



Supplementary information for

Precipitation at Room Temperature as a Fast and Versatile Method for Calcium Phosphate/TiO₂ Nanocomposites Synthesis

Ina Erceg ¹, Atida Selmani ¹, Andreja Gajović ², Borna Radatović ³, Suzana Šegota ¹, Marija Ćurlin ⁴, Vida Strasser ¹, Jasminka Kontrec ⁵, Damir Kralj ⁵, Nadica Maltar-Strmečki ⁶, Rinea Barbir ⁷, Barbara Pem ⁷, Ivana Vinković Vrček ⁷ and Maja Dutour Sikirić ^{1,*}

¹ Laboratory for Biocolloids and Surface Chemistry, Ruđer Bošković Institute, Bijenička Cesta 54, 10 000 Zagreb, Croatia; ierceg@irb.hr (I.E.); aselmani@irb.hr (A.S.); ssegota@irb.hr (S.Š.); Vida.Strasser@irb.hr (V.S.)

² Laboratory for Energy Conversion Materials and Sensors, Ruđer Bošković Institute, Bijenička Cesta 54, 10000 Zagreb, Croatia; gajovic@irb.hr

³ Institute of Physics, Bijenička Cesta 46, 10000 Zagreb, Croatia; bradatovic@ifs.hr

⁴ Department of Histology and Embryology, School of Medicine, University of Zagreb, Šalata 3, 10000 Zagreb, Croatia; marija.curlin@mef.hr

⁵ Laboratory for Precipitation Processes, Ruđer Bošković Institute, Bijenička Cesta 54, 10000 Zagreb, Croatia; lugaric@irb.hr (J.K.); kralj@irb.hr (D.K.)

⁶ Laboratory for Magnetic Resonances, Ruđer Bošković Institute, Bijenička cesta 54, 10000 Zagreb, Croatia; nstrm@irb.hr

⁷ Institute for Medical Research and Occupational Health, Ksaverska Cesta 2, Zagreb, 10000, Croatia; rbarbir@imi.hr (R.B.); bpem@imi.hr (B.P.); ivinkovic@imi.hr (I.V.V.)

* Correspondence: sikiric@irb.hr; Tel.: +385-1-456-0941

Content of listed material:

Figure SI 1. Volume size distributions of TiNPLs (a,b) and TiNWs (c,d) in c-SBF (a,c) and anionic reactant solution ($c(\text{Na}_2\text{HPO}_4) = 8 \cdot 10^{-3} \text{ mol dm}^{-3}$, $\text{pH}_{\text{init}} = 7.4$, $\vartheta = (25.0 \pm 0.1)^\circ\text{C}$).

Figure SI 2. Representative pH vs time curves obtained in the control system (without TiO₂ nanomaterials) and in the presence of different concentrations of TiO₂ a) nanoplates (TiNPLs) and b) nanowires (TiNWs). $c(\text{CaCl}_2) = c(\text{Na}_2\text{HPO}_4) = 4 \cdot 10^{-3} \text{ mol dm}^{-3}$, $\text{pH}_{\text{init}} = 7.4$, $\vartheta = (25 \pm 0.1)^\circ\text{C}$.

Table SI 1. Average induction time obtained from pH vs time curves from 3 measurements with standard deviations in the control system (without TiO₂ nanomaterials) and in the presence of different concentrations of TiO₂ nanoplates (TiNPLs) and nanowires (TiNWs). $c(\text{CaCl}_2) = c(\text{Na}_2\text{HPO}_4) = 4 \cdot 10^{-3} \text{ mol dm}^{-3}$, $\text{pH}_{\text{init}} = 7.4$, $\vartheta = (25.0 \pm 0.1)^\circ\text{C}$.

Figure SI 3. SEM micrographs of the calcium deficient hydroxyapatite (CaDHA) formed in control system after 60 min reaction time. $c(\text{CaCl}_2) = c(\text{Na}_2\text{HPO}_4) = 4 \cdot 10^{-3} \text{ mol dm}^{-3}$, $\text{pH}_{\text{init}} = 7.4$, $\vartheta = (25 \pm 0.1)^\circ\text{C}$.

