Ultrathin Single-crystalline MgO (111) Nanosheets

Pengxin Liu,^{*1} Paula M. Abdala,² Guillaume Goubert,¹ Marc-Georg Willinger,^{*3} and Christophe Copéret^{*1}

¹Department of Chemistry and Applied Biosciences, ETH Zürich, Zürich, Switzerland.

²Department of Mechanical and Process Engineering, ETH Zürich, Zürich, Switzerland.

³The Scientific Center for Optical and Electron Microscopy (ScopeM), ETH Zürich, Zürich, Switzerland.

E-mail: pengxin@ethz.ch; marc.willinger@ethz.ch; ccoperet@ethz.ch

Abstract: Synthesizing high-quality two-dimensional nanomaterials of non-layered metal oxide is a grand challenge because it requires long range single-crystallinity and clean high-energy surfaces. Here, we report the synthesis of single-crystalline MgO(111) nanosheets via a two-step process involving the formation of ultrathin Mg(OH)₂ nanosheets as precursor and their selective topotactic conversion upon heating under dynamic vacuum. The defect-rich surface displays terminal -OH groups, 3-coordinated O²⁻ sites, low-coordinated Mg²⁺ sites as well as single electrons trapped at oxygen vacancies, that render MgO nanosheets highly reactive as evidenced by the activation of CO molecules at low temperatures and pressures, with formation of strongly adsorbed red-shifted CO and coupling of CO molecules into C₂ species.

Introduction

After the exfoliation of graphene from graphite in 2004,¹ ultrathin two-dimensional (2D) nanomaterials have attracted tremendous research interests. The unique structure endows ultrathin nanosheets with high specific surface area, defect-rich surfaces, strong 2D quantum confinement of electrons among many other unconventional properties, which makes them distinct from bulk and other nanostructured counterparts.^{2,3} In the past decade many synthetic approaches have been developed to prepare high-quality nanosheets. For layered compounds that have strong bonding within planes and weak interlayer interaction (hexagonal boron nitride, h-BN; graphitic carbon nitride, g-C₃N₄; transition metal dichalcogenides, TMDs to name a few), top-down methods based on mechanical cleavage or exfoliation from bulk materials are well-documented.^{4,5} However, for non-layered compounds like most oxides, these methods are not applicable.

Due to the intrinsic isotropic structure of most non-layered materials, the synthesis of corresponding ultrathin nanosheets is significantly more challenging.⁶⁻⁸ Currently available strategies are mostly based on templated bottom-up synthesis, by which the final product inherits the structure from a 2D sacrificed-template or a layered-structured precursor. For instance, graphene oxide (GO) has been used as template to prepare 2D γ -Al₂O₃,⁹ MgO¹⁰ and SiO₂¹¹ nanosheets. Topotactic conversion is another efficient method to prepare ultrathin nanosheets by surface modification, heat treatment, nitrogenization, and molecules/ions intercalation of/into the layered precursor nanosheets.^{7,8,12,13} Nevertheless, it remains difficult to grow high-quality single-crystalline nanosheets via these methods. The single-crystallinity is important if one tries to use nanosheets as a material model for establishing detailed structure-property relationships, especially for surface-sensitive applications like catalysis and sensing. Single-crystalline nanosheets with no grain boundary or amorphous composition is thus highly desired to reduce the complexity.

