Fluorescent silica nanoparticle-based probe for the detection of ozone via fluorescence resonance energy transfer

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Experimental

Reagent and materials

Indigo carmine was purchased from J&K Scientific Ltd. (Beijing China). Ozone was obtained by an LW-001 ozone generator from Jilin Lvjin Environmental Science & Technology Co., LTD (Jilin, China). Ozone solutions were prepared in ice water and the concentrations were determined by neutral buffered potassium iodide (NBKI) method.[1] Tris(2,2'-bipyridyl)dichlororuthenium(II) hexahydrate ($Ru(bpy)_3Cl_2 \cdot 6H_2O$), tetraethyl orthosilicate (TEOS), 3-aminopropyltriethoxysilane (APTES) and Triton X-100 were purchased from Sigma-Aldrich. 1-Hexanol was obtained from Beijing Yili Chemical Reagent Factory (Beijing, China). Cyclohexane was purchased from Beijing Chemical Reagent Factory (Beijing, China). Ammonium hydroxide (25 wt %) was purchased from Sinopharm Chemical Reagent Co. Ltd. (Beijing, China). Phosphate buffer solutions of pH 2 were used to control the acidity of the system and prepared by dissolving 28g $NaH_2PO_4 \cdot H_2O$ and 35g H_3PO_4 (85 wt %) in 1.0 L doubly distilled water. Other chemicals were of analytical grade and used as received. All solutions were prepared with doubly distilled water.

Apparatus and measurements

Fluorescence spectra were recorded on a Perkin Elmer LS55 Luminescence Spectrometer. Ultraviolet-visible (UV-vis) absorption spectra were employed in a UNICO UV/VIS 2802PC spectrophotometer. Scanning electron microscopy (SEM) images were taken using an FEI XL30 ESEM FEG scanning electron microscope operated at 25 kV. A drop of the concentrated RuSiNPs solution was deposited on ITO glass and dried at room temperature for SEM measurements. Fluorescent photographs of RuSiNPs solution under the irradiation of 365 nm visible light were operated with ZF-20D ultraviolet analyzing equipment from Gongyi City Yuhua Instrument CO., LTD.

Synthesis of RuSiNPs

RuSiNPs nanoparticles were prepared with W/O microemulsion method as previously described with a little modification.[2-4] Firstly, it was prepared by mixing 15 mL of cyclohexane, 3.2 mL of 1-hexanol, 3.54 mL of Triton X-100 and 800 μL of water. Then 160 μL 0.1 M $Ru(bpy)_3^{2+}$ aqueous solution was added into the mixture and kept magnetically stirred for 15 min. Secondly, 200 μL of TEOS was added and kept stirred for 30 min and then a polymerization reaction was initiated by adding 120 μL of $NH_3 \cdot H_2O$ (25 wt %). The reaction was allowed to stir for 24 h. Finally, 100 μL of APTES was added and kept stirred for another 24 h in order to make RuSiNPs modified with amino group. After the reaction was completed, the resultant nanoparticles were collected by centrifugation and washed three times with ethanol and water, respectively and then resuspended with 15 mL water.

General procedure

Firstly, 100 μL of phosphate buffer (pH 2) was added into a 0.5-mL plastic tube. Then 20 μL of 1.0 mM indigo carmine, an appropriate amount of water, and different amount of ozone solution were pipetted out into tubes. The whole mixture was vortex-mixed immediately and then kept at 4 ^{o}C for 10 min because ozone is relatively stable at low temperature. The volume of the above mixture was kept at 480 μL. After that, 20 μL of RuSiNPs was added into the mixture and then fluorescence spectra were recorded immediately at room temperature.

Ozone detection in indoor air

2.5 mL of 1.0 mM indigo carmine was diluted in 2.5 mL phosphate buffer (pH 2). Then buffer solutions were then moved to a ventilated photocopy room that contained five multi-functional printers and kept there for eight hours. This sample was divided into several parts and diluted with water to keep the final concentration of IDS at 40 μM. One part was used for fluorescence measurement of ozone according to the procedure as mentioned above. The other parts were used for the determination of recovery by adding given amount of ozone into the sample solutions. Fluorescence measurements were carried out according to the procedures as mentioned above. The experiment was performed in triplicate.

Refercences

1. K. Takeuchi and T. Ibusuki, *Anal. Chem.*, 1989, **61**, 619.

2. L. Zhang and S. Dong, *Anal. Chem.*, 2006, **78**, 5119.

3. Y. Zhang, Q. Yuan, T. Chen, X. Zhang, Y. Chen and W. Tan, *Anal. Chem.*, 2012, **84**, 1956.

4. S. Santra, P. Zhang, K. Wang, R. Tapec and W. Tan, *Anal. Chem.,* 2001, **73**, 4988.