Response to Reviewer 1

We are very grateful to Reviewer for your all very valuable comments and additional suggestions. The manuscript has been substantially reformatted and modified based on your all suggestions. Reviewer comments are in black and the responses to the reviewer comments are in blue, as well as the corrections in manuscript are also in blue.

Comments and Suggestions for Authors:

I believe that the overall quality and merit of the revised manuscript are still too low to be published in Materials.

1. Based on the authors' reply to my previous comments, I assumed that authors want to discuss the impacts of stabilizing agents (EN and NH) and Mn doping on the photocatalytic activities of synthesized ZnS nanowires. Although authors separate the paragraphs 3.2 "Photocatalytic activity" into 3.2.1 and 3.2.2, there are still a lot of issues that need to be addressed.

Response:

In fact, our intention to separate the paragraphs 3.2 "Photocatalytic activity" into 3.2.1 and 3.2.2 was the detailed and more precisely discussion of the impacts of stabilizing agents (EN and NH) and Mn doping on the photocatalytic activities of synthesized ZnS nanowires. In present version of manuscript additional remarks and modification have been done according to Reviewer's comments.

- Overall, the results of photocatalytic activities of various samples were not correlated with the discussions of characterization results. Besides, characterization results of various samples should be more carefully examined and the way of presentation of datum needs to be improved (including data selection displayed in one graph for comparison).

Response:

In the present form of paper we correlated the characterization results of prepared ZnS and ZnS:Mn NCs with photocatalytic activities of various samples, please see the paragraphs 3.2. Additional, we have modified all charts and the description of individual results point by point in accordance with the Reviewer's request (please see below). We hope that manuscript in the present form including both overall quality and merit will be sufficient to be published in Materials.

[XRD patterns]

- Selection of stabilizer (EN or NH) resulted in different XRD patterns regardless of Mn doping, although XRD patterns of all the ZnS samples exhibited characteristic peaks of crystalline ZnS. The relative peak ratio of (002) to those of (100) and (001) decreased when NH was used as a stabilizer instead of EN. It is not mentioned or explained, either.

- If ZnS was synthesized using the same stabilizer, variation of Mn doping did not seem to induce significant changes in XRD patterns, excepting for the slight 2theta shift of the entire XRD pattern of ZnS_NH upon the Mn doping (ZnS_NH vs ZnS_NH_Mn0.01 in Figure 1b)).

It seemed that a similar 2 theta shift upon Mn doping was not observed in the case of the ZnS_EN sample (Figure 1a) (at least it is not clear). However, the authors mentioned that "However, the diffraction peaks of (100), (002) and (101) planes of the Mn-doped ZnS NCs showed a slight shift towards the higher 2theta side compared with undoped ZnS" (line 203-204) which can mislead the readers. Moreover, in the following lines (line 204-207), the authors attributed the 2 theta shift upon Mn doping which was only observed in the case of ZnS_NH to the incorporation of the Mn (Mn2+) having a different ion radius from Zn (Zn2+). This cannot explain why the ZnS_EN sample did not exhibit any noticeable peak shift upon the Mn doping. Even the ZnS_En_Mn0.02 sample with the highest amount of Mn doping (3.7447 at%) among all the samples studied in this work showed similar XRD patterns with the ZnS_En sample. In addition, there was also no shift of XRD peak positions of the ZnS_K_NH_Mn0.01 sample from those of ZnS_NH. Do those mean that it was only the ZnS_NH_Mn samples Mn2+ ions substituted the Zn2+ sites upon Mn doping? Those needs more careful examination of datum and explanations.

Response:

In order to present carefully the XRD results in a clearer way as possible, the new XRD graphs of selected samples according to the Reviewer's suggestion were prepared. Please see Figure 1. In fact, now some very important differences on XRD graphs are much more visible compare to our previous graphs. Figures 1 indicate now XRD patterns of ZnS and ZnS:Mn NCs including samples prepared with different content of manganese and ethylenediamine as a stabilizer (Fig. 1a); with different types of using the heat source (Fig. 2b) and with a different stabilizer (Fig. 2c). Figure 1a shows the XRD results for samples ZnS_En_Mn0.02, Zn_EN_Mn0.01, ZnS_EN_Mn0.001 and ZnS_EN. We deliberately omitted the attempt of sample ZnS_EN_Mn0.005 which has a similar XRD pattern as other Mn-doped ZnS_EN samples, to make a Fig. 1a transparent and clear as possible. Figure 2b presents the XRD results for samples Zn_K_NH_Mn0.01 and ZnS_NH Mn0.01 having the same stabilizer (hydrazine) and the same nominal Mn concentration. And finally, Figure 1c presents the XRD results of samples ZnS_NH and ZnS_EN. The text was modified and added in the manuscript (please see line 205-241). In paper we added the information that the relative peak ratio of (002) to those of (100) and (001) decreased when NH was used as a stabilizer instead of EN. Additionally, the discussion about the impact of exact Mn doping on the XRD results of nanocrystals has been added.

