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1 **Layered Double Hydroxide-Borate Composites Supported on Magnetic Nanoparticles:**
2 **Preparation, Characterization and Molecular Dynamics Simulations**

3

4 **Ahmet Nedim Ay,*¹ Birgul Zumreoglu-Karan,¹ Andrey G. Kalinichev,^{2,3} Vicente Rives,⁴**
5 **Raquel Trujillano,⁴ and Abidin Temel⁵**

6

7 **Abstract** Magnetic nanocomposites involving tetraborate ion (TB)-intercalated Mg-Al-
8 layered double hydroxide (LDH) shell supported on magnesium ferrite (MF) core particles are
9 synthesized, characterized, and compared with their non-magnetic analogues. The
10 compositions of the obtained nanocomposites were determined and structural investigations
11 were made by powder X-ray diffraction (PXRD) and Fourier transform infrared spectroscopy
12 (FT-IR). Particle characteristics were examined by size distribution, specific surface area
13 measurements, scanning electron microscopy (SEM) and transmission electron microscopy
14 (TEM). Room-temperature magnetic measurements were performed with a vibrating sample
15 magnetometer (VSM). The dynamics and structure of the interlayer water molecules and
16 borate ions were studied by molecular dynamics (MD) simulations. Analytical and modeling
17 studies verified that the TB ions were arranged between the LDH layers in oblique positions.
18 The products were found to carry ca. 6% boron (10^{17} B atom/ μg nanocomposite). The
19 magnetic nanocomposite showed superparamagnetic properties and can potentially find
20 applications in biomedical fields for the site-specific delivery of bio-potent boron agents.

21

22 **Keywords** Magnetic nanocomposites · Layered double hydroxides · Intercalation · Boron ·
23 Borate composites · Molecular dynamics simulations

24

25

26

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36

37 **1 Introduction**

38 Layered double hydroxide (LDH) materials have unique adsorption and transport
39 properties and high surface areas allowing accommodation of anionic components in the
40 interlayer space [1]. Over the last decade, LDH-based hierarchical architectures have gained
41 an increasing interest for various specific applications due to their multifunctional properties
42 [2,3]. The introduction of oxoanions or polyoxoanions in the LDH structure is a growing area
43 of research for applications in energy, catalysis, biomedical and environmental sciences [4,5].
44 The uptake of borate ions from aqueous solutions has been studied most widely with Mg-Al-
45 LDHs, and several LDH-borate composites have thus been suggested for miscellaneous
46 purposes [6]. Shi et. al. [7] reported a borate pillared Mg-Al-carbonate-LDH with flame-
47 retardant and smoke-suppressant properties. Elmaci et. al. [8] showed that Mg-Al-LDH can
48 be used in boron isotopic enrichment applications. Boron containing Ca-Al-LDH has been
49 suggested as an active, selective and recyclable catalyst in Beckmann type reactions [9].
50 However, because of the strong interactions between the charged LDH sheets and the inherent
51 interlayer anions (nitrate, carbonate, etc.), direct intercalation of the large polyborate anions is
52 a difficult task. Li et. al. [10] reported a hydrothermal method for the intercalation of
53 tetraborate (TB) ions into Mg-Al-NO₃-LDH. It was later shown that polyborate anions can be
54 intercalated by the ion exchange method [11] and well textured materials containing TB ions
55 can be obtained around pH 9, either with or without using interlayer space expanding long
56 chain organic anions [12].

57 LDHs are biocompatible materials [13] while boron is a vital element not only for
58 plants but also for human body with many physiological and therapeutic functions [14-19].
59 The role of boron in preventing arthritis and fungal infections, regulating pheromone levels,
60 enhancing cognition and bone health, and treating cancer has been emphasized among the
61 many beneficial effects of boron. A nanohybrid of a boron compound with non-toxic LDH is

62 expected to act as an effective agent for boron neutron capture therapy (BNCT) [20]. To
63 provide a satisfactory boron concentration at the desired target site, carborane derivatives
64 [21,22] or inorganic polyborate ions can be used as the intercalating species. In biological
65 systems, boron is present as un-dissociated boric acid $[B(OH)_3]$ and as borate ion $[B(OH)_4]^-$
66 [23,24]. The use of polyborate ions from borax or similar borate salts is therefore attractive
67 due to their good water solubility, relatively low toxicity and the simplicity in their
68 implementation.

69 Boron has the capacity to bind covalently to biological targets and a promising site-
70 specific application is the direction of boron to the target by means of an external magnetic
71 field [25]. Supporting a polyborate-LDH nanohybrid on a magnetic core can further help site-
72 specific concentration of boron in biomedical applications [3]. In the past few years, several
73 magnetic core-shell nanohybrid systems have been described for boron-delivery including
74 anionic boron cluster-graphene oxide [26], vitamin C-borate [27], carborane-layered double
75 hydroxide (LDH) [18], carboranylphosphinate [28], and rare earth-borate [29].

76 This work reports the preparation, characterization and atomistic computer simulations
77 of nanocomposites involving TB-intercalated Mg-Al-LDH and its magnetic core-shell
78 counterpart supported on $MgFe_2O_4$ particles.

