Convenient synthesis of Mn-doped Zn (O,S) nanoparticle photocatalyst for 4-nitrophenol reduction

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Abstract. The conversion of 4-nitrophenol as a toxic and waste pollutant to 4-aminophenol as a non-toxic and useful compound by photocatalytic reduction is highly important. In this work, the solid-solution concept by doping was involved to synthesis earth-abundant and green material of Mn-doped Zn(O,S). Zn(O,S) with different Mn doping contents was easily synthesized at low temperature 90°C for 4-NP reduction without using the reducing agent of NaBH₄. The Mn-doped Zn(O,S) catalyst exhibited the enhancements in optical and electrochemical properties compared to un-doped Zn(O,S). It was found that 10% Mn-doped Zn(O,S) had the best properties and it could totally reduce 4-NP after 2h photoreactions under low UV illumination. The hydrogen ion was proposed to involve the 4-NP reduction to 4-AP, which is hydrogen ion and electron replaced the oxygen in amino (NO₂) group of 4-NP to form the nitro (NH₂) group. We also proposed the incorporation of Mn in Zn site in the Zn(O,S) host lattice could make the oxygen surface bonding weak for easily forming the oxygen vacancy. The more oxygen vacancy for more hydrogen ion would be generated to consume for 4-NP reduction.

1. Introduction

The development of industry such as pesticides, dyes, drugs, etc has improved the quality of human life on one side. In the other side, it also contributes the pollution to the environment. One of the waste from those industries especially pesticides industry is 4-nitrophenol (4-NP). The 4-NP is well known as nitroaromatic compounds with high toxicity level and hazardous waste [1]. Therefore, the US government through environmental protection agency (EPA) lists the 4-NP as one of the toxic pollutant. By considering these negative effects, the conversion of 4-NP to another compound with less toxic and useful is absolutely needed. One of the ways to convert the 4-NP is a photocatalytic reduction with 4-aminophenol (4-AP) as a product. 4-AP known as non-toxic chemical is largely used for pharmaceuticals, dyestuffs, paracetamol, and antipyretic drugs in industries [2, 3].

Several kinds of semiconductor photocatalysts have been widely used for the 4-NP reduction. However, most of them used the noble metal such as silver, gold, and platinum to improve the catalytic activity [4-7]. In large-scale application, the utilization of noble metal is inefficient due to the high cost in production. In addition, some of the noble metal like silver or gold is not so stable. Sometimes after being re-used for several times, the silver or gold nanoparticle aggregated and lowered the catalytic activity. To overcome this issue, the researchers introduce the stabilizing reagent. However, it makes the synthesis process a little complicated, inefficient and expensive. Therefore,
designing a photocatalyst with material’s criteria of earth abundance in precursors, simple processing, no noble metals, high activity, and good stability is highly important. To specifically point out, the previous reports had generally used the sodium borohydride (NaBH₄) as a reducing agent in facilitating the conversion of the 4-NP to 4-AP. They proposed NaBH₄ as a hydrogen source to accelerate the reaction. Although the NaBH₄ is a cheap chemical, the excess of its chemical might cause environmental pollution.

In the previous report, we had synthesized the Zn(O,S) solid solution by combining the ZnO and ZnS for hydrogen evolution reaction [8]. In this work, we tried to optimize the application of Zn(O,S) by doping concept for 4-NP reduction. Doping concept has been widely applied in many applications in order to obtain the desired properties from a material. The better properties such as electronic and optical properties could be achieved by introducing the small amount of dopant so-called impurity into the host lattice. Manganese is one of the proper candidate dopant from transition metal group. In literatures, manganese had been shown as dopant to enhance the catalytic performance. For example, manganese doped hematite (α-Fe₂O₃) nanorods could enhance the efficiency of photoelectrochemical water splitting [9]. Abdouhadriz also had reported that Mn-doped WO₃ had the higher catalytic activity compared to un-doped WO₃ for methylene blue degradation [10]. Another report by Faouzi et al. showed that Mn-doped ZnO increased the surface area, decreased electron-hole recombination, and finally improved the catalytic activity for methylene orange degradation [11]. Based on the above considerations, we choose the manganese as a dopant to improve the performance of Zn(O,S). By combining the doping and solid solution concepts, the Mn-doped Zn(O,S) photocatalyst was systematically synthesized at low temperature with different Mn contents. Since our catalyst could produce hydrogen, NaBH₄ was not been used in this work. The hydrogen ion from the photoreaction Mn-doped Zn(O,S) was proposed for 4-NP reduction and the possible mechanism was elucidated in this paper.

