

Accelerated bioactive behavior of Nagelschmidtite bioceramics: Mimicking the nano and microstructural aspects of biological mineralization

Figure 1. Microstructural characteristics at different magnifications of Nagel ceramics (a,b) before and after (c,d) 6 days of immersion in Hank's solution.

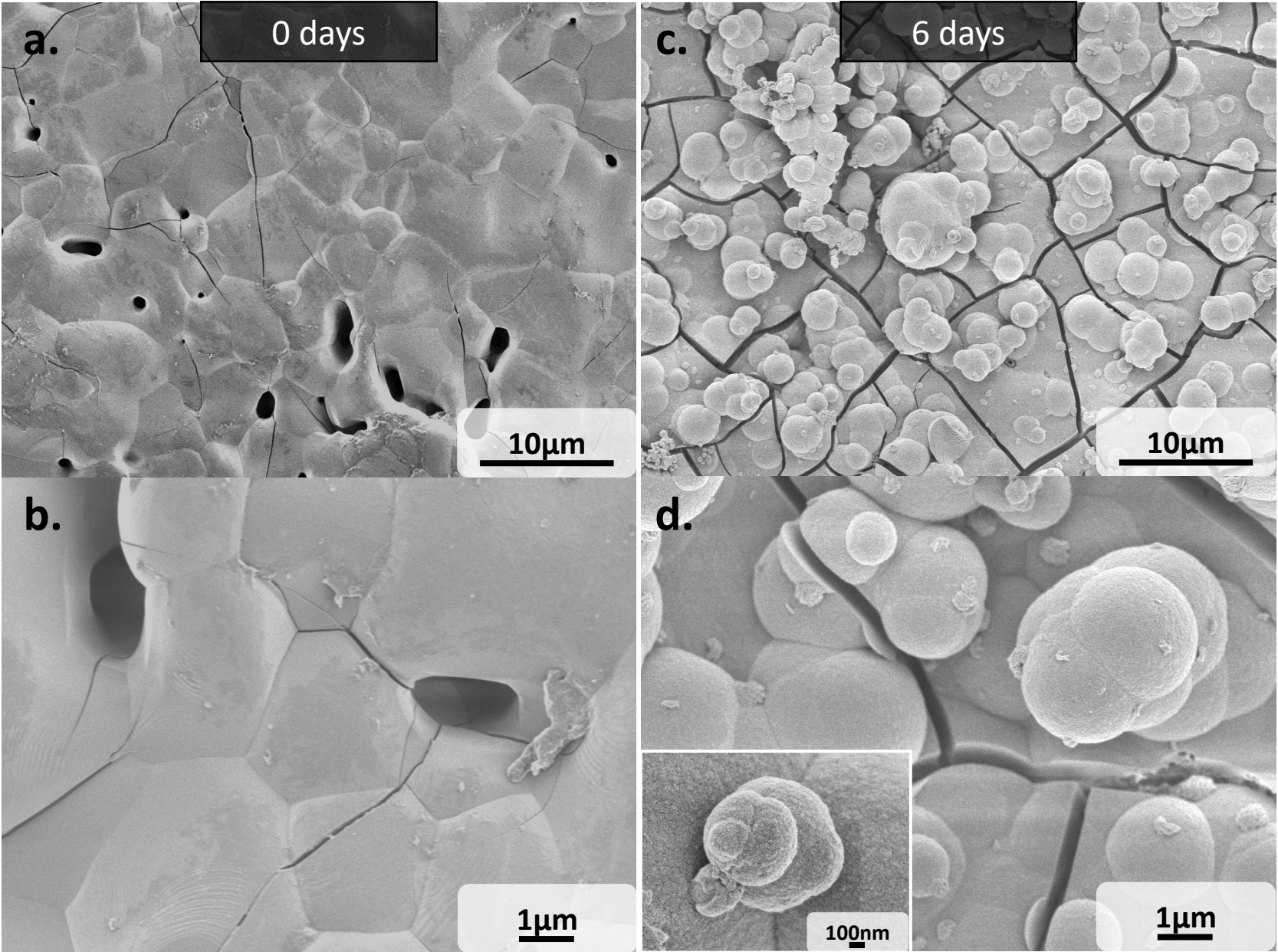


Figure 2. Morphological features of the apatite layer growth on Nagel ceramics after 14 days of immersion in Hank's solution. a) Ceramic's surface covered by crystals with different morphologies, in a closer look (b, c) worm-like and needle-like structures were identified. d) Cross-section of the apatite layer indicating the composition of the crystals.

