# Investigations on Synthesis, Linear and Nonlinear Optical Properties of Some Noble Metal Nanoparticles and Nanocomposites

*A Thesis*

*Submitted in Partial Fulfillment of the Requirements for the Degree of*

**Doctor of Philosophy in Science (Physics)**

**of the**

**National Institute of Technology Durgapur**

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**September, 2022**

# ABSTRACT

In 1959 at the yearly gathering of the American Physical Society, Dr. Richard Feynman (Nobel Laureate, 1964, Physics) in his popular discourse "There's Plenty of Room at the Bottom", anticipated that composing the whole 24 volumes of the Encyclopaedia Britannica on the top of a pin is conceivable. What appears to be incomprehensible then currently transforms into a reality. Presently a day's everybody concurs that the twenty first century is without a doubt a 'nano era'. The gigantic advancement in the fabrication and control techniques for the nanometer-sized objects somewhat recently have permitted us to go into the captivating scene even at the length scale of molecules. The structure blocks of this nano world are the metallic nanoparticles (NPs) and colloids. Through literature studies it has been found that the capacity to manipulate or control light with light at the nanometer scale through the metal nanostructures upsurge plenty of additional potential applications as different as detecting and imaging, information capacity and handling, optoelectronics, photovoltaics, optical limiting and switching. Moreover, the investigation of optical phenomena connected with the electromagnetic reaction of metal NPs, which is the subject of this thesis, prompted the improvement of the quickly developing exploration fields like nano-photonics and optoelectronics. The focal point of this thesis lies on the synthesis and optical properties of metallic nanoparticles, specifically the way that they influence or interact with their surroundings and external monochromatic EM radiation and how we can make these occasions productive for the development of the photonic or optoelectronic devices.

The distinctiveness of metals at the nanoscale have attracted scientists from very long time, atomically precise metal nanocluster (NCs) having size < 2 nm are found to be very effective in achieving high photoluminescence (PL) and multiphoton absorption. On the other hand, metal NPs are known for their shape and size dependent surface Plasmon resonance characteristics and their corresponding high local field (LF) that can result in high and versatile nonlinear optical (NLO) response. In recent time, high resolution three–photon absorption (3PA) based biomedical imaging has been demonstrated using 6-aza-2-thiothymine stabilized Au NCs. On the other hand, Au and Ag NPs heterostructures with 2D nanomaterials are found to possess high NLO properties due to the formation of the complex band structure after the formation of the hybrid structures which is not possible in case of single component materials. Therefore, keeping in mind the high potentiality of metal NPs and metal based hybrid nanostructures, elaborated research work is going on in different directions to make this material potentially useful for mankind.

However, in this thesis, by focusing our attention to get high visible PL emission we have carried out the synthesis of aggregation induced enhancement (AIE) type DMF stabilized AuNCs using low cost, environment friendly chemical reduction method. Through the AIE strategy 51 % PL quantum yield (PLQY) has been achieved. These aggregated AuNCs with strong blue emission are utilized as an efficient donor in Förster or fluorescence resonance energy transfer (FRET) based white light generation where DCM dye is used as the acceptor. Finally, designing of a rare earth element free white LED (WLED) is also being demonstrated utilizing this white emitting aggregated AuNC-DCM duo, and with the help of a green emitting nitrogen doped graphene quantum dot, an excellent spectral quality with CIE coordinates of (0.33, 0.32) and CCT of 5620 K is achieved. Also a good emission spectral matching value with AM 1.5 solar spectra, stable emission in long time operation and repeatability of the fabrication process are shown, which showed that the designed WLED will be capable of driving a commercial lighting and display device.

Unlike the discrete electronic band structure in metal NCs, metal NPs shows strong Plasmonic UV-Vis. absorption band. The Plasmon resonance band is the unique and productive characteristic of metal NPs and the apparently countless promise of Plasmonic metal NPs that has sparked a surge of interest in the creation, characterization, and understanding of Plasmon resonances in metal nanostructures. To tune the Plasmonic response of metal NPs people are working to synthesized NPs of different shape and size however, in Chapter 4 we have demonstrated the post synthesis tuning of the Plasmon band of metal nanostructures using the laser ablation (LA) technique by utilizing laser-matter interaction. One can fine tune as well as abruptly tune the plasmon band by changing the interaction time and incident laser fluence.

