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Green tide deactivation with layered-structure cuboids of Ag/$CaTiO_3$ under UV light

Soo-Wohn Lee [a], L.M. Lozano-Sánchez [b], V. Rodríguez-González [b,*]

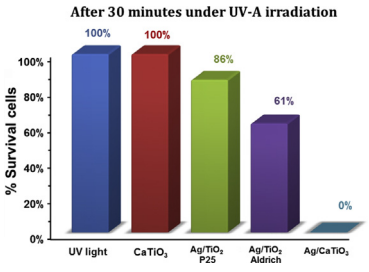
[a] Global Research Laboratory, Sun Moon University, Galsan-Ri, Tangjung-Myon, Asan Chungnam 336-708, South Korea
[b] División de Materiales Avanzados, Instituto Potosino de Investigación Científica y Tecnológica, Camino a la Presa San José 2055 Col. Lomas 4a sección, C.P. 78216 San Luis Potosí, S.L.P., Mexico

HIGHLIGHTS

- An alternative to deactivate harmful green tide is proposed by employing Ag/$CaTiO_3$.
- Particles of perovskite-like have rectangular prisms morphology with AgNPs ~13 nm.
- The cuboids achieve complete inactivation of *Tetraselmis suecica* algae in 12 min.
- AgNPs functionalization induce fatal irreversible damages on the algae surface.

GRAPHICAL ABSTRACT

Synergic reasons such as mass transfer, morphology, biocide properties, UV-A photoresponse, and electron trapping that reduce recombination on Ag/$CaTiO_3$ nanocomposites, have the potential for the generation of reactive radicals that promote the fatal irreversible deactivation of *Tetraselmis suecica* algae in 12 min under UV-A irradiation.



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ABSTRACT

In this work, an alternative to deactivate noxious green tide *Tetraselmis suecica* in the short-term is proposed by employing Perovskite-like cube-shaped, crystalline $CaTiO_3$ semiconductors functionalized with atomic silver nanoparticles. $CaTiO_3$ was prepared by a microwave-assisted hydrothermal method and then Ag^0NPs (1 wt% of $CaTiO_3$), were added by the photoreduction method. The XRD results show that crystalline $CaTiO_3$ has an orthorhombic unit cell with a Perovskite-like structure. Images obtained by FESEM and HRTEM microscopies show well-faceted $CaTiO_3$ rectangular prismatic morphology functionalizated with silver nanoparticles ~13.5 nm. XPS and EDS-FESEM has confirmed the composition of $CaTiO_3$ and silver occurring mainly as reduced metal. The UV inactivation of noxious *T. suecica* with Ag/$CaTiO_3$ nanocomposites formed on bare materials results in complete deactivation of the algae in 12 min. The direct contact between harmful algae and Ag/$CaTiO_3$ nanocomposite is necessary to deactivate the algae and inhibits algae viability.

1. Introduction

Adverse environmental effects from some marine microorganisms now seriously impact our lives. Marine microbes, which are responsible for approximately half of the Earth's primary production of nutrients, play an enormous role in global nutrient cycling [1]. Marine microorganisms are small, and acellular or unicellular. Some phytoplankton are bacteria, some are protists, and most are single-celled plants. Among the common kinds are cyanobacteria, silica-encased diatoms, dinoflagellates, green algae, and chalk-coated coccolithophores [2,3]. Diatoms are one of the most common types of phytoplankton. Dinoflagellate *Tetraselmis suecica* is one kind of toxic green tide. Dinoflagellate blooms

* Corresponding author. Tel.: +52 4448342000x7295.
E-mail addresses: vicente.rdz@ipicyt.edu.mx, vicenrg@hotmail.com (V. Rodríguez-González).

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produce potent toxins that accumulate in marine animals which can have harmful effects on the surrounding sea life that feeds on diatoms. Because of their rapid growth, in the blooming phase, the toxins can be quickly carried up by the food chain and indirectly pass onto humans via fish and shellfish consumption, sometimes resulting in gastrointestinal disorders, permanent neurological damage, or even death [3,4].

Blooms of blue-green toxic dinoflagellates algae have been linked to a particular disease syndrome in raceway-reared blue shrimp [5]. The ingestion of blue-green toxic dinoflagellates algae varies from autotrophy to absorption of organic matter to mixotrophy [5].

Many environmental factors affect bacterial growth but the most important ones are food, water, pH, oxygen, and temperature. So, deactivation of the marine algae in the short-term needs to be achieved in conjunction with inhibition of regrowth at the coastal temperature [1,4]. Photo-inactivation seems to be a good option because it can work in conditions analogous to the marine environmental conditions, and also can mineralize the pathogenic marine algae [6,7]. There are several reports that certain nanostructured materials can achieved complete UV-deactivation of some harmful blooms like *Cochlodinium polykrikoides* using UVA/TiO_2 [7]. Significant degradation of brevetoxins (PbTxs), the PbTxs products that are associated with red tide, were deactivated with TiO_2 under UV and solar irradiation [8]. Partial photocatalytic inhibition of *Oedogonium*, a sessile filamentous algae, was decomposed using Pt-WO and Pt-TiO_2 photocatalytic coatings [9]. Other semiconductors or UV degradation also show acceptable activity in the deactivation of hazardous marine algae [10–13]. However, longer time is required for practical application for harmful blooms or the synthesis of the materials requires high temperature solid-state reactions [11–13].

