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Title Page

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ZnS-based dual nano-semiconductors (ZnS/PbS, ZnS/CdS or ZnS/Ag2S): a green synthesis route and photocatalytic comparison for removing organic dyes

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Conflict of Interest
The authors have no conflicts of interest.
Abstract

Organic dyes generating from many industries are considered as a potential source of water-pollution and have negative effects on human health. The present study was aimed to construct a green synthesis method for fabrication of ZnS-based dual nano-semiconductors and to compare the photocatalytic properties for removing cationic and anionic dyes. ZnS nanoparticles were synthesized using a template synthesis in Bovine Serum Albumin (BSA) solution and then ZnS/PbS, ZnS/CdS and ZnS/Ag$_2$S dual nano-semiconductors were prepared using ion-exchange method. Prepared nano-semiconductors were characterized by using HR-TEM, XRD, FTIR, TG/DTA and AAS. Moreover, photocatalytic activity of prepared nano-semiconductors was tested against Rhodamine B (cationic dye) and Methyl Orange (anionic dye). Results revealed that a controllable ZnS/PbS, ZnS/CdS and ZnS/Ag$_2$S ratio in nano-semiconductors can be achieved by adjusting the ion-exchange time. Prepared ZnS based composites exhibited higher photocatalytic efficiency than that of ZnS alone. In addition, photocatalytic activity of ZnS-based dual nano-semiconductors was found to be dependent upon composition and ratio of sulfides in nano-semiconductors with environmental pH. It was concluded that the combination of template synthesis and ion-exchange method is a feasible approach to fabricate new photocatalysts with higher photocatalytic activity.

Keywords

Photocatalysts • dual nano-semiconductors • template synthesis • Ion-exchange • sulphide
1. Introduction

With every year passing, problem of water pollution is increasing because of industrialization. Industrial wastes contain different organic solvents, dyes, residues of products such as waste from pharmaceutical industry may contain drug or residues[1,2]. Out of them, dyes are rendering serious problems as they are not naturally degradable and difficult to degrade by using routine physical or chemical methods of water purification, however, these methods can reduce the concentration of these dyes[3]. Retention of these dyes in water can cause serious health problems such as methyl orange (MO), a widely used azo-dye, can induce DNA damage[4,5].

In addition to that, metabolite of methyl orange is more toxic and is one of the causes for intestinal tumor induction[6,7]. Therefore, it is necessary to remove such toxic organic dyes from water in order to reduce their health hazards. In this regard, photocatalysis process was emerged as a promising approach for degradation of such dyes[3]. In photocatalysis, free electron-hole pair generation due to light absorption lead to production of free radicals which have superior oxidizing property leading to decomposition of organic contaminants [8]. To achieve higher photocatalytic activity, photocatalysts are commonly employed during photocatalysis process, therefore; development of suitable photocatalysts is promising research area and different kinds of photocatalysts have been reported[9]. Metal sulfide nano-semiconductors have gathered a significant attention due to their exceptional chemical and physical characteristics[9].

Zinc sulfide (ZnS) is an II-VI compound semiconductor with a broader energy gap of 3.68 eV[10]. ZnS based semiconductors, being non-toxic, have been applied as photocatalyst for removal of organic contaminants through photodegradation process[9]. As a photocatalyst, it has ability to rapidly produce electron hole pair under
irradiation of light and also have been reported to have good photostability under UV light irradiation[9,11]. Nano-sized ZnS structures have shown enhanced photocatalytic activity due to enhanced surface area[12]. Doping technique to synthesize hybrid sulphides was reported to be one of feasible methods in order to enhance photocatalytic activity of ZnS. For instance, Wang et al. successfully synthesized ZnS/CdS core/shell nanotubes by combining hydrothermal treatment and ion exchange conversion. They found that the hybrid sulphide nanotubes exhibited about 11.02 and 5.56 times of photocatalytic rates than pure ZnS nanotubes and pure cadmium sulfide (CdS) nanotubles, respectively[13]. In another report, C. Fenget al. synthesized ZnS/CuS nanowires with efficient photocatalytic activity against RhB and MO[14]. Different physicochemical process have been reported for production of ZnS based hybrid nanostructures such as co-precipitation, sol-gel process, thermal evaporation, solvothermal process, microemulsion etc[9,15]. Apart from ZnS and CdS, silver sulfide (Ag_{2}S) and lead sulfide (PbS) were also reported as photocatalyst in degradation of organic dyes[16]. In recent decade, green synthesis methods for synthesis of inorganic nanoparticles have gathered attention of many researchers in order to produce desired products using eco-friendly procedures[17].