79 **2 Materials and methods**

80 **2.1 Chemicals**

81 $Mg(NO_3)_2 \cdot 6H_2O$ (Sigma), $Al(NO_3)_3 \cdot 9H_2O$ (Carlo-Erba), NaOH (Merck),
82 $(NH_4)_2B_4O_7 \cdot 4H_2O$ (Aldrich), and $Fe(NO_3)_3 \cdot 9H_2O$ (Sigma), were used as received. All
83 experiments were performed under nitrogen atmosphere in decarbonated deionized water
84 (DDW) to prevent the incorporation of atmospheric carbon dioxide as carbonate species into
85 the LDH structure.

86 Magnesium ferrite (MF) particles were synthesized as described by Ay et. al. [30]. A
87 100 mL solution of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.04 mol) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.08 mol) and a second
88 solution (220 mL) containing NaOH (0.38 mol) and Na_2CO_3 (0.32 mol) were simultaneously
89 added into a three-neck flask. The resulting suspension with a pH of ca. 9 was stirred for 6 h
90 at 100 °C. The final precipitate, a non-stoichiometric Mg-Fe- CO_3 -LDH (CO_3 -LDH), was
91 separated by centrifugation, washed several times with deionized water, dried at room
92 temperature and then calcined at 900 °C for 2 h to give the magnetic core material, MgFe_2O_4 .

93 **2.2 Nanocomposite synthesis**

94 Nanocomposite synthesis was carried out in a stepwise manner. Mg-Al- NO_3 -LDH was
95 in situ deposited on MF core particles and then the interlayer nitrate ions were exchanged
96 with TB ions [12].

97 *Syntheses of Mg-Al- NO_3 -LDH and Mg-Al-TB-LDH*

98 Mg-Al- NO_3 -LDH and Mg-Al-TB-LDH were prepared as reference materials. A 12
99 mL solution of 2 M KOH was added dropwise onto 60 mL of a solution containing
100 $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (20.51 g, 0.08 mol) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (15.01 g, 0.04 mol) (Mg/Al molar
101 ratio=2). The resulting suspension was refluxed for 4 hours. The pH of the suspension was
102 adjusted to 9.5 with KOH. The precipitate formed was aged for 6 days at room temperature
103 under nitrogen atmosphere, then washed with DDW and filtered. A 250 mL portion of DDW
104 was added onto the filtered precipitate (NO_3 -LDH) and the final suspension was kept for
105 further studies. 100 mL of 0.26 M ammonium tetraborate solution was added to 75 mL of the
106 NO_3 -LDH suspension under nitrogen atmosphere (pH=8.8) and refluxed for 4 hours. The
107 product (TB-LDH) was filtered, washed and dried in a vacuum desiccator.

108 *Deposition of NO_3 -LDH shell on MF core particles*

109 A 34 mL solution containing $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (5.27 g, 0.02 mol) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$
110 (3.86 g, 0.01 mol) (Mg/Al molar ratio =2) and 30 mL of 2 M NaOH solution were added
111 dropwise to 30 mL aqueous dispersion of 0.2 g MF (pH 9.5). The mixture was refluxed and
112 then aged for 6 days at room temperature under nitrogen atmosphere. The product (LDH/MF)
113 was filtered, washed and kept dispersed into 120 mL of water (50 mL of this suspension
114 contains 0.61 g LDH/MF).

115 **2.3 Intercalation of TB anions into the LDH-MF structure**

116 50 mL of the LDH-MF suspension was added to 100 mL of 0.23 M ammonium
117 tetraborate solution and the suspension was refluxed for 4 hours. The product (TB-LDH/MF)
118 was filtered, washed and dried in a vacuum desiccator.

119 **2.4 Characterization studies**

120 Powder X-ray diffraction analyses of the samples were performed with a Rigaku
121 D/MAX-2200 diffractometer instrument using graphite-filtered $\text{CuK}\alpha$ radiation
122 ($\lambda=1.54056 \text{ \AA}$) at a scanning rate of 4° min^{-1} , from 3 to $70^\circ (2\theta)$. FTIR spectra were recorded
123 with a Perkin Elmer Spectrum One instrument using the KBr pellet technique in the $4000 -$
124 400 cm^{-1} range. Thermogravimetric and differential thermal analyses (TGA and DTA) were
125 performed under dynamic nitrogen atmosphere (30 mL min^{-1}) at a heating rate of $10^\circ\text{C min}^{-1}$
126 on a Shimadzu DTG-60H thermal analysis system. Mg, Al, Fe and B contents of the samples
127 were determined in a Yobin Iyon Ultima II model ICP-OES instrument. Particle size
128 distribution analyses were performed with a Malvern Mastersizer 2000 instrument with a
129 Mastersizer software programme. Analyses were carried out according to Lorenz-Mie theory
130 by using 1.33 and 1.52 refractive indexes for water and for the samples, respectively. Specific
131 surface area measurements were performed by recording the nitrogen adsorption-desorption
132 isotherms at -196°C with a Micromeritics Gemini VII 2390t equipment, Surface Area and

133 Porosity analyser. All samples were degassed before analysis at 110°C in a Micromeritics
134 Flowprep 060 Sample Degass System for 2 hours. Scanning Electron Microscopy (SEM)
135 images were recorded on a FEI Quanta 200 FEG SEM system. Transmission Electron
136 Microscopy (TEM) images were recorded with FEI Tecnai G2 F30 instrument at 300 or 100
137 kV. Room temperature magnetization measurements were performed on a Quantum Designed
138 Physical Property Measurement System with a vibrating sample magnetometer in a magnetic
139 field range of 30 kOe.

