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Tuning the carbon nanotube photoluminescence enhancement at addition of cysteine through the change of external conditions

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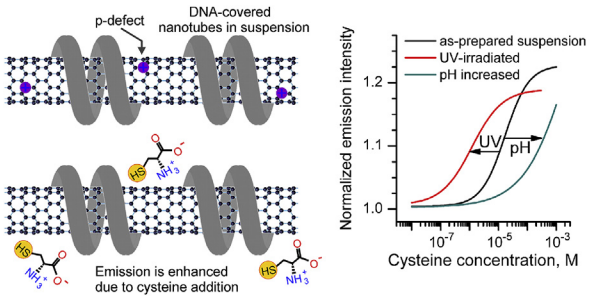
HIGHLIGHTS

- Cysteine doping enhances carbon nanotube emission more than other amino acids do.
- SWNT emission dependence on cysteine concentration is tuned by UV irradiation and pH.
- Type of sonication treatment influences SWNT PL dependence on cysteine concentration.
- Polymer coverage and defectiveness of nanotubes effect on nanotube emission.
- Graphic abstract.

GRAPHICAL ABSTRACT



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ABSTRACT

The enhancement of the photoluminescence (PL) from the semiconducting single-walled carbon nanotubes suspended with single-stranded DNA (ssDNA) in water observed after amino acids doping is the largest at cysteine addition. The PL intensity increased through the passivation of p-defects on the carbon nanotube sidewall by the cysteine molecules due to thiol group. The effect of several external factors on the cysteine-induced enhancement of PL from carbon nanotubes covered with ssDNA was studied: UV irradiation, tip or bath sonication treatment of the suspension, the ionic strength and pH of aqueous suspension. It turned out that all these factors have an essential influence on the dependence of the PL enhancement on the cysteine concentration through inducing of additional defects on nanotube as well as a change of the nanotube surface coverage with polymer. The obtained experimental results demonstrated that PL from carbon nanotubes can be exploited successfully for the monitoring of cysteine concentration in aqueous solution.

1. Introduction

Photoluminescence (PL) from semiconducting single-walled carbon nanotubes (SWNTs) is characterized by high photostability with low photobleaching and photoblinking effects [1]. The nanotube PL is very sensitive to environment and can be employed for various applications including biological sensors and imaging [2–4]. Nanotubes also have an important advantage over other organic fluorophores because their emission is observed in the near-infrared (NIR) range in which the tissue has the transparency window. This property allows to use the semiconducting SWNTs as fluorescent contrast agent in the imaging of living cells [5].

PL from semiconducting SWNTs has an excitonic origin [6–8]. The energy of coulombic interaction between components of an electron-hole pair in semiconducting nanotube is in the order of

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400 meV [6–8]. Such huge binding energy provides the high exciton mobility at room temperature with the large diffusion length (more than 120 nm) [9–12]. The excitonic migration along the nanotube surface is influenced by defects in the nanotube structure which act as traps or scattering centers for excitons, quenching the nanotube emission. High sensitivity of PL to the nanotube surface perturbations makes SWNTs highly interesting for optical sensor applications especially in biosensing as SWNTs emit in aqueous environment [13,14]. However, oxygen molecules present in water can form p-defects on the nanotube surface, which serve as effective traps for excitons [13,14]. These trapped excitons deactivate to the ground state mainly in nonradiative way. Recently it was shown that such p-defects are passivated by some small organic molecules (like dithiothreitol (DDT) or Trolox) and the quantum yield (QY) of the nanotube PL is enhanced [14–16]. It was supposed that these reducing agents donate electrons to defective sites on the nanotube surface [14]. Compounds with thiol group are often used as reducing agents as this group donates easily a proton and electron (sulphur ion has small binding energy with hydrogen). Recently, we have demonstrated that such amino acid as cysteine which contains one thiol group in the structure also enhances PL from nanotubes [17]. Note that only cysteine has thiol group in the structure among all amino acid and this circumstance can be used for the selection of cysteine. So, this nanotube PL enhancement can be employed for detection of such important biomolecule as cysteine in aqueous solution.

Since amino acids are the building blocks of proteins and play a crucial role in many biological processes in organism, the quantitative analysis of amino acid levels in the human plasma or urine is important for the investigation of cellular functions and for the early clinical diagnosis of a variety of diseases. Cysteine is widely distributed in biological tissues and plays an important role in protein structure stabilization, cell detoxification and metabolism. This is possible due to presence of reactive thiol (-SH) group in the chemical structure of cysteine and related compounds (homocysteine, glutathione). Among many methods which have been developed to monitor cysteine concentrations in biological sample luminescence offers certain advantages over other types of detection due to a high sensitivity, simplicity of implementation, and a possibility of the real-time monitoring. Luminescence-based sensing often involves reactions between thiol group and organic dyes [18,19] or metal nanoparticles [20,21], which change their spectral properties at addition of cysteine or related compounds. It was also shown that dye sensors allow detection of one specific biological thiol compound, for example glutathione [22], cysteine [19]. Sensitivity of optical methods to small doses of thiols is quite remarkable too [19,21,22] (less or equal to 1 μM).

