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One-pot, template-free syntheses of spherical ZnS nanocrystals using a new S^{2-} source and their photocatalytic study

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Abstract
A facile, one-pot synthesis of template-free ZnS microspheres composed of nanocrystals (NCs) have been successfully synthesized by solvothermal method using 4,4'-dibenzylidisulfide (DBDS = (C_7H_7)_2S_2) as a new temperature controlled in situ source of S^{2-} ions without (S1-S3) and with the use of capping agent (S4). The powder X-ray diffraction measurements of all the four (S1-S4) samples revealed the cubic or zinc blende (ZB) structure of the ZnS microspheres. FESEM analyses showed almost spherical morphology of the ZnS microspheres which are composed of smaller NCs. TEM analyses of the samples S3 and S4 confirmed the ZnS microspheres with assembled NCs. Optical measurements of the samples (S1-S4) showed blue-shift in the UV-vis absorption maxima compared to that of bulk ZnS due to quantum confinement effect. Photoluminescence measurements show intense blue emission of the samples. Photocatalytic investigation of the uncapped (S3) and mercaptoethanol (MCE)-capped (S4) ZnS microspheres for degradation of methylorange (MO) revealed higher photocatalytic activity of S3 over S4 under UV light irradiation. The lower catalytic activity of S4 has been attributed due to the presence of MCE capping agents which acts as a barrier for the interaction of MO molecules with the ZnS NCs. The proposed mechanism for the formation of ZnS microspheres and their photocatalytic activity has also been presented.
1. Introduction

Semiconductor nanocrystals (NCs) continue to attract immense attention due to their unique optical, electrical and catalytic properties.\(^1\) Among the various semiconductor nanomaterials, ZnS with its large direct band gap of 3.66 eV at 27°C is one of the important II-VI group semiconductor with potential applications in optoelectronics and luminescent devices.\(^2\) ZnS exists in two different polymorphic structures namely cubic zinc-blende (ZB) structure and the hexagonal wurtzite (WZ) structure.\(^3\) Between these, the most stable form in the bulk is the cubic or ZB structure which transforms into a thermodynamically meta stable state called the hexagonal WZ structure at temperature of 1020°C. Previously reported studies have shown that the properties of nanomaterials depend on their crystallite’s size, shape and structure.\(^4\) Therefore, synthesis of semiconductor NCs with deterministic control over the size, shape and phase is crucial for realizing their multifunctional nanodevice applications.\(^5\) In this context, extensive efforts have been reported on controlled synthesis of ZnS nanostructures with various morphologies such as, spheres, rods, flowers, sheets, etc.\(^6,7\) The formation of these nanostructures has been mostly driven by self-assembly processes and assisted by template molecules/capping agents. On the other hand, the organic capping ligand-free NCs offer several advantages over capped-NCs.\(^8\) However, it is quite challenging to develop ligand-free routes for synthesis of semiconductor NCs with controlled size and shape.\(^9\)

