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FRET based integrated pyrene-AgNPs system for detection of Hg (II) and pyrene dimer: Applications to environmental analysis

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ABSTRACT

The integrated system of pyrene and cetyltrimethyl ammonium bromide (CTAB) capped silver nanoparticles (AgNPs) with a distance (r) of 2.78 nm has been developed for the detection of Hg (II) and pyrene dimer. The interaction between pyrene and AgNPs results in the fluorescence quenching of pyrene due to the energy transfer, whose mechanism can be attributed to the Forster Resonance Energy Transfer (FRET) supported by experimental observation and theoretical calculations. The developed probe shows a highly selective and sensitive response towards Hg (II) probably due to the amalgam formation, which results in the fluorescence recovery (90%) of pyrene and color change of solution from yellowish brown to colorless. The addition of Hg (II) may increase the distance between pyrene and AgNPs undergoes the 'FRET OFF' process. This system gives a selective response towards Hg (II) over other competing metal ions. Under the optimal condition, the system offers good linearity between 0.1 and 0.6 $\mu\text{g mL}^{-1}$ with a detection limit of 62 ng mL^{-1} . In addition, the system also provides an effective platform for detection of pyrene in its dimer form even at very low concentrations (10 ng mL^{-1}) on the surface of AgNPs. Therefore, it could be used as effective alternatives for the detection of Hg (II) as well as pyrene simultaneously.

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1. Introduction

Pyrene is a polycyclic aromatic hydrocarbon (PAH) in which four benzene rings are fused together to form a flat aromatic system. PAHs are considered as one of the most widely distributed environmental hazardous contaminants due to their fatal effect on human being and the environment as well as their high toxicity and bio-accumulative properties [1–3]. Generally, PAHs are popular because of their strong carcinogenic properties, which signifies the importance of developing a fast and simple method to monitor their concentrations in the environment. During past years, various attempts have been made, and different approaches have been proposed for the qualitative and quantitative analysis of PAHs including HPLC, LC-MS, GC-MS [4–6], capillary electrophoresis [7], quartz crystal microbalance [8], surface-enhanced Raman scattering [9,10], and immunoassay combined with various detection techniques [11–13]. Pyrene shows a spectral feature of fluorescence, which is exquisitely sensitive to the microenvironment present in the homogeneous media. The high molar extinction coefficient of pyrene makes it possible to be used as a probe for the study of conformational changes with protein [14]. The fluorescence spectrum of pyrene molecules in methanol solvent shows two main vibrational

envelope centred at 373 nm and 392 nm with maximum intensity at 373 nm. In addition to these two peaks, it also shows a broad peak at 416 nm. The fluorescence emission spectrum of pyrene molecules is probably due to the $\pi^*-\pi$ transition with a conjugated structure. The emission peaks at 373, 392 and 416 nm are assigned to the emission arising from S_1-S_0 , S_2-S_0 and S_3-S_0 , respectively, which correspond to the fluorescence of pyrene monomer.

Pyrene also shows superior optical and electronic properties when it is being utilized in composite materials with metal nanoparticles [15,16], which has found various applications in light energy conversion process. The reason for an outstanding fluorophore behaviour of pyrene is mostly attributed to its optical spectra, which is extremely sensitive to change in the surrounding environment and oscillation of spectral region with localized Surface Plasmon Resonance (SPR) of noble metal nanoparticles such as silver [17,18] and gold nanoparticles. The fluorescence and absorption spectra of pyrene are markedly altered by various solvents as per the Ham effect [19–24]. Pyrene has also been used to study a wide range of biomolecules, lipids, proteins and nucleic acids due to its high fluorescent sensitivity to the variation of its coordination sphere. Pyrene with close proximity to AgNPs shows special properties by oscillating with Surface Plasmon Resonance (SPR) of AgNPs [25–27].

Mercury (Hg) is one of the most toxic elements for the human health and the environment. It has been proved that all oxidation states of mercury even in low concentrations are severely dangerous for human health [28]. Hg (II) is widely distributed in water, air, soil and dairy

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foods [29–33] and long-term exposure to that causes serious health problems within the brain, kidneys, heart, lungs, central nervous system (CNS) and immune system to all human kinds and animals of all ages [34–36]. Up to date, numerous methods have been reported for detection of Hg (II) including atomic absorption spectrometry [37], stripping voltammetry [38], inductively-coupled plasma atomic emission spectrometry [39], high-performance liquid chromatography (HPLC) [40] and ion selective electrode (ISE) and flame photometry [41]. However, employment of these techniques is thoroughly limited due to their high operation expenses and sophisticated instructions. In addition, use of highly fluorescent chemosensor [42], complex functionalised carbon dots [43] for Hg (II) detection, which requires complicated synthesis procedure.

Current study focuses on developing a simple, cost effective and efficient nanoparticle based sensor with high sensitivity and selectivity to Hg (II) over other competitive interfering ions. In addition, Hg (II) induced changes in pyrene-AgNPs system is also reported, and the fluorescence recovery of pyrene-AgNPs system follows the addition of Hg (II) within short time, which provides effective platform for the quantification of pyrene in its dimer form.

