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Electronic Supplementary Information

Direct bottom-up synthesis of size-controlled monodispersed single-layer magnesium hydroxide nanosheets modified with tripodal ligands

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Experimental

Materials

Magnesium chloride hexahydrate (MgCl₂·6H₂O) was purchased from Kanto Chemical Co., Inc. Tris(hydroxymethyl)aminomethane (Tris-NH₂) and 6 M hydrochloric acid were purchased from FUJIFILM Wako Pure Chemical Ind. Ltd. Ethanol was purchased from Junsei Chemical Co., Ltd. All reagents were used as received. Silicon substrates (Si(100)) were purchased from Silicon Technology Co., Ltd. Semicoclean 23, an alkaline washing solution for cleaning the substrates, was purchased from Furuuchi Chemical Corporation.

Preparation of Mg-Tris-NH₂ nanosheets

Aqueous solutions of MgCl₂·6 H₂O (0.01 M, 25 mL) and Tris-NH₂ (1.0 M, 25 mL) were mixed at room temperature (25 °C) in a polypropylene bottle (250 mL). The closed polypropylene bottle was placed in an oven at 80 °C. After heating for 2 h, the water dispersion containing the nanosheets was obtained. When the nanosheets were analyzed as a powder, this dispersion was filtered by using a membrane filter (pore size: 0.2 μ m) under vacuum. The obtained gel was washed with water and dried in an oven at 80 °C. In order to control the lateral size of the nanosheets, the concentration of Tris-NH₂ before mixing was changed to 0.75 and 1.25 M.

Estimation of the degree of Mg consumption to Mg-Tris-NH₂ nanosheets

The Mg-based conversion Y(%) was calculated as follows:

$$Y = \frac{(m_0 - m)}{m_0}$$

where m_0 and *m* are the amount of added Mg²⁺ (mg) and the amount of remaining Mg²⁺ in the dispersion (mg), respectively. The term *m* was calculated from the Mg²⁺ concentration in the filtrate of the nanosheet dispersion.

The number of nanosheets $N(L^{-1})$ was calculated as follows:

$$N = \frac{n \times S_0}{(\frac{3\sqrt{3}}{8}D^2)}$$

where *n*, S_0 , and *D* are the number of converted Mg atoms to nanosheets per a liter of reaction solution (L⁻¹), area of magnesium hydroxide sheet per Mg²⁺ atom (nm²), and average lateral size of Mg-Tris-NH₂ nanosheets (nm), respectively.

Characterization

Powder X-Ray diffraction (XRD) patterns were recorded with a Rigaku Ultima III diffractometer using Cu Ka radiation (40 kV, 40 mA). Fourier transform infrared (FTIR) spectra were obtained with a JASCO Model FT/IR-6100 system using KBr disks. Atomic force microscopy (AFM) images were recorded on a Digital Instruments Nanoscope III microscope equipped with a silicon cantilever, using the tapping mode. The dispersions of the nanosheets (100 µL) were spin-coated (2000 rpm, 30 s) onto a silicon substrate which was cleaned by Semicoclean 23 prior to use. After the spin coating, the recrystallized Tris-NH₂ was washed through immersing the substrate in ethanol for several times. High-resolution scanning electron microscope (HR-SEM) images were acquired at an accelerating voltage of 1 kV using a Hitachi S-5500 microscope. Transmission electron microscope (TEM) images and the selected area electron diffraction (SAED) patterns were obtained with a JEOL JEM-2010 microscope at an accelerating voltage of 200 kV. The nanosheet dispersions diluted in ethanol were dried on a holey-carbon-coated copper grid. Ultraviolet visible (UV-Vis) absorption spectra were recorded on a V-670 (JASCO) spectrometer. The dissolved magnesium ions in the dispersion of nanosheets were analyzed by inductively coupled plasma optical emission spectroscopic (ICP-OES) analyses with an Agilent ICP 5100 system. The electrophoretic mobility of the nickel hydroxide nanosheets was measured by using an Otsuka electronics ELSZ-1 analyzer. The pH value of the reaction solution was collected with a water quality meter (F-74T, Horiba) using a glass electrode (9618-10D).



Fig. S1 (a) XRD pattern and (b) FTIR spectrum of Mg-Tris- $NH_2_{1.0}$ collected by filtration.



Fig. S2 Reprinted TEM image (without dashed lines) of Mg-Tris-NH₂_1.0 shown in Fig. 1a.



Fig. S3 SEM image of Mg-Tris- $NH_2_{1.0}$ at low magnification.



Fig. S4 SEM image of Mg-Tris- $NH_2_{1.0}$ stored at ambient conditions for approximately 15 d.

synthetic conditions			lateral size		degree of Mg consumption		
Tris-NH ₂	reaction	pH ^a	average	CV ^b	Mg^{2+}	Mg-based	number of
concentration	time		size		concentration	conversion	nanosheets
$[mol \cdot L^{-1}]$	[min]	[-]	[nm]	[%]	$[mmol \cdot L^{-1}]$	[%]	$[10^{14} \cdot L^{-1}]$
1.0	10	10.8	366	12.3	3.63	27	8.1
1.0	30	10.8	495	9.3	2.78	44	7.2
1.0	80	10.8	572	8.4	1.71	66	8.0
1.0	120	10.8	622	7.9	1.57	69	7.1
0.75	120	10.7	847	7.3	2.30	54	3.0
1.25	120	10.8	404	6.6	1.23	75	18.4

Table S1 Synthetic conditions, lateral sizes, and degree of Mg consumption of Mg-Tris-NH₂ nanosheets.

