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Silver Doped Zinc Stannate (Ag-ZnSnO₃) for the Photocatalytic Degradation of Caffeine under UV Irradiation

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Abstract: Contaminants of emerging concerns (CECs) spread across a wide range of organic product compounds. As biorecalcitrants, their removal from conventional wastewater treatment systems remains a herculean task. To address this issue, heterogenous solar driven advanced oxidation process based-TiO₂ and other semiconductor materials has been extensively studied for their abatement from wastewater sources. In this study, we have synthesized by hydrothermal assisted co-precipitation Ag doped ZnSnO₃. Structural and morphological characterizations were performed via X-ray diffraction (XRD), Fourier transform infra-red (FTIR), N2 adsorption-desorption at 77 K by Brunauer-Emmet-Teller (BET) and Barrett, Joyner, and Halenda (BJH) methods, Transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), Scanning electron microscopy coupled with Energy dispersive spectroscopy (SEM-EDS), and UV-visible absorption in Diffuse reflectance spectroscopy (UV-vis/DRS) mode. Crystallite size estimate for Ag-ZnSnO3 and undoped form was 19.4 and 29.3 nm, respectively, while respective TEM particle size estimate was 79.0 nm and 98.2 nm. BET surface area and total pore volume by BJH for Ag-ZnSnO₃ were estimated with respective values of $17.2 \text{ m}^2/\text{g}$ and $0.05 \text{ cm}^3/\text{g}$ in comparison to $18.8 \text{ m}^2/\text{g}$ and $0.06 \text{ cm}^3/\text{g}$ for ZnSnO₃. Derived energy band gap (Eg) values were 3.8 eV for Ag-ZnSnO3 and 4.2 eV for ZnSnO3. Photocatalytic performance of Ag-ZnSnO₃ was tested towards caffeine achieving about 68% removal under (natural) unmodified pH = 6.50 and almost 100% removal at initial pH around 7.5 after 4 h irradiation. The effect of initial pH, catalyst dosage, pollutant concentration, charge scavengers, H₂O₂, contaminant inorganic ions (anions) as well as humic acid (HA) on the photocatalyst activity over caffeine degradation were assessed. In accordance with the probation test of the reactive species responsible for photocatalytic degradation process, a reaction mechanism was deduced.

Keywords: photocatalysis; Ag-ZnSnO₃; emerging contaminants; caffeine; water purification

1. Introduction

Global population explosion with increase demand in food production, energy and adequate healthcare system for improved social welfare has left the natural environment unbalanced [1,2]. Unprecedented waste inflow from rural and urban households as well industrial companies has led to the pollution of the aquatic environment [2–5]. Amongst several sources of water environmental pollution, contaminants of emerging concerns (CECs) remain alarming and issue of public concern [3,5–7]. These are chemicals encompassing wide range of organic products from pharmaceuticals and personal healthcare



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). products (PPCPs) to organic solvents, to flame retardants, to synthetic chemicals, to pesticides, etc.; with low detectable concentration levels $(ngL^{-1}-\mu gL^{-1})$: thanks to sophisticated analytical tools [3,5–7]. Caffeine ($C_8H_{10}N_4O_2$) is an alkaloid of the methylxanthine family; a psychoactive substance example of PPCP and very often detected in municipal wastewater treatment plants (MWWTPs) and surface waters [8,9]. Mostly consumed as beverages in coffee, cola, tea, energy drinks, and drugs; acts as psychomotor stimulant with responses of increase alertness, insomnia, nervousness, dizziness, and headaches under mild dose consumption [10–12]. Caffeine overuse has been reported with side effects of irritability, DNA mutation, anxiety and tremors, and bone mass loss with risk of cardiovascular illnesses [13–15]. Perceived to be harmful in the long run to humans and environment due to their recalcitrant and bioaccumulative nature, research efforts towards removing CECs prior to the end of pipe discharge in conventional wastewater treatment, which they elude by reason of their resistance to such treatment approach, has intensified [16].

For improved efficient, cleaner, and more sustainable integrated wastewater treatment technologies, heterogeneous photocatalysis using solar based advanced oxidation processes (AOPs) have been focused [17-20]. Transition metal oxides and other semiconductors like TiO₂, ZnO, SnO₂, CeO₂, CuWO₄, etc., have been the most common and widely described heterogeneous catalysts for various applications including organic pollutants photocatalytic degradation [4,6,7,21-26]. TiO₂ with outstanding physico-chemical properties of chemical inertness, non-toxicity, cheap, and environmental friendliness has been the most active compound tested for photocatalytic applications [27]. However, high energy band gap (about 3.2 eV), limited activity within the UV spectrum where it cultivates only about 5% of energy, non-visible light range response, and low quantum yield due to fast charge recombination has remains a challenge [28–30]. Modifications ranging from metal cation and non-metallic anion heteroatom doping to transition metal ion addition, to dye sensitization, oxides couplings etc., is aimed at improving its photocatalytic efficiency [4,6,7,31]. Apart from these modification strategies and the consideration of materials with similar physicochemical properties to TiO₂ like ZnO and their based forms for photocatalytic applications, other metal oxide semiconductor (MOS) materials have also been found promising in dealing with environmental pollution problems [32-34]. MOS materials have gained this wide attention due to their low cost, easy method of preparation, high photosensitivity, non-toxicity, tunable morphological properties, safety, and environmental friendliness, etc. [35–37]. Amongst the MOS materials, ternary oxides have had the edge in terms of research investigations over their binary counterparts as they boast of multiple band energies and promising stability in both acidic and basic solutions, thereby allowing for their suitability in many photocatalytic applications [38]. One such example of a ternary oxide seen as a multifunctional material for various other applications in the areas of gas sensing, optoelectronics, Li-ion battery, energy storage, microwave absorbers, etc., is Zinc stannate [38–41]. With other ternary oxides like Bi_2MoO_6 and Bi_2MoO_6 -based composite forms, ZnFe₂O₄, CdWO₄, and BiWO₆; ZnSnO₃ also have been developed, studied, and presented significant photocatalytic efficiency towards organic pollutant removal under visible and or ultraviolet irradiations [42–44]. Just like classical TiO₂, several nanostructured ZnSnO₃ and material-based forms have been synthesized with different modification design strategies for enhanced photocatalytic performance [45]. Liang et al., successfully fabricated a novel chestnut-like Fe₃O₄@C@ZnSnO₃ core-shell hierarchical structured and deployed it as a recyclable photocatalyst for the degradation of 2,5-dichloro phenol [46]. A facile route synthesized $ZnSnO_3$ hollow nanosphere/reduced graphene oxide (RGO) hybrid nanocomposite has been reported showing significant photocatalytic performance for the degradation of metronidazole under visible light irradiation [47]. Lui et al., by solvothermal method synthesized Bi₂MoO₆/ZnSnO₃ as a recyclable heterojunction photocatalyst with enhanced visible light photocatalytic degradation of Methylene Blue [48]. Dien and tepa used as gelling agent in the fabrication of gelled nanostructured ZnSnO₃ has been reported with high photocatalyst activity under UV irradiation for the almost complete decomposition of Acid Brown 14 dye after 2 h of irradiation [49]. Comparative

study for the photocatalytic activity of Zinc stannate nanoparticle and its composite form of ZnO with pH influence over their efficiency rate removal of phenol from water has been reported [50]. Better photocatalytic performance of $ZnSnO_3$ than TiO₂ for Rhodamine B dye degradation has been demonstrated with high degradation rate efficiency [51]. In addition, ZnSnO₃ has been reported 10 times efficient photocatalyst than TiO₂ nanoparticle under identical conditions [52]. Wastewater antibiotics like ciprofloxacin (CIP), sulfamonomethoxine (SMM) along with methylene blue (MB), rhodamine B (Rh B), and methyl orange (MO) dyes have been reported as efficiently degraded under simulated solar light by double-shelled ZnSnO₃ hollow cubes synthesized via different routes of co-precipitation, hydrothermal and template-assisted methods [53]. Li et al., by template-free solvothermal strategy successfully prepared Ag functionalized ZnSnO₃ hollow nanocubes for improved gas sensing capabilities [54]; however, we have, by hydrothermal assisted co-precipitation method, successfully synthesized Ag doped ZnSnO₃ and deployed if for the first time to the best of our knowledge as a photocatalyst for the degradation of caffeine—a contaminant of emerging concern (CEC)—under UV irradiation while evaluating the effects initial pH, catalyst dosage, initial caffeine concentration, H_2O_2 as an external oxidant, contaminants ions (anions), and humic acid on the photocatalyst performance efficiency. Accordingly, for a proposed reaction mechanism, chemical scavengers were finally employed to determine involved reactive species responsible for the photocatalytic degradation of caffeine.

