Synthesis and Performance Analysis of Photocatalytic Activity of ZnIn$_2$S$_4$ Microspheres Synthesized Using a Low-Temperature Method

Mohammad Imran, Waseem Ashraf, Aurangzeb Khurram Hafiz, and Manika Khanuja*

ABSTRACT: In this paper, we report the synthesis of zinc indium sulfide (ZnIn$_2$S$_4$) microspheres synthesized via a low-temperature route, and the as-synthesized material was used for photocatalytic degradation of malachite green (MG), methyl orange (MO), and Direct Red 80 (DR-80) dyes. The as-synthesized material was characterized by powder X-ray diffraction and field-emission scanning electron microscopy for studying the crystal structure and surface morphology, respectively. Fourier transform infrared spectroscopy was performed to determine the functional groups attached. UV−Visible absorption spectrometry was done for light absorbance and band gap analysis, and Mott−Schottky analysis was performed to determine the nature and flat band potential of the material. A scavenger study was performed to analyze the active species taking part in the degradation process. The reusability of the material was tested up to four cycles to check the reduction in efficiency after each cycle. A time-correlated single-photon counting study was performed to observe the average lifetime of generated excitons during photocatalysis. It was found that the as-synthesized porous sample is more efficient in degrading the cationic dye than anionic dyes, which is further explained in the article.

INTRODUCTION

Increasing environmental pollution is one of the major problems for the whole world, in which the percentage of water pollution is much greater. In a survey by World Bank, nearly one-fifth of water pollution comes from textile industries, which generates more waste containing mainly dyes, during their manufacturing and dyeing processes. The wastewater of synthetic textile industries shows low biodegradability and strong color, which have features associated with the dyes, organic pollutants, and other toxic chemicals. These chemical effluents accumulate in water bodies, inhibiting photosynthesis, by which the production of carcinogenic and mutagenic byproducts occur, which cause severe harmful effects to the environment as well as living organisms.

Direct Red 80 (DR-80) and methyl orange (MO) are among a large group of synthetic industrial dyes, whereas malachite green (MG) is an aniline-based dyestuff (a triphenylmethane salt) made by Dobner and Fisher in 1877 that is available in the market. MG, MO, and DR-80 are mostly used for dyeing, printing of textiles, and killing of parasites and fungi in fish tanks. As a dyestuff, all of these dyes are soluble in water bodies and can cause lung cancer, colorectal cancer, asthma, kidney damage, and other diseases directly or indirectly. These anionic dyes are categorized in the azo class, which is the largest group of synthetic industrial dyes, and exhibit coloration because of the presence of certain functional groups in their molecular structure such as chromophores (−N≡N−) and auxochromes (SO$_3^-$, =O).$^{4-8}$

According to the literature survey, several methods have been used to remove the chemical effluents containing dyes due to their potential damage to the environment. Physical, chemical, and biological processes such as adsorption, microbial decomposition, and enzymatic decomposition have been used for a few decades to degrade these dyes. These processes exhibit certain inefficiencies, as they usually demand high cost and much time or generate toxic and carcinogenic intermediate products. Hence, the effective and alternate method for the degradation of these effluents is photocatalysis, which is a low-cost and lesser time-consuming and eco-friendly process, as it uses the solar spectrum ($E = h\nu$) to generate free radicals such as $^\cdot$OH and $^\cdot$O in the presence of photons that...
Table 1. Reported Results on Photocatalytic Degradation of Various Dyes Using ZnIn$_2$S$_4$ Materials