Interaction of high intensity laser radiation with nanomaterials can alter the optical response of the materials rather it becomes nonlinear in nature. The discrete electronic band structure of metal NCs are found to be suitable for nonlinear multiphoton absorption and it is known that by reducing the size of the NCs or reducing the number of atoms in the NCs we can get high polarizability, ideal for strong NLO response. In Chapter 5 we have demonstrated high 2PA in AuNCs in solution that contains NCs having number of atoms only one or $Au_1$NCs and two or $Au_2$NCs. It is observed that by reducing the number of atoms we have achieved 2PA coefficient of 0.15 cm/GW with very high 2PA cross-section of $9.2 \times 10^4$ *GM* under 532 nm, *fs* pulse excitation. This high 2PA cross-section makes these ultra-small AuNCs useful in optical limiting (OL) application and it shows OL threshold value of 0.009 J/cm$^2$. Furthermore, the NLO response of this AuNCs is found to be highly dependent on the pulse width of the excitation, under *fs* pulse excitation it shows pure 2PA whereas, under *ns* pulse excitation it shows free carrier absorption along with the 2PA.

Metal NCs are showing NLO response based on their quantized electronic band structures whereas in case of metal NPs their NLO responses are known to be govern by their LF. In Chapter 6 we have demonstrated huge enhancement in the LF of triangular shaped AgNPs (TrAgNPs) of edge length around 100 nm when it is being coated with Au (TrAg@Au) of thickness 3 nm. The preparation of such a noble TrAg@Au core-shell nanostructure in simple two step chemical method has been demonstrated here in Chapter 6. It is also being demonstrated that the large LF in the designed core-shell TrAg@Au nanostructure have resulted in the strong reverse saturable absorption (RSA) response originated from the unusual 3PA induced 4PA under 532 nm, *fs* pulse excitation. Whereas under 730 nm, *fs* pulse excitation, intensity dependent smart interplay between saturable absorption (SA) and RSA caused by the linear as well as nonlinear 2PA and 3PA processes, along with the intensity dependent switching behaviour of third- and fifth- order NLO phase between the -ve and +ve mode has been observed. Such interesting NLO response under 730 nm excitation along with the $\chi^{(3)}$ value of $\sim 10^{-11}$ *esu* and $n_2$ value of $\sim 10^{-4}$ *esu* the designed TrAg@Au core-shell nanostructure is demonstrated to be useful in optical switching application. On the other hand, strong RSA behaviour under high intensity under both the 532 and 730 nm excitation makes the designed TrAg@Au core-shell nanostructure suitable for OL application as well.

Two-dimensional nanostructured materials like graphene oxide (GO) often have become one of the materials of choice for their interesting linear and nonlinear optical properties, that comes from its zero-bandgap nature. However, such zero-bandgap nature resulted in a significant amount of linear absorption and there is a constant need to improve its optical nonlinearity to ensure adequate signal output from the devices. In this regard, metals especially the Au and Ag NPs those can significantly influence the optical properties of the surroundings are often being ignored. Here in Chapter 7, we have demonstrated that by integrating Au and AgNPs together with the GO nanosheet (GO_Au_Ag), one can achieve a robust NLO response attributed to the combined 2PA and 3PA process, unlike the only 2PA in the GO nanosheet alone. With this GO_Au_Ag composite we have achieved the $\chi^{(3)}$ value of $\sim 10^{-9}$ *esu* that is found to be two order larger than the $\chi^{(3)}$ value in GO nanosheet only, under 800 nm, *fs* pulse excitation, with repetation rate of 80MHz. This GO_Au_Ag also exhibited remarkable OL performance with OL threshold of $\sim 4.6$ μJ/cm$^2$. Furthermore, people have studied the NLO response of graphene quantum dot (GQD) that is the smaller counterpart of the GO and its modified version such as doping with other elements, to get enhanced NLO response by altering the ratio of $sp^3$ carbon atoms. However here we have demonstrated that making composite of GO with two noble metal NPs is much more favorable to achieved more stronger NLO response that its size reduction.