

# Supporting Information

## Interfacial Water Induced Formation of Amorphous PbCrO<sub>4</sub> Nanoparticles in Water-in-Oil Microemulsions

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## 18 **Experimental Methods**

19 Water-in-oil microemulsions were prepared by mixing appropriate amounts of the nonionic  
20 surfactants C<sub>12</sub>E<sub>5</sub> (pentaethyleneglycol monododecylether, M<sub>w</sub> = 406.61 g/mol, ≥ 98%, Sigma-  
21 Aldrich) or C<sub>12</sub>E<sub>4</sub> (tetraethyleneglycol monododecylether, M<sub>w</sub> = 362.54 g/mol, ≥ 98%, Sigma-  
22 Aldrich), aqueous phase, and *n*-hexane (>99.0% Fluka) as oil. Salts Pb(CH<sub>3</sub>COO)<sub>2</sub> (Fluka) and  
23 Na<sub>2</sub>CrO<sub>4</sub> (Fluka) that were employed to prepare the aqueous salt solutions, were purchased at  
24 their highest commercially available grade. All chemicals were used as obtained. Ultrapure water  
25 was prepared using a Millipore purification unit (Milli-Q).

26 The synthesis was performed by solubilizing aqueous solutions of either Pb(CH<sub>3</sub>COO)<sub>2</sub> or  
27 Na<sub>2</sub>CrO<sub>4</sub> in a reverse micellar solution of surfactants (C<sub>12</sub>E<sub>5</sub> or C<sub>12</sub>E<sub>4</sub>) in the oil phase (*n*-hexane)  
28 in a capped test tube at room temperature and 1 atm pressure. The concentration of surfactants in  
29 the oil phase was kept constant at 13.6 wt%, and the salt concentration of the aqueous solution  
30 was 0.3 M with variable water-to-surfactant ratios *W/S* (molar ratio). The sealed test tubes for  
31 reactions were placed in a thermostatted water bath at 33 °C. To follow the morphogenesis of the  
32 PbCrO<sub>4</sub> nanoparticles, small amounts were periodically collected from the continuously stirred  
33 reacting microemulsion, for inspection by TEM. In order to minimize the drying effect in  
34 preparing the specimen on the TEM grids, we put one drop of particle solution onto a copper grid  
35 and then quickly dried the grid by putting it in an oven at 50 °C. The solvent is volatile hexane,  
36 so the evaporation of solvent is done in a few seconds.

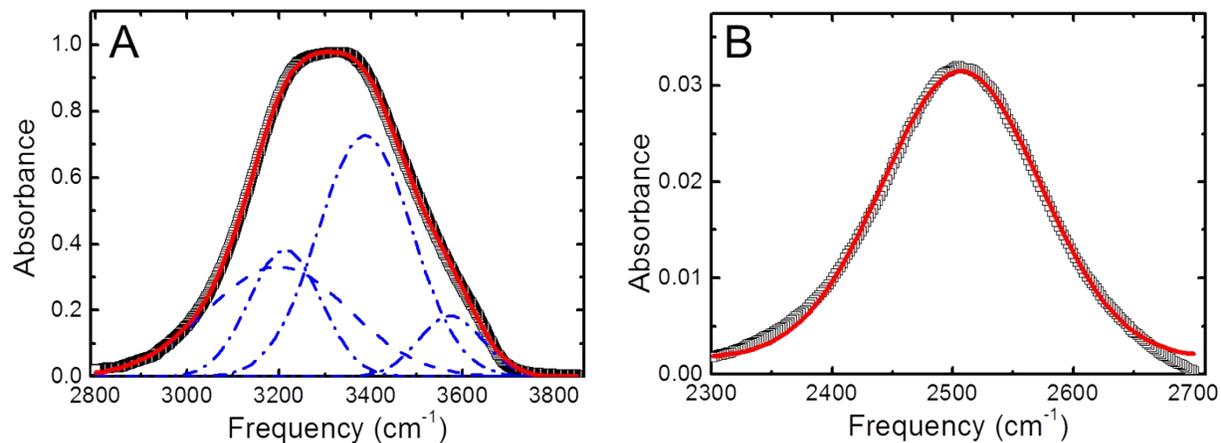
37 The instrument that has been used to study the morphology of the nanoparticles is a Zeiss  
38 LIBRA120 transmission electron microscope operated at 120 kV, equipped with a Gatan  
39 Ultrascan 1000 2k x 2k CCD camera.

