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Fluorescent silicon nanoparticles for sensing Hg^{2+} and Ag^{+} as well visualization of latent fingerprints

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ABSTRACT

We herein used a low cost and facile one-step method for synthesizing fluorescent carbon-doped silicon nanoparticles (Si NPs) under mild reaction conditions. The fluorescence spectra of Si NPs showed maximum excitation and emission wavelengths at 370 nm and 450 nm, respectively. The fluorescence of the obtained Si NPs can be selectively and efficiently quenched by the Hg^{2+} and Ag^{+}. The fluorescent Si NPs showed high sensitivity toward Hg^{2+} and Ag^{+} with detection limits of 2.676 μM and 0.457 μM, respectively. Moreover, the sensing ability of Si NPs for Hg^{2+} and Ag^{+} were successfully carried out in real water samples, which offered the merits of high sensitivity and high selectivity. In addition, Si NPs were also successfully employed as a promising fluorescent label for the visualization of latent fingerprints. As far as we know, this is first time that silicon nanoparticles are used to visualize latent fingerprints. The fingerprints on different surfaces (silicon wafer, patterned coin, glass sheet, copper sheet and rough plastic board) developed with this Si NPs showed very good fluorescent images with the third level under ultraviolet excitation. The method using fluorescent Si NPs as fluorescent marks provides a variety of advantages including enhanced contrast, retaining stability and non-toxicity. In addition, Si NPs showed highly non-toxic for cellular media, the efficient bioimaging of cellular imaging was enabled after incubation of HepG2 cells in the presence of Si NPs.

1. Introduction

The Si NPs are very important fluorescent nanometer materials and drawn extensive attention due to their unique advantages such as, superior optical [1,2], excellent biocompatibility [3], low toxicity [4], low cast [5], and ease of functionalization [6]. For widespread applications of Si NPs, it is essential to be able to facilely prepare fluorescent Si NPs in large quantity at low cost and mild conditions. To date, a number of strategies have been well developed for the preparation of high-quality Si NPs, they invariably require complicated procedures, harsh experiment conditions, and/or costly equipment. We present a facile one-pot approach of synthesizing fluorescent Si NPs by using APTMS as the silicon source and folic acid as reduction reagent. Of particular note the whole reaction is readily performed in a common glass bottle, without the requirement of any additional instruments. Si NPs have shown great promise for widespread applications covering the fields of anti-counterfeiting [4], bioimaging [7], electronics [8], sensing [9] et al. Among them, fluorescent Si NPs are highly promising for sensing and biological applications.

In recent years, the development of sensors for recognizing important biological and environmental heavy metal ions has attracted much attention from environmentalists and chemists [10,11]. Hg^{2+} is known to be one of the most potent neurotoxins for human physiology and it brings detrimental influences on human life. If getting access into the body, it leads to the damage of the brain, nervous system, endocrine system, and other biological system [12–14]. Ag^{+} is widely used in many fields such as electronic applications, chemistry, photographic and fungicides [15–17]. Thus a large amount of Ag^{+} is discharged into the environment from industrial wastes. It is also considered to be one of the most poisonous heavy metal ions because of it would cause argyria and silver deposition [18].

To solve these problems, it is crucial to detect for Hg^{2+} and Ag^{+} in environments and biology, lots of chemo sensors have been evaluated for fast detection of them. Among them the approach of optical

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responses, more specifically the fluorescence responses, has been widely application on detecting $Hg^{2+}$and Ag^{+}. For example, a fluorescence "turn-on" chemo sensor for Hg^{2+} and Ag^{+} based on NBD (7-nitrobenzo-2-oxa-1,3-diazolyl), which demonstrated the detection of Hg^{2+} and Ag^{+} based turn-on of the fluorescence, with the limit of 0.05 μM for Hg^{2+} and 0.12 μM for Ag^{+} [19]. Lv and co-workers reported single-fluorophore-based fluorescent probes enable dual-channel detection of Ag^{+} and Hg^{2+} with high selectivity and sensitivity, with a detection limit of 0.097 μM and 0.142 μM respectively [20]. Although these reports exhibited the advantage of fluorescent materials, the drawbacks such as high cytotoxicity, it was a fatal defect for application in vivo or environment. Compared with above reports, the Si NPs exhibited the excellent merits and have great potential application in the detection. Si NPs are with the advantages of being cheap, being environmentally friendly, and having abundant sources, playing important roles in every aspect of science and technology.

In this study, we have developed an extremely simple and environmentally friendly method for fabrication of Si NPs, and in doing so, have identified a potential application for detection of Hg^{2+} and Ag^{+}. In this work, the fluorescence of Si NPs can be obviously quenched by Hg^{2+} and Ag^{+} at fairly low concentrations. On this basis, the selective and sensitive fluorescent Si NPs probes have been developed for the detection of trace Hg^{2+} and Ag^{+} in real samples. The fluorescent probe constructed by this method was very stable with highly sensitivity and selectivity.

In addition, it is also worthwhile to point out that fingerprints are an important kind of identification, as it is among the few biometric signatures that can be truly unique and invariable for an individual [21]. When a criminal touching any surface in a spot, skin sweat transferred to surface through pores leads to invisible ridge pattern impression, referred to as a latent fingerprint [22]. The detection of latent fingerprints is especially important, because fingerprint evidence historically has been the strongest physical evidence that can be introduced in court [23–25]. In this article, Si NPs were first time employed as a fluorescent regent for the detection of latent fingerprints. It's worth noting that, the Si NPs can harvest both aqueous suspension and solid powers.

