

Sol-gel Preparations of ZnO/SnO₂ Composite Photocatalysts Applied for the Degradation of PAH's under Visible Light

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Abstract— Wastewater treatment challenges faced by conventional methods have necessitated the need for alternative/complementary methods that are environmentally benign and efficient especially toward recalcitrant organic pollutants. In this regard, ZnO/SnO₂ composite photocatalysts were synthesized using sol-gel method and employed in the photocatalytic degradation of Phenanthrene, benzo(a)pyrene and naphthalene, typical PAH's in water solution. The photocatalyst material was characterized with scanning electron microscopy (SEM) and Fourier-transform infrared spectroscopy (FTIR) to confirm the properties of the nanocomposite. The photocatalytic degradation activities of these nanocomposites towards phenanthrene, naphthalene and Benzo(a)pyrene were then investigated by measuring the effects irradiation time. In addition, the first-order kinetic model was used to determine the rate constant for the degradation reaction. The photocatalytic degradation data exhibited a trend fitting the pseudo first-order kinetics as defined by the Langmuir-Hinshelwood model, which allowed prediction of the faster degradation rate by the ZnO/SnO₂ nanohybrid (NH).

Keywords- : Photocatalyst, Polycyclic aromatic hydrocarbons, composite

I. INTRODUCTION

Prior to the widespread use of natural gas, manufactured gas plants (MGPs) supplies gaseous fuel derived from coal, coke

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and/or oil [1;2]. A major by-product of manufactured gas processes is coal tar, which today is often associated with subsurface contamination at former MGP sites [2]. Coal tars are denser than water nanoqueous phase liquids, primarily composed of polycyclic aromatic hydrocarbons [3]. Naphthalene is often the most abundant PAH compound in such coal tars. One of the main disease caused by PAHs viz naphthalene is hemolytic anemia in children [4, 5; 6]. Benzo[a]pyrene which has been found to be persistent organic toxin, is of environmental worry due to its known cancer-causing nature and bioaccumulation potential [7]. Pure, safe and satisfactory freshwater is essential to every single living organism and normal functioning of ecosystems and communities [8-19]. Therefore, special methods which are cost effective and environmental friendly are required to degrade these organic pollutants in water. Numerous efforts have been focused on developing visible-light photocatalysts such as oxides (Cu₂O) [20], sulfides (SnS₂, Cds) [21], nitrides (g-C₃N₄) [10], composite metal oxides (Gd₂O₂CO₃.ZnO. CuO) [22] and Ag-based compounds (ZnO/Ag) [23]. Among them, Semiconductor photocatalysts have drawn much consideration due to their optical properties, Cheapness, long-term steadiness and resistance to photo-corrosion. Tin oxide has gotten a lot of attention as a photo anode in view of its great energy level position, high photoactivity, chemical stability and inexpensiveness [24]. The majority of the properties are beneficial for catalysis and detecting. The principal issue is its moderately extensive bandgap, ~3.5ev, which restricts its photo response to noticeable light, the second is quick recombination of electron-hole pairs in SnO₂ and the third is the challenge related to the reuse of powder photocatalyst [25]. To beat these constraints, different strategies have been utilized, such as doping transition metal ions, including Au, Ag, Fe and Mg or doping nonmetals such as S and N [26]. These days, doping of two kinds of molecules into SnO₂ or TiO₂ has pulled in significant interest, since it could result in a higher photocatalytic activity and enhanced characteristics compared with single-element doping into semiconductor oxides [27]. Among these materials, the ZnO-SnO₂ heterostructural nanomaterials attract much interest in particular due to the low cost of SnO₂ species and the compatibility of some specific crystallographic planes of SnO₂ and ZnO nanocrystals. When the ZnO-SnO₂ heterojunction is radiated by UV light with the photon energy higher or equal to

the band gaps of ZnO and SnO₂, the photogenerated electrons can move to the C_B of SnO₂ and the photogenerated holes to the V_B of ZnO [28]. As a result, the formation of the ZnO-SnO₂ heterojunction could hinder the charge recombination and improve the photocatalytic efficiency [29]. The present study features a facile sol-gel synthesis route for the preparation of ZnO/SnO₂ photocatalysts. In this work, we have chosen naphthalene, phenanthrene and Benzo(a)pyrene as a test probes for remedial experiment. In addition, the functional behavior of the acquired hetero-catalyst in the photocatalytic degradation of naphthalene, phenanthrene and Benzo(a)pyrene is presented in detail. We gauged the photocatalytic properties of ZnO/SnO₂ heterocatalyst and compared it with pure ZnO catalyst. We believe our work can be a premise for further investigations and applications.

