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Modulation of energy/electron transfer in gold nanoclusters by single walled carbon nanotubes and further consequences

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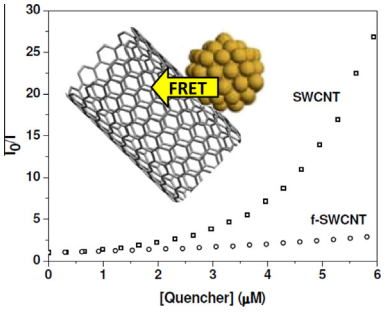
HIGHLIGHTS

- Single walled carbon nanotubes (SWCNTs) can quench fluorescence of gold nanoclusters (AuNCs).
- The quenching of fluorescence depends on their microenvironment.
- Resonance energy transfer and/or excited state electron transfer results into fluorescence quenching.
- Proximity of the donor and the acceptor induces metallic character into the SWCNTs by the AuNCs.

GRAPHICAL ABSTRACT



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ABSTRACT

Semiconductor or metallic character in single-walled carbon nanotubes (SWCNTs) is developed because of their chirality and diameter. Depending upon the extent of these characters in a particular sample of SWCNT, various electronic and mechanical applications are formulated. In this work we used protein protected red emitting gold nanoclusters (AuNCs) to enhance the metallic character in SWCNTs through electron transfer induced by photonic excitation. The AuNCs have been synthesized following a known protocol that generates Au^+ protected Au^0 clusters. Normal and carboxylic acid functionalized SWCNTs were obtained commercially for usage in the experiments. The non-functionalized SWCNTs facilitate intersystem electron transfer while the functionalized ones defer the phenomenon, which, in turn, affects the metallic character in the nanotubes. Steady state and time resolved fluorescence spectroscopy prove the dynamics and electrochemistry supports the intersystem electron transfer process.

Introduction

Fluorescent noble metal nanoclusters are favourable biological markers and energy reservoirs. Many theoretical and experimental works have proven that some percentages of metals with lower oxidation state at the surface of nanoclusters stabilize the neutral metal at core [1–3]. Oxidation state of the Au atoms in protein protected AuNCs were determined by X-ray photoelectron spectroscopy (XPS). The Au $4f_{7/2}$ spectrum was deconvoluted into two distinct components centred at binding energies of 84.0 and 85.1 eV assigned to Au^0 and Au^+, respectively. About 17% presence of Au^+ on the surface of the Au^0 core helps to stabilize the NCs as noted in a structural study on thiol-protected AuNCs [4,5]. Because of the presence of the lower oxidation state elements at the surface, nanoclusters can accept and/or donate electrons to their own counterparts in the neighbourhood [2,6].

Synthesis of noble metal nanoclusters using various templates such as peptides, carboxylic acids, dendrimers, proteins, polymers, and DNA are known [7–9]. Here, we intend to show the effect of interaction between the red emitting AuNCs on non-functionalized and carboxyl functionalized single walled carbon nanotubes

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(SWCNTs) in protein template. CNTs are often functionalized to produce nanocomposites with enhanced physical properties [10–14]. Charlier et al. investigated interaction of AuNCs with isolated CNT to produce metallic clusters that donate or accept fractional charge upon adsorption on a target molecule that modifies electron transport in the nanotube [15]. Earlier reports are available on attachment of nanoclusters to SWCNTs through covalent interactions for different applications [16–18]. Tethered AuNCs were used as linkers between a donor entity and CNT to facilitate photoinduced electron transfer (PET) [19]. Here, we intend to report on intervention of non-functionalized and carboxyl functionalized SWCNTs toward intercluster PET in AuNCs. SWCNTs readily accept electrons from suitable donors, which can then be transported axially [20]. Semiconducting or metallic characters may develop in SWCNTs depending on their chirality and diameter that start when isolated C_2 fragments are brought from infinite distance [21]. Each fragment has two degenerate sets of π and π^* orbitals from the C-fragments that mix during formation of nanotube which decides the energy spread.

Experimental

In the present study we have used bovine serum albumin (BSA) protein as template for the preparation of AuNCs following a protocol described elsewhere [1,2]. The synthesis was carried out at physiological temperature (37 °C). Upon adding $HAuCl_4$ to the aqueous BSA solution, the protein molecules sequestered Au ions and entrapped them. The pH of the solution was adjusted to ~12 so that BSA could act as a reducing agent to produce AuNCs *in situ*. The synthesized AuNCs were found to consist of 25 Au atoms (as depicted by MALDI TOF/TOF mass spectrometry, Applied Biosystems 4800 Proteomics Analyzer) [9] with diameter of the clusters to be around 2 nm (as shown in the transmission electron microscopy (TEM) experiments, C M 12 PHILIPS TEM) (Fig. 1). The number of metal atoms in a given protein encapsulated cluster can be found from the difference between the mass values of free protein and protein-encapsulated clusters observed in MALDI MS. The resulting 25 atom AuNCs in BSA template emit in the red at 645 nm upon excitation at 365 nm [1,2].