2. Experimental

2.1. Reagents and apparatus

All chemical reagents are of analytic grade and used without further purification. Folic acid and (3-aminopropyl) trimethoxysilane (APTMS) were purchased from Aladdin. Chlorinated salts (Ca^{2+}, Fe^{2+}, Fe^{3+}, Ba^{2+}) and nitrate salts (Hg^{2+}, Ag^{+}, Mg^{2+}, Cr^{3+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Mn^{2+}, Pb^{2+}) were used to evaluate the metal ions.

Fluorescence excitation and emission spectra of all samples were recorded on an Eclipse fluorescence spectrophotometer (Varian, USA) at room temperature. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) measurements were taken using a JEOLFETEM-2100 transmission electron microscope operated. All ultraviolet visible (UV) absorption spectra measurements were carried out on a Hitachi, Japan U-2600 spectrophotometer at room temperature. Fourier transform infrared (FT-IR) spectra were obtained on a JASCOFT/IR-420 FT-IR spectrometer. The latent fingerprint images were photographed in situ by using an OLYMPUS FE-350 digital camera. The X-ray photoelectron spectra were recorded using an AXIS Ultra DLD spectrometer.

2.2. Synthesis of Si NPs

The Si NPs were synthesized according to a reported method earlier with modifications by using folic acid as reducing agent [1]. Under the room temperature and atmospheric pressure, 1.6 mL of ATPMS and a solution of folic acid (2 mL 100 mM) were successively mixed by adding into a glass beaker containing 6.4 mL ultrapure water. The mixture was left to stand for 30 min without stirring, during which the folic acid completed dissolution, the solution become clear yellow. Remarkably, the whole procedure is rapidly completed in 30 min in a common glass flask at room temperature (20–25 °C) and atmospheric pressure without requiring harsh conditions and expensive instruments. The as-prepared Si NPs solution was purified with a 1000 Da cutoff dialysis bag against ultrapure water for more than 24 h. Then the processed solution was prepared for TEM testing.

2.3. Selectivity and sensitivity measurement of Hg^{2+} and Ag^{+}

A fluorescent detection for Hg^{2+} and Ag^{+} were performed using the following process. The fluorescent detection probe was obtained by diluting the as prepared Si NPs 500 times using ultrapure water. The detection was just injected into the samples with ratio of volume 1:1, and then the fluorescence spectra of samples were collected on a fluorescence spectrophotometer (slit width of 10 nm). To study the specificity of the sensing probe toward Hg^{2+} and Ag^{+} over other relevant metal ions, the fluorescent properties of the Si NPs in presence of relevant metal ions including Cu^{2+}, Cr^{3+}, Mn^{2+}, Mg^{2+}, Ba^{2+}, Co^{2+}, Cd^{2+}, Zn^{2+}, Fe^{2+}, Ni^{3+}, Pb^{2+}, Ca^{2+}, Fe^{3+} were examined at the same condition. To further evaluate the sensitivity, various concentrations of Hg^{2+} and Ag^{+} (0 μM, 0.001 μM, 0.005 μM, 0.01 μM, 0.05 μM, 0.1 μM, 0.4 μM, 0.5 μM, 1 μM, 3 μM, 5 μM, 8 μM, 10 μM, 15 μM, 20 μM, 30 μM, 40 μM, 50 μM, 80 μM, 100 μM) were added into the fluorescent detection probe in a cuvette, subsequently.

To confirm the practical application of the probes, we collected tap water and lake water in our campus. The lake water was first filtered through a 0.2 mm membrane then analyzed by ICP-AES.

Hg^{2+} ions were not detected in the lake water samples, in good agreement with ICP-AES data. We then prepared a series of samples by spiking them with standard solution [26,27] of Hg^{2+} and Ag^{+} in the range of 0.01–100 μM. Then the detection of tap water samples and lake water samples were also performed according the above process.

2.4. Use of fluorescent Si NPs as agents for latent fingerprints detection

The visualization of fingerprints by Si NPs can not only using Si NPs solution directly but also dusting by Si NPs powder. Before deposition, the hands of fingerprint donors were sufficiently washed in soap and water and air dried. Then the cleaned fingers gently wiped the foreheads of the fingerprint donors and pressed on several different surfaces of objects (silicon wafer, patterned coin, glass sheet, copper sheet and rough plastic board). These latent fingerprints development was carried out by a small volume of suspension, applied to the print using a dropping pipette. After 5 min the excess solution was removed by a dropper with a gentle and smooth motion. The fingerprints were then left to air dry. The Si NPs solution was dried in air, and a faint yellow solid was collected, after fully grinding the solid fluorescent powders were obtained. The latent fingerprints development was carried out by a powder brushing method using fluorescent Si NPs dusting powders as labeling marker. Si NPs powders were applied to fingerprints and quickly deposited on the ridges left on the substrate under the action of physical adsorption. The excess powders were shaking off until a fingerprint image was developed. The resulting fingerprints were visualized by same optical method. When excited by 365 nm ultraviolet radiations, a little Si NPs stained on latent fingerprints showed strong visible fluorescence to enhance contrast. Then fingerprints were photographed by digital camera. The examination is conducted in a darkened room.

2.5. Confocal imaging and MTT assay

The detailed Cell culture, confocal imaging and MTT assay had been described in supporting information.