Development of a microwave-discharge light-emitting diode (MDLED): a novel UV source for the UV-driven microwave-assisted TiO₂ photocatalytic treatment of contaminated wastewaters

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Abstract

This brief article reports on the fabrication of a prototype novel semiconductor digital device, a microwave-discharge light-emitting diode (MDLED), consisting of an LED and a Schottky barrier diode encapsulated in a quartz ampoule. Coating the surface of this ampoule with TiO₂ yielded a new photocatalytic TiO₂ unit (MDLED-TiO₂) for use in treating contaminated wastewaters. To the extent that this MDLED-TiO₂ is driven only by microwave energy, there is no need for electric wires or electrical AC power. As much of the activity of TiO₂ photocatalyst is enhanced and ultraviolet light emission is generated only by irradiating with microwaves, the MDLED-TiO₂ affords a simple water treatment device as demonstrated in the present study. The digital device consisted of 14 pieces of MDLED-TiO₂ units immersed into a model contaminated wastewater toward the decomposition of organic pollutants and sterilization of natural bacteria-contaminated wastewaters performed in an energy-saving manner simply by irradiating the wastewaters with microwaves.

Graphical abstract

Keywords Microwave-discharge light-emitting diodes · Microwave-UV photodegradation · Photocatalyst · Wastewater treatments · 2,4-Dichlorophenoxyacetic acid · *Escherichia coli*

1 Introduction

Considering our daily usage of present-day gadgets, we discover that vacuum-tube technology has been replaced by semiconductor digital technology. For instance, (1) cathode ray tube (CRTs) monitors have been replaced by liquid crystal display (LCD) monitors [1] that have led to the

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fabrication of larger screens, otherwise not possible with CRTs, and (2) fluorescent lights have been replaced by light-emitting diodes (LEDs) [2], all of which have improved the quality of life, have decreased power consumption, and have eliminated potential toxic issues of mercury. Accordingly, various devices no longer use analog vacuum-tube technology, preferring instead the use of digital semiconductors [3].

Our early incursion into microwave-related studies [4–6] focused on the use of microwave energy to improve the activity of photocatalysts, together with the fabrication of prototype new light sources that emit UV light with microwaves that used vacuum-tube technology. Our current research falls in line with the times, in our efforts to change this UV source to an LED-type source—that is, a semiconductor digital light source in response to our overall objective to develop novel TiO_2 -based photocatalytic devices that are driven solely by microwave radiation.

Various photocatalysts have been investigated toward the detoxification of environmental ecosystems and to the production of high-value chemicals and fuels with the overall objective of finding the highly performing Holy Grail photocatalyst that can be activated by UV–Vis light or by sunlight. Among detoxification processes, research into the treatments of waters and wastewaters are also being pursued extensively. In this regard, a current search with the keywords “ TiO_2 ” and “wastewater treatments” in Science Finder resulted in more than 25,000 hits. While many studies have focused on the fundamentals of photocatalysis and semiconductor photochemistry and photophysics, there have been but a few examples that have dealt with the industrial use of photocatalysis to treat large volumes of contaminated wastewaters. The principal reasons are twofold: (1) the TiO_2 nanoparticles must be immobilized on suitable supports when used to detoxify contaminated waters to avoid filtration of the nanoparticulates from the treated waters, and (2) the reaction kinetics of the decomposition of pollutants on the surface of TiO_2 nanoparticulates have tended to be somewhat sluggish. Thus, various attempts are being made to enhance the efficiency of water treatments through chemical engineering means [7].

In our 2000 study [4], we reported that the activity of TiO_2 could be improved significantly by simultaneous irradiation with both microwave radiation and UV light emitted from a microwave-powered (2.45-GHz microwaves) electrodeless mercury-based lamp. For instance, the kinetics of the decomposition of the rhodamine-B dye in aqueous media improved more than threefold by simultaneous irradiating the TiO_2 suspension with both UV and microwaves in comparison to UV alone [5]. Irradiation of contaminated waters with microwaves raises the water temperature, yet even if the waters were heated by conventional means, the increase in temperature had no thermal consequences on the activity of the photocatalyst [6]. However, there was a significant

improvement on the activity of the photocatalyst when irradiating with microwaves and the surroundings were cooled [8]. Interactions between microwaves and TiO_2 contributed to the efficiency of electron transfer involving this photocatalyst [9, 10], and confirmed our inference that the enhanced photoactivity was not due to a thermal effect.

