

Ultrasound assisted fabrication of $\text{InVO}_4/\text{In}_2\text{S}_3$ heterostructure for enhanced sonophotocatalytic degradation of pesticides

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ARTICLE INFO

Keywords:

Ultrasound

InVO_4

In_2S_3

type-II heterostructure

Sonophotocatalysis

Pesticides

ABSTRACT

A cost effective and environmentally benign ultrasonic method has been developed for the synthesis of InVO_4 (InV), In_2S_3 (InS) and the $\text{InVO}_4/\text{In}_2\text{S}_3$ heterostructure (InV/InS). All the designed materials were evaluated for their structural, morphological, spectroscopic, and electrochemical characterizations. Materials were examined for photocatalytic, sonocatalytic, and sonophotocatalytic degradation of carbofuran (CBF) and diazinon (DZN) pesticides under visible light. InV/InS showed enhanced degradation of CBF and DZN when compared to InV and InS. Photocatalytic degradation was accelerated by ultrasonication and found to degrade 97 and 98 % of CBF and DZN in 60 and 70 min, respectively. The reaction conditions, like pH, catalyst dosage, acoustic intensity, and ultrasound power, were carefully optimized. Electron spin resonance (ESR) spectroscopy shows the generation of superoxide radical anion and hydroxyl radicals as reactive species during photoredox reaction. The CBF and DZN degradation intermediates were analyzed using liquid chromatography mass spectroscopy (LC-MS) that shows the mineralization of the CBF and DZN to CO_2 and H_2O . The effect of Cl^- , and PO_4^{3-} were examined towards degradation of CBF and DZN under optimal conditions in the presence of InV/InS. The degradation of CBF and DZN is decreased in presence of Cl^- , CO_3^{2-} and NO_3^- but PO_4^{3-} ions does not show any effect on degradation. The bandgap and Mott-Schottky results suggest the existence of type-II heterostructure between InV and InS through the interface. The synthesis of heterostructure and degradation of pesticides utilizes ultrasonic waves, which prove their multiple applications and attract researchers towards the effective use of sonication.

1. Introduction

Most of the country's development mainly relies on the agricultural industry. Continuous growth in the population essentially demands more food. To meet the high demand for food, farmers are using pesticides, insecticides, and fungicides to increase the quantity of crops in a short time [1,2]. Without sufficient information on how to utilize these pesticides on crops, they have been applied irrationally in massive amounts. Pesticides cause soil toxicity and environmental contamination when they are used frequently and extensively [3,4]. Many pesticides like carbofuran, Ethyl Parathion and dichloro-diphenyl-trichloroethane (DDT) were prohibited in United States of America

due to the toxicity associated with them. Pesticides are dispersed throughout the ecosystem via water and air and concentrate along the food chain, where they can seriously endanger both human health and biodiversity [5,6]. Pesticides cause soil toxicity and environmental contamination when they are used frequently and extensively [7,8]. Unfortunately, pesticides have become so ingrained in contemporary agriculture that they can no longer be avoided. Therefore, it is currently essential to develop advanced technology to degrade pesticide residues to secure both agricultural harvests and ecological civilization [9]. In this sense, developing potent pesticide residue degradation technologies that not only assist environmental restoration but also preserve the long-term growth of the survival habitat is a more prudent option than

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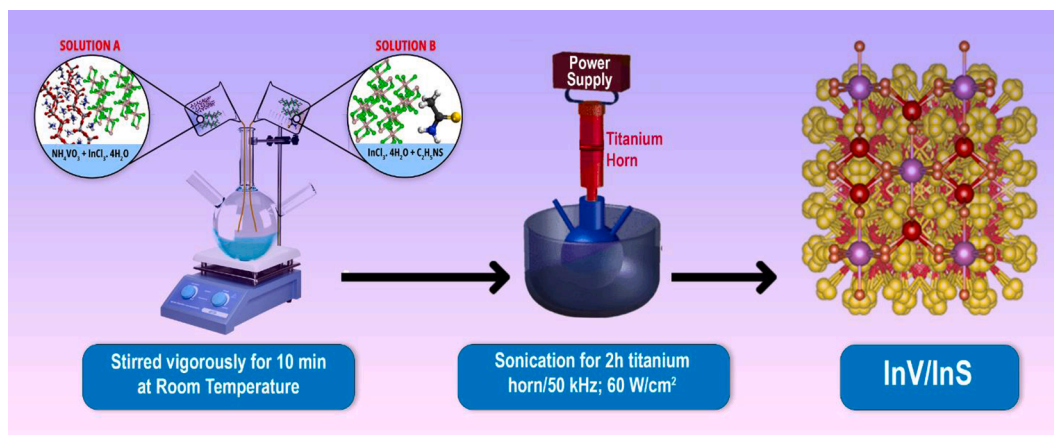
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<https://doi.org/10.1016/j.ultsonch.2023.106615>

Received 21 June 2023; Received in revised form 19 September 2023; Accepted 22 September 2023

Available online 23 September 2023

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Scheme 1. Schematic representation of ultrasonic assisted synthesis of InV/InS.

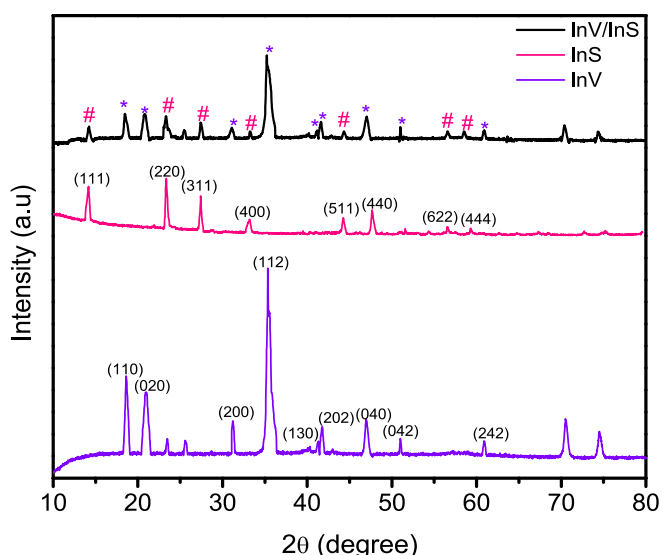


Fig. 1. The X-ray diffraction patterns of InV, InS, InV/InS.

limiting pesticide use [10]. [Scheme 1..](#)

Carbofuran [CBF: 2,3-dihydro-2,2-dimethyl-7-benzofuranyl Nmethyl carbamate] is a type of carbamate pesticide with ester and amide linkage considered to exhibit high toxicity. Because of its broad horizon for suppressing soil dwelling and leaf feeding insects, CBF is

often utilized in agriculture [11,12]. It is known to be quite stable in neutral or acidic soil and water habitats and is hazardous to mammals. CBF can cause mutagenic, cytotoxic, neurotoxic, endocrine-disrupting, dermal-skin, and embryo-toxic issues [13–15]. Additionally, it harms aquatics through acute and chronic toxicity, microbial biomass, and soil fertility. Diazinon (DZN: O,O-Diethyl O-[4-methyl-6-(propan-2-yl)pyrimidin-2-yl] phosphorothioate) is a organophosphate pesticide shows moderate toxicity compared to other highly toxic pesticides [16]. Because of their toxicity to birds and aquatic creatures, organophosphate pesticides are classified as bounded-use pesticides. The upper limit of DZN concentration in water is $0.6 \mu\text{g L}^{-1}$ [17,18]. This pesticide's residues spread to rivers, lakes, and seas by runoff brought on by rain due to the continuous and careless use of this herbicide in agricultural fields close to water sources, damaging these bodies of water. Exposure to DZN can cause cholinergic toxicity and damage to the skin and gastrointestinal tract [19]. Hence, treating pesticides and their residues is highly appreciated. Several reports are available in the literature for the treatment of CBF and DZN using techniques like adsorption, electrocoagulation, membrane technology, and photocatalysis [20–24]. Among all these, photocatalysis is a feasible and effective technique for the treatment of hazardous organic molecules since it not only removes pollutants but also mineralizes them into carbon dioxide and water [25–28]. The photocatalytic approach, which utilizes light for the initiation of redox reactions over semiconductors, still exhibits some disadvantages [29]. Acoustic cavitation is considered an advanced oxidation process (AOP) since the cavitation bubble that contains gas leads to the generation of radicals in the liquid phase have been exploited in environmental remediation for the degradation of contaminants in aqueous solutions [30–32]. In comparison to many other

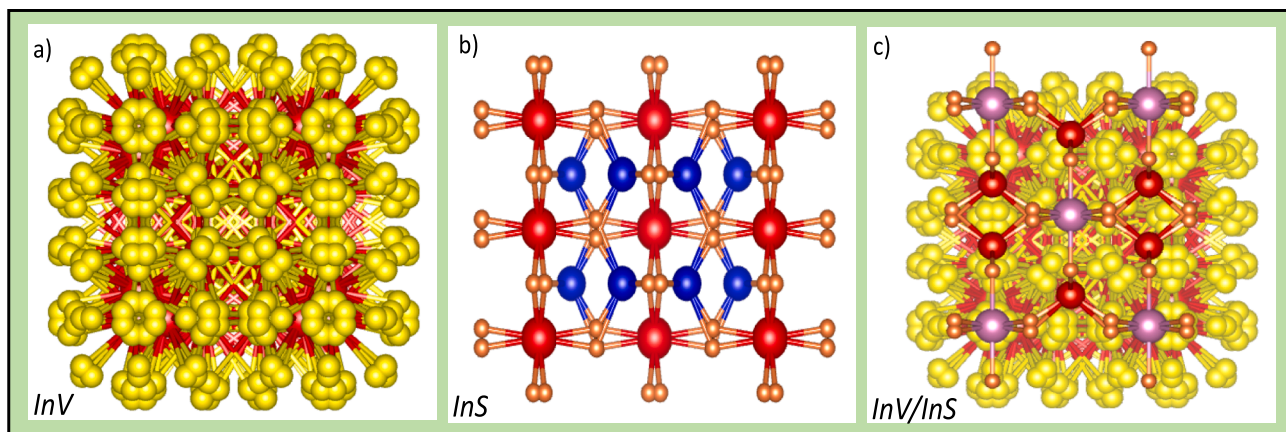


Fig. 2. Crystalline structures of a) InV, b) InS and c) InV/InS.

