Journal of Luminescence 161 (2015) 374–381

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Full Length Article

Rapid fluorometric determination of perfluorooctanoic acid by its quenching effect on the fluorescence of quantum dots

Qi Liu, Aizhen Huang, Nan Wang*, Guan Zheng, Lihua Zhu

College of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, PR China

ARTICLE INFO

Article history:
Received 27 August 2014
Received in revised form
26 December 2014
Accepted 17 January 2015
Available online 28 January 2015

Keywords:
Perfluorooctanoic acid
CdS quantum dots
Fluorescence
Quenching

ABSTRACT

Analysis of perfluorooctanoic acid (PFOA) usually requires a combination of high-performance liquid chromatography and mass spectrometry, which is expensive and time-consuming. In the present work, water-soluble CdS quantum dots (QDs) were employed to develop a simple and rapid fluorometric method for the determination of PFOA. Strongly fluorescent CdS QDs were prepared by using 3-mercaptopropionic acid (MPA) as a stabilizer. It was observed that PFOA strongly quenched the fluorescence emission of the MPA-CdS QDs because PFOA promotes the aggregation of MPA-CdS QDs through a fluorine–fluorine affinity interaction. Under optimum conditions, the fluorescence intensity of MPA-CdS QDs was observed to decrease linearly with an increase in the concentration of PFOA from 0.5 to 40 μmol L^{-1}, with a limit of detection of 0.3 μmol L^{-1}. This new method was successfully implemented for the analysis of PFOA-spiked textile samples, with recoveries ranging from 95% to 113%.

1. Introduction

Perfluorocarboxylic acids (PFCAs) have been widely used as emulsifying agents in fluoropolymer manufacturing and as surfactants in paints, lubricants, photolithography, polishers, food packaging and fire-fighting foams. Within the PFCA group, perfluorooctanoic acid ($C_7F_{15}COOH$, PFOA) is the most commonly detected compound for two reasons: PFOA finds use in numerous applications and PFOA is a stable degradation product of precursor perfluorinated chemicals. PFOA has been widely found in sediment, municipal wastewater, coastal water, and even tap water [1–3]. It was reported that PFOA was detectable in the coastal seawaters of the Pearl River Delta, including the South China Sea, and in Korea, with concentration ranges of 0.24 to 16 and 0.24 to 320 pg L^{-1}, respectively [4]. Much higher concentrations were found in the wastewaters of factories involved in the manufacture or use of PFOA, e.g., concentrations of up to 3.35 mmol L^{-1} were detected in the untreated wastewater from a fluoropolymer manufacturing plant [5]. PFOA exhibits bioaccumulation in wildlife and humans, and it is potentially carcinogenic. Therefore, it is important to develop analytical methods for the determination of PFOA.

The main analytical methods used for PFOA determination are gas chromatography (GC) and high-performance liquid chromatography (HPLC). Due to the high polarity of PFOA, the direct injection of PFOA into a GC system will result in rather severe tailing of the peaks. Therefore, GC determination of PFOA requires appropriate derivatizations [6], which can be carried out with tetrabutylammonium hydrogen sulfate [7], diazomethane [8], isobutyl chloroformate [9] or 2,4-difluoroaniline [10]. Due to a lack of chromophores, PFOA is not easily amenable to traditional HPLC methodologies. Among the reported HPLC methods for PFOA determination, mass spectrometry (MS) detection is employed most frequently. However, HPLC–MS requires expensive instrumentation, a professional operator, complicated sample pretreatment and considerable analysis time [11]. To develop new HPLC methods for simpler detection, Ohya et al. derivatized PFCAs by using laboratory-synthesized 3-bromoacetyl-7-methoxycoumarin for HPLC analysis with fluorescence detection [12]. Based on the use of the commercially available fluorophore 3-bromoacetyl coumarin as a derivatization reagent, Poboży developed another HPLC method with fluorimetric detection [13]. However, the derivatization procedures are time-consuming and the formed derivatives exhibit limited stability, producing a substantial source of uncertainty in PFOA analysis [14].

Recently, Takayose et al. developed a colorimetric method for the detection of PFOA utilizing polystyrene-modified gold nanoparticles (Au NPs) [15]. PFOA with carboxylate groups can be bound to the surface of Au NPs, whereas fluorine–fluorine interactions between PFOA-modified Au NPs encourage interparticle aggregation, causing the color of Au NP suspensions to change from red to blue-purple. However, this colorimetric sensor has very limited sensitivity, and it cannot clearly detect PFOA at concentrations below 250 μmol L^{-1}.

