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Functional Basis of Nanoelectronics

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METHODS OF FORMATION, DIAGNOSIS AND RESEARCH OF NANOSTRUCTURES

FORMATION OF SEMICONDUCTOR QUANTUM DOTS FOR ELECTROCHEMILUMINESCENT ASSAY BY LASER FRAGMENTATION

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The work describes the use of semiconductor quantum dots (QDs) for electrochemiluminescent assay of amine compounds and development of new method for production of shell-free semiconductor nanoparticles using laser fragmentation technique. The strategy of electroanalytical application of QDs is based on electrode modification with polymer films containing CdSe QDs that directly participate in ECL reaction with amine coreactants. We have also described efficient top-down method of fluorescent CdSe nanoparticles synthesis using laser fragmentation of its powder suspension in dimethylformamide, optical properties of produced QDs and discussed the applicability of produced nanoparticles for electroanalytical techniques.

Introduction

The development of new techniques for biologically important substances detection, in particular certain classes of amine compounds, is important considering vital role played by those biological amines in the living organisms. Thus their assay and monitoring are important tasks for biology and medicine, control of foods and beverages quality, pharmacy.

The method of electrogenerated chemiluminescence, also known as electrochemiluminescence (ECL) is a promising detection tool in the analytical chemistry of liquids. In ECL process electrochemically generated intermediates undergo a highly exergonic reaction to produce an electronically excited state that results in light emission. Currently, a number of substances are known as good coreactants for exciting ECL emission in aqueous and nonaqueous media, thus making them good analytes for the detection using ECL method. Among such coreactants are numerous amines, oxalate, peroxydisulfate, hydrogen peroxide and some others [1]. ECL has several attractive features (low background signal, precise control of reaction kinetics by the applied potential, compatibility with solution-phase and thin-film formats) that altogether make it a highly sensitive and selective analytical method.

In order to broaden the application area of ECL assay it is promising to replace commonly used organic luminophores with new emitting species, such as semiconductor QDs. They have a number of advantages over conventional luminophores (broad absorption spectrum, narrow and size dependent luminescence spectrum, high resistivity towards photo bleaching, high quantum yield) making a future assay more efficient and sensitive.

Research on nanomaterials with specific and pre-programmed properties is one of the most expanding fields in nanothechnology, at the crossroad of physics and chemistry and biology. Material properties in this size range are mainly determined by the quantum confinement effects. Ultrapure nanoparticles can be obtained using laser irradiation of solid materials or suspended microsols in liquid media. This green technology has become a reliable alternative to traditional chemical reduction method for obtaining diverse sorts of nanoparticles. The synthesis enables formation of highly stable nanocolloids, nanoparticle size and size distribution control, and direct surface conjugation during the synthesis using a great variety of raw materials [2].

In this work we have developed an ECL approach for detection of amines of interest that is based on the use of amines as direct coreactants for electrochemical excitation of QDs emission. In this case fluorescent nanoparticles can be incorporated into conductive polymer films at the electrode surface and these modified electrodes can be used as compact and efficient ECL sensors.

Laser fragmentation synthesis of CdSe QDs

Laser ablation in liquids is commonly used to generate nanoparticles of noble metals and certain non-metallic substances in suspensions while the number of works devoted to production of semiconductor nanocrystals using laser ablation or fragmentation is relatively scarce [3]. Since our results indicate a number of advantages from using semiconductor QDs for electroanalysis, we believe that development of new methods for generation of ultrapure nanoparticles free from chemical precursors and byproducts is an important objective.

The fragmentation of CdSe nanoparticles was done using Trumpf TruMicro 5050 pulsed laser. Ultrasonicated suspension of CdSe powder in organic solvent was used as a fragmentation target. The target suspension was irradiated in quartz cuvette with the laser beam focused in the solution bulk. The fragmentation process was accompanied by mixing of the suspension to prevent sedimentation of CdSe powder grains (see scheme in Fig. 1).