In that regard, early transmission electron microscopy (TEM) studies revealed a topotactic conversion from Mg(OH)₂ to MgO with orientation relationships {where Mg(OH)₂ (0001) and Mg(OH)₂ [11 $\bar{2}$ 0] are parallel to MgO(111) and MgO[10 $\bar{1}$], respectively}.^{14,15} We thus reasoned that using ultrathin Mg(OH)₂ (0001) nanosheets as template should allow the gram-scale synthesis of ultrathin MgO(111) nanosheets. MgO is especially interesting because it is a key support in heterogeneous catalysis due to its basic properties.¹⁶ The polar MgO(111) surface with intrinsic perpendicular electrostatic field is proposed to have unique catalytic properties,¹⁷ but remains challenging to prepare

due to its thermodynamic instability.¹⁸⁻²⁰ Apart from evaporation-deposition under ultrahigh vacuum to form thin films,²¹ synthetic methods to prepare MgO(111) nanoparticles in batch are limited and lead to materials with surfaces contaminated by stabilizing ligands or ions.²²⁻²⁴

Herein, we report the syntheses of ultrathin Mg(OH)₂ nanosheets and single-crystalline MgO(111) nanosheets (MgO-NS) via a two-step MgO-Mg(OH)₂-MgO transition. The fast nucleation during hydrolysis of MgO precursor leads to formation of ultrathin free-standing Mg(OH)₂ nanosheets, that topotactically decomposed into single-crystalline MgO-NS under dynamic vacuum. The single-crystallinity of MgO-NS that consist of stacked (111) planes is directly observed in high-resolution TEM (HRTEM). *In-situ* powder X-ray diffraction (pXRD) and thermogravimetric analysis (TGA) showed that the reduced partial pressure of water vapor during the dehydration process enabled by vacuum treatment was key for the resultant single-crystallinity. Characterization of MgO-NS by Fourier-transform infrared (FT-IR), diffuse reflectance UV-vis spectroscopy (DRS-UV-vis), electron energy loss spectroscopy (EELS), electron paramagnetic resonance (EPR) and FT-IR with CO as probe molecule reveals that the surface is terminated by isolated -OH groups, under-coordinated Mg²⁺ and O²⁻ sites with abundant O-vacancies.

Results

The Mg(OH)₂ nanosheets are synthesized through hydrolysis of freshly prepared MgO nanoparticles (MgO-NP) with carefully controlled reaction kinetics. Previous studies have shown that rate of dissolution and diffusion determine the morphology of hydrated products: slow dissolution (and diffusion) lead to epitaxial growth^{25,26} and fast dissolution lead to bulky product.²⁷ Thus, the hydrolysis reaction should be fast in both nucleation (fast dissolution and diffusion) and growth (to avoid new nucleation). To meet these kinetic requirements, high surface area MgO-NP, freshly prepared by calcining MgCO₃·3H₂O, was used as the precursor (Supplementary Fig. 1-3). During calcination, water and CO₂ was released, leading to a high porosity and high surface area (120 m²/g, Supplementary Fig. 4). The mean crystallite (particle) size of MgO-NP was determined to be 17 nm from XRD pattern and TEM images. Note that MgO-NP should not be stored too long before use to avoid passivation of its surface by CO₂ and moisture. After adding MgO-NP into deionized water, the pH immediately increased to 10.3 in 5 minutes without apparent induction period (Supplementary Fig. 5), indicating a rapid dissolution and nucleation process.

Figure 1. Characterization of $\text{Mg}(\text{OH})_2$ nanosheets and MgO nanosheets. Representative TEM images and SAED patterns of (a) a freestanding $\text{Mg}(\text{OH})_2$ nanosheet from (0001) direction, (c) MgO-NS and (d) MgO-p. (b) AFM image of a single $\text{Mg}(\text{OH})_2$ nanosheet with sub-monolayer attachment and corresponding thickness along the line. (e) HRTEM image of MgO-NS, insets are fast Fourier transform (FFT) pattern and enlarged image showing the {220} lattice fringes.

Mixed with water at room temperature for one hour, MgO-NP completely converted into $\text{Mg}(\text{OH})_2$ as observed by pXRD. Figure 1a shows a typical TEM image of the produced ultrathin $\text{Mg}(\text{OH})_2$ nanosheets. The product has a hexagonal morphology with an edge length of around 150 nm and a smooth surface judging from the contrast (Supplementary Fig. 6). The selected area electron diffraction (SAED) pattern reveals a hexagonal symmetry and can be indexed as a single-crystalline hexagonal $\text{Mg}(\text{OH})_2$ phase recorded from the (0001) zone axis, which is regular for $P3m1$ space group.