Figure SI 4. Simulated (red) and experimental (dark) EPR spectra of gamma irradiated precipitates formed after 60 min reaction time in control system (calcium deficient hydroxyapatite, CaDHA) and in the presence of 100 mg L⁻¹ TiO₂ nanoplates (CaDHA/TiNPLs), and nanowires (CaDHA/TiNWs).

Table SI 2. EPR spectral parameters extracted by simulation of experimental spectra according to Figures 8 and SI 4 for precipitates formed after 60 min reaction time in control system (calcium deficient hydroxyapatite, CaDHA) and in the presence of 100 mg L⁻¹ TiO₂ nanoplates (CaDHA/TiNPLs), and nanowires (CaDHA/TiNWs).

Figure SI 5. The intensity of DCF fluorescence after incubation in PBS with different concentrations of SIN-1 (NC – negative control; PC – positive control) used for comparison with a) TiO₂ nanoparticles (TiNPs), titanate nanotubes (TiNTs), TiO₂ nanowires (TiNWs), and TiO₂ nanoplates (TiNPLs), and b) precipitates formed after 60 min reaction time in control system (calcium deficient hydroxyapatite, CaDHA) and in the presence of 100 mg L⁻¹ TiO₂ nanoparticles (CaDHA/TiNPs), nanotubes (CaDHA/TiNTs), nanowires (CaDHA/TiNWs), and nanoplates (CaDHA/TiNPLs).

Table SI 3. The percentage of fluorescence quenching and autofluorescence of different concentrations of TiO₂ nanoparticles (TiNPs), titanate nanotubes (TiNTs), TiO₂ nanowires (TiNWs), TiO₂ nanoplates (TiNPLs), and precipitates formed after 60 min reaction time in the control system (calcium deficient hydroxyapatite, CaDHA) and in the presence of 100 mg L⁻¹ TiO₂ nanoparticles (CaDHA/TiNPs), nanotubes (CaDHA/TiNTs), nanowires (CaDHA/TiNWs), and nanoplates (CaDHA/TiNPLs).

Table SI 4. The results of optical interference assay and adsorption assay on different concentrations of TiO₂ nanoparticles (TiNPs), titanate nanotubes (TiNTs), TiO₂ nanowires (TiNWs), TiO₂ nanoplates (TiNPLs), and precipitates formed after 60 min reaction time in the control system (calcium deficient hydroxyapatite, CaDHA) and in the presence of 100 mg L⁻¹ TiO₂ nanoparticles (CaDHA/TiNPs), nanotubes (CaDHA/TiNTs), nanowires (CaDHA/TiNWs), and nanoplates (CaDHA/TiNPLs) in hemolysis test.