„ The influence of the manganese amount on the XRD patterns was shown in figure 1a. On those patterns, a very small shift of the diffraction peaks of (100), (002), and (001) can be observed. All Mn-doped ZnS NCs stabilized with EN showed a very slight shift towards the higher 2θ side compared with undoped ZnS due to the presence of Mn^{2+} instead of Zn^{2+}. The position of (002) peak for ZnS_En_Mn0.02 (1.0622 of Mn wt.%, Tab. 1), for example, is at 28.84° whereas the position of (002) peak for un-doped ZnS_EN NCs is at 28.60°. It is known, that the ion radius of Mn^{2+} cation is bigger than the ion radius of Zn2+ cation. This peak position shift may occur due to the changes that occur in the lattice parameters of the host lattice on the incorporation of the dopant atoms [26]. Those changes can be observed on the XRD patterns of the samples with the increase of the manganese content. The further increase of the exact amount of Mn in the range 0.0944 wt.% (for ZnS_EN_Mn0.001) to 1.0622 wt.% (for ZnS_En_Mn0.02) affects also the very small changes in the XRD patterns of the samples, which are comparable. This effect can be also observed in the case of ZnS:Mn NCs stabilized with hydrazine (please see Fig. S1 in Supporting Information). For ZnS:Mn NCs stabilized with hydrazine this 2 θ shift upon Mn doping in nanocrystals is very well observed. The position of (002) peak for ZnS_NH, ZnS_K_Mn0.01 (0.3857 of Mn wt.%, Tab. 1) and ZnS_NH_Mn0.01 (0.6847 of Mn wt.%, Tab. 1) is at 28.16°, 28.52° and 28.66°, respectively. This shift position of the XRD patterns can demonstrate the successfully Mn doping in ZnS NCs which is more efficient in the case of the ZnS NCs stabilized with hydrazine than ZnS NCs stabilized with ethylenediamine. These results are in good agreement with the results of MP-AES analysis of nanomaterials showed the exact doping contents of Mn in ZnS nanocrystals (see Table 1). Figure 1b shows the impact of the type of the used heat of source on the

XRD patterns of ZnS:Mn samples stabilized with hydrazine. The similar position of the XRD patterns of all samples can indicate that the type of heating techniques do not influence significantly the crystal structure of the NCs. In figure 1c the influence of the used stabilizer on the XRD patterns was shown. The synthesis of the ZnS NCs in the presence of both stabilizers (ethylenediamine and hydrazine) leads to the formation of the NCs with the typical wurtzite structure. However, it can be observed that the relative peak ratio of (002) to these of (100) and (001) decreased when NH was used as a stabilizer instead of EN. Additionally, very small differences in the peak position can be observed. For example, the position of (022) peak for ZnS_NH is 28.10° whereas the position of (002) peak for ZnS_EN NCs is at 28.60°. In the case of the sample synthesized in the presence of hydrazine (Fig. 1c) the peaks (101), (102), and (112) visible on the recorded pattern are higher in comparison to those present on the XRD of the sample prepared with the addition of ethylenediamine. This can be attributed to affected of the presence of bigger crystals in the case of ZnS NCs stabilized with NH. This result is in good agreement with the results of TEM analysis of nanomaterials (see Fig. 2). "

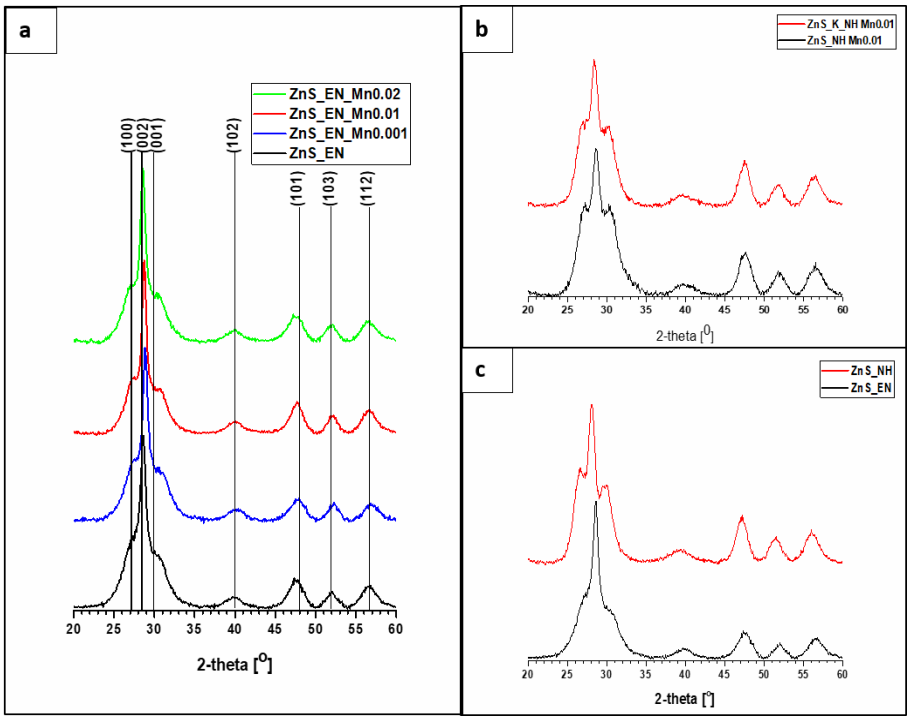

Figure 1. XRD patterns of ZnS samples prepared a) with a different content of manganese and ethylenediamine as a stabilizer b) with different types of the heat source, c) with different stabilizer; the peaks in the pattern matching well with wurtzite structure according to JCPDS#96-110-0045.