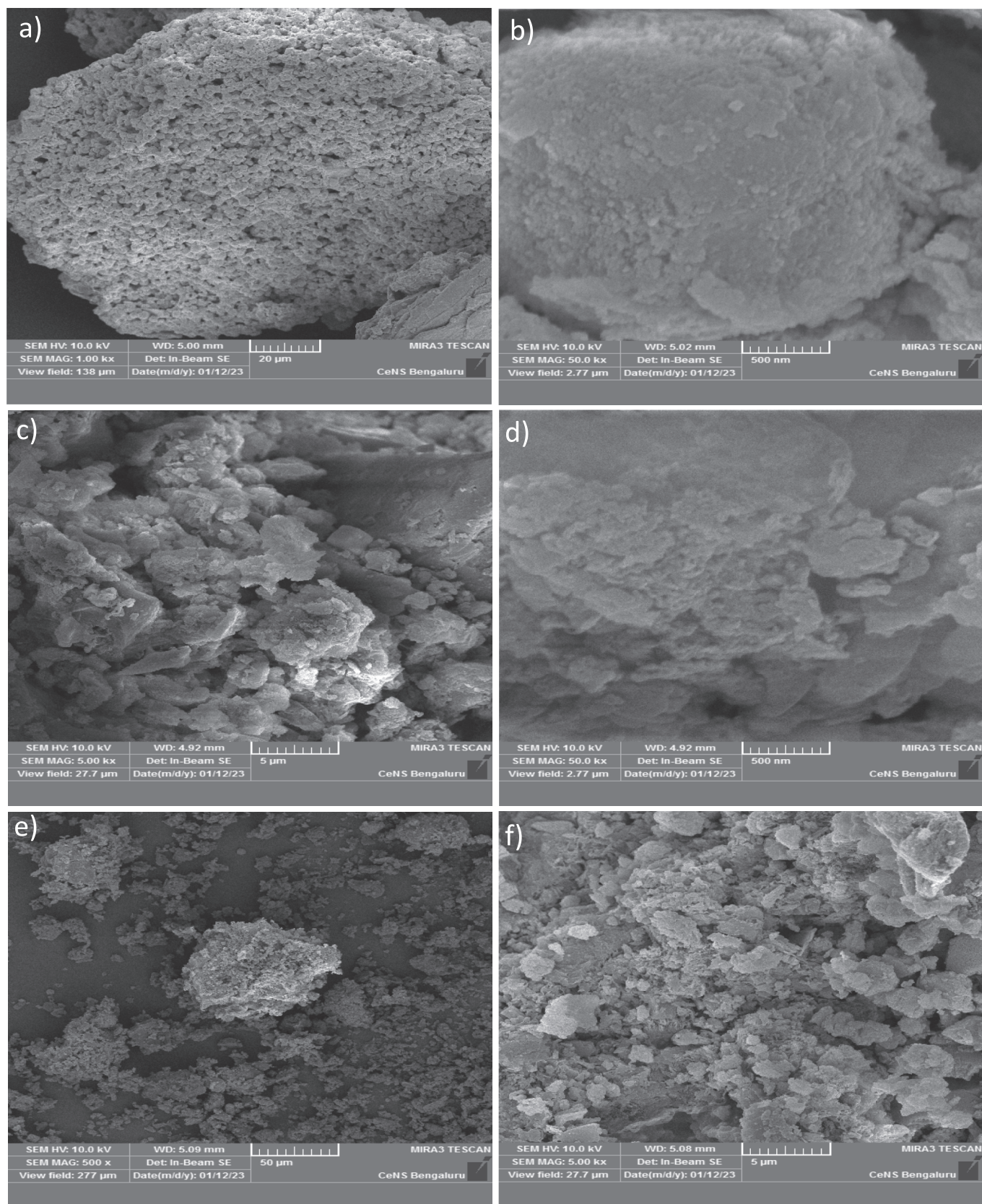


Fig. 3. SEM micrographs of a)&b) InV, c)&d) InS and e)&f) InV/InS.

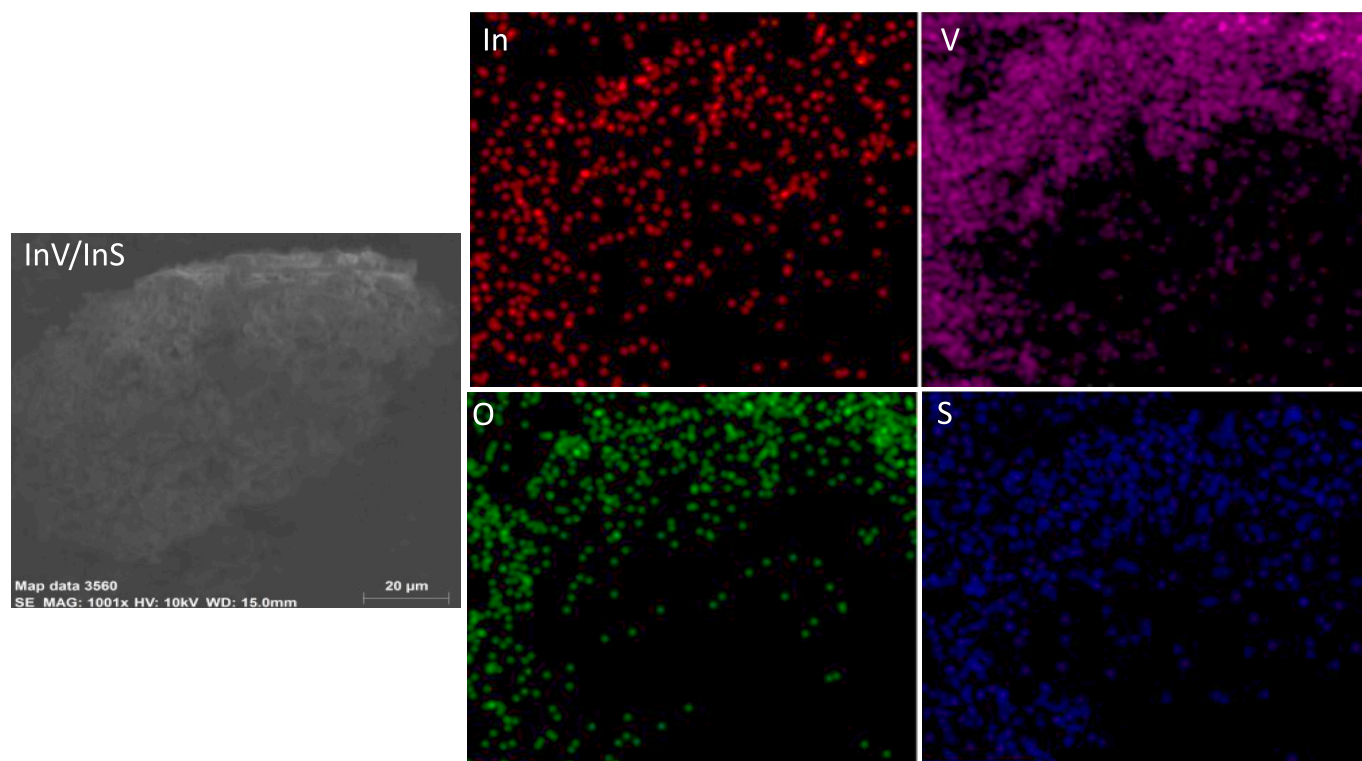


Fig. 4. EDS mapping of InV/InS and constituent, In, V, O and S.

approaches, the sonolysis method that uses ultrasound (US) waves to remediate pollution is has its own limitations. Combining the two processes, known as sonophotocatalysis, could overcome the drawbacks of both sonolysis and photocatalysis [33,34]. The synergistic advantages of a hybrid approach for sonophotocatalysis over separate methods are demonstrated in many reports [35,36].

InVO₄ is a narrow bandgap (~2.0 eV), stable and nontoxic metal vanadate extensively used for catalytic applications for CO₂ reduction, nitrogen fixation, hydrogen evolution, organic molecule degradation [37,38]. InV has strong stability and a small bandgap, but its effectiveness in photocatalytic applications needs to be increased. The main reason for moderate efficiency could be recombination of charge carriers during photocatalysis. Great effort has been devoted to improve the efficiency of InV through combining it with other metal oxides, metal-vanadates, carbonaceous material or any other semiconductor that forms nanocomposite or heterostructure [39–41]. In₂S₃ is a *n*-type metal sulfide with a bandgap 2.0–2.3 eV shows efficient absorption of light in the visible region. Due to narrow bandgap and good ability towards visible light assimilation, InS has been used in optoelectronic devices, water splitting reactions, CO₂ reduction and other photocatalytic applications [42–44]. The edge potentials of InS demonstrate its propensity to build heterostructures with other semiconductors with narrow bandgaps [45]. As a result, there are numerous studies in the literature that combine InS with other visible-light active materials. Due to proper charge carrier separation through the interface, type-II is regarded as the most competent fabrication method among the three types of heterostructures.

InV and InS has been synthesized using hydrothermal, sol-gel and precipitation methods [46,47]. These techniques are widely employed and have been shown to be effective; however, high thermal treatment, several steps, and agglomeration in structures must be taken into consideration. It has been discovered that ultrasonic synthesis of semiconductors is more affordable and unique compared to conventional thermal procedures in terms of quick reaction times without sacrificing structure, particle size, or crystallinity [48–50]. The US synthesis uses

bubbles that form quickly, collapse, and then produce a huge quantity of energy quickly. The semiconductors created in a sonicated solution have diverse properties thanks to the intense heat and quick cooling. Yuan *et al.*, fabricated In₂S₃/InVO₄ heterojunction through in-situ anion-exchange by using Na₂S and pre-synthesized InVO₄. The In₂S₃/InVO₄ heterojunction has been used as photocatalytic degradation of tetracycline [51].

