Local Temperature Measurement in the Vicinity of Remotely Heated Gold Nanoparticles

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ABSTRACT

Remote heating of nanoparticles to induce a selective transformation at the molecular level is emerging as a new technique for controlling biological processes. In this context, measurement of local temperature in the proximity of heated nanoparticles is of interest. This work presents temperature measurements in the vicinity (~3.6 nm) of ultra-small gold nanoparticles suspended in solutions, which are remotely heated by radio frequency (RF) electromagnetic field. Semiconductor CdSe quantum dots (QD) passivated with a layer of ZnS and functionalized with carboxyl group are used as local temperature sensors. They are conjugated to 1.4 nm gold nanoparticles (AuNP) via amine group through standard EDC reaction chemistry. Temperature measurements during RF heating are performed on solutions of conjugated systems as well as control solutions of mixed AuNP and QD. Results suggest that local temperature rise in conjugated solution is up to 7°C higher than the average temperature of the control solution.

Keywords: quantum dot, gold nanoparticle, local temperature

1. INTRODUCTION

Remote heating of bio-conjugated nanoparticles is emerging as a new technology for inducing selective transformations of biological systems at molecular level. For example, Schifferli et al. demonstrated selective de-hybridization of DNA strands employing 1.4 nm gold nanoparticles covalently attached to DNA and subjected to 1 GHz electromagnetic field [1]. Aslan and Geddes [2] have shown 90-fold enhancement in the time response of immunoassays when using substrates covered with silver nanoparticles exposed to 2.45 GHz electromagnetic radiation. Kogan et al. reported on nanoparticle-mediated local control of protein aggregation for dispersing amyloid beta protein deposits [3]. The gold nanoparticles attached to the proteins were 10 nm in diameter and the RF frequency used was 12 GHz. The biological transformations reported in all these studies are typically observed when employing higher reaction temperatures. However, in all cases the reported "bulk" temperature rise of the solutions was less than expected. For example, DNA de-hybridization efficiency observed in the presence of electromagnetically actuated gold nanoparticles reported in Ref. [1] is equivalent to that observed in a "bulk" heated solution, kept at ~13°C above ambient. However, the measured "bulk" temperature of the solution during electromagnetic actuation was negligible. Similarly, the modest bulk temperature rise of 8° degree measured in Ref. [2] could not explain the significant decrease in assay time response, while in Ref. [3] no bulk heating was observed though protein aggregate dissolution typically requires increased temperatures. On the other hand, Keblinski et al. [4] evaluated several methods for heating nanoparticles and found that in most cases, substantial local heating in the vicinity of nanoparticles is not possible. Measuring the local temperature in the vicinity of remotely heated nanoparticles would help resolve these conflicting results. Furthermore, understanding critical parameters that control energy harvesting and dissipation in bio-conjugated nanoparticles is essential for future applications.

This work presents temperature measurements in the vicinity (~3.6 nm distance) of ultra-small gold nanoparticles suspended in solutions. The particles are remotely heated by radio frequency (RF) electromagnetic field. Semiconductor CdSe quantum dots passivated with a layer of ZnS and functionalized with carboxyl group are used as local temperature sensors. They are conjugated to 1.4 nm gold nanoparticles via amine group through standard EDC reaction chemistry. Temperature measurements during RF heating are performed on solutions of conjugated systems as well as control solutions of mixed AuNP and QD (unconjugated).

2. EXPERIMENTAL PROCEDURE

2.1 Materials

Semiconductor quantum dots (Qdot 525 ITK carboxyl quantum dots, 8 µM solution) were procured from Invitrogen Corporation. They consist of a cadmium selenium (CdSe) core covered with a zinc sulphide (ZnS) shell for photo-stability and a polymer coating for effective

dispersion in aqueous solutions. The QD were functionalized with carboxyl groups. Gold nanoparticles, 1.4 nm in diameter, functionalized with primary amine groups were procured from Nanoprobes Incorporated (2022).