40 Transmission FTIR spectra were acquired on an IFS 66v-A Bruker spectrometer. A liquid cell  
41 with CaF<sub>2</sub> windows (Specac) and a Teflon spacer with a typical thickness of 0.5 mm were used.  
42 In order to obtain a good quality of the spectra, 1024 scans were accumulated with a selected  
43 resolution of 4 cm<sup>-1</sup>. The temperature was controlled by circulating thermostated water through  
44 the mounting holder of the cell. Due to the high quality of the spectra, no smoothing techniques  
45 are needed. The spectra have been handled and analyzed by the commercial PC programs  
46 GRAMS/386 (Galactic Industries Corporation, Salem, USA) and RAZOR (Spectrum Square  
47 Associates, Ithaca, USA) run under GRAMS/386. Sample solutions were made by adding 2.5%  
48 (by weight) of D<sub>2</sub>O (99.90 atom % <sup>2</sup>H, and purchased from Merck (Germany)) relative to H<sub>2</sub>O  
49 (H<sub>2</sub>O + D<sub>2</sub>O = 2HDO, *K*~4) and reference samples by adding the same amounts of pure H<sub>2</sub>O.  
50 The purpose of using spectra of isotopically diluted HDO, instead of H<sub>2</sub>O, is to prevent a number  
51 of experimental and interpretative problems caused by complicated H<sub>2</sub>O spectra.<sup>1-3</sup> As shown in  
52 Figure S1, the OH-stretching spectrum of H<sub>2</sub>O (~ 3300 cm<sup>-1</sup>) has to be fit by four deconvolution  
53 peaks, namely symmetric and asymmetric stretching modes in both “close water” and “open  
54 water”,<sup>4</sup> while the spectrum of diluted HDO molecules in the OD-stretching region (~ 2500 cm<sup>-1</sup>)  
55 can be easily fit with one stretching mode of Gaussian peak. This will reasonably simplify the  
56 analysis of the microstructures of water confined in the micellar droplets. All the FTIR data for  
57 the microemulsions presented here have the same conditions as those for reactions, e.g. T=33 °C,  
58 13.6 wt% of surfactant concentration.

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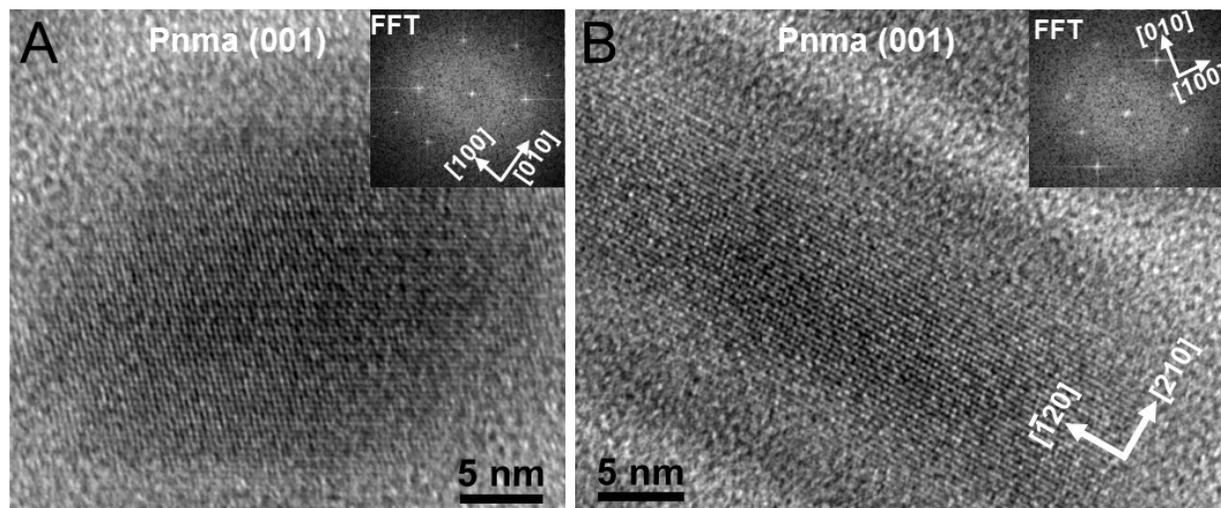
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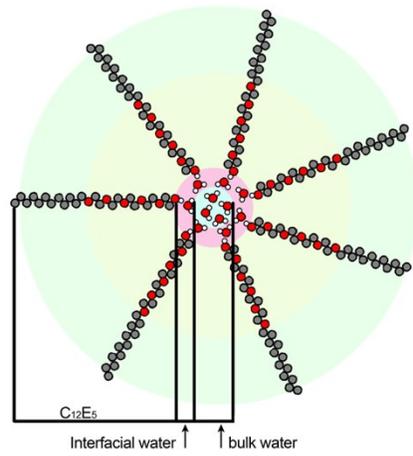
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63 **Figure S1.** FTIR spectra of H<sub>2</sub>O (OH stretching band) (A) and 5% HDO in H<sub>2</sub>O (OD stretching  
 64 band) (B). Red Solid lines are the Gaussian fits and blue dash-dot lines are 4 deconvolution  
 65 peaks for the fit.