II. MATERIALS AND METHODS

A. Preparations of photocatalysts

Zinc acetate dihydrate (Sigma-Aldrich) and tin chloride pentahydrate (Sigma-Aldrich) were used as starting materials. Methanol (Sigma-Aldrich) and 28% ammonium hydroxide solution (Fluka) were used as solvent and additive, respectively. All the chemical products were used as received without any further purification. The synthesis of the ZnO-SnO₂ mixed photocatalysts was carried out by slowly adding 0.1 M methanol solution of Zn(CH₃COO)₂·2H₂O, previously prepared at 70 °C under vigorous stirring, to a 0.1 M methanol solution of SnCl₄·5H₂O prepared in the same conditions. Typically, 8.12g of Zn(CH₃COO)₂·2H₂O were dissolved in 370 mL of methanol and the amount of SnCl₄·5H₂O solution was opportunely determined in order to obtain powders ZnO/SnO₂. The obtained solutions were continuously stirred for 2 h, keeping the temperature at 70 °C. Then, the NH₄OH solution was added dropwise until pH reached the value of 8. The solutions became gels which were dried for 20 h at 110 °C to produce xerogels. Finally, the photocatalysts were obtained by calcining the xerogels for 2 h at 500°C. The pure ZnO was synthesized in the same way by using only the corresponding precursors.

B. Characterization of the composites

Various characterisation methods were conducted to determine if successful synthesis was achieved, and to determine the purity of the catalysts. The morphology of the catalysts was investigated and evaluated by utilising Scanning Electron Microscopy (SEM). Fourier Transform Infrared Spectroscopy, also known as FTIR Analysis or FTIR Spectroscopy, was used to determine the adsorption affinity and potential of each of the photocatalysts. A Perkin-Elmer Spectrum 100 spectrometer (USA) was used for the FTIR analysis utilising the KBr pellet method in the spectral range 4000–400 cm⁻¹ with a resolution of 4 cm⁻¹.

C. Photodegradation experiment

The photocatalytic degradation of PAH's was investigated in a photocatalytic chamber using the prepared photocatalysts (vz, ZnO and ZnO/SnO₂). A UV filter was utilized to cut off

wavelengths <400 nm. All experiments were performed by suspending the photocatalysts into the chamber containing PAH's solution (100 ppm), and the reactions were carried out at 25 °C. After the desired time interval (30 min), the concentrations of residual phenanthrene, Naphthalene and Benzopyrene in each solution were measured by recording the absorbance intensity of the solution at a maximum absorbance wavelength of 271 nm, 288 nm and 400 nm, respectively.

III. RESULTS AND DISCUSSION

A. Structural and morphological characterization

Following preparation of the different photocatalysts, the functional groups present in the prepared samples were then examined by FTIR and the results are presented in Fig. 1. More specifically, in the spectrum of ZnO, the peak observed at the 2163 cm⁻¹ wavelength could be due to the C=C vibration, resulting in a weak bond for the ranges between 2260 cm⁻¹ and 2100 cm⁻¹. Peaks in the range between 665 and 950 cm⁻¹ can be allocated to the N-H wagging, described as a strong broad band between these two wavelengths, which could be the result of the addition of NH₄OH during the synthesis process. The peaks at 1407 and 1556 cm⁻¹ are the results of C-C stretching (in-ring) as well as a N-O asymmetric stretch respectively.

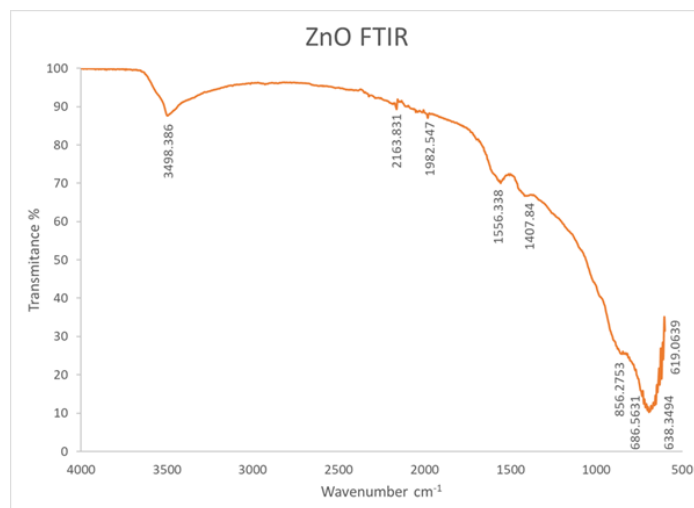
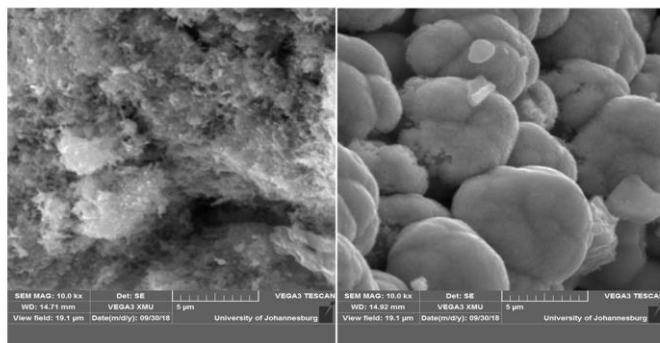


Fig 1. FTIR spectra of the ZnO photocatalyst.

