HYDROGEN PEROXIDE SENZING BY DICHALKOGENIDE QUANTUM DOTS PREPARED BY LPE

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Abstract: Signalling molecules such as hydrogen peroxide (H_2O_2) play crucial role in cellular metabolism. Under pathological conditions, the cell is unable to control enzymatic conversion H_2O_2 into water and oxygen. This fail in cell metabolism could lead to damage of cell. Thus produced H_2O_2 is presented at a nanomolar scale and currently there is a lack of suitable electrochemical sensors for its sensitive detection. Modification of screen printed electrodes (SPE) with 2D-nanomaterial quantum dots prepared by Liquid Phase Exfoliation (LPE). MoS_2, $MoSe_2$, WS_2 and WSe_2 compounds were used for this purpose. Such modified electrodes were characterized and optimized for hydrogen peroxide detection.

Keywords: QUANTUM DOTS, DICHALCOGENIDES, LPE, HYDROGEN PEROXIDE, SENSING, SCREEN PRINTED ELECTRODES

1 INTRODUCTION

Free oxygen radicals (ROS) play an important role in cell metabolism as signalling molecules. The imbalance between the production of reactive metabolites and the antioxidant capacity of organism can lead to DNA damage and the development of a variety of diseases including tumours, diabetes, Parkinson's or Alzheimer's disease [1]. Hydrogen peroxide is converted into water and oxygen when physiological conditions go (work) correctly, on the other side pathological conditions lead to damage of cell structures by oxidizing them. Thus, sensitive measurement of peroxide concentration at very low concentrations (nM) is still challenging and beneficial in terms of studying physiological and pathological cellular processes. Today's approaches to measuring hydrogen peroxide most often include optical methods including fluorimetry [2], spectrophotometry [3], microscopy [4], and electrochemical [5,6]. The development of electrochemical biosensors delivers the benefits of high sensitivity, selectivity, rapid response, low cost and miniaturization [7]. In addition, hydrogen peroxide can be measured directly by amperometric detection. The effect of interferences in complex samples also led to the construction of biosensors with semipermeable membranes [8], redox mediators [9,10] or selective electrocatalysis [11], thereby increases of selectivity and sensitivity to measured redox analytes. The trend in the development of nanotechnologies then gradually led to modifications of electrochemical biosensors using metal nanoparticles [7,12,13], carbon nanomaterials [14-16] or other metal oxide nanostructures [17-19], due to their unique electrical and catalytic properties and stability. However, to date, hydrogen peroxide has been detected electrochemically only in sub-micromolar amounts, which is insufficient to measure the nanomolar concentration of peroxide released from cells. High sensitivity of the biosensors has been achieved with the enzyme horseradish peroxidase [22], mediators [10], and metal nanoparticles [13] which have the disadvantages of reduced operational stability and cost increases. Therefore, new approaches are sought to ensure high stability of biosensors, excellent catalytic effects, high sensitivity, simplicity of preparation, for example in the use of transition metal dichalcogenides. Some dichalcogenides, due to their similarity to graphene, gain weight in the field of nanoelectronics and optoelectronics. However, in the

field of biosensors molybdenum disulfide [23,24] and tungsten disulphide [24] are the most studied, whereas only disulphide molybdenum nanoparticles have been used to construct cellular biosensors. Due to the excellent catalytic properties of molybdenum disulphide a sensitive measurement of hydrogen peroxide was obtained after stimulation of the cells in nanomolar concentration. For this reason, there is a great potential for the study of other dichalcogenides (tungsten diselenide, molybdenum diselenide) in the area of not only cellular biosensors and their comparison of catalytic properties. In this paper, the detection of hydrogen peroxide was investigated with adjusting the screen printed electrode (SPE) by quantum dots of MoS_2, $MoSe_2$, WS_2, and WSe_2 prepared by liquid phase exfoliation and the most suitable material was determined.

2 EXPERIMENTAL

2.1 QUANTUM DOTS PREPARATION

The expanded dichalcogenides MoS_2, $MoSe_2$, WS_2 and WSe_2 were weighed 30 mg and mixed with 10 ml N-methyl Pyrolidone (NMP). The resulting mixture was placed in an ultrasonic bath with power 50W and frequency 37 kHz for 9 hours. When sonication was complete, the mixture was left to settle overnight, after which 80% of the supernatant was collected. This supernatant was then placed in a centrifuge and spun at 4000rpm for 40 minutes to sediment the remaining impurities. The final preparation step was to filter the supernatant through a 450 nm filter.

