Hunting for Monolayer Oxide Nanosheets and Their Architectures

Hyung-Jun Kim1, Minoru Osada1, Yasuo Ebina2, Wataru Sugimoto2, Kazuhito Tsukagoshi1 & Takayoshi Sasaki2

In two-dimensional materials, thickness identification with a sufficient characterization range is essential to fundamental study and practical applications. Here, we report a universal optical method for rapid and reliable identification of single- to quindecuple-layers in oxide nanosheets (Ti0.87O2, Ca2Nb2O9, Ca3NaNbO13). Because of their wide bandgap nature (Eg = ~4 eV) and zero opacity, most oxide nanosheets exhibit a weak white-light contrast (<1.5%), which precludes optical identification. Through a systematic study of the optical reflectivity of Ti0.87O2 nanosheets on SiO2/Si substrates, we show that the use of thinner SiO2 (~100 nm) offers optimum visualization conditions with a contrast of >5%; the contrast is a nonmonotonic function of wavelength and changes its sign at ~550 nm; the nanosheets are brighter than the substrate at short wavelengths and darker at long ones. Such a nonmonotonic optical response is common to semiconducting oxide nanosheets, including Ca2NbO10 and Ca3NaNbO13. The optical contrast differences between the substrates and nanosheets with different numbers of layers were collected, serving as a standard reference from which the number of layers can be determined by optical microscopy. Our method will facilitate the thickness-dependent study of various oxide nanosheets and their architectures, as well as expedite research toward practical applications.

Two-dimensional (2D) nanosheets with atomic or molecular thickness have been emerging as a new frontier of materials science owing to their unique properties. Inspired by the intriguing properties of graphene, many efforts have been devoted to synthesizing 2D nanosheets of various inorganic materials, including transition-metal dichalcogenides (TMDGs)1–3, metal oxides4–8, and hydroxides9–13, as well as primarily investigating their unique electronic structures and physical properties14,15. Among the types of inorganic nanosheets, oxide nanosheets are important and fascinating research targets because of the virtually infinite varieties of layered oxide materials with interesting functional properties, including high-κ ferroelectricity, superconductivity, and magnetism16. A variety of oxide nanosheets (such as Ti1−δO2, Ti1−δCoO2, MnO2, and perovskites) have been synthesized by delaminating layered precursors into molecular single sheets via a soft-chemical process17.

These oxide nanosheets have distinct differences and advantages compared with graphene and other inorganic nanosheets because of their potential uses as insulators, semiconductors, conductors, and even ferromagnets, depending on their composition and structure. Most oxide nanosheets synthesized to date are δ-transmission metal oxides (with Ti4+, Nb5+, Ta5+, W6+) with wide-gap semiconducting or insulating nature17. Current research on oxide nanosheets has thus focused on their use as semiconducting or dielectric nanoblocks in energy, environmental, and electronic applications. Regarding the fundamental study and practical applications of oxide nanosheets, thickness information and sufficient characterization range is particularly important, but still challenging. Localized techniques such as atomic force microscopy (AFM) or transmission electron microscopy (TEM) are commonly used to measure the thickness of oxide nanosheets6,9. However, these techniques are time-consuming and unsuitable for rapid measurement over a large area. In the cases of graphene and TMDGs, mono- and few-layer forms are identified by their optical contrasts and Raman signatures10–13. Little is known about these characteristics for oxide nanosheets. Developing a general and effective thickness characterization scheme is highly desirable in the 2D scientific community because it enables the facile fabrication of monolayer devices based on oxide nanosheets.

