Faraday Discussions

Discussion paper

New route toward nanosized crystalline metal borides with tuneable stoichiometry and variable morphologies

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Supplementary information

Table S1 Reaction conditions for the synthesis of yttrium borides.

Fig. S1 Low magnification TEM picture of the sample obtained with initial ratio $NiCl_2$:$NaBH_4$ = 1:2.

Fig. S2 HRTEM pictures of NiB nanoparticles obtained with initial ratio $NiCl_2$:$NaBH_4$ = 1:2.

Fig. S3 HRTEM picture of Ni_4B_3 30 nm particle, minor product in the sample obtained with initial ratio $NiCl_2$:$NaBH_4$ = 1:2.

Fig. S4 TEM pictures of Ni_4B_3 and Ni_2B particles, obtained for initial ratios $NiCl_2$:$NaBH_4$ = 1:1.2 and 1:1, respectively.

Fig. S5 TEM picture of Ni_3B particles obtained for an initial ratio $NiCl_2$:$NaBH_4$ = 1:0.65.

Fig. S6 EDX spectra of samples NiB, Ni4B_3, Ni_2B and Ni_3B.

Table S1 Reaction conditions for the synthesis of yttrium borides. YCl_3:$NaBH_4$ is the yttrium-to-boron source molar ratio, *T* and *t* are the temperature and dwell time, respectively. The corresponding masses are reported for each synthesis.

YCl_3:$NaBH_4$	T (°C)	t (h)	YCl_3 (mg)	$NaBH_4$ (mg)	LiCl/KCl (g)
1:12	**1000**	**4**	**98**	**227**	**1,25**
1:8	**900**	**4**	**195**	**303**	**2,50**
1:8	900	1	195	303	2,50
1:8	900	0.5	195	303	2,50
1:8	800	4	195	303	2,50
1:8	800	1	195	303	2,50
1:8	800	0.5	195	303	2,50
1:8	700	4	195	303	2,50
1:5	900	4	195	189	2,50
1:5	900	1	195	189	2,50
1:5	900	0.5	195	189	2,50
1:5	800	4	195	189	2,50
1:5	800	2	195	189	2,50
1:5	**800**	**1**	**195**	**189**	**2,50**
1:5	800	0.5	195	189	2,50
1:5	700	4	195	189	2,50

