Flow synthesis and in-channel photocatalysis of antimicrobially active ZnS quantum dots using an efficient planar PMMA microreactor

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Abstract

We report a rapid, robust and efficient technique for the fabrication of poly(methyl methacrylate) based microreactors using laser engraver to synthesize ZnS quantum dots. We also present a comparative study of synthesis and photocatalytic activity of ZnS quantum dots by conventional beaker reactor and microfluidic route. The ZnS synthesized in a microreactor did not show any aggregation, whereas the ZnS synthesized in a beaker reactor showed aggregation and poor reproducibility. The ZnS synthesized in a microreactor revealed the formation of well dispersed quantum dots with uniform size of 2.5 ± 1 nm and higher band gap (4.12 eV) as compared to the quantum dots prepared by beaker reactor method. In comparison to the degradation profile in a conventional reactor, a remarkable enhancement in the photocatalytic activity of ZnS quantum dots in microfluidic reactor has also been observed for degradation of organic dyes (Rhodamine B and Methyl orange) under UV irradiation. The degradation efficiency of ZnS can further be tuned by controlling flow rate of dyes through the photocatalyst coated micro-reactor. Instant degradation with efficiency of 93% and 99% for rhodamine B and methyl orange respectively, were achieved when the flow rate was maintained at 50 µl min⁻¹. The microfluidic reactor also offers the prolonged photocatalyst stability, ensuring its reusability without significantly losing its efficiency. The ZnS quantum dots were also observed to have excellent antibacterial property thus inhibiting the growth of E. coli bacterial colonies even at a very low concentration of 10 µg ml⁻¹.

1. Introduction

In last few decades, nanomaterials have undergone tremendous amount of research to unleash their emergent properties by tuning their shape, size, etc [1–4]. However, still there is a continuous hunt to overcome the challenge of controlled synthesis of high purity nanomaterials with tunable size and shape having monodispersity. Several researchers have meticulously designed synthetic approaches for various nanomaterials that includes chemical (wet chemical, co-precipitation, solvothermal methods etc) as well as physical (laser ablation, physical vapor deposition, lithography methods etc) routes over a period of time [5–9]. Very recently, microreactor based synthesis approach has become one of the emerging route for the preparation of nanostructured materials [10–13]. This technique provides superior control over the morphology of particles through the mere control of flow parameters and reactor design. Moreover, with this technique, faster reaction time, efficient mixing of reagents resulting in lesser chemical waste, better reproducibility and online monitoring can be easily achieved as compared to the conventional synthesis methods [10]. In addition, microreactor synthesis also offers precise control over various reaction parameters such as flow rate of reagents, channel geometry and multiple chemical processing steps (heating, cooling, mixing), making it more suitable for scaling-up to have continuous production of quantum dots or nanostructured materials [11–14]. However,
majority of fabrication processes for microfluidic chips or microreactors use expensive and time consuming photolithographic techniques which often requires clean room environment [15,16]. Achieving a simple, low cost, efficient yet high resolution fabrication method to make microreactors scalable for commercial use is still a challenge for the scientific community. Hence, it was imperative to develop a cost effective and suitable rapid technique for the fabrication of microreactor and its utilization in the synthesis of nanostructured materials for their practical applications. Being a cost-effective material, poly(methyl methacrylate) (PMMA) sheets can be utilized in production, replication and rapid prototyping of such microreactors [17]. Moreover, it is a biocompatible polymer and thus microreactors made from PMMA were also well suited for lab-on-chip and total analytical system (TAS) applications [18].

Nanostructured ZnS is considered as one of the most important semiconductor materials having various applications such as in light-emitting diodes (LEDs), electroluminescent devices, photocatalytic and photovoltaic devices etc [19–25]. Recently, nanostructured ZnS based composites have been intensively studied as the building blocks of nano-electronic systems and biosensors [26,27]. Amongst their widespread applications, ZnS nanostructures have also gained considerable attention in the field of photocatalysis owing to easy tunability in the electronic band structure [28]. When photocatalyst is illuminated with the light energy greater than its bandgap, electrons are excited from the valence band (VB) to the conduction band (CB) to generate electron–hole pairs. The valence band holes (h+) react with water molecules whereas, conduction band electrons (e−) react with the oxygen molecules to reduce them to hydroxyl radicals (OH) and superoxide anion (O2−) respectively. Thus, both the hydroxyl and superoxide radicals attack or react with the organic dyes absorbed on the surface of the photocatalyst, thereby releasing water (H2O) and carbon dioxide (CO2) as by-products.