2. Experimental section
The experimental procedures were similar to our previous work [12], except MnCl₂ at 0, 2.5, 5, 10, and 20% base on the amount of zinc acetate hydrate was added for each Mn-doped Zn(O,S). Briefly, 20 mmol of zinc acetate hydrate, 2 mmol of manganese chloride, and 10 mmol of thioacetamide were dissolved in 800 mL deionized water. This solution was stirred at 400 rpm and heated at 90°C for 4 h. After washing process the precipitation was dried by rotary evaporator. As-prepared catalyst was characterized by XRD, SEM, UV-VIS spectrometer, PL spectroscopy, HPLC and GC.

3. Results and discussion

3.1 X-ray diffraction Analysis (XRD)
The X-ray diffraction patterns of Mn-doped Zn(O,S) with different Mn contents were evaluated, shown in figure 1. Although the ionic radius of Mn (r= 80 pm) was larger than Zn (r= 74 pm), the X-ray pattern did not show any shift before and after being doped with Mn, which can be attributed to the little amount of Mn in the Zn(O,S) host lattice [13]. As confirmed by analyses of energy dispersive spectra (EDS), the actual amounts of Mn were 0.53, 0.89, 1.98, and 2.45 for the Mn-doped Zn(O,S) with the Mn precursors at 2.5, 5, 10, and 20%, respectively. The similar behavior was also found in the previous studies [14]. However, the XRD intensity of the catalyst after being doped was lower than undoped, indicating that Mn was successfully doped to the Zn site in the Zn(O,S) host lattice to disturb the lattice flatness. All the peaks located between those of ZnO (JCPDS#65-2880) and ZnS (JCPDS#05-0566) showed a cubic crystal structure, similar to our previous work [8]. The peaks at 29.36, 48.85, and 58.38 can be assigned as (111), (220), and (311) planes, respectively. There were no other peaks for secondary phases like manganese oxide or manganese sulfide, which revealed that our catalyst was pure Mn-doped Zn(O,S).

3.2 Morphology and microstructure
The morphology of Mn-doped Zn(O,S) was observed by FE-SEM. Figure 2a shows the representative image of Mn-doped Zn(O,S). The morphology of aggregate nanoparticles was clearly observed with some small and big particles. The particle size is actually tiny, about 2.5 nm as confirmed by Scherrer calculation. Due to aggregation of some small particles, the particle size of Mn-doped Zn(O,S) had variation from 10 to 200 nm. There is no big difference of morphology before and after doping Mn even we increased the Mn content to 20%. Figures 2b-e show the elemental mapping for each element in Mn-doped Zn(O,S). The dot patterns explained the existence of zinc, manganese, oxygen, and sulfur as constituents in our catalyst. The manganese as a dopant is not only much less than zinc but also is homogeneously distributed over Mn-doped Zn(O,S) nanoparticles. This provides another evidence that Mn has been successfully doped in Zn(O,S) host lattice.

Figure 1. XRD patterns of Mn-doped Zn(O,S)

Figure 2. (a) Representative of FE-SEM image of Mn-doped Zn(O,S) and elemental mapping images for (b) Zn, (c) Mn, (d) O, and (e) S in 10% Mn-doped Zn(O,S).
3.3 Optical properties
To study the optical properties of Mn-doped Zn(O,S), the DRS and PL spectra were performed. The small amount of Mn could significantly increase the absorbance at UV range (figure 3). The absorbance of 10% Mn-doped Zn(O,S) was 2-fold higher compared to undoped Zn(O,S) and had the highest absorbance. Figure 3b exhibits PL emission of Mn-doped Zn(O,S) with different Mn contents. The emission intensity of catalyst before and after doping is not quite different. However, the lowest emission intensity was found for 10% Mn-doped Zn(O,S). This indicates that it has the lowest charges recombination or the fastest charge separation. To further study the optical properties of Mn-doped Zn(O,S) the Tauc plot was performed to calculate the band gap of catalysts. The band gap values of Mn-doped Zn(O,S) were 3.49, 3.62, 3.62, 3.59, and 3.61 eV for using precursors at 0, 2.5, 5, 10 and 20% Mn, respectively. The substitution of Mn in the Zn(O,S) host lattice only enhanced the absorbance and did not significantly change the band gap energy.