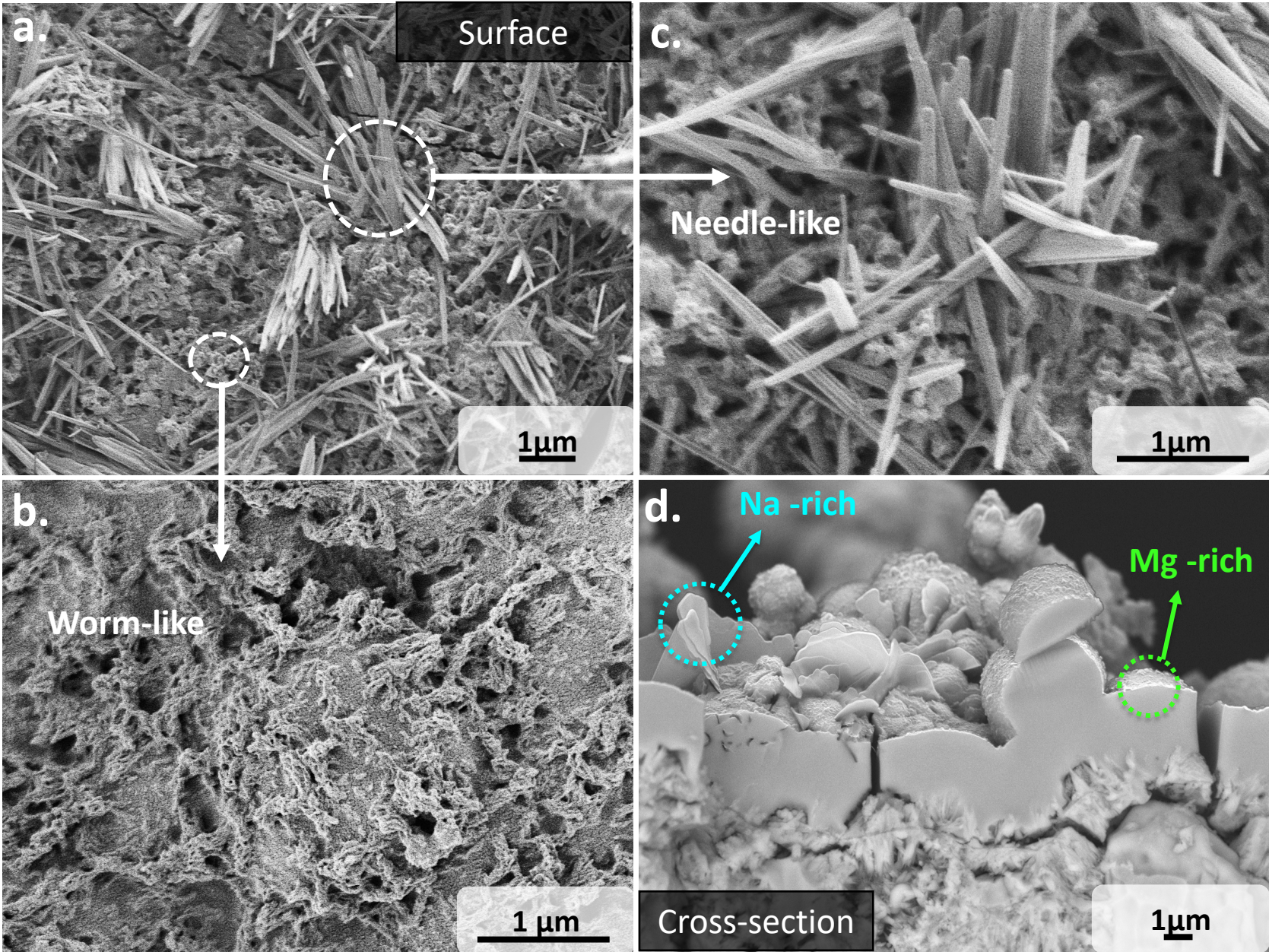


Figure 3. SEM micrographs at the (a,b) surface and (c) cross-section of the apatite layer formed on Nagel ceramics after 28 days of exposure to Hank's solution.