After drying the water dispersion on silicon wafer, pXRD of $\text{Mg}(\text{OH})_2$ nanosheets was measured on the assembled thin-film sample (Supplementary Fig. 7). The (001) diffraction peak at 18.8° is relatively more intense with respect to other peaks, by comparison to standard card (JCPDS 01-076-0667), which is consistent with the preferential orientation of the $\text{Mg}(\text{OH})_2$ nanocrystals. The diffraction pattern shows anisotropic peak broadening of (102) diffraction peak comparing to (100) and (110), in line with the nanosheet morphology. Based on Bragg equation, the lattice spacing of (100) was $4.7 \text{ \AA}$ (Supplementary Fig. 8), which is close to reported experimental and DFT results.²⁸

Atomic force microscopy (AFM) measurements show that the synthesized $\text{Mg}(\text{OH})_2$ nanosheets are 5.5 nm thick (Figure 1b), which agrees well with the estimation from the TEM images of $\text{Mg}(\text{OH})_2$ nanosheets standing on their edges (around 5 nm, Supplementary Fig. 6). Adsorbed sub-monolayer is around 1 nm-thick as the height-profile along line 2 shows (Supplementary Fig. 9). The thickness of one atomic layer of $\text{Mg}(\text{OH})_2$ measured from its crystal structure is $6.5 \text{ \AA}$ (the Van der Waals radius considered). Hence, the sum of one monolayer's thickness and one interlayer distance matches well with the measured value (Supplementary Fig. 8). The thickness of adsorbed adlayer is also close to the measured thickness of previously reported $\text{Mg}(\text{OH})_2$ monolayers synthesized though mechanical exfoliation of bulk crystals, which was $\sim 0.9 \text{ nm}$ when deposited onto SiO_2/Si substrates.²⁸ Based on these values, we estimate that our $\text{Mg}(\text{OH})_2$ nanosheets are composed of 5 atomic layers.

To mimic the topotactic conversion (Supplementary Fig. 10) observed in TEM studies,^{14,15} the gram-scale dehydration treatment of $\text{Mg}(\text{OH})_2$ nanosheets was carried out under dynamic high vacuum. The yielded MgO-NS display a high surface area ($246 \text{ m}^2/\text{g}$, Supplementary Fig. 11). TEM images show that MgO-NS are freestanding and nicely retain the hexagonal shape of $\text{Mg}(\text{OH})_2$ nanosheets (Figure 1c, Supplementary Fig. 12). In previous studies, final decomposed products of $\text{Mg}(\text{OH})_2$ were usually composed of MgO crystallites (typically cubes of 2 nm) attached in the same orientation.^{29,30} Crystal cracking was proposed to originate from the presence of local strain, considering the small shrinkage ($\sim 5\%$) of lattice from $\text{Mg}(\text{OH})_2$ to MgO. For MgO-NS, the observed terrace structures on the surface (Supplementary Fig. 12) is likely due to such a strain built in the lateral dimension and consequent surface reconstruction driven by energy minimization. While along the z-axis, the ultrathin precursor should prevent a large strain, leading to comparably flat surfaces [although oriented attachment of small cubes can't be fully ruled out if several $\text{Mg}(\text{OH})_2$ nanosheets stack when heated (Supplementary Fig. 13)].

The SAED pattern of MgO-NS (Figure 1c, Supplementary Fig. 14) reveals their single crystalline nature and preferential orientation. The hexagonal spot pattern of {220} planes shows MgO-NS are preferentially oriented in [111] direction, which is consistent with the observation by high-resolution TEM (HRTEM) images (Figure 1e, Supplementary Fig. 15). The observed lattice fringes with $1.50 \text{ \AA}$ spacing ascribed to {220} (whose d-spacing in bulk MgO is $1.49 \text{ \AA}$) are in the same direction throughout the lateral dimension of a single piece of MgO-NS. The 3-fold symmetry of MgO(111) is clearly observed in Figure 1e inset.