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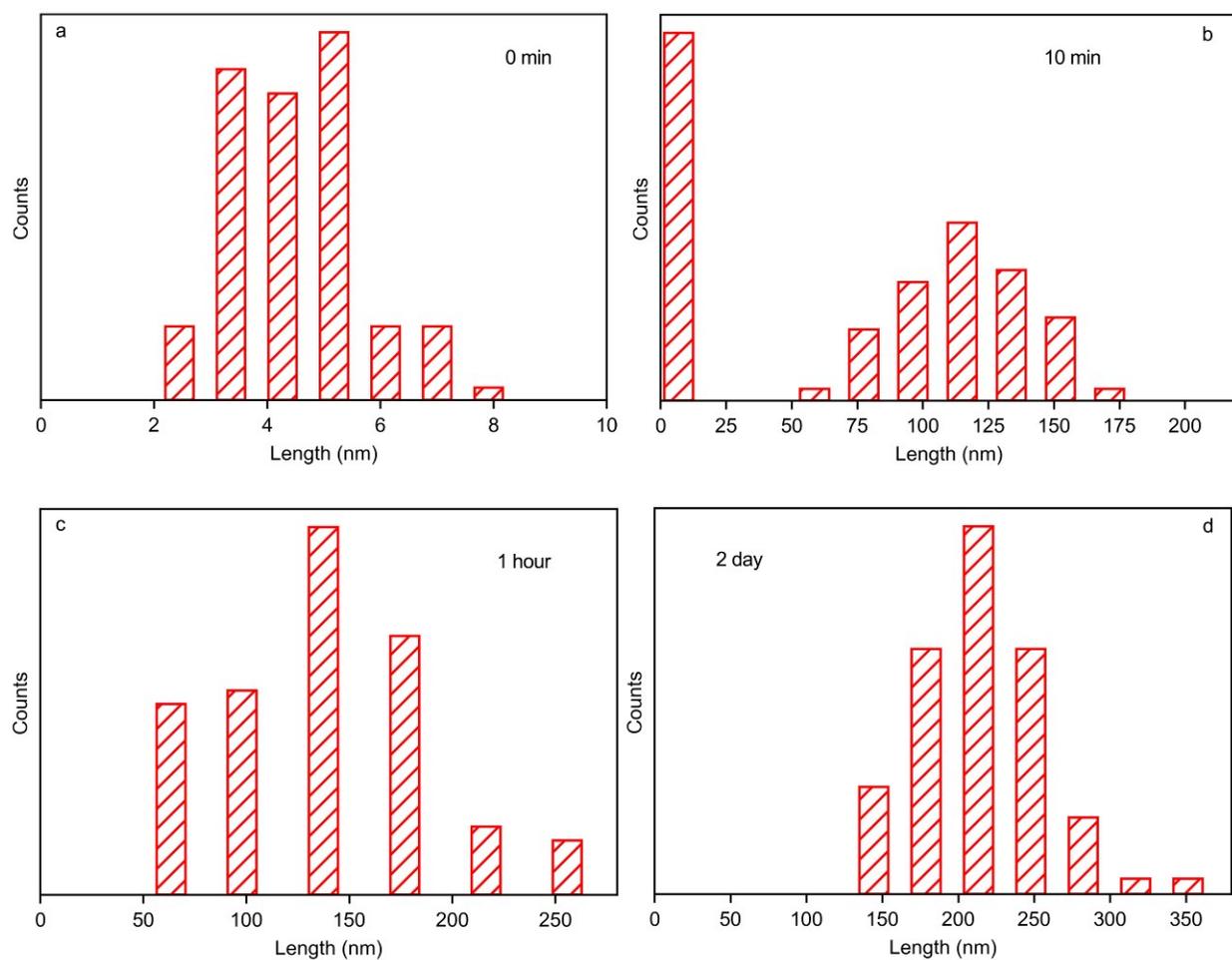