The SWCNTs were procured from Sigma–Aldrich (Catalogue # 704113 and 652490, respectively for the non-functionalized and functionalized variants, TEM image is available in the company website) and used as received without further purification. Functionality of the SWCNTs was verified by FTIR spectroscopy (Perkin-Elmer Spectrum 100) (Fig. 2). BSA was obtained from Sigma in purified form. The protein template for the SWCNTs was constructed by the following protocol. 1.3 mg of the CNT solution was mixed with 300 μL of BSA solution in phosphate buffered saline (PBS) at pH 7.6. The solution was sonicated for few hours and kept undisturbed for a few minutes. 50 μL of the supernatant was dispersed in 300 μL of BSA solution through several hours of vortexing.

All absorption spectra were recorded using a Cary 300 Bio spectrophotometer from Agilent and the steady state fluorescence measurements were done in a QuantaMaster 40 spectrofluorimeter from Photon Technology International, Inc. Time-resolved fluorescence experiments were done using a Horiba Jobin Yvon Fluorocube instrument with a 377 nm diode laser excitation sources. The cyclic voltammetry (CV) studies were carried out with a Princeton Applied Research 263A potentiostat using platinum (Pt) electrode as the working electrode, a platinum wire as counter electrode, and a Calomel electrode as the reference electrode. Nitrogen gas was passed through the solution for 25 min to remove any incipient oxygen. PBS acted as the electrolyte and the measurements were performed at scan rate of 150 mV s^{-1}. Förster distance (R_0) between the donor and the acceptor was calculated using the following equation:

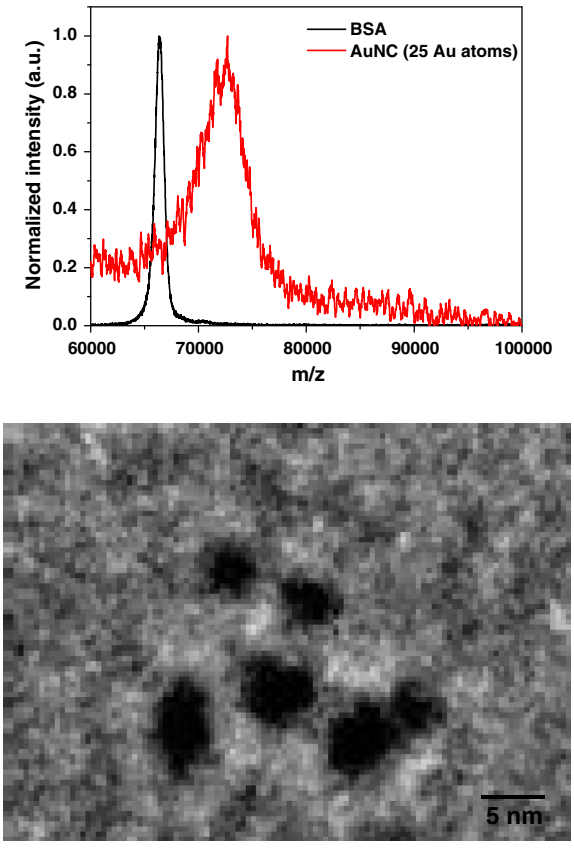

Fig. 1. MALDI-TOF MS data (left) (the spectra were collected in the linear positive mode using a-cyano-4-hydroxycinnamic acid (CHCA) as the matrix) and HR-TEM image (right) of BSA coated red emitting AuNCs.

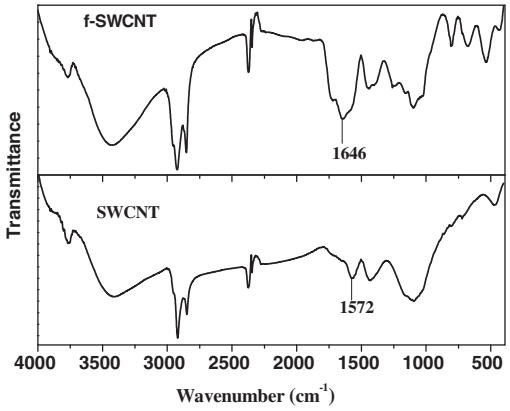

Fig. 2. FTIR spectra for functionalized and non-functionalized SWCNT.

$R_0^6 = 8.79 \times 10^{-5}(\kappa^2 n^{-4} Q_D J(\lambda))$ in $Å^6$, where κ^2 is the orientation factor taken as 2/3, n is refractive index of the solvent taken as 1.4, Q_D is the quantum yield of the donor in absence of acceptor taken as 6.5% and $J(\lambda)$ is the overlap integral calculated as:

$$J(\lambda) = \int_0^\infty F_D(\lambda)\varepsilon_A(\lambda)\lambda^4 d\lambda,$$

$F_D(\lambda)$ is the corrected fluorescence intensity of the donor in the wavelength range λ and $\lambda + \Delta\lambda$ with total intensity normalised to unity and $\varepsilon_A(\lambda)$ is the extinction coefficient of the acceptor at λ. R_0 values for bare and functionalized SWCNT are 97.4 and 87.5 Å, respectively. RET efficiency (E) can be calculated as: