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Metal-enhanced intrinsic fluorescence of nucleic acids using platinum nanostructured substrates

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Abstract

We investigated the feasibility of using platinum nanostructures to accomplish the metal-enhanced fluorescence (MEF) in the UV spectral region. We examine the possibility for detection of the intrinsic fluorescence from nucleotides and G-quadruplex DNA on platinum nanoparticles. Guanosine monophosphate (GMP) showed significant increases (~20-fold) in fluorescence intensities in the presence of platinum nanostructures when compared to quartz controls. G-quadruplex DNA demonstrated ~5-fold increase in fluorescence intensity and higher photostability in the presence of Pt nanostructures. We performed finite element method simulations to explore how Pt nanoparticles interact with plane waves and conformed that the Pt nanostructures are promising for enhancing the fluorescence emission in the UV region.

Keywords

Intrinsic fluorescence of nucleotides; metal-enhanced fluorescence (MEF); plasmonics; metallic nanoparticles; finite element calculations

1. Introduction

Fluorescence detection is a valuable tool in biosciences [1–3]. Many fluorescence studies have taken advantage of the intrinsic fluorescence from proteins, which is due primarily to the tryptophan residues. However in contrast to proteins, nucleic acids and the nucleotides are almost non-fluorescent in water. Most sequencing methods rely on fluorescence detection using extrinsic fluorophores. The labeling of biomolecules is time consuming, expensive, and labor intensive and may cause to additional losses of sample due to purification steps. Additionally, chemical labeling of proteins can cause changes in their characteristics and can affect their biological activity [4–5]. There are extensive ongoing efforts to improve the label-free techniques in order to overcome these problems. Surface plasmon resonance (SPR) [6–7], Raman scattering [8–9], electrochemical methods [10–12] are just a few of these methods, which provide label-free detection.

During the past decade, there has been a growing interest in the use of colloidal metal particles or metal surfaces to enhance fluorescence intensity. Metal-fluorophore interaction

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can be used to increase the brightness, emission rate and photostability of fluorophores near metal particles [13–14]. Previously designed methods to determine the usefulness of fluorophore-metal interactions in the biological applications is mostly based on the silver nanoparticles. In these methods MEF has been observed in the visible and near-infrared wavelength range using silver nanostructures. It would be useful to demonstrate the general usefulness of MEF sensing with metals other than silver. Gold comes out as an attractive alternative with its high chemical stability and facile surface chemistry. Experimental results have shown that gold particles can cause MEF with longer wavelength fluorophore [15]. MEF at shorter wavelength is difficult to reach with particles made from gold or silver, the most commonly used materials in plasmonics. There are several reports on the use of metal nanostructures in the UV region, which indicate that aluminum has better plasmonic properties than silver for enhancement of UV fluorescence [16–18]. This is because aluminum has a low imaginary dielectric constant at wavelengths below 400 nm. In an effort to identify other metals for label free detection of nucleic acids, which may allow DNA sequencing without use of extrinsic fluorophores we have chosen platinum to examine the possibility of MEF using. Reported resonance properties of platinum make it an interesting candidate for short-wavelength region application. Resonances of Pt nanoparticles have been reported under 450 nm. The extinction spectra of Pt substrates are broad and their field enhancement is lower than gold or silver. However, the high chemical stability of platinum makes it a promising candidate for various applications in the UV-region [19].

In this paper, we report the metal-enhanced intrinsic fluorescence of G-quadruplex DNA and four different nucleotides on Pt nanostructured substrates. We investigated the G-quadruplex DNA because of its emerging roles in biological regulation and its potential use as target for designing novel anticancer drugs. G-quadruplexes are four-stranded structures formed by G-rich nucleic acid sequences. Formation of these structures can affect telomere maintenance, gene regulation, transcription, DNA replication and repair. Additionally G-quadruplexes formed by synthetic oligonucleotides may possess anticancer and anti-HIV activity [20–22]. In our study, nucleotides and G-quadruplex DNA are adsorbed onto the platinum nanostructures activated by silanization. A detailed exploration using steady-state fluorescence spectroscopy and near-field enhancement calculations has been carried out to reveal the potential of platinum nanostructured substrates for MEF in UV-blue region. For theoretical calculations Comsol Multi-Physics package (a Finite Element Method package) was used. We determined the scattered part of the field by scattering formalization. For the optical properties of metals we used a lookup table with Piecewise cubic interpolation, based on Handbook of Optical Constants of Solids by Edward Palik.

