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Facile Preparation of β-/γ-MgH₂ Nanocomposites under Mild Conditions and Pathways to Rapid Dehydrogenation

Xuezhang Xiao, Zhe Liu, Sina Saremi Yarahmadi, Duncan H. Gregory

A magnesium hydride composite with enhanced hydrogen desorption kinetics can be synthesized via a simple wet chemical route by ball milling MgH₂ with LiCl as an additive at room temperature followed by tetrahydrofuran (THF) treatment under an Ar atmosphere. The as-synthesized composite comprises ca. 18 mass% orthorhombic γ-MgH₂ and 80 mass% tetragonal β-MgH₂ as submicron-sized particles. The β-/γ-MgH₂ nanocomposite exhibits a dehydrogenation capacity of 6.6 wt.% and starts to release hydrogen at ~260 °C; ca. 140 °C lower than that of commercial MgH₂. The apparent activation energy for dehydrogenation is 115±3 kJ mol⁻¹, which is ca. 46 % lower than that of commercial MgH₂. Analysis suggests that the meta-stable γ-MgH₂ component either directly dehydrogenates exothermically or first transforms into stable β-MgH₂, very close to the dehydrogenation onset. The improved hydrogen release performance can be attributed both to the existence of the MgH₂ nanostucture and to the presence of γ-MgH₂.

1. Introduction

Hydrogen is a promising alternative energy carrier, which can facilitate the transition from fossil fuels to clean energy. Among several tangible advantages are a high energy density, its availability from multiple sources (potentially sustainably) and its utilisation with zero carbon emissions. Implementing a safe, low cost, and fully reversible solid hydrogen storage material with a gravimetric capacity in excess of 7.5 wt.% is major challenge for developing next generation energy storage systems.1, 2 Magnesium is a strong candidate material for solid state hydrogen storage because of its excellent reversibility, earth abundance, low cost and high hydrogen storage capacity (7.6 wt.%). It has thus been the topic of extensive research over the last 50 years.3, 4 However, the stable phase of magnesium hydride (β-MgH₂) possesses a rutile structure with a gravimetric capacity in excess of 7.5 wt.% and starts to release hydrogen at ~260 °C; ca. 140 °C lower than that of commercial MgH₂. The main limitation of the room temperature/pressure phase, β-MgH₂, is the low hydrogen desorption enthalpy of 75 kJ mol⁻¹ (compared to 210 kJ mol⁻¹ for MgH₂). The large desorption enthalpy leads to a high apparent activation energy (115±3 kJ mol⁻¹) for dehydrogenation, which is a major drawback for practical applications.5 Different approaches such as catalysis,6, 7 alloying,8, 9 composite formation10, 11 and nanostructuring12-14 have been employed to improve the hydrogen uptake/release kinetics and thermodynamics of MgH₂. MgH₂ is usually produced using extreme processing conditions requiring high pressure (2.5–8 GPa) and high temperature (250–900 °C) or via ultra-high energy reactive ball milling under ca. 80-150 bar H₂ with a Ti-based catalyst.21, 22, 24 Moreover, a fundamental understanding of the formation and decomposition mechanisms of stable γ-MgH₂ is still lacking.

In the present work, we combined a mechanical ball milling process with THF treatment to prepare a β-/γ-MgH₂ nanocomposite without the need for high (hydrogen) pressure or high temperature. Subsequent studies reveal the likely role of the γ-phase and the β-phase transition in the dehydrogenation of nanostructured β-/γ-MgH₂ as compared with β-MgH₂ itself.

