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Fast and continuous synthesis of nanostructured iron spinel in supercritical water: influence of cations and citrates

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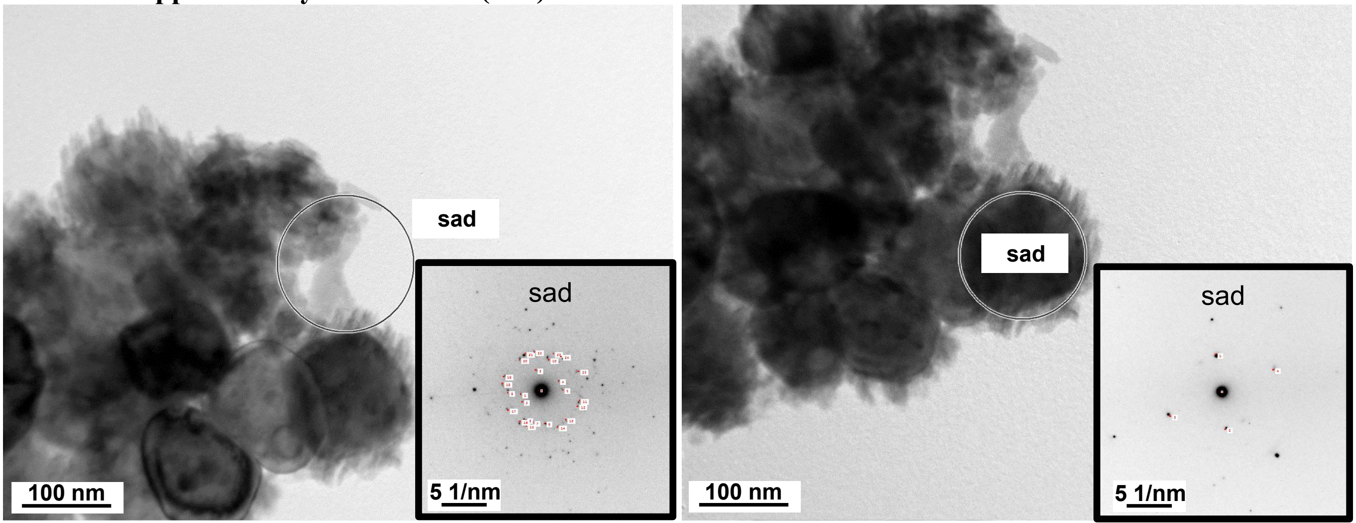
Electronic supplementary information (ESI)



Spot#	d-Spacing (nm)	Mean d (nm)	Theory d (nm)	hkl	Difference between theory and mean d	Iron oxide Phase
1	0.4652	**0.467**	**0.484**	**111**	3.5%	**Spinel**
2	0.4396					
3	0.4577					
4	0.5087					
5	0.4634					
6	0.3026	**0.301**	**0.296**	**220**	-1.3%	**Spinel**
7	0.3005					
8	0.2978					
9	0.2908					
10	0.3122					
11	0.2541	**0.253**	**0.253**	**311**	0.3%	**Spinel**
12	0.2537					
13	0.2627					
14	0.2506					
15	0.2566					
16	0.2633					
17	0.2549					
18	0.2475					
19	0.2427					
20	0.2619					
21	0.2436					
22	0.2503					
23	0.2559					
24	0.2527					
25	0.2377					

Spot#	d-Spacing (nm)	Mean d (nm)	theory d (nm)	hkl	Difference between theory and mean d	Iron oxide Phase
1	0.2591	**0.260**	**0.253**	**311**	-2.8%	**Spinel**
2	0.2615					
3	0.1717	**0.174**	**0.171**	**422**	-1.4%	**Spinel**
4	0.1758					

Figure S1: Analyses of selected area diffraction (sad) of iron oxide nanoparticles synthesized under continuous supercritical water conditions with (Fe^{II}/Fe^{III}) molar ratio of (3/0) without citrates

