ELECTRONIC SUPPLEMENTARY INFORMATION FOR

A fast and simple method for template-free preparation of α-Fe/a-Fe_2B nanosheets

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MATERIALS AND METHODS

-Materials synthesis

All reactions and product isolations were carried out using an inert argon atmosphere in a glove box.

- Reaction of $NaBH_4$ and $FeCl_3$ in water/glycerol mixture

Glycerol (4 mL, 99.5% - Vetec) and $FeCl_3.6H_2O$ (0.82 g, 3.0 mmol, 97% - Dinamica) were dissolved in 50 mL deionized water for 20 min at room temperature (RT ~ 25 ^oC). Then, powder $NaBH_4$ (0.76 g, 20 mmol, 98% - Dinamica) was slowly added to the solution with vigorous stirring for 5 min. The solution became colorless, and a vigorous gas evolution occurred with the precipitation of a black solid. The residue was magnetically separated from the suspension and washed several times with deionized water until reaches a pH 7; a process that aim to remove glycerol and by-products. Then, the water-washed precipitated was transferred to a 250 mL two-necked round-bottom flask attached to a vacuum line of approximately 10^{-3} Torr, and dried at 60 ^oC using a heater blanket (Fisatom) for 48 h. This procedure produced a metallic mixture of α-Fe and amorphous Fe_2B (α-Fe/a-Fe_2B) nanosheets, which are stable in air for several months.

- Reaction of $NaBH_4$ and $FeCl_3$ in pure water

$FeCl_3.6H_2O$ (0.82 g, 3.0 mmol, 97% - Dinamica) was dissolved in 50 mL deionized water for 20 min at RT (~25 ^oC). Then, powder $NaBH_4$ (0.76 g, 20 mmol, 98% - Dinamica) was slowly added to the solution with vigorous stirring for 5 min. The solution became colorless, and a vigorous gas evolution occurred with the precipitation of a black solid. The residue was magnetically separated from the suspension and washed several times with deionized water until reaches a pH 7 in order to remove the

by-products. Then, the water-washed precipitated was transferred to a 250 mL two-necked round-bottom flask attached to a vacuum line of approximately 10^{-3} Torr, and dried at 60 ºC using a heater blanket (Fisatom) for 48 h. The black solid was highly reactive, being completely oxidized into brown maghemite and $Fe(OH)_2$ by air atmosphere.

-Materials characterization

α-Fe\a-Fe_2B composite was analyzed by powder X-ray diffraction (XRD), using a Rigaku Ultima IV, operating with Cu-Ka radiation (λ = 1.5418 Å) and equipped with a graphite diffracted-beam monochromator. The XRD patterns were collected at RT from 20-90º 2θ at a step of 0.5º and with 10 s per step.

^{57}Fe Mössbauer spectra were collected in a broad temperature range (from 15 to 300 K) in a Janis closed-cycle system, with the drive operating in constant acceleration transmission mode and using a 50 mCi ^{57}Co/Rh matrix source. The Mössbauer data were stored in a 512-channel MCS memory unit and were numerically fitted, with NORMOS program [1], using basically two components, i.e., a hyperfine magnetic field distribution superimposed to a crystalline sextet. In Mössbauer experiments, the ^{57}Co/Rh source was kept at 300 K (RT), while the sample temperature was changed, which results in a second-order Doppler shift (SODS) effect in the Mössbauer spectra. The isomer shift (δ) values are quoted relative to metallic Fe at RT.

Transmission electron microscopy (TEM) was carried out on Jeol 2100F (TEM/STEM) instrument operating at an accelerating voltage of 200 kV. The α-Fe/a-Fe_2B nanosheets were dispersed in isopropyl alcohol, and a droplet was placed onto a carbon-coated copper grid and air-dried prior to analysis.

The thermogravimetric analysis was performed on a TA INSTRUMENTS Q600, with aluminum pans, a scanning rate of $10^{o}K\ min^{-1}$ in the air with a flow rate of 30 mL/min.

Differential scanning calorimetry (DSC) analysis was performed in a Shimadzu DSC-50. About 10 mg of material was enclosed in an aluminum pan covered with an aluminum lid (an empty pan with lid was used as reference). The signal was recorded in the heating ramps, with a heating rate of 20 $K\ min^{-1}$, under air flux of 30 $mL\ min^{-1}$.

