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In situ production of silver nanoparticles for high sensitive detection of ascorbic acid via inner filter effect

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ABSTRACT

In the present research, a sensitive biosensing method was proposed for the detection of trace amounts of ascorbic acid (AA). Herein, colloidal silver nanoparticles (SNPs) were successfully in-situ produced by chemical reduction of silver ion in the presence of AA, as a reducing agent. The one-pot in-situ produced silver nanoparticles were characterized by UV–vis, dynamic light scattering (DLS), zeta potential and transmission electron microscopic (TEM). SNPs act as a strong fluorescence quencher for the CdTe quantum dots via an inner filter effect (IFE). Since the absorption band of SNPs entirely covered both emission and excitation bands of QDs. Therefore, the decreasing in the fluorescence signal depends on the AA concentration in the linear range of 0.2–88.0 ng mL^{-1} and with a detection limit of 0.02 ng mL^{-1}. Relative standard deviations of 2.3% and 2.8% (n = 5) were achieved for the determination of 1.8 and 8.8 ng mL^{-1} AA, respectively. This novel QDs nanosensor based on IFE could provide noticeable advantages of simplicity, convenience, cost-effectiveness, and sensitivity. This method was successfully applied for the detection of ascorbic acid in human real samples serums.

1. Introduction

Conventional sensing assays are used for the fluorescent chemosensor [1]. Theses assays are based on charge and electronic energy transfers such as photo-induced electron transfer (PET), intramolecular charge transfer (ICT), twisted intramolecular charge transfer (TICT), metal-ligand charge transfer (MLCT), electronic energy transfer (EET) and fluorescence resonance energy transfer (FRET) [1]. These mechanisms act by the intermolecular interaction present between target species and chemosensor placed at a certain distance and geometry. It can lead to a complicated and time-consuming technique as well as the limits in practical applications. To facile this complicity, fluorescent-based methods, using inner filter effect (IFE), recognize the analyte based on the formation or presence absorber species, which resulted in alterations in the absorption and fluorescence intensities [2].

One of the most effective absorbers/quenchers in fluorescence assays is silver nanoparticles (SNPs) [3]. Dispersion of SNPs in solution caused a substantial UV–visible extinction compared to when the silver used in the bulk form. It can be explained that resonance between the incident photon frequency and the excitation band of conduction electrons leads to mention extinction band. This phenomenon is identified as the surface plasmon resonance (SPR) [4]. SPR obtained from SNPs has a molar extinction coefficient of about (3×10^{11} M^{-1} cm^{-1}), so SNPs with high efficiency of absorption in UV–vis, have strong SPR and act as good energy acceptors in fluorimetric quenching assays [4].

Because of their exclusive electronic and optical specifications, semiconductor nanocrystals or quantum dots (QDs) show great potential, especially in used as probes and luminescent labels in biological detection [5]. They have narrow Gaussian emission with broad excitation spectra. Furthermore, they are bright and photostable and have tunable emission positions in an extensive emission range from UV to NIR, owing to the quantum size effect [6]. Since the surface characteristics, and optical properties of the QDs can change by the surface interaction between QDs and particular spices, can result in high changes in their photoluminescence (PL) efficiency [7–8]. Moreover, the electron/hole acceptors absorbed on the surface of QDs demonstrated efficient quenching effects on its emission [9].

Ascorbic acid is a well-known soluble vitamin and a natural antioxidant [10]. It plays a crucial role in various essential biological functions such as collagen formation, prevention of endogenous oxidative DNA damage, ion adsorption, amino acid metabolism, and the formation of bones, muscle, cartilage and blood vessels [10]. AA has been used for prevention and treatments of common cold, mental illness, infertility, coronary heart diseases, and cancer and in some clinical exhibitions of HIV infections [11]. Additionally, it has a decreasing effect on blood pressure and cholesterol [12]. It has been proved that the concentration of AA in biological fluids can be used to consider the amount of oxidative stress in human metabolism [13], which can be linked to cancer [14], diabetes mellitus and hepatic illness. Extreme consumption of AA can result in diarrhea, hyperacidity and kidney calculi [15]. Consequently, the

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analysis of AA content in human blood has received significant attention, and it is necessary to develop straightforward and sensitive methods for its determination in routine analysis.

Up to now, various procedures have been developed for the determination of AA, including HPLC [16], flow injection analysis [17] and potentiometry [18] and so on. However, they are often cumbersome, time-consuming, expensive and have poor sensitivity or selectivity. Because of their simplicity, low cost, and offer apparent advantages in designing probes/sensors, spectrofluorimetric methods have been used widely for the determination of AA in recent years [2,19–22].

This work provides a novel methodology for a sensitive, rapid and straightforward method for fluorimetric detection of AA, as a mild reducing agent for the generation of direct in situ SNPs, contributing to develop a biosensor. Our approach toward the preparation of the ascorbic acid biosensor is unique in the way that silver nanoparticles were generated in-situ by ascorbic acid and can decrease the fluorescence intensity of CdTe QDs via inner filter effect. The amount of fluorescence quenching strongly depends on upon the concentration of AA.

2. Experimental

2.1. Chemicals

All chemicals were from commercial companies (Aldrich and Merck) and were used without additional purification. 0.010 mol L^{-1} universal buffer solution and deionized water were used throughout the experiments. Precursors for the preparation of CdTe quantum dots (0.040 mol L^{-1} $CdCl_2$ and 0.010 mol L^{-1} Na_2TeO_3) were prepared with the highest purity available chemicals. Universal buffer solution (pH 9.5) was prepared by (0.04 mol L^{-1} each of) citric acid, boric acid and phosphoric acid and an appropriate amount of 0.2 mol L^{-1} sodium hydroxide.