2. Materials and Methods

2.1. Chemicals and Reagents

The following chemicals and reagents were employed for the experimental study- stannic chloride (SnCl₄·5H₂O) (98%), ethanol (C₂H₅OH) (99.9%), sodium citrate (C₆H₅Na₃O₇·2H₂O) (\geq 99%), zinc chloride (ZnCl₂) (\geq 99.99%), sodium hydroxide (NaOH), (\geq 98%), zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O) (\geq 99%), AgNO₃ (\geq 99%), caffeine (1,3,7-Trimethylxanthine; C₈H₁₀N₄O₂) (99%), hydrogen peroxide (H₂O₂) (30% *v*/*v*), sodium carbonate (Na₂CO₃), sodium hydrogen carbonate (NaHCO₃), sodium nitrate (NaNO₃), sodium sulphate (Na₂SO₄), and sodium humic acid salt, all of high purity (\geq 99%), p-benzoquinone (BQ) (\geq 98%), isopropyl alcohol (IPA) (\geq 99%), ethylene diamine tetraacetic acid di sodium salt (EDTA) (\geq 99%), and hydrochloric acid (HCl) (37% wt./v). All chemicals and reagents were purchased from Sigma-Aldrich (Darmstadt, Germany), of analytical grade and used without further purification. Milli-Q water has been used for all the photocatalytic experimental tests.

2.2. Photocatalyst Sample Preparation

Briefly, 2.0 g stannic chloride (SnCl₄·5H₂O) was dissolved in 50 mL ethanol solution to form solution A. Likewise, 0.75 g sodium citrate (C₆H₅Na₃O₇·2H₂O) was dissolved in 50 mL distilled water with subsequent addition of 0.5 g zinc chloride (ZnCl₂) to obtain solution B. In a slow manner and under gentle magnetic stirring at room temperature, solutions A and B were mixed (pH = 2.5), followed by the addition of a 100 mL 0.4 M NaOH solution. Attaining a final pH = 11.60, mixture solution was kept under stirring for 1 h. Formed white suspension was centrifuged, washed with water and ethanol and dried for 24 h in an oven at 60 °C to obtain zinc hydroxystannate (ZnSn(OH)₆). Procedure as above was repeated to the point of obtaining again a mixed solution of A and B (pH = 2.5). Then, the already obtained and dried zinc hydroxystannate (ZnSn(OH)₆) together with a 100 mL 0.4 M NaOH was added into the solution mixture of A and B under magnetic stirring for 30 min till a final pH = 11.60 was attained; 50 mL 2M NaOH was then added dropwise to the resultant solution as final pH = 12 was attained.

Finally, as formed suspension was again subjected to the drying procedures already outlined above to form the $ZnSn(OH)_6$ powder which was calcined in a tube furnace at 300 °C for 3 h to obtain the zinc stannate ($ZnSnO_3$) powder.

Following the same procedure, 1 mol.% Ag doped $ZnSnO_3$ was synthesized. However, instead of zinc chloride ($ZnCl_2$), zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) was used in the preparation of solution B to avoid precipitation of silver chloride (AgCl). About 5 mL

volume equivalent of 0.0062 g representing 1 mol.% silver nitrate (AgNO₃), in drops was added to make up the final 50 mL volume B solution. Synthesized undoped ZnSnO₃, and 1 mol.% Ag doped form (1 mol.% Ag-ZnSnO₃) were on preliminary basis tested for photocatalytic degradation of caffeine and with a better performance, the 1 mol.% Ag-ZnSnO₃ was investigated for further photocatalytic evaluations.

2.3. Instruments

X-ray diffraction (XRD) measurement (RIGAKU Corp., Tokyo, Japan) was performed by a RIGAKU D/Max-IIIC diffractometer with CuK_{α} radiation (λ = 0.1541 nm) over the diffraction angle range of $2\theta = 4^{\circ} - 80^{\circ}$ at conditions of room temperature, 35 kV, and 25 mA and at a scan speed rate of 3°/min. Fourier transform infra-red (FTIR) measurement of samples were performed on a Perkin-Elmer Spectrum one FT-IR (Thermo Fischer Scientific, Leicestershire, UK) using attenuated total reflection (ATR) method. Transmission electron microscopy (TEM) FEITecnaiG2 Spirit (FEI, Hillsboro, OR, USA) was used for the microstructural analysis of the samples. Brunauer-Emmet-Teller (BET) measurement was performed and recorded on a Micromeritics ASAP 2010 System (Micromeritics, Norcross, GA, USA) for the specific surface area of the samples together with pore size analysis obtained with Barrett Joyner Halenda (BJH) application method from the adsorption branch of the isotherms for confirmation of the mesoporosity of the samples. X-ray photoelectron spectroscopy (XPS) was performed for the analysis of the chemical compositions of the samples by a PHI 500 VersaProbe Spectrometer (ULVAC-PHI, Inc., Kanagawa, Japan), operated on an AlK_{α} radiation source. Morphology of the synthesized materials was determined with scanning electron microscopy (SEM) ZEISS EVO LS 10 (Carl Zeiss Microscopy, Hamburg, Germany) with a 0.2–30 kV acceleration voltage and 0.5 pA-5 μ A probe current, coupled to energy dispersive spectroscopy (EDS) detector (Carl Zeiss SmartEDX, Hamburg, Germany). UV-Vis measurement for the optical properties of the samples were recorded in diffuse reflectance spectroscopic (DRS) mode on a Shimadzu UV-2550 (Scintek Instruments LLC., Manassas, VA, USA).

2.4. Determination of pH_{pzc} of Ag-ZnSnO₃ Catalyst Material

According to pH drift method [4,55], pH point of zero charge (pH_{pzc}) of the Ag-ZnSnO₃ catalyst material was determined. Firstly, 50 mL of 0.01 M NaCl solution was measured and introduced into conical flasks. With either 1 M HCl or 1 M NaOH, initial pH of these solutions was adjusted and stabilized at room temperature between 2 and 12 range values. As the stability of these initial pH values is achieved, 0.05 g of the synthesized Ag-ZnSnO₃ powder was then added into each of the measured flask solutions, stirred for 48 h and final stabilized pH values of the solutions recorded with HANNA, edge pH meter at room temperature.

2.5. Photocatalytic Measurement

The photocatalytic performance evaluation of the synthesized materials was investigated for the degradation of caffeine under 365 nm UV irradiation. A 200-degree internal reflector for optimal efficiency (99.9%), UV-A and visible blue wavelength of range 300–475 nm spectral power distribution was fabricated inhouse with a cut off filter at 365 nm for the photocatalytic tests and used a 5- Philips Mercury (Hg) lamps TL-K-40W/10R ACTINIC BL REFLECTOR (Germany) as the light source [4,6,7]. Light intensity as measured with solar power meter Lafayette SPM-7, (Italy) was 1.2 mW/cm². Forty milliliters of working suspension containing 1 g/L catalyst and 10 mg/L caffeine was introduced into 50 mL cylindrically shaped quartz glass sleeve reactor cells and stirred in the dark for 30 min before irradiation to establish adsorption-desorption equilibrium in the meantime the irradiation light source was stabilized. Afterwards, working suspension was maintained under mechanical agitation during irradiation. Following preliminary photocatalytic tests at natural pH values ie unmodified (pHnatural) of 5.60 and 6.50 for ZnSnO₃ and Ag-ZnSnO₃, respectively, other initial pH values of 3, 5, 7.5, 9, and 11 were also tested for Ag-ZnSnO₃ photocatalytic activity evaluation with all other experimental test performed afterwards at initial pH = 7.5 being the best photocatalytic test pH point. pH measurements were performed by HANNA, edge pH meter (USA). A source light to sample distance of about 30 cm was maintained throughout the photocatalytic experiments. At chosen time intervals, about 1 mL sample aliquots were drawn from reactor cells, cooled, and filtered through 0.45 µm CA filter for HPLC analysis for caffeine degradation monitoring on a Kinetex EVO C18, column (150 mm \times 4.6 mm, i.d. 5.0 μ m) Phenomenex (Torrance, CA, USA). From a typical sample run chromatogram shown in (Supplementary Information Figure S1), a retention time (RT) of ~6 min of a ~10 min run time was recorded with an isocratic mobile phase mixture of 60% methanol and 40% milli-Q water at a flow rate of 0.4 mL/min. Caffeine quantification was performed by UV-vis diode array detector (G1315D, 1260 DAD VL), Agilent 1260 infinity at 272 nm absorption wavelength and calibration curve (Supplementary Information Figure S2) using standard caffeine solutions of known concentration $(0.5-10 \text{ mg/L}, \text{R}^2 = 1)$ was used to determine degraded caffeine concentration at a time t, of irradiation exposure. Experimental tests without catalyst, to monitor the effect of photolysis only was performed. Effect of heat with and without catalyst towards caffeine degradation was also performed and executed by covering the reactor cells with aluminum foils to prevent irradiation light penetration. Caffeine degradation kinetic rate constant was evaluated for the remaining concentration of caffeine over irradiation exposure time window of 4 h and data fixed as pseudo-first order kinetic model according to Equation (1).

$$\ln\left(\frac{C_t}{C_0}\right) = -k_{app}t\tag{1}$$

where k_{app} , C_0 , C_t are apparent degradation constant, initial caffeine concentration at t = 0 before irradiation, and caffeine concentration at any time *t* of considered irradiation exposure time window, respectively.

