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Time Resolved Spectroscopic Investigation Of Excited State Dynamics Of Dye/Quantum Dots Near Nanometal Surface.

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Abstract: The use of metal nanomaterials in various applications due to their tunable optoelectric properties are growing and excitement filed. These optoelectric properties of metal nanomaterials are used in various biomedical applications and are highly depend on the size of the nanostructure.[1, 2] These properties of metal nanostructure is due to the oscillation of electrons with in the materials, resulting surface plasmon resonances (SPRs) generates, that makes these materials unique from the bulk. These unique features of nanomaterial can be utilized in molecular sensing, photothermal therapy, tagging.[3-6] These optical properties can vary with the nanomaterials. Among various kind of nanomaterials gold metal nanomaterial have attracted researchers due to their potential application in the field of biomedical technologies, imaging and optical and optoelectronic devices. Moreover, the metal nanostructures are most suitable agent for imaging because of their stability under the light illumination. The surface functionalizations of these nanostructures are very facile with biological groups and chemicals that make them outstanding in the field of targeted imaging.[7] Moreover, the capabilities of nanomaterials to accommodate numerous functional groups, biomolecules, and drugs permit us to customize them for cure of various cancer cells.[8] Bio macromolecules (proteins) are the major part for living organism which carried the information encoded by the genes to the specific site. In biological organisms the self-association of proteins is a common phenomenon that sometime lead to severe side effects. So, the photophysical study on their conformational dynamics in highly crowded environment is of great importance. Therefore, it is essential to design a nanomaterials that would be accurately precise to a given cell and cellular pathway.

Introduction

Fluorescence techniques effectively use to investigate the photophysical and photochemical changes in different systems and the most powerful method for in vitro and in vivo detection, due to their non-invasive and high sensitivity. It can sense the low probe concentration up the level of nano molar quantity and the emission intensity is very sensitive to the surrounding environments. In some cases excited state phenomena lead to change in fluorescence intensity with large Stoke's shift and provide the information about the excited state dynamics such as conformational changes, excited state lifetime etc. These reports will analysis a few studies illustrating the versatility of fluorescence techniques using microscopy, steady-state and time resolved fluorescence measurements. Fluorescent materials, attached with the nanostructure have attracted increasing interest due to their high quantum yield, photostability after coupling with plasmon resonance. These coupled materials near nanostructure will reveal the unique platforms of materials that can open the opportunities to various future technologies, such as sensing, imaging and photothermal therapy.

Gold nanorod optoelectric properties:

The optoelectric properties of nanomaterial are due to the interaction of the incident light leads to change radiative and nonradiative processes. The conduction band electron of nanostructure can oscillate with the frequency of oscillating electromagnetic light; this phenomenon is called surface plasmon resonance (SPR).[9] The consequence to this phenomena leads to change separation of charges between the free electrons and the metal core. The SPR oscillation prompts a strong absorption of light that clearly reflects in the UV–Visible spectrum of a colloidal solution. The condition of this charge separation is depend on the size, shape, structure, dielectric properties of the metal which is used (Gold), and the surrounding medium, as these factors affect the electron charge density on the particle surface.[10] In gold nanorods the electron oscillation can occur in two directions depending on the polarization of the incident light: the short and long axes. The short axis oscillation induces and absorption band in the visible region, called transverse band. This band is similar to the band observed in case of gold nanoparticles. On the other hand the plasmonic oscillation along the long axis induces a stronger absorption band at higher wavelength, designated to longitudinal band. Although the transverse band is not sensitive to the length of the nanorods, while longitudinal band is red-shifted with increasing the length.

