Photocatalyst-incorporated Nonthermal Plasma Sterilization System for Water Treatment

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Abstract. To take advantage of the ultraviolet light emitted by the plasma for sterilization, photocatalysts including tinanium oxide, zinc oxide and graphene oxide (GO) were combined with a dielectric barrier discharge (DBD) plasma reactor. It was found that the combination of the plasma with the photocatalysts resulted in substantial improvements in the sterilization of *E. coli* in biologically contaminated water.

Keywords: Sterilization; Dielectric barrier discharge; Plasma; Photocatalysis

1 Introduction

Conventional sterilization systems utilize heat, chemicals like chlorine and ethylene oxide, irradiation, high pressure, filtration, or the combinations of two or more of these methods. The advantages and drawbacks of the conventional systems are described in many previous articles [1], [2]. Water sterilization using plasma may be a promising cost-effective candidate that may overcome the disadvantages of the conventional systems. In some respects, plasma sterilization systems operate quite differently from the conventional systems because they generate germicidal species such as radicals, ozone and UV photons in situ for killing microorganisms. Recently, the efficiencies of plasma sterilization systems have been reported by many authors. Furthermore, plasma sterilization system is environmentally friendly, compared to common chemical methods like chlorination. The other noteworthy feature of the plasma system is the possibility of catalyzing sterilization action when it is combined with a photocatalyst. Even if plasma-generated UV light itself (mostly UV-A) is not very effective for sterilization, it is strong enough to activate photocatalysts.

The combination of plasma with a photocatalyst can give rise to the formation of highly reactive hydroxyl radicals by taking advantage of plasma-generated UV photons. This led us to consider two types of plasma sterilization systems, i.e., plasma-alone and plasma-photocatalysis combination systems. Many semiconductors including TiO_2, ZnO, CdS and WO_3 can be used as a photocatalyst [3]-[5]. As well, recent studies indicate that graphene oxide (GO) with an apparent band gap of 2.4-4.3 eV can also be used as a photocatalyst [6], [7]. The respective performances of plasma and photocatalysis in sterilization appear to be well understood, and this work

focuses on plasma-photocatalytic combined sterilization process. The plasma sterilization system of this work is based on atmospheric pressure DBD. We investigated the effectiveness of the plasma-photocatalytic combined sterilization with *Escherichia coli (E. coli)* as a model bacterium. Three different photocatalysts including $Ti0_2$, ZnO and GO were comparatively investigated. Commercial TiO_2 and ZnO were used while GO was prepared by modified Hummer's method [8], [9]. Even though ZnO has the similar band gap as TiO_2, the greatest advantage of ZnO is that it absorbs large fraction of solar spectrum and more light quanta than TiO_2 [10], and several researches have evidenced the performance of ZnO on the degradation of organic compounds [11]-[13].

2 Experimental

The components of the DBD-based plasma sterilization system include a DBD reactor, a vessel filled with contaminated water and a 60 Hz AC high voltage power supply. The DBD reactor comprised a quartz tube (inner and outer diameters: 21 mm; 25 mm), a 7.7-mm thick coaxial stainless steel screw electrode and a ceramic gas diffuser connected to the lower end of the quartz tube. The DBD reactor was immersed in biologically contaminated water, thereby the outer surface of the quartz tube being in direct contact with the water. The stainless steel screw acted as a discharging electrode. The effective DBD reactor length was about 22.5 cm. The flow rate of air fed to the DBD reactor was 2 L min^{-1}. The UV light emitted by the DBD can directly irradiate the water since quartz is UV-transparent. Other gas-phase reactive species formed in the DBD reactor were fed to the water through the gas diffuser.

Commercially available TiO_2 and ZnO used as photocatalysts were obtained from Degussa and Kanto Chemical Co., respectively. GO was synthesized with commercial graphite powder (Daejung Chemical Co.). The photocatalyst particles were suspended in the water by the working gas that was continuously bubbled into the water. The initial population density of *E. coli* was around $lx10^7$ colony forming units (CFU) ml^{-1} (volume: 1,000 mL). The water contaminated with *E. coli* was treated at a voltage of 21 kV. To assess the sterilization efficiency, samples were removed from the system at regular time intervals, filtrated to separate the photocatalyst particles, and diluted 10^3, 10^4, 10^5 and 10^6-fold with physiological saline. Characterization of the photocatalysts was performed by using an X-ray diffractormeter, a field emission scanning electron microscope (SEM) and an energy dispersive spectrometer (EDS). The BET specific surface area of the GO prepared was determined by using a surface area analyzer. The concentration of ozone generated in the DBD reactor was analyzed by an UV/visible spectrophotometer at a wavelength of 260 nm.

3 Results

Krishnamoorthy et al. [7] showed that GO exhibits excellent photocatalytic activity by measuring reduction rate of resazurin as a function of UV irradiation time. The photocatalytic properties of TiO_2-GO composite under the irradiation of UV were

studied by Zhang et al. [14], who found out that the photocatalytic properties of their catalyst are superior to that of $Ti0_2$.

