

Referee's report to the dissertation Thesis of R. Blessy Pricilla

Preparation and characterization of carbon dots for versatile applications

Doctoral Thesis deals on one of the hot topics of current nanotechnology world. The carbon based nanodots are known for their versatile applications in many fields including various technologies, medicine as well as anticounterfeiting. There are different approaches for the nanomaterials preparation. The three different so-called bottom-up are presented in the Thesis: The microwave, hydrothermal, and simple heating. All of them are completed at about the same temperature of 200 °C with good or very good yields. As the precursors, proteins, biomass, and organic precursors were studied. The obtained nanodots characterization was examined using numerous techniques. The information about shape, molecular structure and mainly optical properties was achieved. Finally, each of the prepared material was tested for its application potential.

Whole Thesis is composed as set of three publications (one manuscript is under preparation). However the Pricilla's contribution to them is given in the Conclusions, some clarification is needed because many different methods were used and probably not all of them were done by herself.

The short Introduction presents a general feature of nanodots world and their applications. After that, a detailed review of the state of art in the field is given. Because topic is very new, nearly all references are from the last decade. Based on this review, the Thesis motivation and aims are clearly presented.

Chapter 5 brings list of all methods used in the following three chapters (papers). My feeling is that methods had to be presented separately in the sections of each paper because it was not so easy avoid mismatch in the methods used for separate studies. But this is a formal point, only.

Results, as pointed above, are based on the three papers where Pricilla is the first author.

The first study presents results of synthesis and applications of casein-derived carbon based nanodots from casein micelles by a novel method using microwave heating. The high yield and efficient conversion process was obtained that opens a new way for more sustainable and efficient production synthesis for the applications. TEM, TGA, XRD, FTIR, XPS and other techniques were used for the synthesized nanodots characterization. The fluorescence was studied with respect to the applications in anti-counterfeit films and as a potential phosphor material for LEDs exemplifies. Finally, the mechanism of nanodots based on casein precursor is presented.

The second study focused on carbon based nanodots synthesis from *Syzygium cumini* L. seeds. The study of nanodots structural, functional, and optical properties was examined with respect to their efficacy against various bacterial pathogens. This opens a new topic in search of alternative to nano-silver materials commonly used for the purposes. The application was shown by application of nanodots into cotton textile with positive effect. The bacteria elimination mechanism is proposed, too.

The last study deals on carbon-boron nanodots phosphorescence with extended lifetimes. A new approach synthesizing the self-matrix room-temperature material is shown and related mechanisms are proposed, too. The simple heating method was used for the synthesis with high yield. The practical application was demonstrated as anti-counterfeit measures, information encryption, and LED phosphors, too. Additionally, the sensitivity to moisture was observed.

Finally, Conclusion summarizes all Thesis achievements. Here are also presented authors contributions for each of studies. Finally, the last small chapter presents some ideas for the future research in the field.

I have the following comments and questions for the discussion at the defence:

General comments:

1. 5.1.1 – what amount of material was used for XRD measurements? The same information is missing also for some other methods, also in the next experiments.
2. What temperatures were used during materials processing (sonication, stirring, ink preparation etc.)?
3. p. 33 – “7 dilutions were performed” – was it a decadic que or different?
4. 5.2.4 – was cotton cloth pretreated. i.e. washed in some solution etc.? Commonly, these materials are protected by chemicals against microbial contamination. This hat to influence the obtained results.

5. 6.1, 8.1, Fig. 21 – distribution of CND particles was measured, too? Why DLS was not used for the size distribution measurement? And did you try also HRTEM for CND structure visualisation?
6. Fig. 5 – It is surprising that there are no indication of O-H and C-H bounds however these bounds are presented in the precursor structure. Can you explain this?
7. What are the experimental uncertainties of values presented in Tables 2, 3, Fig. 26
8. The CDs antimicrobial effect is photo induced or not? And is any direct evidence for the disruption of membranes (Typically, this is confirmed by SEM where membrane ruptures are visible).
9. 8.2 – how mass losses relate to the XRD measurements? And what was the initial amount? At the beginning, some numbers are given but without reference (original amount).
10. 8.3 - FTIR does not allow surface analysis. The depth is much bigger than particles size.
11. Table 5 – what are the uncertainties? Were tested also smaller amounts of 1,10 phenanthroline than 10 mg?
12. Fig. 40a – why two peaks are observed in the time dependence?
13. 8.6 – “As the scheme demonstrates, they go through internal conversion or intersystem crossing to triplet states through $n-\pi^*$ or $\pi-\pi^*$ transitions to produce fluorescence or phosphorescence, respectively [152]”- this statement is not fully correct. Fluorescence will be most probably back to the ground state, i.e. from singlet to singlet. Exception is, if there is another low energetic triplet state. But this needs further research, probably using molecular numeric modelling.
14. p. 93 – “with the potential for B-C bond formation” – was this observed by XPS measurements?

Technical comments:

1. Purities of the used materials should be given.
2. Table 1 – oxygen should be added here with note that is calculated. And what were experimental uncertainties?
3. Fig. 40c – what were the image exposure conditions?

Formal comments:

1. Sometimes there is non-correct use of capitals.
2. p. 48 – “Hence, zero relaxation energy is observed for $h\nu_{ex} \approx 2.0$.” – unit is missing.
3. Fig. 9 should be presented before Table 2, not 2 pages later. Why double exponential fit was used? Explanation is given in the text later, but this is not clear for the reader immediately.
4. p.67 – “The peaks observed at 284.9, 399, 178, and 530 eV are attributed to C1s, N1s, S2p, and O1s functional groups” – incorrect. These XPS peaks relates to individual atoms. Information about chemical bonds can be obtained using these peaks with high resolution.
5. Fig. 25 – The used resolution should show individual cotton fiber. But they are not visible. Why? The enhanced contrast will be useful to better see the differences.
6. Table 4 – used acronyms are not explained.
7. p.92, eq. 8.1. – what units are used for wavelength? This information is missing.

Finally, I'm warmly recommending this doctoral Thesis for the defence where the main questions will be successfully answered. Thereafter, I'm recommending getting title Doctor to R. Blessy Pricilla.



In Brno, 23. 1. 2024

prof. RNDr. František Krčma, Ph.D.