Synthesis and azo dye photodegradation activity of ZrS$_2$–ZnO nano-composites

Balu Krishnakumar$^a$, Toyoko Imae$^{a,b,}$*, Jonathan Miras$^c$, Jordi Esquena$^c$

$^a$Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, 43 Section 4, Keelung Road, Taipei 10607, Taiwan
$^b$Department of Chemical Engineering, National Taiwan University of Science and Technology, 43 Section 4, Keelung Road, Taipei 10607, Taiwan
$^c$Institute for Advanced Chemistry of Catalonia (IQAC-CSIC) and CIBER en Bioingenieria, Biomateriales y Nanomedicina (CIBER-BBN), C/ Jordi Girona 18-26, 08034 Barcelona, Spain

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**A B S T R A C T**

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 TiO$_2$ 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 TiO$_2$ 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 TiO$_2$. The adequate direct bulk band gap of ZnO (3.37 eV compared to 3.2 eV of TiO$_2$), simple tailoring of structure, ease of crystallization, anisotropic growth, high exciton binding energy (60 meV compared to 4 meV of TiO$_2$), and high electron mobility (200 cm$^2$/V·s compared to 30 cm$^2$/V·s$^{-1}$ of TiO$_2$) give it an edge over TiO$_2$ [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 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$_2$O$_3$ [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$_3$PO$_4$–ZnO [22], MoO$_3$–ZnO [23], Nb$_2$O$_5$–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 semiconductor 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 Ag$_2$S–ZnO as an effective catalyst for removal of an azo dye RR 120. Furthermore, they also found for Ag$_2$S 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
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 H2SO4 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 Kα radiation (λ = 1.5405 Å) with a 2θ step of 0.05° per one second, and a scan range from 2θ = 20° to 80°. Raman spectra were measured with a Horiba spectrometer at 633 nm (1.96 eV) using a 10× objective with 90 s acquisition time. 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 Kα radiation (λ = 1.5405 Å) with a 2θ step of 0.05° per one second, and a scan range from 2θ = 20° to 80°. 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 JEOL JSM-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 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 Na2SO3 (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°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 Na2SO3. 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, 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 ZrS2–loading of ZrS2–ZnO catalysts of different ZrS2 contents. The degradation for 15 min irradiation was 35.2%, 44.4% and 28.6% for ZrS2–ZnO catalysts of calculated 5.6, 11.4 and 17.2 wt% ZrS2 contents, respectively (Fig. 1). Since the catalyst loaded 11.4 wt% ZrS2 was found to be the most efficient, this catalyst was characterized by different methodologies.

The EDS of ZnO and ZrS2–ZnO, shown in Fig. S2, revealed the presence of Zr, S, Zn and O. The contents of elements in both
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 ZrS$_2$–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 ZrS$_2$–ZnO has no difference from that of ZnO, as shown in Fig. 2b. This reveals that ZnO in ZrS$_2$–ZnO also has a wurtzite structure. Aside from this, it should be noted that there were no observation of new peaks for ZrS$_2$ in the ZrS$_2$–ZnO catalyst, while ZrS$_2$ 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 ZrS$_2$ on ZnO and to less intense peaks of ZrS$_2$ 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 ZrS$_2$–ZnO indicates the presence of ZrS$_2$ on the surface of ZnO. In addition, the doping of Zr metal is unlikely because of the difference in ionic radii between Zn and Zr, as previously reported [38].

Table 1

<table>
<thead>
<tr>
<th>Element</th>
<th>ZnO</th>
<th>ZrS$_2$–ZnO</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Weight%</td>
<td>Atomic%</td>
</tr>
<tr>
<td>O K</td>
<td>25.80</td>
<td>58.69</td>
</tr>
<tr>
<td>Zn K</td>
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<td>41.31</td>
</tr>
<tr>
<td>Zr K</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>S K</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Fig. 3. Raman spectra of (a) ZnO and (b) ZrS$_2$–ZnO.

