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ABSTRACT

 ZrS_2 -loaded ZnO (ZrS_2 -ZnO) nano-composites were synthesized by the precipitate-thermal decomposition method. The coexistence of ZrS_2 increased the absorbance of ZnO in UV region. X-ray photoelectron spectroscopic analysis revealed Zr in the form of Zr^{4+} . The prepared catalysts were used for degradation of an industrial pollutant azo dye, naphthol blue black (NBB), under UV light. It was found that the uptake of 11.4 wt% ZrS_2 on ZnO was very efficient for NBB removal and its photocatalytic activity was more efficient than ZnO, ZrS_2 and TiO₂ catalysts. The optimum pH for efficient degradation of NBB was 6.5. Based on the energy levels of ZrS_2 and ZnO, a mechanism was proposed for the higher efficiency of ZrS_2 -ZnO under UV light. This catalyst was reusable.

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1. Introduction

Photocatalysis is a promising technique for the degradation of organic pollutants in air and water. Semiconductor nanostructures have been of interest due to their wide range of applications. Among various semiconductors, metal-oxides such as ZnO and TiO₂ have been studied intensively as photocatalysts because of their suitable band gap, high photocatalytic activity, and stability against photocorrosion [1-4]. In especial, ZnO nanomaterials exhibit a few distinct advantages over TiO₂. The adequate direct bulk band gap of ZnO (3.37 eV compared to 3.2 eV of TiO₂), simple tailoring of structure, ease of crystallization, anisotropic growth, high exciton binding energy (60 meV compared to 4 meV of TiO₂) and high electron mobility (200 cm² V⁻¹ s⁻¹ compared to 30 cm² V⁻¹ s⁻¹ of TiO₂) give it an edge over TiO₂ [5,6].

In order to improve photocatalytic activity of ZnO, several methods have been developed [7,8]. Doping is very useful way to improve the charge separation in the semiconductor system. Many dopants such as transition metals or rare earth metals could enhance the photocatalytic properties of ZnO [9-11]. In addition, coupling of two semiconductor oxides with different band gap

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widths has been demonstrated in many studies as one of the most effective ways to enhance the photocatalytic efficiency. In contrast to the single semiconductor photocatalyst, many coupled semiconductor systems, metal-loaded coupled semiconductors and metal halide-loaded semiconductors such as $ZnO-Fe_2O_3$ [12,13], $ZnO-WO_3$ [12,13], $ZnO-SnO_2$ [14], TiO_2-WO_3 [15,16], TiO_2-SnO_2 [17,18], TiO_2-ZnO [19], CdS-ZnO [5], $WO_3-Ag-ZnO$ [20], AgBr-ZnO [21], Ag_3PO_4-ZnO [22], MoO_3-ZnO [23], Nb_2O_5-ZnO [24], and SrF_2-TiO_2 [25] have been reported. Mesoporous materials are also used for effective environmental remediation [26–28].

The layered transition metal dichalcogenides exhibit a variety of electrical properties, and especially ZrS_2 (group IVB of the transition metal dichalcogenides) is a very good semiconducting dichalcogenide. The transition metal is coordinated to six chalcogen anions and has a D_{3d} point group symmetry, and ZrS_2 is found to have a stoichiometry near the ideal chalcogen-to-metal [29] ratio of 2 and band gap 1.68 eV [30]. Many researchers have used metal sulfides as photocatalysts for effective environmental remediations [5,31–34]. Recently, Subash et al. [34] reported Ag₂S–ZnO as an effective catalyst for removal of an azo dye RR 120. Furthermore, they also found for Ag₂S to be reusable. This stimulated us to prepare ZrS_2 –loaded ZnO. To the best of our knowledge, this is the first report on the synthesis of ZrS_2 –ZnO and its use in the degradation of naphthol blue black dye under UV light illumination. Among azo dyes, naphthol blue black (NBB) is one of the frequently

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used dyes in textile industries and becomes a potential threat to the aquatic environment due to its poor biodegradability [35,36].

2. Experimental section

2.1. Materials

The commercial azo dye NBB (Fig. 1, absorption band: 320 nm) obtained from Aldrich was used as received. Oxalic acid dihydrate (99%), zinc nitrate hexahydrate (99%), zirconium(iv) chloride (anhydrous) and sodium sulfide nanohydrate were obtained from Acros Chemicals. TiO₂ (Merck) was used as received. The double distilled water was used to prepare experimental solutions. The pH of the solution before irradiation was adjusted using an aqueous H_2SO_4 or NaOH solution.

2.2. Analytical methods

The crystal phase analysis was done by a wide-angle X-ray diffraction (XRD) (Bruker D2 Phaser, USA) at 10 mA current and 30 kV voltage with a monochromatic Cu K α radiation (λ = 1.5405 Å) with a 2θ step of 0.05° per one second, and a scan range from $2\theta = 20^{\circ}$ to 80°. Raman spectra were measured with a Horiba spectrometer at 633 nm (1.96 eV) using a $10 \times$ objective with 90 s acquisition time. The thermal gravimetric analysis (TGA) was carried out on a TGA thermal analyzer (TA Instruments Q500, UK). Under the 100 mL/ min air/N₂-flow, the temperature was raised up to 1000 °C at a constant rate of 10 °C min⁻¹. The transmission electron microscopic (TEM) observation was carried out on a Hitachi H-7000, Japan, with an acceleration voltage of 100 kV. The specimens were prepared by depositing a drop of the suspension of sample powder, which was ultrasonically dispersed in acetone for 10 min, on a carbon-coated copper grid, followed by drying at room temperature. On an observation with a IEOL ISM-6500F cold field emission scanning electron microscope (FE-SEM), the samples were mounted on a gold platform placed in chamber. Elemental analysis was performed by means of energy dispersive X-ray (EDX) analyzer (JEOL, JSM-6500F, Japan). The nitrogen adsorption experiment (BET) was performed at 77 K using a surface area analyzer (Quantachrome Autosorb-iQ porosimeter, UK) after degassed at 55 °C for 12 h. X-ray photoelectron spectroscopic (XPS) analysis was done



Fig. 1. Photodegradation of NBB with different contents of ZrS_2 on ZnO; [NBB] = 30 ppm, catalyst suspension = 10 mg/50 mL, pH = 6.5, irradiation time = 15 min.

on a PHI Quantera. The spectra were referenced to the binding energy of C1s (285 eV). The absorption spectra were recorded using a Jasco V-670 series UV spectrometer.

2.3. Preparation of ZrS₂-loaded ZnO

ZrS₂-loaded ZnO was prepared by precipitate-thermal decomposition method (Scheme S1, see Supplementary data). Aqueous solutions (100 mL) of zinc nitrate hexahydrate (0.4 M) and oxalic acid (0.6 M) were heated at 80 °C separately. The zinc nitrate solution was added rapidly to the oxalic acid solution to prepare zinc oxalate. ZrCl₄ (0.466 g, 2 mM) in 5 mL water was mixed with Na₂S (0.960 g, 4 mM) in 5 mL water. The prepared ZrS₂ solution was added to the zinc oxalate solution. The mixture was stirred for 4 h, and then the precipitated mixture was sonicated for 1 h (Amplitude = 50, power = 55–59 W). The zinc oxalate dehydrate crystals with ZrS₂ were filtered, washed several times with water, and air-dried for 2-3 days. The crystals were calcined in the muffle furnace at the rate of $20 \,^{\circ}$ C min⁻¹ to reach the decomposition temperature of zinc oxalate (450 °C). After 12 h, the furnace was allowed to cool down to room temperature. The ZrS₂-loaded ZnO catalyst was collected and used for further analysis. The calculated content of ZrS₂ in this catalyst is 11.4 wt%. The decomposition of zinc oxalate around 400 °C and the stability of ZrS₂ have been confirmed by TGA (Fig. S1, see Supplementary data), although ZrS₂ was reported to be stable at 450 °C [37]. ZrS₂–ZnO catalysts with calculated 5.6 and 17.2 wt% ZrS₂ contents were prepared by the same procedure using appropriate amounts of ZrCl₄ and Na₂S. The ZnO was prepared without addition of ZrS₂.