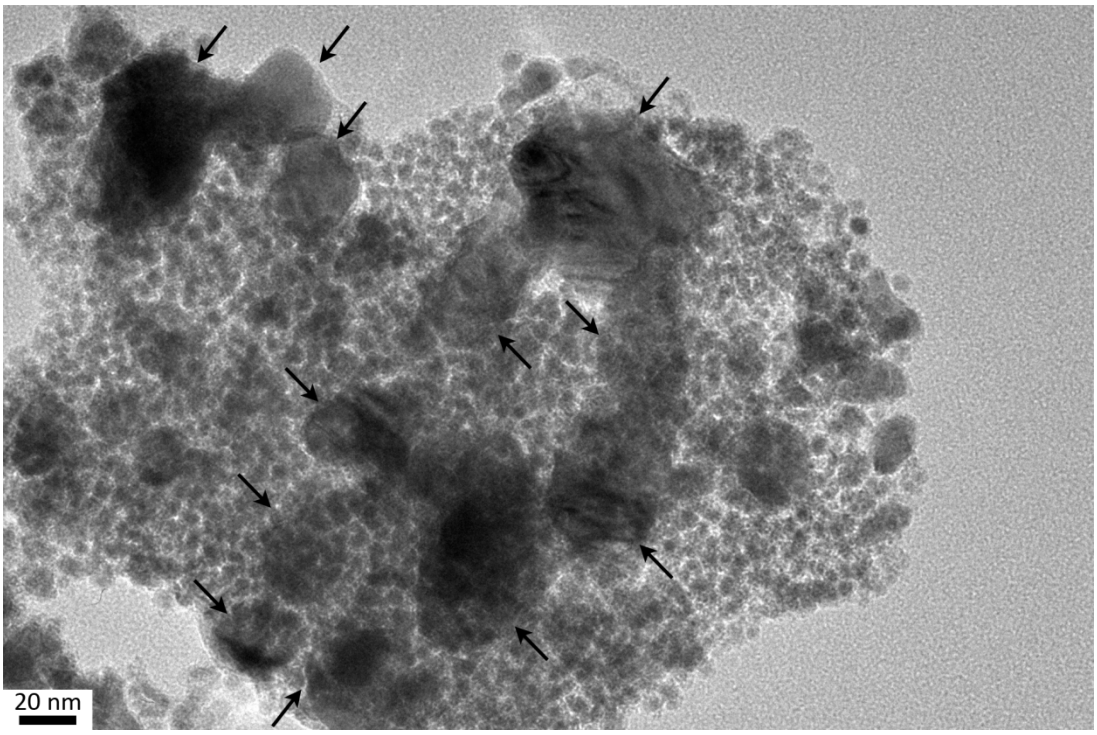

Fig. S1 TEM picture of the sample obtained with initial ratio $NiCl_2$:$NaBH_4$ = 1:2. The sample is composed of crystalline particles dispersed in an amorphous boron phase. The particles can be divided in two groups, depending on size and morphology: the major one is composed of particles around 5 nm in diameter, with a spherical morphology, that are NiB particles according to HRTEM (Fig. S2 and Fig. 3). Other particles in minority exhibit diameters above 20 nm (black arrows) and are slightly faceted. They are indexed on the Ni_4B_3 structure. (Fig. S3).

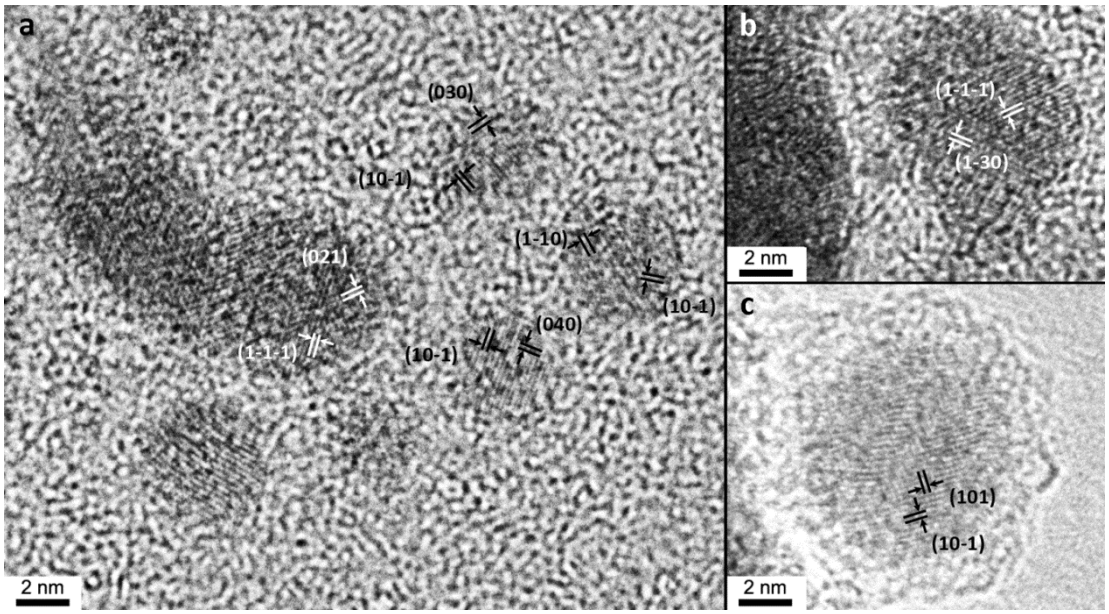

Fig. S2 HRTEM pictures of NiB nanoparticles obtained with initial ratio $NiCl_2$:$NaBH_4$ = 1:2. Spherical particles 2 to 6 nm in diameter are indexed along the NiB structure. Some crystal defects are observed in the particles. c) The crystalline spheres are surrounded by a *ca.* 1.5 nm thick amorphous shell.