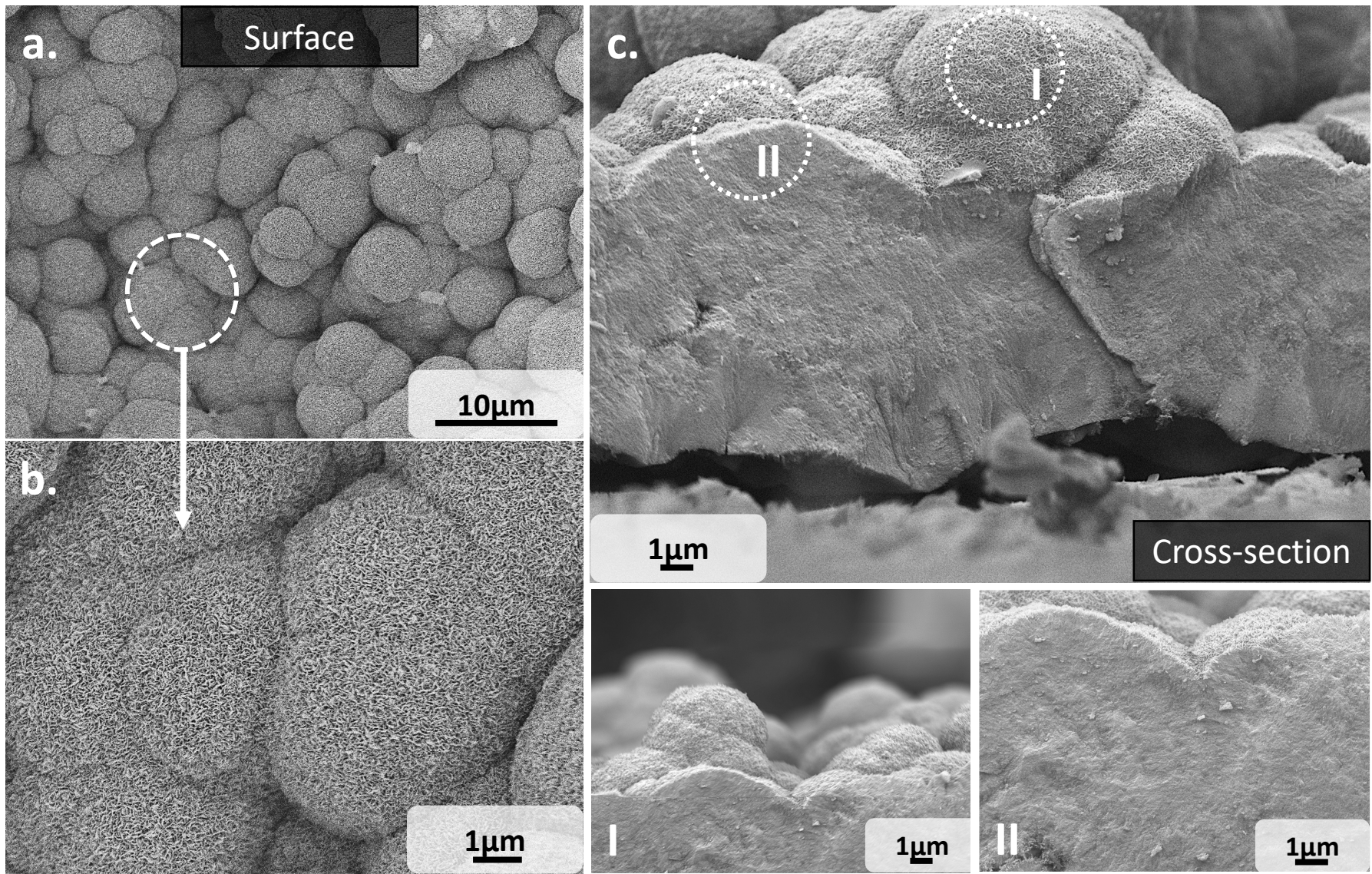


Figure 4. a) XRD pattern, b) inset and c) Rietveld refinement adjust of Nagel ceramics after 0, 6, 14, 21 and 28 days of immersion in Hank's solution.

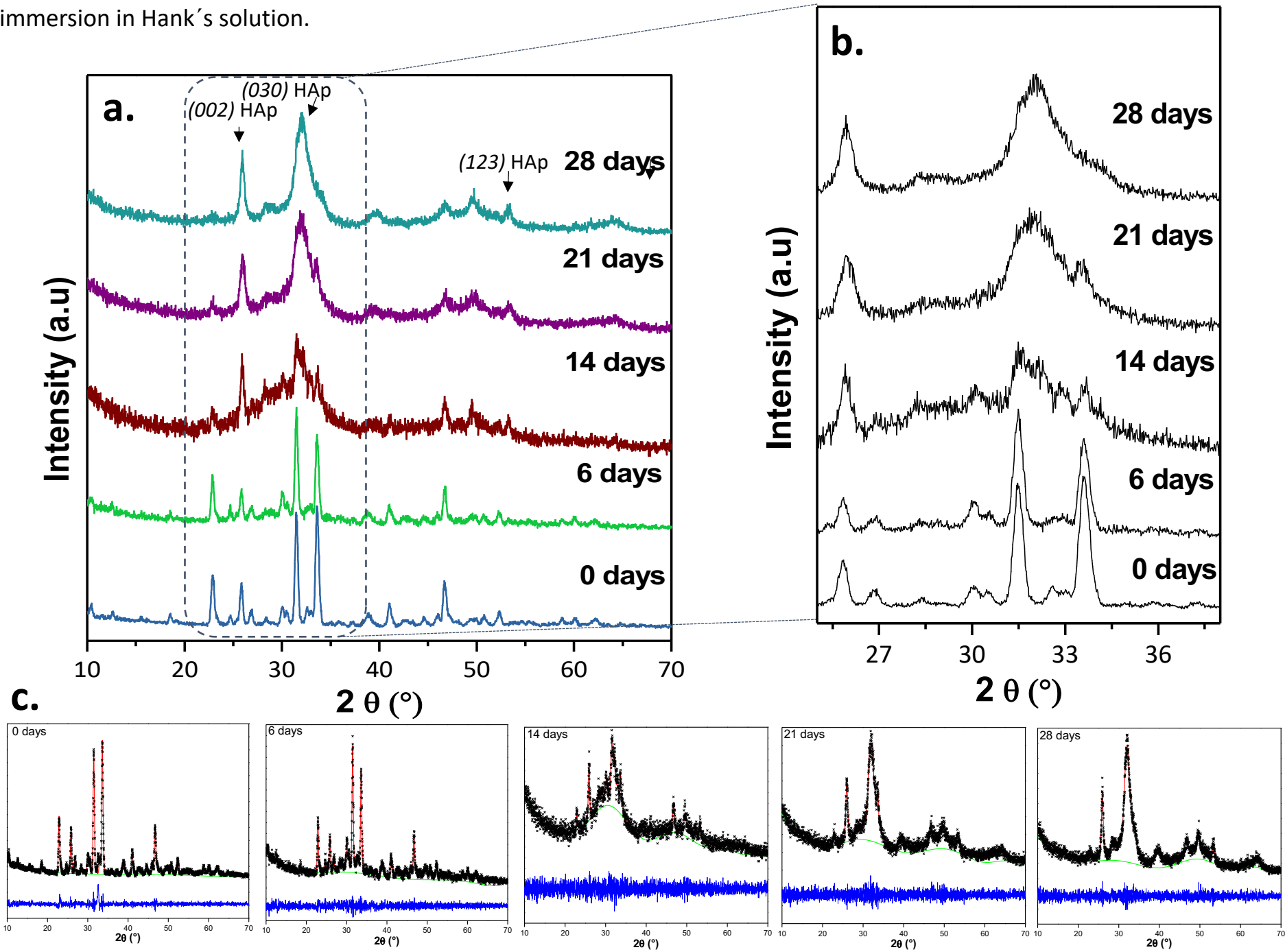


Figure 5. *a,b*) High resolution TEM and Inverse FFT (inset in *b*) images and *c*) electron transmission diffraction pattern of Nagel before bioactivity test.

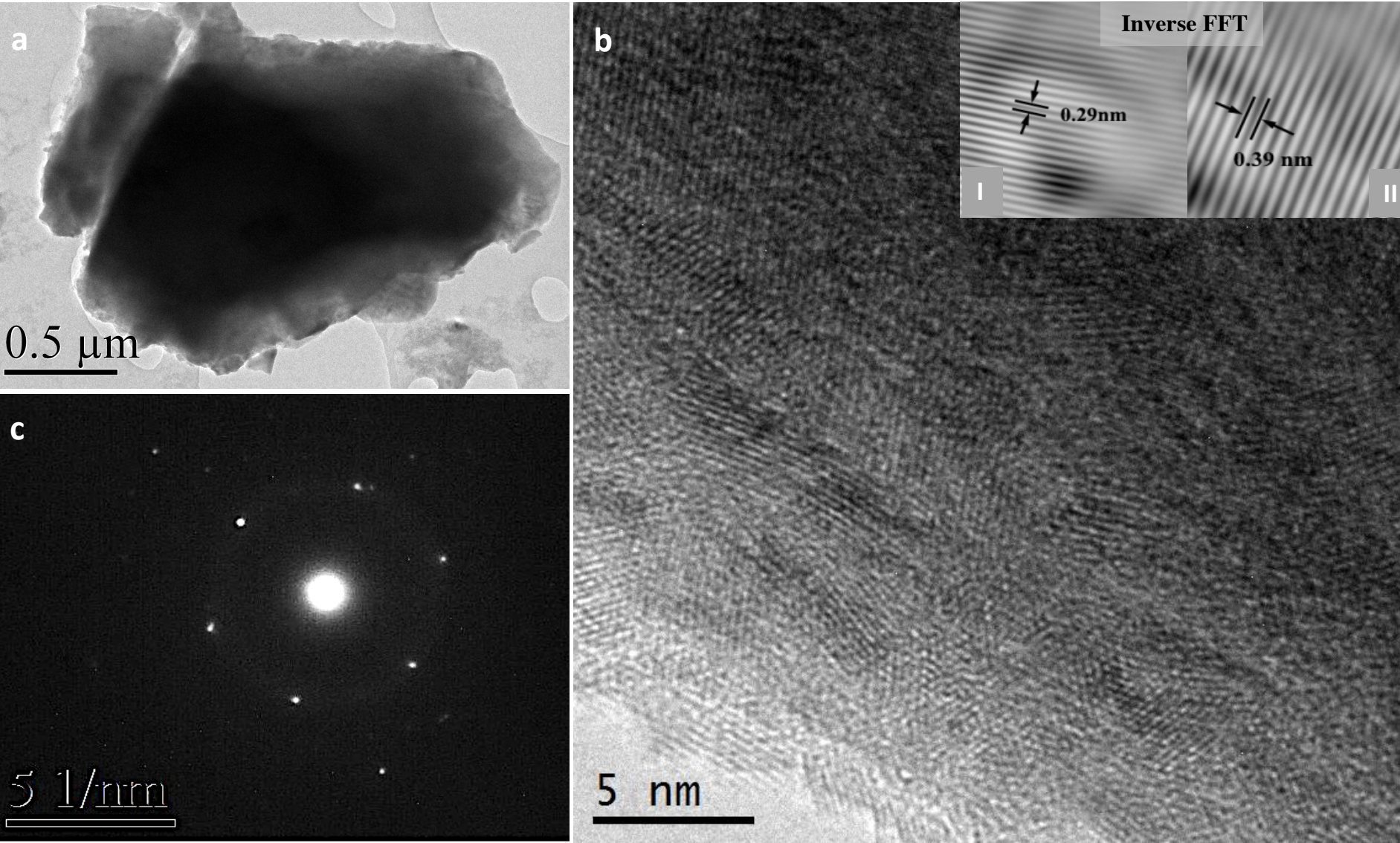


Figure 6. High resolution TEM images of Nagel after 6 days of exposure in Hank's solution, showing in a) morphology of the particles composed by b) overlapping crystal layers.