By considering the above discussions, the authors made an attempt to fabricate the InVO₄/In₂S₃ heterostructure through ultrasonic synthesis. It has been investigated for the structural, morphological, and electrochemical characterizations of synthesized InV, InS, and InV/InS heterostructure. All three synthesized materials were subjected to photocatalytic degradation of CBF and DZN pesticides. Various parameters that affect the degradation, pH, pesticide concentration, amount of catalyst, acoustic intensity and ultrasound power were carefully optimized. The effect various anions on the degradation has been evaluated. Based on the results of LC-MS and ESR studies, detailed mechanism of sonophotocatalysis has been discussed. The current study provides insight into the effective production of stable heterostructures using ultrasonic waves as well as the increased breakdown of dangerous pesticides into less hazardous end products.

2. Experimental

2.1. Materials

InCl₃·4H₂O, NH₄VO₃, HNO₃, C₂H₅NS, ethanol, triethanolamine, isopropanol, 1,4-benzoquinone, 5,5-Dimethyl-1-pyrroline-*N*-oxide, acetonitrile were purchased from Merck India Pvt Limited and used without any further pretreatment. Deionized (DI) water was used to prepare solutions.

2.2. Synthesis of InS, InV and InV/InS heterostructure

Sonochemical approach was chosen for the synthesis of InVO₄/In₂S₃

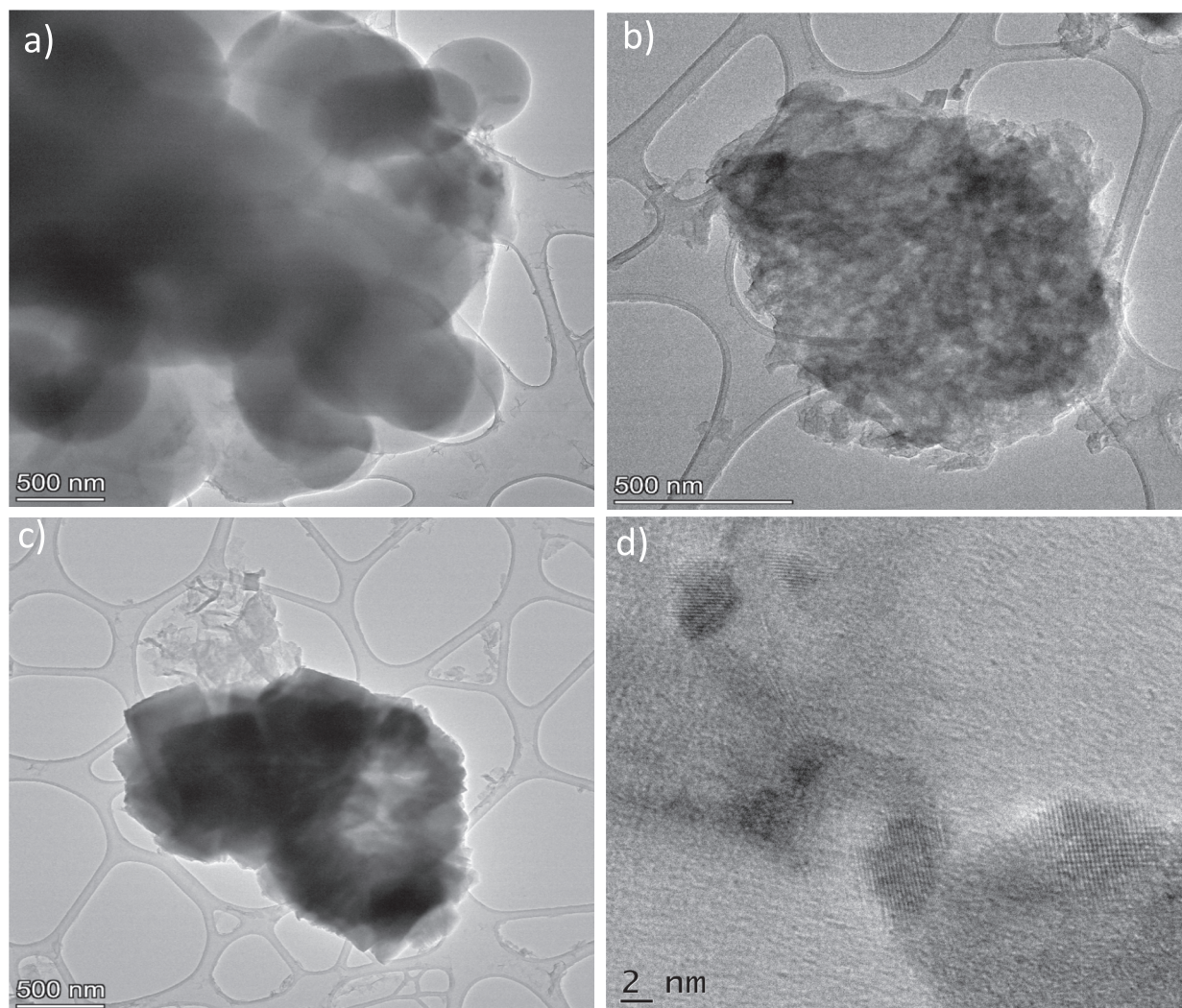


Fig. 5. TEM micrographs of a) InV, b) InS, c) InV/InS and HRTEM of InV/InS.

heterostructure. In a typical synthesis, 100 mL of distilled water was used to dissolve an equal volume of $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ and NH_4VO_3 , and then 5 % HNO_3 was slowly added while the mixture was vigorously stirred. The obtained suspension was named as “solution A” for convenience. Solution B was prepared by dissolving an equal amount of $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ and $\text{C}_2\text{H}_5\text{NS}$ in distilled water. After that, solution A and B were mixed in a 250 mL beaker and stirred vigorously for 10 min using a magnetic stirrer. For the next two hours, the reaction mixture was exposed to ultrasonic irradiation at room temperature in air using a high-intensity ultrasonic probe (Xinzhi Co. model: JY92-2D, titanium horn/20 kHz; 60 W/cm^2). The precipitate thus obtained was collected by centrifugation and then washed three times with double-distilled water and ethanol. After that, the precipitate was dried in an oven at 60°C . Pure InVO_4 and In_2S_3 were also synthesized using the aforementioned method, and solutions A and B were made independently for use in controlled studies.

2.3. Sonophotocatalytic degradation of pesticides

A CBF and DZN standard stock solution of concentration 0.5 mmol/L (100 mg L^{-1}) was prepared, kept in the refrigerator, and used as per requirement. In a 250-mL quartz vessel, 200 mL of 10 mg L^{-1} CBF and DZN solutions were taken for degradation studies. Once the pH of the solution was adjusted, the required amount of catalyst was added to the quartz vessel. A Xe lamp of 300 W with 6170 lm and a mercury vapor

lamp of 250 W (12250 lm) were used as visible and UV light sources, respectively. The light source was placed just outside the vessel. Under this condition, the solution was allowed to attain adsorption/desorption equilibrium for 30 min in the absence of light. The samples were illuminated with light, collected at an interval of 10 min, and centrifuged for 5 min at 8000 rpm. Then the absorbance of the catalyst-free solution was measured using a UV–visible spectrophotometer. Eq (1) was used to get the.

$$\% \text{degradation} = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

percent degradation of CBF and DZN. Where, C_0 and C are initial and final concentrations of the CBF/DZN, respectively. For sonophotocatalysis an ultrasonic probe in the Xinzhi Co. model: JY92-2D with a titanium horn was used as a source for US sound waves. The reaction conditions were optimized for pH 3–10, 10–40 mg catalysts, initial concentration of the CBF and DZN, a US frequency of 20–1142 kHz, and a US power of 20–120 W. The probe was placed at the center of the quartz vessel at a distance of 3 cm from the bottom. Later, the above mentioned procedure was followed and measured the absorbance of CBF and DZN and estimated the % degradation.