In the present study, a green synthesis method was used to prepare ZnS based dual nano-semiconductors i.e. ZnS/Ag_{2}S, ZnS/PbS, ZnS/CdS. ZnS nanoparticles were synthesized by template synthesis using bovine serum albumin (BSA) followed by ion-exchange method to get different dual nano-semiconductors. Furthermore, their photocatalytic activity was compared against Rhodamine B (RhB) and methyl orange (MO). Photocatalytic activity was found to be dependent upon composition and ratio of hybrid sulfide nano-semiconductors which can be adjusted by varying ion-exchange time.

2. Experimental section
2.1. Materials

Zinc nitrate hexahydrate (>99%, MW=297.49, A.R.), silver nitrate (≧ 99.8%, MW = 169.87 A.R.), cadmium chloride (>99.99%, MW=183.32, A.R.), lead nitrate (>99.99%, MW=331.21, A.R.) and thioacetamide (TAA) (≧ 99.0%, Mw=75.13, A.R.) were purchased from Tianjin Chemical Reagent Factory (Tianjin, China). BSA (≧ 98%, Mw = 68,000) was purchased from sigma (St. Louis, MO, USA). All other solvents and reagents used were of analytical grade.

2.2. Green synthesis of ZnS-based nano-semiconductors

2.2.1. Template synthesis of ZnS nano-semiconductors

ZnS nano-semiconductors were synthesized by a template method using BSA as the structure-directing reagent. Briefly, 15 mL of 19.8 mg/mL zinc nitrate aqueous solution was drop-wise added into 40 mL of 1.25 mg/mL BSA aqueous solution under stirring. The mixture was kept static in dark for 12 h at 37 °C. Following that, 15 mL of 10 mg/mL TAA solution was drop-wise supplemented under stirring. The pH value of the mixture was adjusted to 7.5 using NaOH (2 M) solution. After 3 days of reaction at 37 °C, the prepared sample was separated by centrifugation at 10,000 rpm for 10 min. The collected product was washed with double distilled water and lyophilized for 8 h.

2.2.2. Ion exchange for controllable synthesis of dual nano-semiconductors

ZnS-based dual nano-semiconductors were fabricated by the ion-exchange method. Briefly, the prepared ZnS nano-semiconductors were dispersed into 25 mL of 40 mM solutions of cadmium chloride, silver nitrate, lead nitrate solution, separately. The ion exchange process was allowed to carry out at 37 °C for pre-determined time i.e. 1, 3, 4 and 6 h. The final products were separated by centrifugation at 10,000 rpm for 10 min. The collected product was washed with double distilled water and lyophilized.
for 8 h. These nano-semiconductors were named according to ion-exchange time.

2.3. Characterization

Content of nano-semiconductors was determined using atomic absorption spectrometer. High-resolution transmission electron microscopy was used to observe the size and crystal lattice structure (HR-TEM, JEM 2010, JEOL, Japan).

The presence and content of BSA in samples were measured using Fourier transform infrared spectra (FTIR) and Thermo gravimetry-Differential Thermal Analysis (TG/DTA). Potassium bromide pallets of samples were prepared with ratio of 3:100 (sample:KBr) and FTIR spectra were recorded using Fourier transform infra-red spectrophotometer (BIO-RAD, FTS-40, China) within wavenumber range of 4000-650 cm\(^{-1}\) at 2 cm\(^{-1}\) resolution with 128 scan. The TG/DTA thermograms were recorded for each nanocomposite using TG/DTA analyzer (Seiko Instrument Inc., EXSTAR6300 TG/DTA, Japan) in presence of oxygen.

