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# Anti-bacterial activity of indoor-light activated photocatalysts

Damian W. Synnott[a,b], Michael K. Seery[b], Steven J. Hinder[c], Georg Michlits[b], Suresh C. Pillai[a,*]

[a] Centre for Research in Engineering Surface Technology (CREST), FOCAS Institute, Dublin Institute of Technology, Camden Row, Dublin 8, Ireland
[b] School of Chemical and Pharmaceutical Sciences, Dublin Institute of Technology, Kevin St. Dublin 8, Ireland
[c] The Surface Analysis Laboratory, Faculty of Engineering and Physical Sciences, University of Surrey, GU2 7XH, United Kingdom

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ABSTRACT

Nanocrystalline photocatalysts, prepared under ambient conditions using a microwave assisted synthesis, show indoor light photocatalytic activity for the degradation of *Staphylococcus aureus* and *Escherichia coli*. The zinc sulphide (ZnS) nanomaterials, prepared by a microwave assisted synthesis, are shown to be cubic blende structure with an average crystallite size of 4–6 nm. The anti-bacterial activity of these nanomaterials is investigated under irradiation from a 60 W light bulb and photocatalytic activity is revealed to be due to the defects present in the crystal structure. The ZnS shows anti-bacterial action as both a bacteriostatic and bacteriocidal (88% reduction in the amount of bacteria in 5 h) material and the methods of bacterial degradation on the ZnS is discussed. The anti-bacterial actions of these materials were also compared with commercial ZnS and Evonik-Degussa P-25. A detailed mechanism for the light absorption in the visible light region of the microwave prepared ZnS is proposed based on the luminescence spectroscopy.



## 1. Introduction

Semiconductor photocatalysis has been shown to be an effective method of removing bacterial contamination, including *Escherichia coli* and *Staphylococcus aureus*, in hospitals and in the food industry. [1–9] Zinc sulphide is an important II–VI semiconductor with a band gap of 3.8 eV. [10,11] Zinc sulphide has a great potential as an anti-bacterial semiconductor due to its relatively deeper conduction and valence bands compared to other semiconductors including $TiO_2$ and ZnO [3,12]. The comparatively negative positions of the conduction and valence bands of ZnS *versus* the NHE are located at −2.3 and +1.4 eV respectively. ZnS was one of the first semiconductors discovered and is of major interest in biomedical, electronic and photovoltaic devices due to its luminescent and catalytic properties [13,14]. It has been used as an important component in ultraviolet light emitting diodes [15], injection lasers, flat panel displays [16], solar cells [17], and as a photocatalysts in many situations including a visible light activated water-splitting agent [18].

ZnS has been synthesised in a number of ways including by precipitation method [19], by spray pyrolysis [20], by hydrothermal synthesis [21], in solution [22], using ligands [23], with conjugated

* Corresponding author.
*E-mail address:* suresh.pillai@dit.ie (S.C. Pillai).

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polymers [24], using ultrasonic irradiation [25], and employing microwave heating [26]. Microwave heating as a synthetic route is of great interest to materials scientists due to the capability of molecular level heating, which leads to homogenous and quick thermal reactions [12]. Microwave reactions have been used to prepare zinc sulphide but mostly these reactions require the use of pressurised containers made of quartz or Teflon [26–28].

Semiconductor photocatalysts have been established as viable materials for the creation of self-sterilising environments and for the destruction of bacteria. This self-sterilisation is an important part of combating healthcare associated infections, which are a serious problem at every level of healthcare systems [29]. The incidence of healthcare associated infections, HAIs is growing worldwide, especially the number of cases of methicillin-resistant *S. aureus* (MRSA) in Europe [30], North America [31], and Australasia [32,33]. This increase is mainly due to the epidemics of highly transmissible clones [34]. Studies have shown that prevention techniques such as cleaning and the use of barriers, gloves and gowns, can be effective but that behavioural practices limit the effectiveness of these methods [29]. This creates the need for a material on location which will create a sterile environment, and semiconductor photocatalysts are an ideal solution.

When the semiconductor is irradiated by a photon of light, which matches or exceeds the bandgap energy, $E_g$, an electron is promoted from the valence band to the conduction band leaving a positive hole. The photo-generated hole in the valence band and the photo-generated electron in the conduction band can serve respectively as oxidation and reduction species [35]. Titanium dioxide, $TiO_2$, is the most widely studied semiconductor photocatalyst has been shown to kill bacteria on its surface [36,37], has been incorporated into tiles to create self-cleaning surfaces [38] and into medical devices such as catheters [39]. The major advantage of using photocatalytic self-cleaning surfaces as a treatment for HAIs is that they operate in a passive manner, that is, without the need for chemicals or electric power, with only light, oxygen and water from the atmosphere required. The semiconductor surface is non-toxic and does not produce harmful by-products unlike some of the chemical reagents and cleaning products used as anti-bacterial agents [40].