Several organosulfur compounds such as, thiourea, thioacetamide, L-cysteine, etc have been utilized as in situ source of S\(^{2-}\) ions for the synthesis of phase pure ZnS nanostructures.\(^7\) However, the literature survey on ZnS nanostructures synthesized from various organosulfur sources revealed that it is quite difficult to obtain NCs with ultrasmall (~ 2 nm) size without the use of template/capping ligand (Table 1). It has been suggested that for synthesizing nanomaterials with controlled size, it is necessary to separate the nucleation stage from the growth step.\(^10\) In this context, we thought that use of organosulfur compounds with temperature controlled release of S\(^{2-}\) ions would be beneficial for controlling the growth of NCs. Our previous attempts in these lines on utilizing temperature controlled sulfur source resulted semiconductor NCs with ultrasmall (2-5 nm) size without the use of template/capping ligand. In continuation of our efforts, we investigated for the first time the utility of DBDS (dibenzyl disulphide = (C\(_7\)H\(_7\))\(_2\)S\(_2\)) with temperature controlled release of S\(^{2-}\) ions for the synthesis of phase pure ZnS nanostructures. In support of this, we have been able synthesize ZnS NCs with smaller (3-6 nm) crystallite’s size highlighting the merits of DBDS as sulfur source. Herein, we report the synthesis, characterization and photocatalytic activity
of phase pure cubic ZnS NCs of 3-6 nm size using DBDS as a new in situ source of Br2 ions without the use of template/capping agent (S1-S3). Further, to study the effect of capping agents on the crystallite size, shape and the photocatalytic activity of ZnS NCs, we have also synthesized mercaptoethanol (MCE) capped cubic ZnS NCs (S4). Optical measurements of the samples (S1-S4) showed blue-shift in the UV-vis absorption maxima compared with that of bulk ZnS due to quantum confinement effect. Photocatalytic investigation of both uncapped (S3) and MCE-capped (S4) ZnS microspheres for degradation of MO under UV light irradiation revealed higher photocatalytic activity of S3 over S4. The relatively lower photocatalytic activity of S4 has been attributed due to the effect of MCE capping agents which acts as a barrier for the interaction of MO molecules with the ZnS NCs. The unique features of the synthetic procedure followed here are a facile, template-free, one-pot route for synthesis of phase pure ZnS NCs with high yield and almost uniform morphology.

2. Experimental

All the starting materials were commercially available and used as received without further purification. Zn(NO3)2.6H2O and 4,4'-dibenzyl disulphide (DBDS) were purchased from Sigma–Aldrich Chemical Co. Methyl orange (MO) was purchased from Alfa Aesar.

2.1 Synthesis of ZnS microspheres

The ZnS microspheres (S1-S4) were synthesized by solvothermal route as follows. To a 6 mL DMF solution of Zn(NO3)2.6H2O (0.029 g, 0.1 mmol), 3 ml ethanolic solution of DBDS (0.024 g, 0.1 mmol) was added. The mixture with a solvent ratio 2:1 was stirred for 15 minutes and then transferred into a stainless steel teflon lined autoclave and heated at 180°C for 6.5 hrs. After being cooled to room temperature naturally a white precipitate was collected by centrifugation and thoroughly washed with methanol then the products were dried under vacuum (yield of S1:80%). Samples, S2 and S3 were prepared by following the procedure similar to S1, except that the reaction temperature was maintained at 200°C (yield of S2:72%) and 220°C (yield of S3:70%) respectively. The MCE-capped ZnS sample (S4) was prepared by using the procedure similar that of S3 except that, the synthesis was carried out in the presence of 5 equivalents (1 mmol, 35µL) of MCE capping agent (yield of S4:75%)

2.2 Characterization

Powder X-ray diffraction (XRD) patterns of the as-prepared samples were recorded on a PANalytical’s X’PERT PRO diffractometer. Field-emission scanning electron microscopy (FESEM) images were recorded on a Carl zeiss ultra 55 FE SEM. Transmission electron microscopy (TEM), high-resolution TEM (HRTEM) and selected area electron diffraction (SAED) measurements were recorded on JEOL JEM-2100F Field Emission TEM. UV–vis
spectra were recorded on a Perkin Elmer Model Lambda 900 spectrophotometer. Fourier-transform infrared (FT-IR) measurements were recorded on Bruker TENSOR-27 spectrometer. Photoluminescence measurements were recorded at room temperature on a Perkin Elmer LS55 fluorescence spectrophotometer.

2.3 Photocatalytic investigation

Photocatalytic activity of the as-prepared samples of ZnS microspheres for the photocatalytic degradation of an aqueous solution of MO was carried out as follows. As-prepared sample of ZnS microspheres (S3/S4) (40 mg) was suspended in a solution of MO (5.0 x 10^{-5} M) in 50 mL of H2O in a quartz tube at ambient temperature. A 400 W high pressure mercury lamp was used as the UV-vis light source. The lamp was equipped with double walled quartz jacket for constant water circulation and as a water filter to remove the heating effects. The distance between the UV light source and the quartz reaction tube was maintained at 13 cm. Before irradiation, the mixture was stirred well in the dark for 30 minutes to establish an adsorption–desorption equilibrium between the ZnS NCs and MO then the photocatalytic reaction was initiated. The reaction was started after the intensity of the mercury lamp became stable. At regular time intervals, aliquots of the sample were withdrawn and the catalyst was separated through centrifugation and analyzed for MO dye concentration. The percentage degradation of MO dye was determined using the following relation.