2. Material and Methods

2.1. Numerical Techniques

We used, Finite Element Method (FEM) for simulation to determine the mean-fields around the Pt particles induced by UV plane-wave illumination. FEM is a numerical procedure for finding approximate solutions of partial differential equations (PDE) over a model with specified boundary conditions. It is thereby a procedure that may be used to solve much different kinds of problems in physics. The principle of the method is to replace an entire continuous domain by a number of sub domains, called elements. In these elements the unknown continuous functions are represented by simple interpolation functions with unknown coefficients. By doing so the number of degrees of freedom are reduced to a finite number, i.e. the solution of the entire system is approximated by a finite number of unknown coefficients. The solution is then obtained by linear or non-linear optimization. One major advantage of FEM is that high resolution and accurate measurements can be obtained at various desired areas (e.g. interfaces or curves) by changing the size of elements in this model. Our simulation was done by using commercial software Comsol® Multiphysics

version 3.4. The most important part of the model is the boundary conditions. These conditions describe how the interfaces affect and are affected by the electromagnetic fields, e.g. induced surface currents. They may be divided into subgroups, the internal and the external boundary conditions. Weak formulation, total field formulation or scattered-field formulation are alternative methods. In our calculation we used scattered-field formulation.

An alternative to the total-field formulation is the scattered-field formulation [23–25], where the incident field is introduced directly on the scatterer. The implementation of the scattered-field formulation uses the weak formulation (variational calculation). When considering a volume V bounded by the surface S , the electromagnetic fields generated by an internal current density J_i can be described with the curl-curl equation obtained from Maxwell's equations,

$$\nabla \times \left[\frac{1}{\mu} \nabla \times E \right] + \varepsilon \frac{\partial^2 E}{\partial t^2} + \sigma \frac{\partial E}{\partial t} = -\frac{\partial J_i}{\partial t} \quad r \in V \quad (1)$$

Where the magnetic field has been eliminated with aid of the constitutive relations and σ is the conductivity of the media. By substituting E with $E_{inc} + E_{sc}$ into Equation 1 with $J_i = 0$, the incident field E_{inc} may be separated from E_{sc} according to,

$$\nabla \times \left[\frac{1}{\mu} \nabla \times E_{sc} \right] + \varepsilon \frac{\partial^2 E_{sc}}{\partial t^2} + \sigma \frac{\partial E_{sc}}{\partial t} = -\nabla \times \left[\frac{1}{\mu} \nabla \times E_{inc} \right] - \varepsilon \frac{\partial^2 E_{inc}}{\partial t^2} - \sigma \frac{\partial E_{inc}}{\partial t} \quad (2)$$

The right hand side may now be replaced by an equivalent current source, J_{eq} according to Equation 1, i.e.

$$\frac{\partial J_{eq}}{\partial t} = \nabla \times \left[\frac{1}{\mu} \nabla \times E_{inc} \right] + \varepsilon \frac{\partial^2 E_{inc}}{\partial t^2} + \sigma \frac{\partial E_{inc}}{\partial t} \quad (3)$$

When applying Equation 3 in Equation 2,

$$\nabla \times \left[\frac{1}{\mu} \nabla \times E_{sc} \right] + \varepsilon \frac{\partial^2 E_{sc}}{\partial t^2} + \sigma \frac{\partial E_{sc}}{\partial t} = -\frac{\partial J_{eq}}{\partial t} \quad (4)$$

J_{eq} is only nonzero in the region when μ, ε or σ are different from the ambient media, according to Equation 1 where J_i is zero due to the absence of currents. Together with an impedance boundary condition according to,

$$\hat{n} \times \left[\frac{1}{\mu} \nabla \times E_{sc} \right] + Y_c \frac{\partial}{\partial t} [\hat{n} \times \hat{n} \times E_{sc}] = 0 \quad (5)$$