140 **2.5 Computational Molecular Modeling**

141 To better understand the molecular mechanism of borate ions intercalation into the
142 Mg-Al-LDH interlayers, their swelling behavior, and equilibrium interlayer water content,
143 molecular dynamics (MD) computer simulations were carried out at ambient conditions
144 ($T = 300\text{K}$; $P = 0.1\text{ MPa}$) for several hydration states using standard MD algorithms for the
145 NPT statistical ensemble (constant number of atoms, constant pressure, and constant
146 temperature) [31].

147 Based on the experimentally determined sample composition, the computational
148 models were constructed using the same approach as in earlier simulations of Mg-Al-LDH
149 intercalated with organic anions [32, 33]. The experimentally known Mg-Al-LDH crystal
150 structure [34] was taken as the initial configuration of the primary layers in our models.

151 Guided by available X-ray absorption spectroscopy (XAS) and nanoscale imaging
152 experimental data, indicating significant short-range cation ordering within the LDH layers
153 [35,36], a completely ordered Mg, Al cation distribution in the hydroxide layers was assumed,
154 and the simulation supercell consisted of $6 \times 6 \times 1$ crystallographic unit cells with rhombohedral
155 ($R\bar{3}m$) symmetry. However, these simulation supercells were eventually converted to the
156 lowest $P1$ symmetry and each crystallographic parameter was allowed to vary independently
157 during energy minimization and the subsequent MD simulation using the NPT statistical

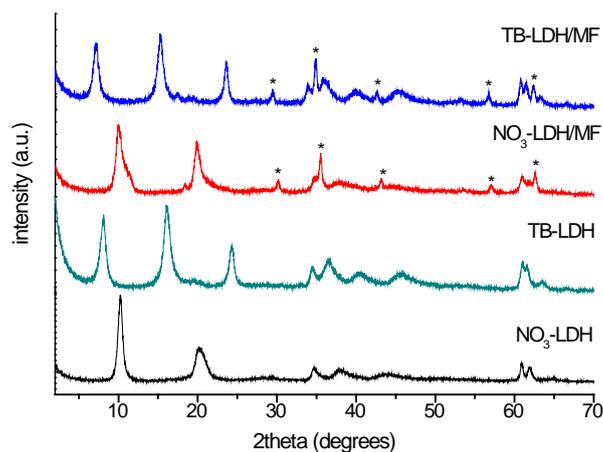
158 ensemble. Thus, in the simulated models each Al octahedron had six nearest-neighbor Mg
159 octahedra, and each Mg octahedron has three nearest-neighbor Mg-octahedra and three
160 nearest-neighbor Al-octahedra (see Fig.3 below).

161 ClayFF force field [37] was used to describe the interatomic interactions among the
162 LDH layers and water, while the DREIDING force field [38], was adopted for the borate ions
163 and their interaction with H₂O molecules and LDH layers, because ClayFF does not include
164 atomic parameters for boron. The atomic partial charges for the borate ions were determined
165 using the *Qeq* charge equilibration procedure [39]. Both DREIDING and ClayFF force fields
166 have already been proven successfully accurate in multiple simulations of LDH materials
167 intercalated by a wide range of inorganic and organic anions [32,33,40,41]. (A complete list
168 of the force field parameters describing the energy of interatomic interactions in the simulated
169 systems is provided in Supplementary Information). All simulations were performed using the
170 *Forcite Plus* module of the Materials Studio molecular modeling software package [42] and
171 started from energy- and stress-minimized structures. As usual, periodic boundary conditions
172 were applied and Ewald summation was used to account for the long-range electrostatic
173 interactions in the system (e.g., [31]). The equations of atomic motion were numerically
174 integrated with a time step of 1 fs. The initial 50 ps period of each MD-simulated trajectory
175 was used for equilibration, while the subsequent 100 ps of each trajectory was recorded every
176 10 fs for further statistical analysis.

177

178 **3 Results and discussion**

179 **3.1 Structural characterization of TB-LDH/MF nanocomposites**



180

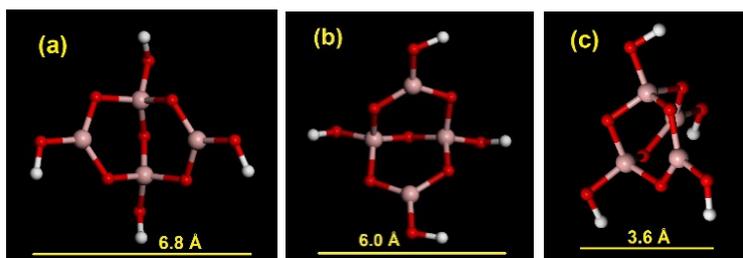
181 **Fig. 1** Powder XRD patterns of NO₃-LDH, TB-LDH, NO₃-LDH /MF and TB-LDH /MF. MF
 182 reflections are marked as *

183

184 Fig.1 and Fig.S1 show the powder XRD patterns of the samples. The pattern for NO₃-LDH
 185 is characteristic for Mg-Al-LDH having exchangeable nitrate ions [43]. The *d*-spacing of this
 186 LDH sample was calculated as 8.6 Å from the *d*₀₀₃ reflection observed at 2θ=9.9°, using the
 187 Bragg equation, suggesting that the nitrate anions are not located flat, parallel to the layers,
 188 but somewhat tilted. This tilted orientation expands the LDH structure and favors exchange
 189 even with bulkier ions [11,44]. After exchanging the interlayer nitrate ions with the larger TB
 190 ions, a swelling of the interlayer space is observed, the position of the *d*₀₀₃ peak changed and
 191 the *d*-spacing increased to 10.89 Å. The height of the interlayer was calculated as 6.09 Å after
 192 subtracting the layer thickness (4.8 Å) from the *d*-spacing value [45]. The XRD pattern of
 193 NO₃-LDH/MF displayed both the LDH (2θ= 9.9°, 19.8°, 34.6°) and MF (2θ = 30.2°, 35.5°,
 194 43°, 57°, 62.6°) reflections, indicating the composite nature of the sample. The pattern for
 195 TB-LDH/MF was quite similar to that of TB-LDH, but with additional MF reflections, with a
 196 interlayer space of 6.09 Å.

