Electronic Supplementary Information

: For the manuscript entitled with **"Water-Floating Nanohybrid Films of Layered Titanate–Graphene for Sanitization of Algae without Secondary Pollution"** by *In Young Kim, Jang Mee Lee, Eui-Ho Hwang, Yi-Rong Pei, Woo-Bin Jin, Jin-Ho Choy, and Seong-Ju Hwang**

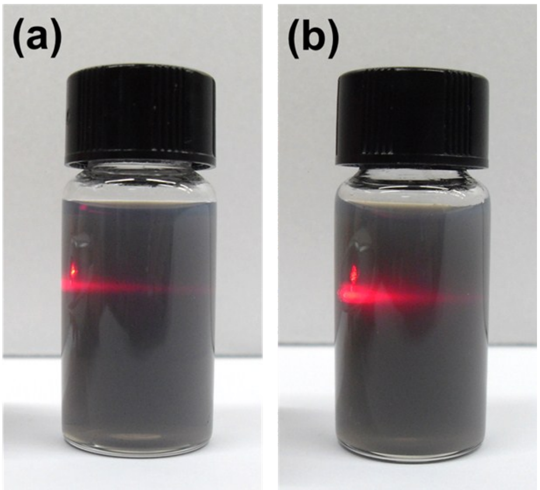
Details of Experimental Methods

Extraction of Chlorophyll A. The freestanding films were removed from the corresponding algal solutions after the algae-killing test. The resulting algal solutions were filtered through GF/C filters (Whatman, glass microfiber filter binder free, pore size = 1.2 μm). The glass filters containing algae were dried at room temperature for 12 h and were crushed to destruct the wall of algal cells. The fragments of glass filter with algae were dispersed in 90% acetone (10 mL) and the subsequent sonication was applied to the resulting suspensions for 15 min. chlorophyll A of the algae was extracted in 90% acetone after the storage of the previous suspensions at 4 °C for 24 h in the dark. The absorbance at 664, 647, and 630 nm was monitored with a UV–vis spectrometer to quantify the concentration of chlorophyll (concentration of chlorophyll A = $11.85A_{664\ nm} - 1.54A_{647\ nm} - 0.08A_{630\ nm}$).

Detection of Reactive Oxygen Species (ROS) Generation. 0.2 mM 2,3-bis(2-methoxy-4-nitro-5-sulfophenyl)-2H-tetrazolium-5-carboxanilide (XTT, Sigma-Aldrich, USA) solution in phosphate-buffered saline (PBS) was prepared at pH = 7.0. All the present freestanding films with the same sizes were soaked in the XTT solution under UV–vis illumination from Xe lamp for 12 h. The change in absorbance of the XTT solution at 470 nm was monitored with UV–vis spectrometer (Shinco S-4100, Shinco, Korea).

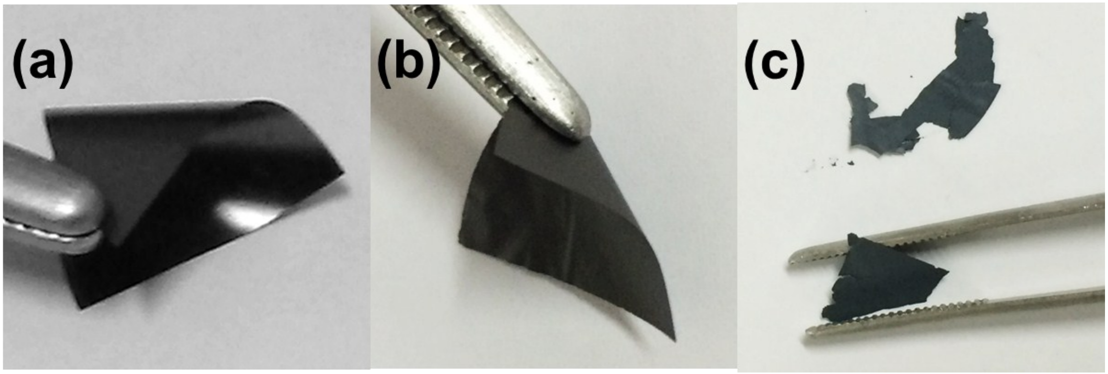
Monitoring of the Morphological Change of Algae. Algae on the films were fixed with 2.5% glutaraldehyde for 30 min and then washed with PBS followed by the fixation of algae with 1% osmium tetraoxide for 30 min. After the fixation, algae were gradually dehydrated with sequential washing treatments with 30, 50, 70, 80, 90, and 100% ethanol. Every washing treatment was taken for 15 min. The dried freestanding films were sputter-coated with platinum for field emission-scanning electron microscopy (FE-SEM) measurement (JSM-6700F, Jeol, Japan).