ZnS has been widely used as photocatalyst in form of quantum dots [29,30], hollow particles [31], core–shell structures [32] and doped ZnS microspheres [33]. ZnS has been employed as photocatalyst for the complete degradation of several organic dyes within a time span of few hours [34,35]. Taking into account the band alignment of composites of ZnS with silver sulphide (Ag2S), cadmium sulphide (CdS), zinc oxide (ZnO), reduced graphene oxide (rGO) and carbon nanofibers, enhanced photocatalytic degradation of organic dyes has been achieved by utilization of maximum solar spectrum range [36–40]. Here, we have chosen to utilize the microreactor based in-channel photocatalysis using ZnS quantum dots for our study. This approach provides various advantages such as large surface area, rapid heat and mass transfer thus shorter reaction time, uniform light irradiation and efficient photon transfer during the photocatalytic reaction in comparison to the conventional bulk reactors [41–47].

The antifungal, antiviral and antibacterial activities of sulphide and oxide materials have also been widely investigated [48,49]. Recently, many groups have successfully demonstrated the antioxidant, antibacterial and antifungal activities of ZnS nanostructures [50,51]. Pillai and co-workers have demonstrated the bactericidal activity of nanocrystalline ZnS against Staphylococcus aureus and Escherichia coli (E. coli) [52]. Satish Kumar et al have reported the antibacterial activity of biosynthesized zinc sulphide against various pathogenic bacteria by disc diffusion method [53].

Hence, in the present study, we have demonstrated the laser engraved rapid fabrication of microreactors which were further elaborated for ZnS quantum dots synthesis and tested for their in-channel photocatalytic activities. A comparative study was also carried out with conventional bulk method in order to fully understand the effect of reactor on the synthesis and reactivity of nanomaterials. Furthermore, antibacterial activity of ZnS quantum dots has been tested against E. coli (O78:K80:H11) bacteria by plating colony forming unit method.

2. Experimental section

2.1. Materials

Zinc chloride (ZnCl2·5H2O, Sigma-Aldrich, 98%) and sodium sulphide (Na2S·9H2O, Sigma-Aldrich, 95%), were utilized for the synthesis of ZnS quantum dots. All chemicals were used in the condition as received without any further purification. Distilled water was used as solvent while commercially available PMMA sheet (Polyglass International Mfg. Corp.) of thickness 0.118 inch was used for fabrication of microreactors. Rhodamine B (Rhb, C28H37ClN2O3, Fisher Scientific, ≥95%) and methyl orange (MO, C14H14N3NaO5S, Sigma, ≥95%) were used as standard dyes for the photocatalytic study.

2.2. Fabrication of PMMA based microreactors

All the microreactors were fabricated using CO2 laser engraver unit (8028 Trotec Speedy 100 flexx). Designs of microfluidic reactors were developed using professional designing software (CorelDRAW Graphics Suite 2018) and interfaced with the laser using the Trotec Job Control™ software. Typically, a PMMA sheet was placed on z-translatable stage and focused with the laser by moving the stage up or down. The microchannels of two
different designs were engraved to specified dimension of 200 μm (width) X 200 μm (depth) for synthesis and 300 μm (width) X 200 μm (depth) for photocatalytic study using optimum laser operation speed (15 mm s⁻¹), frequency (1000 PPI/Hz), power (40 W) and number of passes (12). The digital photographs of the fabricated microchannels are depicted in figure 1.

The microchannels shown in figure 1(a) was used for ZnS quantum dots synthesis whereas that of figure 1(b) was utilized for the inline photocatalytic study. It is to be noted that the fabricated microchannels are open channels. Therefore, the channels were closed through lamination and inlets/outlet openings were connected with silicon tubes in order to flow the reactants or dye solutions.

2.3. Preparation of ZnS quantum dots
In 2-inlets PMMA based microreactor (figure 2(a)), ZnS quantum dots (designated as ZS-1) were synthesized by injecting equal volume (5 ml) of zinc chloride (0.15 M) and sodium sulfide (0.15 M) at the flow rate of 500 μl min⁻¹ into the microreactor using a software controlled syringe pump (neMESYS, Cetoni GmbH). ZnS quantum dots (designated as ZS-2) were also prepared via conventional beaker method by mixing equal volume (5 ml) of 0.15 M sodium sulfide and 0.15 M zinc chloride in a beaker with continuous stirring for 30 min, as depicted in figure 2(b), for understanding the effect of preparation route [43]. Finally, all the products were
washed thoroughly using distilled water to eliminate any unreacted reagents and collected after drying at 50 °C for 5 h.

2.4. Characterization

ZnS nanostructures were studied using Bruker D8 Advance x-ray diffractometer (XRD) with Cu kα radiation (λ = 0.15405 nm) operating at 40 kV and 25 mA with scan rate of 1 degree min⁻¹ in the range of 20°–80°. Microstructural studies were examined using transmission electron microscope (TEM, JEOL, JEM-2100) operating at an accelerating voltage of 200 kV. The Brunauer–Emmett–Teller (BET) surface area of the samples was determined using Autosorb iQ2 TPX instrument. Prior to (nitrogen) N₂ adsorption–desorption measurements, the samples were treated in vacuum at 70 °C for 8 h to remove any unwanted adsorbents from the surface. The optical properties of all the samples were also investigated using ultraviolet-visible (UV–vis) diffuse reflectance spectrometer (Shimadzu UV-2600) in the wavelength range of 200–800 nm employing barium sulfate (BaSO₄) as a reference reflectance. The optical absorption spectrum of semiconductor may be used to calculate its optical band gap (Eg) through Tauc plot [54]. The Tauc relation is expressed as follows;

\[(\alpha hv)^{\frac{1}{2}} = A(hv - E_g)\]

(1)

where \(\alpha\), h, \(\nu\) and A are absorption coefficient, Planck’s constant, frequency of vibration and a constant relative to the material, respectively. \(n\) represents the nature of electronic transition; for direct transition, \(n = 1/2\) and for indirect transition \(n = 2\). The absorption coefficient can be related to the reflectance data by using Kubelka-Munk function (equations (2) and (3)), as follows [55];

\[F(R) = \frac{(1 - R)^2}{2}; \quad R = \frac{\alpha}{S}\]

(2)

\[R = \frac{R_{\text{Sample}}}{R_{\text{BaSO₄}}}\]

(3)

where \(F(R)\), R, and S are the Kubelka-Munk function, reflectance, and scattering coefficient, respectively. So, \(\alpha\) in the Tauc equation can be replaced with \(F(R)\) and the band gap of each sample can be estimated from the plot of \((F(R)h^2\nu)^{2}\) versus \(h\nu\), by extrapolating the linear portion of the curves to \(F(R) = 0\).

2.5. Photocatalytic study

The catalytic performance of ZnS quantum dots were evaluated by recording the photocatalytic degradation of aqueous RhB and MO solutions using 200 W Hg lamp as UV light source. In order to understand the role of reactors on photocatalytic activity, a systematic and comparative photocatalytic studies were done using microreactor and conventional glass beaker as reactor. In a conventional photocatalytic experiment, 20 mg of photocatalysts (ZS-1 and ZS-2) were dispersed in 20 ml of aqueous 10 \(\mu\text{M}\) dye solutions. Prior to light irradiation, the suspensions containing photocatalyst and organic dyes were vigorously stirred for 30 min in dark to make the uniform dispersion of photocatalyst and to achieve an adsorption/desorption equilibrium between catalyst and dye. The solution was subsequently irradiated with mercury (Hg) lamp to undergo photocatalytic reaction as illustrated in figure 3(a). The degradation of dyes was monitored by analyzing the absorption peaks at 464 nm (MO) and 553 nm (RhB) in the UV–vis spectra of the reaction aliquots (2 ml), extracted at every 5 min after the light irradiation. In case of microreactor based photocatalytic study, a pre-dispersed photocatalyst (20 mg) in 5 ml of ethanol was infused in the microreactor (figure 1(b)) and subsequently dried in order to coat the microchannels uniformly. After that, the dye solutions were allowed to flow through the photocatalyst coated microchannel at the specified flow rate (30, 100, 200 or 300 \(\mu\text{ml min}^{-1}\)) under UV light irradiation as shown in figure 3(b). Like the conventional way, here also the degradation of dye solutions collected from outlet at different time intervals were also recorded through UV–vis spectrophotometer [56–58].