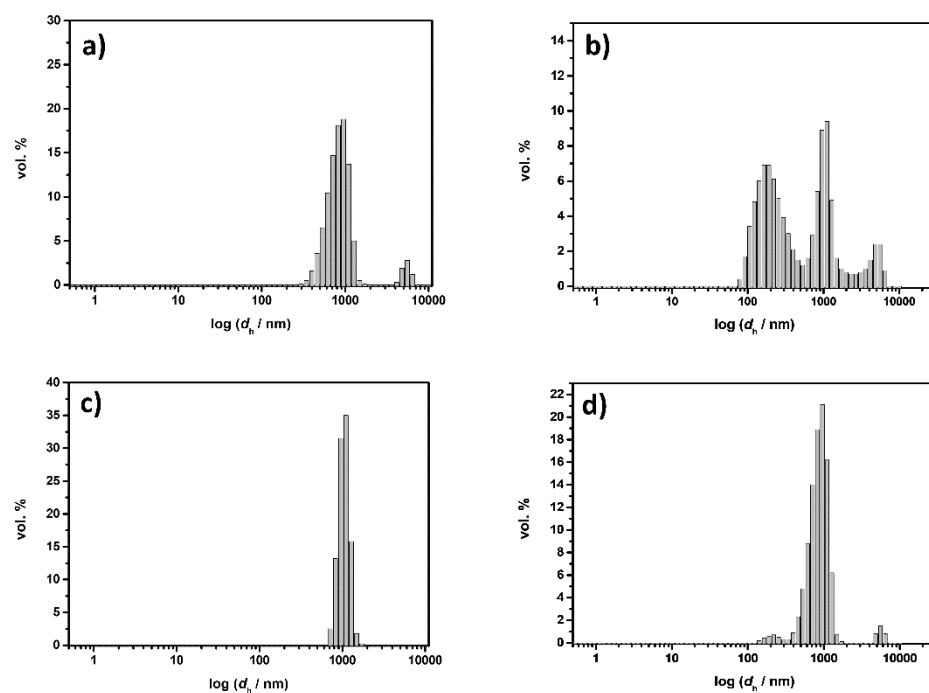


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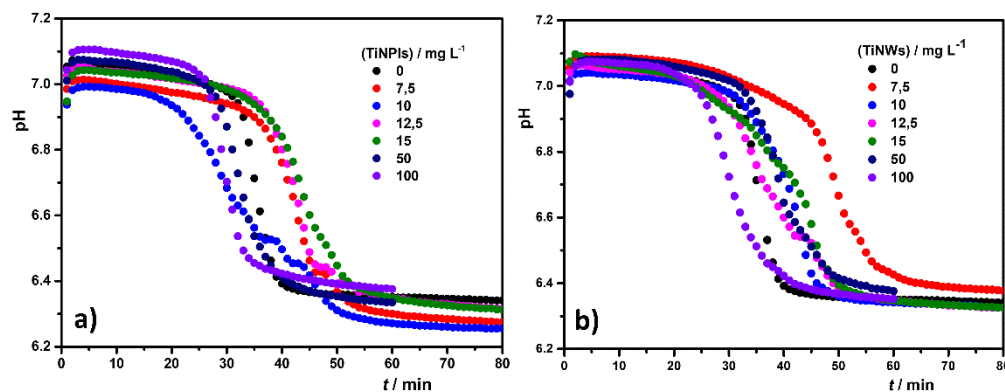


Figure SI 2. Representative pH *vs* time curves obtained in the control system (without TiO₂ nanomaterials) and in the presence of different concentrations of TiO₂ a) nanoplates (TiNPIs) and b) nanowires (TiNWs). $c(\text{CaCl}_2) = c(\text{Na}_2\text{HPO}_4) = 4 \cdot 10^{-3} \text{ mol dm}^{-3}$, $\text{pH}_{\text{init}} = 7.4$, $\vartheta = (25 \pm 0.1) ^\circ\text{C}$.

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$\gamma / \text{mg L}^{-1}$	$t_{\text{ind}} / \text{min}$	
	TiNPIs	TiNWs
0	29.4 ± 3.2	
7.5	36.4 ± 2.0	36.4 ± 4.0
10.0	35.0 ± 4.8	33.7 ± 2.4
12.5	35.8 ± 2.7	24.1 ± 4.5
15.0	36.1 ± 1.0	36.9 ± 2.3
50.0	27.1 ± 0.6	29.2 ± 1.34
100.0	25.3 ± 0.9	23.2 ± 1.6

