

Supporting Information

MgH₂ nanoparticles confined in reduced graphene oxide pillared with organosilica: a novel type of hydrogen storage material

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Synthesis of rGO-BTB heterostructure

The layered heterostructure of reduced graphene oxide and organosilica was prepared with a soft-template method. The synthesis of graphene oxide (GO) from graphite flakes was based on a modified Staudenmaier's method, as described in our previous publications.^{1,2} A suspension of 2.5 mg mL⁻¹ of GO in water was adjusted to the pH of 7.5 by adding small amounts of 0.1 M NaOH solution while monitoring with a pH meter (Mettler Toledo, FP20-Meter); the color of suspension changed from brownish yellow to dark brown. A surfactant, dodecylamine, was mixed with the GO suspension in a weight ratio of 3.0 (dodecylamine/GO) for a prepillaring step, which ensures that the graphene oxide interlayer space is sufficiently opened. After stirring for 24 h, the dodecylamine-intercalated graphene oxide was separated by centrifugation at 4500 rpm and washed three times with ethanol/water (v/v = 1:1) to remove the excess dodecylamine, before being vacuum dried at room temperature. For the intercalation of the phenylene-bridged organosilica precursor into the interlayer space of GO, 100 mg of dodecylamine-intercalated GO were dispersed in 5 mL n-butanol, and the organosilica precursor BTB was added dropwise to the solution while vigorously stirring for 2 h. Then water was added while keeping the molar ratio of silica precursor/H₂O/n-butanol constant at 1/4/54. The sol-gel reaction was performed at 50 °C by stirring for 2 h. The obtained gel was placed in the oven at 50 °C and dried overnight. The layered heterostructure of reduced graphene oxide and organosilica (rGO-BTB) was obtained by removing the amine-surfactant with a calcination step of 370 °C in air for 2 h, with the heating rate of 1.0 °C min⁻¹.