2.4. Photodegradation experiments

Photocatalytic activities of the as-obtained photocatalysts were evaluated by the degradation of NBB azo dye under a HOYA-SCHOTT Ex 250 photoreactor (Super high pressure mercury lamp (250 W), dimensions (mm) (235 (W) × 295 (H) × 250 (D)), initial intensity (5500 mW cm⁻²), long-pass filter (cut-off position 395 nm)). The dye solution was kept approximately at 8-10 cm gap under the UV light source. In each experiment, the reaction suspension containing photocatalyst (10 mg) in a 50 mL NBB solution (30 ppm) was magnetically stirred in the dark for 30 min to ensure the adsorption equilibrium between photocatalyst powders and NBB. Then the solution was exposed to the UV light irradiation, and aliquots (4 mL) were sampled at given time intervals and centrifuged to remove photocatalyst powders. The filtrates were analyzed by recording the absorbance variations of an absorption band (320 nm) in the UV-visible spectrum of NBB. After complete degradation of each run, the catalyst (ZrS₂–ZnO) was centrifuged and washed with water for several times, followed by rinsing with ethanol. The catalyst was dried in a vacuum oven at 80 °C for 5 h and used for next run.

3. Results and discussion

3.1. Characterization of catalyst

Primary analysis of photocatalytic degradation of NBB was carried out with ZrS_2 -loading of ZrS_2 -ZnO catalysts of different ZrS_2 contents. The degradation for 15 min irradiation was 35.2%, 44.4% and 28.6% for ZrS_2 -ZnO catalysts of calculated 5.6, 11.4 and 17.2 wt% ZrS_2 contents, respectively (Fig. 1). Since the catalyst loaded 11.4 wt% of ZrS_2 was found to be the most efficient, this catalyst was characterized by different methodologies.

The EDS of ZnO and ZrS_2 –ZnO, shown in Fig. S2, revealed the presence of Zr, S, Zn and O. The contents of elements in both

Table 1EDS results of ZnO and ZrS2-ZnO.

ZnO		ZrS ₂ –ZnO	
Weight%	Atomic%	Weight%	Atomic%
25.80	58.69	21.29	53.24
74.20	41.31	69.64	42.62
-	-	8.87	3.89
-	-	0.20	0.25
100.00	100.00	100.00	100.00
	ZnO Weight% 25.80 74.20 - - 100.00	ZnO Weight% Atomic% 25.80 58.69 74.20 41.31 100.00 100.00	ZnO ZrS2-ZnO Weight% Atomic% Weight% 25.80 58.69 21.29 74.20 41.31 69.64 - - 8.87 - - 0.20 100.00 100.00 100.00

catalysts are listed in Table 1. Whereas the atomic ratio of Zn and O was nearly 1:1 (1:1.4 for ZnO, 1:1.2 for ZrS_2 –ZnO), the atomic ratio of Zr and S in ZrS_2 –ZnO was not 2:1. The reason of the unaccomplished atomic ratio may be sulfur deficiency in the lattice, as previously reported [38].

XRD patterns of ZnO and ZrS₂-ZnO are shown in Fig. 2. The diffraction peaks of ZnO (Fig. 2a) at 31.69°, 34.36°, 36.18° and 56.51° correspond to (100), (002), (101) and (110) planes of wurtzite ZnO (JCPDS 89-0511). The diffraction pattern of ZrS₂-ZnO has no difference from that of ZnO, as shown in Fig. 2b. This reveals that ZnO in ZrS₂–ZnO also has a wurtzite structure. Aside from this, it should be noted that there were no observation of new peaks for ZrS₂ in the ZrS₂–ZnO catalyst, while ZrS₂ showed four peaks at 30.14°, 50.33°, 59.87° and 62.66° (Fig. S3) [37]. This may be due to the low concentration of ZrS₂ on ZnO and to less intense peaks of ZrS₂ as compared to ZnO. If the zirconium or sulfur is substituted in place of Zn, corresponding peak shifts in XRD are expected. The lack of such shifts in the XRD of ZrS2-ZnO indicates the presence of ZrS₂ on the surface of ZnO. In addition, the doping of Zr metal is unlikely because of the difference in ionic radii between Zn²⁺ (0.72 Å), and Zr^{4+} (0.79 Å).