2. Experimental

2.1. Chemicals

The chemicals used throughout the experiments were of analytical grade and used as received without further purification for synthesis and sample preparation. Deionized water was used throughout the experiment. Silver nitrate (AgNO_3), cetyltrimethyl ammonium bromide (CTAB), sodium borohydride (NaBH_4) and pyrene were purchased from sigma Aldrich. Stock solution of pyrene was prepared in methanol and water. Solutions of all coexisting substance were prepared by dissolving their common salt in water and stored at room temperature. Lake water and tap water were collected from campus and used as practical samples.

2.2. Instrumentation

The absorbance spectra was acquired on a UV–vis. Spectrophotometer (PGENERAL-T6 new-century) with a 1.0 cm quartz cuvette. All the fluorescence measurements were carried out on a PC based fluorescence spectrophotometer (Shimadzu, RF-5301PC) equipped with a Xenon lamp source and 1.0 cm quartz cell. Both excitation and emission slit widths were fixed at 5 nm with medium sensitivity. TEM images were recorded on the Tecnai™ transmission electron microscope (TEM, FEI Tecnai 300). The decay time of pyrene was measured on Time-Resolved Fluorescence Spectrofluorometer (Photon Technology International, USA). The photos of all samples were taken on a Canon digital camera.

2.3. Synthesis of Functionalized CTAB Capped Silver Nanoparticles (CTAB-AgNPs)

CTAB stabilized AgNPs was synthesized by a simple chemical reduction method at room temperatures. Firstly, AgNO_3 , CTAB and NaBH_4 were dissolved in deionized water separately. CTAB was used for capping and NaBH_4 was used as the reducing agent. In a synthetic procedure, 5.0 mL AgNO_3 (0.1 mol L^{-1}) was added to the round-bottom flask containing 2.5 mL CTAB (0.1 mol L^{-1}) with continuous magnetic stirring. The reaction mixture was allowed to stir for about 10 min to become a nearly colorless solution. Finally, 10 mL NaBH_4 (0.1 mol L^{-1}) was added drop wisely into the mixture of AgNO_3 and CTAB with fast magnetic stirring. Then, the reaction aliquots became yellowish brown, which indicates complete reduction and formation of AgNPs. After stirred overnight (12 h), resultant aliquots were diluted up to 100 mL with water and stored in a freezer at 4°C for further use. The

concentration of the resultant AgNPs was $5 \times 10^{-3} \text{ mol L}^{-1}$ (calculated using the concentration of AgNO_3 added).

2.4. Fluorescence Measurement

Initially, the pyrene solution was prepared by dissolving it in an equimolar mixture of methanol and water. The interaction study of pyrene with AgNPs was studied by following procedure: 0.05 mL of pyrene ($1 \mu\text{g mL}^{-1}$) solution was added to a standard flask (5 mL), followed by addition of increasing concentration of AgNPs. Then, the solution was diluted to the working volume (5.0 mL) and mixed thoroughly. After 5 min., the mixed solution was transferred to the sample quartz cell. The fluorescence emission was measured by exciting the solution at $\lambda_{\text{ex}} = 330 \text{ nm}$. Both slit widths for excitation and emission were maintained at 5 nm. Similar methodology was employed for detection of Hg (II) in water by a standard addition method.

2.5. Selectivity Study

The selectivity of the developed probe was checked towards Hg (II) detection and evaluated by following experiment: An individual stock solution of various analytes, which are commonly present in practical water samples, was prepared by dissolving pure substances and salts in water accordingly. To a standard volumetric flask containing mixture (pyrene and AgNPs) solution, the known standard concentration of interfering ions and Hg (II) were added. Then, the solutions were diluted with water to 5.0 mL and mixed thoroughly and fluorescence spectra was measured after 5 min.

3. Results and Discussion

3.1. Characterization of CTAB-AgNPs and Pyrene

The optical properties of CTAB capped AgNPs and pyrene solution were examined and subsequent results are shown in [Fig. 1 (a) and (b)]. The pyrene molecule shows strong emission peaks at 373, 392 and 416 nm, which is assigned to the emission arising from S_1-S_0 , S_2-S_0 and S_3-S_0 , respectively, as shown in Fig. 1 (a). The synthesized AgNPs were characterised by UV–vis. Absorbance spectroscopy and shows strong maximum absorption at $\lambda_{\text{max}} = 408 \text{ nm}$, which confirms the formation of colloidal suspension of AgNPs [Fig. 1 (b)]. TEM experiments were carried out to measure the particle size of AgNPs and virtually spherical particles of highly dispersive and uniform nature with various sizes ranging from 8 to 15 nm was observed as shown in Fig. S1 (a).

3.2. Fluorescence Quenching Mechanism

The fluorescence quenching is one of the most effective tools for elucidation and understanding of interaction between two molecules. Based on the fluorescence quenching, we have undertaken the interaction study of pyrene with increasing concentration of AgNPs. Generally, the reduction in quantum yield of a donor molecule results in the fluorescence quenching due to the variation of molecular interaction with an acceptor molecule [44]. The fluorescence quenching can be classified as two main types: static and dynamic quenching. The interaction of fluorophore with quencher at ground state level results in the static type of quenching and the interaction at the excited state level turns to dynamic type of quenching. The FRET technique is well explained in literature to understand the energy transfer processes [45]. Here, the fluorescence quenching of pyrene with increasing concentration of AgNPs is supposed to follow the FRET process. To confirm the FRET, the steady state fluorescence emission of pyrene with increasing concentration of AgNPs was studied. The concentration of pyrene was kept constant throughout the study. It was observed that the fluorescence of pyrene (donor) goes on decreasing during the experiment.

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