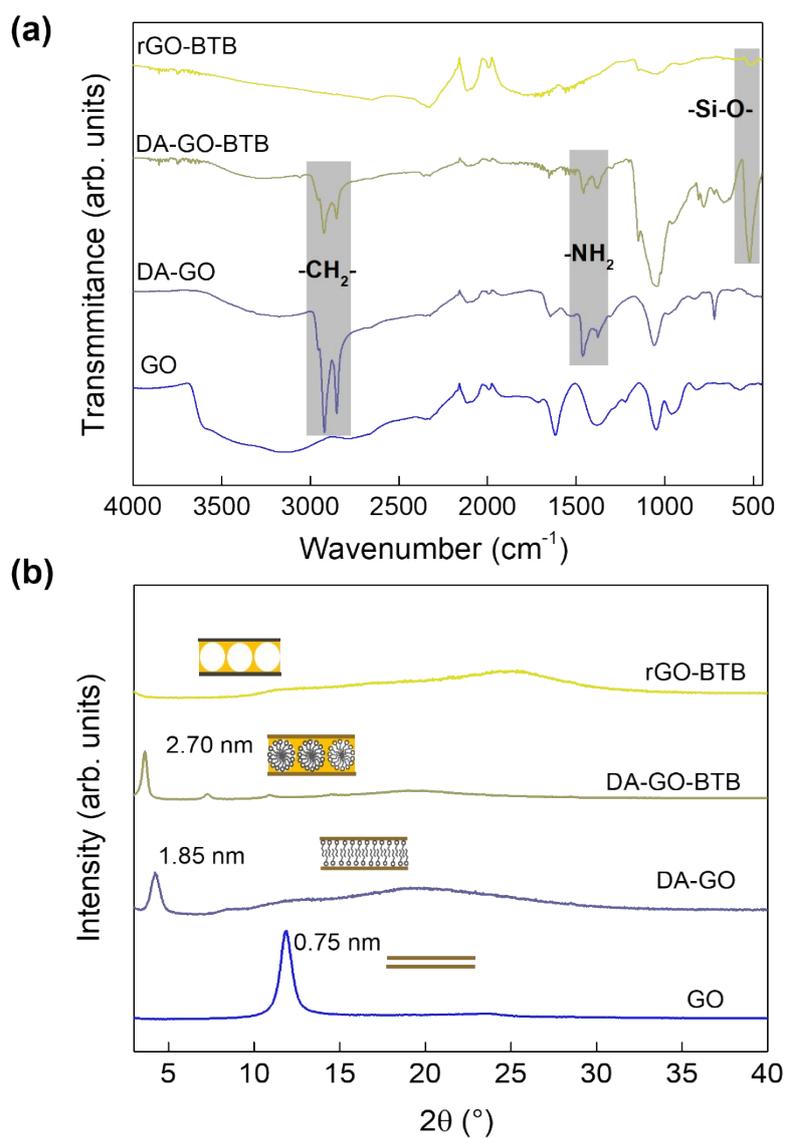


Figure S1. (a) FTIR spectra of GO, dodecylamine-intercalated GO (DA-GO), GO intercalated with both dodecylamine and BTB (DA-GO-BTB) and rGO-BTB; (b) X-ray diffraction patterns of GO, GO intercalated with dodecylamine (DA-GO), GO with dodecylamine and BTB (DA-GO-BTB) and rGO-BTB.