In sharp contrast, $\text{Mg}(\text{OH})_2$ nanosheets heated under N_2 flow decomposed into polycrystalline MgO-p instead of single-crystalline MgO-NS. TEM images show that the sheet-like structure is retained in the product but not the hexagonal shape (Figure 1e, Supplementary Fig. 16). The circular diffraction ring observed in the inset SAED pattern is assigned as a diffractogram

projected from [111] direction, which means that MgO-p is polycrystalline with small domains in the same orientation. To study why the different synthetic conditions largely changed the crystallinity of MgO product, TGA measurements were carried out to analyze the thermal behavior during the decomposition process. Atmosphere and ramping rates were controlled as the same with that of material preparation. TGA conducted under vacuum show a 30% weight loss [theoretic value when $\text{Mg}(\text{OH})_2$ fully dehydrated is 31.0%] in the temperature range of 265 – 328 °C (Figure 2a). Such a range is noticeably lower than that of commonly reported values,³⁰ which may be due to the ultrathin structure of $\text{Mg}(\text{OH})_2$ nanosheets. However, in the N_2 flow (Figure 2b), the major weight loss occurs in the temperature range of 300–360 °C. Another significant difference is that an endothermic peak is observed in the differential scanning calorimetric (DSC) analysis at this range in N_2 atmosphere, which is not observed when TGA was conducted under vacuum. We believe that dynamic vacuum helped to remove the produced water from MgO surface, thus preventing the reversible $\text{MgO} + \text{H}_2\text{O} \rightleftharpoons \text{Mg}(\text{OH})_2$ reaction and ensuring the topotactic conversion to form single-crystalline product.

Figure 2. Characterization of $\text{Mg}(\text{OH})_2$ decomposition process coupled with phase transition. TGA and DSC results (a) under dynamic vacuum and (b) under N_2 flow. (c) *In-situ* pXRD patterns during the decomposition of $\text{Mg}(\text{OH})_2$ along with a phase transition under dynamic vacuum.

In-situ pXRD operated under dynamic vacuum (Figure 2c) was conducted to probe the simultaneous phase transition during decomposition. From room temperature (25 °C) to 290 °C, the diffraction peaks of $\text{Mg}(\text{OH})_2$ (001) at 32.76°, (101) at 37.9° and (110) at 58.61° show almost invariant integrated intensities and only slight shifts in peak positions toward lower angles (less than

0.2°). While the (102) diffraction peak observed at 50.9° at 25 °C shifts to lower angle by 0.5° at 290 °C, indicating an anisotropic lattice relaxation along this plane. At ca. 300 °C peaks due to MgO appear, initially as broad Bragg peaks due to the nanocrystalline nature of the MgO product, with a concomitant and sudden decrease in the intensity of peaks due to $\text{Mg}(\text{OH})_2$. At 320 °C, all the peaks due to $\text{Mg}(\text{OH})_2$ disappear. The temperature range for phase transformation (300–320 °C) is in line with the decomposing temperature range determined from TGA.