Room temperature DC magnetization measurements were performed using a vibrating sample magnetometer (VSM) facility of the Quantum Design/Evercool-II Physical Property Measurement System (PPMS). M(H) curves were recorded for a maximum applied field (H) of 10 kOe, with a step field of 100 Oe.

RESULTS AND DISCUSSION

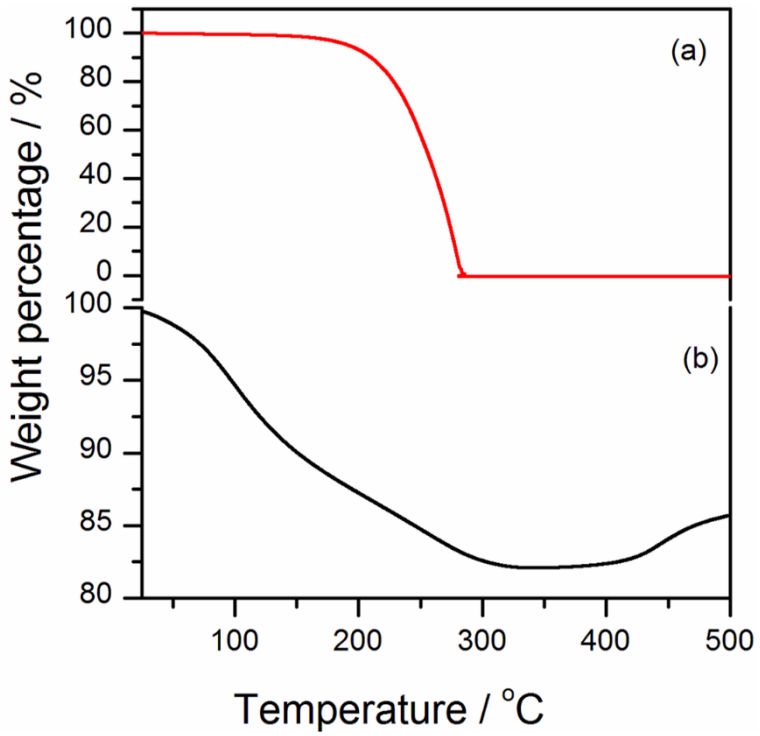


Fig. S1. TGA profiles of the (a) neat glycerol, and (b) α-Fe/a-Fe_2B nanosheets.

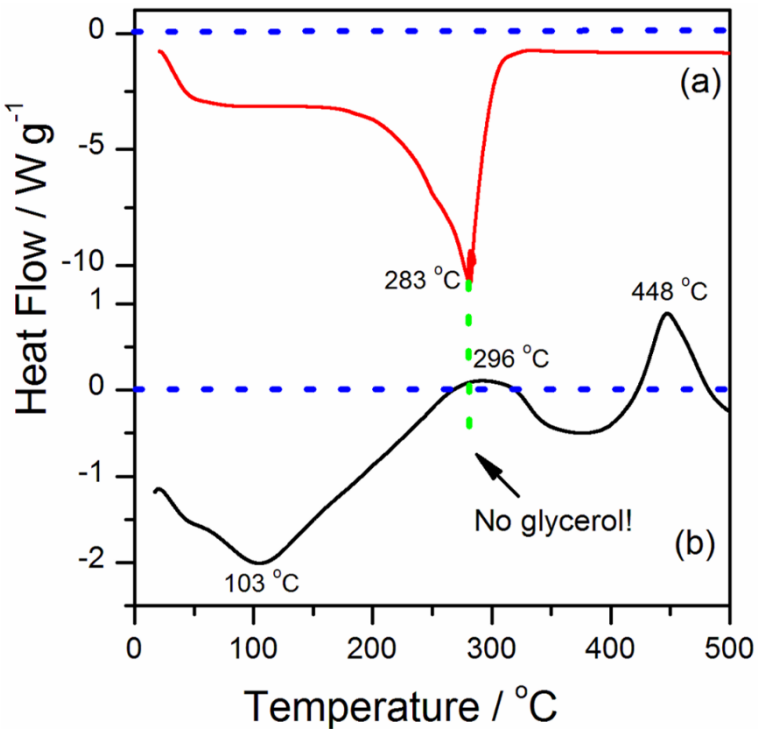


Fig. S2. DSC profiles of the (a) neat glycerol, and (b) α-Fe/a-Fe_2B nanosheets.