It is worth mentioning that two non-Mn doped ZnS samples synthesized with EN and NH, respectively (denoted as ZnS_EN and ZnS_NH in this manuscript), did exhibit different photocatalytic activities towards RhB degradation under 265 nm irradiation. In addition, the other results indicated that two samples (ZnS_EN and ZnS_NH) were different in terms of light absorption at UV region, PL emission, surface area, and pore width. However, those were not compared and discussed properly.

Response:

In fact, samples ZnS_EN and ZnS_NH exhibit different photocatalytic activities towards RhB degradation under 265 nm irradiation. According to the Reviewer's request the UV-Vis, PL emission, surface area, and pore width of both samples were compared and discussed in the manuscript. Please see Table 1, Figure 1c, 5b and 6b and line 335-337.

[the Mn at% in table 1]

- As the authors mentioned in lines 231-233, the exact doping contents of Mn in ZnS can differ from the nominal values which were determined based on the relative amount of Mn precursors used in the synthetic process. The results also indicated that the natures of stabilizers can result in different effectiveness of the Mn doping in ZnS. NH seemed to be more effective for Mn doping in ZnS compared to EN; 0.4705 Mn at% of ZnS_EN_Mn0.01 vs 0.6847 Mn at% of ZnS_NH_Mn0.01. In addition, MW was more effective than conventional heating regardless of the types of stabilizers. The related discussions can be also included in this work.

Response:

First of all, at this point, we would like to apologize the Reviewer for the error which appear in the paper and it concerning the sample named in the text "ZnS_EN_Mn0.02. During the preparation of the answer and the corrections, we thoroughly checked all the values once again. We realized that exact concentration of Mn in sample is 1.0622 wt.% and not as stated previously 3.7447 wt.%. During the preparation of the table 1, the value from the column named "Intensity" was taken accidentally instead of the value in the actual column named ,,Calculated Concentration". As proof for this fact we would like to enclose the original reports from the MP-AES experiment. The files were named as followed: Analyte Results_DSM1M2. All data provided in Table 1 were once again checked. In order to avoid another mistake, the results of the Mn doping of ZnS NCs were added to the table 1 in the original, total values obtained in the ppm (according to MP-AES measurements) and after conversion in wt.%. This error was corrected in manuscript.

Secondly, in fact, the exact doping contents of Mn in ZnS is differ from the nominal values which were determined based on the relative amount of Mn precursors used in the synthetic process. When we compare the efficiency of Mn doping it is clear that the type of used stabilizer plays a key role and the results indicated that hydrazine to be more effective than ethylenediamine. According to the Reviewer's request, this information was added in the text, please see the line 298-302

,,Moreover, these results also indicated that the natures of stabilizers can result in different effectiveness of the Mn doping in ZnS. NH seemed to be more effective for Mn doping in ZnS compared to EN; 0.4705 Mn wt.% of ZnS_EN_Mn0.01 vs 0.6847 Mn wt.% of ZnS_NH_Mn0.01. In addition, MW was more effective than conventional heating regardless of the types of stabilizers."

[the TEM images, Figure 2]

- It is better to present TEM images in the same magnification (at least placing the same scale bar), especially for those authors who want to make direct comparisons (e.g., figure 2a vs 2c vs 2e,f,g, and figure 2b vs 2d). It seemed that ZnS_EN_Mn0.01 exhibited a similar structure with ZnS_K_EN_Mn0.01 if one compared figure 2h and figure 2e in similar magnification (although figure 2h is STEM image whereas figure 2e is TEM image). I wonder what the TEM image of ZnS_EN_Mn0.01 looks if it is in the same magnification as the TEM image of ZnS_K_EN_Mn0.01 (figure 2e).

- One may notice differences in structures by comparing the images of various samples, such as ZnS_En_Mn0.01 (Figure 2a), ZnS_NH_Mn0.01 (Figure 2c), ZnS_K_NH_Mn0.01 (Figure 2e), ZnS_K_NH_Mn0.01 (Figure 2 f and g). However, those differences can be hardly attributed to a particular factor among the types of stabilizer, heating methods (MW or conventional), and doping levels of Mn, since those samples were even different in exact Mn doping levels as shown in table 1.