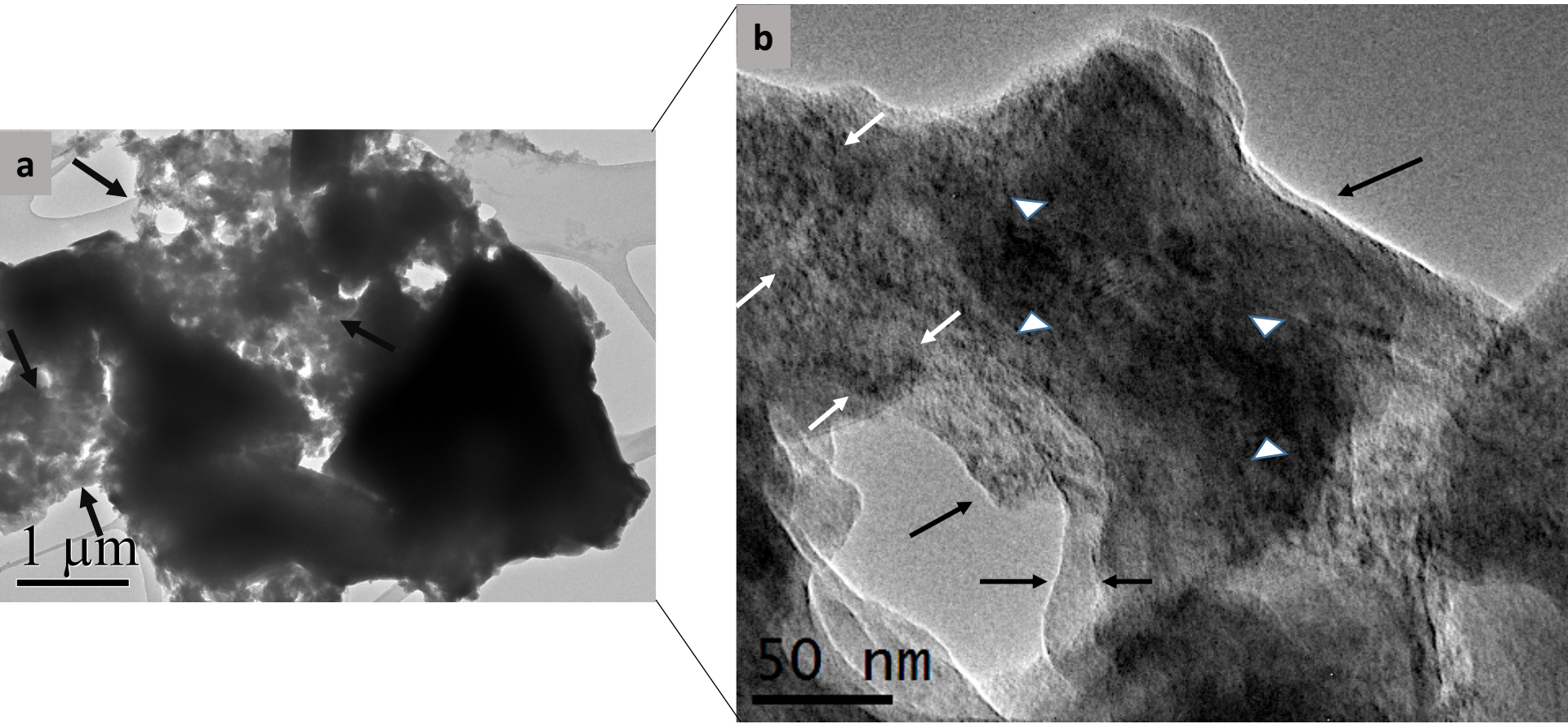


Figure 7. High resolution TEM images of Nagel after 6 days of exposure in Hank's solution, showing in a) layer-by-layer growth, b–d) nanocrystals randomly distributed with 2 different lattice fringes (IFFT insets I–II in d)) and FFT image of a zone in b)

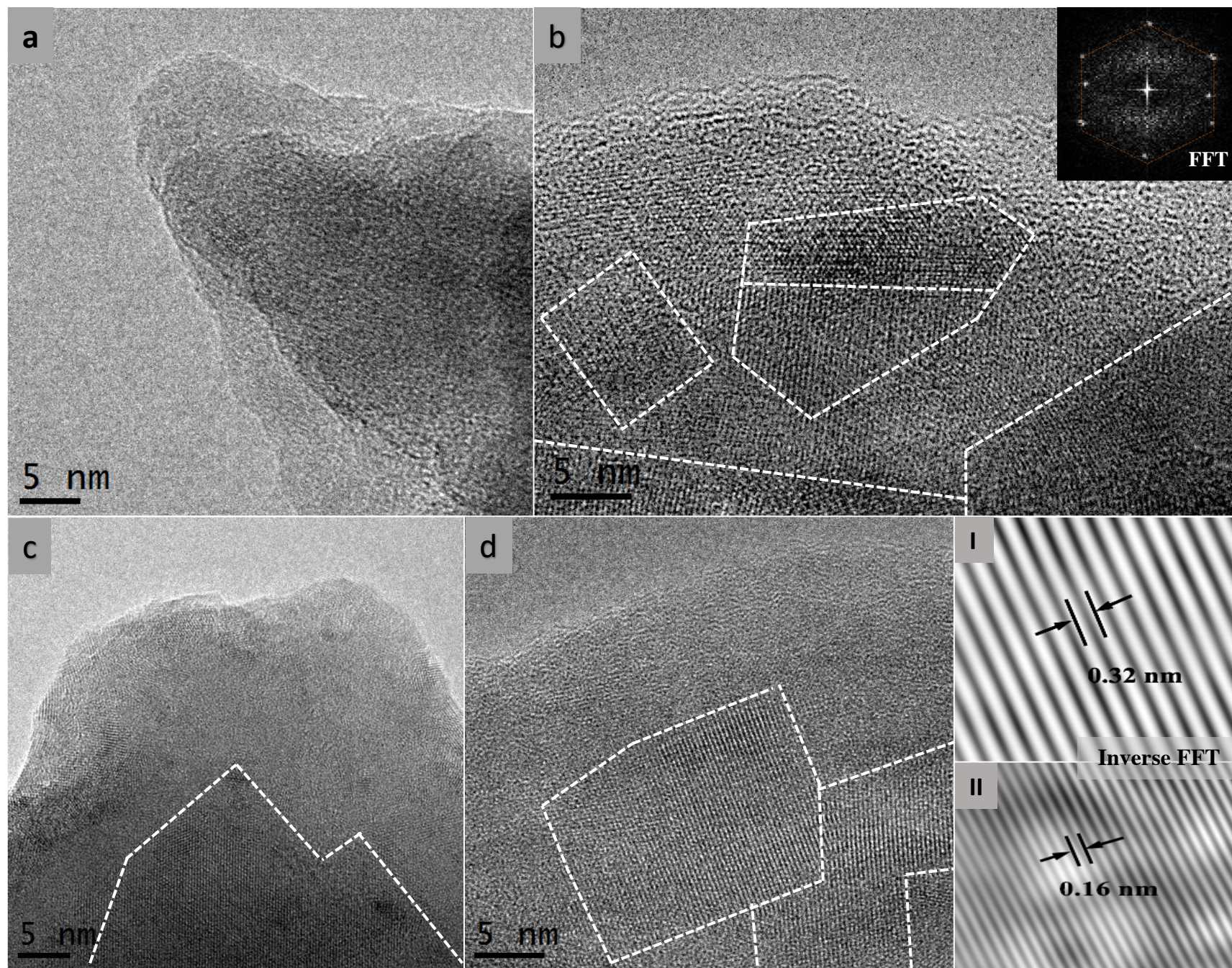


Figure 8. *a, b) High resolution TEM images of different areas from Nagel particles after 28 days of immersion. c) SAED pattern of a)*