197 The TB ion consists of a hybrid configuration of two trigonal (BO₃) and two tetrahedral
 198 (BO₄) groups (Fig. 2a-c). (NH₄)₂B₄O₇·4H₂O (which is also called ammonium borax), presents

199 a very similar structure to that of borax [46,47], it therefore seems probable that the crystal
200 contains B_4O_9 groups $[B_4O_5(OH)_4]^{2-}$ rather than $B_4O_7^{2-}$ ions. Considering the dimensions of
201 the horizontal (Fig. 2a), vertical (Fig. 2b) or oblique (Fig. 2c) configurations of the TB ions
202 [48-50], oblique positioning appears to be reasonable in the interlayer space of 6.09 Å width.
203



204
205 **Fig. 2** Geometry-optimized atomic structure of the TB ion, $[B_4O_5(OH)_4]^{2-}$, in three different
206 orientations (a: horizontal, b: vertical, c: oblique). (Pink - boron; red - oxygen; white -
207 hydrogen)

208
209 Although the *d*-spacing was large enough to allow accommodation of TB ions, it is not
210 exactly diagnostic for the characterization of the intercalated borate ions as polymerization of
211 borate species is very sensitive to pH and the molecular sizes of the polyborate ions are also
212 very similar. So, the nature of the species can best be determined by ^{11}B MAS NMR analysis.
213 Considering the previous ^{11}B MAS NMR studies on borate-LDH systems prepared via similar
214 synthetic procedures and experimental condition [10,11], we can here conclude that the nature
215 of the interlayer ion would be the same, namely tetraborate.

216 The FT-IR spectrum (Fig.S2) of the NO_3 -LDH sample is characteristic for LDHs
217 containing nitrate ions between the layers. The strong and sharp peaks at 1384 and 826 cm^{-1}
218 refer to the ν_3 and ν_2 vibration modes, respectively, of the interlayer nitrate ion. The strong
219 and broad bands around 3450 cm^{-1} are due to the O-H stretching vibrations of the hydroxyl
220 groups in brucite layers and interlayer water molecules. After ion exchange with the TB ions,

221 the intensity of the nitrate bands decreased while new bands appeared at 1478 and 1353 cm^{-1}
222 $\{\nu_{\text{as}}(\text{B}_3\text{-O})\}$, 1200-850 cm^{-1} {tetrahedral borate vibrations}, 1022 cm^{-1} $\{\nu_{\text{as}}(\text{B}_4\text{-O})\}$, 934 cm^{-1}
223 $\{\nu_{\text{s}}(\text{B}_3\text{-O})\}$ and 811 cm^{-1} $\{\nu_{\text{s}}(\text{B}_4\text{-O})\}$ confirming the incorporation of the TB ions into the
224 LDH structure [47]. The spectrum recorded for the TB-LDH/MF hybrid displayed the
225 characteristic bands of the TB-LDH structure, while the characteristic spinel ferrite vibrations
226 at 570 cm^{-1} (ν_1) and 439 cm^{-1} (ν_2) probably overlapped with the Mg-O and Al-O bands in the
227 same region (Fig. S2).

228

229 **3.2 Chemical composition**

230 The samples were analyzed for their Fe, Mg, Al and B contents by ICP-OES and for their
231 H_2O content by TGA. TGA data were also useful for the verification of the thermal stabilities
232 of the composites [51].

233 The general behavior observed in the TGA curves shown in Fig.S3, can be interpreted as
234 follows: surface water was removed up to ~ 150 $^{\circ}\text{C}$, followed by the removal of the water
235 molecules between the layers up to ~ 250 $^{\circ}\text{C}$. Dehydroxylation of the brucite layers and the
236 decomposition of the interlayer anions took place at higher temperatures up to ~ 600 $^{\circ}\text{C}$ for
237 $\text{NO}_3\text{-LDH}$ and ~ 700 $^{\circ}\text{C}$ for TB-LDH. The shift in the decomposition offset temperatures
238 indicated an increase in the thermal stability of the structure due to the pillaring effect of the
239 incorporated TB ions. The total mass loss (54%) recorded up to 600 $^{\circ}\text{C}$ for the $\text{NO}_3\text{-LDH}$
240 sample was higher than the total mass loss (32%) recorded up to the same temperature for the
241 TB-LDH sample. The interlayer nitrate ions thermally decomposed to gaseous NO_x species
242 and were removed out with the carrier gas while the TB ions transformed into B_2O_3 , which
243 remains as a permanent species. This difference (evolution of gases and formation of
244 permanent solid species) would account for the difference observed in the mass losses

245 recorded. The thermal analysis curve recorded for the TB-LDH/MF sample was quite similar
 246 to that of the TB-LDH sample.