To further study the surface state of prepared MgO-NS, we used combined IR, DRS-UV-vis, EPR, EELS and CO-probed IR to characterize the material. To systematically study the decomposition process in the sense of surface structure evolving, we prepared a series of MgO samples by heating $\text{Mg}(\text{OH})_2$ nanosheets at different temperature under dynamic vacuum and characterized them by IR (Figure 3a, Supplementary Fig. 17). The stretch frequencies of surface -OH species show strong dependence on the dehydration temperature. In the range of 300–600 °C, a sharp peak at 3753 cm^{-1} is assigned to one-coordinated isolated -OH, slightly higher than reported 3750 cm^{-1} on (001) terminated MgO cubes.^{31,32} This specie is quite stable up to 700 °C when -OH at 3750 cm^{-1} is observed. Combined with BET (215 m^2/g) and TEM measurements, we find that the sheet-like structure collapsed at temperature above 700 °C. The observation is consistent with a previous hypothesis that MgO (111) surface is likely stabilized by surface -OH groups.³³ The measured -OH density through titration is consistent with this statement. The -OH density drops from ~2.0 -OH/ nm^2 (500 °C treated) to ~1.3 -OH/ nm^2 (700 °C treated). Note that compared to previously reported MgO(111) systems,²³ MgO-NS have symmetric -OH stretching peaks, likely indicating a more well-defined surface.

Figure 3. Characterization of the decomposed MgO product under different temperatures. (a) FTIR spectra and (b) DRS curves of prepared MgO through $\text{Mg}(\text{OH})_2$ decomposition. (c) Scheme representing the topotactic transition and corresponding surface structure.

Similar to the observation of Knözinger *et al.* during evacuation at temperatures between 300–400 °C,³¹ a component in the interval between 3740–3690 cm^{-1} disappears, along with low-frequency

bands at 3513 and 3374 cm^{-1} . These associated bands are assigned to H-bonded -OH groups, that could recombine to water at temperature below 400 $^{\circ}\text{C}$. Note that such a process is reversible if water is not removed by vacuum. As shown in TGA (Figure 1f), the temperature range for massive water releasing matched well with 300-400 $^{\circ}\text{C}$ observed in IR. Another band at 3620 cm^{-1} is still observed after dehydration at 500 $^{\circ}\text{C}$; it is seldom found on (001) terminated MgO cubes, and is assigned to H-O_{3c} on three coordinated O^{2-} on (111) surface.

Figure 3c shows a scheme of the decomposition process of $\text{Mg}(\text{OH})_2$. Heated up to 400 $^{\circ}\text{C}$, most of H-bonded -OH groups are removed from the surface, leaving isolated -OH groups. Considering the stoichiometry of the reaction, a complete removal of water would result in 0.5 monolayer coverage of terminal O^{2-} anions, leaving 50% 4-coordinated Mg^{2+} cations (Mg_{4c}) and 50% 5-coordinated Mg^{2+} cations (Mg_{5c}) sites on the surface. We propose that partially dehydrated surface have both Mg_{4c} and Mg_{5c} exposed (vide infra).

DRS-UV-vis measurements were then conducted to detect these surface defect sites. Although the energy to generate bulk excitation for MgO is 7.7 eV in the far-UV region, nanosized MgO with high surface area usually show optical absorptions at significantly lower energies due to defects.³⁴⁻³⁶ The presence of defects (O-vacancies, under-coordinated sites, dopants, etc.) would give rise to electronic transitions upon light absorption. In our system (Figure 3b), for MgO-NS dehydrated at 400, 500 and 600 $^{\circ}\text{C}$, the observed UV resonance absorption bands at 5.6 eV (221 nm) are assigned to a charge transfer between O_{3c} to Mg_{4c} , close to the absorption of corner sites of cubic MgO nanoparticles (5.5 eV, 225 nm).³⁵ This absorption band disappear on MgO-NS-cal, when calcined in synthetic air; it is replaced by an absorption band at higher energy, indicating a higher coordination of surface Mg^{2+} cations (Supplementary Fig. 18). For MgO_{700} , the adsorption at 5.8 eV (214 nm) and 4.4 eV (282 nm) matches with those of surface anions on edges (5.5 eV) and on corners (4.6 eV) of MgO nanocubes, respectively.³⁶ This further supports the collapsing of nanosheets into small domains above 700 $^{\circ}\text{C}$.

Figure 4. Characterization of surface structure of MgO-NS. FTIR spectra using CO as probe molecule adsorbed on (a) MgO-NS and (b) calcined MgO-NS-cal.