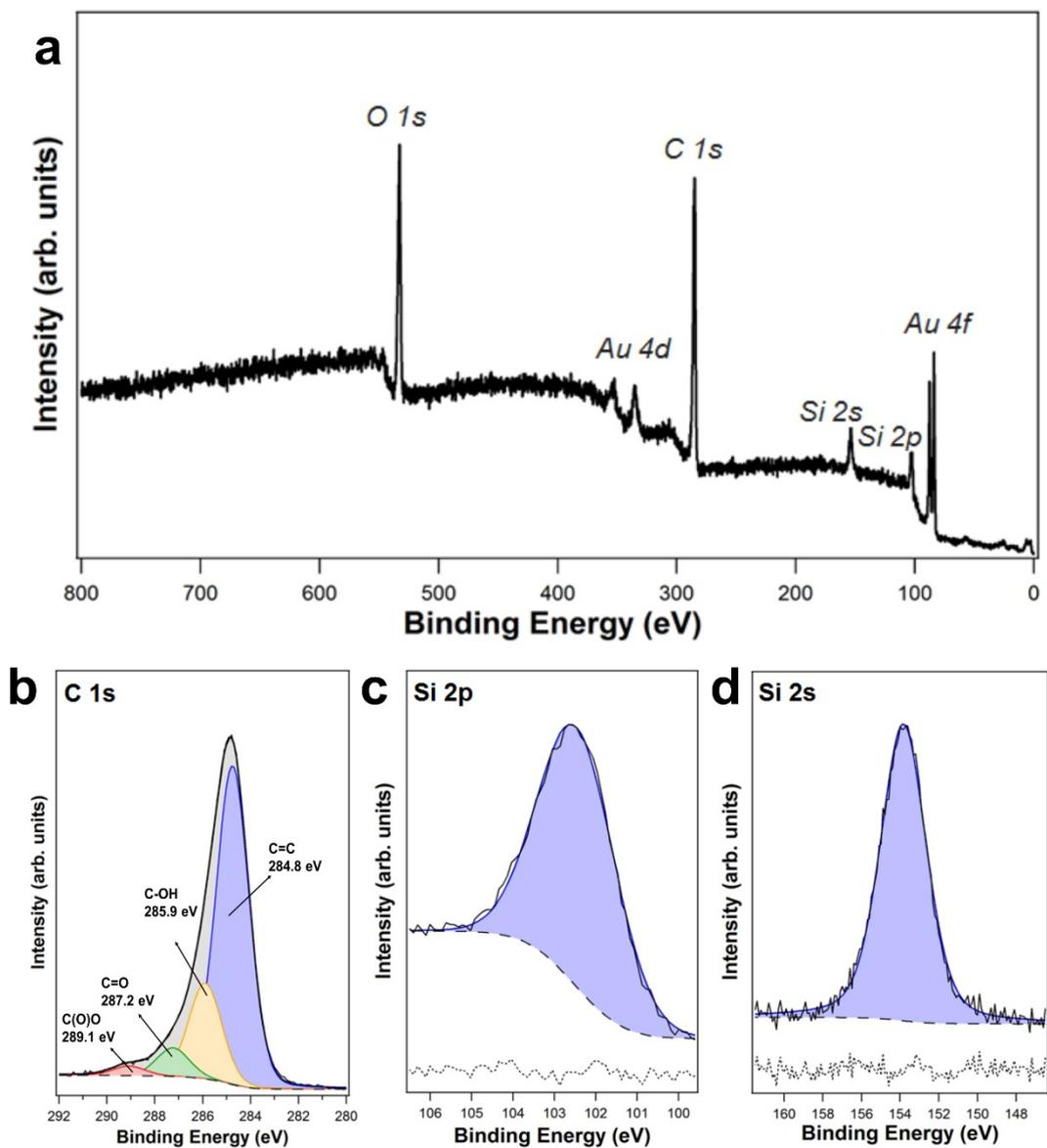


Figure S2. X-ray photoelectron spectra of rGO-BTB (a) wide scan, (b) C1s, (c) Si2p and (d) Si2s core level regions.

Table 1 Specific surface area, pore volume of rGO-BTB, and of the MgH₂/rGO-BTB-10 and MgH₂/rGO-BTB-20 composites

Samples	specific surface area (SSA) [m ² g ⁻¹]			pore volume [cm ³ g ⁻¹]		
	S _{total}	S _{t-plot micro}	S _{t-plot external}	V _{total}	V _{micro}	V _{meso}
rGO-BTB	342	236	76	0.145	0.091	0.054
MgH ₂ /rGO-BTB-10	212	147	65	0.096	0.072	0.024
MgH ₂ /rGO-BTB-20	75	24	51	0.093	0.012	0.081