3. Results and Discussion

3.1. Material Sample Charcaterizations

The XRD pattern of synthesized ZnSnO₃ and Ag-ZnSnO₃ samples obtained within diffraction angle (2 θ) range of 10–80° is presented in Figure 1a. The identified peaks at 110 and 300 crystallographic planes of respective 2 θ values of 33.9° and 60.7° were the two main peaks for both samples. These peaks confirmed the rhombohedral (cuboid) structured ZnSnO₃ (JCPDS cart # 00-052-1381) [56,57]. The lack of sharpness and intensity of these two peaks (Figure 1a), confirm the amorphous characteristics of the synthesized sample materials after calcination and has been reported [57,58]. The crystallite sizes of the obtained samples were 29.3 nm and 19.4 nm for ZnSnO₃ and Ag-ZnSnO₃, respectively (Table 1). This was derived by the Debye-Scherrer function as stated in Equation (2) using the XRD line broadening of the most intense peak (Figure 1a).

$$D = \frac{K\lambda}{\beta \cos \theta}$$
(2)

where D is average crystallite size, K is the shape factor constant of value 0.9, $\lambda = 0.1541$ nm is the wavelength of the CuK α source, β is the line width obtained at full width half height maximum in radians, and θ is the diffraction angle in degree.



Figure 1. (a) XRD patterns, and (b) FTIR spectra of ZnSnO₃, and Ag-ZnSnO₃ sample materials.

Table 1. Textural/structural and morphological characteristics of synthesized sample materials ^{x,y}.

Materials	d _{XRD} (nm)	d _{TEM} (nm)	S_{BET} (m ² /g)	V _p (cm ³ /g)	d _p (nm)	E _g (eV)
ZnSnO ₃	29.3	98.2	18.8	0.06	11.5	4.2
1 mol.% Ag-ZnSnO ₃	19.4	79.0	17.2	0.05	12.8	3.8

^x d_{XRD}, crystallite size estimated by XRD; ^y d_{TEM}, particle size estimated by TEM; S_{BET}, surface area; V_p, total pore volume; d_p, average pore size; E_g, energy band gap.

The disparity between the crystallite sizes of the materials where $ZnSnO_3$ sample showed a higher crystallite size than Ag-ZnSnO₃ can be attributed to possible induced changes of interaction between heteroatoms upon the addition of the low loaded Ag atom, dispersed for the formation of Ag-ZnSnO₃ [59]. However, the obtained crystallite sizes of the samples in this study agree with already reported ZnSnO₃ and modified forms in crystallite size range of 10–30 nm [50]. Absence of characteristic Ag peak in the XRD pattern of Ag-ZnSnO₃ might be attributed to the low Ag loading amount in the sample. Though, the Ag modification, did not alter the phase structure of the synthesized Ag-ZnSO₃ sample with respect to the pristine state ZnSnO₃; the calcination treatment of the samples precursor (ZnSn(OH)₆) due to the dissociation of hydrogen-oxygen bond after dehydration led to the development of weakly attached dangling bonds (Figure 1a). This surface phenomenon together with the disordering of the internal lattice arrangement has been reported and confirms the amorphous nature of such calcinated ZnSnO₃ and modified forms with accompanied surface defects for enhanced catalytic activities [60].

The FTIR spectra of the synthesized sample materials are depicted (Figure 1b). Observed chemical bond and functional group at around 846.19 cm⁻¹ and 1369.92 cm⁻¹ has been reported and attributed to the Zn-O or Sn-O tensile modes [48,53,57,61] and similarly coincided at the same band point of Ag-ZnSnO₃ sample (Figure 1b). Observed bonds in the both ZnSnO₃ and Ag-ZnSnO₃ samples (Figure 1b), within respective 1496–1628.77 cm⁻¹ and 3326–3440 cm⁻¹ band range confirms the presence of H-O-H bond bending vibrations linked to surface adsorbed water, free water and or hydrate -OH functional groups, and stretching vibrations of the hydroxyl (-OH) functional groups in the as synthesized samples [48,53]. Overall, observed peak signal match and coincidence reveals that obtained ZnSnO₃ pristine structure on synthesis in terms of chemical bond group functionality did not make a noticeable difference upon the addition of Ag in the derived Ag-ZnSnO₃. In addition, just as in the case of XRD measurements, the low loading amount in the Ag doped sample as expected made no difference in the introduction of added value to the modified Ag-ZnSnO₃ sample as can be seen from the FTIR spectra (Figure 1b).

The specific surface areas of the sample materials and their pore size distribution were analyzed respectively by N_2 adsorption-desorption isotherm and BJH distribution curves (Figure 2a,b). The observed isotherm of the material samples (Figure 2a) can be described as the type IV isotherm with the H3 hysteresis loop documented for mesoporous

materials by the International Union of Pure and Applied Chemistry (IUPAC) [62,63]. Bare ZnSnO₃ showed slightly a higher BET surface area of 18.8 g/cm² in comparison to the Ag-ZnSnO₃ sample with 17.2 g/cm² BET surface area (Table 1). Similarly, total pore volume was 0.06 cm³/g, and 0.05 cm³/g for the ZnSnO₃ and Ag-ZnSnO₃ samples, respectively (Table 1). Minor differences in pore size were found for both samples with respective average pore sizes of 11.5 nm, and 12.8 nm for bare ZnSnO₃ and Ag-ZnSnO₃ samples (Table 1). In line, similar approximate pore size values have been reported [53]. The PSD curves of both samples (Figure 2b), recorded pore size maxima of more than 3 nm; a further confirmation for their mesoporous nature already supported by their type IV BET isotherm curves (Figure 2a). However, the different shape of pores as noticed from the hysteresis loop (Figure 2a), and a broader bi-modal PSD (Figure 2b) of ZnSnO₃, can respectively be linked to a typical ZnSnO₃ derived from the ZnSn(OH)₆ precursor and obtained via hydrothermal co-precipitation with a characteristic sharp inflection loop point and uncontrollable pore size collapse in a hydrothermal synthetic route for $ZnSnO_3$ materials [53,64]. In all, noticeable differences in the estimated values for the textural/structural properties of the synthesized sample materials (Table 1), absence of inflection point in the BET isotherm curve of Ag-ZnSnO₃ (Figure 2a), and presence of a sharp peak maxima in the Ag-ZnSnO₃ PSD (Figure 2b) can be attributed to the modification of $ZnSnO_3$ with Ag along the synthesis protocol culminated by heteroatom interactions with possible effects on the growth of the nanoparticles [21,53,59].



Figure 2. (a) N₂ adsorption-desorption isotherm curve, and (b) BJH pore size distribution (PSD) of synthesized sample materials.

To observe the microstructural morphology of the sample materials, transmission emission spectroscopy (TEM) was used. Homologous nanocube shaped ZnSnO₃ was obtained in line with previously reported studies at two different magnifications of 200 nm and 500 nm. (Figure 3a,b) [41,45,53]. Following the Ag modification of ZnSnO₃, the nanocubed morphology of ZnSnO₃ readjusted to a hollow nanocube structure in the obtained Ag-ZnSnO₃ nanocomposite (Figure 3c,d). The hollow nanocube structure maintained; however, the defined frame outline of the ZnSnO₃ but with a uniformly distributed white patch on the surface which can be observed and attributed to the Ag nanoparticles. (Figure 3c,d). Estimated particle sizes of the ZnSnO₃ and Ag-ZnSnO₃ nanocomposite obtained by ImageJ Software Version 8 were 98.2 nm and 79.0 nm, respectively (Table 1). Disparity in particle size estimate of bare ZnSnO₃ nanoparticle in comparison to that of Ag-ZnSnO₃ nanocomposite has been reported and attributed to induced microstructural changes due to alterations in synthesis protocols [64,65]. The obtained particle size estimates of the synthesized nanoparticles in our study agree with already reported sizes of ZnSnO₃ nanocube and forms in the range of few nanometers to tens of nanometers (Table 1) [53].