To further confirm the presence of low-coordinated Mg^{2+} sites on the defect-rich surface of MgO-NS, we used CO as a probe molecule since CO can distinguish among surface Mg^{2+} sites of different coordinative unsaturation. In the range of 2200-1300 cm^{-1} , bare MgO-NS showed only a broad band of -OH bending at 1421 cm^{-1} . As the dosing of CO increased, bands assigned to CO adsorbed on Mg^{2+} sites and newly formed anionic species (carbonates, $\text{C}_2\text{O}_3^{2-}$ etc.) are observed. The observed C-O stretch at 2110 and 2090 cm^{-1} red-shifted relative to that of gas-phase CO (2143 cm^{-1}), is distinct from what is typically observed on commonly studied MgO cubes or polycrystals, where adsorbed $\text{C}\equiv\text{O}$ is blue shifted^{37,38} to +60, +27 and +14 cm^{-1} for CO adsorbed on Mg_{3c} , Mg_{4c} , and Mg_{5c} , respectively.³⁹ The red-shifted C-O bands indicate a weakened C-O bond, which implies that electron transfer from MgO surface to CO molecules dominates, similar to π back-donation in low valent transition-metal carbonyl complexes. The possible electron donor could be surface O^{2-}_{3c} , single electrons trapped at oxygen vacancies (F^+ centers) or density of state near Fermi level.^{40,41} EPR and EELS spectra of MgO-NS confirmed the presence of single electrons at oxygen vacancies (Supplementary Fig. 19, 20).^{41,42} An alternative explanation for red-shifted C-O stretch is the Stark effect considering the interaction between the dipole moment of the bond and the external electric field on polar MgO(111) surface.⁴³ Typically, CO on lower-coordinated Mg^{2+} showed higher vibration frequency, thus the two peaks at 2110 and 2090 cm^{-1} were ascribed to CO on Mg_{4c} and Mg_{5c} , respectively. After long evacuation time, the two peaks remain unchanged, unlike the reversible desorption in previous studies, suggesting that CO is comparably strongly adsorbed.

Besides Lewis acid Mg^{2+} , CO is also sensitive to basic O^{2-} sites, which allow us to probe the low O coverage on MgO-NS. Bands in the range of 1700-1300 cm^{-1} are assigned to anionic species and polymeric CO clusters produced by nucleophilic attack of basic O^{2-} on CO.^{44,45} Surface reactions originated from the formation of CO_2^{2-} species, followed by oligomerization and disproportionation. The hypothesized reaction sequence was:

For CO-adsorbed MgO-NS (Figure 4a), the strongest band at 1608 cm^{-1} is assigned to COO asymmetric stretching, which is formed via the primary attack of CO by the low coordinated O^{2-}_{3c} sites (eq. 1). The intensity of bands at 1678, 1380 and 1320 cm^{-1} increase simultaneously as the dosing of CO increased, suggesting that these bands are correlated. These bands are assigned to $\text{C}_2\text{O}_3^{2-}$ species (eq. 2), since the IR spectrum of $\text{MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ with bidentate oxalate ions showed bands at 1675, 1380 and 1320 cm^{-1} .⁴⁶ EPR spectra of MgO-NS in CO atmosphere clearly showed the evolution of CO radical species (Supplementary Fig. 20),⁴⁷ which may relate to the formation of $\text{C}_2\text{O}_3^{2-}$ species through C-C coupling. Another band at 1375 cm^{-1} is assigned to unidentate carbonate groups (eq. 3, 4), because it was also observed on CO_2 adsorbed MgO.⁴⁶ All the formed species cannot be removed by vacuum and indicate that the Mg(111) facet is characterized by O vacancies and the presence of available electrons.