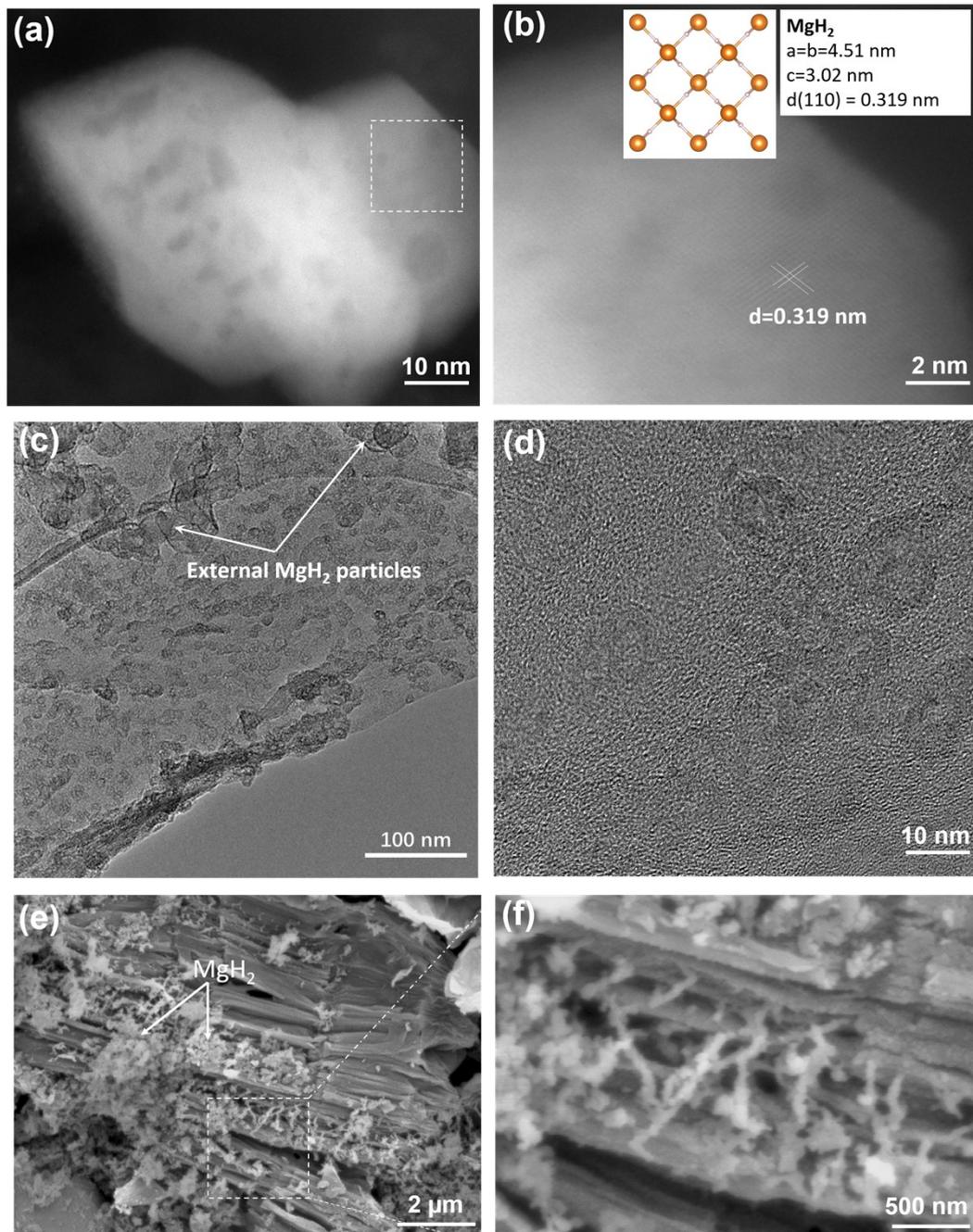


Figure S3. (a) Residual MgH_2 particles located outside of rGO-BTB heterostructure of $\text{MgH}_2/\text{rGO-BTB-20}$; (b) enlargement of the area marked with a dashed white line in (a), inset: structure of crystalline MgH_2 ; (c) and (d) TEM images of $\text{MgH}_2/\text{rGO-BTB-20}$; (e) and (f) SEM images of $\text{MgH}_2/\text{rGO-BTB-20}$.

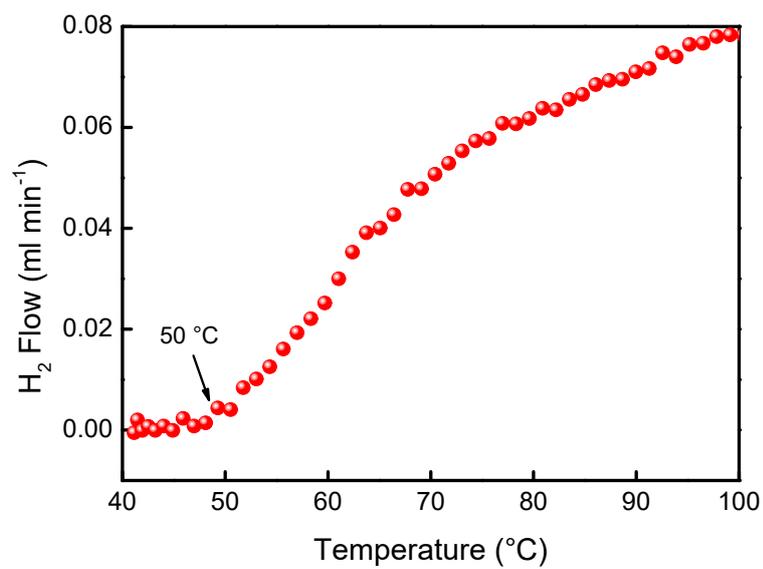


Figure S4 Temperature programmed desorption (TPD) spectrum of MgH₂/rGO-BTB-10 in the region of 40-100 °C recorded with a heating rate of 5 °C min⁻¹.