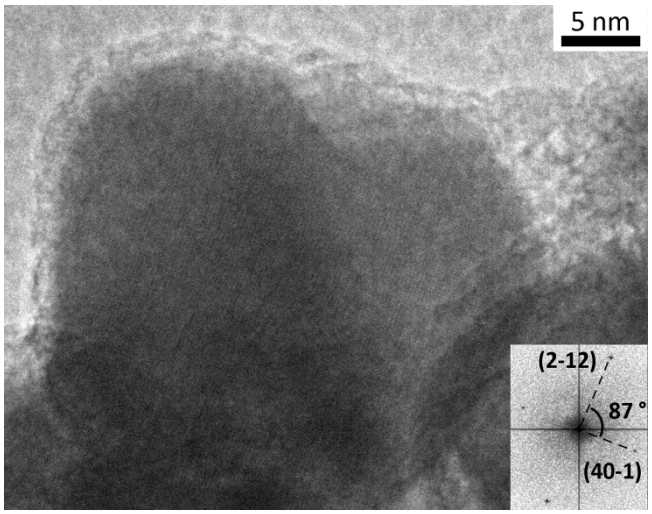

Fig. S3 HRTEM picture of a 30 nm particles, minor product in the sample obtained with initial ratio $NiCl_2$:$NaBH_4$ = 1:2. The inset shows the corresponding Fourier transform indexed on the Ni_4B_3 structure.

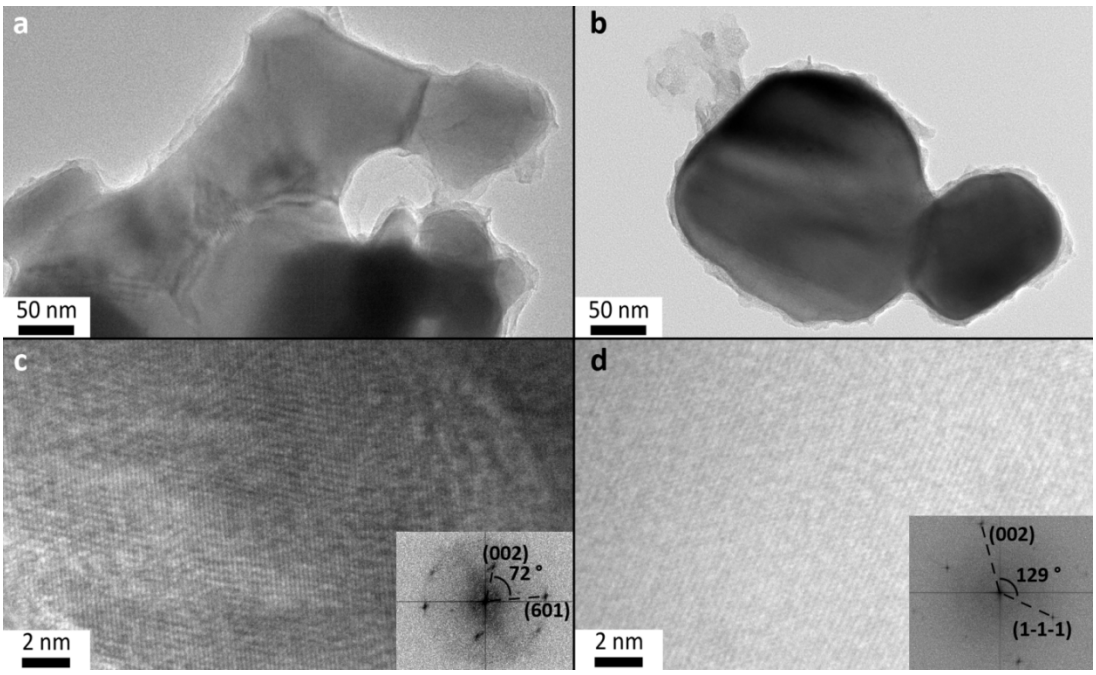

Fig. S4 TEM pictures of (a) Ni_4B_3 and (b) Ni_2B particles, obtained for initial ratios $NiCl_2$:$NaBH_4$ = 1:1.2 and 1:1, respectively. The particles are faceted and exhibit diameters between 50 nm and 200 nm. They form dense aggregates and show evidences of sintering with clear grain boundaries. They are embedded in an amorphous shell that crystallizes under the electron beam, possibly related to nickel hydroxide. HRTEM pictures and corresponding Fourier transforms (insets) highlight the crystal structures of c) Ni_4B_3 for $NiCl_2$:$NaBH_4$ = 1:1.2 and of b) Ni_2B for $NiCl_2$:$NaBH_4$ = 1:1.