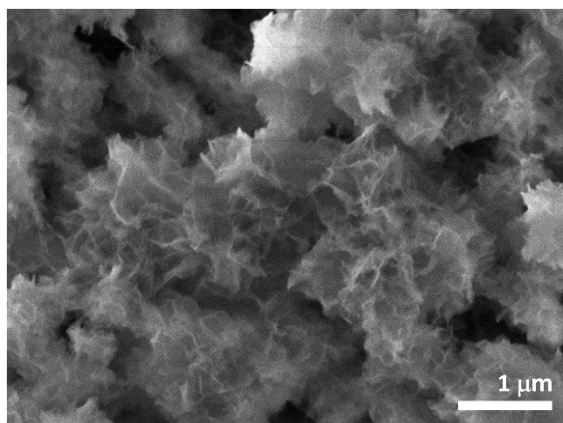


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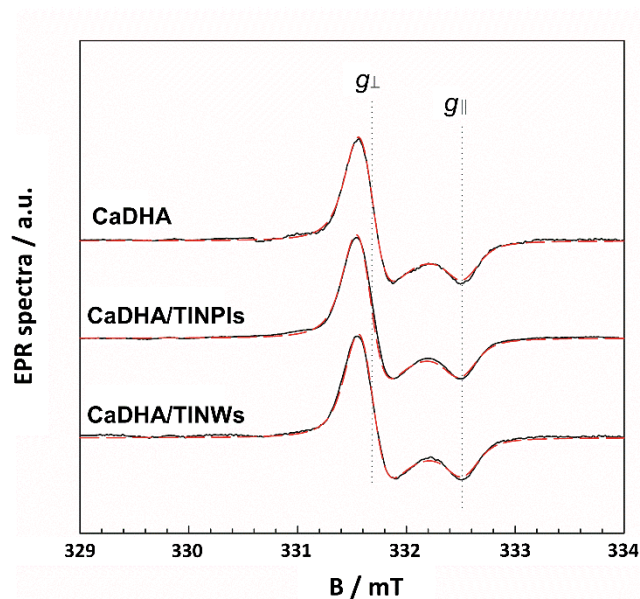


Figure SI 4. Simulated (red) and experimental (dark) EPR spectra of gamma irradiated precipitates formed after 60 min reaction time in the control system (calcium deficient hydroxyapatite, CaDHA) and in the presence of 100 mg L⁻¹ TiO₂ nanoplates (CaDHA/TiNPIs), and nanowires (CaDHA/TiNWs). Extracted spectral parameters are listed in Table SI 2.

Table SI 2. EPR spectral parameters extracted by simulation of experimental spectra according to Figures 8 and SI 4 for precipitates formed after 60 min reaction time in the control system (calcium deficient hydroxyapatite, CaDHA) and in the presence of 100 mg L⁻¹ TiO₂ nanoplates (CaDHA/TiNPIs), and nanowires (CaDHA/TiNWs).

Sample	g_{\perp}	g_{\parallel}	ΔH_{Gpp}^*	ΔH_{Lpp}^*
CaDHA	2.0025	1.9972	0.186	0.125
CaDHA/TiNPIs	2.0025	1.9971	0.186	0.127
CaDHA/TiNWs	2.0026	1.9972	0.186	0.126

*The determined line widths refer to peak-to-peak Gaussian, ΔH_{Gpp} and Lorentzian, ΔH_{Lpp} line shape