Raman studies were performed to investigate the vibrational spectroscopic properties of ZnO and ZrS_2 –ZnO nanostructures. The Raman spectra of ZnO and ZrS_2 –ZnO are given in Fig. 3a and



Fig. 2. XRD patterns of (a) ZnO and (b) ZrS₂-ZnO.



Fig. 3. Raman spectra of (a) ZnO and (b) ZrS₂-ZnO.

b, respectively. The bands at 236, 433 and 639 cm^{-1} are attributed to optical phonons of ZnO. These bands correspond to E_2 and second-order Raman bands arising from zone boundary phones of the hexagonal ZnO [39]. The band at 639 cm⁻¹ can also be assigned to the A_1 (lattice oxygen) mode of the hexagonal ZnO. The Raman bands in the region from 1000 to 1400 cm⁻¹ are attributed to the optical overtones and associated with the second-order Raman active modes. The additional band at 1696 cm⁻¹ was also observed for ZnO, although the origin of this band is not clear at the present moment [40]. No new distinctive bands were observed for ZrS₂ in ZrS₂–ZnO (Fig. 3b). It has been reported that ZrS₂ can give very less intense Raman bands (A_{1g} and E_{g} modes) at 249 and 331 cm⁻¹ and no additional bands are observed [30]. On the contrary, ZnO can present a very intense Raman band at 236 cm⁻¹, Moreover, since the concentration of ZrS₂ is also less, ZrS₂ bands could not be distinguished from a ZnO band. It is evident even from these results that ZrS₂–ZnO is dominated by a wurtzite-phase of ZnO.

The morphology of ZnO and ZrS₂–ZnO was observed by TEM and FE-SEM, as given in Fig. 4. TEM photographs displayed only a texture of aggregates but the morphology of particles can be confirmed by FE-SEM images for both ZnO and ZrS₂–ZnO, although the identification of ZrS₂ in ZrS₂–ZnO was impossible. The particle sizes were in the range of 10–100 nm for both ZnO and ZrS₂–ZnO.

The diffuse reflectance spectra (DRS) of ZnO and ZrS₂–ZnO are shown in Fig. 5a and b, respectively. ZrS₂-loading on ZnO caused a small red-shift in the absorption edge from 410 to 425 nm. This result can be interpreted as a possible evidence for favorable interaction between ZnO and ZrS₂ and for the reduction of band gap of ZnO, since the absorption bands of Zr⁴⁺-doped metal oxides have been reported to be shifted towards longer wavelength compared to metal oxides [41,42]. The band gap energies *E* of ZnO and ZrS₂–ZnO were found to be 3.02 and 2.91 eV, respectively, using Plank's radiation low $E = hc/\lambda$, where *h* is Plank's constant, *c* is the speed of light and λ is the wavelength of absorption edge. That is, the ZrS₂-loading on ZnO decreases the band gap energy of ZnO. Additionally, it should be noted that the ZrS₂-loading on ZnO increased the absorbance of ZnO in UV region, indicating the increased UV-shielding effect.

XPS was measured in order to know the chemical state of elements in the catalyst. The survey spectrum (Fig. 6a) of ZrS_2 -ZnO indicated the existence of elements Zn, O, Zr, and S. The C1s peak is attributed to the residual carbon from the sample and/or adventitious hydrocarbon during the measurement. Zn2p occurred at 1023.8 and 1047.2 eV, which confirms the presence of Zn^{2+} in the catalyst. The O1s profile displayed two symmetrical peaks



Fig. 4. TEM images of (a) ZnO and (b) ZrS₂-ZnO and FE-SEM images of (c) ZnO and (d) ZrS₂-ZnO.