2. Experimental Section

All manipulations were carried out under inert atmosphere in an Argon-filled Saffron Scientific recirculating glovebox (< 10 ppm O₂ and H₂O). MgH₂ (Sigma-Aldrich, 98 %) and LiCl (Sigma-Aldrich, ≥99.9 %) were used as received. Approximately 0.5 g of MgH₂ and LiCl were weighed into a 250 mL stainless steel vessel and ground ball milled in a Fritsch Planetary Ball Mill (Pulverisette 6) with 10 mm diameter alumina balls for 12 hours. The grinding media was THF and the samples were ball milled for 24 hours until no further exothermic reactions were observed. The as-prepared composite was dried under vacuum at 100 °C for 12 hours. The as-prepared composite was then degassed under vacuum at 100 °C for 12 hours to remove any residual THF and water. The resulting β-/γ-MgH₂ nanocomposite was then characterized by X-ray diffraction (XRD), thermogravimetric analysis (TGA), and hydrogen adsorption/desorption measurements.
of MgH$_2$/LiCl (1:1 molar ratio) was ball milled for 4 h at 400 rpm with a ball-to-powder ratio of 40:1 under 1 bar Ar atmosphere using a Retsch PM100 planetary ball mill. Then, the black ball-milled MgH$_2$/LiCl mixture was washed with tetrahydrofuran (THF) to remove LiCl using centrifugation. This process was repeated several times until a dark brown precipitate was observed. In addition, the precipitate was dried at room temperature under dynamic vacuum using a Schlenk line. For comparison, the as received MgH$_2$ was first pre-ball milled and then washed with THF and dried subsequently under the same conditions. Hereafter, the as received MgH$_2$ is denoted as MgH$_2$-A, the ball milled MgH$_2$ as MgH$_2$-B, the ball milled MgH$_2$/LiCl mixture as MgH$_2$-C, the ball milled MgH$_2$ after treatment with THF as MgH$_2$-D, and the ball milled MgH$_2$/LiCl mixture after treatment with THF as MgH$_2$-E.

The phase and structural characterisation of samples was performed by X-ray diffraction in glass capillaries (PX; Bruker D8 Advance) over a 2θ range of 10-85° with a step size of 0.016° using Cu Kα radiation. Full profile structure refinement was performed for the MgH$_2$-E sample via the Rietveld method using the GSAS and EXPGUI software packages. Fourier Transform Infrared (FTIR) spectroscopy was conducted on ~1 mg solid samples using a Shimadzu 8400S spectrometer equipped with the IR-solution software package, scanning from ca. 500-4000 cm$^{-1}$ with a resolution of 2 cm$^{-1}$. The solid state samples were measured by Attenuated Total Reflectance (ATR) by pressing the samples on to the diamond crystal of a MIRacle (PIKE) sample holder. Particle size and morphology were probed by scanning electron microscopy (SEM, H Carl-Zeiss Sigma V3) with an accelerating potential of 10 kV. The samples for SEM were mounted on carbon tabs under an inert atmosphere and sputter coated with gold.

The dehydrogenation behaviour of all the samples was measured by simultaneous thermogravimetric-differential thermal analysis (TG-DTA; Netzsch STA 409 instrument contained within an Ar-filled MBraun UniLab recirculating glovebox with <0.1 ppm H$_2$O, 0.1 ppm O$_2$) coupled to a Hiden HPR20 mass spectrometer. Heating rates of 2, 5, 8 and 10 °C min$^{-1}$ respectively were employed from room temperature to 99.999 % purity, 60 mL min$^{-1}$).

3. Results and discussion

PXRD was performed in order to investigate the effects of ball milling and THF treatment on the structure and composition of the MgH$_2$ samples. Patterns of MgH$_2$-A (as-received MgH$_2$), MgH$_2$-B (ball-milled MgH$_2$) and MgH$_2$/LiCl mixtures before and after THF treatment (MgH$_2$-C, -D, -E) are shown in Fig. 1. As shown, the as-received hydride is composed mainly of β-MgH$_2$ along with a small amount of Mg (Fig. 1(a)). β-MgH$_2$ is still present as the main phase after ball milling in MgH$_2$-B, although possible minor traces of γ-MgH$_2$ can be detected in this sample and Mg reflections become subsumed into the broader β-MgH$_2$ peaks and increased background (Fig. 1(b)). Interestingly, the PXD peaks of γ-MgH$_2$ become slightly more prominent after THF treatment (MgH$_2$-D) as shown in Fig. 1(d).

However, it should be noted that the intensities of the γ-MgH$_2$ diffraction peaks in MgH$_2$-B and MgH$_2$-D are weak compared to the β-MgH$_2$ reflections, suggesting that the conversion to the γ-phase is very limited in samples milled without additive. This is perhaps not surprising since γ-MgH$_2$ is a non-equilibrium, meta-stable phase. Its presence as a minor phase might be explained from two competing processes during ball milling: one promotes the formation of γ-MgH$_2$ via the mechanically (pressure) driven θ→γ transformation, whereas the other favours the reverse, thermally driven γ→θ transformation.

