**Optimal Loading of Porphyrin in Porphyrin@Bi12O17Cl2 heterojunction: Application in Photocatalysis**

Osemeikhian Ogbeifun a\*, Shepherd M. Tichapondwaa, Evans M. N. Chirwaa

*aWater Utilization and Environmental Engineering Division, Department of Chemical Engineering, University of Pretoria, Pretoria, 0002, South Africa*

*\*osemeikhianosi@yahoo.com*

Abstract

The recombination of photogenerated electrons (e-) and holes (h+) and under-utilisation of the visible light spectrum (>420 nm) are significant challenges in photocatalysis involving Bi12O17Cl2. In this study, the photocatalytic efficiency of Bi12O17Cl2 was significantly enhanced in the fabrication of novel porphyrin@Bi12O17Cl2 heterostructure photocatalyst. Aggregated porphyrins have emerged as photosensitisers in light-dependent applications like photocatalysis. The excellence of porphyrin is fully harnessed when combined with inorganic photocatalysts such as Bi12O17Cl2 to form organic-inorganic junctions, thereby enhancing the visible light absorption, charge separation and transport in the material. Various amounts of aggregated rod-shaped 5,10,15, 20-Tetrakis (4-carboxyphenyl) porphyrin (0.02% wt., 0.1% wt., 0.4% wt., 1% wt. and 10% wt.) were coupled to Bi12O17Cl2 and the optimum loading of porphyrin in terms of photocatalytic efficiency was determined for Porphyrin@Bi12O17Cl2 heterostructure. The photocatalytic degradation efficiency of Porphyrin@Bi12O17Cl2 was tested on Rhodamine B dye as a representative pollutant. The highest and lowest performances were reported for 1% wt. and 10% wt. of porphyrin loading in Bi12O17Cl2, respectively, representing 3.1 and 0.5 times increases compared to pure Bi12O17Cl2. The findings offer a new option for improving the photocatalytic performance of Bi12O17Cl2 through photosensitisation and heterojunction strategies for use in numerous photocatalysis applications.

**Keywords**: Bi12O17Cl2, aggregated porphyrin, photosensitisation, heterostructure, charge recombination, photogenerated

* 1. Introduction

Bi12O17Cl2 is an attractive semiconductor photocatalyst with comparatively low bandgap energy, visible light or infrared activity (Chen *et al.*, 2013). With these properties, Bi12O17Cl2 is a choice material for mitigating environmental contamination via photocatalytic degradation technology. However, a drawback to applying Bi12O17Cl2 in photocatalytic technology is the quick recombination of photogenerated charge carriers (e- and h+) as fast as they are produced. (Passi and Pal, 2022). This phenomenon limits the capacity of the material to degrade target contaminants oxidatively (Zheng *et al.*, 2018). To enhance the photocatalytic degradation ability of Bi12O17Cl2, various strategies have been employed, including heterojunction fabrication (Bi *et al.*, 2016), ion doping (Yang *et al.*, 2022), plasmon resonance effect (Zhang *et al.*, 2017), solid solution (Zhang *et al.*, 2020) and photosensitization effect (Ye *et al.*, 2014).

The photosensitization strategy, which is the focus of this study, involves applying a photosensitizer such a porphyrin, to photocatalysts to increase visible light utilization. Porphyrin is a group of organic molecules made of four pyrrole rings that are linked with methine bridges to form a planer macrocyclic structure known as porphyrin ring (Araki *et al.*, 2013). Porphyrin strongly absorbs visible light, producing a photochemical reaction (Joseph and Haridas, 2020), that generates triplet (activated state) that can oxidize contaminants in the medium (Neves *et al.*, 2019). When porphyrin is irradiated, excited electrons move from highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) (Moshari *et al.*, 2016). The LUMO electrons are transferred and injected into the conduction band (CB) of the host material, bringing about the separation of holes and electrons, boosting photocatalytic performance (Zhang *et al.*, 2017).

In this study, self-assembled rod-shaped 5,10,15, 20-Tetrakis (4-carboxyphenyl) porphyrin was prepared and anchored to Bi12O17Cl2. The photocatalytic activity of the surface modified- Bi12O17Cl2 was evaluated by measuring the degradation of Rhodamine B under visible light. The optimum composition of porphyrin in the composite and their photocatalytic efficiency was determined.

* 1. Method
     1. Synthesis of Bi12O17Cl2

Bi12O17Cl2 was synthesized by dissolving 4.84 g (0.01 mol) of Bi (NO3)3·5H2O in 25 mL of acetic acid solution (acetic acid: H2O 2:1 v/v) with stirring for complete dissolution. Next, 3.2 g (0.01 mol) of cetyltrimethylammonium chloride (CTAC) was dissolved in 25 mL of deionized water and added to the nitrate solution. The resulting solution was stirred for 30 min. The pH was then adjusted to 13 using a 10M NaOH solution. After an additional 30 min of stirring, the reaction mixture was subjected to microwave treatment (1000 W; 2450 Hz) for 10 min at atmospheric pressure. The resulting product was collected by centrifugation, washed several times with ethanol: water, and dried in an oven at 60 oC for 18 h.