Here, we report the optical properties of mono- and few-layer titania nanosheets (Ti1−δO2) obtained by solution-based exfoliation of a layered titanate14,15. Because of their zero opacity (the band gap is ~4 eV), Ti1−δO2

1International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS), Tsukuba, 305-0044, Japan. 2Materials and Chemical Engineering, Shinshu University, Ueda, Nagano 386-8567, Japan. Correspondence and requests for materials should be addressed to M.O. (email: osada.minoru@nims.go.jp)
nanosheets exhibit a low degree of optical contrast, even if interference enhancement using oxidized Si wafers is employed. We show that the use of thinner SiO₂ (∼100 nm) offers optimum visualization conditions with a contrast of ∼5% per layer, and this contrast level is sufficient to detect the monolayers under a microscope. To show the versatility of our optical technique, we have extended our research to other oxide nanosheets (Ca₂NaNb₄O₁₃, RuO₂, MnO₂) and heterostructures (RuO₂/TiO₂₋₀.₈₇O₂, MnO₂/TiO₂₋₀.₈₇O₂).

Results and Discussion
Optical properties of titania nanosheets. Titania nanosheet Ti₁₋ₓO₂ (x ≈ 0.09)¹⁴,¹⁵, the initially developed model system of oxide nanosheets, was chosen as the specimen (Fig. 1a,b). Ti₁₋ₓO₂ nanosheets are a new class of nanometer-sized titanium oxide prepared by delaminating a layered titanate into single molecular sheets. Elemental Ti₁₋ₓO₂ nanosheets are characterized by a 2D structure; the thickness is ∼0.75 nm, corresponding to two edge-shared TiO₆ octahedra¹⁶. The compositions of the exfoliated 2D nanosheets slightly deviate from the stoichiometry of TiO₂, with a general formula of Ti₁₋ₓ□ₓO₂ₓ⁻² (where □ represents vacancies) depending on the starting layered compounds¹⁴,¹⁵,¹⁷. Theoretical and experimental investigations have demonstrated that Ti₀.₈₇O₂ nanosheets act as a high-κ dielectric, and its multilayer films exhibit a high dielectric constant (ε̃) of ∼125 at thicknesses as low as 10 nm¹⁸,¹⁹.

Because of their unique 2D structure and high-κ dielectric nature, Ti₀.₈₇O₂ nanosheets exhibit some distinctive optical properties in comparison with their bulk counterparts²⁰. As shown in Fig. 1c, a sharp absorption peak centered at ∼265 nm was observed for Ti₀.₈₇O₂ nanosheets. An analysis of the square root of the absorption edge [i.e., (√hν)²] against photon energy (hν) provides the information to estimate a band gap energy (E₉) of 3.85 eV, considerably larger than those of bulk anatase, rutile, and the layered parent titanate²⁰. We also note that Ti₀.₈₇O₂ nanosheets possess a high transmittance (>99%), higher than those of graphene (>98%)²¹ and MoS₂ (>95%)²². Fig. 1d depicts the spectral function of the refractive index (n) and extinction coefficient (k) of a Ti₀.₈₇O₂ nanosheet. Ti₀.₈₇O₂ nanosheet possessed a higher n (>2) and nearly a zero extinction coefficient (k), which agree well with the high permittivity value¹⁹ and previous studies on Ti₀.₉₁O₂ case²³. Due to its high opacity (the band gap is ∼4 eV), Ti₀.₈₇O₂ nanosheet exhibited a low degree of optical contrast, even when employing interference enhancement using oxidized Si wafers. For the standard oxide thickness of 500 nm of SiO₂, Ti₀.₈₇O₂ showed a white-light contrast of <1.5%, which precludes identification using conventional optical microscopy (Supplementary Fig. S1).

Thickness identification of titania nanosheets by optical microscopy. To model the optical contrast of Ti₀.₈₇O₂ nanosheets, we employed an analysis based on the Fresnel law, which has been proven to be valid for graphene¹⁰. In our simulation, we used a matrix formalism of interference in a multilayer system, where the light incident from the air is assumed to be normal to the Ti₀.₈₇O₂/SiO₂/Si structure (Fig. 2a). The reflected light intensity can be expressed as...
\[ R(\lambda) = \frac{r_1e^{i(\phi_1 + \phi_2)} + r_2e^{-i(\phi_1 - \phi_2)} + r_3e^{-i(\phi_1 + \phi_2)} + r_4e^{-i(\phi_1 - \phi_2)}}{e^{i(\phi_1 + \phi_2)} + r_1r_2e^{-i(\phi_1 - \phi_2)} + r_3r_4e^{-i(\phi_1 + \phi_2)} + r_2r_3e^{i(\phi_1 - \phi_2)}} \]

where the subindexes 0, 1, 2, and 3 refer to the medium (air), \( Ti_{0.87}O_2 \) nanosheet, SiO\(_2\), and Si, respectively. \( \lambda \) is the wavelength of the inspection light. \( r_i = (n_i - n_{i-1})/(n_i + n_{i-1}) \) are the relative indexes of refraction at the top of the nanosheet surface, the interface between the nanosheet and SiO\(_2\) and between the SiO\(_2\) and the Si substrate, respectively. \( n_i \) is the refractive index of a given medium, \( \phi_i = 2\pi n_i d_i/\lambda \) is the phase shift due to the light passing through a given medium, where \( d_i \) is the thickness of the medium \( i \).

The optical contrast of the system can be defined as

\[ C(\lambda) = \frac{R_0(\lambda) - R(\lambda)}{R_0(\lambda)} \]

where \( R_0 \) and \( R \) are the intensities of reflected light from the SiO\(_2\)/Si substrate and the nanosheets, respectively. We used spectroscopic ellipsometry data for 5-layer films of Ti\(_{0.87}O_2\) nanosheets and found \( k \sim 0 \) and \( n \sim 2.1 \). Assuming that the optical properties of monolayers change little with respect to 5-layer films, we obtain the dependences shown in Fig. 2b. The developed theory allows us to predict the SiO\(_2\) thickness at which the optical contrast for monolayer Ti\(_{0.87}O_2\) nanosheets would be maximal; here, a contrast peak is predicted at a thickness of 100 nm. In this case, the contrast remains relatively strong (>5%) over a wide range of visible wavelengths (400–550 nm). Moreover, the contrast changes from negative to positive when crossing from the blue-light to the red-light region of the spectrum, going through zero in the green-light region.

This prediction has been confirmed experimentally by imaging monolayer Ti\(_{0.87}O_2\) nanosheets on a 100 nm SiO\(_2\)/Si substrate (Fig. 3a). We also investigated the optical contrast of monolayer Ti\(_{0.87}O_2\) nanosheets on SiO\(_2\)/Si substrates with different SiO\(_2\) thicknesses (90 and 285 nm) (Supplementary Fig. S2). Several observations can be made from these data. The contrast for Ti\(_{0.87}O_2\) nanosheets can be both negative and positive depending on the wavelength, with a zero crossing in between. A contrast of zero means that the nanosheet is invisible at that wavelength, i.e., it has the same reflectivity as the substrate. The negative contrast was stronger, with a peak observed at \( \sim 450 \) nm, while the positive contrast appeared at \( >550 \) nm. On the bottom panels (Fig. 3b), we show optical images of Ti\(_{0.87}O_2\) nanosheets taken at selected wavelengths centered at 400, 450, 500, 550, 600, and 700 nm. To acquire the image, we have taken optical micrographs using illumination through narrow bandpass filters (with a
which is on the order of 10 min.

700 nm.

wavelength (450 nm) can be used for rapid and reliable characterization of the thickness of Ti0.87O2 nanosheets. Of the optical contrast is persistent up to the theoretical prediction (Fig. 4e). In this study, we evaluated thicknesses up to 4 layers. A trend of a linear increase of the optical contrast at 450 nm reaches ~5% per layer, and this contrast level is comparable to those of graphene and TMDCs.

