DECLARATION

I, Dewan Shahidur Rahman, hereby declare that the thesis entitled "**Photophysical Properties of Molecular Probes near Nanostructured Metallic Surfaces**" has not been submitted either in whole or in part previously to any other institution for the award of any degree or qualification and does not contain any previously published material or written by another person, except where due reference is made in the text.

Place: Silchar

Date: 16.05.2016 Dewan Shahidur Rahman

Dedicated to My Beloved Parent

Mrs. Joynab Begom

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Preface

The aim of this work is to investigate the unique photophysical properties of fluorophores and semiconductor materials near the metal nanostructures of various sizes and shapes and their formation of metal-fluorophore hybrid assembly, metal-semiconductor assembly and their studies of various photophysical and thermodynamic properties. For this purpose, the present Ph. D thesis entitled **“Photophysical Properties of Molecular Probes near Nanostructured Metallic Surfaces”** has been chosen. This thesis includes the synthesis of gold and silver nanoparticles of various sizes and shapes (spherical, dogbone nanorods, multispikes shaped nanostar) and the formation of metal-fluorophore hybrid assembly using various fluorophores and their photophysical properties based on Förster resonance energy transfer and electron transfer mechanism including the studies of relative contribution of electron transfer. Moreover, size selective metal nanoparticles-semiconductor assembly and their various physical properties have been studied using microscopic (transmission electron microscopy, scanning electron microscopy) and spectroscopic (UV-visible spectroscopy, steady state and time resolved fluorescence spectroscopy, Raman spectroscopy, energy dispersive X-ray analysis, Fourier transform infrared spectroscopy, X-ray diffraction, and selected area electron diffraction) techniques and their catalytic and other application has been tried to develop in the present work. The complete work of the thesis has been divided into seven chapters.

Chapter 1

This chapter includes the general introduction about the current literature related to the research work presented on plasmonic metal nanoparticles and fluorophore molecules near to the surface of the nanostructures.

Chapter 2

The chapter two presents a brief description about the chemicals and reagents used during the experiments and various techniques and analytical instruments used for the characterization of the synthesized materials and their hybrid-assemblies.

Chapter 3

In this chapter, the synthesis of gold nanoparticles with variable sizes and their aggregation phenomena and fluorescence enhancement as well as fluorescence quenching have been described. This chapter consists of two sub-chapters: (i) synthesis of ultra-small gold nanoparticles with size ranges of 1-5 nm and compared the fluorescence enhancement by following the spontaneous and induced aggregation and (ii) synthesis of gold nanoparticles with variable sizes (1-55 nm) and their quenching phenomena have been explained by using different models like FRET and NSET mechanism and their critical limits.

Chapter 4

This chapter describes the relative electron transfer in fluorescence quenching of pyrene derivatives with silver nanoparticles of variable sizes. Here, relative electron transfer contribution of the fluorophore molecules and the size effect of the Ag NPs have been explained in the metal-probe hybrid system.

Chapter 5

This chapter consists of anisotropic gold nanostructures with two sub-chapters. Sub-chapter (i) explains the synthesis of dogbone shaped gold nanorods with variable aspect ratio and their effect in quenching process. Sub-chapter (ii) describes the synthesis of multispiked gold nanostructures and their various properties like fluorescence quenching, laser heating shape transformation, excess surface energy at the tips and stability based on thermodynamics.

Chapter 6

This chapter highlighted about the metal-semiconductor assembly and their photophysical behavior with size and composition in two separated sub-chapters. Firstly, the photophysical and catalytic properties of the composites made of zinc oxide quantum dots and gold nanospheres with different sizes have been studied. Secondly, the assembly formations of silver and zinc oxide of different compositions and their photophysical, microscopic and spectroscopic bahaviour have been studied

Chapter 7

The important outcomes of the completed research are summarized and the future scopes of the work are mentioned in this chapter.

