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Facile synthesis of near-infrared-excited $NaYF_4:Yb^{3+}$, Tm^{3+} nanoparticles for label-free detection of dopamine in biological fluids

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ABSTRACT

Rare-earth-doped upconversion nanoparticles (UCNPs) behaved advantages such as non-autofluorescence, environment-friendly synthetic route, low cost and simple detection procedures. In addition, the UCNPs show unique upconvering optical property of converting low-energy infrared photons to high-energy visible ones. Here in our work, water and ethylene glycol at the ratio of 1/1 (v/v) were chosen as solvent. Polyethyleneimine (PEI) was chosen as surface additives to synthesize the $NaYF_4:Yb^{3+}$, Tm^{3+} UCNPs by one-pot route at 200 °C. The as-prepared UCNPs exhibited a strong emission at 473 nm under the continuous excitation at 980 nm. Dopamine (DA), one of the important catecholamine neurotransmitters, shows a crucial role to regulate the memory and attention in brain, renal and hormonal systems. DA molecules could be gently oxidized to quinone structure (ox-DA) in air-containing buffer solution under alkaline condition. In this study, a label-free luminescent probe based on the luminescence energy transfer (LET) between the $NaYF_4:Yb^{3+}$, Tm^{3+} UCNPs and ox-DA was developed for highly sensitive and selective detection of DA. The luminescent response ratios (I_0/I) increased linearly with the concentration of DA increasing in the ranges of 0.25 − 150 μM. The relative standard deviation (RSD) for 11 replicate detections of 25 μM DA was 0.48%, and the limit of detection was 124 nM. The developed method was applied for detection of DA in biological fluids with the quantitative spike recoveries from 94.8% to 103.6%.

1. Introduction

Upconversion nanoparticles (UCNPs), which can convert near-infrared radiation (NIR) to short wavelength emission, show many advantages, such as high tissue penetration depth, good photostability and thermal stability, long luminescence lifetime, narrow emission band width and good signal-to-noise ratios [1–7]. In consequence of these good properties, the UCNPs have been widely applied in bioimaging. Recently, attentions have been focused on UCNPs for detection of biomolecules and metal ions. There were many examples as follows, the UCNPs were applied to detect uric acid based on enzymatic catalysis-induced filter effect between the UCNPs and oxidized o-phenylenediamine [3]. MnO_2-nanosheet-modified UCNPs were applied to detect glutathione based on the fluorescence resonance energy transfer. The UCNPs luminescence was recovered by introducing glutathione to reduce MnO_2 into Mn^{2+} [5]. Furthermore, detection of tyrosine was based on photoinduced electron-transfer between UCNPs and melanin-like polymers which were obtained from catalytic oxidation of tyrosine by tyrosinase [8]. Silica coated UCNPs were modified by fluorescein to detect cysteine. In the presence of cysteine, the fluorescein was transformed into 5(6)-carboxyfluorescein with an emission band which was different from UCNPs [9]. Moreover, dye-assembled UCNPs were developed for the detection of Zn^{2+}. The UCNPs luminescence was quenched by the chromophores via a fluorescence resonant energy transfer process and then turned on by the addition of Zn^{2+} [10]. Besides, polypeptide functionalized UCNPs had been developed for the real-time monitoring of ATP-responsive drug release [11]. Nevertheless, there were no relevant reports about detection of dopamine (DA) using UCNPs as luminescent probes.

Dopamine (DA), which is one of the extremely significant catecholamine neurotransmitters, plays a key role in hormonal systems, the central and peripheral nervous system of human and other mammals [12,13]. DA, containing two hydroxyl groups and one amino group, is produced by decarboxylation of 3,4-dihydroxy phenylalanine in some areas of the brain, including the ventral tegmental and the substantia nigra area. Neurons containing the monoamine neurotransmitter DA are concentrated in an area called as substantia nigra in the midbrain. The human brain uses five known types of DA receptors, labeled as D 1, D 2, D 3, D 4 and D 5 [13], respectively. The role of DA in brain would adjust the memory and attention, control people's behavior, and be

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helpful to heal the alzheimer schizophrenia [14–16]. The deficiency of DA may result in Parkinson's disease and alzheimer schizophrenia [15,16]. On the contrary, excessive DA in the brain would make people keep pleasurable and sometimes even euphoric [16,17]. Owing to its important roles, great efforts have been made to develop efficient methods for monitoring and controlling the DA content in biological samples.