Fig. 5. DRS of (a) ZnO and (b) ZrS₂-ZnO.

(α and β locating at 530.0 and 533.0 eV, respectively), indicating two different kinds of O species. These peaks should be associated with lattice oxygen of ZnO and chemisorbed oxygen caused by the surface hydroxyl (OH), respectively [34]. Thus, the existence of ZnO was confirmed. Figs. 6b and c show the binding energy peaks of Zr3d and S2p, respectively. The binding energy peaks of Zr3d at 180.9 and 185.2 eV correspond to $3d_{5/2}$ and $3d_{3/2}$ of Zr⁴⁺, respectively [42]. Four binding energy peaks of S2p were observed in the range of 159.9–171.9 eV [34]. The results suggest the formation of ZrS₂.

In general, the surface area of the catalyst is one of the most important factors influencing the catalytic activity. The surface areas of ZnO and ZrS_2 –ZnO were determined using the nitrogen gas adsorption method. N₂ adsorption–desorption isotherms of ZnO and ZrS_2 –ZnO are presented in Fig. S4a and b, respectively.

They revealed a type II hysteresis loop. The BET surface area and pore volume of ZnO and ZrS_2 –ZnO are given in Table 2. After loading of ZrS_2 on ZnO, the BET surface area increased 40%, but the average pore diameter shrank 26%, although the pore volume did not change, indicating the influence of ZrS_2 -loading on ZnO. The increase of the surface area after ZrS_2 -loading may be due to the retardation of the aggregation and therefore the less occupation of the intrinsic surface area of ZnO.

3.2. Photodegradability of NBB

3.2.1. Effect of catalyst

The UV–vis spectra, at different irradiation time, of an aqueous NBB (30 ppm) solution in the presence of ZrS_2 –ZnO are shown in Fig. 7. There was no significant change in absorption band positions during irradiation, but the absorbance of bands at 320 and 615 nm decreased gradually due to the degradation. Such variation is apparent even the color fading of the corresponding solutions, as seen in an inset of Fig. 7.

The NBB degradation was calculated from the decrease of absorbance at 320 nm and shown as a function of irradiation time in Fig. 8, where the photodegradability of NBB was compared among those from different photocatalysts. Almost complete photodegradation of the dye took place at 45 min with ZrS₂-ZnO (curve a). However, when the experiment with ZrS₂-ZnO was performed in the dark environment without UV light power, no decrease in dye concentration occurred (curve b). Negligible degradation (0.2%) was also observed, when the reaction without any catalyst was allowed in the presence of UV light (curve c). From these observations, it can be clearly noted that both light energy and photocatalysts are needed for the effective degradation of NBB. The efficiency of the present catalyst was compared with ZnO, ZrS₂ and commercial TiO₂ (see Fig. 8). While ZrS₂ did not display any catalytic efficiency (curve e) and TiO₂ reached 77% of degradation after 75 min (curve f), ZnO took the irradiation time up to 75 min, until the almost complete degradation occurs (curve d).



Fig. 6. XPS of ZrS₂–ZnO (a) survey, (b) Zr3d and (c) S2p.

Table	2
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Surface	properties	of ZnO	and	$7rS_{2}-7nO$
Junace	properties	UI ZIIU	anu	2132-2110.

Sample	$S_{\text{BET}}(m^2/g)$	Pore volume (cm ³ /g)
ZnO	15.7	0.21
ZrS ₂ -ZnO	22.1	0.22

This indicates that ZrS_2 –ZnO is more efficient on the NBB degradation than other catalysts.

3.2.2. Effect of solution pH

Since textile industries usually drain wastewater off at a wide range of pH, the influence of solution pH must be considered on the pollutant degradation by photocatalysis. Moreover, since the solution pH determines the surface charge properties of ZnO, the charge of dye molecules and the adsorption of dyes onto the



Fig. 7. UV-vis spectra of NBB on UV light irradiation in the presence of ZrS_2 -ZnO; [NBB] = 30 ppm, pH = 6.5, ZrS_2 -ZnO suspension = 10 mg/50 mL, irradiation time = (a) 0 min, (b) 15 min, (c) 30 min and (d) 45 min.