The weak form of Equation 5 will be,

$$\begin{aligned}
& \iiint_V \left\{ \frac{1}{\mu} (\nabla \times N_i) \cdot (\nabla \times E_{sc}) + \epsilon N_i \cdot \frac{\partial^2 E_{sc}}{\partial t^2} + \sigma N_i \cdot \frac{\partial E_{sc}}{\partial t} \right. \\
& \left. + \frac{1}{\mu} (\nabla \times N_i) \cdot (\nabla \times E_{inc}) + \epsilon N_i \cdot \frac{\partial^2 E_{inc}}{\partial t^2} + \sigma N_i \cdot \frac{\partial E_{inc}}{\partial t} \right\} dV + \\
& \iint_S \left[\gamma_e (\hat{n} \times N_i) \cdot \frac{\partial}{\partial t} (\hat{n} \times E_{sc}) - \frac{1}{\mu} (\hat{n} \times N_i) \cdot (\nabla \times E_{inc}) \right] ds = 0
\end{aligned} \quad (6)$$

where the intrinsic admittance of the infinite medium Y_c is $\sqrt{\epsilon/\mu}$, N_i is the interpolation vector functions and $\hat{n}$ is the outward normal to the surface S . When written in this form, the incident field is involved in the volume integral over the entire computational domain V as well as in the surface integral over S . To increase the efficiency of the calculations, the knowledge of the incident field outside the scatterer, in terms of fulfilled equations, may be utilized to reduce the weak form to,

$$\begin{aligned}
& \iiint_V \left[\frac{1}{\mu} (\nabla \times N_i) \cdot (\nabla \times E_{sc}) + \epsilon N_i \cdot \frac{\partial^2 E_{sc}}{\partial t^2} + \sigma N_i \cdot \frac{\partial E_{sc}}{\partial t} \right] dV + \\
& \iiint_{V_s} \left[\frac{1}{\mu} (\nabla \times N_i) \cdot (\nabla \times E_{inc}) + \epsilon N_i \cdot \frac{\partial^2 E_{inc}}{\partial t^2} + \sigma N_i \cdot \frac{\partial E_{inc}}{\partial t} \right] dV + \\
& \iint_S \left[\gamma_e (\hat{n} \times N_i) \cdot \frac{\partial}{\partial t} (\hat{n} \times E_{sc}) \right] ds - \iint_{S_s} \left[\frac{1}{\mu} (\hat{n}_s \times N_i) \cdot (\nabla \times E_{inc}) \right] dS = 0
\end{aligned} \quad (7)$$

where S_s is the surface of the scatterer, V_s is its volume and $\hat{n}_s$ is its outward normal. From Equation 7, it is seen that the incident wave only will be introduced in the weak terms inside the scatterer and on its outer boundaries. By introducing the incident wave into the weak formulation directly there will be an increase in accuracy when extracting the amplitude of the reflected wave, since no subtraction will have to be made. On the other hand, when looking at the transmitted field the incident field will have to be added to the result, since the field obtained from the finite element calculation will be the difference between the total field and the incident field.

For calculations involving fluorophores, it is assumed that excitation of the fluorophore has already occurred and the fluorophore is now emitting dipole radiation. Hence the fluorophore is modeled as a time-windowed, oscillating point dipole source for the electric field, with frequency content spanning the spectral range (200–800 nm) of interest. For calculating the radiative power, the dipole is placed in water (refractive index ~ 1.33) and measured the power over a sphere around the dipole. FEM calculations are also performed for a dipole near a semi-coin like metal particle ($n \sim 1.33$) as shown in the schematic. The dipole is placed at the origin so that it is at equal distance from each metal surface. We calculate the total radiated power enhancement as P_{rad}/P_0 , where P_{rad} is the integral of the Poynting vector over a surface enclosing the dipole and metal nanoparticle(s), and P_0 is the result of this integral with only the dipole present. For every normalization we used $\sqrt{(E_x^2 + E_y^2 + E_z^2)}$ which include the average around the dipole for 3 dimensions.