The diffraction peaks of β-MgH$_2$ become broader and relatively weaker for MgH$_2$-C. Cl is the strongest X-ray scatterer in the sample and so LiCl dominates the powder pattern, but nevertheless the data indicate that ball-milling using LiCl can further decrease the particle size and potentially increase the concentration of crystal defects in MgH$_2$. LiCl has a high solubility in THF (1.14 mmol g$^{-1}$) and as expected, LiCl is completely removed after treating the MgH$_2$/LiCl mixture with the solvent. The MgH$_2$-E sample is composed of MgH$_2$ with Mg (presumably remaining from the original as-received material) present as a minor phase (Fig. 1(e)). Notably, the relative intensity of the γ-MgH$_2$ diffraction peaks increases after ball milling and treatment with THF. Other variations of the preparative process in which milled samples were mixed with LiCl without washing, washed with THF without adding LiCl or treated with both LiCl and THF, but milled for different times, all resulted in lower (or negligible) γ-MgH$_2$ content compared to MgH$_2$-E (ESI; Figure S1).

Rietveld refinement against PXD data was performed for MgH$_2$-E in order to obtain further information on the phase abundance and cell parameters of the ball-milled MgH$_2$/LiCl sample after THF treatment. The results are shown in Fig. 2 and Table 1. The quantitative analysis confirms that the MgH$_2$-
The E sample is composed of two different polymorphs of MgH$_2$: 18 wt.% orthorhombic γ-MgH$_2$ (space group: Pbcn) and 80 wt.% tetragonal β-MgH$_2$ (space group: P4$_1$/mmm) (in addition to 2 wt.% Mg as minor phase). It is well known that the γ-MgH$_2$ is a high pressure non-equilibrium phase, which is commonly formed by the transformation of β-MgH$_2$ at high pressure (typically 2.5–8 GPa) and high temperature (250–900 °C) or by ultra-high energy reactive ball milling under H$_2$ pressure with a Ti-based catalyst for long durations.\[^{22, 24, 25}\]

FTIR spectra were collected for MgH$_2$-E to provide further insight in our evaluation of the effect of THF treatment on the formation of the tetragonal δ-MgH$_2$ nanocomposites (Fig. 3). By means of comparison, the FTIR spectrum of MgH$_2$-A (commercial MgH$_2$) displays two broad Mg-H bands in the range of 1400-800 and 800-500 cm$^{-1}$.\[^{30}\]

FTIR spectra were collected for MgH$_2$-E, MgH$_2$-A and Mg phases respectively (from top to bottom). They display the strong C-H stretching bands at 2853 and 2978 cm$^{-1}$ and the very strong bands at 1400-800 and 800-500 cm$^{-1}$.\[^{30}\] From this previous evidence and our own, we propose that the THF treatment of the milled hydride material.

Furthermore, as the drying process was performed, it was observed that MgH$_2$ powder was almost uniformly deposited on the inner wall of the Schlenk flask while water condensed and ice formed on the outer surface of the flask. These observations would be consistent with the endothermic vapourisation of THF under dynamic vacuum.

While there are several reports of the synthesis of γ-MgH$_2$ under relatively high pressure and high temperature,\[^{21-23}\] to the best of our knowledge, the meta-stable γ-phase has not been synthesized previously under such mild conditions as we observe here (ball milling with LiCl for 4 h under 1 bar Ar atmosphere and treating with THF at room temperature). Previously, the room temperature synthesis of 11 wt.% γ-MgH$_2$ (with the remainder of the hydride present as β-MgH$_2$) via hydrogenation of Mg in THF solution has been reported but this required a hydrogen gas pressure of 8 MPa for 1-2 days.\[^{31}\]

From this previous evidence and our own, we propose that the THF solution (and likely formation of the polymeric hydride THF adduct) plays a vital role in the synthesis of the meta-stable γ-MgH$_2$ phase. The formation of γ-MgH$_2$ under mild conditions therefore must be attributable to a combination of ball mill-induced nanostructuring using LiCl together with the THF treatment of the milled hydride material.

