

FOR THE AUTHORS

ABSTRACT

1. It is obvious that under SEM observation, particles will certainly appear as agglomerates and not single particles. So stating that the “SEM analysis revealed particles as agglomerates” is not a scientific deduction.

Author's response: It is an established fact that was also observed by the authors, hence the need to include it.

2. It is wrong to describe increase in band gap energy as being blue shifted

Author's response: No, it is a technical phrase that is used to describe an increase in band gap of nanocrystals/nanoparticle relative to the energy band gap of the bulk compound. The blue shift in energy implies the shift in the energy spectrum towards the blue portion of the electromagnetic spectrum when compared to the bulk material. There are many literatures that have used the phrase in this context.

Reviewer: It is a technical term to describe shift in the absorption peak towards the blue portion of the electromagnetic spectrum when compared to the bulk material but Band gap energy can only be described as DECREASED or INCREASED not with respect to color (blue).

Author's response: I do not agree with the submission, I still maintain my earlier position, please see: Nirmala Jothi and Sagayaraj, 2012 pg 1084; Planelles-Arego *et al.*, 2008, pg 5195; Lu *et al.* 2001, pg 75; Warad *et al.* 2005, pg 298; Corrado *et al.* 2009, pg 3830. It is also logical to see an increased band gap energy (shorter wavelength) referred to blue shift and energy decrease (longer wavelength) referred to red shift.

3. Instead of “S2 sample”, why not “sample S2”

Author's response: Advice is taken.

Reviewer: The authors are yet to make this correction (e.g see the Abstract)

Author's response: suggestion now completely effected in the abstract.

INTRODUCTION

1. Line 38-39 “relative stability”. The cited reference only describes the advantage of non toxicity of ZnS relative to other chalcogenides, CdS and CdTe. Authors should cite the relevant literature to support the relative stability of ZnS (If at all it is true).

Author's response: Relevant literature is now cited.

2. Line 53 -57 Ref [10] does not exist, making the statement questionable

Author's response: It does exist, read carefully the cited article (i.e. Ref. 10 now 12).

Reviewer: Cited reference does not exist. What is the volume number and full page number of the cited reference 10 now 12?

Author's response: The volume is there it is in Roman numerals 'XLI' which is '41' and number 4. See the reference 12 again.

Materials and methods

1. Queries 1 and 2 in the previous review still applies

Author's response: grams now changed into ml (cm³)

Reviewer: Authors are yet to fully address the query raised e.g the authors started with the phrase "In the present work". Do we have a previous work by the authors where similar methodology was used? If there is any, then proper reference is necessary.

Author's response: Yes, the work by Luna-Martinez *et al.* 2011, I think the phrase is justified.

2. Line 94-95 Is there any scientific reason why the samples were kept for 6 months before characterization? This statement was absent in the first draft of the manuscript

Author's response: Yes, it was deliberately done to observe the level of degradation with respect to the amount of CMC used to cap the ZnS nanocrystals.

Reviewer: Good justification but this point should be made in the text to allow readers appreciate the high stability of the prepared samples.

Author's response: From the sample labels and methodology, it is clear.

RESULT & DISCUSSION

Authors still haven't carried out the necessary TEM analysis of the samples. The SEM micrographs only give the surface morphology of the samples and has no relevance in the optical and electronic properties of particles in the nanometric domain. For example the sem only gives the shape of the particles as a bulk powder, and gives no information on the morphology of the nanoparticles.

Author's response: TEM images now included and explained. If you require the images for sample S₂ and S₃ I shall provide as additional material.

Line 173 Authors should give reference for other reported CMC images

Author's response: Reference now included

Line 176 Is smoothness of surface a proof for good passivation? The EDX for the pure CMC should be removed since the authors can not give scientific reasons for the source of the foreign elements.

Author's response: Just an added observation which could possibly support the effect of capping. I have justified the presence of impurity like Au. The TEM machine uses gold grid hence the appearance gold in the EDX spectrum of raw CMC.

