8	0	K	41.2	10.1	32.9	7.1
13	Al	K	0.1	< 0.1	0.2	< 0.1
14	Si	K	6.2	1.5	8.7	1.8
15	Р	K	0.1	< 0.1	0.2	< 0.1
16	S	K	0.2	< 0.1	0.3	0.1
22	Ti	K	12.4	2.4	29.5	4.6
29	Cu	K	1.6	0.3	5.1	0.8

Table S4. Elemental composition of pristine TiO₂-NPs as determined by EDX.

Table S5. Elemental composition of wastewater-borne TiO_2 -NPs as determined by EDX.

Z	Element	Family	Atomic fraction [%]	Atomic error [%]	Mass fraction [%]	Mass error [%]
6	С	K	29.8	4.1	14.9	1.2
7	N	K	3.8	1.0	2.2	0.5
8	0	K	37.9	9.1	25.2	5.4
13	Al	K	1.0	0.2	1.1	0.2
14	Si	K	1.5	0.4	1.8	0.4
15	Р	K	0.6	0.1	0.7	0.2
16	S	K	0.5	0.1	0.6	0.1
20	Ca	K	0.2	< 0.1	0.3	< 0.1
22	Ti	K	18.5	3.5	36.8	5.6
29	Cu	K	6.3	1.2	16.5	2.5

h	k	1	Ag-NPs – Pristine		Ag		Deviation [%]		
			Displacement [nm ⁻¹]	Norm. intensity	Displacement [nm ⁻¹]	Norm. intensity	Displacement	Intensity	
1	1	1	4.21	1000	4.32	1000	- 2.5	0	
2	0	0	4.90	388	4.99	505	- 1.8	- 23	
2	2	0	6.86	141	7.05	342	- 2.7	- 59	
3	1	1	8.04	156	8.27	392	- 2.8	- 60	
2	2	2	8.37	58	8.64	111	- 3.1	- 48	
4	0	0	9.77	13	9.98	48	- 2.1	- 74	
3	3	1	10.61	32	10.87	135	- 2.4	- 76	
4	2	0	10.84	37	11.15	121	- 2.8	- 70	

99 Table S6. Comparison of structure factors of pristine silver nanoparticles (Ag-NPs – Pristine)
100 and silver (Ag).

h	k	l	Ag-NPs – WWTP		Ag_2S	5	Deviation [%]		
			Displacement [nm ⁻¹]	Norm. intensity	Displacement [nm ⁻¹]	Norm. intensity	Displacement	Intensity	
-1	0	1	2.55	355	2.53	8	0.8	4340	
1	1	1	3.28	400	3.25	380	0.9	5	
-1	1	2	3.54	496	3.53	715	0.3	-31	
1	2	0	3.80	236	3.76	353	1.1	-33	
0	2	2	3.88	454	3.88	583	0.0	-22	
1	2	1	4.12	1000	4.10	1000	0.5	0	
-1	0	3	4.23	751	4.20	668	0.7	12	
0	3	1	4.54	239	4.53	510	0.2	-53	
2	0	0	4.80	187	4.80	593	0.0	-68	
1	0	3	4.86	293	4.88	289	-0.4	2	
1	1	3	5.10	317	5.09	233	0.2	36	
-2	2	2	5.86	239	5.82	197	0.7	22	
-2	2	3	6.35	56	6.34	56	0.2	0	
1	4	2	6.90	97	6.93	135	-0.4	-28	
1	3	4	7.43	58	7.43	203	0.0	-71	

102 Table S7. Comparison of structure factors of wastewater-borne silver nanoparticles (Ag-NPs –
103 WWTP) and silver sulfide (Ag₂S).