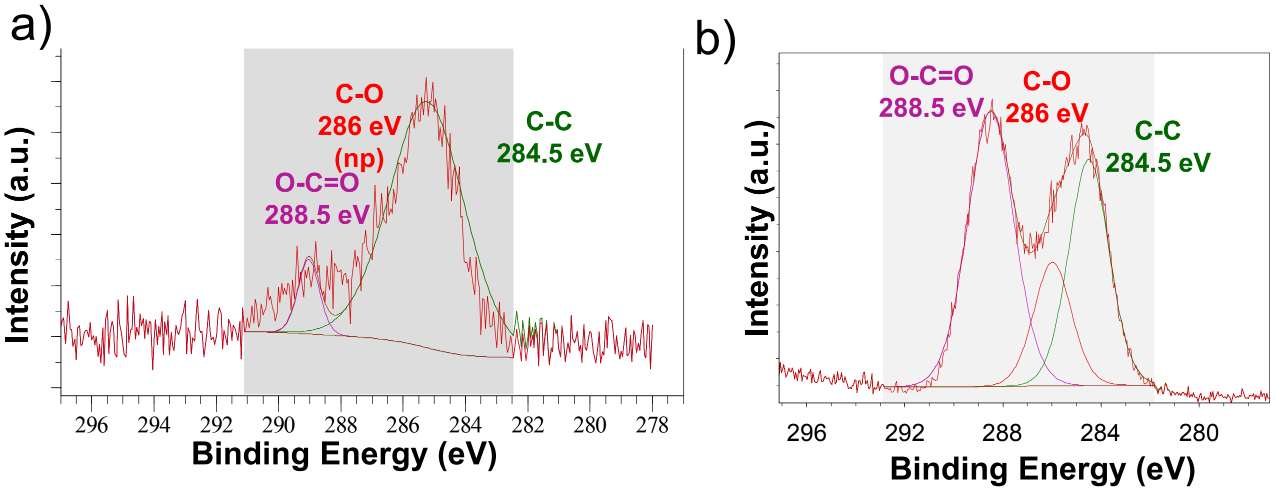


Figure S2: XPS spectra of a) iron oxide nanoparticles synthesized with citrates under supercritical water conditions ($3Fe^{II}$: $0\ Fe^{III}$) and b) in another study in hydrothermal conditions ($1Fe^{II}$: $2\ Fe^{III}$)[1]. Fe/citrates mass ratio was 100% in the both cases. (np): not present

No evidence of citrate coating onto the spinel structured iron oxide nanoparticles (Fe^{II}:Fe^{III} = 3:0 and mass ratio citrates/Fe = 100%) was proven either by FTIR (more intense band usually present at 1625 cm^{-1} and attributed to C=O vibration is missing) nor by a change in colloidal stability or Zeta potential measurement (data not shown). Moreover, thanks to XPS analyses (C1s level, Figure S2) we can see that just a small contribution could come from citrate compared to the C1s signature of citrated iron oxide nanoparticles synthesized earlier and published previously[1]. There is very few Carbon contribution of this peak due to the carboxyl group (O-C=O in Figure S2-a) as it should be as important as the (C-C) peak contribution (Figure S2-b). Furthermore, the fitting of the spectra of Figure S2-a is not good enough to even see any peak of the C-O groups of citrates whereas we see it well in Figure S2-b.These three characterizations could not prove the presence of citrates on the surface of the iron oxide obtained in continuous supercritical water conditions. These molecules may be both partially degraded during hydrothermal synthesis and eliminated during washing procedure. However the anti-oxidative contribution of this organic molecule is crucial to obtain spinel structured iron oxide nanoparticles under supercritical water conditions.

1. L. Maurizi, F. Bouyer, J. Paris, F. Demoisson, L. Saviot, and N. Millot, *Chem. Commun.*, 2011, **47**, 11706–11708.