\[
\% \text{ Degradation} = \frac{(C_i - C_f)}{C_i}
\]

where, \(C_i\) and \(C_f\) are the initial and final concentrations of MO, respectively

3 Results and Discussions

3.1 Synthesis and Characterization

As mentioned before, the ZnS NCs (S1-S4) were synthesized by solvothermal route using DBDS as an \textit{in situ} sulfur source. For the sake of comparison, we have tabulated some of the literature reports of ZnS nanostructures synthesized using various organosulfur sources (Table 1).\textsuperscript{11} It is evident from the Table 1 that hardly there have been any reports of synthesis of ZnS NCs with smaller crystallite’s size (2-5 nm) in the absence of a template/capping ligand. On the contrary, our synthesis route resulted ZnS NCs with ultrasmall (~ 2nm) size even in the absence of any stabilizing ligand. Further, the synthesis can be carried out in air to obtain phase pure ZnS NCs with high yield and almost uniform morphology.

Powder XRD pattern of the as-prepared samples of ZnS microspheres (S1-S4) are shown in Fig.1(a). The diffraction peaks were observed at \(2\theta = 29.07^\circ, 48.31^\circ\) and \(56.77^\circ\) which can be assigned due to (111), (220) and (311) planes of cubic or ZB structure of ZnS (JCPDS...
The broadness of the diffraction peaks suggest the finite size of these crystallites. The absence of any additional diffraction peaks corresponding to either Zn(NO$_3$)$_2$ or any other impurities indicate high purity of the sample. The mean crystallite’s size (D) of the NCs calculated using the Scherer equation, $D = \frac{0.94\lambda}{B\cos\theta}$ (where, $D =$ crystallite size, $\lambda =$ wavelength of X-ray (1.540598 Å), $B =$ value of full width at half maxima (FWHM) and $\theta$ is the Bragg’s angle) are 2.34, 5.92, 6.66 and 3.66 nm for the samples S1, S2, S3 and S4, respectively. The composition of the samples (S1-S4) was determined by energy dispersive X-ray spectroscopy (EDX). As shown in the Fig. 1b only peaks due to Zn$^{2+}$ and S$^{2-}$ were observed for the uncapped sample S3. Whereas the MCE-capped sample, S4 shows additional peaks originating from oxygen and carbon atoms of MCE capping agent. The quantitative analysis confirmed the atom ratio of Zn$^{2+}$/S$^{2-}$ to be 1:1. Furthermore, FT-IR spectra of the uncapped sample S3 shows only the stretching bands due to the solvent molecules and in case of sample S4, additional stretching bands at 2879, 2809, 1104, 1038 and 695 cm$^{-1}$ corresponding to C-H, S-H, C-O, C-C and C-S stretching frequencies were observed due to MCE-capping agent, (Figs. S1 and S2, ESI). Thus, the above mentioned analyses clearly support the formation of uncapped (S1-S3) and MCE-capped (S4) ZnS microspheres with phase pure cubic ZB structure.

The morphology of the as-prepared samples, S1-S4 was examined by FESEM and TEM analyses. As shown in Fig. 2 FESEM images of all the samples show the presence of almost uniform solid spheres with diameters in the range of 0.35 to 1.2 µm. The broad size distribution of ZnS microspheres particularly in case of samples S1-S3 can be attributed to self-agglomeration of NCs due to the absence of capping agent. Moreover, the magnified FESEM images of individual ZnS microspheres of the samples S1-S4 unveiled the presence of assembled smaller NCs (Fig. 3). Furthermore the precise value of the crystallite’s size was determined by TEM analyses. Fig.4a shows the low-magnification bright-field TEM image of a single uncapped ZnS microsphere, S3 whose size is about 400 nm. The TEM image of a selected region on the surface of the sphere shows the presence of ZnS NCs whose crystallite size lie in the range of 6-10 nm (inset of Fig. 4a) which is in near agreement with the crystallite’s size value calculated from XRD (ca. 6.66 nm). The diffraction planes obtained from the SAED pattern match well with the XRD patterns (Fig. 4b). HRTEM image shows structurally uniform lattice fringes of ZnS NCs suggesting crystalline nature of the sample and the calculated fringe spacing of 0.31 nm corresponds to the (111) lattice plane of cubic ZnS (Fig. 4c). Fig. 5a shows low-magnification bright-field TEM image of a single MCE-capped ZnS microspheres, S4 with a size distribution of about 360 nm. The TEM image of a
selected region on the surface of the sphere shows the presence of ZnS NCs whose crystallite’s size lie in the range of 4-8 nm (inset of Fig.5a), which is in line with the value of crystallite size calculated from XRD (ca. 3.66 nm). The diffraction planes obtained from the SAED pattern match with the XRD patterns (Fig.5b). HRTEM image shows structurally uniform lattice fringes of ZnS NCs, suggesting crystalline nature of the material and the calculated fringe spacing of 0.31 nm corresponds to the (111) lattice plane of the cubic structure of ZnS (inset (c) of Fig. 5). Therefore, the above mentioned data strongly supports the formation of ZnS NCs.

3.2 Formation of ZnS microspheres

The formation of ZnS microspheres can be explained as shown in Scheme 1. In situ generation of S$^2^-$ ions by the C–S and S-S bond cleavage of DBDS linker at temperatures of 180-220 °C followed by reaction with Zn$^{2+}$ ion to form ZnS NCs. Then self-aggregation of these NCs results in the formation of ZnS microspheres as depicted in Scheme 1. Here, DBDS molecule acts as a clean source of S$^2^-$ ions which are released in a controlled fashion by in situ cleavage of C–S and S-S bonds. Therefore the formation of ZnS microspheres S1-S4 is driven by self-aggregation of individual ZnS NCs due to surface energy minimization as shown in Scheme 1.

3.3 Optical properties

The room temperature UV-vis absorption spectra of ZnS microspheres S1–S4 dispersed in methanol is shown in Fig. 6. The spectra show sharp band edge absorptions in the UV region with absorption maxima at 240, 275, 280 and 255 nm for S1, S2, S3 and S4, respectively. The blue shift in the absorption edge of the NCs in comparison with that of bulk ZnS (334 nm) can be attributed due to quantum confinement effect. Similar observation of blue-shift in the absorption edge for ZnS microspheres has been reported suggesting that the UV-vis absorption mainly depends on the size of primary particles and the hierarchical ZnS microspheres exhibit the activity of their nanoscale building blocks. The values of direct band gap energy (E$_g$) of ZnS NCs was estimated from a plot of $\alpha h\nu$ vs photon energy (h$\nu$) following the Tauc relationship, $\alpha h\nu = A(h\nu-E_g)^n$ where, $h\nu = $ photon energy, $A = $ constant, $\alpha = $ absorption coefficient, $k = 4\pi k/\lambda$; $k$ is the absorption index, $\lambda$ is the wavelength and $n$ depends on the type of transition, $n=1/2$ for the allowed direct band gap. The direct band gap values estimated by extrapolating the absorption edge by a linear fitting method were 5.00, 4.25, 4.61 and 4.92 eV for sample S1, S2, S3 and S4, respectively (Fig S2).