The optical contrast also depends on the number of layers (N) of Ti0.87O2 nanosheets. From a similar analysis as the one presented in Fig. 2, we investigated the layer dependence of the optical contrast for Ti0.87O2 nanosheets on a 100 nm SiO2/Si substrate (Fig. 4a, Supplementary Fig. S3). This calculation suggests that the use of the 450-nm light is suitable for monitoring the layer dependence in Ti0.87O2 nanosheets. In Fig. 4b, we show the optical image taken with the 450-nm light, which is near the negative peak. The AFM image (Fig. 4c) revealed different thicknesses ranging from 1 to 4 layers. From the line profiles at the selected area (Fig. 4d), the optical contrast increased in integer steps (by a factor of \(100\%\) per layer, and this contrast level is comparable to those of graphene and TMDCs.

Optical identification of Ti0.87O2 nanosheets. (a) Optical contrast of monolayer Ti0.87O2 nanosheets on a 100 nm SiO2/Si substrate (blue circle: experimental value, pink line: theoretical prediction). (b) Optical images of Ti0.87O2 nanosheets were taken at selected wavelengths centered at 400, 450, 500, 550, 600, and 700 nm.

Optical identification in 2D oxide nanosheets and their architectures. Through a systematic study of the optical reflectivity of Ti0.87O2 nanosheets on SiO2/Si substrates, we show that the use of thinner SiO2 (~100 nm) offers optimum visualization, with an optical contrast of >5%. A particular feature of the Ti0.87O2 nanosheets is that the contrast is a nonmonotonic function of \(\kappa\) and changes its sign at \(\kappa\approx500\) nm; the nanosheets are brighter than the substrate at short wavelengths and darker at long ones. These features are different from those of graphene and TMDCs, in which the contrast is either positive or negative. We note that the non-monotonic optical response is common to 2D nanosheets with wide-gap semiconducting or insulating nature, including h-BN, Ca2Nb3O10, and Ca3NaNb4O13. A particular feature of these materials is zero opacity, causing a nearly zero extinction coefficient (\(k\)). Actually, perovskite nanosheets (Ca3Nb3O10, Ca3NaNb4O13) with higher \(\kappa\) (>200) also showed a nonmonotonic response of the optical contrast; the nanosheets were brighter than the substrate at short wavelengths and darker at long ones (Fig. 5). The optical contrast also depends on the number of layers (N) of perovskite nanosheets, a situation being similar to that of Ti0.87O2 nanosheets (Fig. 4, Supplementary Fig. S5). The calculation on the thickness dependence suggests that the use of the 450-nm light is suitable for monitoring the layer dependence in Ca2Nb3O10 nanosheets; a trend of a linear increase of the optical contrast is persistent up to \(N\approx15\). These results imply that the contrast observation at a single wavelength (450 nm) can be used for rapid and reliable characterization of the thickness of Ti0.87O2 nanosheets. We also note that the typical acquisition time for an optical image is ~500 ms, much shorter than that of AFM, which is on the order of 10 min.

Optical identification in 2D oxide nanosheets and their architectures. Through a systematic study of the optical reflectivity of Ti0.87O2 nanosheets on SiO2/Si substrates, we show that the use of thinner SiO2 (~100 nm) offers optimum visualization, with an optical contrast of >5%. A particular feature of the Ti0.87O2 nanosheets is that the contrast is a nonmonotonic function of \(\kappa\) and changes its sign at \(\kappa\approx500\) nm; the nanosheets are brighter than the substrate at short wavelengths and darker at long ones. These features are different from those of graphene and TMDCs, in which the contrast is either positive or negative. We note that the non-monotonic optical response is common to 2D nanosheets with wide-gap semiconducting or insulating nature, including h-BN, Ca2Nb3O10, and Ca3NaNb4O13. A particular feature of these materials is zero opacity, causing a nearly zero extinction coefficient (\(k\)). Actually, perovskite nanosheets (Ca3Nb3O10, Ca3NaNb4O13) with higher \(\kappa\) (>200) also showed a nonmonotonic response of the optical contrast; the nanosheets were brighter than the substrate at short wavelengths and darker at long ones (Fig. 5). The optical contrast also depends on the number of layers (N) of perovskite nanosheets, a situation being similar to that of Ti0.87O2 nanosheets (Fig. 4, Supplementary Fig. S5). The calculation on the thickness dependence suggests that the use of the 450-nm light is suitable for monitoring the layer dependence in Ca2Nb3O10 nanosheets; a trend of a linear increase of the optical contrast is persistent up to \(N\approx15\). These results imply that the contrast observation at a single wavelength (450 nm) can be used for rapid and reliable characterization of the thickness of Ti0.87O2 nanosheets. We also note that the typical acquisition time for an optical image is ~500 ms, much shorter than that of AFM, which is on the order of 10 min.
application of this imaging method; we extend our research to heterostructures such as RuO$_2$/Ti$_{0.87}$O$_2$ and MnO$_2$/Ti$_{0.87}$O$_2$. These structures are basic components of nanocapacitors and photo conversion devices. In this study, we prepared hetero-assembled structures on SiO$_2$/Si substrates by a drop-casting method. Through a systematic