Two specimens were prepared from these materials: 1) a solution of conjugated AuNP-QD and 2) a control solution of quantum dots mixed with gold nanoparticles (that will be referred to as "mixed" or "unconjugated" specimen). In conjugated solution the quantum dots were covalently linked to gold particles. The distance between the edges of the two particles is estimated to be ~ 3.6 nm [5], hence their temperature is thought to represent the actual temperature in the proximity of heated nanoparticle. In mixed solution, the quantum dots move freely around gold particles. Since the temperature decreases when moving farther from heated nanoparticle, the temperature of QD in mixed solution is the average or bulk temperature of the solution. In both specimens, the quantum dots concentration was 208 nM and their ratio to gold nanoparticles was 1:1. A total volume of 150 µL of each specimen was prepared according to following procedure. To synthesize the sample consisting of mixed quantum dots and gold nanoparticle (unconjugate), 3.89 µL of the 8 µM stock solution of quantum dots was added to 145.6 µL of borate buffer. The buffer was prepared from boric acid and borate and its pH was adjusted to 7.6. Next 100 µL of borate buffer were added to 6 nmoles of gold nanoparticles to create 60 µM stock solution of AuNP. From this stock solution, 0.52 µL were taken and mixed with the 149.49µL quantum dots in borate buffer solution.

To prepare the conjugated sample, the same recipe was followed except that the borate buffer was reduced this time to 144.7 µL. In addition, 0.89 µL of 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) stock solution was added to the mix to facilitate reaction between carboxyl and amine groups (the EDC stock solution was synthesized by adding 1 mg of EDC to 100 µL of borate buffer). The solution was left to incubate for more than 12 hours at room temperature under gentle magnetic stirring. The conjugation reaction is shown in Fig. 1. Both samples were stored in the refrigerator prior to measurements.

2.2 Experimental Procedure

For temperature measurements, the solution was placed in a quartz cuvette fitted in a special holder that allowed a copper wire to be wrapped around it to form a coil. The coil was later used to apply an RF electromagnetic field to the nanoparticle quantum dots solutions.

Before evaluating the RF heating of gold nanoparticles, a calibration experiment was first performed. A Fluorolog-3 (Horiba Jobin Yvon) fluorometer equipped with a Peltier module for temperature control was used to measure the emission spectrum as function of temperature of the fluorescent quantum dots. During calibration, the temperature of the cuvette was increased from 15ºC to 40ºC
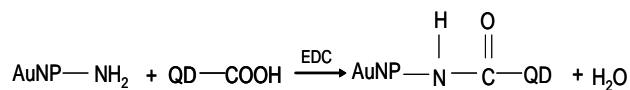

Figure 1: Quantum dot-gold nanoparticle conjugation reaction chemistry.

in 5ºC increments. After waiting 45 minutes to achieve thermal equilibrium, the emission spectrum of the quantum dots was collected for an excitation wavelength of 390 nm. Following calibration, the sample was immediately returned to 15ºC and maintained for 45 minutes to reach equilibrium. Then alternative current (AC) of 600, 800 and 1000 kHz respectively was applied to the coil surrounding the cuvette. The AC signal was generated with an HP 1Hz-20MHz pulse/function generator (model 8111A) and was amplified by an RF power amplifier connected directly to the coil. A digital voltmeter was used to measure the voltage drop across the coil. This experiment was repeated for each specimen. All experimental data during calibration and measurement was collected using same settings on the Fluorolog.

3. RESULTS AND DISCUSSION

3.1 Calibration

Figure 2 a&b shows the fluorescence intensity versus emission wavelength of the quantum dots at each temperature set-point for mixed and respectively conjugated quantum dots-gold nanoparticle solutions. For both specimens, it is observed that the intensity of the fluorescence emission decreases and its peak shifts towards red at higher temperatures, as reported previously [6]. In addition, at the same temperature the QD in the conjugated sample exhibit a wavelength red shift and more than 10-fold decrease in fluorescent intensity when compared with mixed specimen, attributed to the proximity of metal nanoparticle [7].