Figure 3. TEM images of ZnSnO₃ at (**a**) 200 nm and (**b**) 500 nm, and Ag-ZnSnO₃ at (**c**) 200 nm and (**d**) 500 nm resolutions.

The chemical state and surface chemical composition of the synthesized sample materials was analyzed by XPS. As presented in the Figure 4I, XPS survey spectra reveal as expected the presence of Zn, Sn, and O in ZnSnO₃ spectrum. In addition, Ag amongst all the other elements made the difference in the Ag-ZnSnO₃ spectrum after modification. XPS results of Figure 4a, show two corresponding peaks at 1042.0 eV and 1019.2 eV for $2p_{\frac{1}{2}}$ and $2p_{3/2}$ of elemental Zn in the ZnSnO₃ spectrum. These binding energies (BE) agree with previously reported values with ~23.0 eV splitting energy between the Zn $2p_{1/2}$, and Zn $2p_{3/2}$ phases and attributed to the existence of Zn atom as a divalent metal ion [4,48,53,54,61]. In Figure 4b, identified Sn 3d peaks centered at 494.0 eV and 485.4 eV binding energies for the respective Sn $3d_{3/2}$, and Sn $3d_{5/2}$ phases in the bare ZnSnO₃ agree with already reported BE data value of ~9.0 eV spin orbit splitting energy for these phases and attributed to the Sn⁺⁴ ion state [48,53,54]. In Figure 4c, is O 1s peak of pure ZnSnO₃ fitted into two peaks at 528.3 eV, and 529.8 eV BEs. These binding energy (BE) values agree with already reported O 1s BE attributed to surface hydroxyl (-OH) groups [61]. For Ag-ZnSnO₃ XPS chemical environment and state evaluation, the added Ag 3d peak was identified and fitted for the Ag $3d_{3/2}$, and Ag $3d_{5/2}$ phases at BE values of 372.2 eV and 367.3 eV, respectively (Figure 4g). The BE of these Ag 3d phases were in agreement with previously reported data for Ag 3d phases [54]. The shift to lower BE of these phases in this study as compared to reported Ag $3d_{3/2}$ (374.2 eV) and Ag $3d_{5/2}$ (368. 2 eV) BEs of the Ag⁰ bulk phase confirms the good interaction between Ag and ZnSnO₃ upon modification [54]. Comparing the Zn, Sn, and O XPS spectra in Figure 4d–f of Ag-ZnSnO₃ to that of Figure 4a-c of ZnSnO3; though, respective deconvoluted phase of these elements were all in agreement with already reported BE energy for these elements. However, noticeable shift in their BE by reason of their chemical environment alteration due to Ag modification of ZnSnO₃ occurred [4]. Between the Zn $2p_{1/2}$ (1042.0 eV BE), Zn $2p_{3/2}$ (1019.2 eV BE) of ZnSnO₃ spectra (Figure 4a), and that of Zn $2p_{1/2}$ (1044.9 eV BE), Zn $2p_{3/2}$ (1021.7 eV BE) of Ag-ZnSnO₃ spectra (Figure 4d); a respective spin splitting energy of 2.9 eV, and 2.5 eV in phase shifts can be observed. Similarly, Sn $3d_{3/2}$ (495.2 eV BE), and Sn $3d_{5/2}$ (486.6 BE eV) of Ag-ZnSnO₃ (Figure 4f), in comparison to the same phases at Sn $3d_{3/2}$ (494.0 eV BE), and Sn $3d_{3/5}$ (485.4 eV BE) of ZnSnO₃ (Figure 4b) displayed a phase shift with respective splitting energy of 1.2 eV each in BE phase shifts. The identified O 1s peak of 530.5 eV BE, and 532.4 eV BE for the Ag-ZnSnO₃ (Figure 4f) in comparison to the O 1s at 528.3 eV BE, and 529.8 eV BE for the ZnSnO₃, made respective

shifts of 2.2 eV and 3.6 eV of BE. The O 1s fitted peaks at 530.5 eV BE, and 532.4 eV BE in the Ag-ZnSnO₃ nanocomposite has been reported and ascribed to Zn-O, O-Sn bond functionalities, weak bonded -OH, and or crystal surface induced hydroxyl species (-OH_c), chemisorbed, or dissociated surface oxygen [53,54,61]. These oxygen species have also been reported of their role in enhanced photooxidation reactions of organic compounds following modification of photocatalysts [5,21,22]. Core level C 1s spectrum (Figure 4h) showed peaks at 285.0 eV and 288.5 eV BEs which have been reported and attributed to C-H and or C-C bond functionalities linked to adventitious carbon and free carboxyl group (-COOOH)/its coordinated Ag atom form, respectively [48,61].



Figure 4. (I) XPS survey spectrum of ZnSnO₃ and Ag-ZnSnO₃, and deconvoluted spectra of (**a**) Zn 2p, (**b**) Sn 3d, and (**c**) O 1s in ZnSnO₃, and deconvoluted spectra of (**d**) Zn 2p, (**e**) Sn 3d, (**f**) O 1s, and (**g**) Ag 3d in Ag-ZnSnO₃, and (**h**) C 1s spectra of both samples.

From Table 2, the XPS measurement reflected the elemental chemical phase composition of the constituent elements in the synthesized material samples. Between the ZnSnO₃ and 1 mol.% Ag-ZnSnO₃, the respective elemental compositions in wt.% and at.% were in agreement. However, some differences in wt.% and at.% compositions amongst the elements across the samples is related to change of the atoms chemical environment upon modification [4,7]. The Ag atom making the difference between the ZnSnO₃ and 1 mol.% Ag-ZnSnO₃ was in approximate amount equal to the initial Ag dopant content amount in the nanocomposite in wt.%. This can further be confirmed from the SEM-EDX measurement of samples for a more precise in-depth bulk characterization of the composite discussed hereafter.

ZnSnO ₃			1 mol.% Ag-ZnSnO ₃		
Chemical Phase	wt.%	at.%	Chemical Phase	wt.%	at.%
Sn 3d	41.59	9.31	Sn 3d	38.00	8.83
Zn 2p	19.10	6.86	Zn 2p	25.55	9.85
O 1s	24.92	43.95	O 1s	23.73	55.26
C 1s	14.39	39.88	C 1s	9.59	25.34
			Ag 3d	3.12	0.71

Table 2. XPS elemental chemical phase composition of synthesized material samples.

Since XPS data obtained on dry samples do not represent a perfect description of the surface composition of nanoparticles and present the likelihood of different configuration while present in solution, information both of surface chemistry and variation of surface reactivity of modified nanomaterials may display remarkable differences in sample conditions.

As such, for further confirmation of the morphology of the sample materials, SEM measurement with associated elemental mapping by EDS was performed. From Figure 5A,B, the morphology of ZnSnO₃ sample showed similar cube shaped structure obtained of the TEM measurement (Figure 3a,b), while that of Ag-ZnSnO₃ sample retained the hollow-cube shaped structure assembled in stacked form. This observation is also in line with obtained TEM image of Ag-ZnSnO₃ (Figure 3c,d), where the Ag particles are seen decorated on the hollow cube structure. Additionally, the SEM -EDS mapping pattern revealed as expected homogeneous distribution of O, Zn, Sn, and Ag as main elements in the ZnSnO₃ and Ag-ZnSnO₃ samples, respectively. Mapped Au element originated from the use of Au during preparation of both samples for SEM-EDS measurement while carbon presence in samples can be attributed partly to carbon origin in sample holder during preparation as well as reasons already explained from the core C 1s XPS image pattern of samples (Figure 4h). In all, the microstructural measurement, chemical environment as well as the surface morphological results of the samples, confirmed their successful synthesis (Figures 3–5).



Figure 5. SEM images of (A) ZnSnO₃ and (B) Ag-ZnSnO₃ samples and their respective EDS patterns.

Optical properties of a potential photocatalyst material to a large extent do play crucial role in the photocatalytic process to which such materials are subjected [48].

Therefore, to obtain the optical energy band gap (Eg) of the photocatalyst materials, UV-Vis spectroscopy in diffuse reflectance (DR) mode was performed.