A major difference in surface structure between MgO-NS and previously studied MgO cubes and polycrystals was the relative amount of undercoordinated surface sites. For a perfect cube, five coordinated sites (Mg^{2+}_{5c} and O^{2-}_{5c}) on flat (001) faces are main surface sites, with four coordinated sites (Mg^{2+}_{4c} and O^{2-}_{4c}) on step and edge and three coordinated sites (Mg^{2+}_{3c} and O^{2-}_{3c}) on

corners. While on (111) surface, O^{2-}_{3c} is the most abundant species, making the surface strongly basic and highly active interacting with CO. Hence, we did not observe the evolution of different species in IR spectra of CO-adsorbed MgO-NS after prolonged duration.

After calcined in synthetic air, the surface oxygen coverage of MgO-NS-cal likely increases, as observed by the peak ranging from 200 to 500 °C in TPO experiment (Supplementary Fig. 21). In the IR spectra of MgO-NS-cal with CO as probe, bands in the range of 1700-1300 cm^{-1} are similar to those of MgO-NS, while a strong band at 1648 cm^{-1} assigned to bidentate carbonate groups appeared^{46,48} and the bands at 1678 cm^{-1} from $\text{C}_2\text{O}_3^{2-}$ species disappeared. This indicates that the reactions according to eq. 3-4 are much more favored with more O^{2-}_{3c} surface sites. The higher oxygen coverage also makes the surface more polar, leading to a slightly more redshifted CO stretching to 2108 and 2088 cm^{-1} .

Conclusion

Ultrathin single-crystalline MgO nanosheets with a preferential orientation stacked by (111) planes are prepared via thermolysis of ultrathin $\text{Mg}(\text{OH})_2$ precursor under dynamic vacuum. The topotactic transition of $\text{Mg}(\text{OH})_2$ takes place at 300 °C according to TGA and *in-situ* XRD carried out under the same conditions. The well-defined surface as evidenced by high-resolution TEM exposes 3-coordinated O^{2-} sites, 4- and 5-coordinated Mg^{2+} sites and isolated -OH groups according to multiple spectroscopic techniques in combination with probe molecules. Adsorbed CO is easily activated by single electrons trapped at oxygen vacancies and O_{3c}^{2-} sites, thus forming strongly bonded red-shifted CO as well as coupled C_2 and polymeric species. This simple way to synthesize ultrathin single-crystalline MgO(111) nanosheets on gram scale opens the possibility to explore their surface chemistry and to generate on these unconventional surfaces functional materials such as heterogeneous catalysts.

Author contribution

P. L. and C. C. conceived the project. C. C. supervised the research. P. L. performed the preparation and characterization of samples; P. M. A. performed *in-situ* XRD measurements; G. G. performed AFM measurements; M. G. W. performed HRTEM and EELS measurements. All authors discussed the results and contributed to the final manuscript.

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Competing interests

Authors declare no competing interests.

Methods

Preparation of Materials. The synthesis of ultrathin MgO-NS was achieved in three steps: production of high surface-area MgO nanoparticles (MgO-NP) through calcination of $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$, hydrolysis of MgO-NP to produce $\text{Mg}(\text{OH})_2$ nanosheets and decomposition of $\text{Mg}(\text{OH})_2$ to MgO-NS under dynamic vacuum. 100 mL Na_2CO_3 aqueous solution (0.5 M) was rapidly added into 400 mL of $\text{Mg}(\text{NO}_3)_2$ aqueous solution (0.125 M) under vigorous

stirring at room temperature. Scaling up was also possible when concentration of both solutions remained the same. After 10 minutes, the precipitation was collected via filtration, washed with deionized water and ethanol, then dried under reduced pressure. The yielded white powder was transferred into an alumina crucible and calcined at 500 °C for 2 hours under air atmosphere. The ramping rate was controlled at 2 °C·min⁻¹. After cooled to room temperature, MgO-NP was collected and used for next step (avoid long-time storage).