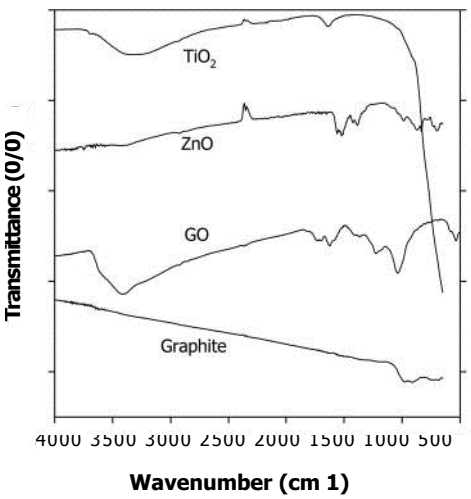

Fig. 1. FTIR spectra of photocatalysts used.

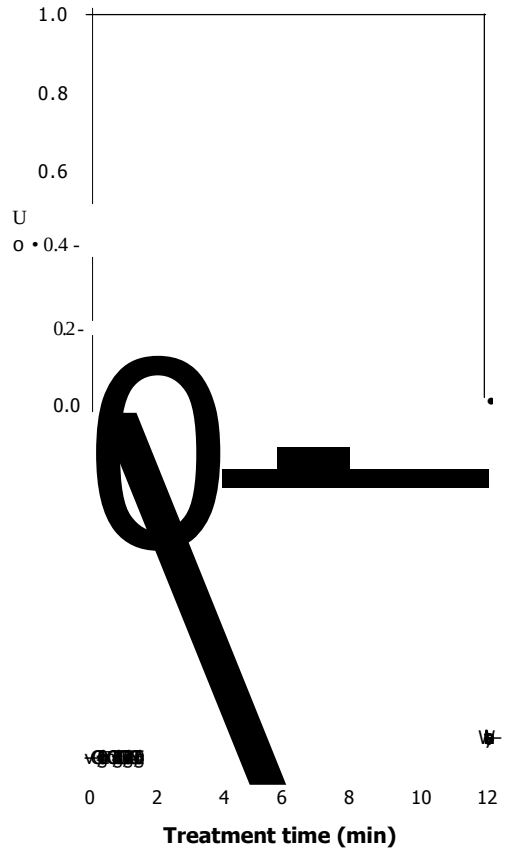

Fig. 2. Concentration of E-coli as a function of treatment time (7.8 W).

Fig. 1 shows FTIR spectra of the three photocatalysts. The spectra exhibited well-defined absorption bands of TiO_2 and ZnO. Regarding GO, characteristic bands around 1060 cm^{-1}, 1220 cm^{-1}, 1370 cm^{-1}, 1620 cm^{-1}, and 1720cm^{-1} are related to CO stretching, phenolic C-OH stretching, tertiary alcoholic C-OH bending, water H-OH bending and C=0 stretching, indicating the presence of phenol and carboxylic acid. The EDS measurements of the photocatalysts are summarized in Table 1. The composition in Table 1 confirms that the graphite was oxidized during the oxidation treatment. Based on the FTIR spectrum of the prepared GO, the oxygen-containing functional groups are mainly carboxyl and OH groups.

Table 1. EDS results for the compositions of the photocatalyst

Photocatalyst	Element	Composition (atomic %)
Graphene oxide	C	55.1
	0	40.5
	impurities	balance

Fig. 2 shows the profiles of

dimensionless *E-coli* concentration as a function of the elapsed time at different GO contents. Since the apparent band gap of GO is quite broad 2.4-4.3 eV, the GO can serve as a photocatalyst with UV or visible light irradiation. Without the addition of GO, the microorganism is mainly inactivated by ozone produced in the DBD plasma reactor. Under this experimental condition, ozone can not only directly attack the cell but also act as an oxidizing agent for the photocatalytic degradation. Kopf et al. [15] investigated the influence of ozone on the photocatalytic oxidation of organic compounds with TiO_2, and they found that the

photocatalytic ozonation leads to much higher degradation rate than without ozone. According to Kopf et al. [15], the photocatalytic ozonation may be summarized as

$$\text{Photocatalyst} + h\nu \quad h^+ + e \tag{1}$$

$$h^+ + H_2O \; 4 \; OH + fr \tag{2}$$

$$e^- + 0_2 \quad 02 \tag{3}$$

$$0_3 \pm 0_2 \; 4 \; 0_3 \pm 0_2 \tag{4}$$

$$0_3 + 1\text{-}1^+ \text{ -› } H0_3 \tag{5}$$

$$H0_3 \quad OH + 0_2 \tag{6}$$

Here, reaction (1) accounts for charge separation of electron (e)-hole (h^+) pairs while the others are charge transfer reactions leading to the formation of highly oxidative OH radical. From Fig. 2, it is obvious that the increase in the GO content substantially improved the sterilization. In principle, the GO can absorb more photons emitted by the DBD when its content is higher, but the increase in its content also increases the solution turbidity, thus in turn decreasing the penetration depth of UV irradiation.

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