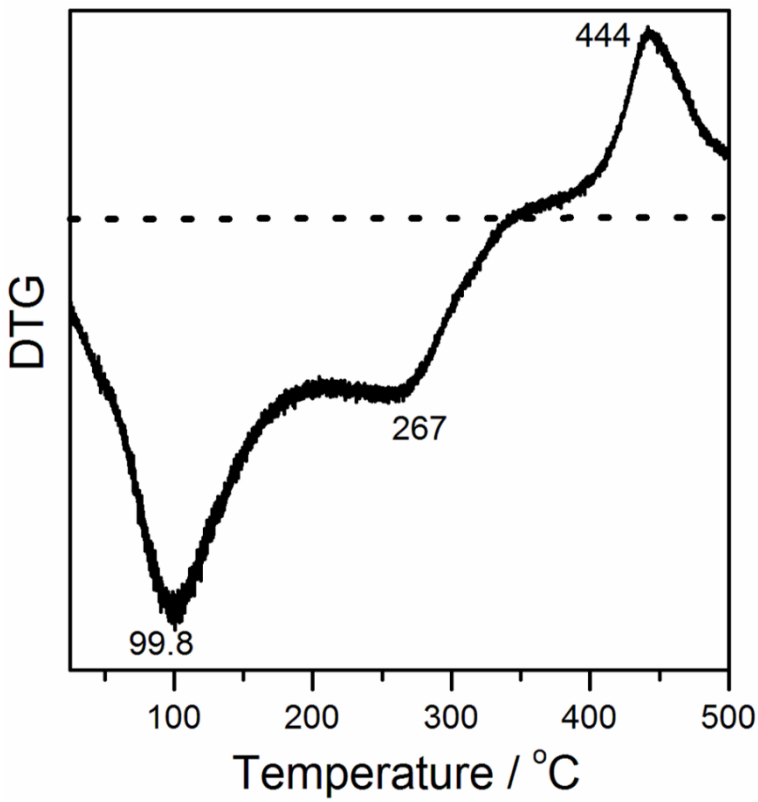
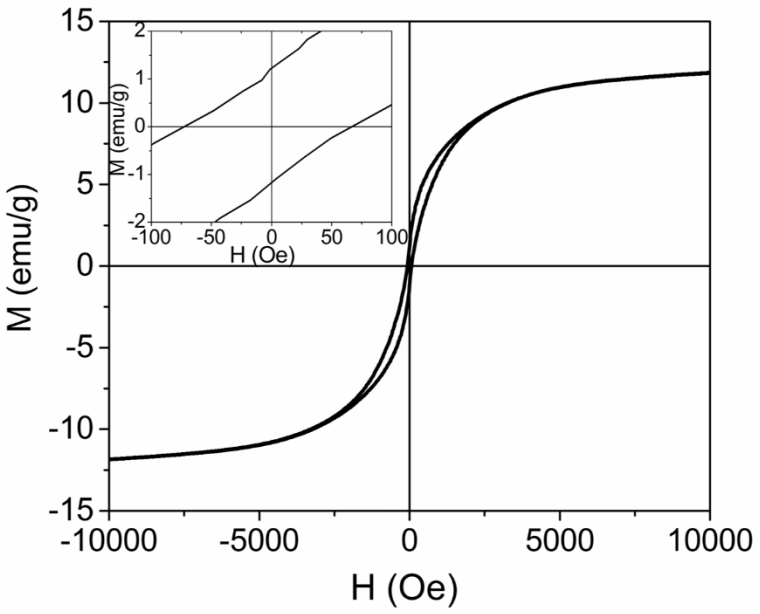
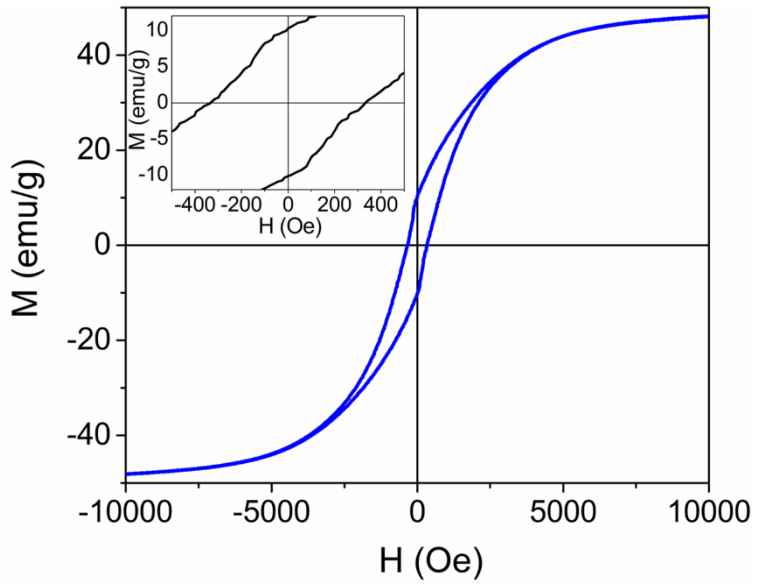