2.2 QUANTUM DOTS CHARACTERIZATION

The height and size of individual quantum dots were characterized by atomic force microscopy (AFM) on a Dimension Icon from Bruker Corporation. The measurement was performed in semi-contact mode using the Scan Asyst tip, which allows very accurate semi-automatic measurement with atomic resolution. The data were processed in Gwiddion software. A thermogravimetric method (TGA) was used to determine the concentration of individual quantum particle solutions. The essence of the thermogravimetric method is a very accurate mass measurement during gradual evaporation of the carrier liquid. Due to the use of NMP which have a high evaporation point, the end temperature of the experiment was set to 200 °C. The entire measurement process took 65 minutes with a heating rate of 10 °C per minute.

2.3 CYCLIC VOLTAMMETRY MEASUREMENT

Screen printed electrodes modified with individual quantum dots were characterized by cyclic voltammetry in terms of oxidation and reduction properties. The measurement setting was from -700 to 1000 mV. Prior to the measurement, the individual electrodes were voltammetrically activated in Phosphate-buffered saline solution with 0.1 M NaCl. Upon activation, an amount of hydrogen peroxide was added to the solution to form a 5 mM mixture in which the measurement was performed. A clean electrode was also measured to compare it with the modified one.

3 RESULTS

Quantum dots from MoS_2, $MoSe_2$, WS_2 and WSe_2 used for electrode modification were prepared by exfoliation in liquid NMP. The concentration of nanoparticles in NMP solution was determined from TGA measurements. The nanoparticle concentration in NMP was 0.5 mg/ml for MoS_2, 1.21 mg/ml for $MoSe_2$, 0.2 mg/ml for WS_2, and 0.8 mg/ml for WSe_2. Measurement of AFM of individual quantum dots showed strong polydispersity of the prepared particles, see Figure 1.

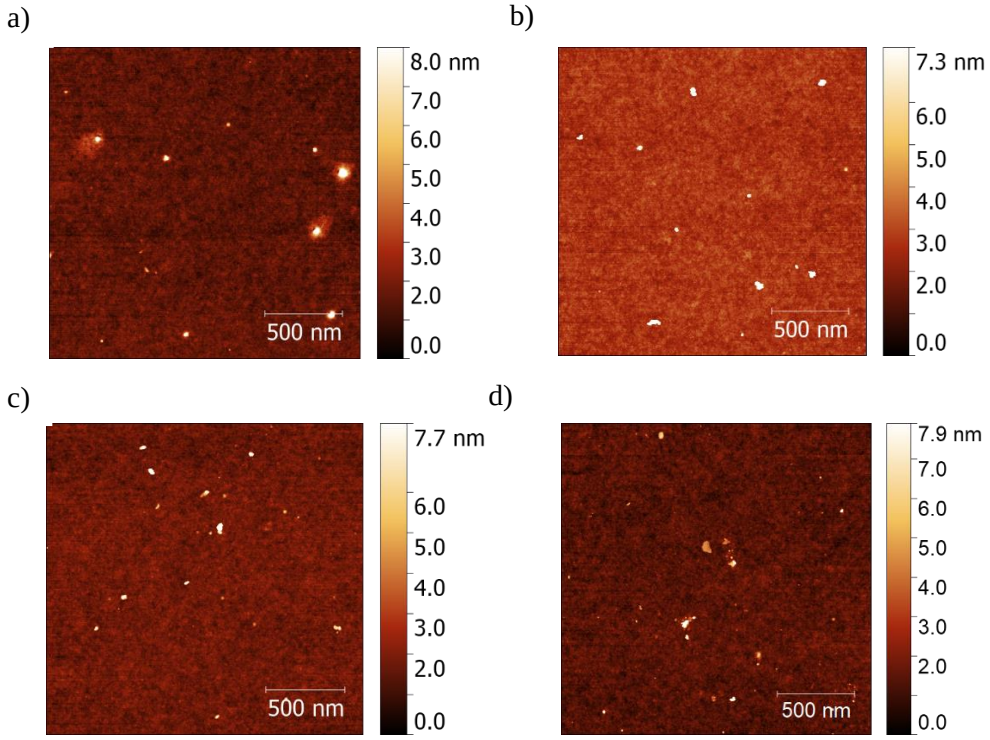

Figure 1: AFM measurements of LPE quantum dots from a) MoS_2, b) $MoSe_2$, c) WS_2 and d) WSe_2.