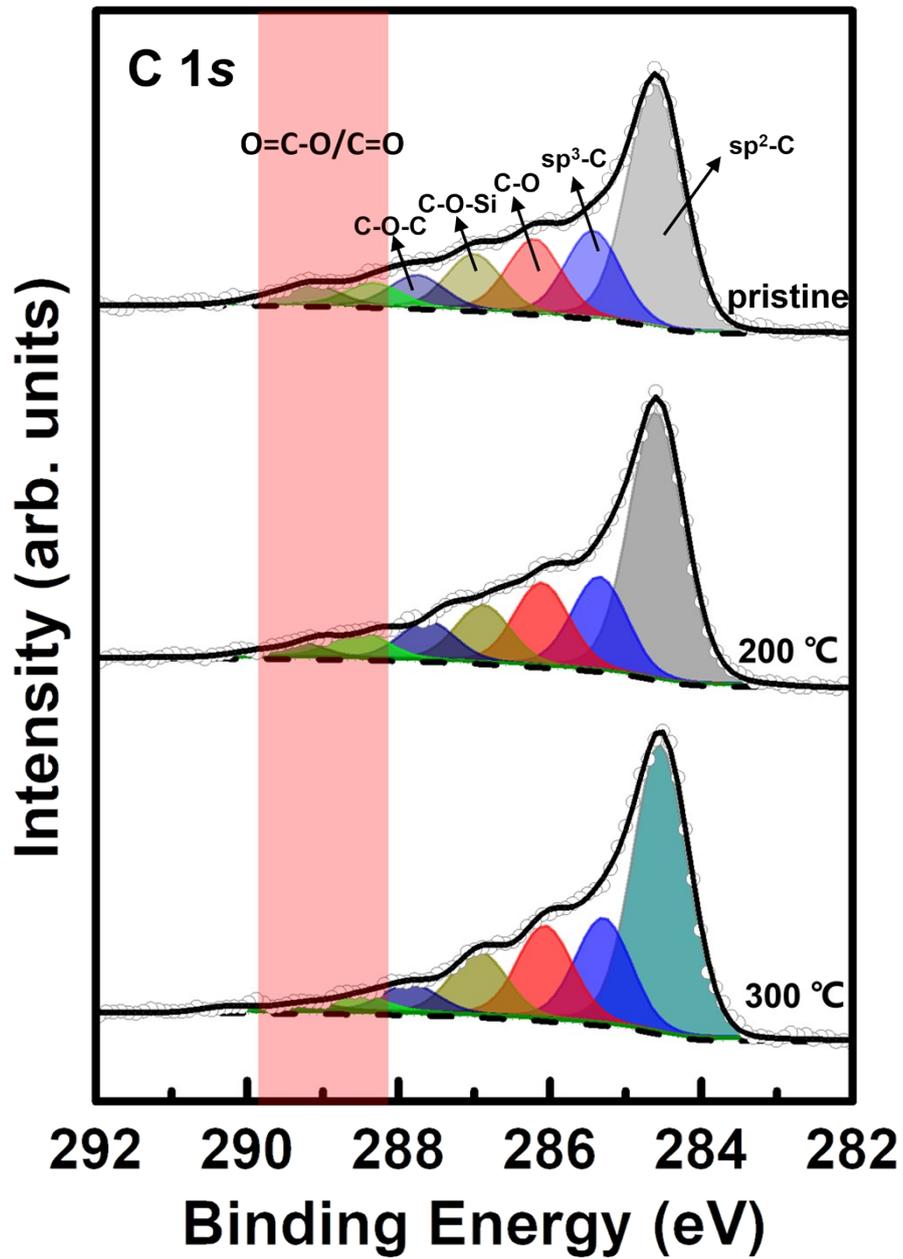


Figure S5. XPS spectra of the C1s core level region of MgH₂/rGO-BTB-10 recorded on the pristine material and after heating to 200 and to 300 °C.