2.4. Characterization

X-ray diffraction studies were conducted to understand the structural

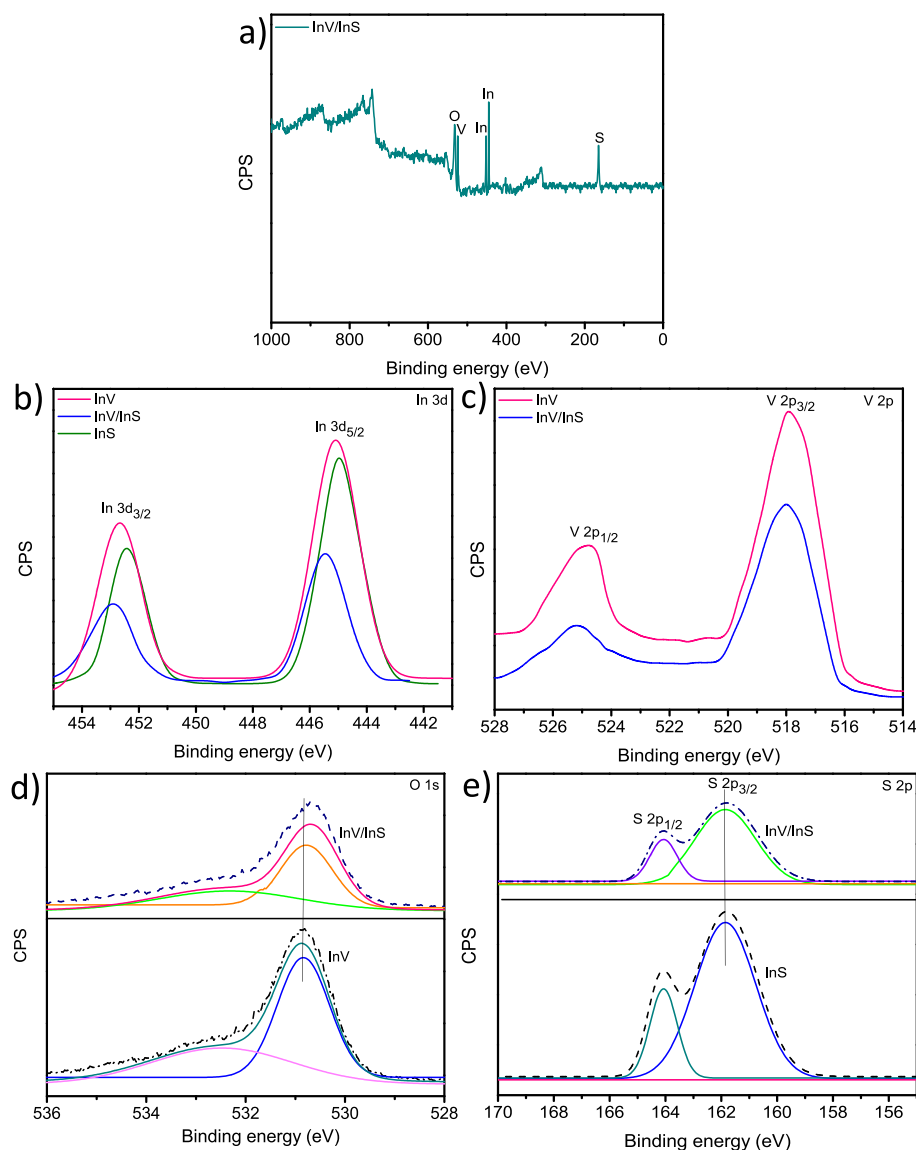


Fig. 6. XPS spectrum of InV/InS, a) Survey spectrum, b) In 3d, c) V 2p, d) O 1 s and e) S 2p.

characteristics of the synthesized materials using Bruker D2 Phaser XRD equipment with Cu-K α radiation. SEM and FESEM energy-dispersive X-ray spectrometer (EDX) images were recorded using a JEOL JSM 840A with a 5 kV acceleration voltage. TEM images were recorded in JEOL/JEM 2100 at an acceleration voltage of 200 kV. The Shimadzu UV-1600 model was used to record the absorbance of prepared samples (UV-DRS) and degradation studies of pesticide solutions. A photoluminescence study was conducted in the RF-6000 spectrofluorometer. A fusion UV/persulfate Total Organic Carbon (TOC) analyzer (Teledyne Tekmar, USA) was used for TOC removal studies. The photoelectrochemical characterization of the synthesized materials was evaluated using a CHI 660 D electrochemical workstation. The unit consists of a three-electrode system where Ag/AgCl and Pt wire are the reference and counter electrodes, respectively. A working electrode was fabricated using 10 mg of the material and subjected to sonication in Nafion solution (0.5 %). From the suspension, 20 μ L was dropcasted, dried in the oven, and used for photocurrent, electrochemical impedance, and Mott-Schottky studies.

2.5. CBF and DZN degradation intermediate analysis

The sonophotocatalytic degradation intermediates of CBF and DZN

were analyzed using a Perkin-Elmer Sciex API 365 LC/MS/ System. A Millipore syringe filter (0.22 μ m) was used to filter the samples. Atlantis C18 column (50 $\times$ 4.6 mm-5 μ m) was used in LC-MS analysis and the silica was used as stationary phase. The acetonitrile:water (80/20; v/v) mixture was used as mobile phase. The elution flow rate was 0.7 mL min⁻¹, and the injection volume used was 20 μ L. The column eluent was made to pass through the UV-visible diode array detector and the mass analyzer. Mass spectral analysis was performed in the mass range of 0 to 500 m/z and in positive ion mode.

3. Results and discussion

Through XRD analysis, we were able to study the phase compositions and crystal characteristics of the as-prepared samples (Fig. 1). Crystal planes (110), (020), (200), (112), (130), (202), (040), (042), and (242) of pure InV are completely indexed to the orthorhombic structure with the JCPDS: 48-0898, and the characteristic peak at 2 θ 18.6, 20.9, 31.2, 35.3, 41.3, 41.8, 46.9, 51.0 and 60.9° is seen [52]. The sharp and strong diffraction peaks indicate the crystalline nature of the sample. While the XRD image of InS shows the peaks at 2 θ 14.24, 23.32, 27.41, 33.21, 44.06, 47.71, 56.61 and 59.3° correspond to the (111), (220), (311), (400), (511), (440), (622), and (444) planes. In accordance

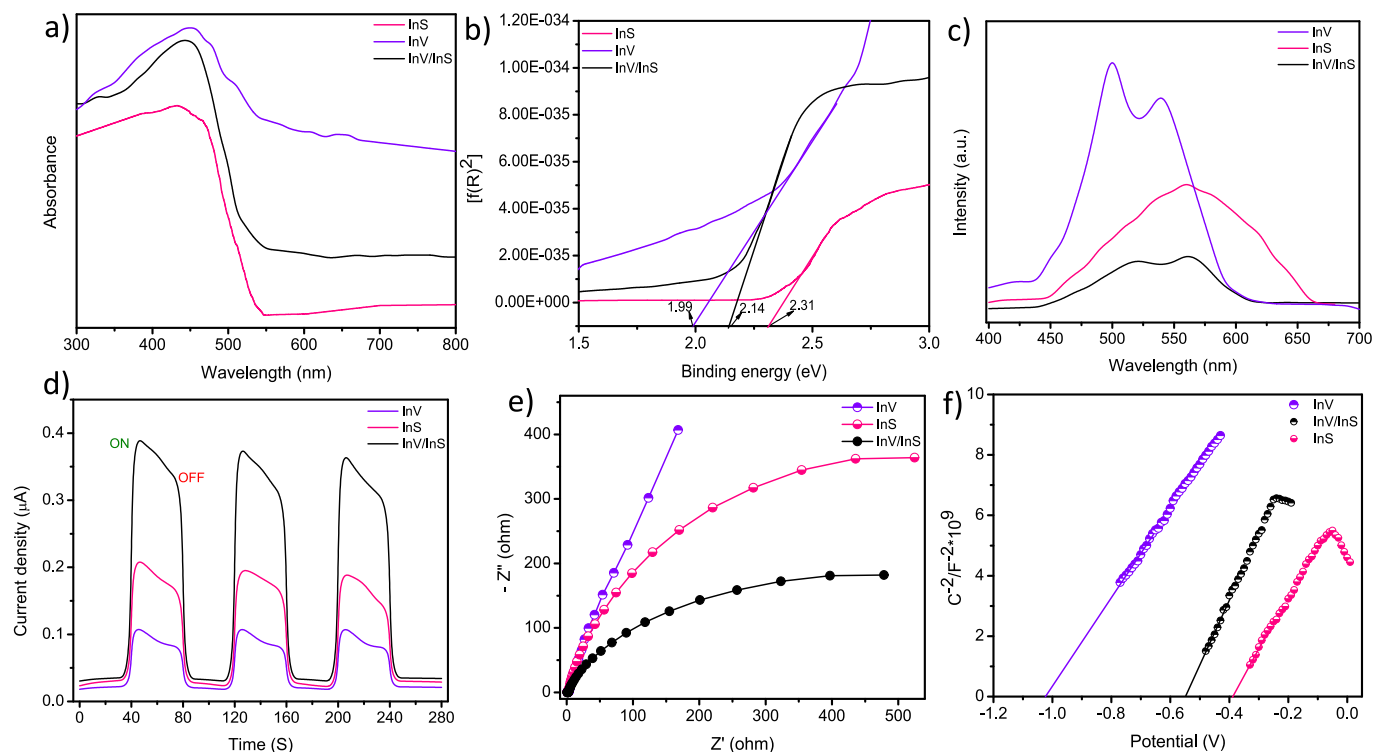


Fig. 7. InV, InS and InV/InS's a) UV-Vis spectra b) Kubelka-Munk curves c) PL studies d) Photocurrent response e) EIS studies f) Mott-Schottky plot.

with the reference standard, JCPDS No. 65-0459, all peaks were detected, and the sample possesses a cubic crystal structure [53]. The small size effect and weak crystalline nature likely contributed to lower intensity and a wider peak width in the XRD patterns when compared to InV. Furthermore, a series of distinctive peaks can be seen in the XRD patterns of InV/InS, suggesting the orthorhombic phase of InV and the cubic phase of InS. This means that pure InV and InS can couple efficiently. The absence of contaminants and the successful interaction of the constituent materials may be seen in the strong crystallinity of the binary composite, as evidenced by the decreasing peak intensities of InS with its loading.

Using the VESTA program, the crystal structures of the orthorhombic InV and cubic InS systems were rendered in polyhedral representation (Fig. 2) to illustrate the coordination number associated with the structural transitions. Fig. 2a demonstrates that the orthorhombic phase crystal structure consists of InO_6 octahedra and VO_4 tetrahedra, with a V-O atomic distance of around 1.63 Å. Likewise, the In-O distance was 1.98 Å and the O-In distance was 2.04 Å. Six tetrahedron vertices and two octahedron edges join the InO_6 octahedron together. When InS crystallizes, it forms a deformed mixture of corner and edge-sharing cubic structures due to the presence of two inequivalent In^{3+} sites (Fig. 2b); the first In^{3+} site is bound to six equivalent S_2 atoms. The second In^{3+} site is a mixed corner and edge-sharing InS cubic, with In^{3+} linked to six comparable S_2 atoms. In-S-In bond angles in a shared corner are 101.25°, and S-In-S bond angles are 72.21°. In-S bond length is in a range of 2.14–2.23°. The potential crystal structure of the InV/InS heterostructure material is depicted in Fig. 2c. This demonstrates that InS is firmly fixed to the uneven InV surface and also suggests that InS is positioned in the cavities of the InV crystals. The above-explained results are in accordance with the experimental XRD and EDX results.

