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Remarkable fluorescence enhancement of upconversion composite film and its application on mercury sensing

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Abstract: To achieve a stable, sensitive, and high-efficiency biological probe, a novel $NaYF_4$:Yb,Er nanocrystals/TiO_2 inverse opal composite film was designed by self-assembly and solvent evaporation methods. 32-fold enhanced upconversion (UC) emission was investigated under 980 nm excitation. According to size-dependency, excitation power density-dependency as well as photonic stop band (PSB)-dependency upconversion spectra, the enhancement mechanism of the composite film was put down to the stochastical diffraction of IOPCs multi-layered structure to the excitation laser. On the basis of the enhancement effect of the composite film, energy transfer between upconversion nanoparticles (UCNPs) and quantum dots (QDs), and the sensitive sensing of CdTe QDs on mercury, the UC composite film was used for sensing of Hg^{2+} in serum. The solid sensor as a mercury detector owns lots of superiorities such as feasible operation, good linear relationship (R=0.997), low limit of detection (70.5 nmol/L) and thus may have broad prospects in the biosensing field.

Keywords: upconversion enhancement; composite film; solid biosensor; mercury detection; rare earths

Upconversion nanoparticles have gained considerable attentions because of their current and future application values in the fields of biological imaging, bio-sensing, infrared photo-dynamical therapeutics, three-dimensional display, fingerprint identification, solar cells, temperature thermometry and so on[1–9]. With the further development of life science, rare-earth (RE) doped UCNPs in the field of biosensing have aroused great interests. UCNPs have been successfully used as sensors to detect deoxyribonucleic acid (DNA), anions, and molecules[10–13]. Compared with traditional luminescence materials commonly used in the biosensing field such as the organic dyes, QDs, lanthanide complex, UCNPs have many unique advantages such as sharp emission lines, high signal to noise ratio, and large penetration depth into biological tissues[14]. Unfortunately, for practical applications, due to small absorption cross sections of UCNPs, they generally possess low excitation efficiency. Meanwhile, the structural defects and dipole forbidden transitions also limit their emission efficiency[15]. For example, the bulk $NaYF_4$:Yb^{3+},Er^{3+} is usually considered as one of the most efficient UC materials; its UC efficiency is only about 3% under 980 nm excitation, however, the UCL efficiency of $NaLuF_4$:Tm^{3+},Yb^{3+} UCNPs with sizes ranging from 10 to 20 nm is lower than 0.4%[16]. So improving the UC luminescent efficiency of NPs is very important to realize their practical applications on biosensing. Until now, researchers have expended great efforts to enhance the luminescent efficiency of UCNPs, for instance, looking for more efficient matrix, coating UCNPs with inert shells, and using surface plasmon effect[17–23]. In recent years, UC emission enhancement induced by photonic crystals (PCs) effect has been reported by many researchers. PCs are materials with a periodic optical nanostructure which can control the spread of electromagnetic waves[24]. They have attracted extensive interests since the concept was first proposed by Yablonovitch in 1987 due to their applications on photonic device[25]. PCs can be used to modulate the radiative rate, direction, emission wavelength, and have also been utilized to improve the UC luminescence intensity. In the year of 2013, Yin et al. designed a novel $NaYF_4$:Yb,Tm UCNPs/PMMA PCs composite film, which can enhance the UC luminescence as high as 32-fold. They attributed the enhancement effect of UC luminescence to the effective coupling of UCNPs with PMMA PCs[26]. Besides, Yan and his co-workers obtained an enhancement of UC luminescence by the improvement of the energy transfer (ET) in

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inverse opal photonic crystals (IOPCs)[27]. So, the effect of PCs modulation on UC luminescence of NPs is expected to be applied on the future device of biosensor.

Inspired by the above ideas, in this work, we introduced an efficient strategy to improve emission intensity of $NaYF_4:Yb^{3+},Er^{3+}$ UCNPs based on the combining of $NaYF_4:Yb^{3+},Er^{3+}$ UCNPs with three-dimensional TiO_2 IOPCs. Moreover, benefited by this unique structure and the superior biological compatibility of nanocrystalline TiO_2, the composite film can also be developed as a sensitive UC biosensor for mercury detection in serum, which was expected to be a stable, feasible and applicable UC sensor.