In the case of the ZnO/SnO₂ heterocatalyst as shown in Fig 2, The peak seen at the 1733 cm⁻¹ wavelength falls within the C=O stretching vibration, which is described as a strong bond, it can thus be said that the pure oxide has formed and in turn successful synthesis of a heterogenous catalyst was achieved. therefore, the infrared spectra indicate that the absorptions at 3469 cm⁻¹ are evidently related to the presence of hydroxyl groups of water molecules on the outer surface of SnO₂ nanoparticles. In addition, the weak band at 633 cm⁻¹ for ZnO-SnO₂ heterocatalyst is assigned to O-Sn-O.

Fig 2. FTIR spectra of ZnO/SnO₂ photocatalysts.

The morphologies and sizes of ZnO NPs and ZnO/SnO₂ heterocatalyst were investigated by SEM. Typical SEM images of as-prepared ZnO NPs and ZnO/SnO₂ NH are displayed in Fig. 3. ZnO exhibited mixed morphologies of smaller nanoparticles (40-120 nm) and nanorods with ~6.5 μm length and 100-230 nm width (see Fig 3a). ZnO morphology appeared to be fibrous or crystalline due to the presence of acetate groups which are directing the growth of ZnO crystals. For ZnO/SnO₂, it can be clearly seen that the morphology is dominated by oval beads resulting from the gelation of SnO₂ NPs which entrapped ZnO crystals (see Fig 3b).



A)

B)

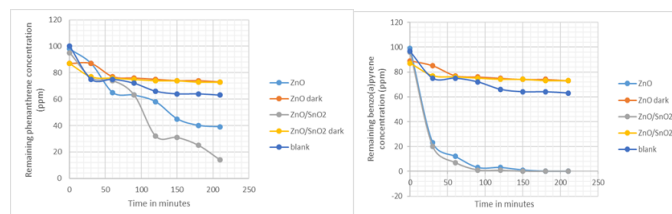
Fig 3. SEM image of ZnO NPs(a), SEM image of ZnO/SnO₂ NH(b)

As shown in Fig. 3b, it can be concluded that the morphology of ZnO/SnO₂ particles was mainly influence by the formation of SnO₂ during the synthesis.

B. Evaluation of the photocatalytic activities of the prepared photocatalysts

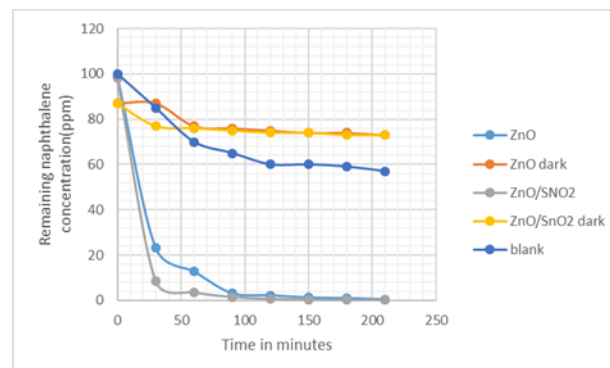
The photocatalytic activity of the synthesized photocatalysts were evaluated through degradation of phenanthrene, benzo(a)pyrene and naphthalene under visible light in a chamber. It is clear from the results that pure oxide showed less degradation as compared to the heterocatalyst (see fig 4). As shown in Fig. 4(a-c), the rate of PAH's degradation

increased with time due to the adsorption of PAH's molecules on the catalyst surface and their subsequent degradation. However, in the absence of visible light or a catalyst, no significant degradation of PAH's was observed, thereby indicating that phenanthrene, benzo(a)pyrene and naphthalene are relatively stable under the above mentioned conditions. These results confirm that both visible light and a photocatalyst are required for the effective degradation of above mentioned PAH's.