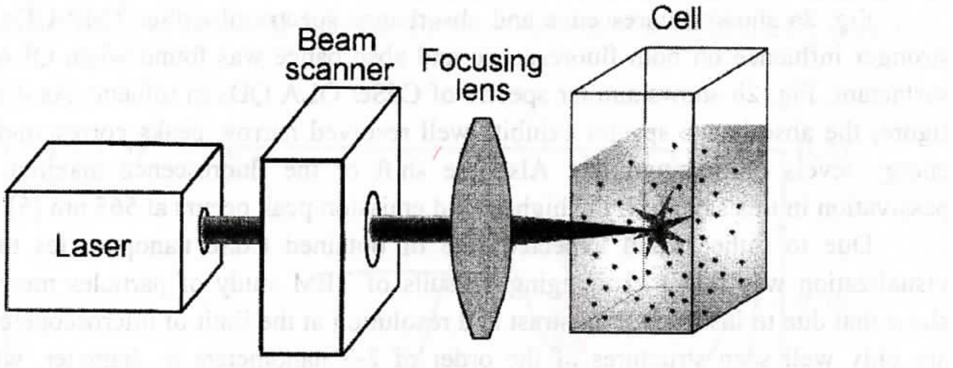

***Fig. 1** - Scheme of laser fragmentation experiment*

In order to choose appropriate media for laser fragmentation a number of solvents were first tested for their stability under laser irradiation. During preliminary studies several solvents were considered as potential media: nonpolar aprotic (toluene, chloroform, cyclohexane); lowpolar aprotic (dichloromethane); polar aprotic (dimethylformamide); polar protic (methanol, ethanol). These tests revealed strong damage of some solvents. Dimethylformamide (DMF), methanol and ethanol showed minimum changes of optical properties. When excited by 405 nm laser diode DMF showed weak fluorescence, while ethanol and methanol gave no emission.

Preliminary testing of CdSe nanoparticles synthesis revealed that only in DMF a distinct absorbance peak at 405 nm is present. This absorbance peak was rather unstable and was decaying with time. It was also noticed that depending on the concentration of fragmentation products there was different tendency towards aggregation. Flocculation of CdSe nanoparticles was only starting at relatively high concentrations when absorbance peak had value above 1.5 units.

Considering presence of fluorescent products of DMF degradation after laser irradiation in all studies the fragmentation products were removed from the original solution by centrifugation and redispersed in a new DMF solvent. Obtained quantum dots possess weak broadband fluorescence with the peak position at about 660 nm. The position of absorption peak (~400nm) is characteristic for core-type CdSe quantum dots with the diameter below 2 nm [4].

The stability and fluorescent activity of CdSe nanoparticles in DMF is attributed to their surface stabilization with dimethylamine which is commonly present in DMF as its synthesis reagent and main product of decomposition during storage while it is well known that amines belong to the group of capping ligands that efficiently passivate CdSe surface and block nonradiative recombination centers.

In order to stabilize the properties of produced nanocrystals their surface modification was applied. Substances, commonly used for such purpose, mostly belong to the classes of phosphines and amines. In this study the modification of CdSe quantum dolts was performed by trimethylolphosphine (TMP) and oleylamine (OLA) to provide their solubility on polar and nonpolar solvents accordingly. The reaction with TMP and OLA was performed in DMF at room temperature during 24 hours. After that quantum dots were separated by centrifugation and redispersed in appropriate solvent. Nanoparticles covered with OLA showed good solubility in toluene whereas those covered by TMP were well soluble in DMF.

The coverage of nanoparticles significantly enhanced their fluorescence efficiency due to blocking of surface defects. This is common behavior considering extremely high surface to volume ratio of nanoparticles of this size scale when surface states essentially contribute to the overall energetic structure of the nanoparticle. In all cases there was observed a shift of fluorescence maxima towards shorter wavelengths comparing to unmodified samples, especially in the case of modification with OLA.

Fig. 2a shows fluorescence and absorbance spectra of CdSe/ TMP QDs. An essentially stronger influence on both fluorescence and absorbance was found when OLA was used as a surfactant. Fig. 2b shows similar spectra of CdSe/ OLA QDs in toluene. As it is seen from the figure, the absorbance spectra exhibits well resolved narrow peaks corresponding to different energy levels of quantum dot. Also the shift of the fluorescence maxima due to surface passivation in this sample is the highest and emission peak occurs at 565 nm [5].