Employing Kubelka-Munk function (Equation (3)), obtained reflectance spectra data was transformed into UV-vis absorption spectra data and subsequently, a Tauc's plot of hv vs. $[F(R)hv]^2$ was realized [4,40,48,53]. In the Figure 6, the band gap energy (Eg) is obtained from the Tauc's plot by linear extrapolation of $[F(R)hv]^2$ axis to corresponding point zero reading hv axis for each sample material. Eg values of 4.2 eV, and 3.8 eV were obtained for ZnSnO₃ and Ag-ZnSnO₃ materials, respectively (Table 1; Figure 6). These Eg values are within the range of reported wide optical band gap for ZnSnO₃ semiconductor due to phase differences, nanostructure shapes and sizes as well as quantum confinement effects [4,66].

$$F(R) = \frac{S(1-R)^2}{2R}$$
(3)

where F(R), R, and S are absorbance, reflectivity, and scattering factor, respectively. The scattering factor (S) has been taken as a unit due to powder form nature of materials.



Figure 6. Tauc's plot for energy band gap of ZnSnO₃ (black line), and Ag-ZnSnO₃ (red line).

3.2. Photocatalytic Activity

3.2.1. Effect of pH

pH Point of Zero Charge (pH_{pzc}).

pH plays a crucial role in the photodegradation process of organic compounds specially in aqueous media [4]. The formation of reactive species like hydroxyl radicals ([•]OH) together with some changes in surface properties of catalysts depend on pH and affect efficiency of catalysts [50]. In Figure 7, is the pH_{pzc} plot of Ag-ZnSnO₃ nanocomposite with estimated value of 7.40 obtained as the point where the final pH line intersects the initial pH.



Figure 7. pH point of zero charge (pH_{pzc}) determination plot of Ag-ZnSnO₃ photocatalyst (broken line: final pH points, and solid line: initial pH points).

Firstly, and for a preliminary test, unmodified (pHnatural) of pH = 5.60, and pH = 6.50, were measured for ZnSnO₃ and Ag-ZnSnO₃ aqueous suspension systems, respectively. With 1 g/L for each catalyst dosage, 40 mL working suspension volume with an initial concentration of 10 mg/L caffeine was employed to evaluate the photocatalysts ability. Under these conditions, ZnSnO₃ and Ag-ZnSnO₃ removed 33% and 68%, respectively, of the initial caffeine concentration after 4 h of 365 nm UV irradiation exposure (Figure 8). Other initial pH values of 3, 5, 7.5, 9, and 11 were further evaluated and their effects on photocatalyst performance discussed in line with the pHpzc of Ag-ZnSnO₃ and pKa value of caffeine (Figures 7 and 9a; Table 3). pH values were adjusted with 1M each of HCl as acid pH control agent and NaOH as alkaline pH control agent. At initial pH = 7.5, photocatalytic efficiency improved and the Ag-ZnSnO₃ degraded almost 100% initial caffeine concentration at 4 h irradiation (Figure 9a; Table 4). The pH_{pzc} of Ag-ZnSnO₃ and the pK_a value of caffeine reported as 10.4 (Table 3) [67,68] are important factors that will affect the adsorption process during the photocatalytic degradation of caffeine. When the pH of the aqueous reaction media is below the pH_{pzc} of Ag-ZnSnO₃ as 7.4 (Figure 7) and below the pKa value 10.4 of caffeine, the surface of the catalyst acquires positive charge, and the caffeine molecule is protonated bearing a positive charge at the functional amine (-NH) group (Table 3) [67,68]. On the contrary, when the pH of the aqueous reaction media is above the pH_{pzc} and above the pK_a value, the catalyst surface is negatively charged, and the caffeine molecule is deprotonated bearing a negative charge at the functional amine group (-NH) (Table 3) [67,68]. In the same sense, possible bond localization within the benzene ring of the caffeine molecule can also lead to a negative charge uptake by the O atoms creating either an attraction or repulsion effect with respect to the catalyst surface charge to either improve or suppress photocatalytic degradation based on the prevailing initial pH condition of suspension media (Table 3). Corroborating this surface charge phenomenon with the degradation efficiency of Ag-ZnSnO₃ against caffeine at initial pH = 7.5, the catalyst surface will be negatively charged, and the caffeine molecule protonated, and thereby the established force of attraction will lead to the strong adsorption of caffeine molecules to the surface of the catalyst for a favored photocatalytic degradation process (Figure 9a). At initial pH = 9, and initial pH = 11, impressive performance by

the catalyst was still recorded and at 4h irradiation, over 90 and 80% of initial caffeine concentration were degraded, respectively. At initial pH = 9 such a performance can be attributed to also the enhanced adsorption of caffeine molecule onto the photocatalyst favored within the pH range of 7.4–10.4 (Figures 7 and 9a; Tables 3 and 4). The degradation pH effect witnessed at initial pH = 11 in the presence of the Ag-ZnSnO₃ photocatalyst can be attributed to reported enhanced surface adsorption mechanisms of ZnO based photocatalysts at such advanced alkaline pH values [4,69]. Hence, caffeine degradation is not only limited to hydroxyl radicals (OH) photocatalytic transformation but also hydrated surface electrons and favored hydroxyl ions (⁻OH) generation in alkaline pH condition of aqueous suspension systems [50,69]. For the case of low acidic initial pH = 3 and moderate acidic initial pH = 5, caffeine photocatalytic degradation was suppressed in comparison to the other initial pH values of 7.5, 9, and 11 (Figure 9a; Table 4). The suppression effects of initial pH = 3 and initial pH = 5 on the photocatalytic degradation efficiency where about 72% of initial caffeine concentration was degraded at 4 h irradiation can be attributed to the fact that while acidic proton environment do promote and facilitate the generation of more reactive species (OH, HO_2, H_2O_2) (Equations (6) and (9)) for photocatalytic degradation of pollutants in some cases; in others, it has been reported that such acidic conditions can hamper photooxidation as the hydrogen cations binds with hydroxyl radicals (OH) reducing as such their availability as reactive species to drive photocatalytic degradation process [70].



Figure 8. Degradation of 10 mg/L caffeine by 1 g/L ZnSnO₃ (blue line) at $pH_{natural} = 5.60$, and 1 g/L Ag-ZnSnO₃ (red line) at $pH_{natural} = 6.50$.



Figure 9. (a) Initial pH effect and corresponding apparent degradation rate constant (inset) on Ag-ZnSnO₃ over 10 mg/L caffeine, and (b) Dark, photolysis, heat effect with and without catalyst on Ag-ZnSnO₃ over 10 mg/L at initial pH = 7.5.

Table 3. Characteristics of Caffeine (CAF) as the tested model CEC compoun	۱d.
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Chemical Property/Name	Caffeine		
Chemical structure	H_3C N		
Molecular formula	$C_8H_{10}N_4O_2$		
CAS No.	58-08-2		
Molecular weight, g/mol	194.19		
Solubility in water, g/L	18.7		
pKa	10.4		

Test	Degradation Rate Constant k (h $^{-1}$)	R ²			
	pH effects on Ag-ZnSnO ₃ #,*				
pH = 3	0.36	0.98			
pH = 5	0.35	0.97			
pH = 7.5	1.01	0.97			
pH = 9	0.64	0.98			
pH = 11	0.44	0.99			
Catal	yst dosage effects on Ag-ZnSnO ₃ ^{#,*}				
0.5 g/L	0.54	0.97			
0.75 g/L	0.75	0.96			
1 g/L	1.01	0.96			
1.25 g/L	0.80	0.99			
2 g/L	1.10	0.98			
Pollutan	t concentration effects on Ag-ZnSnO ₃ #,*				
5 mg/L	2.20	0.99			
10 mg/L	0.87	0.99			
15 mg/L	0.62	0.99			
20 mg/L	0.42	0.99			
25 mg/L	0.42	0.99			
Reactive oxy	rgen species (ROS) effects on Ag-ZnSnO ₃ ^{#,*}				
No scavenger	0.96	0.99			
1 mM Benzoquinone (BQ)	0.10	0.87			
1 mM Isopropyl alcohol (IPA	.) 0.15	0.98			
1 mM Ethylenediamine acetic a (EDTA)	0.12	0.94			
1 mM Sodium sulphate (Na ₂ So	D ₄) 0.15	0.98			
Hydrogen	peroxide (H ₂ O ₂) effects on Ag-ZnSnO ₃ $^{\#,*}$				
0 mM H ₂ O ₂	0.96	0.99			
1 mM H ₂ O ₂	0.20	0.99			
1 mM H ₂ O ₂	0.20	0.99			
Ion effects (anions) on Ag-ZnSnO ₃ #,*					
No anion	1.10	0.99			
1 mM HCO ₃ ⁻	0.44	0.99			
1 mM CO ₃ ²⁻	0.41	0.99			
1 mM SO ₄ ²⁻	0.35	0.99			
1 mM NO ₃ ⁻	0.33	0.99			
Humic acid (HA) effects on Ag-ZnSnO ₃ ^{#,*}					
0 mg/L HA	0.96	0.99			
5 mg/L HA	0.23	0.99			
10 mg/L HA	0.20	0.98			

Table 4. Degradation rate constant k (h^{-1}) and associated correlation factor (R^2) values of controlled photocatalytic parameters.