247 Table 1 summarizes the proposed formulae for non-magnetic and magnetic
 248 nanocomposites based on the chemical analysis results, TGA water contents and assuming
 249 that TB ions were intercalated as $[B_4O_5(OH)_4]^{2-}$. The experimental and calculated values are
 250 in good agreement.

251

252 **Table 1.** Chemical compositions of the samples with some analytical data. (Values in the
 253 parentheses are calculated from the proposed formulae).

Sample	Formula	Mg (%)	Al (%)	B (%)	Fe (%)	H ₂ O (%)
TB-LDH	$[Mg_{0.67}Al_{0.33}(OH)_2][B_4O_5(OH)_4]_{0.165} \cdot 0.7H_2O$	15.1 (15.5)	8.19 (8.63)	6.97 (7.00)	-	14.5 (14.13)
TB-LDH/MF	$\{[Mg_{0.68}Al_{0.32}(OH)_2][B_4O_5(OH)_4]_{0.160} \cdot 0.7H_2O\} \cdot 0.03MgFe_2O_4$	14.9 (15.1)	7.87 (7.98)	6.16 (6.50)	3.10 (3.42)	14.8 (12.88)

254

255

256

257 3.3 Molecular simulations of TB-LDH structure and its hydration

258 Based on the experimentally determined sample composition (TB-LDH:
 259 $[Mg_{0.67}Al_{0.33}(OH)_2][B_4O_5(OH)_4]_{0.165} \cdot 0.7H_2O$), the computational models were constructed
 260 assuming the presence of only tetraborate anions $[B_4O_5(OH)_4]^{2-}$ and H₂O molecules in the

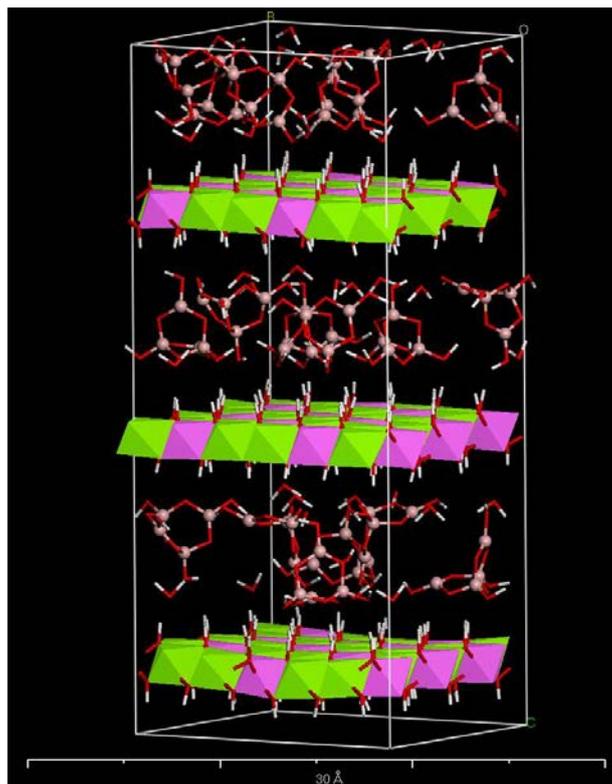
261 interlayers of Mg₂Al-LDH. Thus, the computational models corresponded to the structural
262 formula Mg₄Al₂(OH)₁₂[B₄O₅(OH)₄] · nH₂O, and each simulation supercell contained three
263 metal-hydroxide layers, 18 [B₄O₅(OH)₄]²⁻ anions (Fig. 2a), and a variable number of water
264 molecules, *n* = 0, 2, 4, 6, 8, 10 (Fig. 3).

265 Quantitative analysis of the LDH structural swelling upon hydration and determination
266 of the equilibrium water content in the interlayers represents a sensitive test of the quality of
267 the developed atomistic models [32,33]. The structure and energetics of LDH layer expansion
268 upon hydration was analyzed here by computing hydration energy defined as:

$$\Delta U_{\text{hydr}}(N_w) = \frac{\langle U(N_w) \rangle - \langle U(0) \rangle}{N_w}$$

269 where *N_w* is the total number of water molecules in the simulated system, *U(N_w)* is the total
270 potential energy of the system, and *U(0)* is the total potential energy of the same system with
271 no water molecules. The hydration energy Δ*U(N_w)* offers a simple and effective way to
272 quantitatively assess the affinity of water for the interlayers of clays and other swelling
273 materials [32-33, 52-53]. Since Δ*U(N_w)* is the difference of energies between two structures
274 that differ only by their water content, one can expect that most of the possible inaccuracies in
275 the description of the crystal energy would cancel out. This is particularly true for the TB-
276 LDH systems simulated here, because the dominant contributions to the hydration energy
277 arise from long range electrostatic interactions and formation of hydrogen bonds between the
278 O-H groups of the metal hydroxide layers, the interlayer anions, and the H₂O molecules.