Considering the potential applications of this new method to drive/activate the photocatalyst by microwaves and UV light simultaneously led to our development of new UV light sources, namely the Microwave Discharge Electrodeless Lamp (MDEL) filled with a gas that once excited by the microwaves emitted light in the vacuum-UV (183 nm) and in the UVC region (252 nm) [11]. The structure of the MDEL consisted of argon gas (Ar) and mercury (Hg) sealed in a synthetic quartz lamp bulb, which proved to have a long lifespan as it required neither a power supply, nor electrode sockets, nor electrodes. What's more, it presented no risk of electrical leakage even when submerged in waters. However, that technology was historically not in line with the International Treaty known as *The Minamata Convention on Mercury* established in 2013 and enacted in 2017, which aimed to regulate the manufacture, import, and export of mercury-laden products [12]. This Convention required that all countries regulate the manufacturing and sales of Hg-based lamps by 2020. Accordingly, current commercially available mercury-based UV lamps are now subjected to the enacted mercury regulations. As a result, our later study [13] developed MDEL lamps filled with Kr/Br₂ as the new filler gases that when exposed to microwaves emitted UVC light at 207 nm, 222–228 nm, and 291 nm.

The present article reports on our development of a novel mercury-free MDEL-type light source that comes to terms with present-day semiconductor digital technology: a prototype of a microwave discharge light emitting diode (MDLED) activated solely by microwave energy. Also developed is a new photocatalytic TiO_2 -based device, the MDLED- TiO_2 lamp, fabricated by coating the outer surface of this new MDLED with Evonik P-25 TiO_2 and whose performance was evaluated by treating wastewaters contaminated with the 2,4-dichlorophenoxyacetic acid (2,4-D) herbicide and with the *Escherichia coli* (*E. coli*) bacteria.

2 Experimental section

2.1 MDLED and microwave system

The microwave discharge light emitting diode (MDLED) consists of a loop antenna fabricated by connecting a Nichia LED (Nichia Co. Can Type LED; diameter 4.7 mm) and two ultra-small Schottky barrier diodes (Akizuki Denshi Tsusho Co. Ltd.; 2 mm × 1 mm), after which the LED is lit by the microwave current flowing through the loop antenna

(Fig. 1a). The UV light emitted by this LED spanned the wavelength range 350–400 nm, with maximal emission at 365 nm [14]. Note that the principle of combining Schottky barrier diodes and color LEDs to light them with microwaves was first reported by Nikawa and coworkers [15] in their study of microwave visualization sensors. When the microwave magnetic field is interlinked with the metal loop, the potential (e) generated in the loop is maximized when the magnetic field is orthogonal to the metal loop surface, as described by Eq. (1) [15]:

$$e = \frac{1}{\sqrt{2}} A \omega \mu_0 H \text{ (volts)}, \quad (1)$$

where A is the loop area, ω is the microwave angular frequency, μ_0 is the magnetic permeability, and H is the magnetic field strength.

The structure described above with the visible-light LED was replaced by a UV-LED enclosed in a capsule of synthetic quartz (Fig. 1a), henceforth referred to as a MDLED. The outer hybrid TiO₂ coatings consisted of the microwave-responsive Evonik P-25 TiO₂ particles and a sol–gel TiO₂, which acted as an inorganic binder for the P-25 TiO₂ [16]. Loading the P-25 titania onto the outer walls of the MDLED quartz capsule was achieved by dipping the capsule in a colloidal sol of P-25 TiO₂ particles (1 mg) in ethanolic media (50 mL), followed by drying and heating with a heat gun. Originally, the TiO₂ P-25 was fixed to the MDLED surface by sintering in an electric furnace heated to about 500 °C; however, the LED tended to break at this temperature so that a lower temperature had to be used. However, coating the P-25 titania onto the MDLED's outer walls through physical adsorption caused the TiO₂ nanoparticles to be easily removed by simple rubbing, which led us to use the sol–gel TiO₂/P-25 TiO₂ hybrid method to bind the P-25 titania.