Due to rather small expected size of obtained CdSe nanoparticles the task of their visualization was rather challenging. Results of TEM study of particles modified with OLA show that due to insufficient contrast and resolution at the limit of microscope capabilities there are only well seen structures of the order of 2-3 nanometers in diameter, whereas diameter calculated on the base of the position of first absorbance peak corresponds to 1.5-1.6 nm.

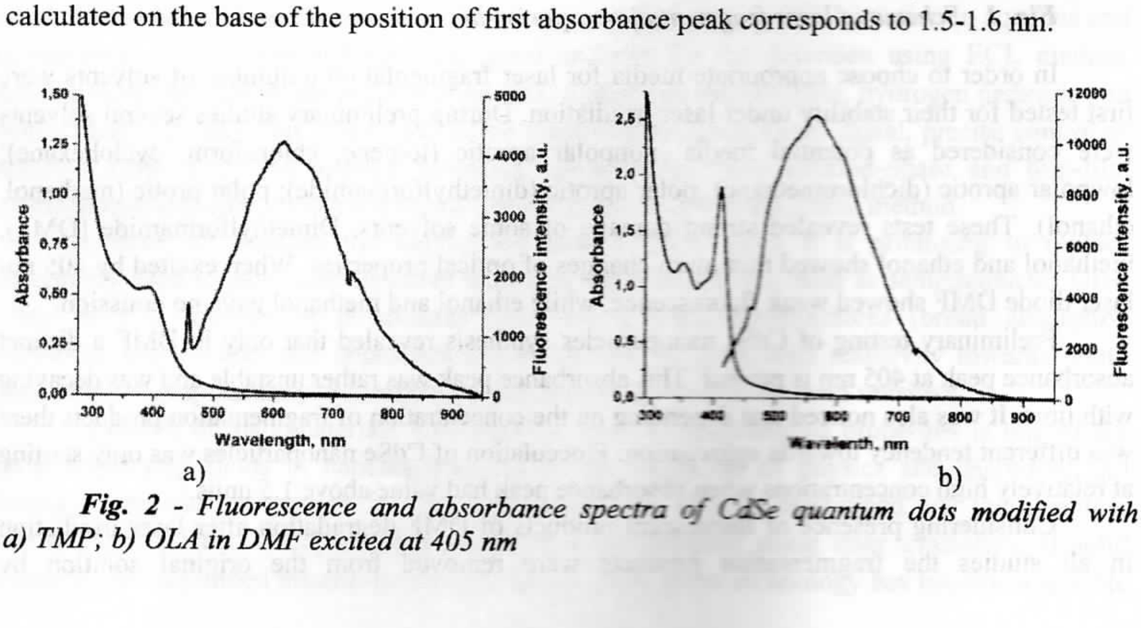

Fig. 2 - Fluorescence and absorbance spectra of CdSe quantum dots modified with a) TMP; b) OLA in DMF excited at 405 nm

ECL sensor for amines detection based on QDs

In analytical sciences there is a trend towards miniaturization of the instruments and their conversion into small, inexpensive and simple sensors. Many expectations for electrochemical and ECL analysis are related with the modification of sensor's electrodes by functional film comprising components for carrying out analytical reaction. The emissive properties of thin film can be achieved by its doping with nanomaterials such as semiconductor QDs acting as either redox mediators or emissive centers. The study was aimed at confirming the idea that polymeric films with CdSe QDs can generate ECL emission in reaction with amine coreactants.

CdSe/ZnS QDs stabilized with TOPO (diameter of 4 nm, λem = 630 nm) were deposited on conductive ITO glass substrates by spin coating technique in poly(9,9-di-n-octylfluorenyl-2,7-diyl (PFO) conductive polymer matrix. ECL experiments were carried in 3-electrode electrochemical cell with film modified ITO glass working electrode, glassy carbon plate counter electrode and Ag/AgCl reference electrode. ECL was excited using cyclic linear potential sweep in phosphate buffer solution (pH = 6.85) as a supporting electrolyte with tripropylamine coreactant using ELAN-3D apparatus.