| materials/dose   | synthesis solvent | reaction temperature and time | synthesis method                  | morphology              | pollutants/dose (ppm) | photocatalytic degradation activity | ref |
|-----------------|-------------------|-----------------------------|-----------------------------------|-------------------------|------------------------|-------------------------------------|-----|
| ZnIn$_2$S$_4$/100 mg | pyridine          | 160 °C, 16 h                | solvothermal method               | nano/ micropeony (hexagonal) | MB/50                  | η = 99.98% (90 min)                 | 34  |
| ZnIn$_2$S$_4$/80 mg | ethylene glycol   | 200 °C, 10 min              | microwave, solvothermal approach  | monodispersed spheres   | MB/10                  | —                                  | 35  |
| ZnIn$_2$S$_4$/40 mg | water             | 80 °C, 6 h                  | thermal solution method           | microsphere             | MO/10                  | C/C$_0$ ≈ 0 (2.5 h)                 | 36  |
| ZnIn$_2$S$_4$/40 mg | water             | 80 °C, 6 h                  | hydrothermal                      | marigold-like microsphere | MO/10                  | C/C$_0$ ≈ 0 (3 h)                   | 37  |
| ZnIn$_2$S$_4$/40 mg | water             | 120 °C, 10 h                | hydrothermal method               | nanoparticles (cubic)    | MO/20                  | C/C$_0$ ≈ 0 (5 h)                   | 38  |
| ZnIn$_2$S$_4$/40 mg | water             | 195 °C, 10 min              | microwave-assisted hydrothermal method | marigold-like microspheres (hexagonal) | MO/10                  | η = 100% (2 h) or C/C$_0$ ≈ 0 (2 h) | 39  |
| ZnIn$_2$S$_4$/100 mg | water             | 65 °C, 16 h                 | hydrothermal method               | microspheres (hexagonal) | MO/10                  | η = 100% (2.5 h) or C/C$_0$ ≈ 0 (2.5 h) | 40  |
| ZnIn$_2$S$_4$/0.1 g | water             | 210 °C, 1 h                 | solvothermal method               | nanoparticles (hexagonal) | MO/40                  | K = 0.89 h$^{-1}$, annealed         | 41  |
| ZnIn$_2$S$_4$/— | water             | 200 °C, 12 h                | hydrothermal                      | nanopowder              | Ce(VI)/—               | η = 99.7% (40 min)                  | 42  |
| Zn$_{65.5}$S$_{100}$ (3 mL solution) | water | 280 °C, 60 months | colloidal chemistry               | nanoflakes              | R6G/(100 μmol/L)/(3 mL solution) | η = 100% (10 min) | 43  |
| ZnIn$_2$S$_4$/50 mg (100 mL DI) | water | 110 °C, 4 days | one-step wet-chemical method     | nanowire                | MO/20                  | η = 76% (210 min)                   | 44  |
| ZnIn$_2$S$_4$/60 mg (CH$_2$OH)$_2$ | water | 95 °C, 12 h                | biomolecule-assisted method       | flower-like hollow microspheres | MO/40 (120 mL DI) | η = 100% (210 min) or 0.045 min−1 (k) | 45  |
| ZnIn$_2$S$_4$/0.3 g (600 mL DI) | ethanol | 160 °C, 24 h               | solvothermal method               | flower-like microspheres | MO/25                  | 99% (100 min)                       | 46  |
| ZnIn$_2$S$_4$/0.04 mg (2 mL DI) | water | 300 °C, 24 h               | thermolysis                       | nanocrystals            | MB/(0.02 mmol/L)       | η = 66% (25 min)                    | 47  |
| ZnIn$_2$S$_4$/100 mg (100 mL DI) | water | 60 °C, 6 h                 | ionic liquid microemulsion-mediated hydrothermal method | microsphere | MO/10                  | η = 98.5% (10 min)                  | 48  |
| ZnIn$_2$S$_4$/0.1 g (400 mL DI) | water | 80 °C, 6 h                 | hydrothermal method               | marigold                | RhB/15                 | η = 97.8% (90 min)                  | 49  |
| ZnIn$_2$S$_4$/20 mg (100 mL DI) | water | 80 °C, 6 h                 | low-temperature method            | marigold               | MG/10                  | η = 99.68 (30 min)                  | 50  |
|                  |                   |                             |                                   |                        | DR-80/10               | η = 99.12 (75 min)                  |      |
in the aqueous solution. The microspheres were synthesized with a fixed amount of zinc, indium, and sulfur precursors. The structural and optical properties and photocatalytic activity on MG, MO, and DR-80 were studied.

**Synthesis of ZnIn$_2$S$_4$ Microspheres.** All chemicals used were analytical grade. In a normal reaction, ZnSO$_4$.7H$_2$O (4.0 mmol) and In$_2$(SO$_4$)$_3$ (4.0 mmol) were added by stoichiometric ratio, and thioacetamide C$_2$H$_5$NS (TAA) (20.0 mmol) was mixed in a conical flask with 250 mL capacity containing 80 mL of distilled water. Then the conical flask was put into a water bath and maintained at 80 °C for 6 h after sealing it with a ground glass stopper. After completing the reaction, the conical flask was cooled to room temperature. The yellowish precipitate was collected and washed with deionized water, absolute ethanol, and acetone several times. The final sample was dried in a vacuum oven at 60 °C for 6 h; the powder was collected for characterization, and further photocatalytic studies were performed. Figure 1 shows the synthesis of ZnIn$_2$S$_4$.

**Characterizations.** X-ray powder diffraction (XRD) was performed with a XRD Smart Lab Guidance Rigaku diffractometer (40 kV, 40 mA) using Cu Kα X-ray radiation (λ = 1.5418 Å) at a scanning rate of 0.02 deg/s. The obtained pattern was used to analyze the phase constituents in samples. UV–vis spectra were obtained with a Varian Cary 500 UV–NIR spectrophotometer to analyze the energy band gap using the Tauc plot. The Mott–Schottky plot was obtained to determine the flat band potential ($E_F^0$) using Metrohm auto lab. The scanning electron microscopy (SEM) images were captured on a Zeiss Sigma field-emission scanning electron microscope (FE-SEM), at an accelerating voltage of 10 kV to examine the morphology of the obtained sample. Energy-dispersive X-ray spectrometry (EDX) was carried out to analyze the chemical composition using an EDX spectrometer attached to the same microscope. Fourier transform infrared spectroscopy (FTIR) was analyzed using Vertex 70 V, Bruker spectrometer to study the functional groups and bond structure. Time-correlated single-photon counting (TCSPC) was performed on a Horiba DeltaFlex-01-DD measurement spectrometer to evaluate the lifetime of charge carriers at an excitonic emission wavelength of 401 nm. The biexponential kinetic model was used to fit the decay curves of the sample, and the best fitting was done with χ² equal to 2.712. All of the measurements were carried out at room temperature.

**Photocatalytic Activity Measurement.** The photocatalytic degradation activity of hexagonal structure-type material ZnIn$_2$S$_4$ was performed in an aqueous solution on anionic and cationic dyes such as anionic MO, DR-80, and cationic MG in the presence of sunlight. In this activity, each dye such as MO, MG, and DR-80 was taken (10 ppm) separately in three different 250 mL capacity beakers with 20 mg of ZnIn$_2$S$_4$ containing 100 mL of distilled water. Before irradiation, the solution was stirred in the dark for 30 min to ensure the establishment of an adsorption and desorption equilibrium. During irradiation, nearly 2–3 mL of the suspension was collected, centrifuged, and filtered through a Millipore filter to separate the photocatalyst particles. The filtrate was placed on a Varian Cary 500 Scan UV–Vis–NIR spectrophotometer to analyze the absorption peaks at a maximum absorption wavelength of dye. The abatement percentage of the dye concentration is described as C/C$_0$, where C is the value of the absorption peak point of dye at each irradiated time interval and C$_0$ is the value of the absorption peak point of the dye when adsorption and desorption equilibrium was achieved.