Figure 4. Thickness identification of Ti$_{0.87}$O$_2$ nanosheets by optical microscopy. (a) Calculated optical contrast of Ti$_{0.87}$O$_2$ nanosheets as a function of the wavelength of light and number of layers (N). (b) Optical image for Ti$_{0.87}$O$_2$ nanosheets on a 100 nm SiO$_2$/Si substrate. Image was taken with the 450-nm light, which is near the negative peak. (c) AFM image taken from the same film as (b). This image clearly revealed different thicknesses ranging from 1 to 4 layers. (d) A line profile at the selected area in (b). The trace shows step-like changes in the contrast for 1, 2, 3, and 4 layers. (e) Comparison between the observed (blue circle) and theoretically predicted (pink line) optical contrast for Ti$_{0.87}$O$_2$ nanosheets. A trend of a linear increase of the optical contrast is persistent up to N ≈ 15.
study of the optical reflectivity of RuO₂/Ti₀.₈₇O₂ and MnO₂/Ti₀.₈₇O₂ on SiO₂/Si substrates, we show that the use of thinner SiO₂ (∼90 nm) and shorter wavelength light (λ = 470 nm) offers optimum visualization; RuO₂ and MnO₂ cause the positive contrast at ∼470 nm, while Ti₀.₈₇O₂ the negative contrast (Supplementary Fig. S5, S6). RuO₂ and MnO₂ are either metallic or semi-metallic, causing a strong positive contrast (5∼10%) with respect to Ti₀.₈₇O₂ and SiO₂/Si substrate. We also emphasize that our technique offers rapid thickness identification with a sufficient characterization range (even on the sub mm scale). These results imply the versatility of our optical technique for the rapid and reliable characterization of various 2D oxide nanosheets and their architectures.

Methods

2D Oxide Nanosheets. A colloidal suspension of Ti₀.₈₇O₂ nanosheets with a lateral dimension of 5–10 µm was prepared by delaminating a layered titanate (K₀.₈Ti₁.₇₃Li₀.₂₇O₄) according to previously reported procedures²⁴,²⁵,²⁷. Ti₀.₈₇O₂ nanosheets were deposited on SiO₂/Si substrates (SiO₂ thicknesses: 90, 100, 285, and 300 nm) by a modified Langmuir-Blodgett (LB) technique²⁸ (Supplementary Fig. S7). In usual LB experiments, densely packed monolayer films were obtained with an optimized surface pressure (∼15 mN/m). In this study, films having dispersed nanosheets were obtained by controlling the surface pressure (∼3 mN/m). The as-fabricated films were irradiated by UV/white light from a Xe lamp (4 mW/cm²) for 48 h to decompose the tetrabutylammonium ions used in the exfoliation process. Repeated LB deposition yielded multilayer structures. The main data