The wavelength corresponding to maximum intensity was determined fitting the Gaussian profile of the fluorescent intensity using a commercial software (Origin). Figure 3 a&b shows the wavelength corresponding to maximum emission intensity as function of temperature for mixed and respectively conjugated specimens. As shown in Fig. 3, two temperature calibrations were carried out for each specimen. For mixed sample, the two temperature scans were performed one after another. For the conjugated sample, the calibration experiments were carried out before after RF heating respectively. However in both cases the results were found to be repeatable, although the intensity of fluorescent emission changed. For example, the fluorescent intensity of mixed sample in first calibration experiment (Test 1 in Fig. 3 a) was ~350x10^3 cps at 15°C, while in Test 2 was ~275x10^3 cps at the same temperature. Similarly, the fluorescent intensity at 15°C of conjugated sample in first and second calibration experiments (Test 1
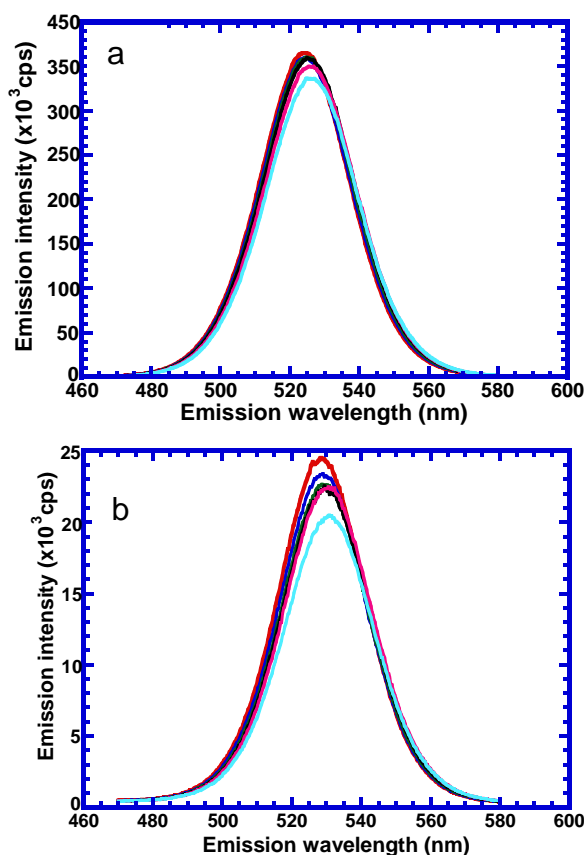
Figure 2: Fluorescent emission intensity as a function of emission wavelength at different temperatures for: a) mixed and b) conjugated specimen.

and Test 2 in Fig. 3 b) were ~ 25 x10³ cps and ~10 x10³ respectively.

3.2 Measurement

Figure 4 a&b shows the wavelength of maximum emission intensity of mixed and conjugated specimen as function of the square AC voltage applied to the coil (used as an indicator of the applied power). For all frequencies tested, as applied power was increased the wavelength corresponding to maximum emission intensity shifted towards red. This indicates that gold nanoparticles absorb energy from the RF field, heating the solution. Furthermore, the temperature measured in mixed solution is consistently smaller than that measured in conjugated solution under same experimental conditions. As a reminder, in mixed solution the quantum dots move freely, hence they measure an average temperature. In solution of nanoparticles conjugated to quantum dots, the quantum dots are covalently liked to the gold particles and their temperature is thought to represent the local temperature in the proximity of the particle (~3.6nm distance). For example at 600 kHz and highest applied power, the temperature measured in mixed solution is 29°C, while the temperature measured in conjugated solution was 32°C as calculated based on calibration curves (Fig. 3 a&b). Similarly, at

highest applied power and 800kHz there is 7°C difference between the local and the average temperature rise (from 25° to 32°), while at 1000 Hz the temperature difference is ~5°C. Keblinski et al. have evaluated the heating of electromagnetically excited nanoparticle [4]. The steady-state temperature difference between the temperature at the particle surface and the average temperature of the surrounding medium can be calculated as [4]:

$$\Delta T = \frac{dQ_{nano}/dt}{4\pi k r_p} \tag{1}$$

where dQ_{nano}/dt is the total power generated by the particle, k is medium thermal conductivity and r_p is particle radius. Although it is not clear what is the mechanism responsible for nanoparticle heating, induction heating (produced by eddy-currents on the particle surface) and magnetic heating (caused by magnetic relaxation [8]) are two possible candidates. Gold is a diamagnetic material, however gold nanoparticles may exhibit chemisorption-induced magnetic dipole [9]. Keblinski et al. estimated the upper limits of
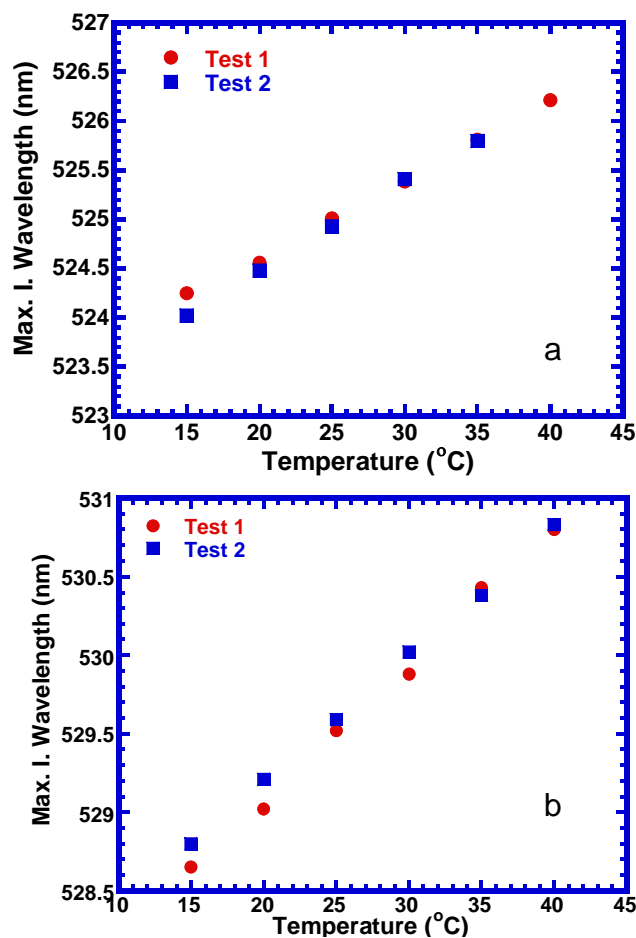