The XRD patterns were taken using Powder X-ray diffractometer (Bruker, D8 Advance, Germany) with graphite monochromatized graphite monochromatized CuK\(\alpha\) radiation (\(\lambda=0.15406\) nm) between 2\(\Theta\) angle range of 10-80\(^\circ\) at 0.05\(^\circ\) s\(^{-1}\) scan rate.

The ultraviolet-visible absorption and fluorescent spectra of different concentration of prepared nano-semiconductors were measured at room temperature by UV-Vis spectrophotometer (Beijing Purkinje General Instrument Co., Ltd., TU-11900, China) and spectrofluorometer (JASCO, FP-6500, Japan).

2.4. Photocatalytic activity of ZnS-based dual nano-semiconductors

2.4.1. Design of photocatalytic device

The following photocatalytic experiments were carried out by using our in-house made photo-catalysis device as shown in Fig. 1. This device contains four sections,
including light source, condensing system, 18 sample cells with magnetic stirrers. The photocatalytic operation for different samples could be simultaneously performed, which would avoid effect of any uncertain factor due to multiple experiments.

2.4.2. Effect of environmental pH

Both cationic (1.0×10^{-5} mol/L Rhodamine B, RhB) and anionic (1.0×10^{-5} mol/L methyl orange, MO) dye solutions were prepared for the photo-degradation tests, respectively (n=3). Briefly, the nano-semiconductors were dispersed into the organic dye solution in a quartz glass tube, with a final concentration of 1 mg/mL. Here, the pH values of the reactive system were maintained at 5.0, 6.0, 7.0, 8.0, and 9.0. After illumination with 500 W of mercury lamp for the regular intervals, the kinetic photo-decomposition process was described by measuring RhB concentration at 554 nm and MO concentrations at 464 nm, respectively, using UV-visible spectrophotometer. As a control, dye solutions without any photo-catalyst were used in order to evaluate the self-decomposition of dyes.

2.4.3. Dye adsorption effect

The dye adsorption on dual nano-semiconductors was evaluated in the dark environment without illumination (n=3). The adsorption kinetic was quantified by measuring RhB concentration at 554 nm and MO concentrations at 464 nm, respectively, using UV visible spectrophotometer.

2.4.4. Recycling of photocatalysts

In order to study the recycling capability of ZnS-based dual nano-semiconductors, photocatalytic activity of nano-semiconductors were evaluated for 5 cycles. The initial concentration of dye was 1.0×10^{-5} mol/L and the pH value was set as 6.0. Nano-semiconductors were obtained by centrifugation at 10,000 rpm for 10 min and their photocatalytic ability against RhB and MO were determined.
3. Results and discussion  

In this study, the combination of the template synthesis and ion exchange technique was used to synthesize the ZnS-based dual nano-semiconductors. This study was mainly based on the following advantages: (1) A synthetic route that allowed fabrication of nano-composites under eco-friendly and gentle conditions, which will reduce the dubious factors from organic system and investment cost from special equipment. (2) The ion exchange technique which offered a facile method to synthesize ZnS based nano-composite semiconductors in a controllable manner without changing the initial morphology. (3) Comparison of photocatalytic activity of different ZnS based nanocomposites against cationic and anionic dye.