In the present work an effect of several external factors on the cysteine-induced enhancement of PL from SWNTs covered with single-stranded DNA (ssDNA) (UV irradiation, type of sonication treatment of the suspension, ionic strength and pH of aqueous suspension) was studied. Also, the comparison between influences of different amino acids on the nanotube PL was performed (see also our preliminary study [17]). The main purpose of changing of all external factors applied to the nanotube suspension was to tune certain parameters (mainly linearity range) of the dependence of the nanotube PL enhancement on the cysteine concentration. Such tuning can be useful for effective monitoring of cysteine concentration in aqueous solution in the range of 50–1000 μM.

2. Experimental details

2.1. Preparation of nanotube aqueous suspensions

SWNTs used in the experiments were produced by CoMoCat method [23] (SouthWest NanoTechnologies, USA). Semiconducting SWNTs with (6,5) chirality (SWNT® SG 65) prevailed in the starting material. ssDNA (obtained from the native double-stranded DNA [24]) dissolved in 0.005 M Na^+cacodylate buffer (pH7) (Serva, Germany) with 0.005 M NaCl was used for the preparation of SWNT aqueous suspensions. Steady SWNT aqueous suspensions were prepared through sonication of nanotube bundles in solution with the biopolymer. Suspensions with SWNT:ssDNA 1:1 wt ratio were prepared using tip sonication (8 W, 22 kHz, 45 min) or bath sonication (0.7 W, 22 kHz, 30 min). As a result of the sonication treatment ssDNA was fragmented [25]. Ultracentrifugation (70000*g*, 60 min) followed the sonication treatments.

2.2. UV irradiation of nanotube suspensions

UV irradiation of nanotube suspensions was performed using high-pressure mercury lamp (electric power 1000 W). Light source was focused on the nanotube suspension in 3 mm quartz cuvette. To avoid the sample heating a special filter (cuvette with aqueous solution of $CuSO_4/CoSO_4$) was used, which transmitted light in range of 280–420 nm [26], but absorbed the IR part of the lamp irradiation. Resulting light power that reached cuvette containing nanotube suspension was not above 3 W and was distributed over 12 × 8 mm surface area. Cuvettes were air-cooled, the temperature of the cuvette with nanotube suspension was not above 50 °C. Sample was irradiated for 5 h.

2.3. Change of nanotube suspensions pH values

The pH of suspensions was varied by adding either hydrochloric acid or sodium hydroxide of different concentrations to achieve the desired pH. To test pH of various samples, a pH-meter (model 150 MI, Russia) with an Ag/AgCl internal reference electrode was used.

2.4. Titration of nanotube suspensions

Stock cysteine (Realab, Russia) aqueous solutions at concentrations ranging from 2×10^{-6} to 5×10^{-2} M were prepared before titration of SWNT suspensions. In titration experiments 2 μL of 2×10^{-6} M solution was the minimal dose added into the suspension portion (400 μL). Spectroscopic measurements followed after up to 5 min delay required to reach the thermodynamic equilibrium. Cysteine concentration in the suspension varied from 10^{-8} to 10^{-3} M. Similar preparations and measurements were performed with other amino acids studied.

2.5. Spectroscopic measurements

PL from semiconducting SWNTs was analyzed using a NIR spectrometer with the signal detection by a thermocooled CCD camera. Emission was excited with a diode-pumped solid-state (DPSS) green laser ($\lambda_{exc} = 532$ nm (2.33 eV), 5 mW). Spectrometer was calibrated with Ne lamp spectrum before and after measurements.

The absorption spectra of nanotube suspensions were obtained using NIR spectrometer equipped with thermocooled InGaAs photodiode (900–1600 nm). Quartz cuvettes with 2 mm path length were used in experiments.

Raman scattering of the nanotube suspensions was excited with He–Ne gas laser ($\lambda_{exc} = 632.8$ nm, 25 mW), spectra were analyzed using double monochromator and detected with a thermocooled CCD camera. The peak positions of the G^+ band (in the spectral range between 1500 and 1630 cm^{-1}) corresponding to the tangential mode and of D band in spectra were determined with the accuracy not worse than 0.3 cm^{-1}. This level of accuracy has