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Materials

Surface modification of up-conversion luminescence material $Na[Y_{0.57}Yb_{0.39}Er_{0.04}]F_4$ with hydrosulfide group

Lili Cui[1)], *Huili Fan*[1)], *Junping Xiao*[1)], *Xiaowei Xu*[2)], *and Dong Su*[3)]

1) Applied Science School, University of Science and Technology Beijing, Beijing 100083, China
2) Materials Science and Engineering School, University of Science and Technology Beijing, Beijing 100083, China
3) Civil & Environment Engineering School, University of Science and Technology Beijing, Beijing 100083, China
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Abstract: A new method was reported for surface modification of an up-conversion luminescence material with hydrosulfide group. The factors that may influence the surface modification, such as reaction time, amount of catalyzer and modifier, and reaction solvent, were investigated. The optimal conditions were that the reaction time, the quantity of the basic catalyzer, the quantity of modifier and the volume of reaction solvent were 40 min, 1.0, 1.0, and 40 mL, respectively. The results indicated that hydrosulfide group content modified on the surface of up-conversion luminescence material reached to 0.1430 mmol/g, and this modified up-conversion luminescence material could be widely used in the study of structure of protein and the property of microenvironment.

Key words: upconversation; surface modification; luminescence material; hydrosulfide; react condition

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1. Introduction

Up-conversion material could emit visible light when excited by infrared light, and it could also be named as anti-stocks' law luminescence material because the absorbed energy is lower than that of emission photons, which disobeys stocks' law [1]. Recently, the appearance of the fluorescence probes of inorganic luminous quanta dots [2-3], fluorescent nanometer latex ball [4-5] and illuminophore adulterated by SiO_2 [6] will provide a new research direction for biological tag [7-8]. The composite materials, which are obtained by embedding organic dyestuff in SiO_2, have unique optical property, but there are some disadvantages for the application to biological tag. Up-conversion luminescence material (UCP) has optical stability, and is unaffected by biological fluid and environment and can derive from biomolecule, so it can be used as fluorescence labeling material in fluorescence probes [9]. Hydrosulfide group, which is the most active group in cells, especially the part that is used as the philic nuclei and reduction reagents, can protect the cell from violation by anoxia, toxin, mutagenic, radiation and carcinogen [10]. Hydrosulfide group as fluorescence probe could directly measure the reaction rate of the compounds and reagents containing hydrosulfide group (–SH), and could be used as the indication system for the research of biological structure, hence it is widely used to research the structure of protein and property of the microenvironment [11].

In this article, a new method is reported for the surface modification of a up-conversion luminescence material with hydrosulfide group by silane coupling agents, and the proposed method is very good because of its merits, such as high efficiency, stability, and reactability for the hydrosulfide group activation on UCP surface.

2. Experimental

2.1. Reagent

Isopropanol, normal butyl alcohol, chloroform, glacial acetic acid, potassium hydroxide, and

Corresponding author: Huili Fan, **E-mail:** Fanhl@sas.ustb.edu.cn
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3-mercaptopropyl-trimethoxysilane were analytical grade. Water used in the experiments was de-ionized water. The up-conversion material used was self-made in lab [12].

2.2. Experimental procedure

0.1g Up-conversion material modified by SiO_2 was added to 40 mL chloroform, and dispersed under ultrasonic conditions for 30 min, then catalyzer and 1.0 mL 3-mercaptopropyl-trimethoxysilane were added. The mixture above was slowly evaporated, and then aged in 150°C to get up-conversion luminescence material modified with hydrosulfide group, shown as Fig. 1.

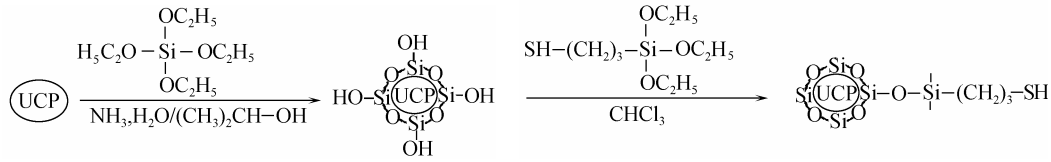

Fig. 1. Modified process of the up-conversion luminescence material with hydrosulfide group.