---

Figure 5. Optical identification of perovskite nanosheets. (a) Calculated optical contrast of Ca₂Nb₂O₁₀ nanosheets as a function of the wavelength of light and SiO₂ thickness. (b,c) Optical images for Ca₂Nb₂O₁₀ and Ca₉NaNb₂O₁₃ nanosheets on a 100 nm SiO₂/Si substrate. Images were taken at selected wavelengths centered at (1) 450 nm, (2) 550 nm, and (3) 600 nm. Insets in (b-1) and (c-1) present the line profiles of multilayer parts.
were obtained from Ti<sub>0.87</sub>O<sub>2</sub> nanosheets with different thicknesses ranging from 1 to 4 layers. Complementary data were obtained from perovskite nanosheets (Ca<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub>, Ca<sub>2</sub>NaNb<sub>4</sub>O<sub>13</sub>), RuO<sub>2</sub>, MnO<sub>2</sub>, and heterostructures (RuO<sub>2</sub>/Ti<sub>0.87</sub>O<sub>2</sub>, MnO<sub>2</sub>/Ti<sub>0.87</sub>O<sub>2</sub>). The films with dispersed nanosheets were prepared by a drop-casting method. The synthesis and characterization of these nanosheets were described elsewhere<sup>30,33–35</sup>.

Optical Microscopy of 2D Nanosheets. Optical images of 2D oxide nanosheets were obtained by a bright-field optical microscope (Olympus, BX51 with a 100×, 0.9 NA objective lens). Monochromatic images were acquired using illumination through narrow bandpass filters (with a width of ±5 nm). A CCD camera head (Nikon, DS-1) with a digital camera control unit was used to capture color optical images of the 2D nanosheets at the resolution of 1280 × 960 pixels. The typical acquisition time was ∼500 ms; in low-contrast cases, acquisition times were varied between 100 ms and 30 s to avoid overexposure. The color optical images were processed by Image-J software (version 1.48, National Institutes of Health, USA). For color images (RGB images), the contrast value of each pixel (C<sub>CV</sub>) was calculated using the following equation:

\[
C_{CV} = (C_{VR} + C_{VG} + C_{VB})/3
\]

where C<sub>VR</sub>, C<sub>VG</sub>, and C<sub>VB</sub> are the R, G, and B values per pixel, respectively (0–255, corresponding to darkest to brightest). The contrast levels of the R, G, and B channels were extracted and converted to a gray-scale image, where 0 is black and 255 is white.

To model the optical contrast of oxide nanosheets, we employed an analysis based on the Fresnel law, which has been proven to be valid for graphene<sup>40</sup>. In our simulation, we used a matrix formalism of interference in a multilayer system (Fig. 2a). We used spectroscopic ellipsometry data for 5-layer films of oxide nanosheets. Ellipsometric measurements were performed by a spectroscopic ellipsometer (J.A. Woollam Japan, M-2000).

Thickness Measurements by AFM. An AFM (SII Nanotech, E-Sweep) was used to confirm the number of layers of 2D oxide nanosheets by measuring the film thickness with tapping mode in air.
References

1. Chhowalla, M. et al. The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets. Nat. Chem. 5, 263–275 (2013).
2. Xu, M., Li, T., Shi, M. & Chen, H. Graphene-like two-dimensional materials. Chem. Rev. 113, 3766–3798 (2013).
3. Ma, R. & Sasaki, T. Nanosheets of oxides and hydroxides: ultimate 2D charge-bearing functional crystallites. Adv. Mater. 22, 5082–5104 (2010).
4. Wang, L. & Sasaki, T. Titanium oxide nanosheets: graphene analogues with versatile functionalities. Chem. Rev. 114, 9455–9486 (2014).
5. Ma, R., Liu, Z., Li, L., Iyi, N. & Sasaki, T. Exfoliating layered double hydroxides in formamide: a method to obtain positively charged nanosheets. J. Mater. Chem. 16, 3809–3813 (2006).
6. Osada, M. & Sasaki, T. Exfoliated oxide nanosheets: new solution to nanoelectronics. J. Mater. Chem. 19, 2503–2511 (2009).
7. Osada, M. & Sasaki, T. Two-dimensional dielectric nanosheets: novel nanoelectronics from nanocrystal building blocks. Adv. Mater. 24, 210–228 (2012).
8. Schlom, D. G., Chen, L.-Q., Pan, X., Schmehl, A. & Zurbuchen, M. A. A Thin film approach to engineering functionality into oxides. J. Am. Ceram. Soc. 91, 2429–2454 (2008).
9. Kumagai, K., Sekiguchi, T., Fukuda, K. & Sasaki, T. Secondary electron imaging of monolayer titania nanosheets. Appl. Phys. Exp. 2, 105504 (2009).
10. Blake, P. et al. Making graphene visible. Appl. Phys. Lett. 91, 063124 (2007).
11. Ni, Z. H. et al. Graphene thickness determination using reflection and contrast spectroscopy. Nano Lett. 7, 2758–2763 (2007).}