### RESULTS AND DISCUSSION

**Structural Analysis.** The XRD pattern of the sample prepared at 80 °C for 6 h is shown in Figure 2. The diffraction peaks of the 2θ angle at 21°, 27.6°, 30.1°, 39.5°, 47.2°, 52.2°, and 55.6° correspond to the (006), (102), (104), (108), (110), (116), and (022) planes of hexagonal ZnIn$_2$S$_4$ (JCPDS No. 03-065-2023), respectively, and a small diffraction peak of 2θ angle at 33.6° (shown in Figure 2 through a letter c) corresponds to the (400) plane of cubic ZnIn$_2$S$_4$ (JCPDS No. 22996).
00-048-1778). Crystallographic planes of hexagonal ZnIn₅S₄ (JCPDS No. 03-065-2023) and cubic ZnIn₅S₄ (JCPDS No. 00-048-1778) indicate the formation of nearly pure hexagonal ZnIn₅S₄. The particle size of the as-synthesized microsphere was calculated by Scherrer’s formula using eq 1.51

\[ D_{hk} = \frac{0.9\lambda}{\beta \cos \theta} \]  

(1)

where \(D_{hk}\) (nm) symbolizes the crystallite size of a particular \(hkl\) plane, \(\lambda\) is the Cu Kα radiation wavelength of X-ray radiation \((\lambda = 1.540 \text{ Å})\), \(\beta\) denotes the full width at half-maxima (FWHM) of the \(hkl\) plane peak, and \(\theta\) (radian) denotes Bragg’s diffraction angle.

In the hexagonal lattice, the relationship between interplanar spacing \(d\) of \(hkl\) planes and the lattice constants \(a\) and \(c\) is as shown in eq 2.

\[ 1/d^2 = \frac{(4/3)((h^2 + hk + k^2)/a^2) + l^2/c^2}{a^2} \]  

(2)

The lattice constants \(a\) and \(c\) of ZnIn₅S₄ microspheres were calculated using (006) and (110) planes, as shown in Table 2. The calculated lattice parameters agreed with the standard values \(a = 3.85 \text{ Å}\) and \(c = 24.68 \text{ Å}\) corresponding to the hexagonal ZnIn₅S₄ sample.

### Table 2. Lattice Constants (\(a\), \(c\)) and Average Crystallite Size (\(D_{hk}\)) for ZnIn₅S₄ Microspheres

| sample     | \(a\) (Å) (lattice constant) | \(c\) (Å) (lattice constant) | crystallite size \(D_{hk}\) (nm) average | \(d\)-spacing |
|------------|-----------------------------|-----------------------------|-----------------------------------------|--------------|
| ZnIn₅S₄   | 25.50                       | 4.91                        | 4.25                                    | d₀₀₀ = 4.25   |
|           |                             |                             |                                         | d₁₁₀ = 1.92   |

Surface Morphology. The FE-SEM images of ZnIn₅S₄ microspheres are shown in Figure 3a–c, which show clear microsphere morphologies containing nanoflower-like petals around it in Figure 3b. Microspheres look like puffy flowers with densely packed petals. The average dimensions of microspheres have a ~1 μm radius and ~18 nm thick petals, as clear from the Figure 3c.

Energy-dispersive X-ray spectroscopy was used to check the chemical composition of the as-synthesized sample ZnIn₅S₄ shown in Figure 3d. The EDX spectra verified the existence of Zn, In, and S elements in the ZnIn₅S₄ microsphere. The chemical composition mapping of the ZnIn₅S₄ microsphere is given in Table 3.

UV–Vis Absorption and Band Gap. Optical absorption and band gap of the prepared sample were analyzed by UV–vis absorption spectroscopy using a Varian Cary 500 UV–Vis–NIR spectrometer. The UV–Vis absorption spectra were plotted in terms of absorption versus wavelength (nm), as shown in Figure 4a, and the Tauc plot \((\alpha \nu = (\alpha \nu)^2)\) of the prepared sample ZnIn₅S₄ microsphere is shown in Figure 4b, where \(h\) is the Planck constant \((h = 6.626 \times 10^{-34} \text{ J} \cdot \text{s})\), \(\nu\) is the frequency, and \(\alpha\) is the absorption constant, defined as \(\alpha = 2.303A/\ell\), where \(A\) and \(\ell\) are absorbance and thickness of the cuvette, respectively. The band gap of the ZnIn₅S₄ microspheres was estimated as \(E_g = 2.1 \text{ eV}\) with the help of a Tauc plot.

To understand the process of charge transfer in the ZnIn₅S₄ microsphere semiconductor and the flat band potential \((E_{fb})\), the Mott–Schottky (MSK) analysis was performed. The \(E_{fb}\) was obtained by extrapolating the positive slope of the MSK plot to the x-axis, as shown in Figure 5c, and the positive slope of the as-synthesized photocatalyst depicts the n-type electronic nature of the semiconductor. Hence, due to the n-type nature, the degradation efficiencies of the cationic dyes are much better than those of anionic dyes, which can be seen through rate kinetic studies, as well, in Figure 6. The value of the \(E_{fb}\) was obtained as 1.7 V versus the normal hydrogen electrode (NHE).