Table S8. Comparison of structure factors of pristine titanium dioxide nanoparticles and titanium
dioxide (TiO₂). Structure factors refer to anatase (white background) and rutile (grey
background).

	h	k	l	TiO ₂ NPs - I	Pristine	TiO	2	Deviation	n [%]
				Displacement [nm ⁻¹]	Norm. intensity	Displacement [nm ⁻¹]	Norm. intensity	Displacement	Intensity
	1	0	1	2.86	1000	2.84	1000	0.7	0
	1	0	3	4.17	259	4.11	43	1.5	503
	0	0	4	4.25	328	4.20	227	1.2	45
	2	0	0	5.32	219	5.29	392	0.6	-44
	1	0	5	5.95	334	5.88	271	1.2	23
tase	2	0	4	6.79	171	6.75	203	0.6	-16
Ana	1	1	6	7.34	62	7.33	74	0.1	-16
	2	2	0	7.45	130	7.47	121	-0.3	7
	2	1	5	7.90	83	7.91	189	-0.1	-56
	3	0	1	7.97	119	8.00	39	-0.4	204
	2	2	4	8.60	59	8.58	82	0.2	-29
	3	2	1	9.59	42	9.59	37	0.0	15
	1	1	0	3.08	1000	3.08	1000	0.0	0
tile	1	0	1	4.06	1443	4.02	406	1.0	255
Rui	1	1	1	4.58	483	4.57	292	0.2	65
	2	1	0	4.89	406	4.87	115	0.2	253

109	Table S9. Comparison of structure factors of wastewater-borne titanium dioxide nanoparticles
110	and titanium dioxide (TiO ₂). Structure factors refer to anatase (white background) or rutile (grey
111	background).

	h	k	l	TiO ₂ NPs - '	WWTP	TiO	2	Deviatio	n [%]
				Displacement [nm ⁻¹]	Norm. intensity	Displacement [nm ⁻¹]	Norm. intensity	Displacement	Intensity
	1	0	1	2.86	1000	2.84	1000	0.7	0
	0	0	4	4.23	263	4.20	227	0.7	16
	2	0	0	5.31	272	5.29	392	0.4	-31
	1	0	5	5.98	283	5.88	271	1.7	5
se	2	0	4	6.80	126	6.75	203	0.7	-38
nata	1	1	6	7.35	72	7.33	74	0.3	-3
\mathbf{A}_{1}	2	2	0	7.47	96	7.47	121	0.0	-21
	2	1	5	7.89	53	7.91	189	-0.3	-72
	3	0	1	7.97	117	8.00	39	-0.4	201
	2	2	4	8.58	53	8.58	82	0.0	-35
	3	2	1	9.60	108	9.59	37	0.1	193
tile	1	1	0	3.08	1000	3.08	1000	0.0	0
Rut	1	0	1	4.06	876	4.02	406	1.0	116

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113 Quantification of NPs used for electron diffraction. The total amount of nanoparticles that 114 were used to generate the respective electron diffraction patterns was determined by considering 115 the number of particles and the corresponding particle density. For both pristine and wastewater-116 borne Ag-NPs, the particles were simply counted. Due to high levels of agglomeration, the 117 number and mass of TiO2-NPs were estimated by taking into account the total projected area and 118 the modal diameter, the latter of which was determined from a fraction of the sample. Assuming 119 a monolayer of TiO₂-NPs, the results for total mass of TiO₂-NPs are an underestimate (see Table 120 S10).

122 **Table S10.** Quantification of NP number and mass used for electron diffraction.

Sample	Chemical composition	Density [g cm ⁻³]	Number of NPs	Diameter [nm]	Mass of NPs [fg]
Ag-NPs - Pristine	Ag	10.49	164	16.3 ± 1.8	3.94 ± 1.17
Ag-NPs – WWTP	Ag ₂ S	7.22	223	15.4 ± 2.1	3.07 ± 1.24
TiO ₂ -NPs – Pristine	TiO ₂	4.23	96/ 848*	25.1 ± 6.4	29.6 ± 23.0
TiO ₂ -NPs - WWTP	TiO ₂	4.23	106/ 1672*	23.3 ± 5.5	46.7 ± 33.8

123 * estimated

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