Response:

In order to present carefully the TEM results in a clearer way as possible, the new TEM graphs of selected samples according to the Reviewer's suggestion were prepared. Please see Figure 2. The TEM images was presented in the same scale bar (50 nm). We also separate the EDX analysis and TEM images. Now at Fig. 2 we compare the morphology of the synthesized NCs images of Mn-doped ZnS NCs with the same Mn nominal concentration (the molar ratio of used Zn/S/Mn precursor was 1:2:0.01) stabilized with ethylenediamine (Fig. 2 a, sample ZnS_K_EN_Mn0.01) and hydrazine (Figure 2 b; sample ZnS_K_NH_Mn0.01) prepared in a conventional heating as well as in the microwave reactor (Fig. 2 c, e, sample ZnS_EN_Mn0.01; and Fig. 2 d, f, sample ZnS_NH_Mn0.01), respectively. We also agree with Reviewer that interesting will be to compare the TEM analysis of nanocrystal with the same, exact Mn doping. Unfortunately we do not have direct access to TEM analysis and resources as the project has now been completed. In fact, ZnS_EN_Mn0.01 exhibited a similar structure with ZnS_K_EN_Mn0,01 this information has been added in text (line 258 – 268).

„ Additionally, it seemed that ZnS:Mn stabilized with ethylenediamine and prepared in MW-assisted reaction (sample ZnS_EN_Mn0.01) exhibited a similar structures with a sample prepared in a conventional heating (sample ZnS_K_EN_Mn0.01). However, the product is an agglomeration of one-dimensional nanowires with a longer length. In turn, the morphology of the samples ZnS_K_NH_Mn0.01 is different when compared to the sample ZnS_NH_Mn0.01 synthesized in MW. In the case of the ZnS_K_NH_Mn0.01 nanocrystals are larger and less regular in comparison with the NCs synthesized in MW-assisted syntheses. Moreover, the crystals of ZnS:Mn NCs stabilized with hydrazine are less regular and bigger than the NCs stabilized with EN in the same conditions and is the mixture of 1D and 2D NCs."

- Line 248-251 reads "In the case of ZnS:Mn stabilized with EN, the products is an agglomeration of one-dimensional nanowires with a longer length. In turn, the morphology of ZnS:Mn NCs stabilized with hydrazine is less regular than the NCs stabilized with EN and is the mixture of 1D and 2D NCs". It is not clear whether the authors made a comparison between TEM images of ZnS_K samples (conventional heating) synthesized with EN and NH or those of ZnS samples synthesized with EN_NH (MW).

Response:

This information was added, the text was modified in manuscript (line 264 -267):

„ In the case of the ZnS_K_NH_Mn0.01 nanocrystals are larger and less regular in comparison with the ZnS_NH_Mn0.01 NCs synthesized in MW-assisted syntheses. Moreover, the crystals of ZnS:Mn NCs stabilized with hydrazine are less regular and bigger than the NCs stabilized with EN in the same conditions and is the mixture of 1D and 2D NCs."

[the isotherms of N_2 adsorption/desorption, Figure 3a]

- There are so many isotherms displayed in one graph as figure 3a, which made it very difficult to check the shapes of isotherms. It seemed that adsorption and desorption curves were almost

overlapped in the case of some samples, but it is difficult to see it. Relating to the isotherm curves, the authors only mentioned that all the samples exhibited a typical type-IV isotherm with a distinct hysteretic loop.

Response:

The new graphs have been prepared (please see Fig. 4). Now Figure 4. present the N_2 adsorption–desorption isotherms for ZnS and ZnS:Mn NCs; a) samples with the different amount of the Mn^{2+} ions synthesized MW heating and in the presence of ethylenediamine as a stabilizer; b) comparison of the sorption isotherms of the samples synthesized in the presence of the ethylenediamine and the hydrazine with the assistance of traditional heat source (K) and the MW heating; c) sorption isotherms of the samples with a different Mn^{2+} content synthesized in the presence of hydrazine as a stabilizer with a assistance of microwaves. We hope that diagrams in the present form will be more transparent for readers.

- In lines 268-269, the authors concluded that "the key factor influencing the size of the surface is the selection of heating method by comparing the four Mn-doped ZnS samples having same nominal Mn doping values. The exact doping levels of Mn were different among those four samples as already mentioned earlier in this letter, and results summarized in table 1 clearly implied that the exact doping levels of Mn can affect the surface area value (comparing surface area values of ZnS_En or ZnS_NH samples with different Mn at%). Therefore, authors need to select samples prepared with two heating methods (MW and conventional heating methods) having similar actual Mn doping levels to make such a conclusion.

According to the Reviewer's suggestion this text was modified, we compare the samples having similar exact Mn content. We compare sample ZnS_NH_Mn0.001 (0.3706 wt.% Mn) with ZnS_K_NH_Mn0.01 (0.3857 wt. % Mn). Please see lines 323-327.

"The comparison of samples with a similar, actual manganese concentration of about 0.38 wt.%, assigned as ZnS_NH_Mn0.001 (0.3706 wt.% Mn), ZnS_K_NH_Mn0.01 (0.3857 wt. % Mn) the relevant values of specific surface area and average pore width have been compared in Table 1) allows to conclude that the key factor influencing the size of the surface is the selection of heating method."