In the current investigation, a novel ambient pressure microwave assisted method of producing zinc sulphide nanocrystals, which is a quick and straightforward water based reaction, where the product is collected and used as it is, is presented. The ZnS were characterised in detail and the anti-bacterial photocatalytic activities of these materials were tested against *E. coli*, and *S. aureus* and *P. aeruginosa.*

## 2. Experimental

### 2.1. Preparation of photocatalysts

In a typical synthesis, 200 mL of a 0.2 M zinc acetate dihydrate aqueous solution was added to 200 mL of a 0.2 M thiourea aqueous solution at room temperature. The beaker containing these solutions was placed in a MARS 5 microwave system and was irradiated at 600 W for 30 min under ambient pressure followed by a 5 min cool down period. After this time had elapsed the water had completely evaporated and a dry yellow powder was collected and characterised without further treatment. Samples prepared in this way are referred to by their irradiation power, *e.g.* ZnS450W – ZnS prepared at 450 W irradiation power.

### 2.2. Characterisation

The obtained ZnS was investigated using a combination of characteristic techniques including X-ray diffraction using a Siemens D 500 X-ray diffractometer with the diffraction angles scanning from $2\theta = 20–80°$, using a Cu Kα radiation source. The diffuse absorbance spectra of the samples were measured by a UV–vis-NIR PerkinElmer Lambda 900 spectrometer between 800 and 200 nm with samples prepared in a KBr disc with a sample to KBr ratio of 1:10. Luminescence measurements were taken, with samples suspended in ethanol, by a PerkinElmer LS 55 luminescence spectrometer. X-ray photoelectron spectrometer measurements were taken with a Thermo VG Scientific (East Grinstead, UK) Sigma Probe spectrometer using a monochromated A1 Kα X-ray source ($h\nu = 1486.6$ eV), which was used at 140 W and the area of analysis was approximately 500 μm in diameter. Infrared spectra were obtained using a Spectrum GX Infrared Spectrometer. SEM images were obtained using a Hitachi SU-70 FE-SEM. Surface area measurements were measured using a Quantachrome Nova 2200 with the samples degassed at 300 °C for 2 h.

### 2.3. Anti-bacterial testing – agar test method

Agar plates were prepared using Mueller Hinton agar plate mix. The loading of the powder samples in the agar was 1% (w/w). The agar was autoclaved at 120 °C prior to testing. After autoclaving the agar was heated to 100 °C and the photocatalyst was added to the molten agar with stirring and dispersed with sonication before being poured onto a plate. Each of the agar plates were inoculated with 50 μL *E. coli*, 50 μL of *S. aureus* and 50 μL of *P. aerginosa* suspension. Each of these suspensions was diluted to approximately 1000 colony forming units/mL (CFU/mL). Each plate was prepared in triplicate with one sample irradiated with a 60 W light bulb (*i.e.* 3 plates irradiated) and one sample kept in the dark (*i.e.* three plates not irradiated). After irradiating the samples for 3 h with a 60 W light bulb, both sets of plates were placed in an incubator at 37 °C for 24 h to allow any growth of the bacteria to take place.

### 2.4. Anti-bacterial testing – suspension test method

The suspension test measures the bactericidal effect of the photocatalyst and makes it possible to determine a time frame for the reduction in the bacterial colonies. The reference sample for these tests contained no catalyst or powder. The reference sample consisted of 4.5 mL multi-recovery diluents, MRD, and is inoculated with 500 μL of $10^6$ CFU/mL of bacteria. This gives a theoretical concentration of $10^5$ CFU/mL at time zero. The test sample contains 10 mg of photocatalyst suspended in 4.5 mL of MRD, which was then inoculated with 500 μL of $10^6$ CFU/mL of bacteria. The reference and sample both were exposed to light from a 60 W light bulb for a total of 5 h. Samples from both were taken at 0 min, 30 min, 1 h, 3 h and 5 h.

## 3. Results and discussion

The ZnS materials were prepared with microwave irradiation powers of 300, 450 and 600 W. In each preparation, a solution of zinc precursor and a solution of sulphur precursor were mixed in an open beaker. The solutions were irradiated in the microwave and at the end of the irradiation period of dry yellow powder was collected and used for all tests without further washing or synthesis steps. The simplicity of this reaction allows for the production of nanomaterials in a cost effective and easily scalable reaction scheme.

The solutions undergo dielectric heating upon irradiation in the microwave and the following mechanism is believed to lead to the formation of the zinc sulphide.

$$H_2NCSNH_2 + 2H_2O \rightarrow CO_2 + H_2S + 2NH_3 \quad (1)$$