Fig. 3 shows ECL emission from QDs/ PFO film modified ITO electrode when electrode potential is swept in the 0 - 2.0 V range. The onset of weak ECL emission occurs at a potential of only 1.1V which is probably associated with the TPA oxidation itself while the main emission raise occurs at 1.4V (with peak at 1.55 V) that is probably associated with QDs oxidation. Presented results suggest that CdSe/ZnS QDs participate in redox reaction of oxidation at ITO electrode with further oxidative-reduction type ECL reaction with trypropylamine coreactant. Thus we believe that such QDs/polymer film modified electrodes are suitable for ECL detection of certain amines and for development of analytical ECL procedures on their base.

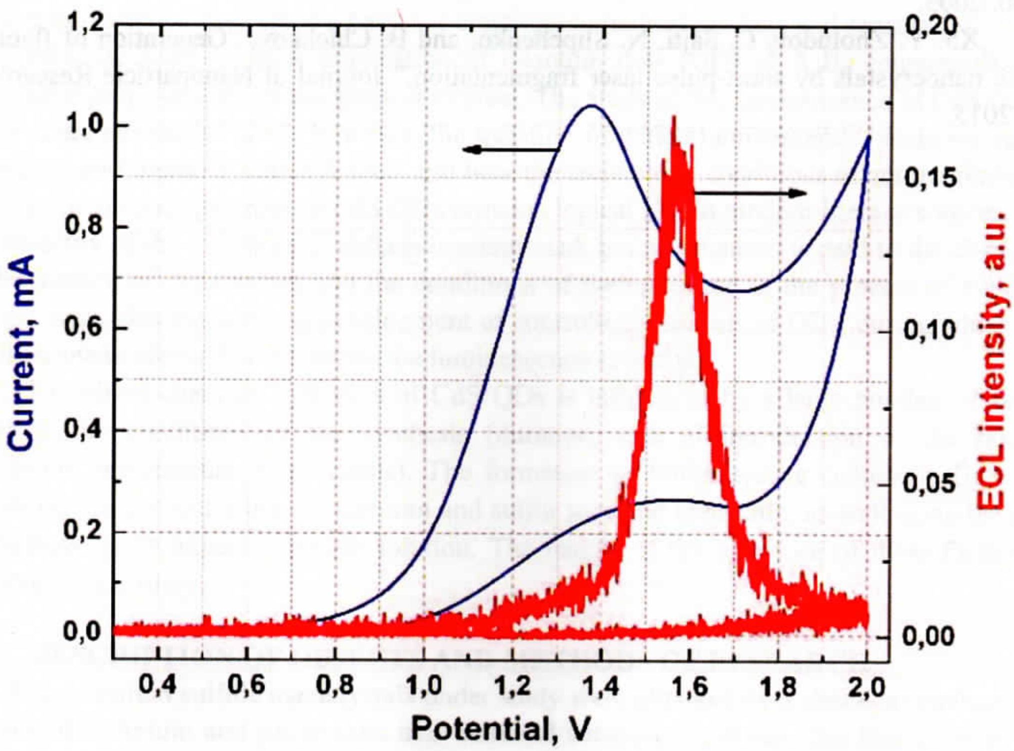

***Fig. 3** - Cyclic voltammogram and ECL response from ITO electrode modified with PFO film containing CdSe/ZnS QDs, coreactant: 20 µM trypropylamine*

Conclusion

In this work we have demonstrated an approach for ECL detection of certain amine compounds using semiconductor quantum dots as emitters. We have shown that polymer films containing CdSe QDs can be used as a base for of new analytical ECL procedures and sensors. Feasibility of such approach was verified using ECL reaction with tripropylamine coreactant as a model of amine analyte. We have also shown that laser fragmentation is a new promising method for rapid and efficient production of shell-free semiconductor nanoparticles with high monodispersity and purity that possess unique optical properties and that can find their application in electroanalytical techniques.

Acknowledgment

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