The hydrolysis of MgO was conducted at room temperature, MgO-NP was added into deionized water (1 mg/mL) under stirring. The dispersion gradually turned into a colloidal suspension showing apparent pearlescent effect, which indicated formation of lamellar structure. After 1 hour, the product was collected via filtration and dried under reduced pressure. The highest scale trial of this reaction was 1L, in which case 1.4 g $\text{Mg}(\text{OH})_2$ nanosheets was produced quantitatively.

Single-crystalline MgO-NS was prepared using $\text{Mg}(\text{OH})_2$ nanosheets as precursor for heat treatment under high vacuum. During both ramping and heating process, the reactor was evacuated with pressure lower than 10⁻⁵ mbar. The ramping rate was 1 °C·min⁻¹. After heated at 600 °C for 12 hours, the white powder was collected and stored in an argon filled glovebox, noted as MgO-NS. A series of MgO calcined at varied temperatures (300, 400, 500 and 700 °C) were prepared using the same ramping rate and heating duration, noted as MgO_x where X means the used temperature. Another sample using same heating program without high vacuum was conducted under flow of N_2 (40 mL/min), noted as MgO-p. Calcined MgO-NS was obtained by calcining MgO-NS under dried synthetic air at 400 °C for 6 hours, noted as MgO-NS-cal.

Characterization. Transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM) and selected-area electron diffraction (SAED) was conducted on a FEI Talos F200X microscope under 200 kV and JEOL Grand ARM within the facilities of ScopeM.

DRS spectra were measured at room temperature using an Agilent Cary 5000 UV-vis-NIR spectrometer (200-800 nm, 10 nm·s⁻¹ scan rate) equipped with a Harrick Scientific Praying Mantis diffuse reflectance accessory. Samples were placed in a sample chamber with quartz windows to preserve the inert (argon) atmosphere.

TGA was carried out on a NETZSCH STA 449 Jupiter. Under either N_2 (5.0) used as feed gas or vacuum in respective experiments. In a typical analysis, 20 mg of finely grounded powder was loaded into the alumina crucible. Then the reaction chamber was flushed with N_2 (flow 40 mL·min⁻¹) for 30 min at 30 °C. The sample was then heated to 900 °C with a rate of 2 °C·min⁻¹. While for decomposition of $\text{Mg}(\text{OH})_2$ under vacuum, a turbo pump was connected to the TGA and the chamber was pumped for 2 h prior to the experiment to pressure of 2 × 10⁻⁴ mbar. Then the sample was heated 2 °C·min⁻¹ under dynamic evacuation.

In-situ pXRD experiments were performed in a PANalytical Empyrean equipment using a Cu K α radiation (45 mA and 40 kV) equipped with a X'Celerator Scientific ultra-fast line detector. Approximately 0.1 g of the material was placed in the reaction chamber (XRK 900, Anton Paar). The chamber was evacuated by a 2-stage rotary slide pump to 1 × 10⁻⁴ mbar. The diffraction patterns during decomposition experiments (following the procedure of the TGA experiments) were recorded in the 2 θ range of 20–60° using a step size of 0.02° (acquisition time ca. 5 min/scan) at every 20 °C.

FTIR spectroscopy experiments were performed on self-supporting wafers using a Bruker Alpha spectrometer in transmission mode (24 scans, 4 cm⁻¹ resolution) under Ar atmosphere. FTIR spectra with adsorbed CO (Nicolet NEXUS 6700 infrared spectrometer; 2 cm⁻¹ resolutions, 1200–4000 cm⁻¹, average of 32 scans) of MgO at different CO coverage were collected in transmission mode. A wafer of the sample (~0.01 g·cm⁻¹) was pressed into an aluminum ring, which was placed into a glass vacuum cell with CaF₂ windows. The cell was exposed to desired pressure of CO at room temperature for 5 min. The IR spectrum of the cell was collected with the aluminum ring in the middle of the optical path or out of the optical path (as background).

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