3.1. Green synthesis of ZnS-based dual nano-semiconductors

From the typical HR-TEM and selected area electron diffraction (SAED) patterns of ZnS/PbS\(^{@1h}\), ZnS/CdS\(^{@4h}\) and ZnS/Ag\(_2\)S\(^{@2h}\) (Fig. 2), it can be seen that three kinds of ZnS-based dual nano-semiconductors have well dispersity and less than 10 nm size in diameter (Fig. 2A\(_1\), Fig. 2B\(_1\) and Fig. 2C\(_1\)). Both the clear lattice fringes in HR-TEM and typical diffraction spots in the SAED images revealed that crystalline structure of nano-semiconductors (Fig. 2A\(_1\)-2C\(_2\)). The inorganic components in nano-semiconductors were confirmed by XRD spectra. Before ion exchange, the diffraction peaks for ZnS can be clearly distinguished and consistent with the values of the standard (JCPDS 65-0309), with characteristic peaks at (20) 28.608°, 47.589° and 56.471° corresponding to (111), (220) and (311) crystal plane of sphalerite, respectively (Fig. 2A\(_3\)). Because PbS (\(K_{sp}=8.0\times10^{-28}\)), CdS (\(K_{sp}=8.0\times10^{-27}\)) and Ag\(_2\)S (\(K_{sp}=6.3\times10^{-50}\)) have the lower solubility product (\(K_{sp}\)) than ZnS (2.93\(\times10^{-25}\)), the ion-exchange method is feasible in theory to fabricate the hybrid nano-semiconductors based on ZnS by ion-exchange method [18] with the increase in
ion exchange time, the diffraction peaks of PbS (standard JCPDS 05-0592), CdS (standard JCPDS 41-1049) and Ag$_2$S (standard JCPDS 14-0072) were observed on XRD patterns due to composite formation (PbS/ZnS, CdS/ZnS and Ag$_2$S/ZnS) as shown in Fig. 2A to 2C. Moreover, diffraction peak intensities of PbS, CdS and Ag$_2$S in corresponding nanocomposites were found to increase with further increase in time of ion-exchange while intensities of ZnS related peaks was decreased due to replacement of ions. The difference in solubility product ($K_{sp}$) of PbS, CdS and Ag$_2$S results in the different ion-exchange rate, in order of Ag$_2$S $>$ PbS $>$ CdS.

The existence and content of BSA in ZnS-based dual nano-semiconductors was measured by FTIR and TG/DTA. The FTIR results from Fig. 3A indicate that three kinds of ZnS-based dual nano-semiconductors have the same FTIR spectra in the range of 4000 cm$^{-1}$-600 cm$^{-1}$, characterizing with the stretching vibration of amide I and amide II in the typical protein adsorption peaks at 1637 cm$^{-1}$ and 1511 cm$^{-1}$, respectively. The TG measurement reveals the BSA content in ZnS/PbS@1h, ZnS/CdS@4h and ZnS/Ag$_2$S@2h gets to 22.5%, 50.0% and 25.0%, respectively corresponding to weight loss due to protein decomposition (Fig. 3B1-Fig. 3B3).

The UV-visible absorption spectra and fluorescent spectra of ZnS-based dual nano-semiconductors were shown in Fig. 4A. It can be seen that ZnS/PbS and ZnS/Ag$_2$S dual nano-semiconductors have a strong absorption in the UV-light region, with an absorption peak at around 205 nm. The UV absorption intensity increases with the increase of sample contents. ZnS/CdS dual nano-semiconductors show two absorption peaks at around 205 nm and 240 nm. The optical band gap of ZnS-based dual nano-semiconductors was estimated from the Tauc plot and presented in the insets of Fig.4A1-Fig.4A3[19]. From the absorption values, the calculated band gap is 5.68 eV for ZnS/PbS@1h and 5.59 eV for ZnS/Ag$_2$S@2h (the insets in Fig. 4A1 and A3).
respectively. As for ZnS/CdS$^{@4h}$, there are two different band gaps, which are 4.41 eV and 5.45 eV corresponding to CdS and ZnS, respectively. Figure 4B shows the room-temperature PL spectral of ZnS/PbS$^{@1h}$ dual nano-semiconductors, ZnS/CdS$^{@4h}$ dual nano-semiconductors and ZnS/Ag$_2$S$^{@2h}$ dual nano-semiconductors. It is clear that ZnS-based dual nano-semiconductors have the similar PL spectra of and exhibit strong emission in the red region.