The sol–gel TiO₂ binder was prepared by mixing titanium tetraisopropoxide (28.4 g), diethanolamine (21.0 g) and ethanol (200 mL) under an inert atmosphere in a glove box previously purged with dry nitrogen gas. Subsequently, ethanol (4.6 g) and water (18 g) were added to the mixture under vigorous stirring for 1 h at room temperature that yielded the desired sol–gel. Later, the MDLED quartz capsule was dipped into the hybrid TiO₂ sol–gel/P-25 TiO₂ and then dried with a heat gun. An EDX elemental analysis (Shimadzu Co. EDX-8100 ED) of the surface of the TiO₂-coated MDLED showed the quantity of Ti as 4.33% of total. Dimensions of the devices were 26–30 mm (length) by 7 mm (external diameter).

The flow reactor consisted of a synthetic quartz cylindrical vessel (length, 130 mm; diameter, 30 mm) with high microwave transmission; the solution was introduced from the upper part of the reactor through the silicone tubing (Fig. 1b, c) fixed with a silicone stopper. Note that silicone

Fig. 1 Photographs of the **a** MDLED and MDGEL-Hg with the scale in cm units, and **b** the experimental setup showing the microwave multimode applicator containing the reactor with the MDLED-TiO₂; **c** schematic image of the location of the MDLED-TiO₂ and MDGEL-Hg setup in the reactor

tubing and silicone plugs remained cool under microwave irradiation. An assembly of 14 pieces of MDLED-TiO₂ devices was added to the reactor to be used to decontaminate

200 mL of each model contaminated wastewater in a reservoir bottle. The wastewater from this reservoir bottle was circulated through the MDLED-TiO₂ assembly at a rate of 0.35 L min⁻¹ using a peristaltic pump located outside the microwave device, and then collected in the reservoir bottle through the silicone tubing attached at the bottom of the reactor. Continuous microwave irradiation of the MDLED-TiO₂ devices was provided by a Tokyo Rikakikai Co., Ltd MWO-1000S microwave apparatus consisting of a multi-mode applicator and a 2.45-GHz microwave generator; the microwave power was fixed at 65 W.

The photolytic experiments implicated two model wastewater systems: the first consisted of an aqueous solution of the herbicide 2,4-dichlorophenoxyacetic acid (0.05 mM; High-purity grade; Fujifilm Wako Chemical Co.), while the second was an aqueous solution of *E. coli* bacteria.

To assess the performance of the novel MDLED-TiO₂ devices, 14 pieces of MDLEDs (not coated with TiO₂) were also examined under otherwise identical experimental conditions; for comparison, 48 pieces of the mercury-laden microwave discharge granulated electrodeless lamps (MDGEL-Hg; not coated with TiO₂) were also used to treat the two model contaminated wastewaters (see Fig. 1c). The MDGEL-Hg devices were fabricated using a vacuum-UV transparent synthetic quartz vessel and a mixture of Hg and Ar as the gas-fills; dimensions of the vessel were 10 mm (length) by 5 mm (external diameter). After evacuating the MDGEL quartz envelope to 133×10^{-7} Pa, the system was purged with argon gas (133×10^{-3} Pa) followed by addition of a small quantity of liquid mercury (ca. 0.3 mg). Subsequent microwave irradiation of the latter MDGEL-Hg devices generated UV light in the vacuum-UV region at 185 nm and in the UVC region at 254 nm [17]. The need to use 48 MDGEL-Hg was so that the height of the MDGELs (ca. 55 mm) packed in the reactor was the same as the height when 14 MDLED-TiO₂ units (ca. 55 mm) were packed in the reactor. In experiments that involved the light emitting MDLEDs, the microwave output power was fixed at 65 W and irradiation was performed under conditions otherwise identical to the case of MDLED-TiO₂ devices. In contrast, in experiments with continuous microwaves that involved the MDGEL-Hg devices, the microwave output power was 220 W in order to obtain stable UV light emissions.