Figure 3: Wavelength corresponding to maximum intensity of the fluorescence emission as function of temperature for a) mixed and b) conjugated specimen.

heating rates produced by each of these two mechanisms and concluded that maximum possible temperature difference between local and bulk heating is less than 0.1mK. However, these predictions were made based on diffuse heat conduction modeling, which may not apply readily at the nanoscale [10]. To better understand these apparent discrepancies more experimental and theoretical investigations of these systems are needed.

4. SUMMARY

This work presents preliminary temperature measurements in the vicinity (~3.6 nm distance) of ultra-small gold nanoparticles suspended in solutions and heated remotely by RF electromagnetic field. Temperature measurements were performed on solutions of conjugated systems as well as control solutions of mixed gold nanoparticle and quantum dots (unconjugated). In mixed solution, the temperature of the quantum dots represents the average temperature of the solution. When conjugated to gold particles, the quantum dots measure local temperature in the vicinity of the particle. Up to 7°C difference was observed between the local and the average temperature when the particles were heated by 800 kHz electromagnetic field. These results suggest that local temperature in the vicinity of electromagnetically excited nanoparticles may be several degrees higher than bulk temperature of the solution.

Acknowledgment

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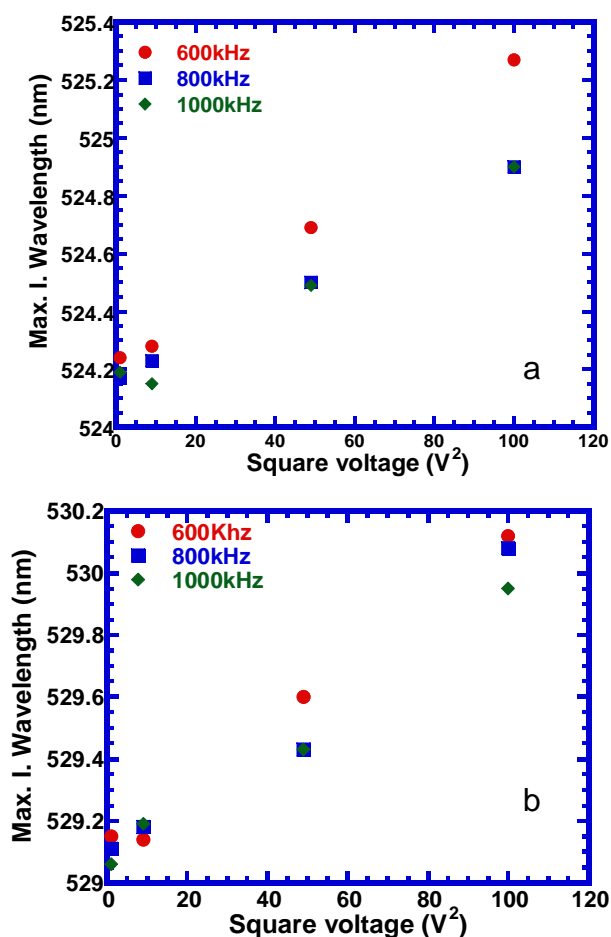
Figure 4: Wavelength corresponding to maximum fluorescence intensity as function of square voltage applied across the coil for a) mixed and b) conjugated sample.