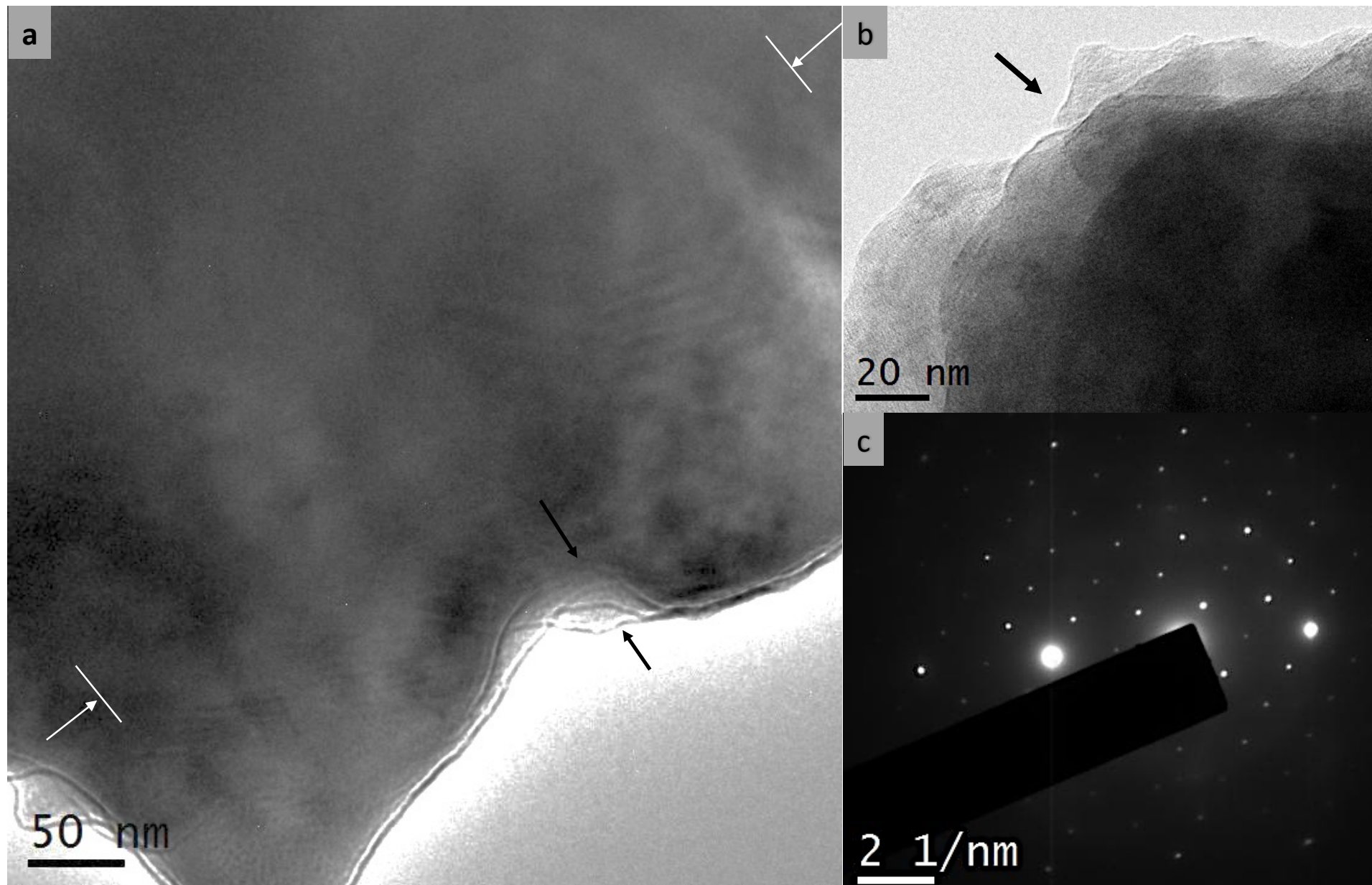


Figure 9. a) High resolution TEM image of Nagel particles after 28 days of Immersion (inside of figure 8a). b-c) Inverse FFT of different zones in a.