3.4 Photoluminescence studies
Photoluminescence spectra of as-synthesized ZnS samples (S1-S4) dispersed in methanol were recorded at room temperature. As shown in the Fig. 7 intense blue emission with maxima centered around 450 nm along with two shoulder peaks located around 385 and 466 nm were observed with the excitation wavelength of 240, 275, 280 and 255 nm for S1, S2, S3 and S4 respectively. Similar observation of multiple emission bands from ZnS samples has been reported earlier. In our studies, the dominant blue emission observed around 450 nm can be assigned due to the recombination of free charge carriers at the surface defect sites of the ZnS. Furthermore, the weak shoulder peaks located around 385 nm and 466 nm can be attributed due to sulphur and zinc vacancies, respectively. Similarly, Hu and co-workers have reported ZnS nanobelts that show fluorescence emission band at 401 nm along with shoulder peak at 470 nm when excited with 250 nm. Kar and Chaudhuri have reported the synthesis of wurtzite ZnS nanostructures that exhibit an intense blue emission consisting of two bands at 394 and 456 nm when excited again at 250 nm wavelength. Moreover, it has also been reported that ZnS microspheres that display strong blue emission band around 415 nm with weak shoulder peak appearing at 466 nm wavelength.

### 3.5 Photocatalytic activity of ZnS NCs

The degradation of toxic and non-biodegradable organic dyes using nanomaterials has attracted significant current interest for the removal of environmental pollutants from waste water. In this regard, photocatalytic activity of uncappped (S3) and MCE-capped (S4) ZnS NCs was investigated for degradation of MO in aqueous solution under UV light irradiation. MO dye was chosen for the study since it is one of the major organic pollutants from textile and dyeing industries. Furthermore, it is a carcinogenic and resistant to direct degradation by sunlight or ultraviolet light. However, it can be photoreduced to harmless organic compounds using photocatalysts. The degradation can be easily monitored with decrease in the intensity of the characteristic absorption band at 463 nm. To rule out the possibility of decolouration by UV light, blank experiments were carried out in the absence of the catalyst which showed negligible degradation of MO suggesting the necessity of catalyst for the degradation process. Figs. 8a and b show the changes in the optical absorption spectra of MO at different time intervals under UV light irradiation catalyzed by ZnS NCs. As it can be seen, with increase in irradiation time the concentration of MO decreases and at the end of 120 min the % degradation of MO was found to be 80.0% and 71.0% catalyzed by un-capped (S3) and MCE-capped (S4) ZnS NCs, respectively indicating higher photocatalytic performance of S3 over S4 (Fig. 8c). The relatively lower photocatalytic activity of S4 can be attributed due to the effect of MCE capping agents which acts as a barrier for the interaction of MO molecules.
with the ZnS NCs. Furthermore, the kinetics of photocatalytic degradation of MO using ZnS NCs can be best explained using pseudo first order reaction, \( \ln(C_o/C_t) = K_{app}t \) where, \( C_o \) is the concentration of dye after keeping in darkness after 30 min and \( C_t \) is the concentration of dye at given time interval \( t \). The plot of \( \ln(C_o/C_t) \) vs \( t \) is shown in Fig. 8d. The estimated value of rate constant for the photocatalytic reaction catalyzed by uncapped (S3) and MCE-capped (S4) ZnS samples are \( 1.278 \times 10^{-2} \) and \( 1.033 \times 10^{-2} \) min\(^{-1} \) respectively supporting higher catalytic activity of S3 over S4. Similar observation of higher catalytic activity of uncapped NCs over organic ligand-capped semiconductor NCs for the photocatalytic degradation of MO has been observed before.\(^9\) The catalytic activity of ZnS NCs observed here is comparable or higher than some of the reported examples of ZnS nanostructures utilized for photocatalytic degradation of MO (Table. 2)\(^{21}\) Moreover, the catalytic rate is also comparable to the best known ultraviolet light photocatalyst, ZnO whose rate constant for catalytic degradation of MO is reported to be \( 1.7 \times 10^{-2} \) m\(^{-1}\).\(^{22}\)

In order to determine the stability and recyclability of the catalysts, the ZnS samples (S3 and S4) were isolated after the catalytic cycle by centrifuging the dispersed solution and washing several times with methanol. The powder XRD spectra of the recycled samples match very well with those of original samples confirming the photostability and recyclability of both uncapped (S3) and MCE-capped (S4) ZnS samples (Fig. S7)