1 Experimental

1.1 Synthesis of $NaYF_4$:Yb,Er

Hydrophobic UCNPs were synthesized on the basis of a conventional solvothermal method[28]. Different sizes of $NaYF_4$ NPs were obtained by controlling the reaction temperature at 290, 300, and 320 ºC. The preparative nanoparticles were centrifuged with cyclohexane/ethanol mixture thrice, then the final outcomes were preserved in cyclohexane solution for future use.

1.2 Preparation of TiO_2 IOPCs

The TiO_2 IOPCs were synthesized using self-assembled and template removal methods. First, different sizes of monodispersed polymethylmethacrylate (PMMA) latex spheres were prepared by controlling the reaction time. Then a piece of glass sheet was vertically placed into a beaker containing 5% solid content colloid suspension of PMMA spheres and put into a 34 ºC stove for 20 h. The PMMA spheres self-assembled on the glass substrate into highly ordered arrays slowly. Then the opal temples were put into a 120 ºC stove for 40 min to enhance their mechanical strength. Next, 10 mL butyltitanate, 10 mL absolute ethanol, and 1 mL nitric acid were stirred mixing for 1 h to form a transparent solution for the preparation of TiO_2 precursor sol. Then the precursor solutions were dropped into the interspaces of the PMMA template through capillary force. After infiltration, the resulting products were annealed at the temperature of 500 ºC for 3 h. The PSB of IOPCs was well controlled by tuning the sizes of PMMA spheres in the former experimental section. Moreover, the reference sample (TiO_2 powder) was obtained by grinding the sample of the IOPCs to destroy the 3D ordered structure.

1.3 Preparation of $NaYF_4$:Yb,Er UCNPs and TiO_2 IOPCs composite films

For preparation of the composite film, the glass substrate with partial TiO_2 IOPCs was placed vertically into the 0.5 mg/mL UCNPs/cyclohexane mixture and placed in a 25 ºC oven for 2 h. Actuated by the capillary force, the solvent evaporated slowly and the UCNPs were self-assembled into the interspaces of TiO_2 IOPCs or deposited on the glass surface directly.

1.4 Modification of hydrophobic UCNPs with PEI

The procedure of modifying OA-$NaYF_4$:Yb,Er with poly(ethylenimine) (PEI) was as follows: 30 mL diethylene glycol/PEI mixture solution was heated to 110 ºC under argon. The cyclohexane solution containing 1 wt.% UCNPs was slowly injected into the solution and then refluxed at 150 ºC for 2.5 h. Subsequently, the cyclohexane was evaporated by heating the solution to 240 ºC for 30 min. The as-prepared UCNPs were collected via centrifugation with alcohol and deionized water thrice.

1.5 Synthesis of CdTe QDs

CdTe QDs were prepared following the previous literature[29]. In simple terms, $CdCl_2·2.5H_2O$ (0.04 mol/L, 16 mL) was diluted in 200 mL deionized water in a flask, and sodium citrate (400 mg), Na_2TeO_3 (0.01 mol/L, 4 mL), mercaptosuccinic acid (200 mg), and $NaBH_4$ (400 mg) were added into the flask under a stirring. Then the solution was refluxed under open air for 6 h after the solution color changed to light green. The as-prepared QDs were separated by centrifugation and washed with ethanol thrice. The final products were dissolved in water for the following experiment.

1.6 Detection of Hg^{2+} with QDs/UCNPs/IOPCs composite films

The QDs/UCNPs/IOPCs composite films were prepared as a biosensor for sensitive detection of Hg^{2+}, the preparation process was as follows: a certain amount of CdTe QDs and 6 nm PEI coated UCNPs were mixed in the buffer, after being stirred for 30 min at room temperature, the TiO_2 IOPCs was vertically placed into the mixed solution and placed in a 25 ºC oven for over 4 h.

Mercuric chloride was used for the Hg^{2+}-sensitivity studies. 20 μL serum solutions containing different concentrations of Hg^{2+} were dropped on the composite films, after incubation for 10 min at room temperature, the luminescence spectra of the composite film were recorded under 980-nm laser excitation.

2 Results and discussion

2.1 Morphology and structure of TiO_2 IOPCs/$NaYF_4:Yb^{3+},Er^{3+}$ composite film

Different sizes of $NaYF_4:Yb^{3+},Er^{3+}$ NPs were synthesized by a typical solvothermal method, and the TiO_2 IOPCs were fabricated by template removal method. The $NaYF_4:Yb^{3+},Er^{3+}$ NPs were assembled layer-by-layer on