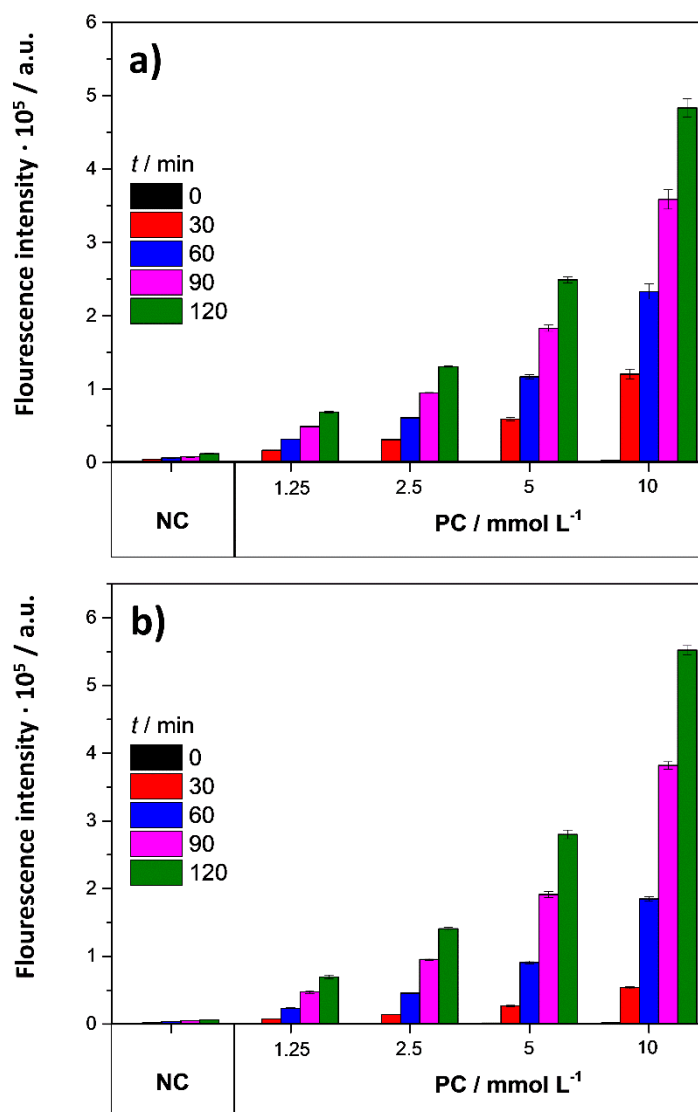


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Nanomaterial	Concentration / mg L ⁻¹	% quenching	% autofluorescence
TiNPs	10	0%	102%
	100	5%	81%
	500	11%	86%
TiNTs	10	1%	101%
	100	11%	73%
	500	14%	67%
TiNWs	10	5%	227%
	100	23%	68%
	500	31%	75%
TiNPIs	10	1%	106%
	100	3%	97%
	500	6%	81%
CaDHA	10	4%	106%
	100	16%	71%
	500	21%	32%
CaDHA/TiNPs	10	1%	117%
	100	17%	53%
	500	31%	17%
CaDHA/TiNTs	10	1%	113%
	100	12%	71%
	500	27%	55%
CaDHA/TiNWs	10	5%	99%
	100	26%	31%
	500	30%	14%
CaDHA/TiNPIs	10	5%	104%
	100	15%	59%
	500	32%	18%

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Material	Concentration (mg/L)	% absorbance (optical interference test)	% Hb recovery (adsorption test)
Blank (PBS)		100.00 ± 0.79%	100.00 ± 2.47%
Negative control (PEG)		N.A.	N.A.
Positive control (Triton)		N.A.	N.A.
TiNPs	10	98.73 ± 10.06%	87.21 ± 5.49%
	100	88.37 ± 10.40%	89.04 ± 5.61%
	500	100.61 ± 2.42%	98.30 ± 2.22%
TiNTs	10	96.30 ± 0.60%	97.78 ± 2.30%
	100	96.42 ± 6.39%	100.09 ± 1.82%
	500	107.33 ± 5.72%	98.99 ± 0.02%
TiNWs	10	97.93 ± 4.93%	106.27 ± 7.25%
	100	105.51 ± 3.68%	104.00 ± 1.76%
	500	101.38 ± 3.17%	99.61 ± 1.11%
TiNPIs	10	96.49 ± 4.20%	95.73 ± 0.45%
	100	100.67 ± 7.02%	94.44 ± 7.52%
	500	94.36 ± 7.91%	100.15 ± 2.92%
CaDHA	10	98.96 ± 0.58%	107.88 ± 9.39%
	100	101.49 ± 2.18%	104.46 ± 5.78%
	500	100.98 ± 0.88%	104.52 ± 5.04%
CaDHA/TiNPs	10	99.72 ± 1.14%	85.72 ± 7.00%
	100	108.46 ± 7.31%	99.71 ± 2.68%
	500	101.44 ± 2.15%	97.09 ± 1.66%
CaDHA/TiNTs	10	99.93 ± 1.12%	93.14 ± 4.16%
	100	102.63 ± 1.66%	94.33 ± 5.62%
	500	106.04 ± 4.64%	98.04 ± 0.55%
CaDHA/TiNWs	10	100.61 ± 1.52%	106.14 ± 3.21%
	100	104.66 ± 5.03%	95.19 ± 1.80%
	500	111.54 ± 9.69%	101.74 ± 0.68%
CaDHA/TiNPIs	10	100.73 ± 0.93%	107.91 ± 5.07%
	100	107.18 ± 1.65%	92.96 ± 1.91%
	500	104.49 ± 1.93%	106.54 ± 5.17%