The position of the conduction band edge potential \(E_{CB}\) and the valence band edge potential \(E_{VB}\) for the ZnIn₅S₄ microsphere was calculated by using the Butler and Ginley equation, as given below in eqs 3 and 4.52

\[ E_{vb} = X - E_e + 0.5E_g \]  

(3)

\[ E_{cb} = E_{vb} - E_g \]  

(4)

where \(X\) represents the absolute electronegativity of the semiconductor determined as the geometrical mean of electronegativity of the constituent atoms \((i.e., X_{ZnInS₄} = 4.84)\), \(E_e\) (4.5 eV) represents the free electron’s energy on the hydrogen (H₂) scale, and \(E_g\) represents the band gap energy of the semiconductor. The obtained values of \(X_{ZnInS₄}\), \(E_e\), \(E_g\), \(E_{vb}\) versus NHE, and \(E_{cb}\) versus NHE corresponding to ZnIn₅S₄ are presented in Table 4 and Figure 8.

Optical Studies. FTIR analysis was carried out to find the functional groups and impurities, attached to the surface of the catalyst, as shown in Figure 5. A broad strong peak present at 3400–3550 cm⁻¹ represents OH and NH stretching vibrations. Peaks present at 2922 and 2852 cm⁻¹ represent aliphatic CH stretching vibration of CH, CH₂, or CH₃. The peak at 1635 cm⁻¹ was assigned to the deformation vibration of N–H. The C=O stretching vibration occurs at 1650–1450 cm⁻¹. The peak present at 1161 cm⁻¹ occurs due to the hydroxyl group. FTIR spectra confirm that our synthesized sample does not contain any impurity contents.

Photocatalytic Activity. An absolute study of as-synthesized material ZnIn₅S₄ with three different dyes, i.e., MO, MG, and DR-80, was conducted to test the photocatalytic behavior and the degradation efficiencies of organic dyes, as shown in Figure 6.

The procedure to study photocatalytic behavior is as follows. First, the dark reaction (in the absence of light) was performed using DR-80 aqueous dye solution, such that ZnIn₅S₄ catalyst was allowed to react with the dye in the absence of light. The UV–vis absorption spectra were calculated for time \(t = 0\) and 30 min in the dark, as shown in Figure 6a–c. It was clear from the figure that there was no change in the absorption intensity even after 30 min, confirming that the degradation does not occur in the dark due to the surface adsorption phenomenon.

The \(C/C_0\) versus time graph is plotted as shown in Figure 6g. It is observed that the cationic dye MG is more degraded than anionic dye MO and azo dye DR-80. The \(C/C_0\) is the ratio of absorbance intensity at any recorded time (say, \(t = 0, 15, 30, 45, 60, 75,\) and 90 min) to the absorbance intensity at zero time \((t = 0\) min). Here, the photocatalytic degradation process follows the first-order rate kinetics as defined by the given eqs 5, 6, and 7.
where $C$ stands for the intensity of absorbance at any recorded time ($t$), $C_0$ is the initial intensity of absorbance at time ($t = 0$ min) and $k$ is the rate constant of reaction. The rate constant $k$ was determined by plotting a graph between $-\ln(C/C_0)$ versus time ($t$) and by drawing the corresponding slope. The rate constants were observed to be 0.55, 0.199, and 0.065 min$^{-1}$ for MO, MG, and DR-80, respectively, using 20 mg of the catalysts and 10 ppm of the above-mentioned dyes, as shown in Figure 6h.

As obvious from Figure 7, ~57.54, 99.68, and 90.79% of the dyes (MO, MG, and DR-80, respectively) were degraded in the first 30 min using ZnIn$_2$S$_4$ photocatalyst, and from the rate constants, it was also observed that the ZnIn$_2$S$_4$ photocatalyst was more active for the cationic group, such as MG, than for the anionic group, such as MO and DR-80.

The photocatalytic degradation efficiency was calculated using the following formula, as shown in eq 8.

$$\eta = \{1 - (C/C_0)\} \times 100\% \tag{8}$$

where $\eta$ is degradation efficiency, $C$ is the intensity at a recorded time ($t$), and $C_0$ is the intensity at time ($t = 0$ min).

The photocatalytic degradation efficiencies ($\eta$) were 99.43% for MO, 99.68% for MG, and 99.12% for DR-80 within 90, 30, and 75 min, respectively, as shown in Figure 7, using 20 mg of ZnIn$_2$S$_4$ photocatalyst and 10 ppm dyes in 100 mL of DI water.
Active species trapping experiment was performed to get a deep insight into the primary and secondary species responsible for the degradation of MG, MO, and DR-80 dyes during the photocatalysis process. Different scavengers like tetrabutanol (TBA) for $\cdot$OH, 1,4-benzoquinone (BQ) for $\cdot$O$_2^-$, and potassium iodide (KI) for both $\cdot$OH and h$^+$ were used in this experiment. As can be seen from Figure 9, the TBA and KI have a least considerable effect on the degradation process, suggesting $\cdot$OH and h$^+$ as secondary species in the degradation, whereas BQ shows a great impact on the degradation process, suggesting $\cdot$O$_2^-$ as the main primary species helping in the degradation process.