Fig. 8. Photodegradability of NBB; [NBB] = 30 ppm, catalyst suspension = 10 mg/50 mL, pH = 6.5, (a) ZrS₂–ZnO, (b) ZrS₂–ZnO (dark, without irradiation), (c) no catalyst, (d) ZnO, (e) ZrS₂, and (f) TiO₂.



Fig. 9. Effect of solution pH; [NBB] = 30 ppm, ZrS_2 –ZnO suspension = 10 mg/50 mL, irradiation time = 15 min.



Fig. 10. Effect of initial dye concentration; pH = 6.5, ZrS_2 –ZnO suspension = 10 mg/ 50 mL, irradiation time = 15 min.

surface of photocatalyst, the degradation of NBB by ZrS₂-ZnO was carried out at different initial pH of the dye solution. It was found from Fig. 9 that the degradation strongly depended on the solution pH. The degradation by ZrS₂–ZnO at pH 2.9, 6.5, 9.2 and 11 were 21.3%, 44.4%, 34.2% and 33.6%, respectively, for 15 min irradiation, indicating that the optimum pH for efficient removal of NBB by ZrS₂–ZnO is 6.5. Degradation efficiency of a catalyst depends on the adsorption of dye molecules, which is influenced by ionic nature of the dye and pH_{zpc} (pH of zero point charge) of the catalyst. The pH_{zpc} for ZnO and Zr⁴⁺-loaded ZnO is found to be below 9, and the ZnO surface is positively charged below this pH value [42,43]. Because the dye has two sulfonic acid groups in its structure, it exists as negative ions above pK_{H2SO4} ($pK_{\alpha 1} = -5$ and $pK_{\alpha 2}$ = 1.99). The electrostatic attraction between positively charged ZrS₂-ZnO and negatively charged dye at pH region below pH_{zpc} and above pK_{H2SO4} can lead to the strong adsorption of dye on ZrS₂–ZnO surface, and therefore the reaction at catalyst surface with abundant adsorbed dyes may lead to the higher degradation at this pH range. An experiment to verify the dark adsorption of NBB under different pH was carried out, and the adsorption at pH 2.9, 6.5, 9.2 and 11.0 were 13.0%, 18.5%, 8.2% and 1.8%, respectively, after the attainment of adsorption equilibrium (30 min) (Fig. S5). It is apparent that the degradation of NBB is consistent with the adsorption of NBB on catalysts. The strong correlation of photocatalytic efficiency with the doping of guest (analyte) on catalyst surface has been reported for the system of dendrimer-protected TiO₂ [44,45]. The less removal efficiency at high acidic pH range is due to the reaction of charged ZnO with acids to produce the corresponding salt at [20,21].

3.2.3. Effect of initial dye concentration

Since most of the industrial effluents have higher concentration of the pollutant, an application point of view to study the effect of initial dye concentration is very important for any environmental remediation by means of photocatalysis process. The effect of initial dye concentration on degradation of dye NBB by ZrS₂-ZnO was examined under UV light illuminations. Fig. 10 showed that the increase of dye concentration from 20 to 50 ppm decreased the percentages of degradation from 60.4% to 30.0%. The degradation depends upon 'OH (hydroxyl radical) formation on catalyst surface and probability of 'OH reacting with dye molecule. As the initial concentration of the dye increases, the path length of photons entering the solution decreases and thus the photocatalytic degradation efficiency decreases [21,25], while the path length of the photons is enough long at the low concentration of dye, that is, the increasing of the photon absorption leads higher degree of degradation by the catalyst.