Fig. S3. DTG profiles of the α-Fe/a-Fe_2B nanosheets.



(a)



(b)

Fig. S4. Magnetic hysteresis loops of the samples (a) control (without glycerol), and (b) α-Fe/a-Fe_2B nanosheets collected at 300 K. The inset shows zoomed low-field region.

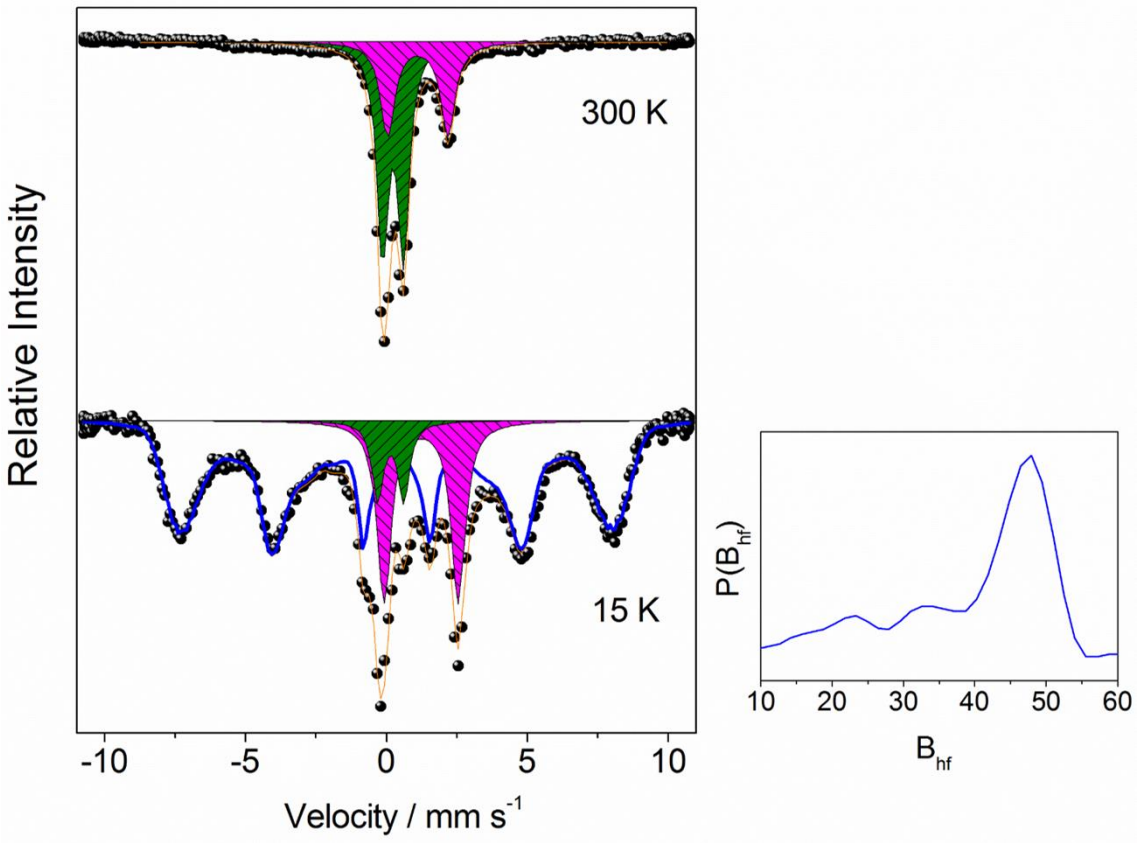


Fig. S5. ^{57}Fe Mössbauer spectra recorded at 300 and 15 K (left side), and the corresponding