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Symbols

2D	two dimensional	3D	three dimensional
Å	angstrom	A_e	surface area of ellipsoidal tip-head
A_p	surface area of protrusion base	A_{cone}	surface area of prolong conical arm
A_{core}	surface area of spheroidal core		
c	velocity of light	°C	celsius
cm	centimeter	C	concentration
e	ellipticity of the tips of nanospikes		distance of the emitter from the metal surface
E_g	band gap	eV	electron volt
E_{tip}	surface energy on tip	ε, ε_A	extinction co-efficient
E_{pc}	cathodic potentials	E_{pa}	anodic potentials
	energy transfer efficiency		Fermi energy level
ΔE_P	potential difference		real dielectric of the medium
( )	real components of the dielectric function	( )	imaginary components of the dielectric function
f	packing fraction	$F_D(\lambda)$	fluorescence intensity of donor
Φ_{dye}	quantum yield of the donor dye	fcc	face-centered cubic
φ_f	quantum yield		modified quantum yield
	radiative decay rate		nonradiative decay rate
h	hour	hν	photon energy
i_{pa}	anodic peak current	i_{pc}	cathodic peak current
	intensity of the exciting source beam	k	solvent interaction energy parameter
$J(\lambda)$	overlap integral	K_{app}	apparent association constant
K	kelvin		energy transfer rate
kDa	kilodalton	kV	kilovolt
K_S	static quenching constant	K_D	dynamic quenching constant
K_{SV}	Stern-Volmer constant	K_{cat}	catalytic rate constant
	Fermi wave-vector	λ_{ex}	excitation wavelength

λ_{max}	maximum wavelength	λ_{abs}	maximum absorption wavelength
λ_{em}	maximum emission wavelength	M	molar
mM	millimolar	mL	milliliter
meV	millielectron volt	min	minutes
N	numbers of nanoparticles per milliliter	nm	nanometer
		nM	nanomolar
	Avogadro’s number		refractive index
μM	micromolar	μA	microampere
	dipole moment		quantum yield of the donor
r	radius of atoms	R	average radii of the particles
R_0	Förster distance		lifetime of the donor
	lifetime of the dye		excited state radiative lifetime of the donor
Γ_0	excited state life time		
	extinction of the particles	V_0	volume of the particles
ω	angular frequency		plasma frequency
	vibrational frequency of the dipole	W	watt

Abbreviations

A	acceptor
APY	aminopyrene
Au NPs	gold nanoparticles
Ag–APY	silver-aminopyrene assembly
Ag–PY	silver-pyrene assembly
CTAB	cetyltrimethylammonium bromide
D	diameter
DNR	Dogbone-shaped nanorod
FTIR	Fourier transform infrared spectrum
FRET	Förster resonance energy transfer
HRTEM	high resolution transmission electron microscopy
NIR	near infrared
NSET	nanosurface energy transfer
PY	pyrene
PVP	poly(*N*-vinyl-2-pyrrolidone)
PZC	point of zero charge
QD	quantum dot
SPR	surface plasmon resonance
TEM	transmission electron microscopy
TOAB	tetraoctylammonium bromide
UV-vis	ultraviolet visible
UV-vis-NIR	ultraviolet visible near infrared
AMPY	aminomethylpyrene
AR	alizarin red
Ag NPs	silver nanoparticles
Ag–AMPY	silver-aminomethylpyrene assembly
CV	cyclic voltammetry
D	donor
DNA	deoxyribonucleic acid
EB	Evans blue
FITC	fluorescein isothiocyanate
FDTD	finite difference time domain
GDNR	gold dogbone nanorod
LSPR	localized surface plasmon resonances
NPs	nanoparticles
NCs	nanocomposites
PET	photoinduced electron transfer
Q	quencher
SP	sphere
SR7B	sudan red 7B
SAED	selected area electron diffraction
UV	ultraviolet
XRD	X-ray diffraction
ZnO QD	zinc oxide quantum dot
ZnO–Au	zinc oxide-gold
ZnO–Au NCs	zinc oxide-gold nanocomposites