^{*a*} pH was measured immediately after mixing at room temperature. ^{*b*} CV is defined as a standard deviation divided by the average size.



Fig. S5 (a) AFM image of the spin-coated Mg-Tris- $NH_2_{1.0}$ obtained immediately after mixing the solutions. (b) Height profiles of Mg-Tris- $NH_2_{1.0}$ obtained immediately after mixing the solutions on the dashed line indicated in (a). (c) SEM image of Mg-Tris- $NH_2_{1.0}$ obtained immediately after mixing the solutions.



Fig. S6 SEM images of Mg-Tris-NH₂_1.0 aged for (a) 10 min, (b) 30 min, and (c) 80 min.



Fig. S7 Height profiles of Mg-Tris- $NH_2_{1.0}$ aged for (a) 10 min, (b) 30 min, and (c) 80 min on the dashed lines indicated in Fig. 2a–c in the main text.



Fig. S8 Photographs of the dispersion of Mg-Tris- $NH_2_{1.0}$ aged for (a) 10 min, (b) 30 min, (c) 80 min, and (d) 120 min. Photographs of the filtrate of the dispersion of Mg-Tris- $NH_2_{1.0}$ aged for (e) 10 min, (f) 30 min, (g) 80min, and (h) 120 min. Green laser light exthibits the Tyndall effect.



Fig. S9 XRD patterns of (a) Mg-Tris- $NH_2_0.75$ and (b) Mg-Tris- $NH_2_1.25$ collected by filtration. FTIR spectra of (c) Mg-Tris- $NH_2_0.75$ and (d) Mg-Tris- $NH_2_1.25$ collected by filtration.



Fig. S10 Height profiles of (a) Mg-Tris- $NH_2_0.75$ and (b) Mg-Tris- $NH_2_{1.25}$ on the dashed lines indicated in Fig. 3a–b in the main text.



Fig. S11 SEM images of (a) Mg-Tris-NH₂_0.75 and (b) Mg-Tris-NH₂_1.25.



Fig. S12 Size distribution histogram of (a) Mg-Tris-NH₂_0.75, (b) Mg-Tris-NH₂_1.0 and (c) Mg-Tris-NH₂_1.25. The size in (a)–(c) was defined by the diagonal length of hexagonal particles and measured from SEM images (N= 200).



Fig. S13 SEM images of (a) Mg-Tris-NH₂_2.0 and (b) its magnified image.



Fig. S14 (a) AFM image of the spin-coated Mg-Tris- $NH_2_0.5$. (b) Height profiles of Mg-Tris- $NH_2_0.5$ on the dashed line indicated in (a). (c) SEM image of Mg-Tris- $NH_2_0.5$. (d) XRD pattern and (e) FTIR spectrum of Mg-Tris- $NH_2_0.5$ collected by filtration.

Estimation of the change in the lateral size by light scattering

Coleman's group has demonstrated that the non-resonant regime of extinction spectra of the dispersions of nanomaterials with wide bandgap correlates with the mean lateral sizes of the nanosheets.^{1,2} Here, the light scattering in the dispersions of Mg-Tris-NH₂ nanosheets at visible light region was measured by using a UV-Vis spectrophotometer without an integrating sphere.

The extinction spectra of the dispersion of Mg-Tris-NH₂ nanosheets are shown in Fig. S15a–c. Because Mg(OH)₂ does not absorb light at wavelength from 300 to 700 nm, the extinction spectra at this region can be interpreted as scattering profiles.¹ We note that the Tris-NH₂ solution does not display any observable absorption or scattering (Fig. S15d). When the effect of optical absorption can be ignored, the scattering coefficient σ (L·g⁻¹·m⁻¹) is defined from the transmittance:

$$T \cong 10^{-\sigma cl}$$

where *c* and *l* are the mass concentration of converted Mg to nanosheets $(g \cdot L^{-1})$ and the cell length (m), respectively. The term *c* is calculated from the *m*. The scattering coefficient spectra of the water dispersion of Mg-Tris-NH₂ nanosheets are shown in Fig. S15e–g. As the average particle size increases, the scattering coefficient at each wavelength also increases. Because the scattering coefficient has a positive correlation with the average particle size,¹ this results supports the global changes in the lateral size which is locally confirmed from AFM and SEM observations.

Moreover, the scattering coefficient σ tends to vary with wavelength λ (nm) as power law:

$\sigma(\lambda) \propto \lambda^{-n}$

where *n* is scattering exponent.² Using this equation, the values of *n* are preliminaly extracted from the fits of scattering coefficient spectra at wavelength between 300–350 nm where the effect of noise is small. Because the scattering exponent (*n*) plotted versus the average lateral size shows the negative correlation (Fig. S16), the series of analysis may be a good metric for estimating the lateral size of nanosheets as discussed in the literature.^{1, 2}



Fig. S15 Extinction spectra of the water dispersion of (a) Mg-Tris-NH₂_0.75, (b) Mg-Tris-NH₂_1.0, (c) Mg-Tris-NH₂_1.25, and (d) aqueous solution of Tris-NH₂ (0.5 M) measured by UV-Vis spectrophotometer. Scattering coefficient spectra of the water dispersion of (e) Mg-Tris-NH₂_0.75, (f) Mg-Tris-NH₂_1.0, and (g) Mg-Tris-NH₂_1.25.



Fig. S16 Scattering exponent (*n*) plotted versus the average lateral size.

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