magnetic hyperfine field distribution (right side) of the sample prepared by direct Fe^{3+} reduction with $NaBH_4$.

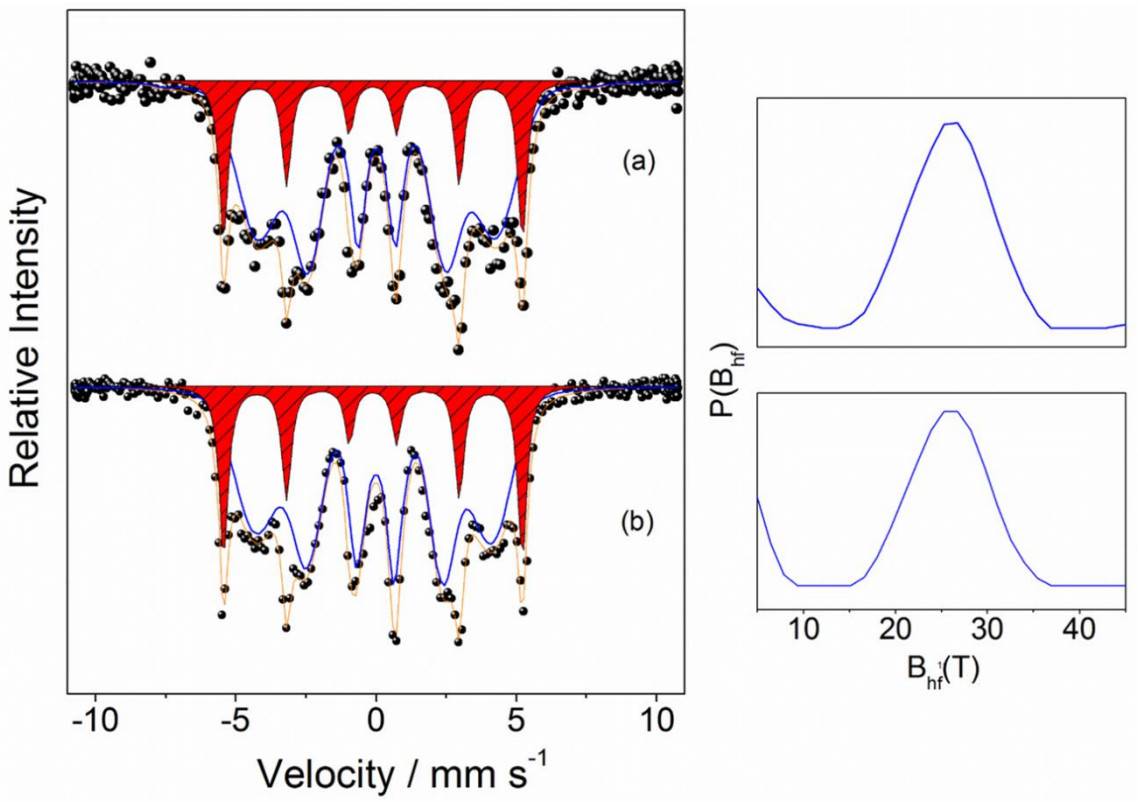


Fig. S6. ^{57}Fe Mössbauer spectra of the Fe/Fe_2B nanosheets (a) fresh, 0 days and (b) after 60 days air exposure, collected at 300 K.

References

[1] R. A. Brand, Laboratorium für Angewandte Physik, Germany, 1992.