In addition, similar control experiments were also performed in both conventional as well as microfluidic reactor without catalyst or in the dark in order to demonstrate that the degradation of dyes is solely because of the photocatalytic process. The photo degradation efficiency of organic dye can be calculated using equation (4) [59];

\[\text{Degradation efficiency} \times 100 = \frac{C_o - C_t}{C_o} \times 100\]

(4)

where \(C_o\) and \(C_t\) are the initial concentration of dye at irradiation time \(t = 0\) and \(t\) min, respectively [53].

2.6. Measurement of antimicrobial activity

Antibacterial activity of ZnS quantum dots was analysed in *E. coli* 078 bacterial strain. Plating colony forming unit assay was performed for the antibacterial experiment and sterile Luria Bertani Broth media (Himedia,
India) and standard Luria Bertani (LB) agar plate (Himedia, India) were used as culture media. Antibacterial activity was investigated by incubating 10^3 CFU ml\(^{-1}\) of bacteria with different concentrations (10, 100 and 500 μg ml\(^{-1}\) while 10 μg ml\(^{-1}\) ampicillin as positive control) of zinc sulphide quantum dots in conical flask for 3 h at 37 °C with continuous shaking at 180 rpm in an incubator shaker. After 3 h of incubation, 0.5 ml of the suspension was separated and diluted 10 times. Further, 100 μl of diluted solution was plated on LB agar plates and incubated overnight at 37 °C followed by counting the number of colonies.

3. Results and discussions

3.1. XRD analysis
The crystal structure and the phase purity of ZS-1 and ZS-2 were investigated using x-ray diffraction (XRD) patterns illustrated in figure 4. The XRD patterns of the samples showed three peaks at \(2\theta = 28.7^\circ, 47.9^\circ\) and \(56.5^\circ\), which can be well indexed with the standard (111), (220) and (311) crystallographic planes of pure cubic ZnS (JCPDS # 00-005-0566) respectively. No other impurity peaks corresponding to oxides or any unreacted reagents were detected. In addition, all the peaks were observed to be very broad, implying that the synthesized ZnS has very small crystallite size. The crystallite size was calculated using Scherrer’s formula was found to be \(\sim 2.0 \text{ nm}\) [60].

3.2. Microstructural studies
In order to decipher the shape and size of ZnS samples (ZS-1 and ZS-2), microstructural investigations were carried out by using TEM. When the reaction was carried out in microreactor, the well separated uniform ZnS particles (ZS-1) of spherical morphology were clearly observed (figure 5(a)). In this case, the average particle size of \(\sim 2.5 \pm 1 \text{ nm}\) was observed as shown in the histogram (figure 5(c)). The estimated d-spacing value measured using high resolution TEM image (figure 5(b)) was 0.31 nm, which corresponds to the (111) plane of ZnS. Whereas, in case of ZnS quantum dots (ZS-2) prepared by conventional beaker method, the particles were observed to be highly agglomerated with elusive spherical morphology as shown in figure 5(d).