2.2. Material and Methods

Platinum slugs, silicon monoxide, 3-(aminopropyl)triethoxysilane (APS), and phosphate buffer solution pH 7.2 were purchased from Sigma-Aldrich-Fluka and used as received. Guanosine 3',5'-cyclic monophosphate sodium (GMP), thymidine 5'-monophosphate disodium (TMP), cytidine 5'-monophosphate disodium (CMP) and uridine 5'-monophosphate disodium salts were obtained from Sigma-Aldrich. G-quadruplex DNA was obtained from Integrated DNA Technology (IDT). Ultrapure water (>18.0 M Ω) purified using a Millipore Milli-Q gradient system was used in preparation of buffers and aqueous solutions.

Quartz slides were cleaned by soaking the slides into “piranha solution” (35% $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$, 1:3) overnight, rinsed with distilled deionized water, and dried with air before thermal vacuum deposition steps. 10 nm of platinum were deposited on quartz slides using AJA sputtering system under high vacuum. The metal deposition step was followed by the deposition of 5 nm of silica via evaporation without breaking vacuum. This step served to protect the metal surface and also it adds a distance of 5 nm from the metal surface. After these coating steps, slide surfaces were activated by immersion in an ethyl alcohol solution of 1% of aminopropyl trimethoxysilane (APS). G-quadruplex DNA, GMP, TMP, CMP and UMP solutions (0.1mg/mL) in phosphate buffer (pH 7.2) were added onto the dried surfaces. The same procedure was used for preparation of control samples using bare quartz slides. After overnight incubation with nucleic acid solutions, slides were washed with phosphate buffer solution to remove unbound nucleotides. Fig. 1 shows the schematic of preparation steps of nucleic acid adsorbed platinum substrates.

Fluorescence spectra of nucleotides and G-quadruplex DNA on platinum substrates were recorded using a Varian Cary Eclipse fluorescence spectrophotometer and compared with the signal of the respective samples on bare quartz. Absorption spectra were collected using a Hewlett-Packard 8453 spectrophotometer.

3. Results and Discussion

Numerical simulations are not only necessary to confirm the experimental output, but also beneficial to understanding physical processes of wave propagation. FEM simulation of electromagnetic fields is currently one of the most popular methods among optical researchers. The expressions for calculation of the cross-sections are rather complex. For this reason we use a commercially available program, Comsol Multi-Physics package (a Finite Element Method package) as mentioned before. In calculations, the simulation environment was a sphere with 250 nm radius filled with water. The power was measured on the top hemisphere where the incident wave was X polarized and traveling in the positive Z direction. We used two different shapes of Pt nanoparticles in simulations. One of them is full cylindrical coin-like nanoparticle, and the second one is semi cylindrical platinum nanoparticles which are obtained by breaking the coin in two parts. In following parts we will call these two type platinum nanoparticles as coin-like platinum nanoparticle and broken-coin/broken-semi-coin platinum nanoparticles. Fig. 2 shows the extinction properties of coin-like and broken-coin Pt nanoparticles with different heights. We obtained two bands for both type Pt particles. The variation in the extinction properties of coin-like Pt nanoparticles by height of particle is shown in Fig. 2a. Obtained values demonstrate those extinction values of Pt particles increase with increased height of the particles. Fig. 2b demonstrates the comparison of extinction properties of semi cylinders in different heights and at 10 nm distances between two broken-semi-coin Pt nanoparticles. We observed a small blue shift by increase in size of the nanoparticles by height. While

Fig. 3a short wavelength bands are remarkable by the polarization along the X-axis, long wavelength bands became larger by polarization along the Y-axis. Fig. 3a shows the experimental absorption spectra of 5 and 10 nm thick platinum nanostructures on quartz substrates. The platinum nanostructures show an absorbance peak around 225 nm. Absorption spectra show increase in extinction over the whole observed wavelength range with the increase of platinum height. The SEM image of platinum substrates reveal that the film is not continuous and platinum forms nanoparticles of various shapes and sizes when deposited on the quartz substrate, presented in Fig. 3b, with an average particle size of approximately 20 nm (a rough estimate).