2.2 Model wastewaters

Analytical grade 2,4-dichlorophenoxyacetic acid (C₈H₆Cl₂O₃; purity 100%; Fujifilm Wako Chemical Co.) was dissolved in ion-exchanged water (pH 6.7; 0.05 mM; 200 mL) to be used as a model of a wastewater contaminated by a herbicide. The solution was circulated through the reactor for about 1 h prior to microwave irradiation; ca. 6% of the 2,4-D had adsorbed onto the metal-oxide surface. The time profiles

of the degradation of 2,4-D were monitored with a JASCO liquid chromatograph (HPLC) equipped with a JASCO UV-2070 UV/visible diode array multi-wavelength detector, and a JASCO CrestPak C18S column; the eluent was a mixed solution of CH₃OH/H₂O (1:4 v/v). The concentration of Cl⁻ ions from the photo assisted dechlorination of 2,4-D was assayed with a JASCO ion chromatograph equipped with a CD-5 conductivity detector and a I-524 anion column; the eluent was a mixed solution of phthalic acid (2.5 mM) and tris-(hydroxymethyl)amino-methane (2.3 mM; pH adjusted to 4). The time profiles of the loss of total organic carbon (TOC) in the degradation of 2,4-D were assayed using a Shimadzu TOC-5000A analyzer.

The *E. coli* contaminated model wastewater used a pure strain of *E. coli* DH5-α obtained from the Takara Bio Inc. The *E. coli* DH5-α was increased in a LB-medium, a standard nutrient media for the growth of bacteria. The LB-medium was prepared by adding 5.0 g of Bacto Trypton (Fujifilm Wako Chemical Co.), 2.5 g of Bacto Yeast Extract (Fujifilm Wako Chemical Co.) and 5 g NaCl (Fujifilm Wako Chemical Co.) to 500 mL distilled water, followed by 100 μL of 10 N NaOH (Fujifilm Wako Chemical Co.). To this LB-medium was then added 15% (w/v) agar, after which the resulting mixture was autoclaved at 120 °C and then cooled to about 60 °C. About 20 mL of the cooled nutrient media was poured into 90-mm petri dishes and fan-dried for about 1 h in a bio-clean bench. The bacterium *E. coli* was linearly applied on agar in the LB medium, and then the *E. coli*-streaked agar plates were incubated at 37 °C for 24 h; one colony inoculated in LB-medium was incubated at 37 °C for 10 h. The *E. coli* plates were then washed with sterile water three times by centrifugation at 10,000 rpm and 4 °C for 3 min. Afterwards, diluting the *E. coli* with 1 L of sterile water resulted in an initial concentration of *E. coli* estimated to be ca. 10⁴ CFU/mL (10⁴ colonies in 1 mL; CFU: colony forming unit). From there, a 200-mL solution was uniformly transferred to a reservoir bottle and circulated through the reactor system by a peristaltic pump at a rate of 0.35 L min⁻¹. Aliquots of the *E. coli* solution were collected at regular irradiation times and subsequently diluted with 20 mL of sterile water; 0.5 mL samples of the diluted solution were spread onto LB agar plates, and then incubated for 24 h followed by manual plate counting that spanned the range 0 to ~200 colonies. The “control *E. coli*” sample that had not been microwave irradiated was placed in a reservoir bottle and allowed to stand at ambient temperature for 30 min, after which the colonies were counted using the same protocol. The sterilization yields of *E. coli* before and after microwave irradiation were determined from Eq. (2),

$$\text{Sterilization yield (\%)} = \frac{C_0 - C_t}{C_0} \times 100, \quad (2)$$

where C_0 is the concentration of the “control *E. coli*” (CFU mL⁻¹) and C_t is the concentration (CFU mL⁻¹) at the specified time, t .