Supplementary information accompanies this paper at http://www.nature.com/srep

Author Contributions

M.O. and T.S. conceived the experiments. H.K. performed the experiments. Y.E. and W.S. synthesized oxide nanosheets. H.K., M.O. and K.T. analyzed the data. H.K. and M.O. wrote the manuscript. All authors reviewed the manuscript.

Additional Information

Supplementary information accompanies this paper at http://www.nature.com/srep

Competing financial interests: The authors declare no competing financial interests.

Acknowledgements

This work was supported in part by the World Premier International Research Center Initiative on Materials Nanoarchitectonics (WPI-MANA), MEXT, Japan. M.O. acknowledges support from the Grant-in-Aid for Scientific research KAKENHI (Nos. 25289232, 15K14134), MEXT, Japan.

Author Contributions

M.O. and T.S. conceived the experiments. H.K. performed the experiments. Y.E. and W.S. synthesized oxide nanosheets. H.K., M.O. and K.T. analyzed the data. H.K. and M.O. wrote the manuscript. All authors reviewed the manuscript.

References

1. Chhowalla, M. et al. The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets. Nat. Chem. 5, 263–275 (2013).
2. Xu, M., Li, T., Shi, M. & Chen, H. Graphene-like two-dimensional materials. Chem. Rev. 113, 3766–3798 (2013).
3. Ma, R. & Sasaki, T. Nanosheets of oxides and hydroxides: ultimate 2D charge-bearing functional crystallites. Adv. Mater. 22, 5082–5104 (2010).
4. Wang, L. & Sasaki, T. Titanium oxide nanosheets: graphene analogues with versatile functionalities. Chem. Rev. 114, 9455–9486 (2014).
5. Ma, R., Liu, Z., Li, L., Iyi, N. & Sasaki, T. Exfoliating layered double hydroxides in formamide: a method to obtain positively charged nanosheets. J. Mater. Chem. 16, 3809–3813 (2006).
6. Osada, M. & Sasaki, T. Exfoliated oxide nanosheets: new solution to nanoelectronics. J. Mater. Chem. 19, 2503–2511 (2009).
7. Osada, M. & Sasaki, T. Two-dimensional dielectric nanosheets: novel nanoelectronics from nanocrystal building blocks. Adv. Mater. 24, 210–228 (2012).
8. Schlom, D. G., Chen, L.-Q., Pan, X., Schmehl, A. & Zurbuchen, M. A. A Thin film approach to engineering functionality into oxides. J. Am. Ceram. Soc. 91, 2429–2454 (2008).
9. Kumagai, K., Sekiguchi, T., Fukuda, K. & Sasaki, T. Secondary electron imaging of monolayer titania nanosheets. Appl. Phys. Exp. 2, 105504 (2009).
10. Blake, P. et al. Making graphene visible. Appl. Phys. Lett. 91, 063124 (2007).
11. Ni, Z. H. et al. Graphene thickness determination using reflection and contrast spectroscopy. Nano Lett. 7, 2758–2763 (2007).