[#] Tests performed under 365 nm near UV-vis irradiation, and * initial pH condition.

In addition, acidic pH has been reported to hamper the photocatalytic degradation of caffeine due to interfering phenomenon of adsorption process, photocatalyst dissolution and decomposition amongst various other factors [50,67,68]. Again, under these initial pH = 3 and 5 conditions, the amine (-NH) functional group of caffeine will be protonated (positively charged) and the surface of the catalyst will also be positively charged, thereby creating a repulsion effect which tends to keep caffeine molecules away from the surface of the catalyst for degradation.

Since of all the tested initial pH values, initial pH = 7.5, delivered the most impressive photocatalytic degradation, other investigative tests on the photocatalyst performance evaluation against caffeine degradation were carried out at initial pH = 7.5 as the best pH performance point. At this initial pH value, dark test condition effect on the photocatalytic degradation of caffeine in the presence of catalyst, effect of photolysis (irradiation light only) without catalyst as well as heat effect with and without catalyst (with irradiation light on but photocatalyst reactor cells covered with aluminum foils to prevent light penetration) were all investigated and found of no significant contribution towards caffeine degradation (Figure 9b).

3.2.2. Effect of Catalyst Dosage and Initial Caffeine Concentration

The effect of different amounts of catalyst on the photocatalytic degradation of 10 mg/L initial caffeine concentration at initial pH = 7.5 was investigated. In addition to 1 g/L, other catalyst amounts of 0.5 g/L, 0.75 g/L, 1.25 g/L, 1.5 g/L, and 2 g/L were tested. As can be seen from Figure 10a, and Table 4, a trend of increase in the photocatalytic degradation rate of caffeine from lowest tested amount of 0.5 g/L catalyst to the highest amount of 2 g/L is observed. Enhanced photocatalytic activity has been reported for the degradation of organic pollutants with increase in catalyst dosage and attributed to increase in total active surface site [69]. An exception was observed in the case of 1.25 g/L showing a lesser photocatalytic degradation rate removal of caffeine after 4 h irradiation than 1 g/L catalyst amount. This observation can be attributed to surface adsorption mechanism at a certain catalyst concentration in aqueous suspensions [69]. Since the catalyst dosage showed a concerted caffeine removal at 4 h irradiation with no outstanding significance in activity between the doses except for the lowest 0.5 g/L dose, 1 g/L was preferred as the effective catalyst amount in keeping the dosage low yet active for caffeine degradation.

Different initial caffeine concentrations in addition to the 10 mg/L were also tested against 1 g/L catalyst dose at initial pH = 7.5. Other initial caffeine concentrations tested were 5 mg/L, 15 mg/L, 20 mg/L, and 25 mg/L. As can be seen from Figure 10b and Table 4 in terms of photocatalytic degradation rate constant, increase in caffeine concentration resulted in a decrease in the catalyst activity. At a lower 5 mg/L caffeine, the degradation rate was faster; while as the initial caffeine concentration increased from 10 mg/L up to 25 mg/L, the photocatalytic degradation rate decreased (Figure 10b). It is noticed that at 20 mg/L, and 25 mg/L caffeine concentrations, photocatalytic degradation maintained the same rate constant value of 0.42 h^{-1} (Table 4). It has been reported that at high pollutant concentration, catalyst efficiency decreases due to light penetration blockage or shielding effect of catalyst surface that reduces number of generated reactive species responsible for pollutant degradation [4,69]. As a more effectively degraded concentration with respect to the other higher tested initial caffeine concentrations at 1 g/L catalyst dose and initial pH = 7.5 conditions, 10 mg/L initial caffeine concentration was considered. Hereafter, at initial pH = 7.5, a 1 g/L Ag-ZnSnO₃ catalyst dosage, and 10 mg/L initial caffeine concentration were focused and discussed in the next sections.



Figure 10. Effects of (**a**) catalyst dosage, and (**b**) initial caffeine concentration and their corresponding apparent degradation rate constant (insets) at initial pH = 7.5.

3.2.3. Reactive Oxygen Species (ROS) Probe

To investigate the main reactive species involved in the photocatalytic degradation process of caffeine, we carried out trapping experiments with benzoquinone (BQ), isopropyl alcohol (IPA), ethylenediamine tetraacetic acid (EDTA), and sodium sulphate (Na₂SO₄) as the chemical scavengers for the reactive species [4,53,61]. Then, 1 mM each of the chemical scavengers of BQ, IPA, EDTA, and Na₂SO₄ were added into the working suspension for the detection of superoxide anion (O_2^{-}) , hydroxyl free radical ($^{\circ}OH$), valence band holes (h_{vb}^+) , and conduction band electrons (e_{cb}^-) , respectively. As can be seen from Figure 11, the chemical scavengers exerted suppressive effects on the catalyst performance once added into solution until 2 h irradiation. At this point, just about 27% of initial caffeine concentration was degraded by the catalyst as compared to the about 83% of initial caffeine concentration degraded in the absence of these scavengers (Figure 11). The suppressive effect of the scavengers was still felt until the 4 h irradiation especially in the presence of BQ and EDTA scavengers for respective superoxide anion (O_2^-), and valence band holes (h_{vb}^+) detection. The observed lapse in suppression effect of both IPA and Na₂SO₄ scavengers for the respective detection of hydroxyl free radical ('OH) and valence band hole (h_{vb}^{+}) species involvement at 3 h and 4 h irradiation was not a significant one compared to the no scavenger addition activity of the catalyst where about 94% and 98% of initial caffeine concentration was respectively removed (Figure 11). Based on this outcome, it can be deduced that in the presence of these employed chemical scavengers, photocatalytic degradation rate removal of caffeine by the Ag-ZnSnO₃ was significantly affected in comparison to no chemical scavenger addition. An approximate photocatalytic degradation rate constant of 0.10 h^{-1} for each of BQ and EDTA, and 0.20 h^{-1} for each of IPA and Na_2SO_4

scavengers as compared to the $0.96 h^{-1}$ photocatalytic degradation rate constant when no scavenger was added, further confirms the suppressive effects of these reactive species on a respective ~10 and ~5 factor fold towards caffeine photocatalytic degradation at 4 h irradiation (Figure 11; Table 4). Though, there has not being an outright selective outcome amongst the employed chemical scavengers in their suppression exhibition effect against the photocatalytic degradation of caffeine; at least up to the 2 h irradiation time (Figure 11). This trend in outcome makes it even more ideal to say that with the employed Ag-ZnSnO₃ photocatalyst, the driving mechanism behind the photocatalytic degradation of caffeine under the investigated experimental condition is a classical one where majority of the reactive oxygen species if not all involved in the photocatalytic degradation of organic pollutants played important role for the photocatalytic degradation of caffeine.



Figure 11. Effect of 1 mM concentration each of chemical scavengers on caffeine degradation (1 g/L Ag-ZnSnO₃, $[CAF]_0 = 10 \text{ mg/L}$, and initial pH = 7.5) and its corresponding apparent degradation rate constant (inset).

This analogy can further be supported by the reported mechanism of the photocatalytic activity of ZnSnO₃ based photocatalyst under UV light according to the equations below [71].

e

$$ZTO - based photocatalyts \rightarrow e^- + h^+$$
 (4)

$$e^- + h^+ \to energy$$
 (5)

$$h^+ + H_2 O \to H^+ + O H^{-} \tag{6}$$

$$h^+ + OH^- \rightarrow OH^-$$
 (7)

$$e^- + O_2 \to O_2^{\cdot -} \tag{8}$$

$$O_2^{\cdot-} + H^+ \to HO_2^{\cdot} \tag{9}$$

$$(OH^{\cdot}, O_{2}^{\cdot-}, HO_{2}^{\cdot}) \rightarrow degradation products$$
 (10)

In Equation (4), ZTO-based photocatalyst refers to zinc stannate based photocatalyst.