280



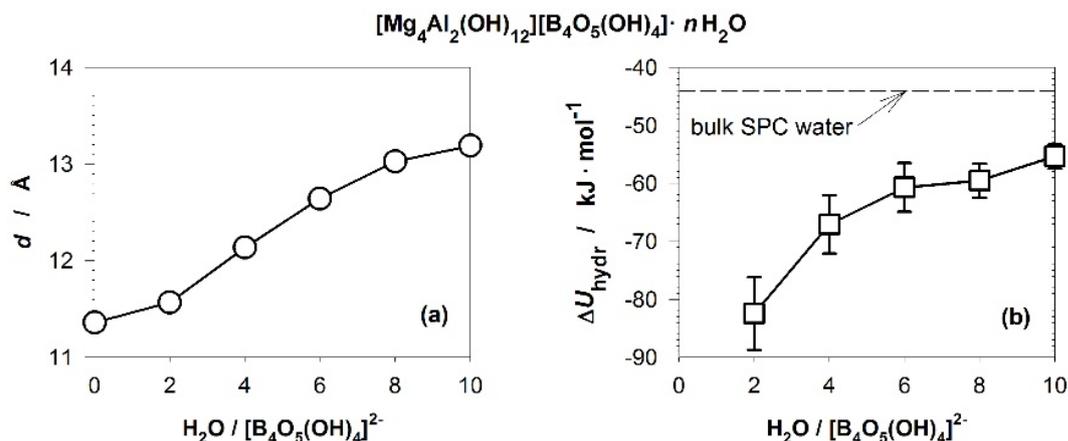
281

282 **Fig. 3** A representative snapshot from MD simulations of Mg₂Al-LDH intercalated with TB at
 283 a normal hydration state of $n=2$. (Light green and pink octahedra: Mg²⁺ and Al³⁺ structural
 284 cations, respectively; TB anions are shown as in Fig.2, while H (white) and O (red) atoms of
 285 H₂O molecules and surface OH groups are shown in stick representation.

286

287 The equilibrium d -spacing (Fig. 4a) of the completely dehydrated TB-LDH in our
 288 simulations is 11.36 Å, and it increases only slightly to 11.57 Å at the hydration state
 289 characterized by H₂O/TB = 2 before growing further upon higher hydration. Both of these
 290 values are somewhat higher than the d -spacing of 10.89 Å determined by XRD, but still
 291 within the accuracy of the current calculations. However, the resulting curves of the system
 292 hydration energy as a function of water content indicate that under ambient conditions the
 293 stable equilibrium hydration state should be expected at $n\sim 2$ (Fig. 4b), while the experimental
 294 data seem to imply that n should be closer to 4. More accurate simulations should clarify this

295 contradiction by developing a more consistent force field parameterization for boron within
 296 ClayFF [37]. However, it is important to note that the simulated swelling behavior of TB-
 297 LDH in Fig. 4 is qualitatively and even quantitatively very similar to the swelling behavior of
 298 Mg-Al-LDH intercalated by glutamate - an anion of the same charge and approximately the
 299 same size [33].

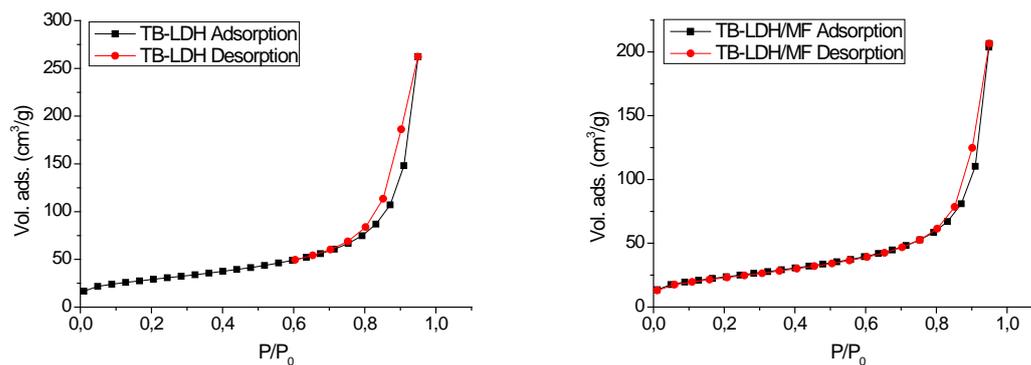


300
 301 **Fig. 4** The equilibrium layer spacing (a) and the hydration energy of the TB-LDH structure
 302 (b) as functions of the water content in the interlayers (number of H₂O molecules per
 303 tetraborate anion).

304

305 3.4 Particle characteristics

306 Fig. 5 shows the nitrogen adsorption/desorption isotherms of TB-LDH and TB-
 307 LDH/MF samples. The measured specific surface areas were 101 and 83 m²/g, respectively.
 308 These values are large compared to typical values for hydrotalcite (HT)-like systems for
 309 which such values can be attained after thermal treatment [54]. The minimal hystereses in the
 310 curves (Type H1) indicated a narrow range of uniform mesopores and the absence of
 311 micropores [55].



312

313 **Fig. 5** Nitrogen adsorption isotherms of TB-LDH and TB-LDH/MF samples

314

315 TB-LDH and TB-LDH/MF suspensions were held in an ultrasonic bath for de-

316 aggregation before particle size distribution analysis. Usually, the maximum size values for

317 large particles are expected to be shifted to lower values as the processing time in the

318 ultrasonic chamber increases. However, different behaviors were observed for these samples,

319 especially for the TB-LDH/MF. A monomodal distribution with a maximum of about 100

320 microns was observed for TB-LDH, while a complex particle size distribution was observed

321 for sample TB-LDH/MF (Fig. S4). It is difficult to quantitatively determine the particle-size

322 distribution for magnetic particles because the presence of aggregates of small crystallites is

323 known to cause problems in the analysis of particle size [56]. The advantage of using SEM

324 and TEM is that one physically observes the particles and obtains information not only about

325 particle size but also their morphology. Fig. 6 shows the SEM images of the samples. The

326 image of the original nitrate clay (LDH) clearly exhibited a layered structure. Stacking of

327 hexagonal platelets with large surface areas in rose morphology is typical for such materials.