To date, several methods have been proposed for the detection of DA, including electrochemistry [18], chemiluminescence [19,20], high performance liquid chromatography (HPLC) [21–23], colorimetry [24,25] and fluorescent spectroscopy [26] and so on. For instance, Sandeep Kumar Jha's group developed an electrochemical method for determination of DA based on the surface functionalized nanostructured nickel oxide platform [15]. Lei's group [20] reported an electrochemiluminescent method for detection of DA based on CdTe quantum dots. In that work, a boronic acid-functionalized pyrene probe was synthesized and was assembled on carbon nanotubes as capture probes on a glassy carbon electrode. Meanwhile, 3,3-dithiodipropionic acid di (N-hydroxysuccinimide ester) (DSP)-functionalized CdTe quantum dots (QDs) were designed as signal probes to detect DA. These methods are fast, but the electrode modification process and the functionalization of QDs were still time-consuming and complicated. Besides, the determination of DA via HPLC [21] can provide good selectivity. However, it is still faced with the problems of requiring expensive equipment and time-consuming in the chromatography separation process. Ai's group proposed a colorimetric method for determination of DA based on the aggregation of gold nanoparticles [27]. Although the method allows convenient naked eye detection of DA, they are heavily interfered from other substances such as cysteine (Cys) and glutathione (GSH).

Herein, the near-infrared-excited $NaYF_4$:Yb^{3+}, Tm^{3+} UCNPs luminescent probe was explored for label-free detection of DA. In our work, water and ethyleneglycol were chosen as the solvent to synthesize the $NaYF_4$:Yb^{3+}, Tm^{3+} UCNPs at the ratio of 1/1 (v/v). Polyethyleneimine (PEI) was chosen as surface additives to synthesize the $NaYF_4$:Yb^{3+}, Tm^{3+} UCNPs by one-pot route at 200 °C. The UCNPs didn't need to functionalize with other materials and emitted blue light at around 473 nm upon 980 nm laser exposure. DA, containing two hydroxyl groups and one amino group, was gently oxidized to quinone structure (ox-DA) in air-containing solution under alkaline condition. The ox-DA has a broad absorption peak overlapping the emission peak of the $NaYF_4$:Yb^{3+}, Tm^{3+} UCNPs. Based on the LET between the ox-DA and the $NaYF_4$:Yb^{3+}, Tm^{3+} UCNPs, the luminescence intensity of $NaYF_4$:Yb^{3+}, Tm^{3+} UCNPs was quenched correspondingly. The system is anticipated to be a promising technique for detection of DA.

2. Experimental section

2.1. Materials

All chemicals mentioned in this study were at least of analytical grade. DA was purchased from Sigma-Aldrich. Rare earth oxides Tm_2O_3 (99.99%), Yb_2O_3 (99.99%) and Y_2O_3 (99.99%) were purchased from China Shanghai Chemical Industrial Co., Ltd. All the rare-earth nitrates: $Re(NO_3)_3$ (RE = Y, Yb and Tm) were dissolving the corresponding oxides into the nitric acid (HNO_3) and entirely evaporating the water. Hydrogen chloride (HCl), ammonium fluoride (NH_4F), sodium hydroxide (NaOH), ethanol and ethylene glycol (EG, 99%) were supplied from Tianjin Kewei Co., Ltd. Polyethyleneimine (PEI, M_W 10000, 99%, liquid), was acquired from Alfa Aesar. Tris-(hydroxymethyl) aminomethane (Tris, 99.5%) was purchased from Beijing Dingguo Biological Technology Co., Ltd. (Beijing, China). Uric acid (UA, M_W = 168.11) and ascorbic acid (AA, 99.7%) were purchased from Tianjin Northern Tianyi Chemical Reagent Co., Ltd (Tianjin, China). Methionine (Met, 99%), glycine (Gly, 98%), histidine (His, 98.5%) and glutamic acid (Glu, 98%) were purchased from Yunni Technology Ltd. (Tianjin, China). Glucose, maltose and xylose were purchased from Tianjin Fengchuan Co., Ltd. (Tianjin, China). Arginine (Arg, 98%), urea and lysine (Lys, 98%) were purchased from Sangon Biotech (Shanghai, China). KCl and $CaCl_2$ were purchased from Tianjin Northern Tianyi Chemical Reagent Co., Ltd (Tianjin, China). NaCl and $MgCl_2$ were purchased from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). Ultrapure water was purchased from the Wahaha Co., Ltd. (Hangzhou, China).