It is known that fluorescent sensors usually provide a considerably higher sensitivity than colorimetric methods. The purpose of the present work was to develop a rapid fluorometric method for the

* Corresponding author. Tel.: +86 27 87543032; fax: +86 27 87543632.
E-mail address: nwang@hust.edu.cn (N. Wang).

http://dx.doi.org/10.1016/j.jlumin.2015.01.045
0022-2313/

determination of PFOA. To this end, we considered another group of NPs, quantum dots (QDs). It is worth noting that QDs have size-dependent and interparticle-distance-dependent optical and electronic properties. By varying the size of QDs, the emission wavelength and fluorescence quantum yield can be tuned. For example, different-sized CdS QDs emit blue to near-UV light [16], whereas the fluorescence quantum yield of CdSe QDs can be changed by varying the particle size (i.e., 18% for 2.8 nm, 38% for 3.3 nm, and 2% for 4.0 nm) [17]. In addition, the luminescence intensity of QDs is also sensitive to the interparticle distance; therefore, it is expected that fluorine–fluorine affinity-induced QDs aggregation may cause a change in fluorescence intensity, which makes QDs-based fluorescence analysis of PFOA feasible. To the best of our knowledge, thus far, no reports have employed the photoluminescence of QDs to detect PFOA. Thus, in the present work, the direct involvement of PFOA in the control of aggregation-dispersion of MPA-CdS QDs was studied and a simple and sensitive MPA-CdS QDs system for the fluorescence detection of PFOA was developed.

2. Experimental section

2.1. Reagents

3-Mercaptopropionic acid (MPA, HS–CH_2–CH_2–COOH) was obtained from Aladdin Chemical Reagent Company, $Cd(ClO_4)_2 \cdot 6H_2O$ was obtained from Alfa Aesar Company, and sodium sulfide nonahydrate was obtained ($Na_2S \cdot 9H_2O$) from Shanghai LingFeng Chemical Reagent Company. PFOA (96%), heptafluorobutyric acid (PFBA, C_3F_7COOH, 99%) and pentafluoropropionic acid (PFPrA, C_2F_5COOH, 97%) were purchased from Acros (New Jersey, USA), perfluoroheptanoic acid (PFHpA, $C_6F_{13}COOH$, 98%) from Alfa Aesar (Lancs, UK), undecafluorohexanoic acid (PFHeA, $C_5F_{11}COOH$, 98%) and perfluoropentanoic acid (PFPeA, C_4F_9COOH, 98%) from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan). Other chemicals were purchased from Shanghai Chemical Reagent Company (Shanghai, China). All reagents were of analytical reagent grade or the highest purity available and directly used without further purification. All aqueous solutions were prepared with double-distilled deionized water. A PFOA stock standard solution (0.5 mmol L^{-1}) was prepared and then stored at 4 °C. A series of pH buffer solutions was prepared by mixing 0.1 mol L^{-1} NaH_2PO_4 and 0.1 mol L^{-1} H_3PO_4 to maintain a pH range of 3.0 to 4.0, 0.1 mol L^{-1} NaH_2PO_4 and 0.1 mol L^{-1} Na_2HPO_4 for a pH range of 5.0 to 8.0, and 0.1 mol L^{-1} Na_2HPO_4 and 0.1 mol L^{-1} NaOH for a pH range of 8.0 to 11.0.

2.2. Preparation of CdS QDs

Water-soluble CdS QDs were prepared with MPA, a capping agent, through the procedures described by Hosseini [18], with some modifications. $Cd(ClO_4)_2 \cdot 6H_2O$ (0.84 g, 2 mmol) was dissolved in 100 mL of water to obtain a 0.02 mol L^{-1} Cd^{2+} solution. MPA (1.6 mL, 20 mmol) was added to the Cd^{2+} solution, resulting in a Cd^{2+}/MPA molar ratio of 10:1. After the solution pH had been adjusted to 10 by adding a 2.0 mol L^{-} NaOH solution, the obtained mixture was transferred to a 500-mL three-neck, round-bottom flask. Under purging with pure nitrogen gas, the mixture was heated to the boiling point and maintained at that temperature for 30 min. Next, 100 mL of 0.02 mol L^{-1} freshly prepared Na_2S solution was added to the solution to reach a Cd^{2+}/S^{2-} molar ratio of 1:1. The bright-yellow colloid was sealed for 2 h of incubation at its boiling point. All steps were carried out under continuous magnetic stirring and purging with pure nitrogen gas. After having been cooled to room temperature, the colloid solution was washed with an equal volume of alcohol and centrifuged to remove excess precursors and contaminants. After having been washed 5 times, the MPA-CdS QD deposits were dried at 60 °C by a vacuum drier.

