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Water disinfection using zinc phosphide nanowires under visible light conditions

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ABSTRACT

Common methods of bacteria disinfection after water treatment include chlorination and ultraviolet irradiation. Although very effective, those methods require continual investment of energy or materials. Previous studies have shown that photocatalysis can enhance water disinfection. This study addressed the potential use of zinc phosphide nanowires to promote water disinfection under visible light conditions as a potentially economical alternative. Disinfection studies were conducted using boron nitride decorated zinc phosphide nanowires, unfunctionalized zinc phosphide nanowires, 1,4-benzenedithiol functionalized zinc phosphide nanowires, and bare zinc foil. Bioreactors inoculated with *Escherichia coli* isolates were exposed to the photocatalysts under visible light. *E. coli* was enumerated at five-min intervals during the disinfection period. At least a 5-log reduction in microbial load was achieved for all materials, with the unfunctionalized zinc phosphide nanowires consistently producing the highest log reduction. For each material, more than a 4-log reduction was observed after only 5 min of exposure. Minimal photoreactivation or dark repair (less than a 1.48-log increase) was observed. Disinfection efficacy did not differ significantly ($p < 0.05$) between the three isolates. Although the specific photocatalytic mechanism is not yet known, this study indicates that zinc phosphide nanowires can enhance disinfection of water using only visible light.

1. Introduction

In the United States, bacteria from fecal material are a leading cause of water impairment [1]. Fecal contamination from humans or animals is a potential source of enteric bacteria. To mitigate health risk, water is disinfected to eliminate fecal-derived pathogens remaining after drinking water or wastewater treatment. Widely used and effective disinfection treatments include chlorination and ultraviolet (UV) irradiation [2–4]. Chlorination is very effective and has the added benefit of residual disinfection, but it may form carcinogenic by-products [5,6]. UV treatment requires neither special handling nor chemicals, but it is moderately expensive and bacterial reactivation often occurs [3], especially with environmental isolates [7]. The ability of photocatalysts to degrade bacteria has been observed since the mid-1980s [8]. For instance, bacterial inactivation by titanium dioxide (TiO_2) under UV light has been studied extensively [8–12]. In most studies, nanomaterials such as ZnO and TiO_2 have tended to be used in conjunction with UV light because the UV radiation spectrum matches the excitation energies of these photocatalysts [10,12–14]. However, ZnO is unstable in water, and bacterial inactivation using TiO_2 under visible light is slow [15,16].

The photocatalytic properties of zinc phosphide (Zn_3P_2) make it attractive for use in water disinfection in the visible light range. Zinc phosphide, an inorganic compound, is useful in photovoltaic applications [17]. Because its components are inexpensive and are available abundantly in the earth's crust [14,18], zinc phosphide can be mass produced in nanowire forms [18]. Also, Zn_3P_2 nanowires have high specific surface areas, which is essential for their use as catalysts [19]. With a bandgap of 1.5 eV (in the infrared regime), these nanowires can be activated by wavelengths in either the visible or the ultraviolet regimes [19].

However, similar to ZnO, zinc phosphide is not stable in water [18,19]. Because Zn_3P_2 is highly toxic, stable forms are needed for use in aqueous environments. In a process developed by Vasiraju, et al. [19], zinc phosphide has been stabilized by non-conformal decoration with boron nitride (BN). Further, functionalization of Zn_3P_2 with organic molecules may enhance stability, as shown by Brockway, et al. [17,18,20] and Ramos-Sanchez, et al. [14]. Stabilization of these nanowires, using either BN decoration or organic molecule functionalization, enhances their suitability for use in aqueous media [17,19].

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Enhancing the stabilities of materials that have high specific surface areas, such as Zn_3P_2 nanowires, makes them suitable for disinfecting water using only sunlight or inexpensive sources of visible light. Also, because these stabilized nanowires are easily activated and made from inexpensive materials, they are potentially useful as photocatalysts for disinfecting water. To our knowledge, the use of Zn_3P_2 nanowires to promote photocatalytic degradation of bacteria in water has not been studied yet.

This study addresses the potential use of various forms of zinc phosphide nanowires to promote the disinfection of *E. coli* photocatalytically under visible light conditions. To evaluate whether different isolates vary in responses or repair mechanism with this treatment, environmental *E. coli* isolates from three sources were used. Disinfection studies were performed, and then photoreactivation and dark repair were evaluated after treatment. Stability studies were conducted to assess any degradation of the treatment materials in water. These preliminary studies show the potential suitability of this class of nanomaterials to disinfect water.

2. Materials and methods

2.1. Microbial strains and culture media

Disinfection experiments were conducted on environmental *E. coli* isolates from three sources: wastewater treatment plant (WWTP), cattle, and feral hog. The WWTP isolate was prepared from the secondary effluent of a domestic wastewater treatment plant in Texas. The cattle and feral hog fecal samples were collected from the Attoyac Bayou (Texas) watershed; *E.coli* identification and isolation were conducted by the Soil and Aquatic Microbiology Laboratory at Texas A&M University. The harvested stock specimens were stored in a −20 °C freezer until use. Isolation confirmation was performed on a modified mTEC (membrane Thermotolerant *E. coli*) medium. For each isolate, a loop full of stock culture was aseptically transferred and then enriched in Luria-Bertani (LB) Broth for 4 to 6 h at 42 °C under aerobic conditions and continuous agitation. After enrichment yielded at least 10^8 CFU/mL, 5 mL of each culture was transferred into 100 mL of sterile water in a separate 200 mL beaker. All glassware and media were aseptically handled before and after autoclave sterilization (121 °C for 20 min).