The particle size ranged from 10-50 nm for MoS_2, 30-60 nm for $MoSe_2$, 10-60 nm for WS_2, and 30-80 nm for WSe_2. The height of the prepared particles ranged from 2 to 8 nm, which corresponds approximately to 2 to 8 monolayers. The nanoparticles prepared in this way were used to modify the platinum electrode using the drop casting method. This method involved applying 10 µl of nanoparticle solution onto the electrode for 24 hours. After this time, the electrode was washed with ultrapure water from the residual solution. For the detection of 5 mM hydrogen peroxide, the cyclic voltammetry (CV) method was used. Voltammogram and graph of each material current density peak with size distribution of used material is shown in Figure 2.

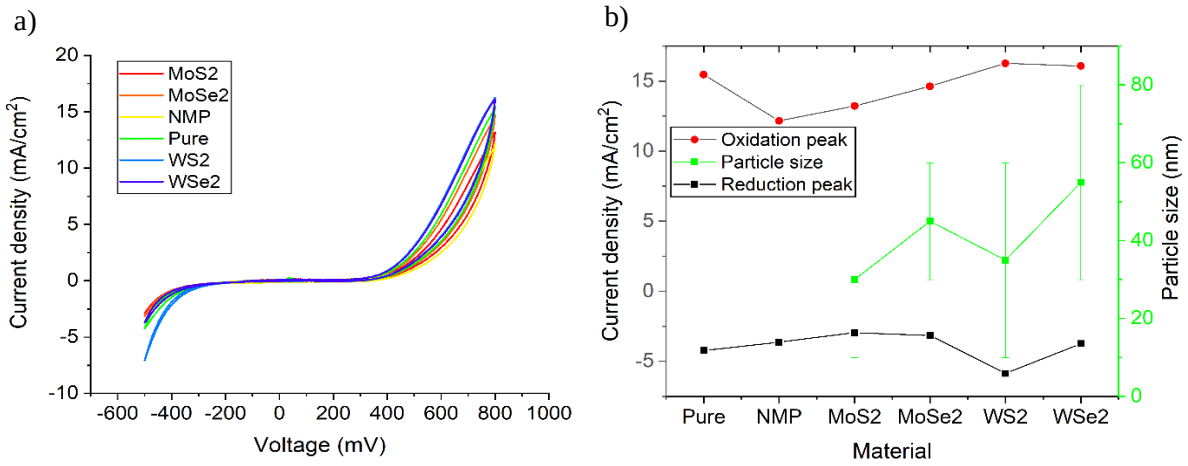

Figure 2: a) Voltammogram of 5 mM H_2O_2 with clear and modified electrodes with b) current density peaks with size distribution of used material.

The obtained data show highest reduction and oxidation peak for WS_2 quantum dots. WSe_2 exhibited almost same oxidation peak as WS_2. Both materials exhibit highest current densities than the rest of tested electrodes. Size particle distribution don't correlate with current density peaks results probably due to strong polydispersity of prepared dichalcogenides quantum dots.

4 CONCLUSION

In the initial research on the detection of hydrogen peroxide by quantum dots from dichalcogenides, the following results were obtained:

1. WS_2, WSe_2, MoS_2, $MoSe_2$ quantum dots were prepared by LPE.
2. AFM shown polydispersity in size (10-80 nm) and height (3 – 8 nm) for all quantum dots.
3. Modified electrode with WS_2 showed highest oxidation and reduction peak.
4. The oxidation peak was very height not only for WS_2, but also for WSe_2 modified SPE.
5. To ensure this effect is not caused by the stabilization solvent, measurements with NMP only were done.

From the obtained data can be seen that the most suitable material from the tested dichalcogenes is tungsten sulphide, which showed better detection values of hydrogen peroxide than others. Due to the large polydispersity of the quantum dots obtained, it is not possible to say unequivocally which nanoparticle size is the most suitable for the detection of hydrogen peroxide. To determine this relationship, follow-up research is needed to reduce polydispersity and affect the detection properties of WS_2.

ACKNOWLEDGEMENT

The research received support from the Ministry of Education, Youth and Sports of the Czech Republic under project INWITE (LO1401). This research has also been financially supported by the Specific University Research grant of Brno University of Technology, FEKT/STI-J-18-5354. Further, the paper was supported from project No. FEKT-S-17-3934, Utilization of novel findings in micro and nanotechnologies for complex electronic circuits and sensor applications. For the actual research, the infrastructure of the SIX Center was used.

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