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One-pot Synthesis of MPA Capped CdTe Quantum Dots for Non-Enzymatic Hydrogen Peroxide Biosensor Application

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Abstract

Mercaptopropionic Acid (MPA) capped CdTe QDs with crystallite size is 0.8 nm were successfully synthesized in aqueous medium by reflux method. The HRSEM demonstrates the spherical shape with varying sizes in the nanometer scales. From the electrochemical studies, the prepared QDs improve the electron transfer between electrode and H_2O_2. The sensor exhibits a linear range from 0.67-8.04 μM with a sensitivity of 0.2833 mA $mM^{-1}cm^{-2}$ with a linear coefficient of 0.9877. The sensor shows detection limit of 6.7 μM with a rapid amperometric response time of 5s and possesses a good reproducibility. It shows the selectivity toward H_2O_2 and interference free phenomenon for other electro active species like oxalic acid and ascorbic acid. MPA capped CdTe QDs sensor was used in rat and human serum samples and cell labeling.

Keywords: CdTe Quantum Dots, Hydrogen peroxide, Sensitivity, Selectivity, Limit of Detection.

1. Introduction

Hydrogen peroxide (H_2O_2) is simplest and colorless peroxide and plays an important role in biological systems. It is widely applicable in biological, industrial, pharmaceutical and environmental [1-3]. H_2O_2 is not only a byproduct of almost all oxidases in mitochondria and separate out freely through membranes and reaches various cellular components [4]. Many analytical tools such as volumetric, photometry, chemiluminescence, chromatography, flurometric and electrochemical have been employed for the detection of H_2O_2. Electrochemical method has attracted considerable interest due to high sensitivity, low cost, lower limit detection, less response time, efficiency, linear range and selectivity [5-7]. In last decades the electrochemical biosensor modified with several metal nanomaterial's and QDs have been studied. The modified TGA capped CdTe QDs based on electrode shows high selective detection of dopamine in the presence of ascorbic acid and uric acid has been proposed by Roushani et al.[8]. Carbon paste electrode modified with CdTe QDs was fabricated and used to study the electro oxidation of dopamine and uric acid in some real samples [9].

II-VI semiconductor nanocrystals also known as quantum dots (QDs) has received extensive attention due to their size dependent optical properties, efficient emission and potential applications in biosensor, nonlinear optics, electronics, light emitting diode, photovoltaic devices, bio imaging and cell labeling [10-12]. In this work, Glassy carbon electrode (GCE) modified with MPA capped CdTe QDs for determination of H_2O_2 in the presence of excess amount of interfaces like oxalic acid (OA) and ascorbic acid (AA).

2. Experimental

2.1. Synthesis of CdTe QDs

Mercaptopropionic Acid (MPA) capped CdTe QDs is synthesis by following method. In a typical synthesis, 0.2279 g of cadmium chloride was diluted in 150 ml of double distilled water in a two-necked flask, followed by the addition of 0.2763 g of MPA and 1M of sodium hydroxide to a final pH value of 11. After that, the solution was stirred under Nitrogen gas (N_2) for 20 min. In addition to that, 0.4842 g of trisodium citrate, 0.0319 g of sodium telluride, 0.0284 g of sodium borohydride were added and refluxed under nitrogen flow (N_2) at 100°C. Subsequently the reaction mixture was heated to reflux for 3 h under N_2. Finally the resulting QD solution was mixed with propanol at the rate of 1:1 and centrifugalized at 10,000 rpm for 10 min and kept at room temperature. The sample is codes as MCQ.

2.2. Material Characterization

XRD pattern was recorded (PANalytical X-pert pro) with CuKα (1.5406 Å) in the range of 20 to 80º and FTIR spectrometer (JASCO FTIR 460 plus spectrometer) was recorded in the range of 400-3500 cm^{-1}. HRSEM image (FEI Quanta FEG 200) was taken. Optical properties like absorption and emission were studies using UV-Visible (Shimadzu 1800) and fluroscence (Floromax) spectrophotometers. Cyclic voltammetry (CV) and amperometric analyses were performed using (BioLogic SP-150) electrochemical workstation.

2.3. Preparation of the Electrode

In the three electrode system, glassy carbon electrode as a working electrode, Ag/AgCl as a reference electrode and Pt wire as a counter electrode were used and 0.1 M of phosphate buffer solution (PBS) were used as a electrolyte. For preparing MPA capped CdTe QDs (MCQ) modified GCE electrode, 1mg of MCQ powder was first dispersed in 50 µl of chitosan solution and then in 0.5 ml of ethanol and sonicated for 30 min. 5 µl of the dispersed solution was dropped on GCE electrode, dried at atmospheric air and then modified electrode was used for H_2O_2 sensing.