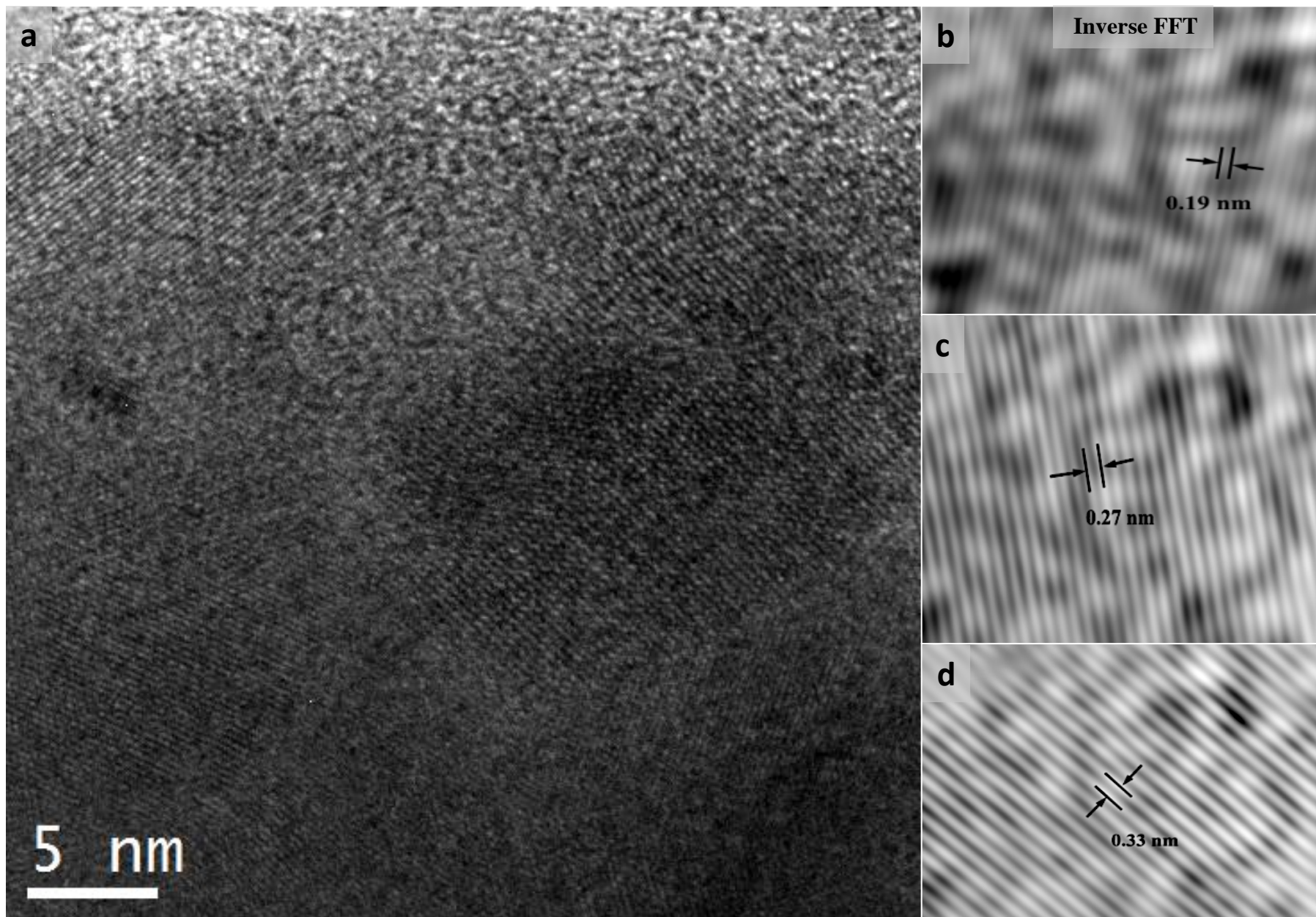


Figure 10. Raman spectra of Nagel ceramics after 0, 6, 14, 21 and 28 days of immersion in Hank's solution.

