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**Title:** Mesoporous CuS nanospheres decorated rGO aerogel for high photocatalytic activity towards Cr(VI) and organic pollutants

**Dear. Editor** (Chemosphere)

Thank you very much for giving us a chance to revise our manuscript. The reviewer’s comments are valuable and very helpful for improving our research paper. We have carefully read all comments and have tried our best to revise the manuscript as per reviewers suggestions, which we hope to meet with acceptance requirements. **Reviewer # 1** **and** **reviewer # 3** comments have been **yellow highlighted** because both the reviewers have almost same comments and suggestions**,** **reviewer # 2 c**omments have been **red highlighted** in the manuscript.

**Response to the reviewer’s comments**

**Reviewer #1**
This submission reported the fabrication of Mesoporous CuS nanospheres decorated rGO aerogel and its photocatalytic performances towards Cr(VI) reduction and organic pollutants degradation. This submission can be considered acceptance subject to addressing the major issues.
**1).** Chemosphere is an internal journal concerning ENVIRONMENTAL SCIENCES. The authors are suggested to shorten the description on material characterizations, and enrich the discussion on the photocatalytic abilities toward Cr(VI) reduction and organic dyes degradation along with the corresponding mechanism. Also, the influence factors of the photocatalysis should be considered.

**Response:** Respected reviewer thank you very much for your valuable suggestions. Your suggestions made a huge improvement in our research paper. According to your comment (1), we have added detailed discussion to photocatalytic mechanism and added different characterization, which are needed to deduce photocatalytic mechanism. Like Scavenger studies, VB-XPS and Mott-Schootty measurements. All the changes are marked in yellow in the revised manuscript for your comments.

**2).** As described in 3.1 "The photoreduction of Cr (VI) and photodegradation of cationic dyes was performed at neutral pH = 7, 0.1M NaOH or 0.1M HCL (note: should be HCl) was used to adjust the pH of the desired solution." The Cr(VI) reduction was performed under pH = 7. The formed Cr(III) was easily precipitated as Cr(OH)3. The reduction mechanism of Cr (VI) should be revised. Under pH = 7, the Cr(VI) specie was primarily presented as CrO4-. The authors should make a major revision to this sector. The authors should study how the pH influence the photocatalytic ability of the photocatalysts. Finally the authors should report the reuse of photocatalysts for Cr(VI) reduction.

**Response:**  Respected reviewer thank you again for your valuable comments. According to your suggestion, we have thoroughly studied the pH effect on Cr(VI) reduction and we have found out from the results that the highest reduction was obtained in acidic pH. So the results have been modified and pH=3 was considered for all the experiments related to Cr(VI) reduction in this manuscript. You can see the results and description discussed in page 18, section 5.1 and line number from 367-368. And the effect of pH on dye degradation is present in supplementary data **Fig. S7**. The obtained results were consistent with the previous reports for pH effect on Cr(VI) reduction(1-5). The modified study is marked in yellow in the revised manuscript.

1. Kumar Padhi, D., et al., Facile fabrication of Gd (OH)3 nanorod/RGO composite: synthesis, characterisation and photocatalytic reduction of Cr(VI). Chemical Engineering Journal, 2014. **255**: p. 78-88.

2. Padhi, D.K., et al., Green synthesis of Fe3O4/RGO nanocomposite with enhanced photocatalytic performance for Cr(VI) reduction, phenol degradation, and antibacterial activity. ACS Sustainable Chemistry & Engineering, 2017. **5**(11): p. 10551-10562.

3. Lu, D., et al., Solvothermal-assisted synthesis of self-assembling TiO2 nanorods on large graphitic carbon nitride sheets with their anti-recombination in the photocatalytic removal of Cr(VI) and rhodamine B under visible light irradiation. Nanoscale, 2017. **9**(9): p. 3231-3245.

4. Hu, X., et al., Simultaneous photocatalytic Cr(VI) reduction and 2, 4, 6-TCP oxidation over g-C3N4 under visible light irradiation. Catalysis Today, 2014. **224**: p. 34-40.

5. Mani, A.D., et al., Effect of fuels on combustion synthesis of TiO2–Towards efficient photocatalysts for methylene blue oxidation and Cr(VI) reduction under natural sunlight. Chemical engineering journal, 2013. **228**: p. 545-553.

**3).** Recently, many papers concerning photocatalytic Cr(VI) reduction and organic dyes degradation over different photocatalysts like MOFs and MOFs composites were published. The authors should make a comparison with the counterpart photocatalysts to highlight the advantages of the photocatalysts in this paper.

**Response:** Dear reviewer after your valuable advice we have added the comparison of our photocatalyst with other photocatalyst and latest MOF composites. We have further compared this aerogel with other techniques like MOF based composites for the reduction of Cr(VI) in **Table S1**. You can find the compared discussion in page 18, section 5 and line 360-365. And the required results are presented in supplementary data **Table S1**. Compared to other techniques this material is more efficient in the sense of its recovery and less time consumption. Other composites are mostly in powder form that’s why it is difficult to recover by simple techniques. While this composite is an aerogel and it can be easily recovered. The required changes are presented in supplementary information **Table S1**.