We compared the emission of G-quadruplex DNA [26] and the five nucleotides on Pt nanoparticles and quartz substrates. G-quadruplex DNA and three different nucleotides thymine monophosphate (TMP), uracil monophosphate (UMP), and guanine monophosphate (GMP) showed significant increases in fluorescence intensity when compared to a control quartz substrate. Cytidine monophosphate (CMP) showed moderate increase in fluorescence intensity according to other three nucleotides. Fig. 4 shows the fluorescence spectra of GMP and CMP on platinum nanostructures and control quartz substrates. The largest enhancement is observed from the GMP-adsorbed platinum nanostructure as ~20-fold. Approximately ~9-fold and 5-fold increase in fluorescence intensities of UMP and TMP on metallic nanostructures were observed, respectively. Approximately 3-fold fluorescence enhancement was obtained from CMP on platinum nanostructures. One factor that may have contributed to the differences in enhancement factor for the CMP and GMP on the platinum nanostructure substrate could be related to the quantum yields of the CMP (1.2×10^{-4}) and GMP (0.8×10^{-4}) [27] respectively. The metal-enhanced fluorescence is due to a through-space interaction, and not thought to be dependent on chemical structure. It is important to note that the enhanced fluorescence observed from the nucleotides on the platinum nanostructures cannot be attributed simply to conventional far-field reflection. The sputtered platinum particles are smaller than the wavelength of the excitation and emission, hence the sputtered platinum films essentially behave like a particulate surface. In this configuration we believe that the excited-state molecule (nucleotides) couples to the plasmons on the surface of the platinum particles and the combined excited fluorophore-metal complex acts as a unified system, which then radiates the emission observed in the experiments [28].

DNA G-quadruplex showed ~5-fold increase in fluorescence intensity when compared to a control quartz substrate. shows G-quadruplex DNA steady-state fluorescence emission (a) and fluorescence emission as a function of time (b). The same initial steady-state intensities were adjusted to make comparison between Pt substrate and quartz substrate. We attribute the decrease in intensities to either photobleaching or conformational changes. In either case the signal is modulated more stable on the Pt substrate.

The ability to observe of nucleotide fluorescence can be achieved by reducing the observed volume around the fluorophore. Background emission and scattering can overwhelm the weak nucleotide or nucleic acid emission. Metal particles can be used to overcome this problem by localization of the fields near the surface of the particles. The localization can be helpful in designing specific fluorophore-metal nanoparticle systems. Fig. 6 shows the effect of 280 nm plane wave excitation on the near-fields around platinum nanoparticles, which have 20 nm radius, 20 nm heights and 10 nm distances between the comparable two semi-coin particles in water. A wavelength of 280 nm was chosen for our calculations with the excitation wavelength of our experimental studies. All of the near-fields are shown along a single plane, that is, the x-y plane ($E_x^2 + E_y^2 + E_z^2$) running through the center of the platinum nanoparticles. Fig. 6 shows the near-fields intensities around a coin-like and broken-semi-coin Pt nanoparticles ($r = 20$ nm) created by its interaction with the plane wave of wavelength 280 nm and 340 nm with its electric field oriented along the x axis. Fig. 6 reveals that the interaction of platinum nanoparticles with 280 nm incident light produces regions of field enhancements around the nanoparticles. Note all images are in the linear scale. Fig. 6 indicates that the fields between broken-semi- coin Pt nanoparticles show higher excitation fields when compared with coin-like Pt nanoparticles. The electric field intensities in the x-y plane of a plane wave of wavelength 340 nm, the near-fields around a coin-like Pt nanoparticles and broken-semi-coin Pt nanoparticles system with a surface-to-surface distance of 10 nm are shown in Fig. 6. Note all images are in the linear scale. Results show that the highest enhanced near-fields can be observed between broken semi-coin Pt nanoparticles by interaction of both plane waves of wavelength 280 nm and 340 nm. These