Fig. S1 Photoimages of the homogeneous colloidal mixtures of rG-O with (a) lepidocrocite- and (b) trititanate-type layered titanate nanosheets.



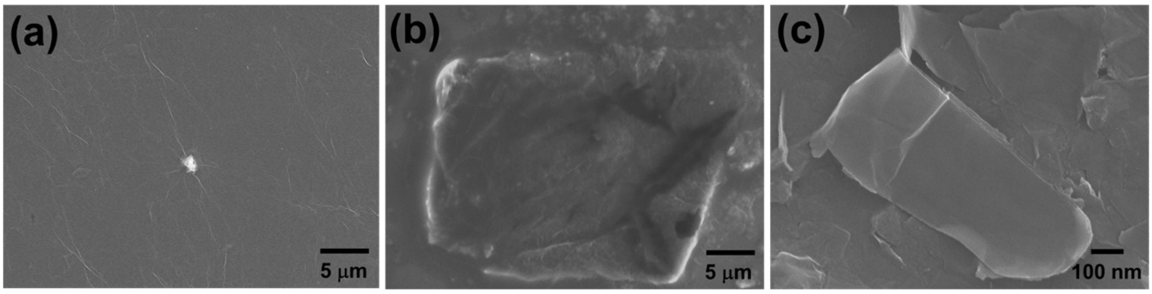
: As shown in **Fig. S1**, the resulting mixed colloidal suspensions of rG-O and layered titanate nanosheets commonly display a good colloidal stability without any phase separation for several weeks, as confirmed by the maintenance of Tyndall phenomenon.

Fig. S2 Photoimages for the flexibility tests of (a) pure graphene film and the rG-O−layered titanate hybrid films of (b) **GLT** and (c) **GTT**.



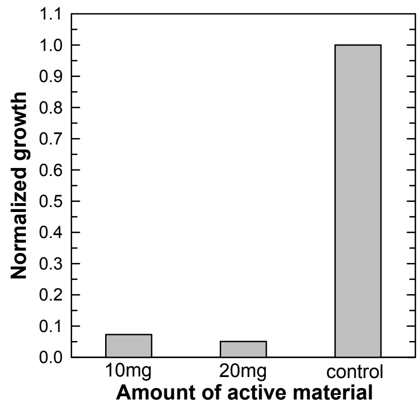
: As illustrated in **Fig. S2**, both pure graphene and **GLT** hybrid films were highly flexible with good stability. In comparison with these films, the **GTT** hybrid film shows lower stability and flexibility, leading to the breakdown of the film in bending state**.**

Fig. S3 FE-SEM images of the precursors of (a) rG-O, (b) lepidocrocite-, and (c) trititanate-type layered titanate nanosheets.



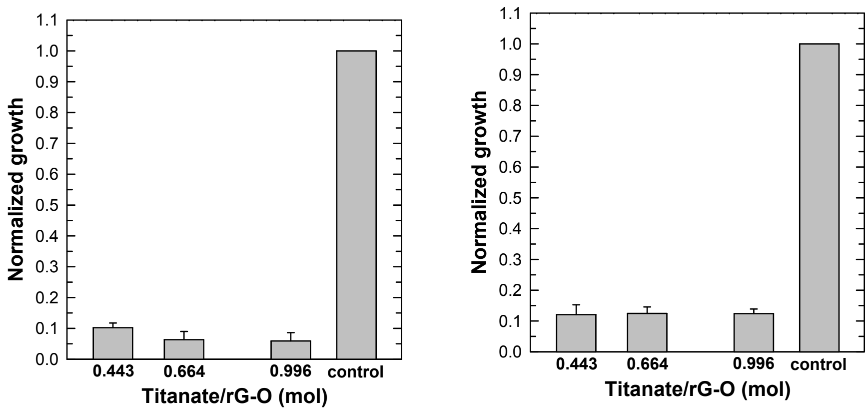
: As can be seen in **Fig. S3**, the lepidocrocite-type layered titanate nanosheet shows wide 2D sheet-shaped morphology with lateral size of ~15 μm, which is quite similar to the 2D morphology of the rG-O nanosheet. Conversely, the trititanate-type layered titanate has 2D belt-shaped lateral shape with the width of ~300 nm and the length of ~1 μm, which is quite distinguishable from the lateral morphology of rG-O. Such a significant difference between the lateral morphologies of trititanate nanosheet and rG-O nanosheet was responsible for the poor mixing between these nanosheets.