67 **Figure S2.** High resolution TEM images of PbCrO<sub>4</sub> nanoparticles in the C<sub>12</sub>E<sub>5</sub> microemulsion of  
 68 W/S=5 at 1 min (A) and 2 h (B). The insets are the corresponding Fourier transformation (FFT)  
 69 on the single particles. The space group Pnma, and indices of crystal faces and zone axes are  
 70 presented.



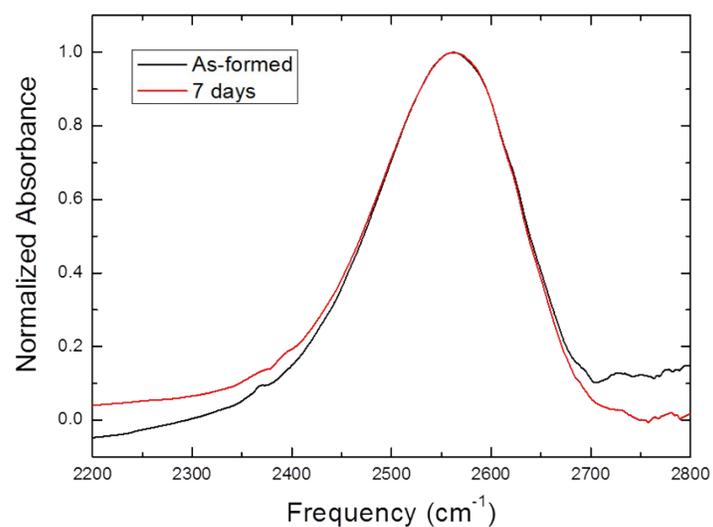
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72 **Figure S3.** Structural scheme of a  $C_{12}E_5$  reverse micelle. The surfactant molecules form a  
73 saturated monolayer around the interior water droplets and the polyethylene oxide chains of the  
74 surfactant do not penetrate into the water volume.<sup>5</sup>