### 3.6 Proposed mechanism for the degradation of MO

The general mechanism of photocatalysis involves absorption of photons by semiconducting material (here ZnS) leading to photoexcitation of electrons from the valence band (VB) to the conduction band (CB) to generate electron–hole (\( e_{CB}^{-}/h_{VB}^{+} \)) pair (eqn (1)).\(^{23}\)

\[
\text{ZnS} + \text{hv} \rightarrow (e_{CB}^{-})_{\text{ZnS}} + (h_{VB}^{+})_{\text{ZnS}} \tag{1}
\]

Then the photogenerated electron–hole pair migrates to the surface of the catalyst (ZnS) and reacts with the adsorbed dye molecules on the surface (eqn (2)–(5)). Followed by transfer of the photogenerated electrons to the dye molecules which is crucial for increasing the activity of a photocatalyst by inhibiting electron–hole recombination.
The reactive species ($O_2^-$, •OH) produced as shown in the eqns (2)–(5) can react with MO to form the degradation products through several possible pathways as has been proposed before eqn (6) (see Scheme S1, ESI).\textsuperscript{24}

\[
\begin{align*}
    O_2 + ZnS (e_{CB}^-) & \rightarrow O_2^- \quad (2) \\
    O_2 + 2(e_{CB}^-)ZnS + 2H^+ & \rightarrow H_2O_2 \quad (3) \\
    (e_{CB}^-)ZnS + O_2^- + 2H^+ & \rightarrow HO^+ + HO^- \quad (4) \\
    H_2O + (h_{VB}^+)ZnS & \rightarrow HO^+ + H^+ \quad (5)
\end{align*}
\]

The observed difference in the photocatalytic activity of uncapped (S3) and MCE-capped (S4) ZnS NCs can be explained as follows. The ZnS NCs in both S3 and S4 are quite active and can produce the electron–hole pairs under UV light irradiation but their contact with air is obstructed by the presence of MCE-capping agents in case of S4. The MCE capping agents act as physical barrier for MO molecules from easy access to catalytically active ZnS NCs in case of S4. Whereas, in the case of S3 the MO molecules can easily access to the surface of ZnS NCs and can interact with the charge carriers (electrons and holes) which is a crucial step in the degradation process. This phenomena clearly supports the relatively higher rate of photocatalytic degradation of MO with uncapped ZnS NCs, S3 ($1.278 \times 10^{-2}$) as compared to that of MCE-capped ZnS NCs, S4 ($1.033 \times 10^{-2}$).

Furthermore, it is noteworthy that the absorption edge of MO shows blue shift to shorter wavelength as shown in Fig.8. This phenomenon suggests that during the course of photocatalysis the MO molecules were oxidized and converted into molecules with lower degree of Π-Π conjugation. The absorption maxima ($\lambda_{\text{max}}$) of these molecules produced during the degradation of MO is shorter than that of original MO molecules. Further oxidation leads to opening of aromatic rings and consequently to degradation of MO to CO$_2$ and H$_2$O (Scheme S1, ESI†).

**Conclusions**

In summary, a facile, one pot, template-free route for synthesis of uncapped (S1–S3) and MCE-capped (S4) ZnS microspheres composed of NCs (3-6 nm) has been developed. For the
first time, dibenzyl disulphide (DBDS) has been utilized as a temperature controlled in situ source of S$^2$- ions for the formation of ZnS NCs. A possible mechanism for the formation of ZnS microspheres has also been proposed. Photocatalytic investigation of both uncapped (S3) and MCE-capped (S4) ZnS microspheres revealed very good photocatalytic activity for the degradation of MO under UV light irradiation. The photocatalytic activity of uncapped ZnS NCs (S3) is higher compared to that of MCE-capped ZnS microspheres (S4). The lower photocatalytic performance of S4 has been attributed to the presence of MCE capping agents which acts as a barrier for the interaction of dye molecules with ZnS NCs. Thus the effect of capping agent on the photocatalytic activity of ZnS NCs has been demonstrated. These results demonstrate the significance of developing capping ligand-free NCs for catalytic applications.