A)

B)



C)

Fig 4. Photocatalytic activity of (a) Phenanthrene, (b) Benzo(a)pyrene, and (c) Naphthalene,

It was additionally discovered that the underlying photodegradation rate was high because of the accessibility of various dynamic synergist sites. The exposure of phenanthrene, benzo(a)pyrene and naphthalene to ZnO resulted in the decrease of their concentrations to 39, 0 and 0.37ppm respectively, while ZnO/SnO₂ heterocatalyst degraded phenanthrene, benzo(a)pyrene and naphthalene to concentrations as low as 14, 0 and 0ppm respectively, subsequently showing that the ZnO/SnO₂ is the most effective photocatalyst for PAH's degradation in a solution under the condition utilized in this study. In fact, when the ZnO/SnO₂ NH was utilized, total naphthalene and benzo(a)pyrene removal was achieved within 120 min. Phenanthrene appeared as a recalcitrant PAH to degrade in a solution under the above conditions (see Fig 4(a).

IV. CONCLUSION

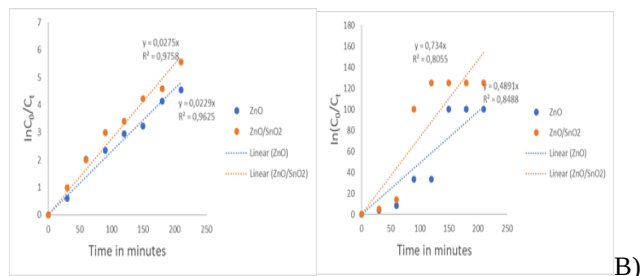
In summary, we have successfully prepared the ZnO/SnO₂ composite photocatalyst via a simple, inexpensive sol-gel method. The photocatalytic experiment indicated that the composite used in this paper was effective for the degradation of PAH's employed herein. Up to 100 ppm concentration of naphthalene and benzo(a)pyrene was removed within 120 min under visible light. From the results above, Photodegradation kinetics followed the Langmuir-Hinshelwood. The composite used in this study is simple and cost effective and might have successful application for treatment of wastewaters.

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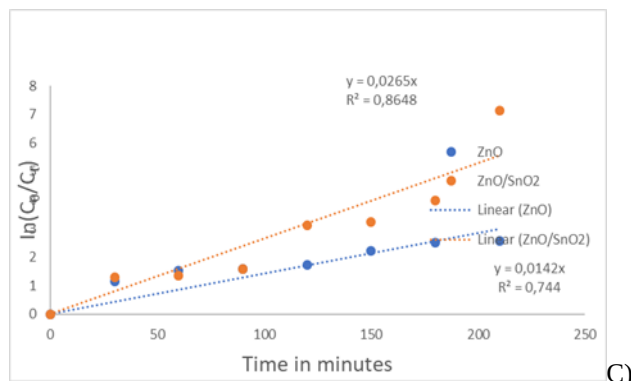
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A)

B)



C)

PAH's	Photocatalysts	R ²	Kmin ⁻¹	(ppm)
Naphthalene	ZnO	0.9625	0.0229	0.37
	ZnO/SnO ₂	0.9758	0.0275	0
Benzo(a)pyrene	ZnO	0.8488	0.489	0
	ZnO/SnO ₂	0.8055	0.734	0
Phenanthrene	ZnO	0.744	0.0142	39
	ZnO/SnO ₂	0.8648	0.0265	14

D)

Fig 5. Degradation kinetics of (a)Naphthalene, (b) Benzo(a)pyrene (c) Phenanthrene (d) table of remaining concentration of PAHs and rate constants.

Photodegradation kinetics followed the Langmuir-Hinshelwood (L-H) model (Fig. 5) [30], The reaction rate is dependent on the concentration of the pollutant according to the equation below:

$$\frac{dc}{dt} = \frac{kK_{PAH'S}C_0}{1 + K_{PAH'S}C_0} \quad (2)$$

$$\ln(C_0/C_t) = kK_{PAH'S}t \quad (3)$$

$$\ln(C_0/C_t) = K_{app}t \quad (4)$$

where K_PAH'S represents the adsorption coefficient of PAH'S on the photocatalyst (L.mg⁻¹), while K_app represents the calculated apparent rate constant (min⁻¹), and t is the reaction time (min). As shown in Fig. 5, plots of ln(C₀/C_t) vs. t gave a linear relationship, thereby indicating that the kinetics data fit well with pseudo first order kinetics. The rate constant of pure ZnO photocatalyst was lower than that of the heterocatalyst when degrading all PAH's. These results indicate that the photocatalytic degradation activity of ZnO NC was extremely low under visible light, potentially due to its high recombination rate of photogenerated charge carriers.

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Mukwevho Nthambeleni started work on the synthesis of nano-structural layered materials and their heterostructures/nanocomposites during his Masters as a chemical engineering student. These nanomaterials will be applied to find sustainable solutions for water purification. He now carries on this work as part of a PhD degree at the North West University under the tutelage of Professors Elvis Fosso-Kankeu, Frans Waanders, Neeraj Kumar and Suprakas Ray. Vhundikha.3@gmail.com