higher near-field enhancements in between the particles suggests that a DNA base molecule (or any other fluorophore) once localized between the particles will experience a much higher excitation field than if it was isolated and directly excited only by the incident light. The phenomenon of MEF includes emission as well as excitation. Hence it is important to understand the effect of Pt particles on nearby fluorophore, which we modeled as a point dipole. We determined the effect by comparing the wavelength dependent power of a dipole near Pt to the power radiated in free space (water). Fig. 7 shows the radiated power enhancements when a fluorophore is placed between broken-semi-coin Pt nanoparticles. For the 20 nm height broken-semi-coin nanoparticles, we examined two dipole- metal distances (s) of 5 and 10 nm. Here we see an increase in the radiative power enhancement approximately 12-fold at 340 nm for the $s = 5$ nm case. For the $s = 10$ nm case, we observe a peak enhancement of approximately 6-fold at 320 nm by polarization along X-axis. These results show that the wavelength of peak radiative power enhancement red-shifts with a decrease in distance between broken-semi-coin Pt nanoparticles. We also investigated the radiative power enhancement of dipoles by polarization along the Y and Z axis. For along the Y and Z axis polarization case, variable in distance didn't affect the radiative power enhancement of dipoles. An important overall conclusion from these calculations is that higher enhancements are expected for dipoles which are located closer broken-semi-coin platinum nanoparticles. Additionally the enhancements are expected over a wide range of wavelengths, especially from 300 to 400 nm where the nucleotides emit. Hence we expect platinum nanostructures to be generally useful in enhancing intrinsic DNA emission.

4. Conclusions

This study demonstrates the potential of Pt nanostructures for DNA detection using intrinsic base fluorescence. We presented experimental and computational studies showing the effect of Pt nanoparticles on fluorophore emission in the UV-region. The platinum nanoparticles were modeled as coin-like and broken-semi-coin and a variety of nanoparticle sizes changing by particle height were studied. We observed that the broken-semi-coins provide higher enhanced near-fields when compared to coin-like platinum nanoparticles. Simulations showed that fluorescence emission enhancement amount from fluorophores which are located between semi-coins increase with a decrease of gap distance between the semi-coins. These results reveal that enhancement amount strongly depend on the gap amount between semi-coins. The experimental studies showed that the presence of Pt nanoparticles causes to increased fluorescence intensity of four nucleotides GMP, TMP, UMP, CMP and G-quadruplex DNA. GMP and UMP showed the highest MEF in the presence of platinum nanostructures. A moderate enhancement obtained from TMP and G-quadruplex DNA adsorbed on platinum nanostructures. CMP exhibited the lowest increase in fluorescence intensity on Pt nanostructures when compared to quartz controls. These experimental and numerical results suggest that platinum nanostructures can potentially be used for enhancing the intrinsic emission from nucleic acids.

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Highlights

1. Enhanced fluorescence from nucleotides and G-quadruplex DNA near Pt nanoparticles
2. Pt nanostructures increase the photostability of nucleic acids.
3. FEM calculations revealed enhancement dependent on Pt particle size and shape.
4. Pt nanostructured substrates for label free nucleic acid detection.

Fig. 1.
Schematic of the assembly of nucleic acids on quartz and Pt nanostructures.

Fig. 2.

(a) Extinction properties of coin-like Pt nanoparticles calculated using scattered-field formulation; (b) Extinction properties of broken-semi-coin Pt nanoparticles calculated using scattered-field formulation in different heights. Continuous lines represent the extinction properties of broken-semi-coins when polarized along X-axis and dashed lines represent the extinction functions when polarized the Y-axis.

Fig. 3.
(a) Absorption spectra of 5 and 10 nm thickness Pt substrates; (b) SEM image of sputtered platinum substrate.

Fig. 4.
Emission spectra of (a) GMP; (b) CMP on quartz and Pt substrates.

Fig. 5. (a) Emission spectra of quadruplex-DNA on quartz and Pt substrates;; (b) Photostability of quadruplex-DNA on quartz and Pt substrates.

Fig. 6. Near-fields around a coin-like and broken-semi-coin Pt nanoparticles (**a**) created by interaction with a 280 nm plane wave (**b**) created by interaction with a 340 nm plane wave.

Fig. 7. Comparison of fluorescence enhancement from fluorophores located between broken-semi-coins.