2.3. Apparatus

Transmission electron microscopy (TEM) images of MPA-CdS QDs were acquired on an FEI TECNAI G^2 20U-TWIN at an accelerating voltage of 200 kV. The colloidal solution of the NPs in water was dropped onto a 0.1-nm-thick carbon-coated copper grid, with the excess solution immediately removed. FTIR spectra were recorded on an Equinox 55 Fourier Transform Spectrometer (Bruker Germany). UV–vis absorption spectra were recorded on a Cary 60 UV–vis spectrophotometer (Agilent Technologies). Fluorescence measurements were performed on an FP6200 fluorescence spectrophotometer (Jasco, Japan). pH measurements were conducted using a Sartorius PB-10 pH meter. All optical measurements were performed at room temperature and under ambient conditions. Zeta potentials and hydrodynamic diameter measurements were performed on a Malvern ZEN 3690.

2.4. Measurements

Unless specified otherwise, the basic reaction conditions for the determination of PFOA were as follows: 1.0 mL of MPA-CdS QDs stock dispersion (200 mg L^{-1}) and a given volume of PFOA standard stock solution were rapidly mixed in a 10-mL test tube, followed by the addition of 1.0 mL of Na_2HPO_4–NaOH buffer to maintain the pH at 10. Then, the mixture solution was diluted to 10 mL with water. After 10 min, fluorescence emission spectra were obtained at an excitation wavelength of 365 nm. Both the excitation and emission slit widths were set to 10 nm, and the photomultiplier tube voltage was 400 V.

2.5. Analysis of textile samples

Untreated textiles were purchased from a local supermarket. Samples of fabric ($\sim$5 cm × 5 cm) were placed into a 50-mL beaker, followed by the addition of 25 mL of water. The samples were then fortified by adding PFOA stock solution, if needed. For example, a recovery study was carried out on samples spiked with 10–30 μmol L^{-1} PFOA to evaluate the developed method. After the mixture had been left at 40 °C under ultrasound irradiation for 40 min, the sample was filtered under vacuum and washed with water. The collected water sample was then diluted to 100 mL for analysis.

3. Results and discussion

3.1. Characterization of MPA-CdS QDs

Hydrophilic MPA molecules were adopted as capping agents to prepare water-soluble CdS QDs. Fig. 1a showed the FTIR spectra of the bare CdS QDs, MPA and MPA-CdS QDs. The characteristic IR absorption bands occurred at 3430 cm^{-1} (O–H stretching vibration, ν_{OH} (adsorbed H_2O)), 1623 cm^{-1} (O–H bending vibration, $\delta_{OH}(H_2O)$), 1117 cm^{-1}(ν_{S-S}), 1013 cm^{-1}($\nu_{S=O}$), and 626 cm^{-1} (ν_{Cd-S}) for the bare CdS QDs (curve 1) and at 3595 (ν_{OH} of free COOH), 3400–3099 cm^{-1} (ν_{OH} of COOH with intermolecular hydrogen bonding), 2947 cm^{-1} ($\nu_{CH}(CH_2)$), 2661 cm^{-1} (ν_{S-CH}), 2569 cm^{-1} (ν_{S-H}), 1710 ($\nu_{C=O}$), 1426 cm^{-1} (δ_{OH} of C–OH) and 1250 cm^{-1} (ν_{C-O}) for MPA (curve 2). In the FTIR spectrum of the MPA-CdS QDs, a broad absorption band at approximately 3376 cm^{-1} was a characteristic peak of $\nu_{OH}(H_2O)$, the strong absorption peaks at 1565 cm^{-1} and 1399 cm^{-1} could be assigned to the asymmetric stretching vibration ($\nu_{as}(COO^-)$) and symmetric stretching vibration ($\nu_s(COO^-)$) of