3. Results and Discussion

3.1. Structural and Morphological

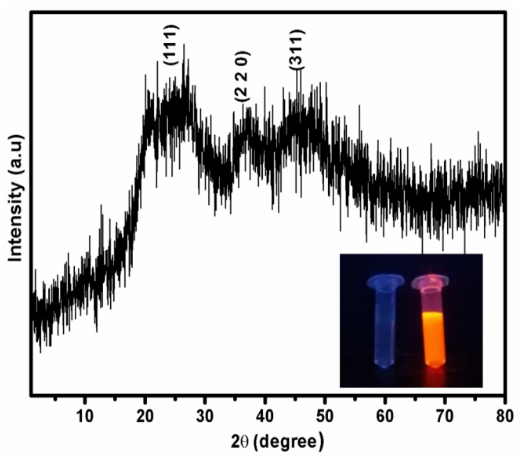

Figure 1. XRD pattern of MPA capped CdTe QDs

Figure 1 shows the XRD pattern of MPA capped CdTe QDs. The diffraction peaks centered at 23º, 39º and 46º are indexed to the (1 1 1), (2 2 0) and (3 1 1) plane respectively, for MPA of cubic CdTe lattice (JCPDS card: 65-0880) [13]. The average crystallite sizes calculated from Scherrer formula was 0.8 nm for MPA capped CdTe QDs. Figure 2. Shows the HRSEM image of MPA capped CdTe QDs with spherical shape. From the histogram, the average particle size is about 50 nm with a range dispersion of 30-90 nm for MPA capped CdTe QDs.

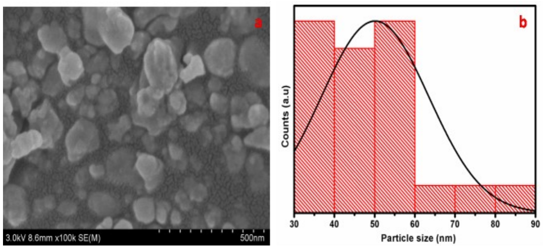

Figure 2. HRSEM image of MPA capped CdTe QDs

To identify the functional groups, FTIR spectra were taken and shown in figure 3. The infrared absorption band observed at 3445 cm^{-1} is due to the overlapping of O-H and N-H stretching. The bands at 2360 and 1586 cm^{-1} denote the existence of C-N asymmetric stretching and carbonyl group respectively. The presence of asymmetric C-H bending and C-S stretching vibrations indicated by the bands at 1384 and 676 cm^{-1} respectively [14,15].

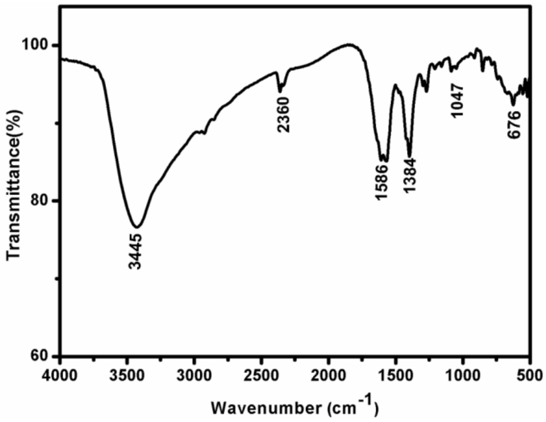

Figure 3. FTIR spectrum of MPA capped CdTe QDs

3.2. Optical Properties

Figure 4 shows the absorption and fluorescence spectra of MPA capped CdTe QDs. An absorption maximum centered at 356 nm is observed for MPA capped CdTe QDs respectively. The line width of the fluorescence spectrum is relatively narrow, and the maximum emission wavelength is 570 nm indicates the consequence of quantum confinement for an excitation wavelength of 350 nm.

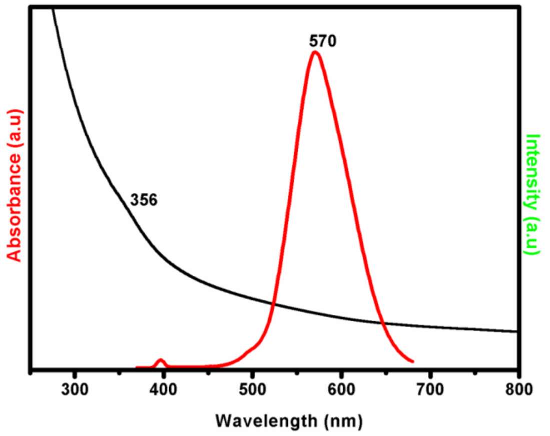

Figure 4. UV-visible spectrum of MPA capped CdTe QDs

3.3. Electrochemical Studies

3.3.1. Cyclic Voltammetry

The electrochemical characteristics of MCQ QDs were analyzed through CV using chitosan as a binder in PBS. Figure 5(a) shows the voltammograms recorded on GCE, MCQ/GCE, and MPCQ/GCE/Chitosan at a sweep rate of 40 mV/s between -1.0 to 1.0 V range. GCE bare electrode shows oxidation peak at -0.70 V and in the presence of MCQ, it shows -0.58 V and -0.57 V for MCQ/GCE/chitosan. Figure 5(b) illustrates the CV for MCQ/GCE/chitosan in deoxygnated PBS at scan rate from 20 to 100 mV/s in the potential range between -1.0 to 1.0 V. It is found that as the scan rate increases the oxidation peak current get decreased from -0.574 V to -0.570 V [16]. Figure 5(c) shows the voltammograms recorded on MCQ/GCE/chitosan in the absence and presence of H_2O_2 with different concentrations. In the absence of H_2O_2, an oxidation peak is found at -0.57 V, while adding H_2O_2 in an electrochemical cell, a decrease is found at -0.63 V. On increasing the H_2O_2 concentration, the redox peak current gets decresed [2].