3 Results and discussion

3.1 Decomposition of 2,4-dichlorophenoxyacetic acid herbicide in aqueous media

Subsequent to the microwave irradiation of the MDLED-TiO₂ devices within the reactor, the extent of decomposition of the aqueous 2,4-D was 18% after 5 min, 27% after 10 min, and 85% after 60 min (Fig. 2a). In contrast, no decomposition of 2,4-D occurred with the uncoated MDLEDs even after irradiation with microwaves for 60 min. The maximal emission of UV light of this MDLED occurred at 365 nm (quantum energy is 3.4 eV) and thus the energy available was unable to photolyze directly (no TiO₂ present) the 2,4-D herbicide through bond breaking, as the bond strengths in this herbicide are significantly greater: for instance, C–C bond (3.82 eV), C=C (11.08 eV), C=O (3.69 eV) and C–Cl (3.48 eV). Therefore, the driving factor that impacts the decomposition of 2,4-D by the MDLED-TiO₂ is the presence of the TiO₂ photocatalyst that is being photoactivated simultaneously by both the microwaves and by the emitted ultraviolet light (absorption band edge of anatase TiO₂ occurs at > 387 nm). However, unlike the uncoated MDLEDs, the microwave-activated MDGEL-Hg decomposition of the 2,4-D herbicide was much faster ($k = 0.30 \pm 0.01 \text{ min}^{-1}$) than with the MDLED-TiO₂ system ($k = 0.024 \pm 0.005 \text{ min}^{-1}$). No less than 76% of 2,4-D was degraded after 5 min and 100% after 20 min of microwave irradiation with the MDGEL-Hg system.

Likewise, dechlorination associated with the decomposition of 2,4-D also failed to occur with the microwave-activated MDLEDs alone, contrary to the dechlorination occurring in the presence of microwave-activated MDLED-TiO₂ after a delay time of about 5–10 min ($k = 0.011 \pm 0.001 \text{ min}^{-1}$; Fig. 2b): the extent of dechlorination was 14% after 20 min of microwave irradiation, 32% after 40 min and 41% after 60 min. In comparison, the microwave-activated MDGEL-Hg led to near-complete dechlorination (90%) of the 2,4-D herbicide after 40 min ($k = 0.056 \pm 0.007 \text{ min}^{-1}$), almost threefold greater and five times faster vis-à-vis the MDLED-TiO₂ system after this time.

The extent of loss of total organic carbon (TOC) associated with the decomposition of 2,4-D (Fig. 2c) was also quantified. No reduction in TOC was observed from the 2,4-D degradation with the MDLEDs alone. In contrast, there was a 12% loss of TOC after 20 min, 18% of after 40 min, and 25% after 60 min with the MDLED-TiO₂ system

Fig. 2 Degradation of continuously recirculated aqueous 2,4-D solutions (200 mL; initial concentration, 0.050 mM) using MDGELHg (48 pieces; irradiated with 220-W microwaves), MDLED-TiO₂ (14 pieces; irradiated with 65-W microwaves), and MDLEDs (14 pieces; also irradiated with 65-W microwaves). **a** Time profiles of the degradation of 2,4-D, **b** time profiles of the formation of Cl⁻ ions, and **c** time profiles of the loss of total organic carbon (TOC)

($k = 0.0048 \pm 0.0003 \text{ min}^{-1}$), whereas TOC loss with the MDGEL-Hg ($k = 0.027 \pm 0.002 \text{ min}^{-1}$) was 44% after 20 min of microwave irradiation, 69% after 40 min and 83% after 60 min. Hence, TOC loss with the latter device was nearly fourfold greater after the 40-min irradiation period.

3.2 Disinfection of an *E. coli*-contaminated wastewater

The performance of MDLED-TiO₂ was also evaluated from the sterilization of wastewaters contaminated with the

Fig. 3 Sterilization yields of wastewaters contaminated with *E. coli* bacteria using the MDGEL-Hg (48 pieces; irradiated with 220-W microwaves), MDLED-TiO₂ (14 pieces; irradiated with 65-W microwaves) and MDLEDs (14 pieces; also irradiated with 65-W microwaves)