Reviewer: I disagree with the authors on the source of the gold. The EDX was obtained from the SEM sample and SEM uses carbon as sample holder. So the likely impurity is carbon and not Gold. TEM analysis was not carried out in the initially submitted manuscript. This reviewer believes that the source of gold is from the coating of the SEM sample which is usually done to reduce the scattering of electron beam during imaging. EDX analysis should have been carried out before the coating for SEM. Comparing the EDX images of ZnS capped with CMC and raw CMC, it is obvious that both analyses were not carried out using the same machine. The authors donot necessarily need to include the later.

Author's response: Sorry, SEM analysis is not exclusively carried out using carbon tape as sample holder. Moreover, the operators of this machine (see methodology) indicated so when I asked them about the source of gold. I agree with you that both analysis were not done at the same place, while the capped sample analysis was done at SHESTCO in Abuja Nigeria, the SEM analysis for the raw CMC was done at the center for nanostructured materials, Pretoria in south Africa. The lead research scientist at the ceneter, Dr James Smith is an expert in microscopy.

Line 281 There is no peak at 381 because the spectra started from 400

Author's response: Correction now effected.

CMC spectrum also contain a peak at 480

Author's response: No! The peak is at 491 cm^{-1} . The shift may be caused by the incorporation of ZnS.

Reviewer: Authors should compare both IR spectra between $400\text{ -}600\text{ cm}^{-1}$ range. The peaks assigned to 480 cm^{-1} in figure 6b is even less pronounced when compared to peaks around this same range in Figure 6a (CMC sample). This makes the Reviewer to conclude that if peak picking is done below 500 cm^{-1} in Figure 6a, authors will pick up the 480 cm^{-1} peak also in this spectrum.

Author's response: Looking at the two spectra, it is clear that they were both recorded within the same range of energy and is slightly below 500 cm^{-1} . Again, more information was obtained within this range. So, we feel the earlier explanation is ok.

Line 310 should be Figure 6 and not Figure 5

Author's response: Correction effected.

Line 313 should be denoted as Figure 6 (a), (b) and (c) .not (1), (11) and (111)

Author's response: The use of Fig. 6(I), (II) and (III) now Fig. 7(I), (II), (III) and (IV) is most appropriate in this case since for example Fig. 7(II) has (a), (b),... and so the other figures.

Line 325 -326 The statement is not true

Author's response: The statement is true, check the cited literature for confirmation.

Reviewer: Reviewer can't see any reference for the statement in question: "The broadness of emission peaks of all samples synthesized in this work suggests smaller particles size distribution. This finding is supported by the average particles sizes calculated from XRD and EMA".

Author's response: Statement reversed in line with another reviewer's suggestion and confirmed from literature. Appropriate literature is also cited.

REFERENCES

The references are carelessly prepared. Author do not follow the standard short forms of some of the cited references. E.g the use of the word "of" is not allowed when writing the short forms of journal names. Why write the doi and the journal websites for reference [7] when the article full pages were already given

Author's response: Recommended standard short forms of the cited references now fully considered.

Reviewer: Authors are still not consistent with the referencing format. E.g reference 4 has no title, full journal names are used in ref 14, 8 etc.

Author's response: I have effected the corrections of those I could. Some journals do suggest while others don't. I do not want to commit any blunder in such cases.

General Observation

Authors have included some questionable results. Particle sizes from XRD are derived from 111 peak of the diffraction pattern. Deriving sizes from several peaks and given size of 2.31 and 27.90 nm for the same nanoparticles is highly inconsistent with particle size estimation.

Author's response: You may recall the context to which this is coming from. However, deriving crystal size using only the (111) reflexion is done by assuming the contribution to size from (220) and (311) peaks are negligible. Note, it is average crystal size. Again, why I had to include sizes calculated from other peaks e.g. (001), (002) and (101) is to indicate were the large average crystal size was coming from. The average of crystal sizes calculated from (111), (220), (331), (001), (002) and (101) peaks gave 15.7 nm. Now, I have replaced them with the average crystal size of 15.7 nm in the table.