Particle size, distribution and the morphology of MgH$_2$-A, MgH$_2$-B, and MgH$_2$-E samples before dehydrogenation were...
characterized using SEM as shown in Fig. 4. Commercial MgH₂ (MgH₂-A) is composed of some laminar structures ranging from 20-150 μm across. In the MgH₂-B sample, the particle size is significantly reduced and ranges from 80-800 nm with an average particle size of ~300 nm due to the agglomeration of the irregular particles that occurs following milling. Interestingly, after ball milling with LiCl as an additive and THF treatment (MgH₂-E), a lamellar microstructure predominates with particle lengths/widths ranging from 50-400 nm and particle thicknesses of the order of 10 nm (Fig 4(c,d)). Moreover, it is apparent that the surfaces of the layer structures in the MgH₂-E sample have a high asperity, which would be expected to lead to an increase in specific surface area compared to the smooth particle surfaces in the MgH₂-B sample (i.e. ball milled without LiCl). Although agglomeration seems more severe after THF treatment, such a surface morphology in MgH₂-E is anticipated to lead to a high concentration of surface defects and coupled with the nanoscaling effects of milling, could enhance diffusion and hence enhance the hydrogen absorption/desorption kinetics.

Fig. 5 shows the TG-DTA curves of the MgH₂-A-E samples. The evolved gas mass spectrum from MgH₂-E is presented in Fig. 6. The desorption temperature of commercial MgH₂ peaks above 400 °C, which is in agreement with previous reports. The weight loss for MgH₂-A (ca. 7.0 wt.%) is slightly lower than the theoretical value, which is due to the Mg impurity present in the commercial sample. Compared with commercial MgH₂, both the desorption temperatures and kinetics of MgH₂-B and MgH₂-C are improved because of the reduction in particle size following ball milling. MgH₂-C exhibited the lowest desorption peak temperature of 306.5 °C. This stems from the fact that the fine MgH₂-C particles were prepared using LiCl as an additive, which should act as a milling aid, further reducing the particle size. It is widely accepted that the smaller the MgH₂ particles, the faster the desorption kinetics and the lower the desorption temperature. However, the experimental gravimetric hydrogen capacity on desorption is reduced from 6.89 wt.% for MgH₂-B to 2.57 wt.% for MgH₂-C, due to the additional mass of “inactive” LiCl in the MgH₂-C sample.

With respect to the DTA curve of MgH₂-D, a ca. 20 °C increase in dehydriding peak temperature was observed compared to that of MgH₂-B. A comparable increase in peak temperature occurs between MgH₂-C and MgH₂-E. In both cases the differences probably originate from the increased particle agglomeration following THF treatment. It should be emphasized, however, that the hydrogen desorption onset temperature of MgH₂-D is ca. 25 °C lower than that of MgH₂-B, as is clear from the TG curves. Even more remarkably, the onset of hydrogen desorption for MgH₂-E decreases to ca. 260 °C, which is almost 150 °C lower than that for commercial MgH₂ (MgH₂-A). Moreover, MgH₂-E exhibits a mass loss of 6.6 wt.% although this is slightly lower than the theoretical value for dehydrogenation of MgH₂, importantly no other impurity gases (such as THF, HCl, CO or CO₂) were observed in the mass spectrum (Fig. 6). Of particular note, is a weak exothermic peak at ~290 °C that occurs in the DTA profile of MgH₂-E before the stronger endothermic signal at ~337 °C (Fig. 5(e)).

One possible explanation for this exothermic peak is the phase transformation from meta-stable γ-MgH₂ to the more stable β-phase. A similar phase transformation phenomenon was also reported in the AlH₃ system, where γ-AlH₃ transforms into the α-phase as an exothermic process. Careful comparison of the DTA profiles additionally suggests that a weaker endothermic event overlaps with the exothermic peak at ca. 300 °C and merges with the stronger endothermic peak at ca. 337 °C. This coincides with a weight loss of ca. 1.16 wt.% in the TG profile for MgH₂-E (Fig. 5). This weight loss at lower temperature presumably corresponds to the decomposition of a fraction of smaller size β-MgH₂ particles that either originate from milling with LiCl (as seen for MgH₂-C) or are generated in situ from γ-MgH₂ (following the exothermic phase transition). The second, strong endothermic peak at ~337 °C in the DTA profile of MgH₂-E thus results from the dehydrogenation of β-MgH₂. Therefore, the improved dehydrogenation characteristics of MgH₂-E could be attributed to the formation of a nanocomposite containing meta-stable γ-MgH₂ as engineered by combining ball milling and THF treatments.