2.[the UV DRS datum, Figure 4a, b, and c]

- Since the photocatalytic activities of various samples were examined under UV light irradiation (254 nm), it is important to analyze/compare the light absorption abilities of samples in the UV light region (close to 254 nm) not in the visible light region. Apparently, light absorption spectra in the UV light region varied among samples depending on types of stabilizers, Mn doping levels, and heating methods (MW or conventional heating). However, those were not compared and discussed at all in the manuscript. For instance, the UV light absorption ability of ZnS_NH and ZnS_EN cannot be compared with figures 4 a and b since they were plotted as two separated graphs with Y-axes in arbitrary units.

Response:

The new DR UV-Vis spectra according to the Reviewer's suggestion (please see Fig. 5) were prepared and added in the manuscript. Figure 5 shows DR UV-Vis spectra of ZnS and ZnS:Mn NCs a) samples with the different amount of the Mn^{2+} ions synthesized MW heating and in the presence of ethylenediamine as a stabilizer; b) samples stabilized in the presence of the ethylenediamine and the hydrazine with the assistance of the MW heating; c) samples synthesized in the presence of the hydrazine with the similar actual Mn doping levels (about 0.38 wt.% Mn^{2+}) with the assistance of traditional heat source (K) and the MW heating. The discussion of the light absorption spectra in the UV light region varied among samples depending on types of stabilizers, Mn doping levels, and heating methods were compared and discussed in the manuscript. Please see lines 370 - 404.

"*Figures 5a and b present DR UV-Vis spectra for samples with the different amounts of the Mn^{2+} ions synthesized MW heating and in the presence of ethylenediamine as a stabilizer; b) samples stabilized in the presence of the ethylenediamine and the hydrazine with the assistance of the MW heating; c) samples synthesized in the presence of the hydrazine with the similar actual Mn doping levels (about 0.38 wt.% Mn^{2+}) with the assistance of traditional heat source (K) and the MW heating. One of the important features influencing the photocatalytic activity of the tested samples is the light absorption abilities of nanocrystals in the UV spectrum near 254 nm since the photocatalytic activities of various samples were examined with a UV lamp with irradiation at 254 nm. All samples were characterized with a strong and broad absorption band in the UV spectrum of light with the maximum at about 300 nm for ZnS and ZnS:Mn stabilized with hydrazine and at 320–330 nm for ZnS and ZnS:Mn stabilized with EN. The comparison of samples with a similar, actual manganese concentration of about 0.38 wt.%, as-signed as ZnS_NH_Mn0.001 (0.3706 wt.% Mn), ZnS_K_NH_Mn0.01 (0.3857 wt. % Mn) allows to conclude that one of the key factor influencing the UV absorbance is the selection of heating method. Sample ZnS_NH_Mn0.001 synthesized under MW-assisted reaction shows higher the light absorption abilities in the UV range of spectrum compare to sample synthesized with the assistance of traditional heat source. Another important factor influencing the optical properties of ZnS NCs is the type of used stabilizer. Figure 5b indicates that the un-doped ZnS nanocrystals stabilized with hydrazine absorb more efficient light in the UV light region of spectrum, including irradiation at 254 nm. Moreover, the UV spectra also clearly indicate that the significant red shift in the UV spectrum into the visible spectrum of light can be observed for the NCs doped with Mn^{2+} ions in the crystal lattice. This phenomenon can be observed for both ZnS NCs stabilized with EN and N_2H_2. However, this effect can be more visible for ZnS:Mn, as it has EN ligands. Additionally, it can be observed that with the increased Mn concentration in the ZnS NCs, the absorption in the visible light increases due to the Mn dopants (Fig. 5a). This enhanced absorbance to the visible region can be probably linked to the in-crease in defect sites in the crystal structure of the doped ZnS NCs [28, 30, 31]. In the UV light spectrum the situation is more complicated. In the case of ZnS_EN, the light absorption abilities first increased as the Mn doping level increased for samples ZnS_EN_Mn0.001 and ZnS_EN_Mn0.005 and again decreased as the Mn doping level kept increasing for samples ZnS_EN_Mn0.01 and ZnS_EN_Mn0.02."*

- The optical band gaps of various samples were determined in this manuscript and those were summarized in table 1. In the case of ZnS_NH, bandgap values decreased as the Mn doping level increased, whereas the changes of band gap values upon the Mn doping levels were more complicated in the case of ZnS_EN; initially, the bandgap decreased with an increase of Mn doping levels, but it decreased and again decreased as the Mn doping level kept increasing. Those were not mentioned and discussed at all. If authors want to compare the Mn doping effects on the optical properties of two ZnS samples prepared with two different stabilizers, authors need to select samples having similar actual Mn doping levels (Mn at%) not nominal Mn doping values.

- The changes of optical band gap upon the nature of stabilizer (EN or NH) were more significant than those induced by Mn doping (it can be clear if one compares ZnS_EN with

ZnS_NH). And the selection of different stabilizers did not induce a significant size difference in synthesized ZnS samples if MW was used instead of conventional heating as implied by TEM analysis results. Those were not correlated with the discussions in lines 322-325 and 330-334 explaining different bandgap values among various samples.