SEM images of pure InV, InS, and InV/InS are displayed in Fig. 3. SEM images of pure InV (Fig. 3a and b) reveal that the material is composed of spherical, well-separated particles and small void spaces that are kept fairly isolated from one another. The particles tend to aggregate and self-assemble into larger particles. Fig. 3c and d show that the InS sample is composed of irregularly shaped particles with sizes

smaller than 50 nm and a wavy flake-like structure, with agglomerations found distributed over the flakes surfaces. The formation of InV/InS heterostructure is depicted by discrete morphological changes in SEM micrographs (Fig. 3e and f). The micrographs clearly display a flake-like structure, and smaller spherical particles may also be seen. Pinecone-shaped particles are generated upon the formation of composites with moderately dense, porous, and rough surfaces. This morphological dissimilarity further proves the existence of probable heterostructure. EDS mapping was also used to study the phase composition of InV/InS as shown in Fig. 4. It shows the presence of In, V, O, and S which are distributed uniformly without any other impurities. In the TEM image, the irregular spherical structure of InV (Fig. 5a) and flake-like structure of InS (Fig. 5b) are confirmed. For the InV/InS, interlaced flakes are prevalent, along with the presence of thinly irregular spherical particles as observed in Fig. 5c. The HRTEM image (Fig. 5d) reveals the shape and additional phase information of the InV/InS heterostructure. Interfringe spacings of 0.26 and 0.28 nm are observed, which are consistent with the (222) and (400) crystal structures of InV and InS, respectively.

In order to determine the precise surface composition and bonding nature of the samples, an X-ray photoelectron spectrometer (XPS) analysis was performed. The survey spectra (Fig. 6a) shows the presence of In, V, O, and S which is in accordance with the EDS mapping. Matching closely with the XPS results of pure InV, two characteristic peaks at 452.65 and 445.12 eV may be assigned to $\text{In } 3d_{3/2}$ and $\text{In } 3d_{5/2}$ of In^{3+} in the 3d XPS spectrum (Fig. 6b). In contrast, the InV/InS displays a distinct shift toward higher binding energy of In 3d to 452.82 and 445.44 eV belongs to $\text{In } 3d_{3/2}$ and $\text{In } 3d_{5/2}$, respectively. It confirms that electrons flow from InV to InS, generating an electric field within the contact that points in the same direction. The creation of an internal electric field at the interface would be heavily influenced by electron migrate on and the related electric field. The creation of heterostructure greatly influences electron migration hence expected to exhibit enhanced photocatalytic activity. The binding energy shifts are greatly sensitive to the changes in electron density after the formation of heterostructure and reveals the direction of electron migration. The work function difference between InV and InS heterojunction leads to electron

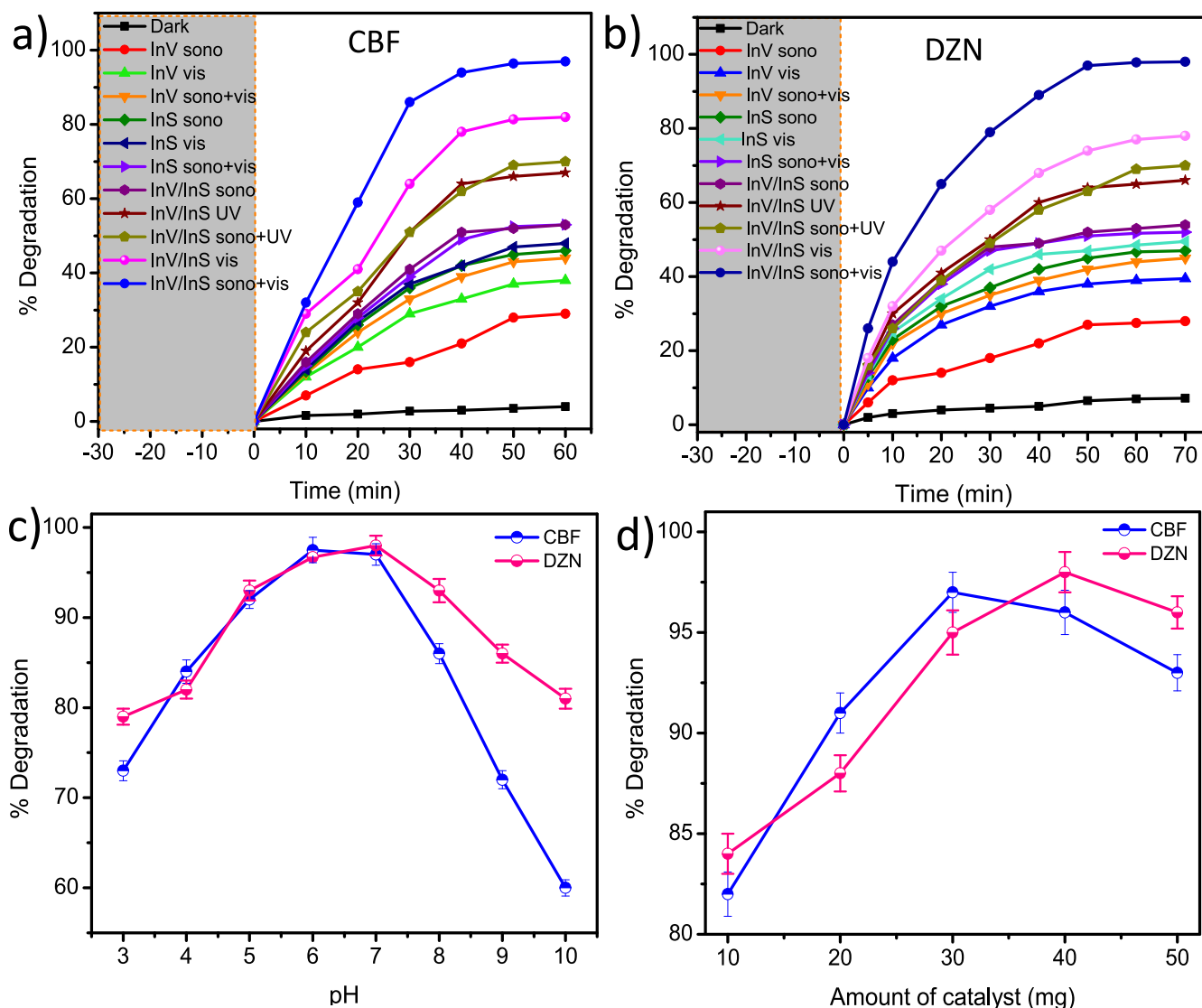


Fig. 8. A) degradation of cbf b) degradation dzn c) effect of ph d) effect of amount of catalyst

Table 1

Degradation of CBF and DZN under different conditions.

Material	Condition	CBF Degradation, % (60 min)*	DZN Degradation, % (70 min)*
InV	Dark	04	07
	Ultrasound	29	28
	Visible light	38	39
	Sono + visible	44	45
InS	Ultrasound	45	47
	Visible light	48	50
	Sono + visible	53	52
InV/InS	Ultrasound	53	54
	UV light	67	66
	Sono + UV	70	70
	Visible light	82	78
	Sono + visible	97	98

*n = Triplicates.

density rearrangement at the interface and results in an induced electric field which separates photoexcited electrons and holes. Fig. 6c shows a spectrum of vanadium V 2p, which shows a doublet peak at 517.86 eV for V 2p_{3/2} and 524.67 eV for V 2p_{1/2} for the V⁵⁺ oxidation state for InV. The V 2p peaks shift to higher binding energy in InV/InS. The O 1s spectra of InV have two peaks at 530.84 and 532.75 eV (Fig. 6d). Again a slight shift to lower binding energy in InV/InS. The S coordinated to In exhibit doublet peaks at 161.85 eV (S 2p_{3/2}) and 164.04 eV (S 2p_{1/2}) it is observed to shift slightly to lower binding energy in InV/InS as observed in Fig. 6e. The XPS results show deviation in the respective peaks of the pure and combined form with varied intensities demonstrating the success of the heterojunction between the two materials.

3.1. Optical/electrochemical characterization

The efficiency of the material towards photocatalysis depends mainly on its light absorption wavelength, bandgap etc. UV-diffusion reflectance spectroscopic (UV-DRS) analysis was performed for all three synthesized materials and is given in Fig. 7a. InS shows the absorption edge at around 525 nm, and InV exhibits the absorption edge at around 580 nm. When both materials were combined, there was a blue shift (w.r.t. InV) as well as a red shift (w.r.t. InS), which showed the absorption edge up to 560 nm. The shift in the absorption observed in