3.3. Proposed mechanism for the synthesis of ZnS quantum dots within a microchannel
The mechanism of synthesis of ZnS quantum dots within a microchannel can be directly correlated to the LaMer’s model of nucleation and growth. According to this model, reactant concentration plays a vital role in the synthesis of nanostructures [61]. There should be a critical concentration of reactant molecules which will initiate the synthesis process [62]. Since higher reactant concentration promotes faster nucleation rates, there is a generation of uniform nanoparticle nuclei. As a result of higher reactant concentration, there is a higher probability of forming larger particles due to diffusion and the Ostwald ripening process. On the other hand, if
the reactant concentration is kept low, the nanoparticles nuclei do not grow larger in size [63]. In the present work, for continuous flow synthesis of ZnS quantum dots, reactants (ZnCl2 and Na2S) at low concentrations (0.15 M each) react inside a channel in the dimension range of ~200 µM. Within the microchannel, laminar flow and diffusive mixing result in the formation of ZnS nanoparticle nuclei without being prone to growth. Such a reaction mechanism solely depends on the extent of mixing, which is somewhat similar to proton exchange in conventional synthesis. Initially, when both the reactants mix at Y-junction of the microreactor at room temperature, nucleation sites are formed which gradually move through the serpentine section ensuring
the reaction completion within the reactor without getting sufficient time for growth. It does not follow the second order reaction kinetics, and the suggested reaction mechanism is shown in figure 6.

3.4. BET surface area analysis
The catalytic activity can greatly be influenced by the surface area of catalyst. Larger surface area is expected to offer more reaction sites, leading to enhancement in the rate of reaction [35]. The BET measurements revealed the surface area value of 337.0 m² g⁻¹ and 48 m² g⁻¹ for ZS-1 and ZS-2 respectively as shown in figures 7(a) and (b). The BET results indicate that the surface area of the quantum dots is greatly influenced by synthesis route and reaction parameters. In other words, it can also be inferred that the microfluidic synthesis route could provide uniform particle size with higher surface area (∼7 fold) as compared to the conventional wet chemical (beaker) route.

3.5. Optical studies
The light absorption properties, which can greatly influence the photocatalytic activity of a catalyst were evaluated using UV–vis diffuse reflectance spectroscopy (UV–vis DRS) of as-synthesized samples. Figures 8(a)

Figure 6. Mechanism for the formation of ZnS quantum dots inside a microreactor.

Figure 7. N₂ adsorption–desorption isotherm of ZnS prepared; (a) via microfluidic route (ZS-1); and (b) by conventional beaker method (ZS-2).
and (b) shows the UV spectrum and the plot of $(F(R)hν)^2$ versus $hν$, respectively. From the figure 8(a), it is evident that ZS-1 and ZS-2 have absorption peaks at 286 nm and 289 nm respectively. The direct band gaps ($E_g$) of ZS-1 and ZS-2 were estimated to be 4.12 eV and 3.99 eV respectively using equation (3). The band gap observed in our experiment was slightly larger than that of the literature reported values (3.5–3.8 eV) [64, 65]. This can be attributed to the quantum confinement in the size regime 2–5 nm, leading to a blue shift in the absorption maximum which results in increase of the band gap [64].

A photocatalytic reaction by quantum dots is associated with the excitation of electrons from valence band to conduction band (generation of electron-hole pairs) driven by absorption of photons with energy equal to or greater than the band gap. In general, the electron of the semiconductor having band gap greater than 3.1 eV can be excited by UV-light irradiation [66].