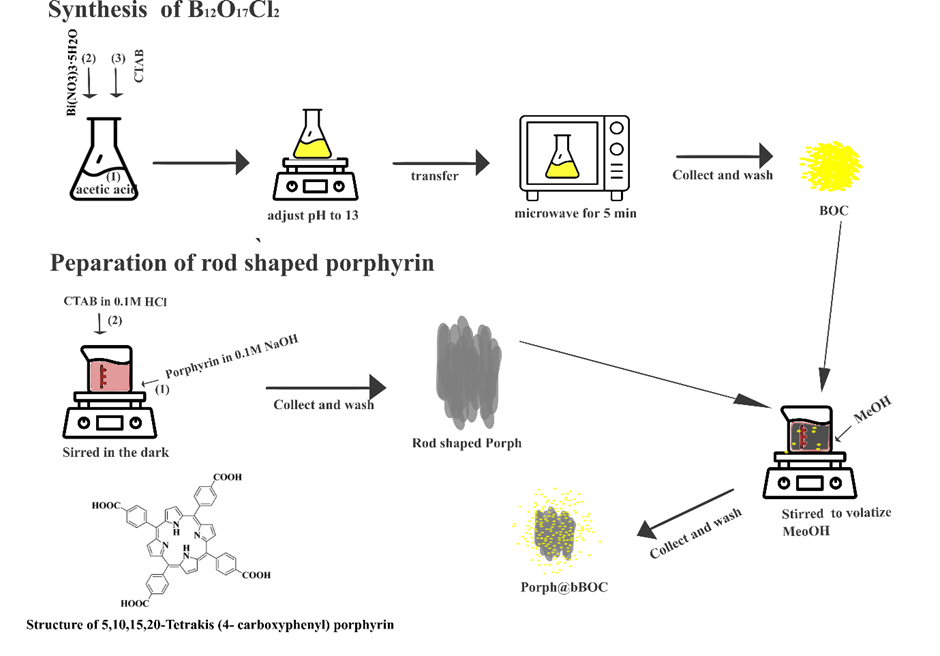
* + 1. Synthesis of aggregated porphyrin

In a typical synthesis, 0.04 g of porphyrin powder was dissolved in 0.5 mL of 0.2 M NaOH (referred to as the host solution). The “guest’ solution was prepared by dissolving 0.036 g of Cetyltrimethylammonium bromide (CTAB) in 10 mL of 0.01 M HCl. The guest solution was quickly injected into the host solution with vigorous stirring for 30 min in the dark. The resulting precipitate referred to as Porph was collected by centrifugation at 9,000 rpm for 10 min and washed with deionized water several times to remove the surfactant.

* + 1. Synthesis of Poprhyrin@Bi12O17Cl2

The preparation of Bi12O17Cl2 containing 0.02% wt., 0.1% wt., 0.4% wt., 1% wt., and 10 % wt. porphyrin was carried out as follows: 0.2 g of as-synthesized BOC was added to 20 mL of methanol containing a certain amount of Porph (0.04 mg, 0.2 mg, 0.8 mg, 2 mg, and 20 mg). The mixture was sonicated for 5 min and then stirred at 60 oC in the dark to completely volatilize the methanol. The resulting materials were collected and washed with water to remove unattached porphyrin and were labelled as *x*%Porph@BOC (0.02%Porph@BOC, 0.1%Porph@BOC, 0.4%Porph@BOC, 1%Porph@ BOC and 10%Porph@BOC), where *x* represents the weight percentage of Porph in BOC.

Scheme 1. shows the synthesis of Bi12O17Cl2, aggregated porphyrin and Poprhyrin@Bi12O17Cl2 heterostructure.



Scheme 1. Synthesis of aggregated porphyrin, Bi12O17Cl2 and Porph@BOC. and structure of 5,10,15,20-Tetrakis (4- carboxyphenyl) porphyrin

* 1. Results and discussion

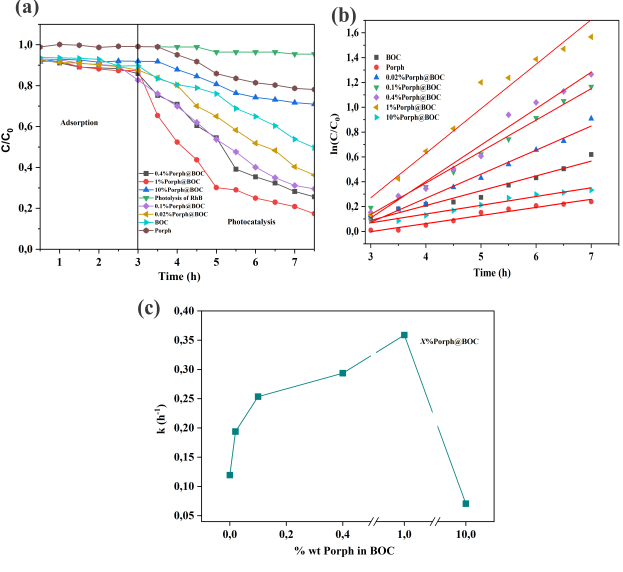
Degradation studies were conducted at room temperature (25oC) on Rhodamine B as a representative contaminant using the synthesised materials described from the preceding section. In doing that, 60 mL of 20 mg L-1 of Rhodamine B dye was placed in a 100 mL-beaker reactor, and 0.025g of photocatalyst material was added to the solution. The mixture was stirred in the dark for 3 h to achieve adsorption-desorption equilibrium. The solution was then irradiated for 4 h 30 min with visible light from six 16W fluorescent tubes (OSRAM, Germany) having a total intensity of 6300 lux. To monitor the degradation of Rhodamine B, 2 ml of aliquots were withdrawn at 0.5 h intervals. The photocatalyst particles were separated using a centrifuge and the absorbance of the remaining dyes solution were measured with a spectrophotometer at 553 nm absorbance. The concentration of Rhodamine B was calculated from the equation of the standard curve. Photolysis experiments were also performed in the absence of photocatalyst to differentiate photolysis from photocatalysis reaction. The percentage degradation was calculated from the following equation:

x 100%

where *C0* and *Ct* are the initial concentration and concentration at time of Rhodamine B.

From Fig. 2(a), after 120 min of irradiation of light, the degradation efficiency of Rhodamine B on BOC, Porph, 0.02%Porph@BOC, 0.1%Porph@BOC, 0.4%Porph@BOC, 1%Porph@BOC and 10%Porph@BOC were reported to be 31.1%, 16.5%, 41.8%, 52.4%, 60.9%, 71% and 23.6%, respectively. Among the modified materials, 1%Porph@BOC performed the best with an efficiency of 71% while, 10%Porph@BOC was the least performing material with an efficiency of 23.6% efficiency, which is less than that of BOC with an efficiency of 31.1%. At the end of the photocatalytic degradation experiment (4.5 h), 82.6% degradation efficiency was achieved on 1%Porph@BOC. It was also demonstrated that photolysis did not contribute significantly to the removal of Rhodamine B and only achieved a removal efficiency of 3.5% by light irradiation. The kinetics of Rhodamine B degradation was determined from the data obtained in the degradation study to be a pseudo-first-order kinetic equation. First-order kinetic –in C/Co = ktwhere C0 and C are the initial and final concentrations of Rhodamine B, *k*, the rate constant, and *t*, the time, was used to fit the experimental data. The linear curve in Fig. 2(b) confirmed the pseudo-first kinetic. The R2 values for 0.02%Porph@BOC, 0.1%Porph@BOC, 0.4%Porph@BOC, 1%Porph-@BOC, 10%Porph@BOC and BOC were found to be 0.9566, 0.97107, 0.97808, 0.99063, 0.97548, 0.94701, 0.97018, respectively. Overall, the degradation of Rhodamine B on 1%Porph@BOC was 3.1 times faster than on pristine BOC.

Fig. 2(c) shows a gradual increase in photocatalytic degradation of Rhodamine B on the materials in the following order: 0.02%Porph@BOC < 0.1%Porph@BOC < 0.4%Porph@BOC < 1%Porph@BOC. This shows that 1% wt. porphyrin-loaded material is the best-performing material. As observed from Fig. 2(c), there was a sharp decrease in the photocatalytic degradation at 10%Porph@BOC. The decrease in the photocatalytic activity of 10%Porph@BOC was caused by blockage of active sites on Bi12O17Cl2 surface and low light penetration in the reaction solution at high porphyrin dose in 10%Porph@BOC.



**Fig. 2.** **(a)** Photocatalytic degradation of Rhodamine B on *x*%Porph@BOC. **(b)** Rate constants of Photocatalytic degradation of Rhodamine B on *x*%Porph@BOC materials. **(c)** Percentage weight of aggregate porphyrin, x, in BOC versus kinetic rate constant, k, of degradation of Rhodamine B.

* 1. Conclusions

The photocatalytic efficiency of porphyrin@ Bi12O17Cl2 heterostructure was tested at various porphyrin loading of 0.02%, 0.1%, 0.4%, 1%, and 10% w/w. The optimum porphyrin dose in the composite to achieve the highest degradation efficiency of Rhodamine B was determined as 1% w/w, which is 3.1 times higher than that of pure Bi12O17Cl2. The enhanced performance was attributed to the synergy between the anchored porphyrin and Bi12O17Cl2. However, at the highest dose of 10%w/w porphyrins, a deterioration of the photocatalytic activity was observed due to blockage of active sites on Bi12O17Cl2 surface and low light penetration on the reaction solution. Two phenomena were found to be crucial to the photocatalytic activity of the composite: Bi12O17Cl2 surface area and the photosensitisation effect of porphyrin. Therefore, it is essential to strike a balance between these effects to harness the synergy between porphyrin and Bi12O17Cl2 in porphyrin@ Bi12O17Cl2 composite to achieve optimum performance. The optimum activity achieved with 1% wt. porphyrin in porphyrin@ Bi12O17Cl2 provided for adequate exposure of active sites on the surface of Bi12O17Cl2 for the photodegradation of Rhodamine B, while still benefiting from porphyrin's photosensitisation effect.

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