3.2.4. Stability of catalyst

The main advantage of the semiconductor photocatalysis is its reusability. The catalyst reusability is an important performance of the photocatalytic process, because a significant cost reduction on the treatment of dye effluent is indispensable. When the catalyst was recycled owing to this reason, a drop in efficiency from 100% (1st run) to 98.5% (4th run) was obtained as shown in Fig. S6. These results indicate that ZrS₂–ZnO catalyst remains



Scheme 1. Mechanism of degradation of NBB by ZrS2-ZnO.

effective and reusable under UV light. Earlier, nano-chain ZnO and Zr⁴⁺-doped ZnO have been reported to have preferable antiphotocorrosive nature [3,42]. Thus, supposed that ZrS₂–ZnO is antiphotocorrosive, this may be the reason for its reusability and photostability. Moreover, the stability of ZrS₂–ZnO was also confirmed by XRD measurements. The XRD patterns of ZrS₂–ZnO before run and after 4th run are shown in Fig. S7. No difference between those XRDs reveals that ZrS₂–ZnO is stable under UV light illumination.

3.2.5. Mechanism of photocatalytic degradation

A mechanism was proposed based on the energy levels of ZrS₂ and ZnO [20,46]. The charge separation and photocatalytic reaction on ZrS₂–ZnO photocatalyst are shown in Scheme 1. When semiconductor is illuminated by UV irradiation, a valance band (VB) electron goes to conduction band (CB) leaving a hole in valance band, although in common, these photogenerated electron and hole are partly recombined and the photocatalytic activity of semiconductors is reduced by this process. Under UV light illumination, when two semiconductors are excited, the charge separation occurs simultaneously, and positions of VB and CB play a vital role for charge separation and photocatalytic efficiency. Since the CB position of ZrS₂ is slightly high in comparison with ZnO, photogenerated electrons are transferred from CB of ZrS₂ to CB of ZnO, and this process will enhance the charge separation of ZnO. Moreover, the CB positions of ZrS₂ and ZnO are more negative than the standard redox potential $E^0 = (O_2/O_2^-)$ (-0.33 eV vs NHE) [47], suggesting that electrons at CB of ZrS₂ and ZnO can reduce O₂ to O₂⁻. The formation of superoxide radical (0^{-}_{2}) is promoted by both semiconductors; this radical is a highly reactive species towards the degradation of NBB dye. In the meantime, the VB of ZnO is more positive than the standard redox potential $E^0 = (OH^-/OH^2)$ (1.99 eV vs NHE) [48]. This suggests that the generated holes in the VB of ZnO can oxidize OH⁻ or H₂O to form OH, then involving the photocatalytic degradation of NBB. The formation of O_2^- and OH[•] is attained due to the charge separation processes described above, and the high reactivity of both radicals leads higher percentage of degradation. However, the VB of ZrS₂ is negative than the standard redox potential of $E^0 = (OH^-/OH^-)$ (1.99 eV vs NHE) [48], suggesting that the generated holes in ZrS₂ cannot oxidize OH⁻ or H₂O to form OH[.]. This is the reason that ZrS₂ alone has scarcely efficiency in photodegradation of NBB, as revealed by photocatalytic experiment (Fig. 8e).

4. Conclusion

It was validated for the first time that the easy synthesis of ZrS₂–ZnO was achieved by the precipitate-thermal decomposition method. This synthetic method is simple and low cost for the production of efficient photocatalyst. EDS showed the presence of Zr and S in the catalyst. Presence of ZrS₂ increased the absorbance of ZnO in UV region. DRS spectra indicated the reduction of band gap of ZrS₂-ZnO, compared to ZnO. XPS revealed the presence of zirconium in the form of Zr^{4+} in the catalyst. ZrS_2 -loading on ZnO increased the BET surface area of the catalyst. Moreover, ZrS₂–ZnO was more efficient than ZnO, ZrS₂ and commercial TiO₂ for the degradation of NBB under UV light. The optimum pH for efficient removal of dve was neutral like 6.5. Increase in the initial dye concentration decreased the efficiency of degradation. Reusability of this catalyst will make the treatment of dye effluent more cost-effective. A degradation mechanism was proposed based on the energy levels of ZrS₂ and ZnO. Furthermore, since the prepared ZrS₂–ZnO had superior photocatalytic activity towards the degradation of NBB, this procedure may be generally used to the treatment of industrial dye effluent in large scale.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.seppur.2014.05. 018.

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