PLASMONIC SYSTEMS WITH MORPHOLOGICAL AND FUNCTIONAL ISOTROPY AND ANISOTROPY

A synopsis submitted to Madurai Kamaraj University, Madurai in partial fulfillment of the requirements for the Degree of

DOCTOR OF PHILOSOPHY IN CHEMISTRY

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TAMILNADU – INDIA

JUNE – 2019

SYNOPSIS

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According Drude-Sommerfield model, electrons in metallic nano structures behaves like incompressible liquid around the positively charged nuclei. When external electromagnetic radiation interacts with this electron cloud, it gets displaced from the equilibrium position. This distortion will lead to oscillations of electron cloud. These oscillations are called plasma oscillations. Quantized form of plasma oscillations is called plasmons. Systematic study and tuning the application of these systems is called plasmonics. Plasmonic systems provide the possibility to confine the energy of electromagnetic field down to nanoscale. Confinement of energy results in extreme increase of the local electromagnetic field. This in turn leads to enhancement of various kinds of light-matter interactions, offering a huge potential in applications. These days have witnessed wide applications of these plasmonic systems viz; sensing , catalysis , bioimaging , photo-thermal cancer treatment, photovoltaic, plasmonic nanolasers, plasmonic logic circuitry and optical data storage. Noble metal nanoparticles (MNPs) are the most exploited material among the family of plasmonic systems. Depending on the applications both bottom up and top down methods are explored for the synthesis of these systems. The metal plasmonic systems have been synthesized and stabilized via wet chemical procedures involving various reactants, in particular using reducing and stabilizing agents. These possess the drawbacks of contamination from precursor chemicals, use of toxic solvents and generation of hazardous by-products. The physical methods leading to the generation of metallic plasmonic systems have the undesirable effects like expensiveness, enormous consumption of energy, maintenance of critical physical parameters viz; pressure and

temperature In addition to these, another fascinating aspects of metallic plasmonic systems is the size and shape-dependent variation in properties. Due to this reason, efficient efforts have been made to find various parameters that directly shake the intrinsic properties of materials at this length scale Among these, shape was found to play a significant role in determining the properties of nanomaterials. Restricted motion of electrons, holes, excitons, phonons, and plasmons with respect to the physical shape of an object lead to exceptional property change of plasmonic systems.

Graphene , graphene oxide, reduced graphene oxide and nano cellulose are the some of the new comers to the nano technology arena. The studies on property evaluation of these materials are not fully understood. Researchers round the globe are trying to analyse the properties of these materials for eco-friendly applications. More over studies on hybrid systems explicitly plasmonic- reduced graphene oxide and plasmonic-nano cellulose are fully unexplored area for environmental and technological applications. In this context it will be worth to evaluate the properties and application potential of the above mentioned systems for the development of active devices for functional applications.

The challenge on hand is to produce new isotropic plasmonic systems, anisotropic plasmonic systems and their hybrid functional versions without harmful properties but at the same time fulfilling the industrial standards. Keeping in mind the advantage of initiating a sustainable and safe nanotechnology, herein an attempt has been made to synthesize isotropic, anisotropic plasmonic systems and their functionalized ones in a greener way and to apply to nonlinear optical and environmental applications.

The thesis consists of six chapters.

Chapter I

Introduction

A general introduction on plasmonic systems, characterization techniques and their application potentials in various fields has been presented. The physical processes are discussed in a more general way with special emphasis on linear and nonlinear optics. The advantages and merits of metallic plasmonic systems and reduced graphene oxide are detailed. Spectroscopic evaluation techniques and optical features of these systems, which are instrumental in arriving at qualitative and quantitative results, are described. A special emphasis is given to explain the importance of wood derived materials and nano forms of wood derived materials. Importance of hybrid forms of plasmonic systems and their functional advantages including packaging industry are also explained. . Objective and scope of the present study are also presented in this chapter.

Objective of the present study are

Green synthesis of isotropic and anisotropic plasmonic systems and their charecterisation

(i) Facile synthesis of metallic plasmonic- reduced graphene oxide system

(ii) Evaluation of capability of plasmonic gold- RGO for reduction of nitrophenols.

(iii) Non- linear optical property evaluation of green synthesized plasmonic systems.

(iv) Evaluation of application potential as novel optical limiters.

(v) Evaluation of morphology dependent photo catalytic and nonlinear optical properties of plasmonic systems.

(vi) Synthesis of transparent plasmonic-cellulose nano fibril Poly vinyl alcohol films for ultraviolet radiation shielding.