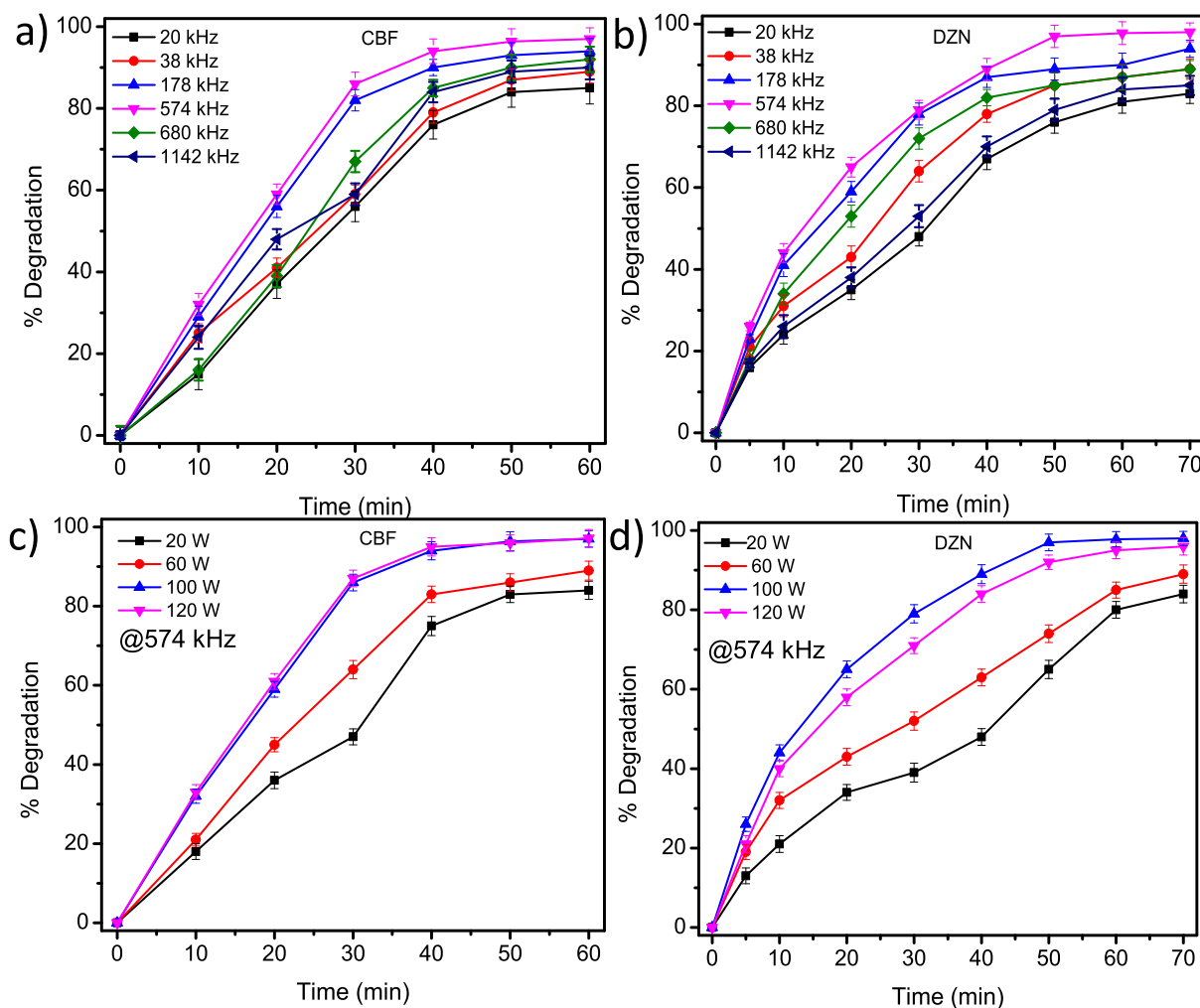


Fig. 9. Effect of acoustic intensity on a) CBF degradation b) DZN degradation c) Effect of US power on CBF degradation d) Effect of US power on DZN degradation.

Table 2

Degradation of CBF and DZN in presence of InV/InS under different ultrasonic frequency and power.

Frequency, kHz	CBF Degradation, %*	DZN Degradation, %*
20	85	83
38	89	85
178	90	89
574	97	98
680	94	94
1142	92	90
US Power, W		
20	84	86
60	89	91
100	97	98
120	97.2	96

*n = Triplicates.

InV/InS shows the combination of two visible active materials. The corresponding Tauc-plot is given in Fig. 7b. The bandgap of InV, InS and InV/InS is found to be 1.99, 2.31 and 2.14 eV, respectively. The bandgap of InV/InS lies in between the bandgap of InV and InS speaks about the formation of heterostructure between them. The photoluminescence (PL) studies of the materials were conducted at the excited wavelength of 390 nm to understand the electron-hole separation ability. Fig. 7c shows the high PL intensity in InV and the emission between 490 and

540 nm. InS exhibits a broad emission spectrum at 560 nm with low PL intensity compared to InV. InV/InS heterostructure exhibit low PL intensity combined spectra of InV and InS with emission in the range of 510–550 nm. The high PL intensity observed in InV is expected to experience fast recombination of charge carriers. InV/InS heterostructure undergo quenching and exhibit much lower PL intensity than pristine InV and InS due to the efficient separation of photoexcited electrons and holes. Further photoelectrochemical studies were conducted to better understand the charge separation characteristics. Fig. 7d shows the photocurrent response of all three synthesized materials. InV, InS and InV/InS show the current response, which indicates their ability to absorb visible light. The current produced is in the order InV/InS > InS > InV in the presence of light. The current density developed by InV/InS and InS is 3.5 and 2 times higher than the current density possessed by InV. The enhanced current established by InV/InS speaks about the efficient separation of charge carriers compared to pure InS and InV. Electrochemical impedance spectroscopy (EIS) was also conducted to understand the charge transfer resistance at the electrode-electrolyte interface. Fig. 7e shows the Nyquist plot of InV, InS and InV/InS. The decreased semicircular nature of InV/InS shows the decreased charge transfer resistance compared to pristine InV and InS. The decreased charge-transfer resistance in InV/InS is due to the formation heterostructure between two visible active InV and InS. It is important to examine the conduction band and valence band edge potentials of the materials for better understanding the photocatalytic mechanism. Fig. 7f shows the Mott-Schottky (M–S) plot of InV, InS and

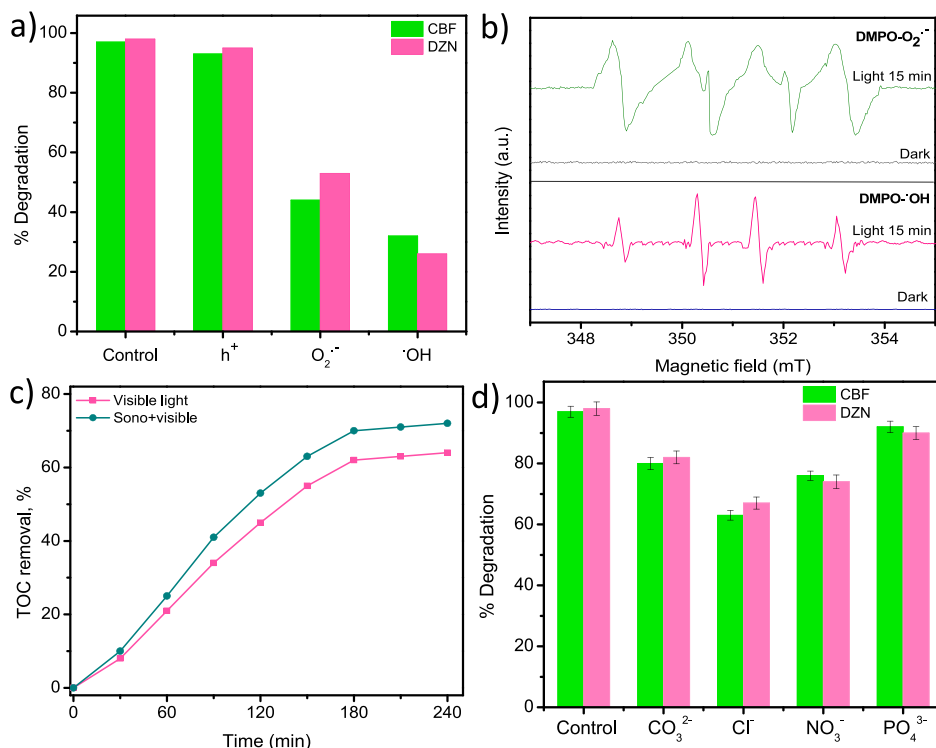
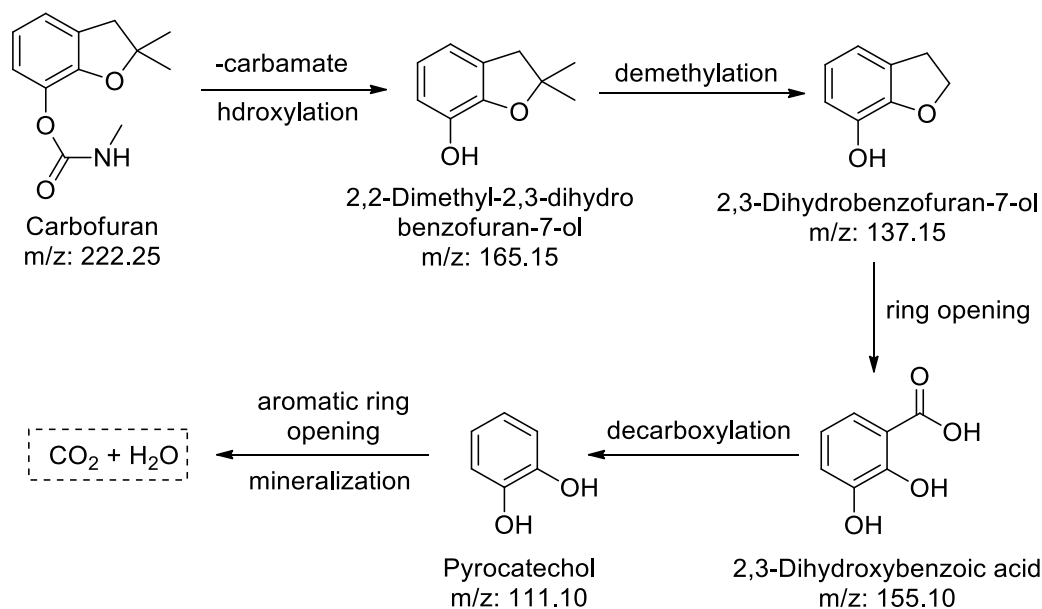


Fig. 10. A) scavenger studies b) esr studies c) toc removal d) effect of common anions on degradation.



Scheme 2. Proposed degradation pathway of CBF.

InV/InS. The nature of the M–S plot shows characteristics of an n-type semiconductor. The conduction band potential (E_{CB}) of InS, InV and InV/InS is -1.02 , -0.38 and -0.54 V, respectively. The E_{CB} of InV/InS lies in between the E_{CB} of pristine InV and InS. From these E_{CB} values and bandgap, one can easily find the valence band potential (E_{VB}) of all three photocatalysts. The E_{VB} of InS, InV and InV/InS is found to be 1.19, 1.51, and 1.50 eV, respectively.