3.2. Photocatalytic behaviors of dual nano-semiconductors

Fig. 5 shows the heatmap of photocatalytic degradation of ZnS-based dual nano-semiconductors against Rhodamine B and Methyl orange at different pH values. pH is an important determining factor for dye degradation as it can increase/decrease amount of reactive free radicals and also associated with dye-photocatalyst interaction [20]. Overall, ZnS-based dual nano-semiconductors can effectively degrade both dyes upon UV illumination. The photocatalytic efficiency of ZnS-based dual nano-semiconductors was found in order of ZnS/CdS>ZnS/Ag$_2$S>ZnS/PbS>ZnS. Moreover, the early ion-exchange products (e.g. ZnS/PbS$^{@1h}$, ZnS/CdS$^{@4h}$ and ZnS/Ag$_2$S$^{@2h}$) have the highest photocatalytic efficiency than the later ion-exchange products. The acid reactive system is more suitable for ZnS-based dual nano-semiconductors to photo-degrade organic dyes.

It has been well documented that photocatalytic processes are based on the efficient generation and separation process of carriers by means of band gap excitation[21]. Therefore, the generation and separation of the photo-induced electron-hole pairs are the key factors to influence a photocatalytic reaction[22]. As for the pure ZnS, these charge carriers might be rapidly recombined leading to a small fraction of the available electrons and holes which can participate in the photocatalytic reaction process [23]. Thus, pure ZnS samples have lower photocatalytic activity. However, in
In the case of dual nano-semiconductor photocatalysts, transfer of photo-generated charges from one semiconductor into the lower lying energy bands of the second semiconductor occurred by thermo-dynamical process [as shown in Scheme 1]. ZnS has a wider band gap of ~3.7 eV with about 2.5 eV of $E_{vb}$ and -0.9 eV of $E_{cb}$. Both CdS ($E_g$=-2.4 eV, $E_{vb}$=1.88 eV, $E_{cb}$=-0.52 eV) and Ag$_2$S ($E_g$=-1.0 eV, $E_{vb}$=1.0 eV, $E_{cb}$=0 eV) have narrow band gap [24,25]. Their conduction and valence bands are located within the energy gap of ZnS. Electron-hole pairs have tendency to localize within CdS or Ag$_2$S, which provides the lowest energy states for both electrons and holes, therefore, separation efficiency of photo-generated electrons and holes can be improved. After that, ·OH radicals would be generated through the reaction between valence band hole and water molecules (and hydroxyl) or by ·O$_2$, which is formed by the combination of conduction band electron with adsorbed oxygen. Finally, ·O$_2$ and ·OH radicals react with organic dyes to produce nontoxic products[26]. Therefore, ZnS/CdS and ZnS/Ag$_2$S showed better catalytic activity than pure ZnS. As for ZnS/PbS dual nano-semiconductor, it possibly performed the same photocatalytic mechanism, and its photocatalytic activity was enhanced by comparison with that of pure ZnS. However, the electrons of PbS could not transfer from conduction band of ZnS to that of PbS due to the lower $E_{cb}$ (-1.19 eV)[27]. Thus, ·O$_2$ couldn’t be generated and the degradation rate was decreased. Therefore, the photocatalytic degradation rate on organic dyes of ZnS/PbS was lower than that of ZnS/CdS and ZnS/Ag$_2$S.