![Fig. 4 SEM images of (a) MgH₂-A, (b) MgH₂-B, (c) and (d) MgH₂-E samples before dehydrogenation.](image-url)
In a bid to understand the dehydrogenation pathway of the \( \delta/-\gamma \)-MgH\(_2\) nanocomposite, we performed a series of ex-situ PXD experiments sampled from the system at different temperatures during dehydrogenation. Fig. 7 presents the ex-situ PXD patterns from the dehydrogenation of MgH\(_2\)-E at five selected temperature points. Prior to the heating process, MgH\(_2\)-E is composed of \( \delta \)-MgH\(_2\), \( \gamma \)-MgH\(_2\) and Mg. On heating to 200 °C (Fig. 7(b)), the intensity of the \( \gamma \)-MgH\(_2\) diffraction peaks increases coupled with a reduction in peak width due to the improved crystallinity of the phase. As the temperature is increased to 310 °C (Fig. 7(c)), the diffraction peaks of the meta-stable \( \gamma \)-MgH\(_2\) phase disappear completely and the \( \delta \)-MgH\(_2\) diffraction peaks dominate the pattern. Moreover, upon further increase of the temperature to 350 °C, the intensity of the \( \delta \)-MgH\(_2\) reflections gradually diminish, while the Mg peaks intensify. Additional heating to 450 °C leads to the formation of the Mg as the major phase and the complete absence of \( \delta \)-MgH\(_2\). A small amount of MgO is also detected in the patterns, possibly originating from a surface layer of oxide on particles of the as-supplied MgH\(_2\),\(^{30}\) or arising from handling of the samples during the diffraction experiments. Taking the TG-DTA data (Fig. 5) into account, the weight loss (1.16 wt.% H\(_2\)) at 300 °C is ~17.6 % of the total hydrogen gravimetric desorption capacity measured for MgH\(_2\)-E (6.6 wt.% H\(_2\)). This figure (17.6 %) is very close to the \( \gamma \)-MgH\(_2\) phase fraction of 18.0(5) wt.% derived from Rietveld analysis of the \( \delta/-\gamma \)-MgH\(_2\) nanocomposite. Although from the data available it is not possible to determine definitively whether the \( \gamma \)-MgH\(_2\) phase dehydrogenates directly to Mg (equation 2) or first transforms to \( \delta \)-MgH\(_2\) prior to hydrogen release (equation 3), there is little doubt that the lower temperature hydrogen release is elicited by the presence of the \( \gamma \)-MgH\(_2\) in the hydride mixture.

\[
x (\gamma \text{-MgH}_2) + (1-x) (\delta \text{-MgH}_2) \rightarrow x \text{Mg} + (1-x) \delta \text{-MgH}_2 + x \text{H}_2 \\
\rightarrow \text{Mg} + \text{H}_2 \tag{2}
\]

\[
x (\gamma \text{-MgH}_2) + (1-x) (\delta \text{-MgH}_2) \rightarrow \delta \text{-MgH}_2 \rightarrow \text{Mg} + \text{H}_2 \tag{3}
\]

A similar \( \gamma \rightarrow \delta \) phase transformation event has already been proposed from in situ PXD experiments in the MgH\(_2\) system.\(^{35}\) We suggest that the release of heat from an exothermic \( \gamma \rightarrow \delta \) transition could provide the means by which dehydrogenation occurs more easily in the \( \delta/-\gamma \)-MgH\(_2\) nanocomposite. Ultimately, a detailed dehydrogenation pathway for \( \gamma \)-MgH\(_2\) is not yet known and thermodynamic data for the \( \gamma \)-phase is also not available. Simultaneous in situ powder diffraction combined with TGA could provide the best means for elucidating the dehydrogenation mechanism of this \( \delta/-\gamma \)-MgH\(_2\) nanocomposite in the future.
MgH2-E were quantitatively determined via the Kissinger method, viz.\(^{37}\)

\[
\ln(\delta/T_p^2) = -E_a/RT_p + \ln(A/R\delta) \tag{5}
\]