2.2. Apparatus

The UV–Vis absorbance spectra were recorded on a Jasco V-570 UV/Vis/NIR spectrophotometer with a 1.0 cm quartz cell. The fluorescence spectra were taken on a Jasco FP-750 spectrofluorimeter. The excitation and emission slit widths were adjusted at 5.0 nm. The size, distribution and zeta potential of the synthesized CdTe QDs and SNPs were characterized by Transmission Electron Microscopy (TEM) using a Philips CM30 300 kV and dynamic light scattering (DLS) Malvern ZEN3600 dynamic light scattering device. For X–ray diffraction (XRD) analyses a Bruker D8/Advance X-ray diffractometer with a Cu-Ka radiation was employed.

2.3. Preparation of CdTe QDs

Glutathione-capped water-soluble CdTe QDs were prepared according to the previous work [9]. Briefly, 2.00 mL of 0.040 mol L^{-1} $CdCl_2$ were diluted to 50 mL. Afterward, trisodium citrate dihydrate (0.050 g), glutathione (0.0250 g), Na_2TeO_3 (2.0 mL, 0.010 mol L^{-1}) and $NaBH_4$ (0.0250 g) were added to the $CdCl_2$ solution along with severely stirring for 2 h at room temperature. Then, the mixture was refluxed for 12 h at 90 °C. Finally, the produced CdTe QDs was transferred to a dark and cold place.

2.4. Measurement process

To obtain the fluorescence spectra, a solution mixture (containing CdTe QDs, $AgNO_3$ and AA solutions in universal buffer (pH 9.5)) was transferred into a 1.0-cm quartz cell and the fluorescence emission spectra were recorded from 480 to 680 nm (excitation wavelength 524 nm) using 5.0 nm slit widths. For the determination of AA at a constant wavelength (575 nm) a freshly prepared mixture containing 100 μL of 0.32 μmol L^{-1} CdTe QDs and 20 μL of 1.0×10^{-7} mol L^{-1} $AgNO_3$ solution in universal buffer (pH 9.5), plus an appropriate volume of a sample solution were added in a vial and they were stirred for 30 min. Then, the mixture was transferred into a 1.0-cm quartz cell and the fluorescence emission was recorded at 575 nm (excitation wavelength 524 nm). The response function (F0-F) values of the sensor were obtained as an analytical signal with different concentrations of AA, where F0 and F referred to the fluorescence intensity at 575 nm in the absence and presence of AA respectively.

2.5. Sample preparation

Real samples of human plasma of three volunteers were prepared from clinic center of the Isfahan University of Technology. Each plasma sample was filtered and was diluted 10 times with water. Standard addition technique was employed for the determination of AA in the plasma samples. Following dilution the sample, 50 μL of the spiked serum sample was added into 2 mL of the testing solution (including 0.32 μmol L^{-1} CdTe-QDs, 10.8 μmol L^{-1} $AgNO_3$ at pH 9.5). After that, the fluorescence response was recorded.

3. Results and discussion

3.1. QDs and silver NPs characterizations

Fig. 1(a) and (b) displays the characteristic UV–visible absorption and fluorescence emission spectra for the CdTe QDs, with extensive absorption and narrow emission spectrum ($\lambda_{emission}$ 575 nm) and full widths at half maximum (FWHM 50 nm).

The average diameter size of the QDs is 5.0 nm, as shown in the TEM image in Fig. 2(a). The CdTe QDs amount was achieved by using Yu's experiential calculation by UV–Vis spectroscopy (at $\lambda = 524$), which was about 3.2 μmol L^{-1} ~ 1.93×10^{13} dots/μL [23]. The XRD pattern of the CdTe QDs defined in Fig. 2(b), shows the characteristic zinc blend cubic crystal structure of the CdTe phase. Three diffraction peaks were observed at Miller crystalline index values of 111, 220, and 311, resulting in the crystalline planes according to JCPDS No. 75-2086. Moreover, dynamic light scattering (DLS) of the as-prepared CdTe QDs showed that the size of the particles is distributed in the range from 3.2 to 7.8 nm, with an average size of 5.0 nm (Fig. 2(c)).

The size, shape, and distribution of the in situ produced SNPs were further characterized by TEM and DLS images (Fig. 3), and the average size of these nanoparticles was estimated to be 60 nm, and Zeta potential was shown to be −5.34 mV.

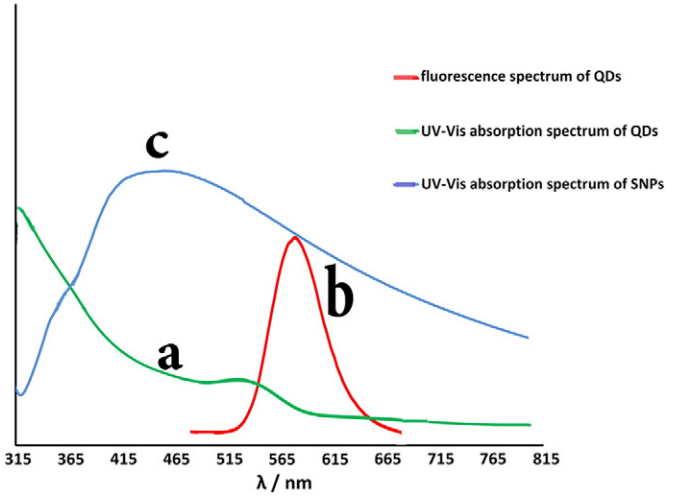

Fig. 1. The UV–vis absorption spectrum of prepared glutathione-capped CdTe-QDs (a). The fluorescence spectrum of prepared glutathione-capped CdTe-QDs (b). The absorption spectrum of produced SNPs (c).