3.2.4. Hydrogen Peroxide (H₂O₂) Effect

The effect of hydrogen peroxide on the photocatalytic degradation process was investigated, whereby 5 mM and 10 mM concentrations of H_2O_2 were added to the working suspension and monitored separately. From Figure 12a, and at 4 h of 365 nm UV irradiation, the photocatalyst degraded about 52% of initial caffeine concentration in the presence of the external oxidant at both concentrations. In comparison to 0 Mm H_2O_2 , about 98% of initial caffeine degradation was achieved. A suppressive effect was exerted on the photocatalytic degradation process under those concentration conditions. It has been reported that the addition of external oxidants like H_2O_2 may not respond with a positive effect due to its extremely low absorption under UV light conditions [4,72,73]. Another reason for the witnessed suppressive effect of H_2O_2 is due to the scavenging behavior of H_2O_2 towards photoproduced holes (h⁺) and its subsequent reaction with hydroxyl radical (OH) at high concentration under certain reaction conditions [4,72,73]. This leads to decrease in photocatalytic efficiency. The observation of Figure 12b, where at both H_2O_2 concentrations of 5 mM and 10 mM under 365 nm UV irradiation and in the absence of photocatalyst there was no significant caffeine degradation; confirms that the reported low absorption of H_2O_2 under UV irradiation and in the presence of some organic pollutants was evident. Hence, in addition, the lesser performance of the photocatalyst at 4 h irradiation at 5 mM and 10 mM H_2O_2 in comparison to no added H_2O_2 in the presence of photocatalyst owes to the scavenger nature of the H_2O_2 towards photoproduced holes and their subsequent hydroxyl ion (OH⁻) generation leading to the suppression of photocatalytic degradation process. At 4 h irradiation, 5 mM H_2O_2 and 10 mM H_2O_2 , an ~0.18 h⁻¹ apparent photocatalytic degradation rate constant was achieved in comparison to ~0.96 h^{-1} for no H_2O_2 addition (Table 4). This represents a fivefold factor of photocatalytic degradation process inhibition in the presence of H₂O₂ with respect to when the reaction took place without.



Figure 12. (a) Effects of H_2O_2 on caffeine degradation (1 g Ag-ZnSnO₃, [CAF]₀ = 10 mg/L, initial pH = 7.5) and its corresponding apparent degradation rate constant (inset), (b) UV/5 mM H_2O_2 , and UV/10 mM H_2O_2 effects only on 10 mg/L CAF degradation at initial pH = 7.5.

3.2.5. Effects of Contaminant Ions (Anions) and Humic Acid (HA)

Investigation into the effects of anions and humic acid on the photocatalytic degradation process was performed as these species are often associated with water matrixes and can impact photocatalytic reactions. Sodium salts of four inorganic anions $(CO_3^{2-}, HCO_3^{-}, NO_3^{-}, and SO_4^{2-})$ at 1 mM concentration each was investigated. As can be seen from Figure 13a, all the four anions at the tested concentration impeded the photocatalytic degradation process in comparison to no added anion. At 4 h irradiation, and

in the presence of 1 mM HCO₃⁻ ion, about 82% of initial caffeine concentration was removed at a photocatalytic degradation rate of ~ $0.44 h^{-1}$ (Table 4). About 77% of initial caffeine concentration was degraded at a rate of ~ $0.41 h^{-1}$ by the photocatalyst in the presence of 1 mM CO_3^{2-} ion. While in the presence of 1 mM NO_3^{-} ion, a 72% of initial caffeine concentration was removed by the photocatalyst at a degradation rate constant of ~0.33 h^{-1} (Table 4) at 4 h irradiation; 76% of initial caffeine concentration was removed by the photocatalyst at a degradation rate constant of ~0.35 h⁻¹ (Table 4) in the presence of 1 mM SO_4^{2-} ion. Comparing these outcomes with no anion addition, over 98% of initial caffeine concentration with a photocatalytic degradation rate of ~0.96 h⁻¹ was delivered of the photocatalyst at 4 h irradiation (Figure 13a; Table 4). Based on the analogy of the tested anions in the presence of their Na counter ion (Na inorganic salts), the inhibition effect trend on caffeine photocatalytic degradation is assumed to take the order: 1 mM NO₃⁻ > 1 mM SO₄²⁻ > 1 mM CO₃²⁻ > 1 mM HCO₃⁻. The presence of the Na⁺ in the tested anions might have introduced some effects to the photocatalyst degradation efficiency of caffeine; but the contribution is seen not significant due to common ion effect of Na at the equal tested concentrations of the anions at 1 mM each. It has been reported of decreased photocatalytic efficiency of photocatalyst on organic pollutants in the presence of inorganic ions, dissolved organic matter (DOM), etc. [4,74]. Diminution of colloidal stability, incoherent mass transfer, surface contact reduction between photocatalyst and pollutant, pH modification of working suspension media, photocatalyst surface fouling as well as scavenging of holes (h⁺) and hydroxyl reactive species, etc., have been reported as contributing factors to photocatalytic reduction efficiency in the presence of inorganic ions [4,74].



Figure 13. (a) Anion effect at 1 mM concentration of each tested anion, and (b) humic acid effect and their corresponding photodegradation rate constant (inset) (1 g Ag-ZnSnO₃, [CAF]₀ = 10 mg/L, initial pH = 7.5).

Under the investigated anion effect test condition of initial pH = 7.5, the added CO_3^{2-} will be effectively absent and rather exist in the HCO_3^{-}/CO_3^{2-} buffer form as the working suspension media initial pH condition was not kept constant. Therefore, the response witnessed of the photocatalyst in the photocatalytic degradation of caffeine in the presence of HCO_3^{-} anion could be linked to a synergistic effect as all initially present 1 mM CO_3^{2-} shifts to HCO_3^{-} ion, doubling in concentration. This inference can be confirmed along the irradiation exposure time window, where amongst the other considered anions and in comparison, to no added anion, HCO_3^{-} showed a lower inhibitory response to the photocatalytic degradation of caffeine (Figure 13a).

The adherence of SO_4^{2-} to photocatalyst surface due to its double charge power via van der Waals forces and hydrogen bonds which in turn leads to the displacement of some surface hydroxyl groups of photocatalysts via ligand transfer mechanism (LTM); has been reported for SO_4^{2-} inhibition to photocatalytic degradation of organic pollutants [4,74]. The scavenging nature of NO_3^- for valence band hole (h_{vb}^+) and hydroxyl radical ('OH) has also been reported and responsible for its organic compound photocatalytic degradation inhibition [4,7].

In all, the suppression of the photocatalytic degradation of caffeine in the presence of the tested anions and under initial pH = 7.5 condition, is evident in comparison to no added anion (Figure 13a) and can be linked to the above outlined reasons.

In Figure 13b, the effect of humic acid (HA) on the photocatalytic degradation process in comparison to 0 mg/L HA can be observed. In the presence of 5 mg/L HA, about 62% of initial caffeine concentration was removed after 4 h irradiation with a photocatalytic degradation rate constant of 0.23 h⁻¹ (Table 4). Upon doubling the concentration of HA to 10 mg/L, the photocatalyst rate of caffeine degradation decreased to a 0.20 h⁻¹ rate (Table 4) with a about 52% of initial caffeine concentration removed at 4 h irradiation. In comparison to no added HA, an ~98% of initial caffeine concentration removal was achieved of the photocatalyst with a photocatalytic degradation rate constant of about 0.96 h⁻¹ (Figure 13b, Table 4). With 5 mg/L HA, photocatalytic degradation rate constant decreased ~4-fold with respect to no HA addition. With 10 mg/L HA, an ~5-fold photocatalytic degradation rate constant decrease was observed with respect to no HA addition. Between tested 5 mg/L HA, and 10 mg/L HA, photocatalytic degradation inhibition of caffeine was not outrightly significant. However, both tested HA concentrations of 5 mg/L and 10 mg/L exerted a photocatalytic degradation in comparison to no added HA.

In the presence of organic carbon compounds (e.g., NOM, DOM, HA, etc.), photocatalytic degradation of organic pollutants is impaired as photocatalyst surface is shielded from adequate photo energy penetration responsible for the generation of reactive species which are essential for photocatalytic processes [4,72,74]. The effect exerted by the tested anions and humic acid under the investigated initial pH = 7.5 on the photocatalytic degradation of caffeine may not represent exactly what is obtainable of a real wastewater sample as well as that of natural waters where dissolved inorganic carbon (DIC) content as per water matrix is different and made up of several chemical species that may vary in quantity at different pH values.

The photocatalytic degradation of caffeine in the presence Ag-ZnSnO₃ photocatalyst and under test conditions of (Sections 3.2.1–3.2.5) may vary due to possible pH variations along and to the end of the 4 h irradiation time window. Such scenario may lead to exertion of different result outcome in the photocatalytic degradation of caffeine than the present one reported under initial pH = 7.5.

Table 4 presents estimated photocatalytic degradation rate constants k, and correlation factor (R²) values of investigated photocatalytic parameters per the Ag-ZnSnO₃ photocatalyst material over caffeine degradation. For all the tested parameters, an average of triplicates has been reported and error bars have been assigned with a standard deviation of ± 0.05 .