2.2. Synthesis of zinc phosphide nanowires

Three nanowire samples and bare zinc foil were used in this study. Boron nitride (BN) decorated zinc phosphide nanowires, unfunctionalized zinc phosphide nanowires, 1,4-benzenedithiol (BDT) functionalized zinc phosphide nanowires, and zinc foil were designated materials A, B, C, and D, respectively. All nanowires were synthesized on top of zinc foils using chemical vapor deposition (CVD) as outlined by Vaddiraju, et al. [14,17–20]. As previously mentioned, to enhance nanowire stabilities in water, a method involving the non-conformal decoration of Zn_3P_2 nanowires with BN ceramic [19] was used. Brief descriptions of these processes follow. Zinc phosphide nanowires were formed when phosphorous vapor was transported onto zinc foils maintained at 380–400 °C. A red phosphorus powder source maintained at 480 °C allowed for this phosphorus vapor transport, and a 20 sccm hydrogen flow aided this transport. All nanowire synthesis was performed at a pressure of 400–500 mTorr. It is thought that nanowire formation results from self-catalysis via zinc droplets [14,17,18,20,21]. After synthesis and before removal from the vacuum chamber, the nanowires were exposed to either 1,4-benzendithiol (BDT) or decomposed tribromoborazine to obtain BDT functionalized [14,17,18,20] and BN decorated Zn_3P_2 nanowires, respectively [19]. For the latter, the amount of tribromoborazine was carefully controlled to ensure a non-conformal BN coating was obtained on top of the nanowires [19].

2.3. Disinfection trials

To assess disinfection, Materials A, B, C, and D were each immersed and suspended in the respective aerobic reactors at 25 °C for the duration of the experiment. The control reactor did not contain any photocatalyst. In the preliminary study, performed on the WWTP isolate, the control was exposed to a low-pressure UV-C germicidal lamp (Bryant Energy, Indianapolis, USA). The average irradiance was approximately 3.26 mW/cm^2. However, each reactor containing a nanomaterial was exposed only to visible light.

Other than in the preliminary study, all disinfection trials were conducted in the presence of visible light. Reactors were exposed to three fluorescent lamps, each with an approximate intensity of 30,000 Lux. For all trials and the control, enumeration of *E. coli* was conducted immediately after inoculation (0 min) and thereafter at 5-min intervals for the duration of the experiment. During the disinfection period, which lasted 20 to 30 min, reactors were continuously mixed using magnetic stirrers under aerobic conditions at 25 °C.

2.4. Reactivation studies

After the disinfection experiments, each culture was split into two reactors. In order to assess dark repair, one reactor was completely covered in foil. The other reactor remained exposed to light in order to determine photoreactivation. The reactors were continuously mixed by magnetic stirrers under aerobic conditions. All reactivation studies were conducted at ambient room temperature. *E. coli* enumeration was conducted after 24 h. Reactivation was assessed as log repair following treatment.

2.5. Enumeration of microorganisms

E. coli was enumerated by spread plating in triplicate on MacConkey agar plates; serial dilution was done when necessary. Plates were inoculated with volumes ranging from 0.1 mL to 1 mL and then incubated for 24 h at 30 °C. After incubation under aerobic conditions, colony-forming units (CFUs) were counted and then multiplied by the dilution factor. The number of cells (N) was reported as the average of the triplicate plate counts. All enumeration values (N_t) at time t were normalized using the initial enumeration (N_o) of *E. coli* prior to treatment. Additionally, a single factor analysis of variance (ANOVA) was performed for each time interval on the normalized replicated plate counts.

2.6. Assessment of nanowire degradation

The synthesized nanowires were characterized using scanning electron microscopy (SEM). A detailed discussion of the X-ray diffraction (XRD) and transmission electron microscopy analyses appears in previous publications by Vaddiraju and coworkers [17–20]. After synthesis, the physical dimensions (diameters and lengths) of the as-obtained nanowires were measured using SEM analysis. Additionally, to determine nanowire photostability, scanning electron micrographs were taken before and after the disinfection trials.

3. Results and discussion

3.1. Preliminary disinfection study

A preliminary proof-of-concept disinfection trial was conducted on only the WWTP isolate (Fig. 1). Because treated wastewater typically undergoes UV disinfection, the control was subjected to UV light during this preliminary study. At least a 5-log reduction in the surviving culturable fraction of *E. coli* was achieved for all materials. The disinfection extent during the initial 20-min exposure provided the basis for the subsequent studies. This preliminary study demonstrated not only that a 20 min exposure time was sufficient to achieve greater than a 7-log