- Authors made a long discussion on the optical band gap values determined by UV-DRS results of various samples (making discussion on the absorption edge extension to the visible light upon Mn doping). However, those were not so important to explain the different photocatalytic activities of various samples since activities were determined under UV light irradiation 254 nm. The light absorption abilities of various samples in the UV light region would be more useful to explain the variation of photocatalytic activities among the samples.

Response:

The discussion about the changes of optical band gap upon the nature of stabilizer, Mn doping and type of used heating methods, according to the Reviewer's suggestion was modified and added in the text of manuscript. Please see lines 410 - 434. The discussion of light absorption abilities of various samples in the UV light region was also added (lines 370 – 404).

„ Table 1 presents the calculated band gaps for all samples. The values are, accordingly, 3.30 eV for un-doped ZnS_EN, 2.93 eV for ZnS_EN_Mn0.001, 3.31 eV for ZnS_EN_Mn0.005, 2.94 eV for ZnS_EN_Mn0.01 and 2.72 eV for ZnS_EN_Mn0.02 with the highest content of Mn. As it can be seen, the band gap values of all ZnS and ZnS:Mn stabilized with ethylenediamine decrease when compared with those of ZnS bulk value materials (3.7 eV) [3,10]. However, the changes of band gap values upon the Mn doping levels were complicated, initially, the band gap decreased with an increase of Mn doping levels than increased for ZnS_EN_Mn0.005 and again decreased as the Mn doping level kept increasing for ZnS_EN_Mn0.01 and ZnS_EN_Mn0.02. In the case of ZnS and ZnS:Mn stabilized with hydrazine, we also observe slightly increased band gap values in comparison with the ZnS bulk value materials, i.e. 3.78 eV for ZnS_NH, 3.81 eV for ZnS_NH_Mn0.001. However, for ZnS:Mn with a higher concentration of Mn^{2+} ions in the NCs, we observe a slightly decreased band gap when compared to ZnS bulk value materials. Moreover, the optical band gap of samples ZnS_NH_Mn0.001 and ZnS_K_NH_Mn0.01 synthesized in the presence of hydrazine with the similar actual Mn doping levels (about 0.38 wt.% Mn^{2+}, Tab. 1) with the assistance of the MW heating and traditional heat source, are 3.81 eV and 3.72 eV, respectively. This can suggest that the doping process of Mn atoms has not so high impact on the engineered ZnS band gap like type of used ligands or type of used heating methods. Its looks that the type of used stabilizer has more significant impact on the changes of optical band gap of nanocrystals. For example, the calculated optical band gap for ZnS_NH is 3.78 eV whereas for ZnS_EN samples was 3.30 eV. And the selection of different stabilizers did not induce a significant size difference in synthesized ZnS samples if MW was used instead of conventional heating as implied by TEM analysis results (Fig. 2).”

[the PL emission spectra, Figure 4d, and e]

- The PL emission spectra would be also useful to explain the variation of photocatalytic activities among the samples since they can provide information on the electron-hole separation efficiency. However, first, the wavelength of excitation light should be provided. And second, emission spectra of ZnS_NH and ZnS_EN should be compared since they can help us to understand the impacts of stabilizers on optical properties and photocatalytic activities regardless of Mn doping. Now two spectra were plotted as two separated graphs with Y-axes in arbitrary units.

The additional figure (fig. 6b) presents the comparison of PL emission of Zn_NH and ZnS_EN on one spectra has been prepared and added in the manuscript. As can be seen the emission of both sample is a very low, compare to Mn doped ZnS NCs. All emission spectra were provided for excitation wavelength at 310 nm. This information has been added in the text.

- Lastly, interpretation of PL peak intensity needs to be checked. During PL emission measurements, the sample surface was irradiated by light. Once light energy was absorbed by the sample, the electron was excited from VB to CB leaving a hole in VB. Then, the excited electron falls back to the hole in VB (electron-hole recombination) emitting energy as light (PL signal). Thus, usually higher the PL intensity from the sample indicated a higher probability of electron-hole recombination, i.e., lower electron-hole separation efficiency. Figures 4 d and e showed the higher PL intensity upon the higher Mn doping levels, however, authors seemed to try to relate the higher PL intensity to improved ZnS activities upon the higher Mn doping levels. Those need further explanations in detail if the authors were certain of it.

Response:

In our opinion the PL emission is above all is the proof of successful Mn doping in ZnS nanocrystals. The emission which can be observed is coming mostly from electron-hole recombination in Mn ions ($^4T_1$-$^6A_1$)., not from ZnS lattice crystals. However, the exact Mn doping concentration in ZnS NCs is still relatively low. Which is why in our opinion, it is not easy to direct interpretive of PL peak intensity of nanocrystals with the variation of photocatalytic activities of samples. In other paper we found that the high PL intensity of Mn-doped ZnS NCs and relatively high photo catalytical activity can be correlated with higher amount of Mn-based surface defects on ZnS NCs nanocrystals surface. This information also was added in the text. Please see liens: 440-470.

