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The photocatalytic properties of zinc phthalocyanines supported on hematite nanofibers for use against methyl orange and *Staphylococcus aureus*

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ABSTRACT

Heterogeneous photocatalysis is a promising approach for environmental remediation from contaminants including microorganisms and organic pollutants. In this work, hematite nanofibers are fabricated and modified with a novel monosubstituted Pc (**4**) as well as an asymmetrical tetrasubstituted Pc (**5**) with the aim of creating hybrid photocataysts. The photocatalytic activities of the unmodified and phthalocyanine modified hematite nanofibers were compared based on their efficacies in the photoinactivation of *S. aureus* and photooxidation of methyl orange. For both applications, the hybrid nanofibers were found to be more efficient photocatalysts than the unmodified hematite nanofibers. Comparison of the modified nanofibers (**4**-Fe_2O_3 and **5**-Fe_2O_3) showed that they have comparable antibacterial activity while the **5**-Fe_2O_3 nanofibers are the best for the photooxidation of methyl orange. The singlet oxygen generation efficiency, high activity, versatility, regenerability and thus reusability of the fabricated hybrid nanofibers makes them ideal candidates for real life water treatment studies.

1. Introduction

Phthalocyanines (Pcs) are macrocyclic dyes encompassing four iminoisoindoline rings with a conjugated 18 π electron system [1]. Their attractive properties including chemical and thermal stabilities as well as the ability to generate singlet oxygen diversify their applications [2,3]. These applications include their use as pigments, nonlinear optical materials, liquid crystals, photovoltaic cells, and photocatalysts amongst others [4–8].

Heterogeneous photocatalysis is a promising approach for environmental decontamination and remediation. Commonly used heterogeneous catalysts for water treatment include zeolites, clays, polymer membranes and hematite (α-Fe_2O_3) [9–12]. As a semiconductor, α-Fe_2O_3 is also the most thermodynamically stable form of iron oxide [13]. It is particularly attractive due to its absorption in a wide wavelength range and it is earth abundant and hence inexpensive [14]. Various α-Fe_2O_3 nanostructures have been fabricated [15–17] but they are limited by concerns over their inadvertent release into the treated water [13].

In this work the photocatalytic properties of the novel zinc(II) 2(3)-mono-(5-oxy) isophthalic acid phthalocyanine (**4**, Scheme 1) when supported on α-Fe_2O_3 nanofibers are reported. For comparison, the previously reported 2-[5-(phenoxy)-isophthalic acid] 9(10), 16(17), 23(24)-tris (*tert*-butyl) phthalocyaninato zinc (II) [18] (**5**, Scheme 1) is also evaluated for the same applications. The α-Fe_2O_3 nanofibers are formed by electrospinning and calcination followed by modification with complexes **4** and **5** by immersion.

We have reported on enhancement of the photocatalytic efficiencies of semiconductor TiO_2 and ZnO nanofibers upon modification with complex **5** [19]. This work therefore continues on that study and demonstrates the effect of modifying α-Fe_2O_3 nanofibers with complex **5** (comparing it to complex **4**) instead. The asymmetry of complexes **4** and **5** is attractive as asymmetry in porphyrin type complexes has been reported to improve their singlet oxygen quantum values [20]. Unlike the asymmetrical tetrasubstituted complex **5** however, complex **4** is monosubstituted. Monosubstituted Pcs have been reported to have higher singlet oxygen generation efficiencies than their symmetrical tetrasubstituted counterparts [21]. This work therefore compares a monosubstituted Pc to an asymmetrical tetrasubstituted Pc when supported on nanofibers for the first time. The α-Fe_2O_3 nanofibers are studied as they are easier to regenerate due to their magnetic response unlike the TiO_2 and ZnO semiconductor nanofibers we reported before [19].

With the aim of creating versatile, heterogeneous and visible light active photocatalysts, the nanofibers reported herein are therefore

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