1. Liu, H., et al., Simultaneous conversion of organic dye and Cr(VI) by SnO2/rGO microcomposites. Journal of Molecular Catalysis A: Chemical, 2015. **410**: p. 41-48.

2. Dhivya, E., et al., Synthesis of titanium based hetero MOF photocatalyst for reduction of Cr(VI) from wastewater. Journal of Environmental Chemical Engineering, 2019. **7**(4): p. 103240.

3. Yi, X.-H., et al., Highly efficient photocatalytic Cr(VI) reduction and organic pollutants degradation of two new bifunctional 2D Cd/Co-based MOFs. Polyhedron, 2018. **152**: p. 216-224.

**4).** The authors should investigate the photocatalytic abilities toward Cr(VI)/MB or Cr(VI)/RhB matrix to effectively use the photo-generated electrons and holes.

**Response:** Respected reviewer thank you again for your comments. According to your suggestion, we have studied the simultaneous removal of Cr(VI) and RhB dye. And presented in the revised manuscript page 23-24, section 6.3 line 488-505 and highlighted in yellow.

**5).** The roles of superoxide radicals during the Cr(VI) reduction and organic dyes decomposition should be studied.

**Response:** Dear reviewer, we have studied the role of superoxide radicles in the reduction of Cr(VI) and organic dye degradation by scavenger studies. The role of superoxide radicles for Cr(VI) is presented in page 18, section 5.2 and **Fig.7e** in the revised manuscript. And role of super oxide radicles for RhB is presented in page 26, section 7 and **Fig. 11d**.

**6).** The active species capture experiments and ESR determination should be added.

**Response:** Dear reviewer thank you again for your valuable suggestions and comments. We have performed the scavenger studies for both Cr(VI) reduction and RhB dye degradation to find out the active species in the photocatalysis. To further confirm this we have performed ESR, the results obtained from ESR are consistent with the scavenger studies as shown in page 26-27, section 7, **Fig.11c** & **11d**.

**Reviewer #2**

There are many improvements to be made in the present manuscript, such as the unit format, subscript format, spaces format, reference format. The major comment is that the photocatalytic mechanism lacks of scientific explanation, which is as follows:
1. Please note that the potential of hydroxyl radicals formed by hole oxidation is ·OH/OH− (+1.99 eV) and ·OH/H2O (+2.27 eV). However, the band gap of the composite material is only 1.35 eV. Thus, it is difficult to generate hydroxyl radicals under visible light irradiation. The authors can test the VB, CB and ESR to further deduce the mechanism.

**Response:** Respected reviewer thank you for your valuable comments and suggestions. We have tried our best to improve this manuscript as per your suggestions. We believe that now the manuscript is in a better condition and we hope that there are no mistakes regarding format, superscripts, subscripts and references. We have tried our best to improve this manuscript.

According to your suggestion, we have performed the ESR, VB-XPS, mott-Schotty measurements and scavenger studies to fully understand the mechanism and find out the active species. According to the ESR and scavenger studies, the active species taking part in the photocatalytic reduction and degradation are superoxides, holes and hydroxyl radicles as shown in **Fig.11c** & **11d**. The formation of hydroxyl radicles can be due to the rGO network structure. The rGO nanosheets not only act as a substrate for CuS-NS but also plays an important role as an electron reservoir, which helps in highly efficient separation of photoinduced charge carriers. The electrons in CB of the CuS-NS or stored on the rGO sheets can react with O2 molecules and produce●O2− superoxide radical ion. And the photoinduced holes in the valence band of CuS can be easily taken by the hydroxyl ions by generating strong●OH radicals. So all the photoinduced active species are responsible for the degradation of organic dyes (RhB and MB) into smaller intermediates. To further confirm the bandgap we have performed the UV-Vis DRS again and the band gaps obtained were 1.73 for CGA-2 and 1.91 eV for CuS-NS which is shown in **Fig.S2** in the revised supplementary data.

Thank you again for highlighting the misunderstandings in our manuscript. The band gap obtained before was an error while calculating the band gap from the tauc’s plot. This time we have carefully calculated the band gap and also performed VB-XPS and Mott-Schottky measurements to confirm the band gap calculations.

1-Qian, J., Wang, K., Guan, Q., Li, H., Xu, H., Liu, Q & Qiu, B. (2014). Enhanced wet hydrogen peroxide catalytic oxidation performances based on CuS nanocrystals/reduced graphene oxide composites. Applied Surface Science, 288, 633-640.

2- Lu, K. Q., Xin, X., Zhang, N., Tang, Z. R., & Xu, Y. J. (2018). Photoredox catalysis over graphene aerogel-supported composites. Journal of Materials Chemistry A, 6(11), 4590-4604.