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References


Scheme 1. The proposed mechanism for the formation of ZnS microspheres

$$\text{Zn(NO}_3\text{)}_2 + (\text{C}_7\text{H}_{17})_2\text{S}_2 \xrightarrow{180-220 \degree C} \text{ZnS}_{\text{NC}_3} + (\text{C}_6\text{H}_5)\text{S}^{-}\text{S}^2.$$  
$$\text{ZnS}_{\text{NC}_3} \rightarrow \text{ZnS}_{\text{microspheres}}$$

- **Nucleation**: $\xrightarrow{180-220 \degree C \text{ } 6.5 \text{ hrs}}$  
- **Self-aggregation**:  
- **Ligand-free ZnS**  
- **MCE**  
- **MCE-Capped ZnS**
Table 1. Comparison chart for synthesis of ZnS NCs using various organosulphur sources

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Metal precursor</th>
<th>Sulphur source</th>
<th>Capping agent/ Template</th>
<th>Temperature (°C)</th>
<th>Crystallite size (nm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Zn(acac)₂</td>
<td>Thioacetamide</td>
<td>Thioglycolic acid</td>
<td>110-180</td>
<td>10-27</td>
<td>7(a)</td>
</tr>
<tr>
<td>2</td>
<td>Zn(NO₃)₂.6H₂O</td>
<td>Thioacetamide</td>
<td>Polyethylene glycol</td>
<td>200</td>
<td>20</td>
<td>11(a)</td>
</tr>
<tr>
<td>3</td>
<td>Zn(NO₃)₂.6H₂O</td>
<td>Thioacetamide</td>
<td>Sodium EDTA</td>
<td>130-230</td>
<td>20-25</td>
<td>11(b)</td>
</tr>
<tr>
<td>4</td>
<td>Zn(SO₄)₂</td>
<td>Thiourea</td>
<td>PVP</td>
<td>150</td>
<td>12.3</td>
<td>11(c)</td>
</tr>
<tr>
<td>5</td>
<td>Zn(CH₃COO)₂.2H₂O</td>
<td>Thiourea</td>
<td>Ethylenediamine</td>
<td>180</td>
<td>12-20</td>
<td>11(d)</td>
</tr>
<tr>
<td>6</td>
<td>ZnCl₂</td>
<td>Thiourea</td>
<td>Ethylenediamine</td>
<td>180</td>
<td>40</td>
<td>11(e)</td>
</tr>
<tr>
<td>7</td>
<td>Zn(CH₃COO)₂.2H₂O</td>
<td>Thiourea</td>
<td>Thioglycolic acid</td>
<td>180</td>
<td>20</td>
<td>11(f)</td>
</tr>
<tr>
<td>8</td>
<td>Zn(CH₃COO)₂.2H₂O</td>
<td>L-Cysteine</td>
<td>Granular Gelatin</td>
<td>100</td>
<td>10-40</td>
<td>11(g)</td>
</tr>
<tr>
<td>9</td>
<td>[Zn(TSC)₂]Cl₂</td>
<td>Thiosemicarbazide</td>
<td>Oleylamine</td>
<td>150</td>
<td>11</td>
<td>11(h)</td>
</tr>
<tr>
<td>10</td>
<td>Zn(CH₃COO)₂.2H₂O</td>
<td>Thiosemicarbazide</td>
<td>Hexamethylenetetraamine (HMTA)</td>
<td>180</td>
<td>2-3</td>
<td>11(i)</td>
</tr>
<tr>
<td>11</td>
<td>Zn(NO₃)₂.6H₂O</td>
<td>Thiourea</td>
<td>No capping agent /template</td>
<td>170</td>
<td>9.3-12.7</td>
<td>11(j)</td>
</tr>
<tr>
<td>12</td>
<td>Zn(NO₃)₂.6H₂O</td>
<td>Dibenzyl disulphide (DBDS)</td>
<td>No capping agent/ template</td>
<td>180-220</td>
<td>2.3-6.6</td>
<td>This work</td>
</tr>
</tbody>
</table>