Fig. S4 Algae-killing activity tests for the **GLT** films with variable loading amounts.



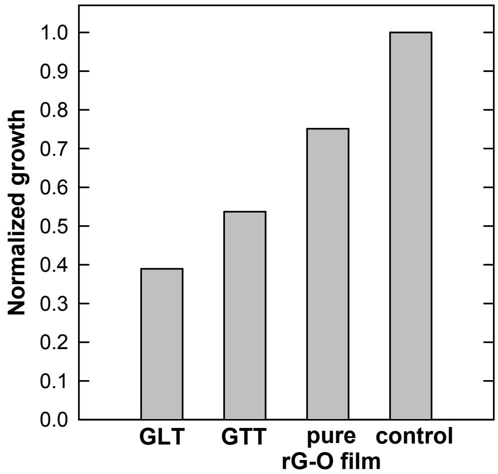
: To verify the efficient algae-killing ability of the present hybrid film, we studied the correlation between the loading amount of hybrid film and the inhibition efficiency of algae growth. As can be seen clearly from **Fig. S4**, the addition of more **GLT** film leads to a notable increase of inhibition efficiency for algae growth, confirming that the observed inhibition of algae growth is surely attributable to the intrinsic sterilization functionality of the rG-O−layered titanate hybrid film.

Fig. S5 Algae-killing activity tests for the (left) **GLT** and (right) **GTT** films with various molar ratios of titanate/rG-O.



: To confirm the critical role of titanate nanosheet in the algae-killing functionality of the present hybrid films, we fabricated additional **GLT** and **GTT** films with several titanate/rG-O ratios of 0.443, 0.664, and 0.996. As plotted in the left panel of **Fig. S5**, the inhibition efficiency of the **GLT** film for algae growth becomes higher with increasing the content of lepidocrocite-type titanate (89.8 ± 1.5, 93.7 ± 2.7, and 94.1 ± 2.7% for the ratio of 0.443, 0.664, and 0.996, respectively), confirming the critical role of lepidocrocite-type titanate nanosheet in the improved algae-killing functionality of the **GLT** film. Also the present result indicates that the titanate/rG-O ratio of 0.664 is an optimal value for optimizing the algae-killing activity of the **GLT** hybrid film. Conversely, as shown in the right panel of **Fig. S5**, there is no significant improvement of the algae-killing activity of the **GTT** film with increasing the content of trititanate nanosheet (87.9 ± 3.2, 87.5 ± 2.1, and 87.6 ± 1.5% for the ratio of 0.443, 0.664, and 0.996, respectively), suggesting the less efficient role of trititanate nanosheet in the algae-killing functionality of the **GTT** film compared with lepidocrocite-type titanate nanosheet. Of noteworthy is that, for all the ratios of layered titanate/rG-O employed here, the **GLT** films show better sterilization activity than do the **GTT** ones, clearly demonstrating the superior role of lepidocrocite-type titanate nanosheet over trititanate nanosheet for optimizing the sterilization functionality of graphene film.

Fig. S6. Algae-killing activity tests for the **GLT**, **GTT**, and pure rG-O films with high concentration of algae.



: The practical applicability of the present hybrid films for the prevention of algae blooming was probed by algae-killing test at higher concentration of algae (7.1×10^7 cells·mL^{-1}). As plotted in **Fig. S6**, even at this ~5 times higher concentration, the **GLT**, **GTT**, and pure rG-O films still show promising inhibition efficiencies for the algae growth of 61.0, 46.3, and 24.9, respectively. Among the present films, the **GLT** film exhibits the best and excellent algae-killing efficiency even for this high algae concentration, underscoring a beneficial role of lepidocrocite-type titanate nanosheet in preventing the growth of algae and the usefulness of this film for the sanitization of practical environment.