Journal of Luminescence 246 (2022) 118863

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

In vitro photoinactivation of *S. aureus* and photocatalytic degradation of tetracycline by novel phthalocyanine-graphene quantum dots nano-assemblies

Yolande Ikala Openda, Sithi Mgidlana, Tebello Nyokong *

Institute for Nanotechnology Innovation, Rhodes University, Makhanda, 6140, South Africa

ARTICLE INFO

Keywords:
Zinc phthalocyanines
Singlet oxygen
Graphene quantum dots
Tetracycline photodynamic antimicrobial therapy
Photocatalytic degradation

ABSTRACT

A novel asymmetrical zinc (II) phthalocyanine (Pc) **4** bearing three dimethoxy groups and one carboxyl group was linked to glutathione capped graphene quantum dots (GQDs) by the reaction of carboxylic acid substituent on Pc **4** with the amino group on the GQDs. On the other side, the symmetrical Pc analog **3** was linked to the same nanoparticles through π-π interactions. The as-formed nano-photosensitizers were fully characterized by spectroscopic methods and their photophysicochemical properties were investigated as well. Photodynamic antimicrobial chemotherapy was performed on the planktonic cells of *S. aureus* strain. And the results show that these nano assemblies were able to completely inhibit the metabolic activity of the resistant bacteria strain *S. aureus* with a 10.26 log reduction in the viable count. Again, asymmetrical Pc showed higher photocatalytic activity compared to the symmetrical complex with higher k_{obs} and fast initial rates for the former. The photocatalysis obeyed the Langmuir-Hinshelwood kinetic model. The target conjugates showed all the advantages of two different groups existing on a single entity.

1. Introduction

The extensive use of antibiotics in humans and animals has led to important environmental pollution. Antibiotics have been detected in soil, waste, and even drinking water [1,2]. Tetracycline (TC), a subject of this work, is an example of an antibiotic that is a water pollutant. Bacteria, commonly the Gram (+) strain *S. aureus*, constitute on their own another form of biological water contaminant. Generally, the greatest microbial risks come from the ingestion of water that is contaminated with microorganisms [3].

Recently, various methods such as membrane separation, physical absorption, chemical oxidation, biodegradation have been developed to eliminate pollution by TC in water [2,4,5]. Among the above methods, photocatalytic degradation shows the most potential because of its low mammalian toxicity and high efficiency [2,6–8]. Photocatalysis is an example of an advanced oxidation processes (AOP) [9], which has been presented as an alternative method for ensuring degradation and mineralization of TC. Whereas photodynamic antimicrobial chemotherapy (PACT) has been reported as the efficient alternative to eradicate the bacteria *via* the photosensitization process [10,11]. Hence photocatalysis and PACT are used in the present work for water purification purposes.

In photocatalysis and PACT, a non-toxic photocatalyst or photosensitizer (PS), gets excited with light of an appropriate wavelength and populates the triplet state where it interacts with molecular oxygen [12] to produce highly cytotoxic reactive oxygen species (ROS). Among these ROS, singlet oxygen ($^1O_2$) is known to damage bacteria cells. Generally, the $^1O_2$ is generated by energy transfer in the triplet state between the photocatalyst or PS and the molecular oxygen [13].

Metallophthalocyanines (MPcs) are effective photosensitizers and photocatalysts [14,15]. MPcs have unique properties thanks to their intense optical and electronic properties, high thermal and chemical stability, catalytic, photophysical, and photochemical characteristics [14,16]. The MPcs employed in this work contain Zn as heavy central metal. The transition of a photosensitizer from the singlet excited state to the triplet excited state happens with a spin-orbit coupling which usually occurs due heavy atom effect caused by the presence of various metal ions, halogen, and even oxygen atoms (the latter are present in the molecules employed in this work) in the macrocycle structure. This results in improved triplet quantum yields, and consequently, high singlet oxygen [17].

Recently, the trend in research is to elaborate conjugated systems

* Corresponding author.
E-mail address: t.nyokong@ru.ac.za (T. Nyokong).

https://doi.org/10.1016/j.jlumin.2022.118863
Received 28 January 2022; Received in revised form 24 March 2022; Accepted 25 March 2022
Available online 26 March 2022