The ZnIn$_2$S$_4$ microspheres, cationic dye MG, and anionic dyes MO and DR-80 were used to study the mechanism of photocatalytic degradation, as shown in Figure 8. When the incident photon, with an energy equal to or greater than the energy band gap of ZnIn$_2$S$_4$ ($E_g = 2.1$ eV) ($h\nu \geq E_g$) strikes the surface of the photocatalyst, the valence band electron (e$^-$) moves toward the conduction band after absorbing energy from incident photon, leaving behind a hole (h$^+$). Thus it creates an electron–hole pair. A reaction between hole (h$^+$) and water (H$_2$O) takes place, yielding hydroxyl radical ($\cdot$OH) and H$^+$ ions, as shown in the following eqs 9, 10, and 11.

$$\text{ZnIn}_2\text{S}_4 + h\nu \rightarrow \text{ZnIn}_2\text{S}_4 (e^-_d + h^+_ab)$$

$$\text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}^+$$

$$\text{OH}^- + h^+ \rightarrow \cdot\text{OH}$$

Similarly, another reaction between electrons (e$^-$) and oxygen (O$_2$) occur, yielding superoxide radicals. These radicals react with toxins and reduce them into harmless or less toxic byproducts, as shown in eqs 12 and 13.

$$e^-_d + \text{O}_2 \rightarrow \cdot\text{O}_2^-$$

$$\cdot\text{O}_2^- + \text{dye} \rightarrow \text{byproduct}$$

Reusability Study. The reusability and the cyclic stability are always an important part of the photocatalysts. The stability and the reusability of the ZnIn$_2$S$_4$ microspheres were determined for four cycles, as shown in Figure 10. In the first cycle, the efficiency is 99.32% using 50 mg of ZnIn$_2$S$_4$ in 10 ppm DR-80 dye in 100 mL of solution. Photocatalysts were separated from the DR-80 dye solution by filtration after each cycle, washed, dried, and reused in the next cycle. The light irradiation time (30 min), dye solution quantity, and concentration were kept the same for each cycle. ZnIn$_2$S$_4$ microspheres possessed good reusability and showed 70.83% efficiency after four cycles. Such decreased efficiency was due to waste of photocatalyst during filtration after each cycle. Therefore, the as-synthesized ZnIn$_2$S$_4$ microsphere is an effective and stable photocatalyst for the degradation of DR-80 dye.

Time-Correlated Single-Photon Counting (TCSPC). Time-resolved transient and steady-state decay were analyzed to study the generation, transfer, and decay of the excitons. Biexponential fitting of the decay curve (Figure 11) was performed using eq 14, with a least $\chi^2$ value of 2.712:

$$I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$$

To obtain the lifetimes of $\tau_1$ and $\tau_2$, I(t) is the intensity, $\tau_1$ is the decay times for faster nonradiative processes, whereas $\tau_2$ is the decay time for slower radiative decay process. It can be seen from Table 5 that $\tau_1$ contributes 89.22% to the deactivation of excited states, which suggests that the degradation process happens due to the nonradiative pathways and radiative pathways having the very least role in the degradation process of dyes.

**CONCLUSIONS AND FUTURE WORK**

An analytical study was performed to understand the photocatalytic performance of ZnIn$_2$S$_4$ on malachite green, methyl orange, and Direct Red-80. The ZnIn$_2$S$_4$ sample was synthesized using a low-temperature solution method inside a water bath. Synthesized microspheres were found to be micron size and indicate the formation of a nearly pure hexagonal
Figure 6. Time-dependent UV–vis spectra of different dyes using 20 mg of ZnIn$_2$S$_4$ photocatalyst (a–c) dark reaction of ZnIn$_2$S$_4$ with DR-80, MG, and MO, respectively, (d) MO, (e) MG, and (f) DR-80. (g) C/C$_0$ versus time graph of the three dyes. (h) Photodegradation kinetics.
ZnIn$_2$S$_4$ structure. Marigold flower-like morphology was obtained, which is depicted from the FE-SEM micrographs. Photocatalytic performance was largely dependent on ZnIn$_2$S$_4$ structure, morphology, and optical characteristics. Degradation efficiency ($\eta$) of 99.68, 99.48, and 99.12 in 30, 90, and 75 min for MG, MO, and DR-80, respectively, was achieved, which makes ZnIn$_2$S$_4$ a potential candidate for degradation of both anionic and cationic dyes. Band gap energy calculated using the Tauc plot was $E_g = 2.1$ eV corresponding to 590 nm wavelength, which makes the photocatalyst suitable in the visible region. MSK analysis was done to find the flat band potential of ZnIn$_2$S$_4$. An average crystallite size of 4.91 nm was obtained from XRD analysis. A reusability study suggests a $\sim$5−10% decrease in efficiency after consecutive cycles, where a part of a reduction in efficiency is due to the quantity of sample decreasing during the collection process after each cycle. All of these observations and analyses suggest ZnIn$_2$S$_4$ is a potential and suitable candidate for degrading both anionic and cationic dyes. In the future, we will work on the synthesis of ZnIn$_2$S$_4$ with some other materials to form a Z-scheme and heterostructure-based photocatalysts to further extend the domain of the photocatalyst in degrading heavy metals and more complex dyes.

Table 4. Energy Band Structure Parameters of As-Synthesized ZnIn$_2$S$_4$ Microsphere

| $X_{ZnInS_4}$ | $E_{FB}$ (eV) | $E_g$ (eV) | $E_{CB}$ (eV) vs NHE | $E_{VB}$ (eV) vs NHE |
|---------------|--------------|------------|----------------------|----------------------|
| 4.84          | −1.7         | 4.5        | 2.1                  | 1.39                 | $−0.71$              |

Figure 7. Comparative efficiencies of the three dyes MO, MG, and DR-80 using 20 mg of ZnIn$_2$S$_4$ and 10 ppm dyes.