Methodology

a. Synthesis of Gold nanoparticles and Nanorods:

Gold nanomaterials synthesis via simple methods is one of the preferred ways. Nevertheless, accomplishing growth control of nanostructures in confined dimension is quite difficult task for researchers. A simple example for the gold nanorods synthesis is seed mediated method, extensive research efforts worldwide have resulted in a plethora of synthetic routes. El- Sayed *et al*. obtained gold nanorods of high yield and varied aspect ratio in solution by using gold seeds which are stabilized by surfactants.[11] Here, we will extend the procedure to yield gold nanorods in a well-disciplined fashion.

b. Surface Functionalization: As the surface area increases by surface functionalization the fraction of absorbed light is increased, which is responsible for the quenching and enhancement of the quantum yield of fluorophore?

c. Fluorescence Quenching/Enhancement of dyes/Quantum Dots with Gold nanorods

The photoluminescence of probe molecules are drastically changed by the coupling with plasmon resonance in adjacent nanostructures. However accomplishing optimistic fluorescence with fluorophores emission ranging near IR is quite difficult task.[12] The metallic nanostructures present near the fluorophore can stabilized the system and enhance the photostability that can further uses in bioimaging application.[13-15] By time-resolved photoluminescence spectroscopy, we will be investigating dyes coupled to Au nanorods. The distance between emitter and metal is adjusted by coating the nanomaterial with silica shells. These observations will be clarifying

Discussion:

It is mentioned earlier that with the variation of the silver nitrate in the methods of preparation, different aspect ratio nanorods can be prepare. These changes are reflected in the spectral features of the gold nanorods. In this project, gold nanorods will be prepared by the seed mediated method by varying the $AgNO_3$ and the growing time of the nanorods solution.

a. Fluorescence from dyes coupled to individual DNA-functionalized metal nanomaterials will be studied

b. Preparation of different Surface functionalized gold nanorods.

c. The spectral and temporal features of the nanomaterials prepared by the techniques mentioned above will be studied. The lifetimes will be determined using the time correlated single photon counting technique and if required, femtosecond fluorescence upconversion. Microscopy experiments will be performing to investigate the blinking features of fluorescent dyes/quantum dots coupled with gold nanorods by using epifluorescence and total internal reflection microscopy (TIRF) methods. Studies will be performed on colloidal solution of nanorods and on surface functionalized/silica coated nanorods with dyes mention above, in order to understand the consequences of the spectral features of varying aspect ratio and different concentration of nanorods on said fluorescent molecules and quantum dots. Since the PL spectrum of probe has been proposed to alter with SPR band (Red end) of nanorods, low temperature studies will also be performed with the same.

Applications: Gold nanorods have unique optical properties say radiative and nonradiative phenomena that leads to a new types of nanomaterials for wide range of applications in the files of listed below.

a. Labelling and imaging: As the dye molecule coupled with gold nanorods. The scattering area of chosen dye will be higher compare to conventional dye molecules,[16-20] making them outstanding candidates for biomedical applications.

b. Biosensing: Gold nanorods are extremely suited for plasmon sensing due to the increasing of absorption surface area.

c. Molecular Imaging: Gold nanorods are well suited for imaging owing to their higher scattering cross section as compare to conventional fluorescent dye molecules.

d. Gene and Drug Delivery: The conventional gene delivery method based on virus mediated and this is very risky due to cytotoxicity and bad immunological response. Due to the limitation of these responses, the discovery of nonviral gene delivery carrier is very necessary. In this context the gold nanorods catch attention in past years.

e. Photothermal Therapy: Gold nanorods have outstanding properties apart from optoelectric properties like stability and small size that makes gold nanorods excellent candidates for using in the field of photothermal therapy, high absorption efficiency, and tunable absorption.

Conclusion:

Coupling with plasmon of nanorods to enhance fluorescence is potential technique to increase efficiency of weak fluorescence. Literature revealed that by plasmon fluorophore combination which can enhance the fluorescence is a quite complex process. However, fluorescence enhancement of weak fluorophore via coupling with surface plasmon resonance of nanorods remains a worthwhile opportunity to increase their potential biological application. We will demonstrate that how these nanomaterials are beneficial to improvement better understanding for interaction with other materials. The main focus of this project is to explore that how gold nanorod optical properties can be exploited for numerous applications.

8. References

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