2.3. Test of modification

(1) Determination of hydrosulfide groups of silanization magnetism particles by Ellman's method

Ellman's method which is usually used to determine hydrosulfide groups in organization and protein is shown in Fig. 2 [13-15].

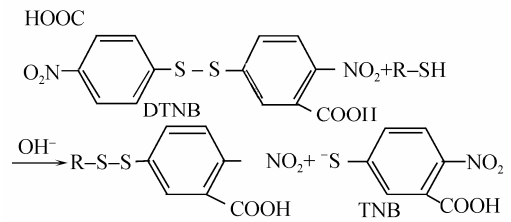

Fig. 2. Principle of Ellman's method for the determination of hydrosulfide groups.

In Fig. 2, R is $Si(OC_2H_5)_3C_3H_7$, the skeleton of silanization reagent. DTNB is Ellman reagent; and it has characteristic absorbance at 325 nm. TNB is produced when DTNB reacted with –SH of silanization reagent or magnetic particles. TNB has strong absorbance at 412 nm under alkalescence condition. Absorption of TNB and concentration of –SH conformed to the Lambert-Beer law. The determining procedure was as follows: 3-mercaptopropyl-trimethoxysilane in anhydrous ethyl alcohol, 200 μL Ellman reagent which was dissolved by PBS buffer solution (pH=7.4) (2 g/l) and 8.0 mL PBS buffer solution were put into 10 mL volumetric flask, and water was added up to the marked line. After 5 min, absorbance at 412 nm was measured. Standard curves were obtained by this method and applied to quantitative determination of hydrosulfide groups of magnetic particles modified by silanization.

(2) Specimen pretreatment

0.10 g Up-conversion material modified with –SH group, 200 μL DTNB reagent and 1 mL PBS buffer solution were put into a 2 mL centrifuge tube. The mixture was reacted for 1.5 h at room temperature in an air vibrator (Oscillation velocity was 190 r/min). Then the mixture was centrifuged, and the solution was transferred to a 10 mL test tube, and water was added to the scale line. The absorbance at 412 nm of solution was measured.

3. Results and discussions

3.1. Infra-red spectrum

Figs. 3 and 4 show the infra-red spectra of the un-modified and modified materials. In Fig. 4, the needle and weak band at 2739 cm^{-1} is the stretching vibration of –SH absorption band. There are two absorption bands at 2975 and 2927 cm^{-1}, which are symmetry and dissymmetry stretching vibration absorption peaks of $-CH_2-$. The absorption of symmetric bending vibration of methylene is 1443 cm^{-1}. Strong absorption band at 1077 cm^{-1} is Si–O asymmetric stretching vibration band. The Si–O–Si symmetrical stretching vibration absorption band is 473 cm^{-1}. The absorption band of stretching vibration of surface association –OH and deformation vibration of remainder H_2O are 3500 and 1693 cm^{-1} [16]. The stretching vibration absorption band of Si–C is 790 cm^{-1}. 1242 cm^{-1} is the non-planar surface wiggle absorption band of CH_2 in $Si-(CH_2)_n$. The difference between two spectra indicated that the surface of materials was successfully modified with hydrosulfide groups.

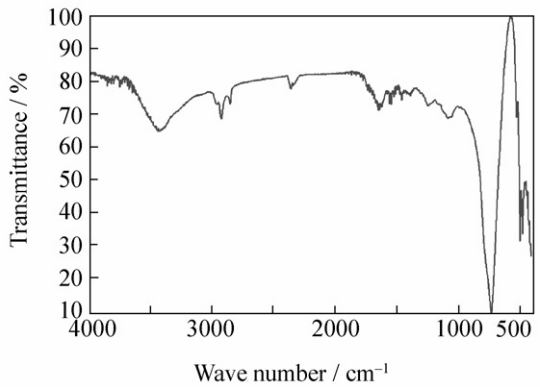

Fig. 3. FI-IR spectrum of the un-modified material.