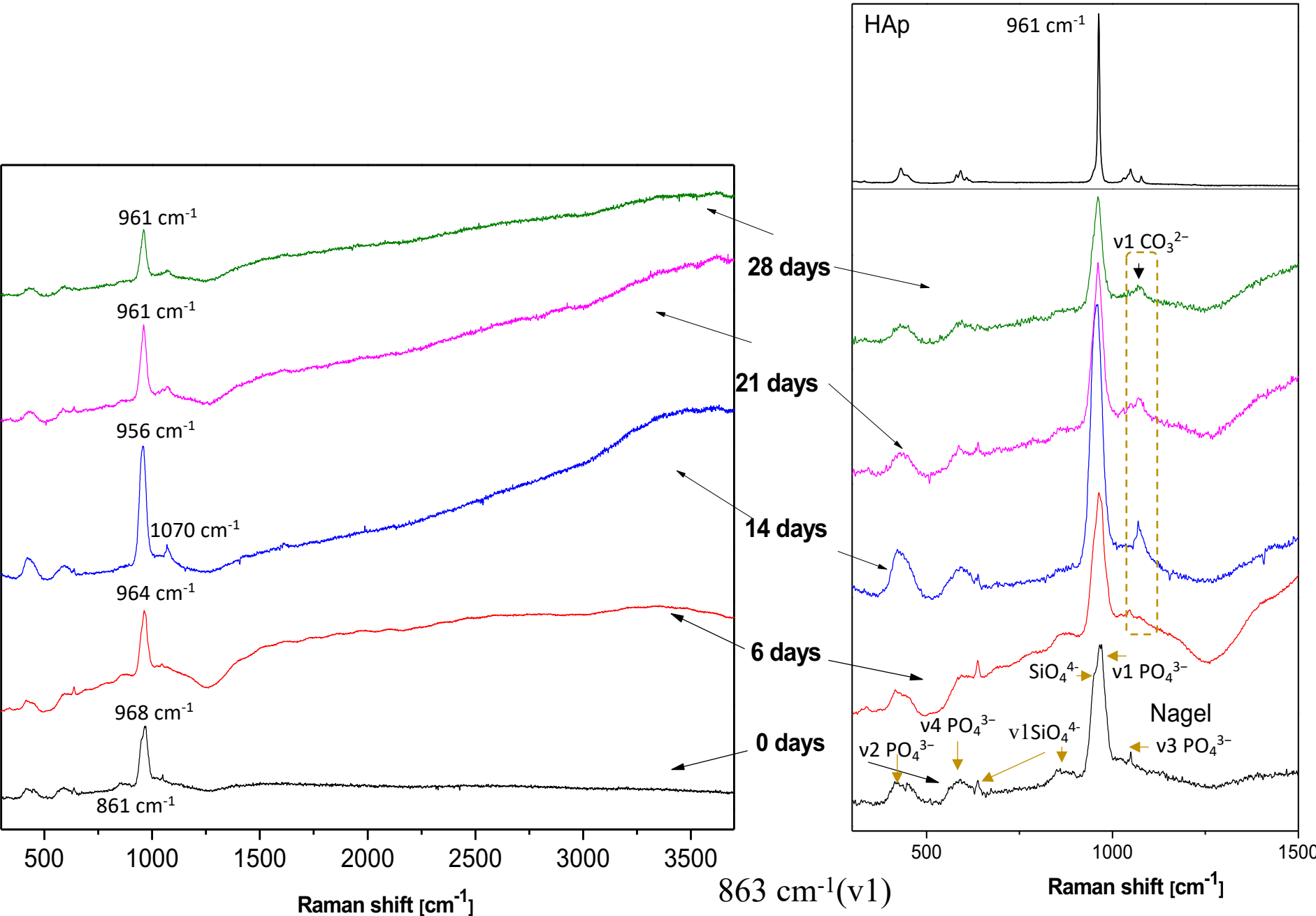


Table 1. Chemical composition by EDX analysis of Nagel ceramics after 0, 6, 14 and 28 days. Composition of stoichiometric Hap is included for comparative purposes

SEM /EDX (wt.%)						
Sample	O	Na	Mg	Si	P	Ca
Control	43.550 ± 2.474	7.420 ± 2.166	0.692 ± 0.239	3.335 ± 0.171	15.544 ± 0.779	29.457 ± 2.963
6 days	46.770 ± 2.394	1.267 ± 0.100	5.418 ± 0.525	0.167 ± 0.128	19.924 ± 0.930	26.423 ± 1.806
14 days (needle-like)	47.201 ± 1.695	26.290 ± 1.328	1.936 ± 0.063	-	10.057 ± 0.492	14.513 ± 0.994
14 days (plate-like)	44.471 ± 0.410	22.312 ± 0.138	2.130 ±0.304	0.426 ± 0.128	13.358 ± 0.798	17.261 ± 0.857
14 days (worm-like)	49.947 ± 1.857	4.714 ± 1.387	3.847 ± 0.050	-	16.355 ± 0.298	25.062 ± 0.118
28 days	37.881 ± 0.590	3.537 ± 1.351	1.272 ± 0.202	1.062 ± 0.677	20.892 ± 0.133	35.320 ± 2.503
Stoichiometric HAp	41.407				18.499	39.895

Table 2. Lattice Parameters, Crystallite Size, Cell Volume, Ca/P Ratio, Goodness Coefficient (χ^2) and Structure Factor (R_f) Obtained from Rietveld Refinement, for BHAp and BHAp/Nagel Composite Samples before and after Immersion

Sample	Immersion days	Phase	% Wt phase	a = b (Å)	c (Å)	% a=b strain	% c strain	Crystallite size (nm)	Volume (Å ³)	Ca+Na/P+Si	χ^2	R_f
Nagel Theoretical values	-	-	-	10.636	21.642	-	-	-	2448.263	1.750	-	-
HAp Theoretical values	-	-	-	9.432	6.881	-	-	-	612.152	1.670	-	-
Experimental values	0	Nagel	100	10.676	21.622	-0.371	0.094	1725.894	2134.000	1.866	1.95	0.05
	6	Nagel	89.762	10.677	21.629	-0.386	0.061	1088.557	2135.410	1.655	1.31	0.09
		HAp	10.238	9.243	6.715	2.007	2.410	76.764	496.816	1.940		
	14	Nagel	49.962	10.663	21.668	-0.254	-0.119	199.425	2133.594	1.851	1.18	0.10
		HAp	50.038	9.439	6.877	-0.073	0.065	472.874	530.575	2.088		
	21	Nagel	34.386	10.717	21.888	-0.763	-1.137	110.138	2177.254	2.167	1.22	0.06
		HAp	65.614	9.455	6.877	-0.248	0.062	136.009	532.465	1.955		
	28	HAp	100	9.456	6.883	-0.252	-0.035	247.486	532.748	1.604	1.18	0.07

^a χ^2 : Goodness coefficient. R_f : Structure factor. % strain = ((Theoretical value - Experimental value) / Theoretical value) x 100

Table 3. Ionic concentrations in ppm after Nagel degradation tests.

Tris solution			Hank's solution	
<i>Ionic species</i>	<i>0 hours</i>	<i>120 hours</i>	<i>0 hours</i>	<i>120 hours</i>
[Ca]	0.514 ± 0.118	6.998 ± 0.102	51.513 ± 1.583	48.255 ± 1.390
[Si]	0.142 ± 0.004	15.704 ± 0.057	0.321 ± 0.156	16.290 ± 0.030
[Mg]	0.175 ± 0.039	0.632 ± 0.002	20.148 ± 0.416	11.614 ± 0.020
[P]	0.709 ± 0.189	7. 042 ± 0.070	25.791 ± 0.682	15.295 ± 3.512
[Na]	5.653 ± 3.763	269.259 ± 1.584	3298.687 ± 50.358	2432.068 ± 38.609