328 The layer stacking in TB-LDH was not very clear since the interlayer space was enlarged by

329 the incorporation of TB ions into the structure. The increase in the interlayer space induced by

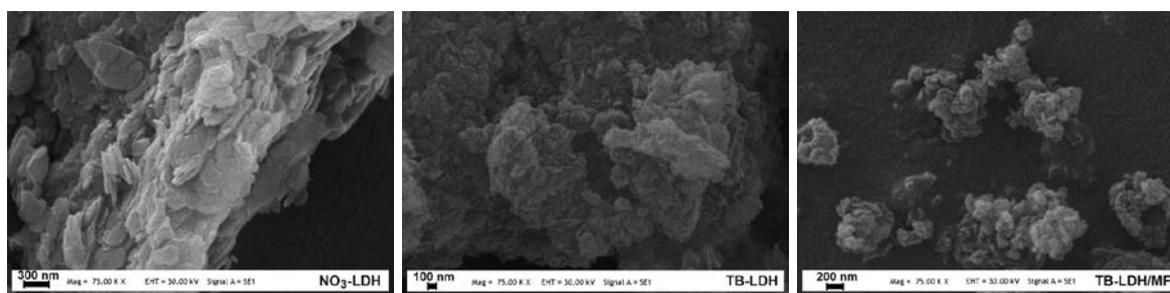
330 swelling due to intercalation of TB (and probably the different ionic strength of the solution

331 where such a NO_3/TB exchange has taken place) lead to a rearrangement of the primary LDH

332 particles' morphology. For the magnetic core-shell TB-LDH/MF sample, a different image
333 was noticed, showing clusters with sizes in the range of 50-150 nm. By electrostatic
334 interaction, LDH layers were coated around magnetic cores in parallel to the surface of the
335 nucleus and TB-LDH/MF nanocomposites having larger diameter were obtained without
336 changing the core morphology.

337 A high resolution TEM image showed the polyhedral morphology of particles
338 containing a TB-LDH shell of ca. 5-10 nm thickness around the polyhedral ca. 50-100 nm MF
339 particles (Fig. 7). Arrangement of LDH plates in a thin shell around the polyhedral core
340 particles resulted in a decrease in the specific surface area.

341 The room temperature magnetization curves for TB-LDH/MF and the core material
342 itself, for comparison, are given in Fig. 8. The saturation magnetization value observed for the
343 magnetic core ($\sigma_s = 29.6$ emu/g) is characteristic for ferromagnetic spinel ferrites prepared by
344 calcination of LDHs [57,58]. Saturation magnetization decreased to $\sigma_s = 2.19$ emu/g when the
345 MF core was coated with the non-magnetic TB-LDH shell which reduced the mole fraction of
346 the magnetic core in the composite material. The enlarged inset of the magnetization curve
347 showed no hysteresis indicating that TB-LDH/MF particles can behave as SPIONs
348 (Superparamagnetic Iron Oxide Nanoparticles).