3.2. Pesticide degradation studies

The optical characterization results indicate the ability of the synthesized materials to absorb light. This has led to further studies on the degradation of hazardous pesticides. Carbofuran and diazinon were the two pesticides used for degradation studies. The degradation profiles of CBF and DZN under different conditions are given in Fig. 8a and b. The degradation of CBF was subjected to sonocatalysis, photocatalysis and sonophotocatalysis. The results show negligible degradation under dark conditions. The nature of efficiency follows the order sonophotocatalysis

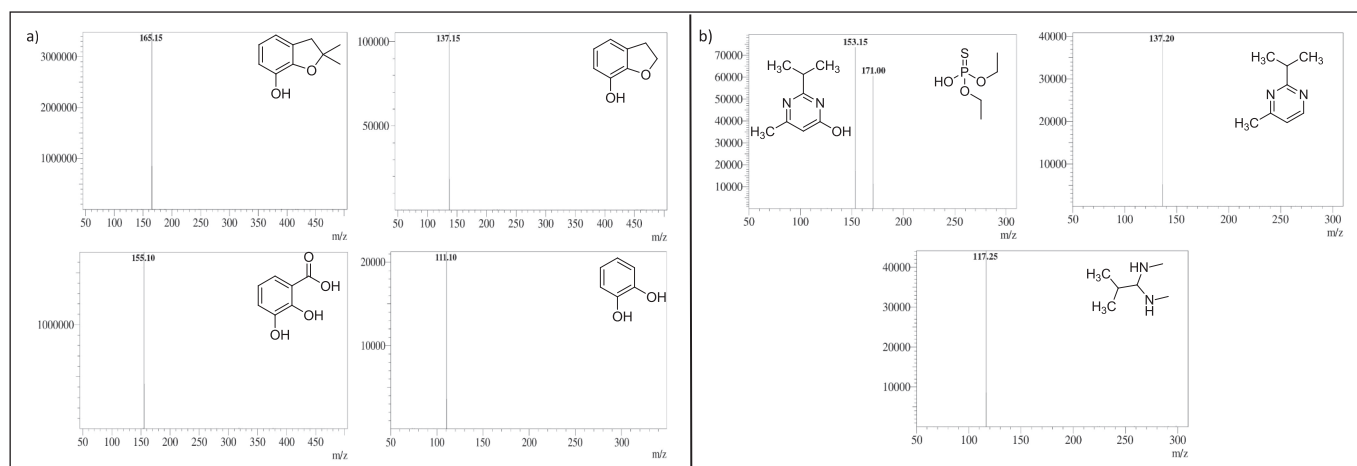
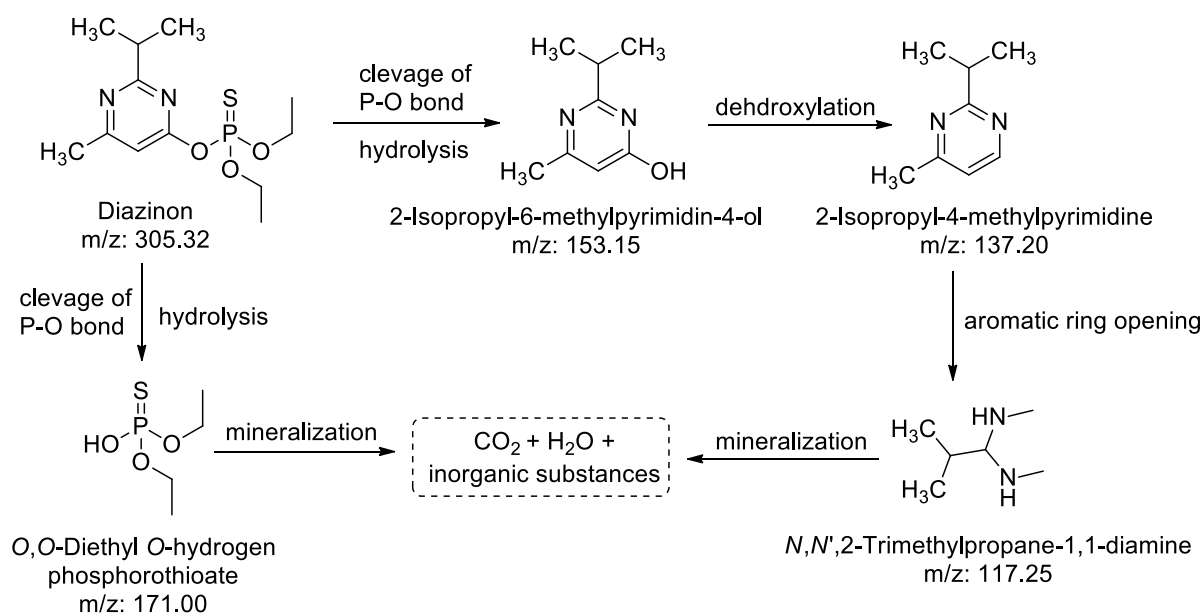


Fig. 11. LC-MS spectra of degradation intermediates a) CBF and b) DZN.



Scheme 3. Proposed degradation pathway of DZN.

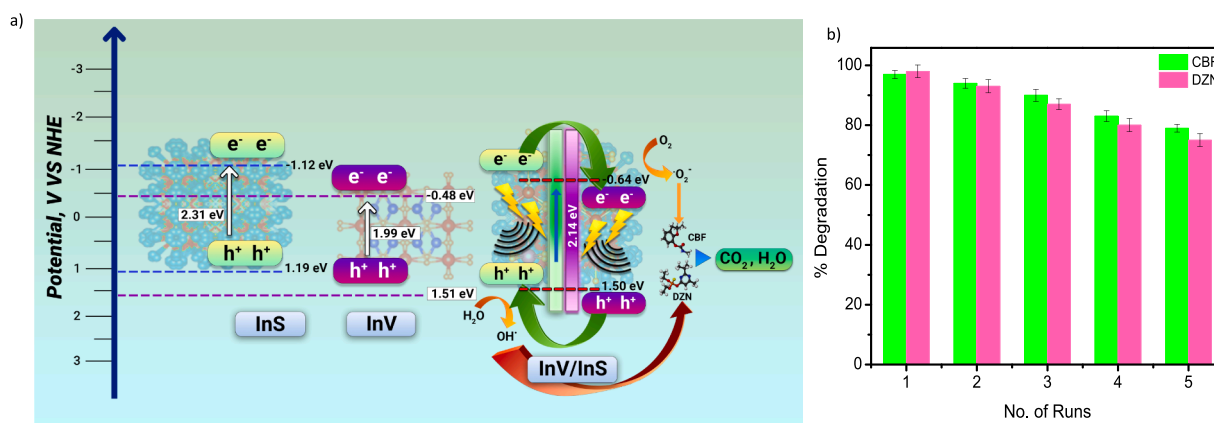


Fig. 12. A) photocatalytic mechanism b) reusability studies.

(visible) > sonophotocatalysis (UV) > photocatalysis > sonocatalysis towards degradation of CBF and DZN. Table 1 shows the detailed degradation percentages of CBF and DZN under different conditions. It was found that InV/InS showed enhanced activity compared to pristine InV and InS under all conditions. InV/InS found to degrade 82 and 78 % of CBF and DZN under visible light, respectively. This enhanced activity under visible light is observed due to the formation of heterostructure that results in efficient separation of charge carriers. Still, no degradation under visible light is observed, even after 60 min. Then enhanced degradation is observed in the presence of ultrasound and visible light, which are found to degrade 97 and 98 % of CBF and DZN, respectively. The enhanced activity could be attributed to the synergy between light and sound waves. The saturation towards the degradation of pesticides is observed under visible radiation due to the entrapment of the active areas on the surface of the catalyst. When energy is supplied to the system through ultrasound irradiation, it results in enhanced degradation of CBF and DZN. The ultrasound waves enhance the turbulence in the liquid, minimizing the mass transfer limitations and deagglomeration. The sonophotocatalytic degradation of organic molecules depends on the pH of the medium. So, the effect of pH has been studied by varying the pH of the medium from 3 to 10 (Fig. 8c). The degradation of both CBF and DZN is less at pH 3 and 4. After pH 6, both showed good degradation up to pH 8 and decreased degradation at pH 9 and above. CBF and DZN showed maximum degradation of 97 and 98 %, respectively, at pH 8. This could be attributed to the electrostatic force of attraction in slightly alkaline medium above pH 8 and below pH 8, where it experiences electrostatic repulsion. The amount of catalyst is another factor that needs to be optimized. Different amounts of InV/InS were added to CBF and DZN (pH 8, 10 mg L⁻¹ CBF and DZN, US frequency 574 kHz, US power of 100 W) and based on absorbance values, the degradation percentage is given in Fig. 8d. The maximum degradation is observed when 30 and 40 mg of InV/InS are used to degrade CBF and DZN. More catalysts showed decreased degradation due to the masking of the catalytically active surfaces of InV and InS. Since the maximum degradation is observed in the presence of US and visible light, it is essential to optimize the US parameters.

The effect of acoustic frequency on the sonophotocatalytic degradation of CBF and DZN has been examined and given in Fig. 9a and b. The degradation percentages of CBF and DZN are detailed in Table 1. The degradation of both CBF and DZN is to be linear with frequency up to 574 kHz. A detrimental effect is observed at higher frequencies (680 and 1142 kHz). The percentage degradation of CBF and DZN was found to be 97 and 98 %, respectively, at 574 kHz. At this frequency, the micro-sized bubbles form, grow, and collapse in a fraction of a second, thus releasing a high magnitude of energy. At this frequency (574 kHz), more time is available to form the bubble with high disintegration, which dissociates water and oxygen to generate free radicals. At higher frequencies, the lower dissociation of water and oxygen due to the shorter time to collapse leads to a lower generation of free radicals. Hence, 574 kHz is set as the optimum frequency for efficient degradation of CBF and DZN in the presence of InV/InS under visible light. Sonophotocatalytic degradation of organic molecules is also affected by ultrasound power. Fig. 9c and d show the effect of US power on the degradation of CBF and DZN, respectively. The results depicted in Table 2 indicate that the maximum degradation of CBF and DZN is observed at a US power of 100 W. The degradation of pesticides was found to increase with the increase in US power up to 100 W. High US power generates more active sites on the InV/InS catalyst and continuously cleans the catalyst surface. A negligible effect is observed at 120 W US power, and hence 100 W US power is found sufficient to collapse the bubbles and show maximum degradation of CBF and DZN through the generation of free radicals.