![Figure 3](image.png)

**Figure 3.** Diffuse reflectance spectra of Mn-doped ZnOS with different Mn contents.

3.4 Electrochemical impedance spectroscopy (EIS) analysis
The EIS analysis is a capable characterization to evaluate the charge transfer at the interface between catalyst and electrode. In the Nyquist plot, the charge transfer ability is indicated by the diameter of the semicircle. The higher diameter indicates slower charge transfer and vice versa. The electrochemical impedance spectra of Mn-doped Zn(O,S) with different Mn contents are shown in figure 4. To determine the charge transfer resistance ($R_{ct}$) of Mn-doped Zn(O,S), the measurement results were fitted to Randle equation circuit model (inset in the figure 4) in Z view software. The values of charge transfer resistance were 44.2, 27.8, 19.6, 11.3, 31.5 kΩ for using 0, 2.5, 5, 10, and 20% Mn precursors in doped Zn(O,S), respectively. The charge transfer resistance constantly decreased with increasing the Mn content up to 10%. This result concurred with the PL data in figure 3b, in which the 10% Mn-doped Zn(O,S) showed the fastest charge separation.
Figure 4. Electrochemical impedance spectra (EIS) of Mn-doped Zn(O,S).

3.5 Photocatalytic 4-NP reduction

Figure 5 shows the time-dependent UV-Vis absorbance spectra of 4-NP reduction at different conditions. It has been known that the peak absorbance of 4-AP and 4-NP located at 300 nm and 317 nm, respectively. In the presence of sodium borohydride the peak of 4-NP shifts to 400 nm due to the formation of 4-nitrophenolate [15]. Since we did not use the NaBH₄ in this work, the peak position for 4-NP was at 317 nm. Figure 4a shows the 4-NP reduction without using any catalyst. It can be seen clearly that the absorbance did not change even after 90 min photoreaction. It means there no 4-NP reduction happened in this condition. Next, we tested the performance of un-doped Zn(O,S) with the existence of 10 % ethanol, as shown in figure 5b. The absorbance slowly decreased and the peak shifted a little to the lower wavelength, indicating that the 4-NP reduction happened. However, the reduction was very slow. After introducing 10% Mn-doped Zn(O,S) catalyst without ethanol, the absorbance did not decrease furthermore, as shown in figure 4c and the reduction did not obviously happen. This can be explained as that more hydrogen ions for the significant 4-NP reduction are needed, while the reduction reaction to produce hydrogen ion was very low without using ethanol as sacrificial reagent, as shown in our previous reports [8, 12, 14]. The figure 5d shows the 4-NP reduction in the presence of 10% Mn-doped Zn(O,S) with 10% ethanol. The absorbance regularly decreased with increasing the photoreaction irradiation time and the peak was clearly shifted from 317 nm to 300 nm. Accordingly, at this condition, 4-NP was significantly reduced to 4-AP after 90 min reaction. To confirm the 4-NP reduction, further characterization was performed by using the HPLC.
Figure 5. UV-Vis absorbance spectra of the 4-NP reduction. (a) without catalyst, (b) with Mn-free Zn(O,S) and 10% ethanol, (c) with 10% Mn-doped Zn(O,S) without ethanol, and (d) with 10% Mn-doped Zn(O,S) with 10% ethanol.