Where \(\delta\) is the heating rate, \(T_p\) is the absolute temperature at the maximum desorption rate (desorption peak temperature), \(A\) is the pre-exponential factor and \(R\) is the gas constant. In this work, \(T_p\) was obtained using DTA with heating rates of 2, 5, 8, and 10 °C min\(^{-1}\) respectively. The salient details of the DTA profiles for samples MgH2-A, MgH2-B and MgH2-E are displayed in Fig. 8 and the dependence of \(\ln(\delta/T_p^2)\) vs. \(1/T_p\) is shown in Fig. 9. The intrinsic linearity of the curves indicates that the hydrogen desorption kinetics of MgH2 follows the non-isothermal Kissinger equation and comprises a first order decomposition reaction.\(^{37}\) The \(E_a\) was calculated from the slope \((-E_a/R\) of the fitted line, as shown in Fig. 9. The \(E_a\) for MgH2-E is calculated to be 115±3 kJ mol\(^{-1}\), which is ~46 % lower than that of commercial MgH2 (213±6 kJ mol\(^{-1}\)) and ~17 % lower than MgH2 that is ball milled only (138±6 kJ mol\(^{-1}\)). This result suggests that the nanostructuring of the \(\delta\)/\(\gamma\)-MgH2 composite may lower the driving force for Mg nucleation, resulting in enhanced kinetics and a reduced dehydrogenation temperature without the need for catalysts or additives.\(^{38}\)

The as-synthesized \(\delta\)/\(\gamma\)-MgH2 nanocomposite offers a capacity of 6.6 wt.% H\(_2\) and superior hydrogen desorption kinetics without the requirement of a catalyst. However, from our preliminary experiments, the re-/dehydrogenation properties of the nanocomposite on cycling are not clear. Given the presence of the exothermic step in the initial hydrogen release, one might expect that the advantages of the \(\delta\)/\(\gamma\)-phase behaviour are lost in subsequent cycles unless the material undergoes further processing. Additional experiments are underway to investigate the reversibility of the hydrogen absorption and desorption in the \(\delta\)/\(\gamma\)-MgH2 nanocomposite system and the feasibility of a catalytic strategy to improve performance and cyclability still further.

\[\text{Fig. 8 DTA curves of (a) MgH2-A, (b) MgH2-B and (c) MgH2-E samples at different heating rates.}\]

\[\text{Fig. 9 Kissinger plots for the dehydrogenation of (a) MgH2-A (commercial MgH2); (b) MgH2-B and (c) MgH2-E.}\]

4. Conclusions

In summary, an MgH2 nanocomposite composed of tetragonal \(\delta\)-MgH2 and 18 % orthorhombic \(\gamma\)-MgH2 has been prepared for the first time without recourse to high pressure or temperature. By optimizing the ball milling conditions, addition of LiCl and use of THF solvent, the \(\delta\)/\(\gamma\)-MgH2 nanocomposite so-produced is capable of releasing 6.6 wt.% H\(_2\) with rapid kinetics, from ca. 260 °C without the use of a catalyst. The apparent activation energy for dehydrogenation of the \(\delta\)/\(\gamma\)-MgH2 nanocomposite is calculated to be 115±3 kJ mol\(^{-1}\), which is almost half that of commercial MgH2 (213±6 kJ mol\(^{-1}\)). PXD, FTIR and SEM analyses demonstrate that the formation of meta-stable \(\gamma\)-MgH2 under relatively mild conditions is achieved from a combination of ball-milling with LiCl and subsequent treatment with THF. The former treatment is extremely effective in reducing the hydride particle size while the latter appears to encourage \(\gamma\)-MgH2 formation from the hydride THF adduct. Only by combining these two treatments does it appear possible to produce appreciable (>15 wt.%) \(\gamma\)-MgH2 in the MgH2 material. It is possible that during the hydrogen desorption process, \(\gamma\)-MgH2 is first transformed into stable \(\delta\)-MgH2 followed by dehydrogenation to Mg. The significant improvement in desorption performance of the \(\delta\)/\(\gamma\)-MgH2 nanocomposite over \(\delta\)-MgH2 itself could be ascribed to two main factors: 1) a reactive, defective nanostructure which could lead to enhanced hydrogen diffusion and 2) an exothermic process associated with the \(\gamma\)- to \(\delta\)-MgH2 transformation, resulting in improved hydrogen desorption kinetics.

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