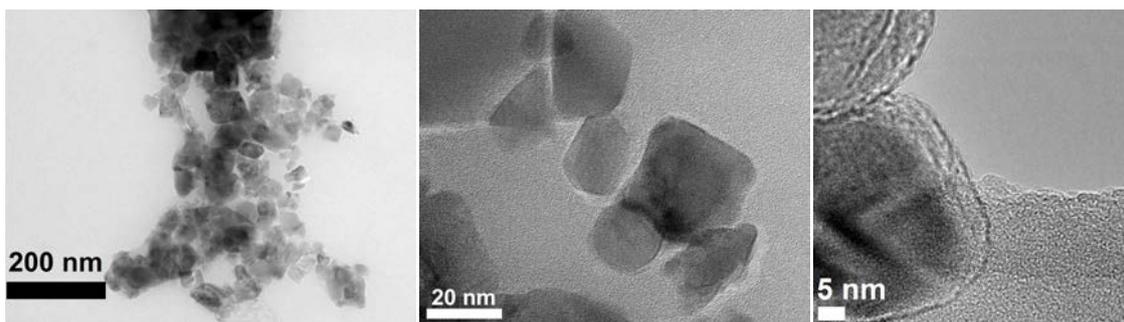


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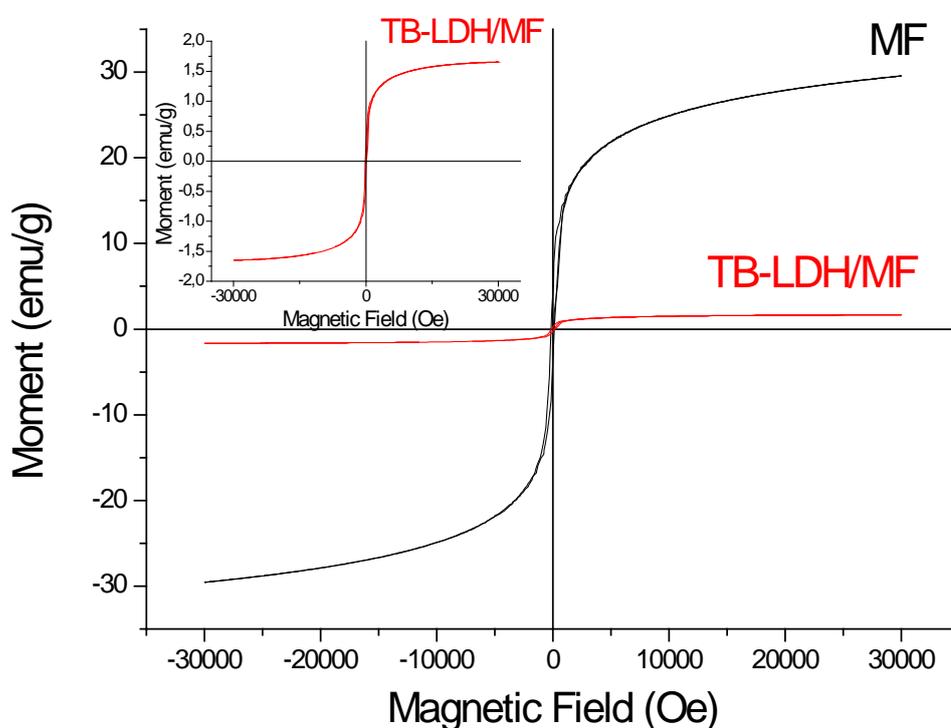
Fig. 6 SEM images of NO₃-LDH, TB-LDH and TB-LDH/MF

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Fig. 7 TEM images of MF (left and middle), and TB-LDH/MF (right)



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Fig. 8. Room temperature magnetization curves for MF and TB-LDH/MF

358 The properties summarized in Table 2 are promising for the use of TB-LDH and TB-
359 LDH/MF composite nanoparticles in potential biomedical applications [59]. Immobilization
360 of the shell around the magnetic core did not cause any significant distortion in the LDH
361 structure. XRD data revealed that the shell retains its layered structure after coating on the MF
362 core. SEM and TEM data helped in explaining the differences in the measured surface areas.

363 The surface areas were comparable but larger for the nonmagnetic composite due to the
 364 stacking of the LDH platelets in rose morphology, which also offers the contribution of the
 365 inner surfaces. Nitrogen adsorption-desorption experiments showed that both materials have
 366 mesopores and can provide facile channels for electrolyte diffusion in drug delivery
 367 applications like mesoporous silica [60]. The sizes of the particles range in 50-150 nm
 368 approaching the range of biological compatibility and meeting the requirement for
 369 administration by injection [61].

370

371 **Table 2** Some characteristic properties of TB-LDH and TB-LDH/MF samples

Sample	d_{003} (Å)	B (% w/w)	Core (% w/w)	σ_s (emu/g)	BET specific surface area (m ² /g)	Particle size distribution (µm)
TB-LDH	10.89	7	-	-	101	100 (monomodal)
TB- LDH/MF	10.89	6.5	6	2.19	83	complex distribution

372

373

374 The LDH component provides a versatile matrix to optimize dosage regimens for local
 375 drug therapy. TB-LDH and TB-LDH/MF nanocomposites carry ca. 6-7% boron (10¹⁷atom
 376 B/µg nanocomposite). A 50 mg of nanocomposite thus contains ca. 3mg of B, the minimum

377 amount recommended for the daily intake of people who are at risk of osteoporosis,
378 osteoarthritis, or cancer [17]. The nanocomposites contain ca. 10^{17} of B atoms (ca. 10^{16} of ^{10}B
379 isotope) per microgram, displaying the potential to be used in targeted BNCT applications as
380 well [20].

381

382 **4 Conclusions**

383 This work covers the preparation and characterization of Mg-Al-LDH and also
384 magnesium ferrite core-Mg-Al-LDH shell nanocomposites as boron carriers and magnetic
385 targeting agents for potential biomedical applications.

386 Powder-XRD and computational modeling results confirmed the intercalation of TB
387 ions in the LDH galleries in nearly vertical (oblique) orientation which stabilizes the LDH
388 structure through hydrogen bonding and electrostatic interactions. The structural behavior of
389 the interlayer TB ions was modelled to assess the H-bonding interactions and energetics of
390 hydration. However, further improvement of the parametrization of interatomic interactions
391 involving TB ions seems to be necessary in order to achieve better agreement with XRD data.

392 Chemical analysis results indicated high entrapment efficiency of the LDH matrix for
393 TB ions. Both the magnetic and nonmagnetic nanocomposites were found to contain 6-7%
394 boron, meeting the dosage requirements for boron medication including BNCT. The
395 nanocomposites were found to have suitable particle characteristics for the emerging medical
396 applications of boron containing compounds.

397 Loading of polyborate ions within the LDH material along with superparamagnetic
398 iron oxide nanoparticles represents another advantage for delivery. TB-LDH/MF
399 nanoparticles can literally drag TB ions to their target site in the body under the influence of
400 an applied magnet field.

401

402 **Supporting Information**

403 Powder XRD patterns, FT-IR spectra and TGA/D-TGA curves of NO₃-LDH, TB-
404 LDH, NO₃-LDH /MF and TB-LDH /MF, Particle size distribution curves of TB-LDH and
405 TB-LDH/MF. A complete list of the force field parameters describing the energy of
406 interatomic interactions in the simulated systems is also provided in Supplementary
407 Information together with the description of how these parameters were used in the present
408 calculations.

409

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415

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