In addition, ZnS-based dual nano-semiconductors exhibited higher photocatalytic activity in acidic condition than in alkaline reactive system as represented by heat map in Fig. 5. Furthermore, in order to compare different composites, kinetic analysis of all composites was done at pH 6.0 against Rhodamine B and Methyl Orange which
showed that early ion-exchange products had better photocatalytic activity with order of ZnS/CdS>ZnS/Ag$_2$S>ZnS/PbS>ZnS as shown in Fig. 6 and table 1 through kinetic data analysis. Non-zero y-intercept as shown in Fig. 6 indicates involvement of both dye adsorption and photocatalysis in remediation process. The photocatalytic efficiency was found to be increased with decrease in pH within range of 5.0-9.0. Variations in pH lead to changes in the ionization degree and surface properties of ZnS-based nano-semiconductors [28]. Surfaces of photocatalysts exhibit positive charge at low pH while negative charge at high pH [28,29]. In case of cationic dye (Rhodamine B), protonation of ZnS based dual nano-semiconductors in the acid reactive system caused the fewer dye adsorbed on its surface due to the electrostatic repulsion, but there will form more hydroxyl on its surface. Therefore, photo-generation of ·OH is considered as a key step for pH-dependent photo-degradation of Rhodamine B by ZnS-based dual nano-semiconductors (Fig. 5). In case of anionic dye (methyl orange), there are two possible reasonable explanations for the pH-dependent photocatalytic behaviour of ZnS-based dual nano-semiconductors (Fig. 5). On one hand, ZnS-based dual nano-semiconductors are partially protonated due to the existence of BSA and thus able to electrostatically interact with the anionic dye (Fig. 3) [30]. From Fig. 3 and Fig. 7, it can be seen that ZnS/CdS dual nano-semiconductors had the most content of BSA, and thus the highest methyl orange adsorption can be expected. In the dark, ZnS/CdS dual nano-semiconductors showed the highest adsorption on methyl orange as depicted in Fig. 6. It means that ZnS/CdS dual nano-semiconductors can more effectively photo-degrade methyl orange than ZnS/PbS and ZnS/Ag$_2$S dual nano-semiconductors. Secondly, an increase in H$^+$ concentration always favours to promote methyl orange forming a colourless hydrazine derivative in a dynamic sense [31]. Thus ZnS-based
dual nano-semiconductors have the higher photocatalytic activity in acid pH system
than in alkaline pH system.

\[(\text{CH}_3)_2\text{NC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{SO}_3^-+2\text{H}^+ + 2\text{e}^-\rightleftharpoons (\text{CH}_3)_2\text{NC}_6\text{H}_4\text{NHNHC}_6\text{H}_4\text{SO}_3^-\]

Lastly, the effects of recycling on the photocatalytic activity were also investigated
while keeping the experimental conditions unchanged. Fig. 8 shows the repetitive
photo-degradation of RhB and MO during five consecutive cycles of reuse for
ZnS-based dual nano-semiconductors. The results showed that the photocatalytic
activity of all ZnS-based dual nano-semiconductors decreased significantly after five
cycles. The loss rate of photocatalytic activity on RhB is in order of
ZnS/CdS<ZnS/Ag$_2$S<ZnS/PbS<ZnS, which were about 28.7%, 35.4%, 51.1% and
63.0%, respectively. As for MO, the photocatalytic activity loss for ZnS/PbS,
ZnS/CdS and ZnS/Ag$_2$S dual nano-semiconductors are almost same i.e. 43.3%, 44.1%
and 42.2%, respectively. ZnS was found to loss more photodegradation activity (upto
61.2%) which is significantly higher than dual nano-semiconductors.

4. Conclusions

In summary, we successfully prepared ZnS-based dual nano-semiconductors by
combining the template synthesis technique and ion-exchange methods. The ratio of
dual sulphides in nano-semiconductors could be easily controlled by adjusting the
ion-exchange time. More importantly, the dual nano-semiconductors exhibited the
higher photocatalytic activity than pure ZnS. Moreover, the environmental pH and
adsorption activity of ZnS-based dual semiconductors are two key factors affecting
their photocatalytic activity. This data can serve as a guide for finding new
photocatalysts with higher photocatalytic activity on dye pollutants.

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Table 1. The kinetic rate constants of rhodamine B and methyl orange degradation over the samples under UV irradiation.

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<th>Methyl orange rate constants</th>
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Figure legends

Figure 1. In-house made photo-catalysis device equipped with 18 sample cells.