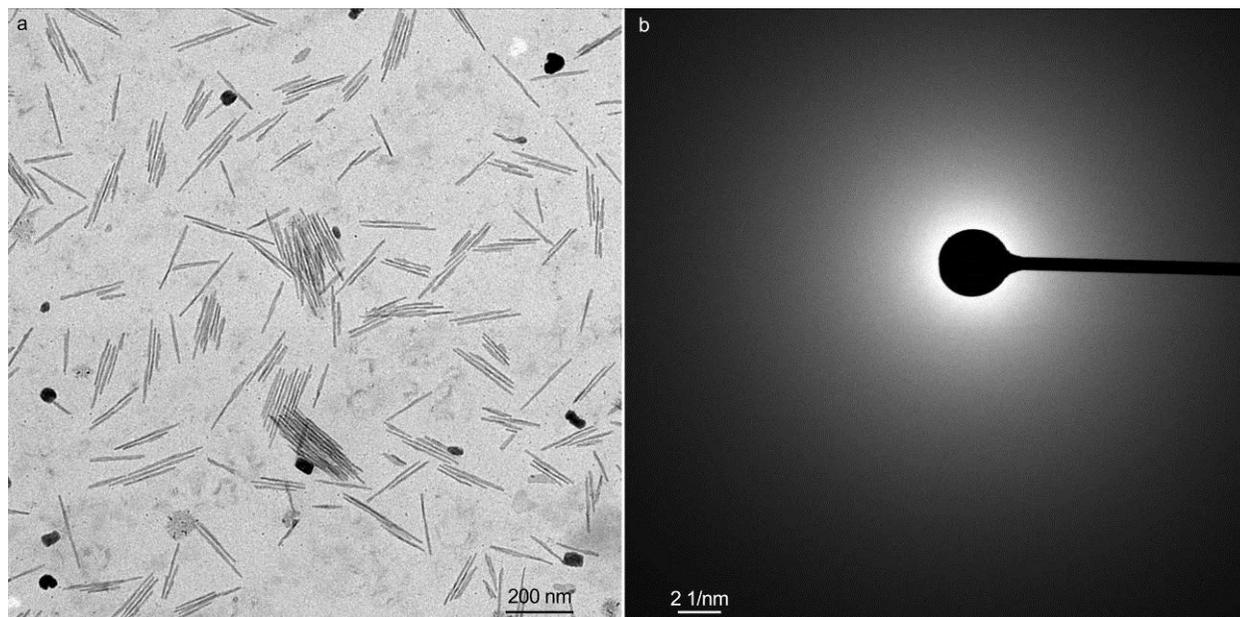
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76 **Figure S4.** Particle size distribution histograms of amorphous  $\text{PbCrO}_4$  particles in the  
 77 microemulsion of  $W/S=1.25$  at different reaction times: 0 min (a), 10min (b), 1 h (c), and 2 d (d).



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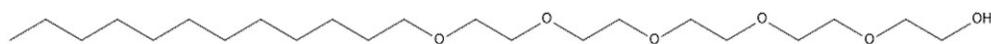
79 **Figure S5.** Normalized FTIR spectra of the OD stretching bands for C<sub>12</sub>E<sub>5</sub> microemulsions of  
80 W/S = 1.25 after storage for seven days.



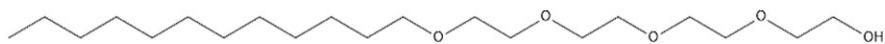
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82 **Figure S6.** TEM images of PbCrO<sub>4</sub> nanoparticles and the corresponding SAD pattern in the  
83 microemulsions at W/S=1.25 for seven days.

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C<sub>12</sub>E<sub>5</sub>



C<sub>12</sub>E<sub>4</sub>

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86 **Figure S7.** Chemical structures of C<sub>12</sub>E<sub>5</sub> and C<sub>12</sub>E<sub>4</sub>.

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88 REFERENCES

- 89 (1) Waldron, R. D. Infrared Spectra of HDO in Water and Ionic solutions. *J. Chem. Phys.* **1957**,  
90 26, 809–814.
- 91 (2) Hornig, D. F. On the Spectrum and Structure of Water and Ionic Solutions. *J. Chem. Phys.*  
92 **1964**, 40, 3119–3120.
- 93 (3) Falk, M.; Ford, T. A. Infrared Spectrum and Structure of Liquid Water. *Can. J. Chem.* **1966**,  
94 44, 1699–1707.
- 95 (4) D'Arrigo, G.; Maisano, G.; Mallamace, F.; Migliardo, P.; Wanderlingh, F. Raman Scattering  
96 and Structure of Normal and Supercooled Water. *J. Chem. Phys.* **1981**, 75, 4264–4270.
- 97 (5) van der Loop, T. H.; Panman, M. R.; Lotze, S.; Zhang, J.; Vad, T.; Bakker, H. J.; Sager, W.  
98 F. C.; Woutersen, S., Structure and dynamics of water in nonionic reverse micelles: A combined  
99 time-resolved infrared and small angle x-ray scattering study. *J. Chem. Phys.* **2012**, 137 (4),  
100 044503.

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