2. Figure 3 is confused. 3b shows the diameter of CuS is ~500 nm, but the black spot CuS in figure 3c showed only <10 nm. And the 3c inset ruler line is missing. Also, the authors did not explain the Figure 9c.

**Response:** Dear reviewer thank you again for highlighting the improvements we need to do. We have corrected the TEM image and scaled the missing part. As the inside of the **Fig.3c** is HRTEM of **Fig.3c**, that’s why the scale bar is 10 nm. And we have also explained the **Fig .9c** in section 6.2, page 22 and line 462-464.

3. The article highlights that the 3D CuS-NS/rGO materials can be easily recovered with tweezers (abstract and conclusion), but the method and results parts in particular are not described in detail, please add.

**Response:** Respected reviewer, according to your suggestion, we have added the description in method and results parts highlighted in red in revised manuscript.

4. Many references need to be inserted in the article, line 194, 243, 369, 407, 482, 489. All the references has been inserted in the required lines. Some lines were blank in my part of manuscript therefore I have inserted references where needed.

**Response:** Dear reviewer we have added the required references in the mentioned lines and also added many other references where needed. All the added references are marked in red in the revised manuscript.

We have added references in line 241,251,257,269,426,461,463, 550. After some additions and modifications in the manuscript the line numbers are changed.

5. Some expression need to rewrite correctly, line 15 (BET? complete spelling for the first time), the line 62, 84, 107, 108, 120, 123, 124, 132, 133, 134, 135, 138, 140, 141, 149-166 (font size is not uniform), 171, 173, 174, 179, 183, 184, 189, 190, 200-201 (please rewrite), 203, 233, 236, 284, 312, 352, 353, 358, 362, 398 (time format), 405 (rewrite), 437, 456, 484 (hydroxyl ions? or H2O?), 516.

**Response:** Dear reviewer thank you again for your valuable comments and suggestions. We have tried our best to fulfill all the required changes. We have corrected the font sizes and formats in the whole manuscript and rewrite all the sentences you asked for. All the modifications according to your suggestions have been marked in red in the revised manuscript.

**Reviewer # 3**

In this manuscript, the authors have prepared 3D CuS-NS/rGO by chemical reduction process and applied to the removal of Cr(VI) and dyes. There are some important questions should be addressed before submitting (as listed below).

Comment 1: Mott-Schottky measurement should be performed

**Response:** Respected reviewer thank you so much for the suggestions and comments you gave us. According to your suggestion, we have performed the Mott-Schotty measurement for CuS-NS and CGA-2 composite as presented in **Fig.S4** in revised supplementary data.

Comment 2: The CB/VB and redox potentials of different reactions should be added in the picture of Graphical abstract.

**Response:** Dear reviewer we have modified and added the redox potentials in the graphical abstract.
Comment 3: A rapping experiment must be added to determined the active species of reaction.

**Response:** Dear reviewer thank you again for your valuable suggestions and comments. We have performed the scavenger studies for both Cr(VI) reduction and RhB dye degradation to find out the active specie in the photocatalysis. To further confirm this we have performed ESR as shown in **Fig.11c** page 26. The results obtained from ESR are consistent with the scavenger studies. The results obtained for scavenger tests are presented in section 5.2, page 18 , **Fig.7e** for Cr(VI) and section 7, page 25-26, **Fig.11d** for RhB. The text is highlighted in yellow.

 Comment 4: Please test the actual content of CuS in your samples.

**Response:** Dear reviewer we have performed the SEM-EDS to find out the actual content of CuS in the composite CGA-2 and the results are presented in **Fig.3d** page 9.

Comment 5: Please test the UV-Vis DRS spectra and the corresponding band gaps of samples.

**Response:** Dear reviewer we have added the UV-Vis DRS and calculated band gaps from the tauc’s plot and the results are presented in section 4.6, page 13, line 270-287 and **Fig.S2**.

Comment 6: Please optimize the Fig. 7. (c) and (d), which are very complicated and not intuitive.

**Response**: Dear reviewer **Fig.7c**&**d** has been clarified and simplified as shown in page 18.

Comment 7: Abstract: the authors have mentioned that "3D CuS-NS/rGO was prepared by chemical reduction process and used for the synergistic removal of Cr(VI) and cationic dyes". Please perform a degradation test contain a mixture of Cr(VI) and cationic dye.

**Response:** Respected reviewer thankyou again for your comments. According to your suggestion, we have studied the simultaneous removal of Cr(VI) and RhB dye. And results are presented in the revised manuscript page 23-24, section 6.3, line 488-505 and highlighted in yellow.

Comment 8: Conclusion: the authors have mentioned that "After several recycles, the morphology of the composite remained invariant". Therefore, the authors should provide The XRD patterns and TEM images before and after the reaction.

**Response:** Dear reviewer thank you again for your valuable suggestions and comments. We have added the XRD (**Fig.S5**) and TEM (**Fig.S6**) results before and after recycling in supplementary data.