Figure 2. HRTEM (1) and SAED images (2), and XRD patterns (3) of ZnS-based dual nano-semiconductors. (A) ZnS/PbS@$^{1h}$, (B) ZnS/CdS@$^{4h}$ and (C) ZnS/Ag$_2$S@$^{2h}$.

Figure 3. FTIR (A) and TG/DTA (B) analysis of ZnS-based dual semiconductors (1) ZnS/PbS@$^{1h}$, (2) ZnS/CdS@$^{4h}$ and (3) ZnS/Ag$_2$S@$^{2h}$.

Figure 4. UV-vis absorption spectra (A) and PL spectra (B) of ZnS-based dual nano-semiconductors with different concentrations in aqueous solution. (1) ZnS/PbS@$^{1h}$, (2) ZnS/CdS@$^{4h}$ and (3) ZnS/Ag$_2$S@$^{2h}$. The insets show the Tauc plots of $(ahv)^2$ vs. photon energy $(hv)$ for ZnS-based dual nano-semiconductors.

Figure 5. Heatmap of photocatalytic degradation rates of ZnS-based dual nano-semiconductors on Rhodamine B and Methyl orange at different pH values.

Figure 6. Degradation kinetics profiles of ZnS-based dual nano-semiconductors on Rhodamine B (1) and Methyl orange (2). (A) ZnS/PbS, (B) ZnS/CdS and (C) ZnS/Ag$_2$S.

Figure 7. Dark adsorption of ZnS and ZnS-based dual nano-semiconductors (all ion-exchange products) on Rhodamine B (1) and Methyl orange (2) after 2 h.

Figure 8. Cycling degradation efficiency of ZnS-based dual nano-semiconductors on Rhodamine B (1) and Methyl orange (2). (A) ZnS/PbS, (B) ZnS/CdS and (C) ZnS/Ag$_2$S.
Scheme 1

Scheme 1. A proposed photo-catalytic mechanism of ZnS-based dual nano-semiconductors for degradation of organic dyes.
Figure 1

Condensate water

Mercury lamp

Magnetic stirrer
Figure 2

A1  ZnS/PbS$^{\text{10 h}}$

10 nm

A2  ZnS/PbS$^{\text{10 h}}$

A3  Intensity (a.u.)

20 (degrees)

B1  ZnS/CdS$^{\text{10 h}}$

10 nm

B2  ZnS/CdS$^{\text{10 h}}$

B3  Intensity (a.u.)

20 (degrees)

C1  ZnS/AgS$^{\text{20 h}}$

10 nm

C2  ZnS/AgS$^{\text{20 h}}$

C3  Intensity (a.u.)

20 (degrees)
Figure 3

Figure 3
**Figure 4**
494 Figure 5

![Figure 5](image-url)

495 Rhodamine B
496 Methyl orange
497
498
499
Figure 6

(A1) ZnS
1h-product
3h-Product
4h-Product
6h-product

(A2) ZnS
1h-product
3h-Product
4h-Product
6h-product

(B1) ZnS
4h-product
12h-Product
24h-Product
48h-product

(B2) ZnS
4h-product
12h-Product
24h-Product
48h-product

(C1) ZnS
2h-product
4h-Product
8h-Product
24h-product

(C2) ZnS
2h-product
4h-Product
8h-Product
24h-product

T/min
\[-\ln(C/Co)\]
Figure 7

(A) Graph showing dark adsorption of Rhodamine B (%).
(B) Graph showing dark adsorption of Rhodamine B (%).
Figure 8
ZnS-based dual nano-semiconductors were successfully synthesized by combining the biomimetic technique and ion-exchange methods. The ratio of dual sulphides in nano-semiconductors was controllable and key factors improving the photocatalytic activity of ZnS photocatalyst.
➢ The green route was developed to prepare ZnS-based dual nano-semiconductors.

➢ The catalytic activity of dual nano-semiconductors was higher than pure ZnS.

➢ Composition and ratio of sulfides were key factors affecting catalytic activity.

➢ Combination of template synthesis and ion-exchange method was a feasible route to develop new composite photocatalysts.