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 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 phonons of the hexagonal ZnO [39]. The band at 639 cm$^{-1}$ can also be assigned to the $A_1g$ (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 ZrS$_2$ in ZrS$_2$–ZnO (Fig. 3b). It has been reported that ZrS$_2$ 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 ZrS$_2$ is also less, ZrS$_2$ bands could not be distinguished from a ZnO band. It is evident even from these results that ZrS$_2$–ZnO is dominated by a wurtzite-phase of ZnO.

The morphology of ZnO and ZrS$_2$–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 ZrS$_2$–ZnO, although the identification of ZrS$_2$ in ZrS$_2$–ZnO was impossible. The particle sizes were in the range of 10–100 nm for both ZnO and ZrS$_2$–ZnO.

The diffuse reflectance spectra (DRS) of ZnO and ZrS$_2$–ZnO are shown in Fig. 5a and b, respectively. ZrS$_2$-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 ZrS$_2$ and for the reduction of band gap of ZnO, since the absorption bands of Zr$^{4+}$-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 ZrS$_2$–ZnO were found to be 3.02 and 2.91 eV, respectively, using Planck’s radiation law $E = h\nu/c$, where $h$ is Planck’s constant, $c$ is the speed of light and $\nu$ is the wavelength of absorption edge. That is, the ZrS$_2$-loading on ZnO decreases the band gap energy of ZnO. Additionally, it should be noted that the ZrS$_2$-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.
(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 3d5/2 and 3d3/2 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 ZrS2–ZnO were determined using the nitrogen gas adsorption method. N2 adsorption–desorption isotherms of ZnO and ZrS2–ZnO are presented in Fig. 5a and b, respectively. They revealed a type II hysteresis loop. The BET surface area and pore volume of ZnO and ZrS2–ZnO are given in Table 2. After loading of ZrS2 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 ZrS2-loading on ZnO. The increase of the surface area after ZrS2-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 ZrS2–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).
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

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$ (m$^2$/g)</th>
<th>Pore volume (cm$^3$/g)</th>
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<tr>
<td>ZnO</td>
<td>15.7</td>
<td>0.21</td>
</tr>
<tr>
<td>ZrS$_2$–ZnO</td>
<td>22.1</td>
<td>0.22</td>
</tr>
</tbody>
</table>

Table 2
Surface properties of ZnO and ZrS$_2$–ZnO.

This indicates that ZrS$_2$–ZnO is more efficient on the NBB degradation than other catalysts.

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) ZrS$_2$–ZnO, (b) ZrS$_2$–ZnO (dark, without irradiation), (c) no catalyst, (d) ZnO, (e) ZrS$_2$, and (f) TiO$_2$.

Fig. 9. Effect of solution pH; [NBB] = 30 ppm, ZrS$_2$–ZnO suspension = 10 mg/50 mL, irradiation time = 15 min.
surface of photocatalyst, the degradation of NBB by ZrS$_2$–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 ZrS$_2$–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 ZrS$_2$–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 Zr$^{4+}$–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 pH$_{zpc}$ (pK$_{a1}$ = 2.4 and pK$_{a2}$ = 1.99). The electrostatic attraction between positively charged ZrS$_2$–ZnO and negatively charged dye at pH region below pH$_{zpc}$ can lead to the strong adsorption of dye on ZrS$_2$–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 TiO$_2$ [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 ZrS$_2$–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 O$_2^-$ (hydroxyl radical) formation on catalyst surface and probability of O$_2^-$ 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 ZrS$_2$–ZnO catalyst remains...
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 valence 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 (O2-) 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 $E^0 = (OH/OH^+)$ ($1.99$ 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 O2- 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 $E^0 = (OH/OH^-)$ ($1.99$ 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. 5e).

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 ZrS2 in the catalyst. ZrS2–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 dye 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.

References