Table 2. Comparison of rate constant (k) values for catalytic degradation of MO by ZnS NCs.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Catalyst</th>
<th>Sulphur source</th>
<th>Temperature of syntheses (°C)</th>
<th>Conc. of dye solution</th>
<th>Catalyst loading</th>
<th>Rate constant (K) value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ligand free ZnS NCs</td>
<td>Thioacetamide</td>
<td>170</td>
<td>10 mgL⁻¹</td>
<td>1.0 gL⁻¹</td>
<td>4.98 x 10⁻² m⁻¹</td>
<td>21(a)</td>
</tr>
<tr>
<td>2</td>
<td>Ligand free ZnS NCs</td>
<td>Thiourea</td>
<td>170</td>
<td>10 mgL⁻¹</td>
<td>1.0 gL⁻¹</td>
<td>3.90 x 10⁻² m⁻¹</td>
<td>21(a)</td>
</tr>
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<td>3</td>
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<td>Commercially bought ZnS</td>
<td>Microwave synthesis</td>
<td>20 mgL⁻¹</td>
<td>0.05 gL⁻¹</td>
<td>7.55 x 10⁻³ m⁻¹</td>
<td>21(b)</td>
</tr>
<tr>
<td>4</td>
<td>Thioglycollic acid-capped ZnS nanorods</td>
<td>Thioacetamide</td>
<td>100</td>
<td>10 mgL⁻¹</td>
<td>0.2 gL⁻¹</td>
<td>1.17 x 10⁻² m⁻¹</td>
<td>21(c)</td>
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<tr>
<td>5</td>
<td>Ligand free ZnS NCs</td>
<td>Dibenzyl disulphide (DBDS)</td>
<td>220</td>
<td>16 mgL⁻¹</td>
<td>0.8 gL⁻¹</td>
<td>1.03 x 10⁻² m⁻¹</td>
<td>This work</td>
</tr>
<tr>
<td>6</td>
<td>MCE-capped ZnS NCs</td>
<td>DBDS</td>
<td>220</td>
<td>16 mgL⁻¹</td>
<td>0.8 gL⁻¹</td>
<td>1.27 x 10⁻² m⁻¹</td>
<td>This work</td>
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Figures with captions

Fig. 1 (a) XRD patterns of the as-prepared ZnS microspheres at temperatures of 180° (S1) 200° (S2), 220°C (uncapped, S3) and 220°C (MCE-capped, S4). (b) EDS spectra of the as-prepared sample of uncapped (S3) and MCE-capped (S4) ZnS microspheres.
Fig. 2 FESEM images of ZnS microspheres, S1 (a), S2 (b), S3 (c) and S4 (d) showing the spherical morphology.

Fig. 3 FESEM images of the surface of ZnS microspheres S1 (a), S2 (b), S3 (c) and S4 (d) showing the presence of NCs.
Fig. 4 (a) TEM image of uncapped ZnS microspheres S3 showing a single ZnS microsphere (inset: magnified image showing the presence of NCs), (b) and (c) shows the SAED pattern and the lattice fringe of ZnS respectively.
Fig. 5 (a) TEM image of MCE-capped ZnS microspheres S4 showing a single microsphere, (inset shows magnified image of the surface of the microsphere showing the presence of ZnS NCs). (b) and (c) shows the SAED pattern and lattice fringe of ZnS respectively.
Fig. 6 UV-vis absorption spectra of the ZnS microspheres S1-S4 in methanol.

Fig. 7 Photoluminescence spectra of ZnS microspheres S1-S4 in methanol.
Fig. 8 Time-dependent UV–vis absorption spectra for degradation of MO (5.0 \times 10^{-5} \text{ M}) in 50 mL H_2O using ZnS (40 mg) microspheres (S3) (a) and S4 (b) under UV light, (c) percentage conversion of MO with time and (d) plot of ln(C_o/C) with time.
For graphical abstract

A facile, one-pot solvothermal method for syntheses of template-free ZnS microspheres composed of nanocrystals (~ 3-6 nm) using (C₇H₇)S₂ as a new in situ source of S²⁻ ions without and with the use of MCE-capping agent has been demonstrated. Photocatalytic investigation of the microspheres revealed very good activity for degradation of MO under UV light irradiation.