„ The room-temperature photoluminescence (PL) spectra of the as-prepared ZnS and Zn:Mn NCs is presented in Figures 6. All emission spectra were measured for an excitation wavelength at 310 nm. Figure 6 presents PL emission spectra for ZnS and ZnS:Mn NCs of ZnS and ZnS:Mn NCs a) samples with the different amount of the Mn^{2+} ions synthesized MW heating and in the presence of ethylenediamine as a stabilizer; b) samples stabilized in the presence of the ethylenediamine and the hydrazine with the assistance of the MW heating and c) samples synthesized in the presence of the hydrazine including the samples with the similar actual Mn doping levels (about 0.38 wt.% Mn^{2+}) with the assistance of traditional heat source (K) and the MW heating. The PL spectra of all the Mn doped ZnS samples stabilized with EN or N2H2 were characterized with one sharp band at about 590 nm and a broad peak with the maximum between at 420–470 nm. The band at about 590 nm is attributed to $_4T^1$-$_6A^1$ transition in the Mn^{2+} ions [28, 30]. The higher concentration of the Mn^{2+}ions in the Zn:Mn samples led to the increased intensity of emission band corresponding to transition in the Mn^{2+} ions (Fig. 6a and 6b). The comparison of samples with a similar, actual manganese concentration of about 0.38 wt.%, assigned as ZnS_NH_Mn0.001 (0.3706 wt.% Mn), ZnS_K_NH_Mn0.01 (0.3857 wt. % Mn) allows concluding that the selection of heating method has also impact on PL emission of ZnS:Mn NCs. Samples prepared in MW reactor show higher PL emission of the band at 590 nm. On the other hand, Fig. 6b shows that the type of used stabilizer for the synthesis of un-doped ZnS NCs does not impact the PL properties of nanocrystals. As can be seen, the emission of both samples is very low, compare to Mn-doped ZnS NCs. As we know, the PL emission spectra can be also useful to explain the variation of photocatalytic activities among the samples since they can provide information on the electron-hole separation efficiency. In most cases, the higher the PL intensity from the sample indicated a higher probability of electron-

hole recombination, i.e., lower electron-hole separation efficiency which mostly decreases the photocatalytic activities. However, in the cease of Mn-doped ZnS NCs, the emission which can be observed is coming mostly from electron-hole recombination in Mn ions ($^4T_1$-$^6A_1$) not only from the sample surface but also from nanocrystals (Fig. 3c). In addition, the exact Mn doping concentration in ZnS NCs is still relatively low. Therefore, it is not easy to direct interpretive of PL peak intensity of nanocrystals with the variation of photocatalytic activities of samples."

[the photocatalytic activity datum]

- Photocatalytic activities of ZnS_EN and ZnS_NH should be compared and discussed in detail with their characterization results since it can help us to understand the impacts of stabilizers on optical properties and photocatalytic activities regardless of Mn doping. Comparison of various samples with Mn doping needs to be more carefully made considering the difference between the nominal values of Mn doping levels and actual values of Mn doping levels.

Response:

The discussion about the changes of photocatalytic activities of ZnS_EN and ZnS_NH versus the nature of stabilizer, according to the Reviewer's suggestion was added in the text of manuscript. We also add a new graph presenting the comparison of degradation efficiency of ZnS_EN and ZnS_NH separately (Fig.9b) . Please see lines 591 - 601.

,, When we compare the un-doped ZnS NCs synthesized in MW reactor, samples ZnS_NH and ZnS_EN (Fig. 9 b) we observe higher photocatalytic performance for the crystals with shorter amine molecules as hydrazine on the surface of the NCs. The specific surface area of ZnS_EN was 218.4 m^2/g (with pore size of 8.76 nm) whereas for ZnS_NH was only 207.5 m^2/g (with a pore size of 5.63 nm). However, Fig. 5b shows that the un-doped ZnS nanocrystals stabilized with hydrazine (ZnS_NH) have better light absorption abilities in the UV light region of the spectrum than ZnS NCs stabilized with ethylenediamine, including the irradiation at 254 nm. These properties make ZnS_NH NCs a more efficient photocatalyst (almost twice).

- The comparison of characterization and photocatalytic experiment results among samples must be made considering the nominal Mn doping values were different from the exact doping amount of Mn. For instance, ZnS_EN_Mn0.01 (0.4705 of Mn at%) has different doping amount from ZnS_NH_Mn0.01 (0.6847 of Mn at%), ZnS_K_EN_Mn0.01 (0.1207 of Mn at%), and ZnS_K_NH_Mn0.01 (0.3857 of Mn at%). However, those were not considered when the author made a comparison among the samples to discuss the impacts of Mn doping on their photocatalytic activities and characterization results.