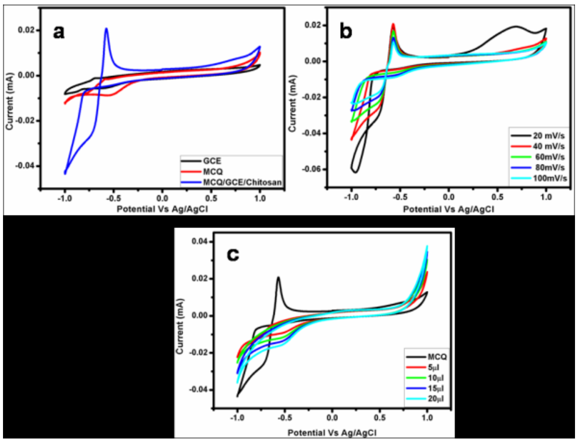

Figure 5(a). CV for bar GCE, GCE/MCQ, GCE/MCQ/chitosan (b) CV of different GCE/MCQ/chitosan at different scan rate (c) CV for GCE/MCQ/chitosan with different concentration of H_2O_2 for MPA capped CdTe QDs

3.3.2. Amperometric Biosensors

Amperometric response to H_2O_2 is shown in Figure 6(a). While maintaining PBS in a stirring condition, different concenteration of H_2O_2 are added at regular intervals. The amperometric analysis was studied on the chemically modified electrode by applying constant potential of -0.4 V. The amperometric responses were linearly increased in the concenteration range of 0.67-8.04 μM with the correlation coefficient 0.9877. With the addition of H_2O_2 into the electrolyte solution and the catalytic current increases and reaches its steady state within 5 s and a plot between H_2O_2 and current exhibits good linearity figure 6(b). The MCQ sensitivity and detection limit of sensor were calculated to be 0.2833 mA $mM^{-1}cm^{-2}$ and 6.7 μM respectively. The Limit of Detection of the sensor was calculated by using the formula is $3s_b/S$ where, s_b is the standard deviation of blank signal and S is the sensitivity [17].

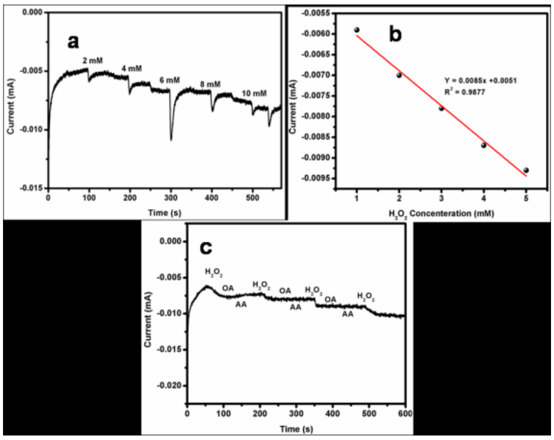

Figure 6 (a). Amperometric analysis for different concentration of H_2O_2 (b) linear relation between current and H_2O_2 concentration (c) Amperometric analysis with the addition of H_2O_2, OA and AA for MPA capped CdTe QDs

The selectivity of the sensor to the determination of H_2O_2 has been investigated in the presence of likely interfering agents. Figure 6(c) showed the amperometric response of the electrode towards 0.67 μM of H_2O_2, OA, AA. The electrode quickly responded to H_2O_2 however, it was insensitive the other species. On the contrary, a rapid and large decrease in current response is observed with the subsequent addition of H_2O_2, suggesting a excellent selectivity of MCQ for H_2O_2 sensor.

4. Conclusion

MPA capped CdTe QDs were prepared by reflux method. XRD confirms the zinc blende cubic structure of CdTe QDs and the average crystallite sizes is 0.8 nm for MPA capped CdTe QDs. HRSEM image show the spherical particles and from the histogram, the average particle sizes is 50 nm for MPA capped CdTe QDs. MCQ electrode exhibits an excellent non-enzymatic electrocatalytic activity towards H_2O_2 in CV experiments. The fabricated sensor exhibits a linear range from 0.67-8.04 μM with a sensitivity of 0.2833 mA $mM^{-1}cm^{-2}$ with a linear coefficient of 0.9877. The sensor shows detection limit of 6.7 μM for the determination of H_2O_2. The MCQ sensor holds great potential for the fabrication of electrochemical sensing applications.

5. References

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