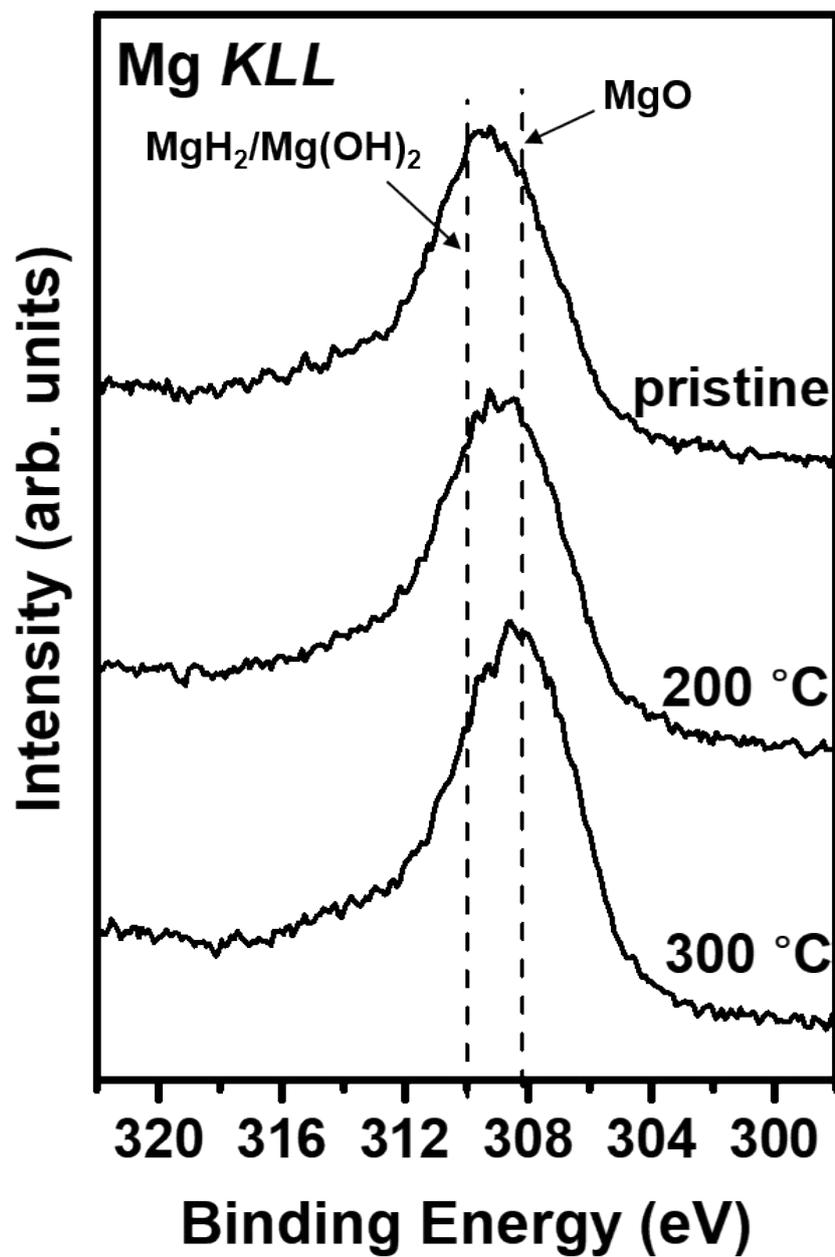


Figure S6. The Mg *KLL* Auger region of the XPS spectra of MgH₂/rGO-BTB-10 recorded before and after heating to 200 and to 300 °C.

Table S1. Binding energies and intensity ratios of C1s core level components as deduced from the XPS spectra collected MgH₂/rGO-BTB-10 recorded before and after heating to 200 and to 300 °C.

species	pristine	200 °C	300 °C
Sp²-C	284.7 eV (44.9%)	284.6 eV (46.0%)	284.5 eV (47.4%)
Sp³-C	285.4 eV (16.0%)	285.3 eV (16.0%)	285.3eV (17.2%)
C-OH	286.3 eV (13.6%)	286.1 eV (14.2%)	286.0eV (15.5)
C-O-Si	287.1 eV (10.3%)	286.9 eV (9.7%)	286.9 eV (10.3%)
C-O-C	287.8 eV (6.0%)	287.6 eV (6.6%)	287.8 eV (4.6%)
C=O	288.5 eV (4.5%)	288.4 eV (4.6%)	288.5eV (2.9%)
O-C=O	289.2 eV (4.2%)	289.2 eV (2.9%)	289.3 eV (2.0%)

References

1. F. Yan, S. Kumar, K. Spyrou, A. Syari'ati, O. De Luca, E. Thomou,; E. M. Alfonsín, D. Gournis, P. Rudolf, *ACS ES&T Water* **2021**, *1*, 157.
2. K. Spyrou, M. Calvaresi, E. K. Diamanti, T. Tsoufis, D. Gournis, P. Rudolf, F. Zerbetto, *Adv. Funct. Mater.* **2015**, *25*, 263.