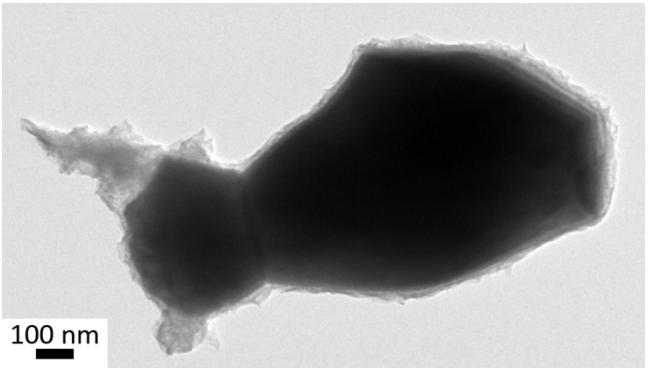

Fig. S5 TEM picture of Ni_3B particles obtained for an initial ratio $NiCl_2$:$NaBH_4$ = 1:0.65.

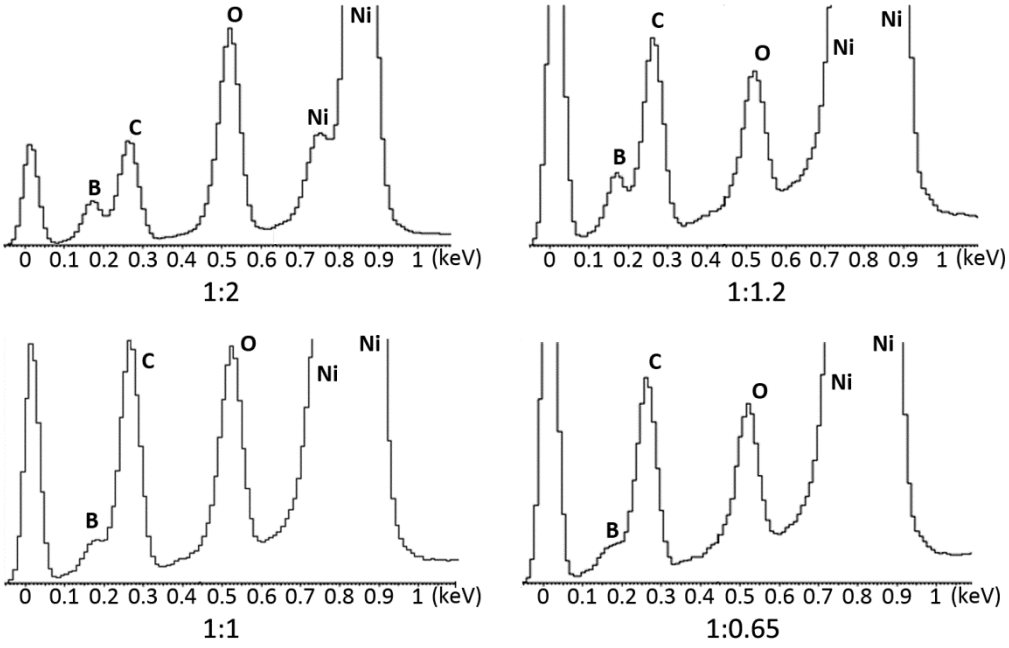

Fig. S6 EDX spectra of samples NiB, $Ni4B_3$, Ni_2B and Ni_3B, obtained with initial ratios $NiCl_2$:$NaBH_4$ = 1:2, 1:1.2, 1:1 and 1:0.65, respectively.