2.2. Instrumentation

Upconversion luminescent spectra of all samples at room temperature were detected on a Cary Eclipse Fluorescence spectrophotometer (Agilent Technologies, USA) equipped with a plotter unit and a quartz cell (1 cm × 1 cm) in the Bio-chemfluorescence mode, but using an external 0–2 W verstellbar 980 nm semiconductor laser (Beijing Hi-Tech Optoelectronic Co. Ltd, China). Powder X-ray diffraction (XRD) measurements were carried on a Bruker D8 diffractometer in the 2θ range of 10–70°. High resolution transmission electron microscopy (TEM, HRTEM) images were carried out by a Tecnai G2 F20 (FEI, USA), which was operated at a stepped-up voltage of 200 kV. The composition quantitative analysis of the $NaYF_4$:Yb^{3+}, Tm^{3+} UCNPs was measured on the ×7 Series Inductively coupled plasma mass spectrometry (ICP-MS) (Thermo Electron Corporation, USA). The zeta potential was tested by Malvern (British) Zetasizer Nano ZS (red badge) with 633 nm He-Ne laser. Fourier transform infrared (FTIR) spectra were performed using a NICOLET 6700 FT-IR spectroscope. UV–Vis spectra were recorded on a UV-2450 spectrophotometer (Shimadzu, Japan). Upconversion lifetime curves were obtained on FLS980 steady state and time resolved fluorescence spectrometers (Edinburgh, British).

2.3. Synthesis of the $NaYF_4$:Yb^{3+}, Tm^{3+} UCNPs

In a typical synthesis of $NaYF_4$:Yb^{3+}, Tm^{3+} UCNPs [1,8,28], 10 mmol NH_4F and 10 mmol NaOH were dissolved in 4.5 mL of water and 3 mL of EG to form a solution A. 1 mmol of $Re(NO_3)_3$ (RE = $Y_{0.75}$ $Yb_{0.25}$ $Tm_{0.003}$) and 0.20 g of PEI were dissolved in 3 mL of water and 4.5 mL of EG to form a solution B. Both solution A and solution B were stirred for 1 h and then were mixed into the homogenized solution at the room temperature. The mixture was stirred for 10 min, transferred to the Teflon-lined autoclave, immediately rose temperature up to 200 °C and maintained at this temperature for 12 h, and then cooled down to room temperature. The resultant nanoparticles were precipitated by the addition of ethanol, washed with ethanol and water three times respectively, collected by centrifugation, and finally redispersed in water for future use.

2.4. Procedure for the detection of DA

The $NaYF_4$:Yb^{3+}, Tm^{3+} UCNPs probe solutions were obtained by diluting the stock solution into ultrapure water and vibrating for 10 min throughout the experiments. For detection of DA, 2 mL $NaYF_4$:Yb^{3+}, Tm^{3+} UCNPs probe solution (0.16 mg mL^{-1}), 1.5 mL H_2O, 400 μL Tris-HCl (pH = 8.4, 100 mM) and 100 μL certain amounts of DA solutions or real samples were sequentially added and mixed thoroughly. The final concentrations of $NaYF_4$:Yb^{3+}, Tm^{3+} UCNPs and Tris-HCl buffer in the test solutions were 80 μg mL^{-1} and 10 mM, respectively. The mixtures were then used for luminescent measurements. The luminescent data were collected after 115 min with an external 980 nm semiconductor laser. The luminescent spectra were recorded in the range of 400–600 nm and the photomultiplier tube (PMT) voltage was set at 700 V. All of the luminescent intensity determinations were carried on at 25 °C. The luminescent intensity of the $NaYF_4$:Yb^{3+}, Tm^{3+} UCNPs with addition of DA was marked as I. The luminescent intensity of UCNPs without addition of DA was marked as I_0. The ratio of I_0/ I was used for quantification.