3.3. Proposed Reaction Mechanism

From the capture experiment that investigated the role of reactive oxygen species (ROS) in the photocatalytic degradation of caffeine (Figure 11; Section 3.2.3), a possible surface reaction mechanism was suggested (Scheme 1). From the trapping experiment (Figure 11); superoxide anion (O_2^{-}) as scavenged by BQ, and conduction band electrons (e_{cb}^{-}) as scavenged by EDTA exerted most prominent suppression effect on the photocatalytic degradation process (Figure 11). Based on the investigation outcome of all the probed reactive oxygen species, namely, superoxide anion (O_2^{-}) , hydroxyl free radical (OH), valence band holes (h_{vb}^+) , and conduction band electrons (e_{cb}^-) , showing no outright significant inhibition effect between them on the photocatalytic degradation process; such a mechanism where all the reactive species are directly or indirectly involved is envisaged (Equations (4)–(10), Scheme 1). Following the irradiation of the Ag-ZnSnO₃ photocatalyst, adequate photon energy ($h\nu$), knocks off electron from the valence band (vb). While this is happening, a charge transfer mechanism in place sees the electrons migrate to the conduction band (cb) with subsequent generation of hole charge carriers at the valence band (vb) energy level (Scheme 1). At both the valence band (vb) and conduction band (cb) energy levels, surface attached Ag atom undergo redox reaction with the release of electron charges (Scheme 1). $ZnSnO_3$ being an n-type semiconductor will accept part of the electron inflows into its conduction band (cb) from the Ag/Ag⁺ redox system. During this time, and at the valence band (vb) energy level, the generated hole carrier (h⁺) will interact with surface adsorbed water molecules producing ($OH/^{-}OH$) reactive species in the process (Scheme 1). At the same time, the conduction band electrons (e^{-}) and a portion of the electron charge carriers generated of the Ag/Ag⁺ redox system will abstract and interact with adsorbed surface oxygen molecules; subsequently producing superoxide anions (O_2^{-}) (Scheme 1). The evolved reactive species of hydroxyl radical/ions (OH/-OH) and superoxide anions (O_2^{-}) are then readily available for the photooxidation of caffeine yielding degraded products and some intermediate nitrogenous compounds (e.g., NH₃, NH₂, etc.), water, and CO_2 in the process (Scheme 1). The surface reaction mechanism for the suggested involved reactive oxygen species (ROS) in the photocatalytic degradation process can be supported with conduction band (E_{cb}) and valence band edge (E_{vb}) potentials of the photocatalyst. Employing the Mullikan function of electronegativity of semiconductors, the band edge potentials of Ag-ZnSnO₃ was estimated according to Equation (11) [75].

$$E_{cb} = \chi - 0.5E_e - E_g$$
 (11)

where, E_{cb} is conduction band edge potential (eV), χ is the electronegativity estimated from the geometric mean of the individual element electronegativity in the Ag-ZnSnO₃ composite (eV), E_e is the energy of free electron on the normal hydrogen electrode (NHE) scale (eV), and E_g is the energy band gap of Ag-ZnSnO₃ (eV). From the function relating energy band gap (Eg), conduction band edge potential, and valence band edge potential in equation 12; the valence band edge potential (E_{vb}) of Ag-ZnSnO₃ is estimated.

$$E_{vb} = E_{cb} + E_g \tag{12}$$

where E_{vb} is the valence band edge potential (eV), E_{cb} is the conduction band edge potential (eV), and E_g is the energy band (eV).



Scheme 1. Proposed Reaction Mechanism of Ag-ZnSnO₃ Photocatalyst.

Estimated values of E_{cb} and E_{vb} were -0.26 eV, and 3.54 eV, respectively.

From Scheme 1, the conduction band edge (E_{cb}) potential (-0.26 eV) of the Ag-ZnSnO₃ photocatalyst is enough negative in value when compared to the E° (O₂/O₂⁻) of value -0.046 eV on the NHE [48,61]. Therefore, at the conduction band (CB) of the photocatalyst, superoxide anion (O_2^{-}) formation via surface adsorbed oxygen is favored to degrade the caffeine molecule. Again, the formation of superoxide (O_2^{-}) via the $(O_2 + H^+/O_2^{-})$ pathway is favored also as part of the electrons in the Ag/Ag⁺ redox reaction at the valence band edge (VB) possesses enough energy of 3.54 eV as compared to the E° (O₂/O₂⁻⁻) with a value of 0.68 eV vs. NHE needed for the generation of these species at this level (Scheme 1). Similarly, the formation of hydroxyl radical (OH)/hydroxyl ion (HO⁻) species at the valence band (VB) energy level is energetically favored also as the band edge potential (E_{vb}) 3.54 eV value is high enough to generate these species when compared to their respective E° values of 1.99 eV and 2.38 eV vs. NHE in their formation either through the (OH/HO^{-}) or (H_2O/OH) pathways (Scheme 1) [48,61]. Moreover, the reported tendency of Ag doped $ZnSnO_3$ nanoparticle catalyzation of the dissociation of molecular oxygen (O_2) to form active oxygen species (O^{-}) and their subsequent transport to the surface of the ZnSnO₃ via spillover effects known of noble metals is in concordance with the proposed mechanism [76].

4. Conclusions

Successfully 1 mol.% Ag doped ZnSnO₃ was synthesized by hydrothermal assisted co-precipitation method. The microstructural and morphological outcome presented cubic shaped microporous material of 79 nm as the average particle size. Thanks to its modified microstructural morphology, chemical state, and optical characteristic, a 1 g/L of 1 mol.% Ag-ZnSnO₃ demonstrated a higher photocatalytic degradation rate for a 10 mg/L of initial caffeine concentration in comparison to bare ZnSnO₃ after 4 h and under near UV-vis

365 nm irradiation. For the photocatalytic degradation of caffeine, effects of different initial pH conditions (pH = 3, pH = 5, pH = 7.5, pH = 9, and pH = 11) in line with the determined pH point of zero charge (pHpzc) of the photocatalyst (7.4) and caffeine pKa 10.4 was investigated. With higher caffeine degradation of over 98% achieved by the photocatalyst at pH = 7.5, and impressive performances also at pH = 9, pH = 11; conditions of pH = 3, and pH = 5, exerted a suppression effect on the photocatalyst performance. Other effects of different catalyst dose, different initial pollutant concentrations (caffeine), reactive oxygen species (ROS), hydrogen peroxide (H_2O_2) , anions, and humic acid in different amounts and concentrations at initial pH = 7.5 were also investigated, and their influence either for or against the photocatalyst performance accordingly elucidated. Based on the outcome of trapping experiments with chemical scavengers for the involved reactive species in the photocatalytic degradation process, a proposed surface reaction mechanism was suggested. Supported empirically, generated superoxide anions (O_2^{-}) along with hydroxyl radicals (OH) as respective primary and integral part of the photocatalytic degradation process were earmarked. However, suggested involvement of the Ag/Ag⁺ redox system for catalytic Ag metal role together with the direct/indirect involvement of conduction band electrons (e_{cb}^{-}) and valence band holes (h_{vb}^{+}) for the generation of other reactive species like H₂O₂, OOH, etc., led to a classical deduction of involved ROS in the proposed reaction mechanism. Exciting results of ZnSnO₃ nanostructure-based materials for the photocatalytic degradation of organic compounds have been reported. However, results of the present study showed further impressive photocatalytic degradation ability in comparison to commonly studied titania and other photocatalysts for caffeine and or other CEC compound degradation. For instance, 42.1% of initial 5 mg/L metronidazole was removed by $ZnSnO_3$ catalyst under simulated solar light after 3 h (180 min) [53], whereas in comparison to our study, about 93% of 10 mg/L initial caffeine concentration at same time of irradiation was removed. With almost 100% of 10 mg/L of initial caffeine concentration removal demonstrated in this study, Arfanis et al., reported about 50% removal of initial 15 mg/L caffeine concentration on TiO_2 nanotubes (TNT) after 4 h (240 min) of UV irradiation under similar range of investigated initial pH values of this study. The satisfactory display of the Ag-ZnSnO₃ over caffeine degradation is worth considering for extended application in the removal of other CEC compounds.

Finally, the Ag-ZnSnO₃ photocatalyst haven shown promising result, will further be investigated of its photocatalytic activity performance dependence on initial pH variation. Additionally, more studies will be performed to understand the mineralization profile of the degraded caffeine compound as to what intermediates and other organic compound end products evolved. As a multifunctional material, its application for energy harvesting, electronic and optical uses, and various sensory profiles will also be explored.

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