Figure 6. High performance liquid chromatography (HPLC) profiles achieved with (a) UV detector and (b) Fluorescence detector.
Figure 6 shows high performance liquid chromatography results for the 4-NP reduction with Mn-doped Zn(O,S) in 10% ethanol. Initially, we monitored the commercially available standard samples of 4-NP and 4-AP to identify their retention time. The retention time of 4-NP was found at 27.3 min by UV detector and for 4-AP at 4.3 min by the fluorescence detector. As soon as the photoreaction started, the 2 mL aliquot solution was taken at the time scale of 0h and was checked by the HPLC. It had the quite high intensity at 27.3 min (figure 6a) and there was no peak at 4.3 min (figure 6b), which means no formation of 4-AP. However, after 1 h photoreaction, the 4-NP intensity was much lower than 0h. The peak intensity of 4-NP dramatically decreased (figure 6a) with the concurrently rapid decrease in the 4-AP peak intensity (figure 6b). The disappearance of peak at 27.3 min after 2h proved that 4-NP was totally reduced to 4-AP. The photographs of colour change from yellowish to the clear solution (shown inset figure 6) also reveal the 4-NP reduction to 4-AP. The additional peak in figure 5b (signed as*) might be caused by the polymerization of 4-AP since it can easily polymerize even at the room temperature [16]. This HPLC results corroborate the reduction of 4-NP to 4-AP over the Mn-doped Zn(O,S) catalyst.

4. Kinetic mechanism

Figure 7 displays the schematic kinetic mechanism for hydrogen evolution-involved reaction and the 4-NP reduction to 4-AP. Once the catalyst is illuminated by the photo with energy larger than 3.6 eV, the photocarrier holes and electrons will be generated in the valence band and conduction band, respectively. Those electrons and holes need to migrate to the surface of the catalyst to participate the chemical reaction before their recombination together. The reaction for 4-NP reduction is initiated by the oxidation reaction of water with the formation of oxygen vacancy. Then following by the reduction of water via oxygen vacancy to form the hydrogen ion (H\(^+\)). We proposed hydrogen ion involved in the reduction of 4-NP to 4-AP which is hydrogen and electron would replace the oxygen in the nitro (NO\(_2\)) group to form the amino (NH\(_2\)) group. Therefore, the hydrogen evolution reaction in figure 8 with 30 ppm 4-NP was much lower compared to without 4-NP. Furthermore, we confronted the photocatalytic hydrogen evolution reaction result in figure 8 with HPLC result in figure 6. During the first hour photoreaction, almost no hydrogen gas evolution since most of the hydrogen ion was consumed to reduce the 4-NP. However, after the first-hour reaction the hydrogen evolution a little increased since the remain 4-NP was less (see figure 6a). Thereby, some of the hydrogen ions reduced the 4-NP to 4-AP and some others produced hydrogen gas. Finally, after the second-hour reaction, hydrogen evolution rate dramatically increased since the 4-NP has been totally reduced to 4-AP and all hydrogen ions now were utilized to produce the hydrogen gas. The better performance of the 10% Mn-doped Zn(O,S) is related to several issues such as the bonding strength, absorbance, charge recombination and charge transfer. As proved by PL result and EIS results, the 10% Mn doping showed the lowest charge recombination and the fastest charge transfer. Furthermore, the incorporation Mn is proposed to weaken the bonding and make the surface more active. Mn-doped Zn(O,S) with the best composition has significantly improved its photocatalytic activity.
Figure 7. Schematic mechanism of the 4-NP reduction with Mn-doped Zn(O,S).

Figure 8. Photocatalytic hydrogen evolution with and without 30 ppm 4-NP.

5. Conclusions
The Mn-doped Zn(O,S) had been successfully synthesized by the convenient method at low temperature with different Mn contents. The incorporation of Mn in the Zn(O,S) host lattice not only increased the absorbance but also decreased the photocarrier electron-hole recombination as confirmed by DRS and PL spectra, respectively. Additionally, the Mn also could significantly decrease the charge transfer resistance. The 10% Mn-doped to Zn(O,S) host lattice was found the best properties and it could totally reduce the 30 ppm 4-NP to 4-AP after 2-hour photoreaction without using the NaBH₄ as reducing agent. The hydrogen ion was proposed to involve the 4-NP reduction to 4-AP, which the hydrogen ion and electron replaced the oxygen in amino (NO₂) group to form the nitro (NH₂) group. The capability of Mn-doped Zn(O,S) to reduce the 4-NP was contributed by the synergetic effect of the high absorbance, low charge recombination, and fast charge transfer. The substitution of Mn in the side of Zn in the Zn(O,S) host lattice also weakened the oxygen bonding to easily forming the oxygen vacancy.

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