In our previous work, TiO_2 photoimpregnated with silver nanoparticles in a slurry or immobilized in foamed waste-glass strips (FWGS), was utilized as a proposed alternative to inactivation of green and red tide algae [14]. The complete deactivation was achieved in 30 min in a slurry system and in 3 h with an immobilized system for green tide [6,14]. The fatal damage to these microorganisms induced by the TiO_2-Ag sol–gel semiconductor occurred faster than those promoted by the Ag/P25 and TiO_2 sol–gel isolated supports due to the biocide properties of silver in aqueous medium. The microalgae *T. suecica* was more resistant than *Amphidinium carterae* [6]. The combination of bacteriostatic effect of noble metals with the homogenous materials seems to be the best option.

In this paper, we analyze the viability of using Perovskite-like cuboid materials, synthesized by a one-step Microwave assisted hydrothermal (MW-AH) process, for the deactivation of hazardous green marine algae. To our knowledge, there are no reports of the use of Perovskite-like materials for the deactivation of hazardous toxic algae. The materials synthesized by microwave hydrothermal process have enhanced physicochemical properties and notable photocatalytic performance [15]. In this study, we discuss the results of the deactivation and destruction of noxious *T. suecica* with silver functionalized $CaTiO_3$ cuboids under UV-A irradiation.

2. Experimental

2.1. Synthesis of $CaTiO_3$ cuboids

The $CaTiO_3$ materials were synthesized by a MW-AH process using aqueous solutions of NaOH (5 M, 80 mL), urea (2 M, 10 mL), and $CaCl_2$ (2.5 M, 10 mL) prepared in distilled water and stirred individually for 10 min. Then, 2 g of commercial TiO_2 P25 were placed in a 150 mL Teflon vessel, into which the solutions of NaOH, urea, and $CaCl_2$, which were previously prepared, were then poured. The mixture was magnetically stirred for 5 min and then placed in an ultrasonic bath for 5 min. The Teflon vessel containing the final suspension was placed in a microwave reactor (Eyela MWO-1000 Wave Magic) and heated by microwave irradiation for 4 h at 180 °C, at a maximum variable microwave irradiation power of 150 W, with stirring at 400 rpm. The resulting precipitated powder was cooled at room temperature inside the microwave reactor and then neutralized to pH 7 with a 5 M HCl solution. Excess liquid was removed by decantation and then filtered using a cellulose filter (Whatman, grade 5). Finally, the solid was dried at 70 °C overnight.

2.2. Preparation of Ag/$CaTiO_3$ photocatalyst

200 mg of Ag/$CaTiO_3$ were prepared by a photodeposition method from 3.2 mg of $AgNO_3$, to obtain 1 wt% of Ag, dissolved in 20 mL of methanol, and stirred magnetically at 500 rpm for 5 min. In addition, 198 mg of $CaTiO_3$, previously prepared by MW-AH method, was placed in a small glass reactor. A methanol solution of $AgNO_3$ was then added to the reactor. The mixture was placed under vigorous stirring for 5 min and then placed in an ultrasonic bath for 5 min to ensure the complete disaggregation of agglomerated particles. Afterwards, the slurry was maintained for 1 h under magnetic stirring at 100 rpm and at the same time irradiated with two 20 W UVC lamps (short wave). Then, the suspension was placed on a hotplate at 70 °C to evaporate the methanol. The solid was completely dried overnight in an oven at 70 °C.

2.3. Photo-deactivation of green tide algae

In a glass reactor of 75 mL capacity, 25 mg of photocatalyst were suspended in 50 mL of a *T. suecica* dispersion (green tide algae) $250 \pm 20 \times 10^3$ cell mL^{-1} (Natural Live Plankton Co., Ltd., 99.9%). Then, the suspension was magnetically stirred and exposed to UV-A irradiation using two 20 W lamps (Sankyo Denky, Japan). The experiments were performed at room temperature for 45 min, and 100 μL aliquots were collected after each irradiation time interval. The collected suspensions were analyzed with a hemacytometer divided in small square regions of 1 mm × 1 mm of dimensions, where an optical microscope equipped with a video camera was focused in order to determine the living cells concentration in an area of ca. 1 mm^2. For all the observations through the microscope, a video of 15 s long, was recorded by the video camera so as to count all the living cells through the direct observation using a mechanical counter. The videos were useful for counting at least 5 times, and each photoinactivation experiment was repeated at least twice under identical conditions in order to increase the number of available data to produce the graphs of cell inactivation as a function of time. For comparative purposes, experiments were performed using $CaTiO_3$ cuboids sample, Ag/TiO_2 Aldrich and Ag/TiO_2 P25 photocatalysts. Control experiments with silver, TiO_2 bare P25 and in dark conditions, were previously described by our group [6]. Finally, to ensure that the noxious green tide algae does not regrow, nutritive water (Natural Live Plankton Co. Ltd.) was added to the system after incubation at 25 °C.

2.4. Characterization of functionalized materials

All of the samples were stored at room temperature inside a vacuum desiccator, away from light to prevent possible light-induced modifications. The crystalline phases were determined by X-ray diffraction (XRD) with a diffractometer (D8 Bruker Advance) using CuKα radiation of 1.5406 Å operated at 35 kV and 25 mA over the 2θ range of 5–70° in a step mode at steps of 0.02° with at a step time of 2 s. The resulting diffractograms were compared with the Powder Diffraction File (PDF) data of the International Centre for Diffraction Data (ICDD) for crystalline phase identification. The average