Escherichia coli bacteria (Fig. 3). The sterilization yield of *E. coli* with the microwave-activated MDLED-TiO₂ devices was 61% following 10 min of microwave irradiation and 92% after 30 min ($k = 0.087 \pm 0.003 \text{ min}^{-1}$). Evidently, the sterilization process was remarkably more effective than the decomposition of the 2,4-D herbicide. The sterilization yield with the MDGEL-Hg system was nearly quantitative (> 99%) in aqueous media after only 1 min of microwave irradiation. Possible causes for such a short time are that in addition to the direct sterilization by the 254-nm UV light emitted by the MDGEL-Hg, sterilization may have been further enhanced by (a) the presence of active oxygen species, such as ozone (O₃), formed from the decomposition of water by the 185-nm vacuum-UV light [18] emitted by the MDGEL-Hg device, and possibly by (b) the heat released by the MDGEL-Hg lamps.

Sterilization of the *E. coli*-contaminated wastewater also proceeded with the TiO₂-uncoated MDLED (experiments repeated three times), albeit less so than the MDLED-Hg and MDLED-TiO₂ systems; the averaged sterilization was 11% in 10 min and 15% in 30 min ($k = 0.0066 \pm 0.0009 \text{ min}^{-1}$). Another experiment used three MDLEDs connected to an external power source and microwave-irradiated to sterilize 10 mL of an *E. coli* solution. Results from the emitted 365 nm radiation by these MDLEDs showed no sterilization of *E. coli* even after 30 min. Accordingly, sterilization must have occurred thermally as the temperature of the MDLED/ aqueous solution that had been irradiated with microwaves for 30 min was ca. 48 °C. To test this hypothesis, 200 mL of the aqueous solution of *E. coli* was heated in a water bath at 50 °C for 30 min, which caused 38% of the wastewater to be sterilized. This demonstrates that sterilization of *E. coli* bacteria by the MDLEDs was caused by the rise in water temperature through microwave heating the aqueous medium. Clearly then, sterilization of the *E. coli*-contaminated

wastewater by the MDLED-TiO₂ devices was caused by both the microwave effects on TiO₂, whose activity was improved by the UV light emitted by the microwaved MDLED-TiO₂s, and by the rise of water temperature following microwave irradiation of the reactor.

4 Concluding remarks

A novel photocatalytic TiO₂-based device, MDLED-TiO₂, was constructed and its performance evaluated by the decomposition of the 2,4-D herbicide and by the sterilization of an aqueous solution contaminated with *E. coli*. In keeping with our earlier proposed MDELs filled with mercury and argon gas, this novel device also requires no electrical wiring and retains the characteristics of a prolonged lifespan. Furthermore, power consumption was reduced from 220 to 65 W by changing the light source from a vacuum-tube technology to a semiconductor digital technology. We note further that such novel devices are easy to manufacture and that chemical substances present no issues, even if it were damaged in the wastewaters. On the other hand, because the generated UV light from the MDLEDs alone does not lead to the decomposition of the 2,4-D herbicide and the full sterilization of *E. coli*-contaminated wastewaters, the MDLEDs alone are not practical in water treatment. In contrast, however, coating these MDLEDs with TiO₂ that respond to the effects of microwaves and to the emitted UV light, the MDLED-TiO₂ devices can indeed detoxify and disinfect contaminated wastewaters and thus will prove useful in water treatment processes. In this regard, it is important to note that although the MDLED-TiO₂ devices have proven less efficient than the MDGEL-Hg counterparts in the mineralization of the 2,4-D herbicide and the sterilization of the *E. coli* bacteria, the fact that the novel systems proposed herein contain no toxic mercury presents significant advantages were the MDLED-TiO₂ devices suffer breakages when utilized in the environment. Moreover, these MDLED-TiO₂ assemblies can prove useful with a household microwave oven and can, in principle, also be used to sterilize low concentrations of viruses by the action of the photoactivated TiO₂. Future development of small MDLEDs that can emit short-wavelength UV light (UVC and vacuum-UV) with high intensity subsequent to microwave irradiation should improve their performance and could be used as a light source in various other fields.

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Author contribution SH planned the research, summarized the data, and wrote the first draft; MK performed the experiments; SH and NS examined and interpreted the data, and wrote the final draft.

Declarations

Conflict of interest The authors have no conflicts of interest to declare.

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