Figure 8. Proposed mechanism of photocatalytic degradation and charge transfer.

Figure 9. Scavenger study of zinc indium sulfide microsphere photocatalysts using BQ, KI, and TBA scavengers.

Table 5. Lifetimes of Generated Carriers

| samples       | lifetime (ns) | $\tau_1$ | $\tau_2$ | $A_1$ | $A_2$ | $\chi^2$ |
|---------------|---------------|----------|----------|-------|-------|----------|
| ZnIn$_2$S$_4$ | 0.0480152     | 1.13987  | 89.22%   | 10.78%| 2.712 |

makes ZnIn$_2$S$_4$ a potential candidate for degradation of both anionic and cationic dyes. Band gap energy calculated using the Tauc plot was $E_g = 2.1$ eV corresponding to 590 nm wavelength, which makes the photocatalyst suitable in the visible region. MSK analysis was done to find the flat band potential of ZnIn$_2$S$_4$. An average crystallite size of 4.91 nm was obtained from XRD analysis. A reusability study suggests a $\sim$5−10% decrease in efficiency after consecutive cycles, where a part of a reduction in efficiency is due to the quantity of sample decreasing during the collection process after each cycle. All of these observations and analyses suggest ZnIn$_2$S$_4$ is a potential and suitable candidate for degrading both anionic and cationic dyes. In the future, we will work on the synthesis of ZnIn$_2$S$_4$ with some other materials to form a Z-scheme and heterostructure-based photocatalysts to further extend the domain of the photocatalyst in degrading heavy metals and more complex dyes.
AUTHOR INFORMATION

Corresponding Author
Manika Khanuja – Centre for Nanoscience and Nanotechnology, Jamia Millia Islamia, New Delhi 110025, India; orcid.org/0000-0001-8019-7621; Email: manikakhanuja@gmail.com

Authors
Mohammad Imran – Centre for Nanoscience and Nanotechnology, Jamia Millia Islamia, New Delhi 110025, India
Waseem Ashraf – Centre for Nanoscience and Nanotechnology, Jamia Millia Islamia, New Delhi 110025, India
Aurangzeb Khurram Hafiz – Centre for Nanoscience and Nanotechnology, Jamia Millia Islamia, New Delhi 110025, India

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.2c00945

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work supported by Science and Engineering Research Board [SERB (No. ECR/2017/001222)] to one of the authors (M.K.) is highly appreciated.