### 3.6. Photocatalytic degradation of organic dyes

Initially, comparative photocatalytic degradation activity of RhB were carried out separately in presence of photocatalyst ZS-1 and ZS-2 by conventional route using beakers. In this study, the intensities of absorption curve were observed to be reduced with increasing irradiation time, indicating decrease in the concentration of RhB solution. The relative change in the concentration of RhB under the irradiation of light was calculated according to equation (4) and shown in figure 9(a). The decolorization of RhB solution after 30 min of irradiation can also be observed in the digital photograph shown as inset in figure 9(a). After 30 min of light irradiation, 77% and 54%, of degradation efficiency could be achieved for ZS-1 and ZS-2 respectively (shown in figure 9(b)). From the results, it is observed that ZS-1 achieved higher degradation efficiency even in beaker reactor. This may be attributed to its high effective surface area (see figure 7(a)) for photocatalytic reaction due to smaller particle size and well dispersed nature. On the other hand, the particles of ZS-2 tend to agglomerate in order to decrease their surface energy, providing less effective surface area for catalytic reaction even after having small particle size also. Thus, keeping in mind the enhanced activity of ZS-1, it was further selected for inline photocatalytic study in microreactor. In the microchannels, similar comparative experiments were carried out using different flow rates (300, 200, 100 and 50 $\mu\text{L min}^{-1}$) of RhB dye keeping the other experimental conditions identical (shown in figure 9(c)). The obtained results revealed that as the flow rate decreases, there is an increase in degradation efficiency of catalyst. In other words, 27, 42, 55 and 93% of dye degradation efficiencies have been achieved for 300, 200, 100 and 50 $\mu\text{L min}^{-1}$ flow rate of dye respectively. This may be attributed to the difference in effective time of interaction between catalyst and dye at different flow rate. In addition, an enhanced 93% degradation efficiency was achieved in microreactor based photocatalysis whereas only 77% of degradation efficiency was attained with the convention beaker based photocatalysis for the same catalyst. The photocatalytic enhancement of ZS-1 in microfluidic channels may be attributed to the higher active surface site of photocatalyst, faster diffusion thus enabling rapid heat, mass and charge transfer, more uniform irradiation of light etc, as compared to the conventional bulk reactor [58]. Thus, the study suggests that microreactor based inline photocatalysis could be a promising method for the enhanced photocatalytic reaction. Similar results have also been observed from the photocatalytic study using MO as the model dye and are shown in figures 9(d)–(f).

The stability and reusability of catalyst are very important for any practical application. Thus, consecutive cyclic (5 times) photo-degradation of MO was performed using ZS-1 in microfluidic channels at the optimized flow rate of dye solution as 50 $\mu\text{L min}^{-1}$.
The same microchannel without altering the coated catalyst was used in every cycle while flowing the fresh dye solution and the results were presented in figure 10. The study revealed that for ZS-1, photocatalytic degradation efficiency declines from 99 to 40% after five cycles, indicating a higher stability of ZS-1 during photocatalytic reaction.

3.7. Antibacterial activity of ZnS quantum dots
Antibacterial activity of zinc sulphide quantum dots was demonstrated against the Gram-negative bacteria (E. coli) at concentrations of 10, 100 and 500 μg ml⁻¹ by performing colony forming unit assay. Results demonstrated a considerable reduction in the number of bacterial colonies in all the treated samples as compared to the control group without any treatment (figure 11). It was further interesting to note that ZS-1 sample in a constrained environment exhibit a significant reduction in the growth of bacterial colonies at a concentration as low as 10 μg ml⁻¹. This is significant enhancement in the antibacterial activity as compared to...
the earlier reports where the anti-bacterial activity was achieved at nanoparticle concentrations ranging as high as mg ml\(^{-1}\)[67].

4. Conclusion

We have efficaciously demonstrated the rapid fabrication of PMMA based microreactors for synthesis of antibacterial ZnS quantum dots and their subsequent inline enhanced photocatalytic activity. ZnS quantum dots, synthesized using microfluidic reactor are more effective in terms of shorter reaction time, uniformity and higher surface area due to smaller particle size. Uniform distribution of quantum dots was observed in case of microreactor based synthesis while highly agglomerated particles were observed in the conventional beaker route. A remarkable enhancement in the photocatalytic activity of ZnS quantum dots was observed when the photocatalytic reaction was performed inline using microfluidic reactor. Instant degradation with efficiencies as high as 93% and 99% were observed for RhB and MO respectively in microfluidic reactor with optimum flow rate of 50 \mu l min\(^{-1}\). The antibacterial investigation performed on \textit{E. coli} also reveal that the ZnS quantum dots (ZS-1) even at concentration as low as 10 \mu g ml\(^{-1}\) are exhibiting good bactericidal activity as compared to the earlier reports.

Hence, the present study demonstrates that these cost effective and rapid fabrication friendly laser engraved microreactors could be viable reactors for the synthesis of semiconductor nanostructures as well as in-channel light-driven enhancement of photocatalytic reactions. These quantum dots may also be useful in heterojunction thin film solar cell or quantum dot sensitized solar cell as photo-absorber/electrode sensitizing material respectively.

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Declaration of conflict of interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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