Chapter 2

Synthesis of AuNPs @ RGO Nanosheets for Sustainable Catalysis toward Nitrophenols Reduction

In this chapter, a facile, green and one-pot synthesis strategy for the convenient preparation of well-dispersed gold nanoparticles (AuNPs) decorated reduced graphene oxide (RGO) without using any other toxic chemicals and reductants is reported herein. The synthesized AuNPs@RGO hybrid nanomaterials were characterized by UV–visible absorption spectroscopy, FT-IR, XRD, Raman, SEM, TEM and EDX analysis. The AuNPs@RGO acts as an efficient catalyst for the reduction of organic nitroaromatics (2- & 4- nitro phenols) in the presence of $NaBH_4$. This newly synthesized hybrid AuNPs@RGO has superior catalytic activity over any other Au-nanomaterials ever reported. The rate of nitro aromatics reduction is found to be dependent on concentrations of substrate, reductant and catalyst. The mechanisms for the synthesis and catalytic reduction have been studied and discussed.

Chapter 3

Green Synthesized Plasmonic Silver Systems for Potential Non-Linear Optical Applications : Optical Limiting and Dual Beam Mode Matched Thermal Lensing

Biosynthesis of silver nanoparticles using *mimosa pudica* leaf extracts as a reducing and a stabilizing agent, and its application in linear and nonlinear optics are discussed in this chapter. The aqueous silver ions when exposed to *mimosa pudica* leaf extract are reduced resulting in the formation of silver nanoparticles. These nanoparticles are characterized using UV-Visible, optical band gap, fluorescence spectroscopy and high resolution transmission electron microscopy techniques. Third order nonlinear optical susceptibility and nonlinear optical absorption studies were measured using open aperture Z-scan technique with a 7 ns, 532 nm pulsed laser. These silver nanoparticles suspended in solution unveiled very strong reverse saturable absorption with low optical limiting threshold. Dual beam mode matched thermal

lensing technique was used to determine the thermo optic properties of the synthesized system. Promising values of optical limiting threshold (242MW/cm^2) and thermal diffusivity parameter (D=1.13 x10^{-7} m^2/S) points to the application potential of the system.

Chapter 4

Morphology Dependent Nonlinear Optical and Photo Catalytic Activity of Anisotropic Plasmonic Silver

Systematic studies on morphology dependent ultra-sensitive thermal diffusivity and photo degradation capability of anisotropic plasmonic silver for are presented in chapter 4. We have performed hydrogen peroxide centered synthesis to prepare anisotropic silver nanosystems spherical(14nm), quasi-spherical(17nm), elliptical(18nm), rods(aspect ratio 2.1), hexagonal (22nm) and prisms (19nm). The synthesized nano systems were characterized using UV–VIS spectroscopy, high resolution transmission electron micrograph (HRTEM) and band gap analysis. Dual beam mode matched thermal lensing method was adopted for evaluating the thermal diffusivity of anisotropic system. The present anisotropic nanoparticle system exhibited strong morphology based thermal diffusivity. An increase of 140% in thermal diffusivity value points to the nonlinear optical application potential of the anisotropic systems. Sun light mediated photo degradation of methylene blue showed a promising increase in the degradation rate for anisotropic systems compared to other similar systems reported in the literature.

Chapter 5

Plasmon Enhanced Cellulose Nano Fibril- PVA Coatings: Ideal hybrid for UV Radiation Blocking

In chapter five, development of novel highly efficient transparent plasmon enhanced ultraviolet radiation blocking films is described. The transparent Cellulose Nano Fibril (CNF)-PVA films were prepared by mixing a colloidal solution of the CNFs with a water solution of PVA in appropriate ratios. Synthesized films exhibited high transparency in the visible region and UV protection capability. Addition of plasmonic silver to the films enhanced UV protection ability by a considerable amount. The defined methods show a straightforward procedure to produce environment friendly UV-light blocking films for practical industrial /commercial/textile applications.

Chapter 6

Summary and Conclusion

Overall summary and conclusions are presented in chapter 6. This research work provides an in depth awareness of the facile methods for isotropic, anisotropic plasmonic systems, metallic plasmonic – reduced graphene oxide system, transparent metallic plasmonic - cellulose nano fibril- PVA films synthesis, characterization and their most promising applications in non linear optics and environments. With the fast and promising advancement, the continuous efforts in developing particle synthesis efficiency and exploring their nolinear optical and environmental applications, it is positive that the implementation of these methods on an increased scale and their commercial applications will definitely take place in the future.