Response:

According to the Reviewer's suggestion the discussion about the characterization and photocatalytic experiment results considering the nominal Mn doping values as well as the exact doping amount of Mn was added in the text in the paragraph . Please see lines 529 – 575 and 611-621

,, The comparisons of the reported photodegradation efficiency of ZnS:Mn stabilized by EN photocatalyst synthesized with the microwave method for the degradation of RhB are summarized in Figure 9a. Obviously, the ZnS_EN_Mn0.02 exhibited much smaller degradation

efficiency compared to standard powder P25 TiO_2 (see also Fig. S2 in Supporting Information). Taking into account the positive impact of Mn doping on the activity in the photocatalytic degradation of RhB we need to consider also the exact Mn doping concentration and characterization in ZnS NCs. As can be seen in Table 1 the nominal Mn concentration is different than the exact doping amount of Mn. For in-stance, ZnS_EN_Mn0.01 (0.4705 of Mn wt.%) has different doping amount from ZnS_NH_Mn0.01 (0.6847 of Mn wt.%), ZnS_K_EN_Mn0.01 (0.1207 of Mn at%), and ZnS_K_NH_Mn0.01 (0.3857 of Mn at%). The photocatalytic activity of these samples in the degradation process of RhB was also different about 36%, 60%, 16% and 30% for ZnS_EN_Mn0.1, ZnS_NH_Mn0.01, ZnS_K_EN_Mn0.01 and ZnS_K_NH_Mn0.01, re-spectively. The highest photocatalytic activity presents sample ZnS_NH_Mn0.01 with the highest effective Mn doping concentration. One of the important parameters in-fluencing the photocatalytic activity of the ZnS:Mn samples is the UV light absorption abilities, band gap properties as well as the specific surface area. All these properties have been discussed in detail in the previous chapters. Table 1 and Figure 5a show that the Mn doping led to a shift of the ZnS optical band gap from 3.30 to 2.72 eV. The band gap of ZnS_EN_Mn0.01, ZnS_NH_Mn0.01, ZnS_K_EN_Mn0.01 and ZnS_K_NH_Mn0.01 samples was 2.94 eV, 3.64 eV, 3.58 eV and 3.72 eV, respectively. On the other hand, the specific surface area of these samples was adequate of 207.4 m2/g, 211.2 m^2/g, 185.1 m^2/g and 194.8 m^2/g for ZnS_EN_Mn0.01, ZnS_NH_Mn0.01, ZnS_K_EN_Mn0.01 and ZnS_K_NH_Mn0.01, respectively. Nanomaterials synthesized in MW-assisted methods show higher specific surface area and also higher light ab-sorption abilities (Fig. 5c). The Mn^{2+} ions doping caused also the enhanced absorbance to the visible region of the spectrum and PL emission at 590 nm. However, the Mn doping in ZnS NCs allows them to be used as effectual UV photocatalysts for the degradation of organic contaminants. This enhancement can suggest a more efficient sep-aration process of the photogenerated charge carriers than that of un-doped ZnS, which can positively influence the photocatalytic activity even under UV light. The Mn2+ ions in ZnS NCs behave like electron sinks, which can effectively trap and transfer the photogenerated electrons, and then improve the separation of electrons and hole pairs. Similar effect has been observed also for other nanomaterials e.g. ZnSe, ZnO, CuO by other authors [30, 36, 37].”

Analyte Results

Label	Solution Concentration	Unit	SD	%RSD	Intensity	Calculated Concentration
Zn (213.857 nm)	Uncal	ppm	N/A	N/A	405410.49	Uncal (ppm)
Mn (403.076 nm)	0.45	ppm	34.61	0.74	15141.20	4705.26 (ppm)

Replicates Concentration

Label	Replicate 1	Replicate 2	Replicate 3	Units
Zn (213.857 nm)	Uncal	Uncal	Uncal	ppm
Mn (403.076 nm)	4687.22	4683.40	4745.16	ppm

Replicates Intensity

Label	Replicate 1 (c/s)	Replicate 2 (c/s)	Replicate 3 (c/s)
Zn (213.857 nm)	400897.82	405887.73	409445.93
Mn (403.076 nm)	15082.98	15070.67	15269.95

Sample Name: DSM1Mn2

Date: 2/27/2020 5:33:36 PM Rack:Tube: 1:2

Weight (g): 0.0105 Volume (mL): 100 Dilution: 1

Analyte Results

Label	Solution Concentration	Unit	SD	%RSD	Intensity	Calculated Concentration
Zn (213.857 nm)	Uncal	ppm	N/A	N/A	415128.72	Uncal (ppm)
Mn (403.076 nm)	1.12	ppm	56.47	0.53	37447.96	10622.04 (ppm)

Replicates Concentration

Label	Replicate 1	Replicate 2	Replicate 3	Units
Zn (213.857 nm)	Uncal	Uncal	Uncal	ppm
Mn (403.076 nm)	10631.46	10561.45	10673.20	ppm

Replicates Intensity

Label	Replicate 1 (c/s)	Replicate 2 (c/s)	Replicate 3 (c/s)
Zn (213.857 nm)	409815.19	414720.37	420850.59
Mn (403.076 nm)	37481.22	37234.12	37628.55