3.3. Scavenger, ESR, TOC removal and effect of anion studies

Photocatalytic degradation of organic molecules depends mainly on

the active species generated during the photoredox reaction in the presence of a photocatalyst. Scavenger studies were conducted to determine the major active species responsible for the photocatalytic degradation of dyes. 1 mM triethanolamine, isopropanol, and 1,4-benzoquinone were used as hole, hydroxyl radical, and superoxide radical anion scavengers, respectively. As shown in Fig. 10a, in the presence of triethanolamine, a negligible decline in degradation of both pesticides was observed. But in the presence of isopropanol and benzoquinone, a considerable decrease in the degradation of CBF and DZN is observed. This indicates superoxide radical anion and hydroxyl radicals are the major active species involved in the degradation of CBF and DZN in the presence of InV/InS and visible light. To further confirm the generation of superoxide radical anion and hydroxyl radicals, an ESR spin-trapping experiment was conducted. 5,5-Dimethyl-1-pyrroline-N-oxide (DMPO) was used as a probe that shows the ability to form detectable and stable free radicals. Fig. 10b shows the absence of peaks in both cases, but proper hyperfine and quartet peaks were observed due to the formation of hydroxyl and superoxide radicals. Under visible light, there are quartet peaks and hyperfine split peaks corresponding to $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$ radicals during photocatalysis. These peaks suggest further reduction of $\text{O}_2^{\cdot-} \gg \text{H}_2\text{O}_2 \gg \cdot\text{OH}$. The extent of degradation of organic molecules for practical applications mainly depends on effective mineralization. The effective mineralization of the pesticides is associated with the removal of total organic carbon (TOC). A fusion UV/persulfate TOC was evaluated under visible light and sonocatalytic conditions in presence of CBF. Fig. 10c shows that the TOC removal is higher under ultrasound and visible light (72 %) than visible light alone (64 %) in 240 min. These results indicate the effective generation of active species leads to the formation of hydroxyl radicals and finally mineralizes the hazardous pesticides into less harmful final products. Usually, water contains a variety of anions, which could affect the degradation of organic molecules since they act as radical scavengers. 10 mM solutions of inorganic Cl^- , CO_3^{2-} , NO_3^- , and PO_4^{3-} were added to the pesticide solutions and examined for the degradation of CBF and DZN under optimal conditions in the presence of InV/InS and results are given in Fig. 10d. The degradation efficiency of CBF and DZN both declined in the presence of anions. In the presence of Cl^- the degradation of CBF and DZN was found to be 63 and 67 %, respectively. The presence of chloride ions greatly affects degradation due to the blockage of surface active sites of catalysts and the consumption of active species. On the other hand, the quenching effect of CO_3^{2-} and NO_3^- on hydroxyl radicals leads to the generation of free radicals in nitrate and carbonate through electron transfer reactions. Due to the lower adsorption ability of PO_4^{3-} ions on the surface of InV/InS, the degradation of CBF and DZN does not affect them much. These results indicate the involvement of radicals in the effective degradation of pesticides.

3.4. Degradation pathway of carbofuran

The degradation pathway of CBF in the presence of visible light and InV/InS has been predicted based on the experimental findings (Scheme 2). LC-MS was employed to identify the intermediate compounds generated during the sonophotocatalytic degradation of CBF. According to LC-MS analysis, the cleavage of the carbamate group from the parent carbofuran yields 2,2-dimethyl-2,3-dihydrobenzofuran-7-ol, which has a peak at m/z 165.15 (Fig. 11a) [54]. Then, 2,3-dihydrobenzofuran-7-ol (m/z : 137.15) was produced through demethylation of 2,2-dimethyl-2,3-dihydrobenzofuran-7-ol. The 2,3-dihydrobenzofuran-7-ol underwent ring opening, leading to the formation of 2,3-dihydroxybenzoic acid (m/z : 155.10), from which further decarboxylation produces pyrocatechol (m/z : 111.10). Finally, pyrocatechol undergoes hydrolysis into smaller aliphatic acids, followed by mineralization into carbon dioxide and water.

3.5. Degradation pathway of diazinon

The proposed degradation route of DZN was formulated on the basis of the findings of the LC-MS analysis. Scheme 3 presents a suggested breakdown of DZN through sonophotocatalysis in the presence of InV/InS. Fig. 11b illustrates the mass spectra of the intermediates. The formation of 2-isopropyl-6-methylpyrimidin-4-ol (m/z : 153.15) and O,O-diethyl O-hydrogen phosphorothioate (m/z : 171.00) is initiated by the cleavage of the P-O (pyrimidine group) bond in DZN, which is then followed by hydrolysis. After that, 2-isopropyl-6-methylpyrimidin-4-ol undergoes hydroxylation and forms 2-isopropyl-4-methylpyrimidine (m/z = 137.20). Later, 2-isopropyl-4-methylpyrimidine undergoes aromatic ring opening, resulting in the production of N,N',2-trimethylpropane-1,1-diamine (m/z : 117.25). Finally, the intermediates O,O-diethyl O-hydrogen phosphorothioate and N,N',2-trimethylpropane-1,1-diamine undergo complete mineralization, which results in the creation of low molecular weight molecules such as carbon dioxide, water, and other inorganic substances.

3.6. Mechanism of sonophotocatalysis

A mechanism of sonophotocatalytic degradation of CBF and DZN has been predicted based on the optical and electrochemical results. Since the M-S plot results show the n -type semiconductor nature of all three materials, it is advised to add + 0.1 V to the obtained values as shown in Fig. 12a. The efficiency of InV and InS towards degradation of CBF and DZN was found to be lower due to recombination of electrons and holes. Enhanced degradation of CBF and DZN is observed when InV and InS are combined through heterostructure. The shift in the edge potential and formation of heterostructure through the interface between InV and InS in InV/InS significantly enhances the degradation of CBF and DZN. In addition, the degradation is boosted by ultrasound waves, which create a good amount of energy and form free radicals. When InV/InS is illuminated with visible light and subjected to ultrasonication, the electrons in the valence band (VB) of InV get excited and reach the conduction band (CB). The recombination of the excited electrons was not allowed due to the transfer of electrons from the CB of InV to the CB of InS through the interface. The electrons accumulated in the CB of InS are readily available for the reduction of dissolved oxygen and form superoxide radicals. These superoxide radicals form hydroxyl radicals in aqueous media and attack the CBF and DZN. On the other hand, the holes on the VB of InV undergo extensive oxidation and form hydroxyl radicals, which in turn degrade CBF and DZN. Hydroxyl radicals undergo the breakdown of CBF and DZN as shown in Schemes 2 and 3, and finally form the less hazardous carbon dioxide and water. In addition, US irradiation aids in simulated water sonolysis and also help in generation of electrons and holes by the InV/InS through the supply of electrons located in VB. In presence of light and US, synergistic effect on the formation of electrons and Second, UV irradiation had a synergetic effect on the induction rate of electrons and improved generation of charge carriers. Due to superior charge carrier mobility the suppression of e^-/h^+ + recombination and extend the lifetime of charge carriers. The formation of heterostructure through the interface helps for the separation of charge carriers and effectively mineralizes CBF and DZN with the aid of ultrasound waves. Ultrasound waves boost the degradation of CBF and DZN through the formation of energy and the generation of free radicals in an aqueous medium. The enhanced degradation of CBF and DZN was achieved in the heterostructure of InV/InS through the formation of superoxide and hydroxyl radicals and ultrasonication. The practicable applicability of any photocatalyst depends on its reusability. The stability studies of the InV/InS heterostructure indicate good stability up to three cycles, which was found to decrease at the fourth and fifth cycles (Fig. 12b). Still, even after five cycles, InV/InS found to degrade 79 and 75 % of CBF and DZN, respectively.

4. Conclusions

A simple and efficient ultrasonic assisted synthetic approach has been well developed for the fabrication of InV, InS, and InV/InS heterostructure. The computational study of the structure of the synthesized materials using the VESTA program gives the nature of bond angles and bond lengths between atoms. The morphological dissimilarity and HRTEM proved the existence of heterostructure between InV and InS. The reaction conditions like pH 8, 30 (CBF) and 40 (DZN) mg catalyst, 574 kHz US intensity, 100 W ultrasound power, and visible light with sonication were found to be optimum for enhanced degradation. The InV/InS heterostructure also showed its ability to mineralize CBF and DZN. The Cl^- considerably decreased the degradation efficiency. Scavenger studies and ESR results show the formation of superoxide radical anion and hydroxyl radical during photocatalytic degradation. The LC-MS results of the degradation pathway have been well utilized in predicting the mechanism of photocatalysis. The good stability, efficiency of InV/InS indicate their versatile nature for future applications.

CRedit authorship contribution statement

K. Yogesh Kumar: Investigation, Methodology, Writing – review & editing. **M.K. Prashanth:** Methodology, Writing – review & editing. **H. Shanavaz:** Methodology. **L. Parashuram:** Data curation. **Fahd Alharethy:** Data curation, Resources. **Byong-Hun Jeon:** Formal analysis, Resources. **M.S. Raghu:** Conceptualization, Methodology, Writing – review & editing, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgement

The authors are immensely elated and wish to express their indebted gratitude to the Management of NHCE, BNMIT and Jain University for providing lab facilities to carry out this work. Authors extend their sincere appreciation to the Researchers Supporting Project Number (RSP2023R160), King Saud University, Riyadh, Saudi Arabia for the Support. This work was funded by the Korea Institute of Energy Technology Evaluation and Planning (KETEP) of the Republic of Korea (RS-2023-00255939).

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