REFERENCES

(1) Holkar, C. R.; Jadhav, A. J.; Pinjari, D. V.; Mahamuni, N. M.; Pandit, A. B. A critical review on textile wastewater treatments: possible approaches. J. Environ. Manage. 2016, 182, 351–366.
(2) Dwivedi, A. K. Researches in water pollution: A review. Int. Res. J. Nat. Appl. Sci. 2017, 4, 118–142.
(3) Kumar, A.; Mittal, H.; Nagar, R.; Khanuja, M. The synergistic effect of acid-etched gC3N4 nanosheets and polyaniline nanofibers for the adsorption and photocatalytic degradation of textile dyes: a study of charge transfer mechanism and intermediate products. Mater. Adv. 2022, DOI: 10.1039/DIMA01218E.
(4) Benkhaya, S.; M’rabet, S.; El Harfi, A. A review on classifications, recent synthesis and applications of textile dyes. Inorg. Chem. Commun. 2020, 115, 107891.
(5) Sarkar, S.; Banerjee, A.; Halder, U.; Biswas, R.; Bandopadhyay, R. Degradation of Synthetic Azo Dyes of Textile Industry: a Sustainable Approach Using Microbial Enzymes. Water. Conserv. Sci. Eng. 2017, 2 (4), 121–131.
(6) Verma, A. K.; Dash, R. R.; Bhuina, P. A review on chemical coagulation/flocculation technologies for removal of colour from textile wastewaters. J. Environ. Manage. 2012, 93 (1), 154–168.
(7) Kallel, F.; Bouazziz, F.; Chaari, F.; Belghith, L.; Ghorbel, R.; Chaabouni, S. E. Interactive effect of garlic straw on the sorption and desorption of Direct Red 80 from aqueous solution. Process. Saf. Environ. Prot. 2016, 102, 30–43.
(8) Manzoor, J.; Sharma, M. Impact of Textile Dyes on Human Health and Environment. In Impact of Textile Dyes on Public Health and the Environment; Wani, K., Jangid, N., Bhat, A., Ed.; IGI Global, 2020; pp 162–169.
(9) Ashraf, W.; Fatima, T.; Srivastava, K.; Khanuja, M. Superior photocatalytic activity of tungsten disulfide nanostructures: role of morphology and defects. Appl. Nanosci. 2019, 9 (7), 1515–1529.
(10) Ashraf, W.; Bansal, S.; Singh, V.; Barman, S.; Khanuja, M. BiOCl/WS2 hybrid nanosheet (2D/2D) heterojunctions for visible-light-driven photocatalytic degradation of organic/inorganic water pollutants. RSC. Adv. 2020, 10 (42), 25073–25088.
(11) Park, J.; Joo, J.; Kwon, S. G.; Jang, Y.; Hyeon, T. Synthesis of monodisperse spherical nanocrystals. Angew. Chem., Int. Ed. Engl. 2007, 46 (25), 4630–4660.
(12) Kumar, S.; Nann, T. Shape control of II-VI semiconductor nanomaterials. Small. 2006, 2 (3), 316–329.
(13) Burda, C.; Chen, X.; Narayanan, R.; El-Sayed, M. A. Chemistry and properties of nanocrystals of different shapes. Chem. Rev. 2005, 105 (4), 1025–1102.
(14) Murray, C. B.; Norris, D. J.; Bawendi, M. G. Synthesis and Characterization of Nearly Monodisperse CdE (E = S, Se, Te) Semiconductor Nanocrystallites. J. Am. Chem. Soc. 1993, 115 (19), 8706–8715.
(15) Peng, Z. A.; Peng, X. Formation of high-quality CdTe, CdSe, and CdS nanocrystals using CdO as precursor. J. Am. Chem. Soc. 2001, 123 (1), 183–184.
(16) Akkerman, Q. A.; Genovese, A.; George, C.; Prato, M.; Moreels, I.; Casu, A.; Marras, S.; Curcio, A.; Scarpellini, A.; Pellegrino, T.; Manna, L.; Lesnyak, V. From binary Cu2S to ternary Cu-In-S and quaternary Cu-In-Zn-S nanocrystals with tunable composition via partial cation exchange. ACS Nano 2015, 9 (1), 521–531.
(17) Khan, M. M. Introduction and fundamentals of chalcogenides and chalcogenides-based nanomaterials. In Chalcogenide-Based Nanomaterials as Photocatalysts; Khan, M. M., Ed.; Micro and Nano Technologies Series; Elsevier: Brunei Darussalam, 2021; pp 1–6.
(18) Rahman, A.; Khan, M. M. Chalcogenides as photocatalysts. New J. Chem. 2021, 45 (42), 19622–19635.
(19) Ashraf, W.; Khan, A.; Bansal, S.; Khanuja, M. Mechanical ball milling: A sustainable route to induce structural transformations in tungsten disulfide for its photocatalytic applications. Phys. E: Low-Dim. Syst. Nanostruc. 2022, 140, 115152.
(20) Fatima, T.; Hussain, S.; Narang, J.; Khanuja, M.; Shetti, N. P.; Reddy, K. R. Novel tungsten disulfide (WS2) nanosheets for photocatalytic degradation and electrochemical detection of pharmaceutical pollutants. J. Water Proc. Eng. 2022, 47, 102717.
(21) de Jesus da Silveira Neta, J.; Costa Moreira, G.; da Silva, C. J.; Reis, C.; Reis, E. L. Use of polyurethane foams for the removal of the Direct Red 80 and Reactive Blue 21 dyes in aqueous medium. Desalination 2011, 281, 55–60.
(22) Wang, A. L.; Chen, L.; Zhang, J. X.; Sun, W. C.; Guo, P.; Ren, C. Y. Ionic liquid microemulsion-assisted synthesis and improved photocatalytic activity of ZnInS2, J. Mater. Sci. 2017, 52 (5), 2413–2421.
(23) Li, P.; Wei, Z.; Wu, T.; Peng, Q.; Li, Y. Au-ZnO hybrid nanopyramids and their photocatalytic properties. J. Am. Chem. Soc. 2011, 133 (15), 5660–5663.
(24) Rajendran, R.; Varadharajan, K.; Jayaraman, V.; Singaram, B.; Jayaram, J. Photocatalytic degradation of metronidazole and methyline blue by PVA-assisted Bi2WO6-Cds nanocomposite film under visible light irradiation. Appl. Nanosci. 2018, 8 (1–2), 61–78.
(25) Grilli, E.; Guzzi, M. Recombination process of photocexcited carriers in ZnInS2, Phys. Status. Solidi. A 1977, 40 (1), 69–74.
(26) Cingolani, A.; Ferrara, M.; Minafra, A.; Adduci, F.; Tantalo, P. Photoelectronic properties of ZnInS2, phys. status. solidi. A 1974, 23 (2), 367–371.
(27) Anagnostopoulos, A. N.; Manolikas, C.; Papadopoulos, D. Comparison of the Structure and the Electric Properties of ZnInS2 (III-) and CdInGaS2-Layered Crystals. Phys. Status. Solidi. A 1983, 77 (2), 595–602.
(28) Ohta, H.; Sato, W.; Sato, K. Thermoelectric properties of homologous compounds in the ZnO-In2O3 system. J. Am. Ceram. Soc. 1996, 79 (8), 2193–2196.
(29) Romeo, N.; Dallatura, A.; Braglia, R.; Sberveglieri, G. Charge storage in ZnInS2 single crystals. Phys. Lett. 1973, 22 (1), 21–22.
(30) Mora, S.; Paorici, C.; Romeo, N. Properties of the ternary compound ZnInS2 at high electric field. J. Appl. Phys. 1971, 42 (5), 2061–2064.
(31) Kalomiris, J. A.; Anagnostopoulos, A. N.; Spyridelis, J. Temperature dependence of the energy gap and some electrical
properties of ZnIn$_2$S$_3$ (II) single crystals. *Semicond. Sci. Technol.* 2018, 4 (7), 536.

(32) Anagnostopulos, A. N. Influence of composition faults on the AC conductivity of ZnIn$_2$S$_3$ (III). *Phys. Status. Solidi.* A 1983, 75 (2), 595–599.

(33) Seo, W. S.; Otsuka, R.; Okuno, H.; Ohta, M.; Koumoto, K. Thermoelectric properties of sintered polycrystalline ZnIn$_2$S$_4$. *J. Mater. Res.* 1999, 14 (11), 4176–4181.

(34) Fang, F.; Chen, L.; Chen, Y. B.; Wu, L. M. Synthesis and photocatalysis of ZnIn$_2$S$_4$ nano/micropeony. *J. Phys. Chem. C* 2010, 114 (6), 2393–2397.

(35) Hu, X.; Yu, J. C.; Gong, J.; Li, Q. Rapid mass production of hierarchically porous ZnIn$_2$S$_4$ submicrospheres via a microwave-solvothermal process. *Cryst. Growth. Des.* 2007, 7 (12), 2444–2448.

(36) Chen, Z.; Li, D.; Zhang, W.; Chen, C.; Li, W.; Sun, M.; He, Y.; Fu, X. Low-Temperature and Template-Free Synthesis of ZnIn$_2$S$_4$ Microspheres. *Inorg. Chem.* 2008, 47 (21), 9766–9772.

(37) Chen, Z.; Li, D.; Zhang, W.; Shao, Y.; Chen, T.; Sun, M.; Fu, X. Photocatalytic Degradation of Dyes by ZnIn$_2$S$_4$ Microspheres under Visible Light Irradiation. *J. Phys. Chem. C* 2009, 113 (11), 4433–4440.

(38) Chen, Y.; Hu, S.; Liu, W.; Chen, X.; Wu, L.; Wang, X.; Liu, P.; Li, Z. Controlled syntheses of cubic and hexagonal ZnIn$_2$S$_4$ nanostructures with different visible-light photocatalytic performance. *Dal. Trans.* 2011, 40 (11), 2607–2613.

(39) Chen, Z.; Li, D.; Xiao, G.; He, Y.; Xu, Y. J. Microwave-assisted hydrothermal synthesis of marigold-like ZnIn$_2$S$_4$ microspheres and their visible light photocatalytic activity. *J. Solid State Chem.* 2012, 186, 247–254.

(40) Guo, M.; Yin, S.; Han, Y.; Wang, C. Low temperature preparation of ZnIn$_2$S$_4$ by hydrothermal method and its visible light photocatalytic property. *Adv. Mater. Res.* 2012, 415–417, 464–467.

(41) Peng, S.; Li, L.; Wu, Y.; Jia, L.; Tian, L.; Srinivasan, M.; Ramakrishna, S.; Yan, Q.; Mhaisalkar, S. G. Size- and shape-controlled synthesis of ZnIn$_2$S$_4$ nanocrystals with high photocatalytic performance. *CrystEngComm.* 2013, 15 (10), 1922–1930.

(42) Wang, T. X.; Xu, S. H.; Yang, F.X. ZnIn$_2$S$_4$ nanopowder as an efficient visible light-driven photocatalyst in the reduction of aqueous Cr(VI). *Mater. Lett.* 2012, 83, 46–48.

(43) Kempken, B.; Dzhagan, V.; Zahn, D. R.; Alcocer, M. J.; Kriegel, L.; Sciotognella, F.; Parisi, J.; Kolny-Olesiak, J. Synthesis, optical properties, and photochemical activity of zinc-indium-sulfide nanoplates. *RSC. Adv.* 2015, 5 (109), 89577–89585.

(44) Shi, L.; Yin, P.; Dai, Y. Synthesis and photocatalytic performance of ZnIn$_2$S$_4$ nanotubes and nanowires. *Langmuir.* 2013, 29 (41), 12818–12822.

(45) Zhang, Y.; Liu, L.; Ying, J.; Qian, J.; Liu, L.; Wang, L. Biomolecule-assisted synthesis of ZnIn2S4 flower-like hollow microspheres. *Mater. Lett.* 2013, 105, 185–188.

(46) Zhou, M. J.; Cui, P. Synthesis and photocatalytic properties of flower-like ZnIn$_2$S$_4$ microspheres by a solvothermal method. *Adv. Mater. Res.* 2014, 881–883, 1101–1104.

(47) Batabyal, S. K.; Lu, S. E.; Vittal, J. J. Synthesis, Characterization, and Photocatalytic Properties of In$_2$S$_3$, ZnIn$_2$S$_4$, and CdIn$_2$S$_4$ Nanocrystals. *Cryst. Growth Des.* 2016, 16 (4), 2231–2238.

(48) Liu, T.; Wang, L.; Lu, X.; Fan, J.; Cai, X.; Gao, B.; Miao, R.; Wang, J.; Li, Y. Comparative study of the photocatalytic performance for the degradation of different dyes by ZnIn$_2$S$_4$; adsorption, active species, and pathways. *RSC. Adv.* 2017, 7 (20), 12292–12300.

(49) Xu, Z.; Li, Y.; Peng, S.; Lu, G.; Li, S. NaCl-assisted low temperature synthesis of layered Zn-In-S photocatalyst with high visible-light activity for hydrogen evolution. *RSC. Adv.* 2012, 2 (8), 3458–3466.

(50) Chen, Y.; Huang, R.; Chen, D.; Wang, Y.; Liu, W.; Li, X.; Li, Z. Exploring the different photocatalytic performance for dye degradations over hexagonal ZnIn$_2$S$_4$ microspheres and cubic ZnIn$_2$S$_4$ nanoparticles. *ACS. Appl. Mater. Interfaces.* 2012, 4 (4), 2273–2279.

(51) Patterson, A. The Scherrer Formula for X-Ray Particle Size Determination. *Phys. Rev.* 1939, 56 (10), 978–982.

(52) Beranek, R. (Photo)electrochemical methods for the determination of the band edge positions of TiO$_2$-based nanomaterials. *Adv. Phys. Chem.* 2011, 2011, 786759.