Chapter 7

This chapter provides a general and comprehensive conclusion of all the chapters.

Conclusion

7.1   General conclusion

This chapter contains the general conclusive remarks drawn from the previous chapters. The general introduction of nanoparticles including historical background, property and applications has been described precisely in the first chapter. The advancement of research in the field of nanoparticle fabrication has been paid an attention. The fabrication of NPs of desired application is one of the challenging deeds in active nano-research. Though plethora of synthetic routes of NP fabrication has been found in literature, yet the colloidal routes are thought to be beneficial for experimentalists due to the user-friendly and candid approach of the methods. Moreover the methods are not only popular for their prudent skill of tuning NPs to preferred size and shape but also functionalizing the surface of NP to make it biocompatible. The quality and the structure of nanoparticles play a pivotal role in determining their functions. Therefore comprehensive characterizations are essential to determine the potentiality of NPs. On this account advanced instrumentations and techniques are required for characterization. In parallel with the experimental techniques theoretical methods have their unique perspectives for precise understanding of the properties that is required for development of new preparation methods for a wide variety of NPs of specific applications. Regarding this, study of electronic structures of NPs to predict their behavior toward various properties is in need. The present study bestows the synergy among the previous aspects that is extended to the field of plasmonics and enlightens the simpler way to achieve the executions.

In the second chapter a brief theoretical framework of the evaluation of optical property of NP has been discussed. Both the classical and quantum mechanical approach have been carried out to explore the optical nature of NPs. For larger NPs (~50 to 200 nm) the classical electrodynamic approach is adapted while for small NPs (~ 1 to 2 nm) quantum mechanical approach is executed. The computational execution to evaluate the nature of surface plasmon resonance of larger NPs has been done by DDSCAT code based on DDA method. For smaller clusters the concept of surface plasmon can be interpreted as density of oscillations in support of TDDFT studies. The excitations in small metal clusters in terms of transitions between distinct molecular states can be manifested by the collective electronic excitations arising from the

oscillations of the valence electrons. The detailed discussion of TDDFT approach along with linear response formalism explores that the implementation of linear-response kernels to TDDFT brings a promising method to calculate the electronic spectra even for extended systems.

The third chapter describes synthesis of $ZnCrO_4$ NPs with controllable morphology in W/O microemulsion template under simple conditions. The synthesized $ZnCrO_4$ particle sizes are in a range of 100 to 200 nm, which is close to the border line dimensions between nano and micro scale. The $ZnCrO_4$ suspensions behave like ordinary solutions obeying Beer's law with molar extinctions which strongly relies upon the water pool size (ω). The enthalpy of the formation of the synthesized $ZnCrO_4$ obtained from ITC was exothermic with the nonlinear dependence on ω. With an appropriate ω, the synthesized $ZnCrO_4$ NPs exhibit good crystallinity with needle-like morphology as revealed by XRD and TEM analysis. The band gap value has been found to be 3.01 eV, which was comparable with many other synthesized nanomaterials.

From fourth chapter, it can be concluded that the Fe_3O_4/Co nanocomposite can be prepared by adapting suggested scheme in the present work. The structure of the as prepared sample has been confirmed through XRD measurement, TEM analysis. The 2θ values appeared in XRD assures the presence of lattice planes of Fe_3O_4, Co and CoFe planes. On the other hand, TEM images have revealed that the monodispersity can be achieved by increasing the precursor concentrations. The fringes appeared in the HRTEM images are well matched with the reflections arise in the SAED experiment. These results unveil the structure of Fe_3O_4/Co nanocomposite, where Co NP is deposited over Fe_3O_4 NP host matrix, with the formation of some CoFe structure. The elemental composition has been confirmed through the EDS spectra analysis. Finally, from the DLS and absorption property analysis, effect of precursor concentration on the progress of reaction, aggregation, stability and size of the colloidal NP has been recognized.

The fifth chapter unravels the effect of surface structure reconstruction and variation in band gap upon their surface plasmon resonance and associated electronic transition of Cu_2O nanoparticles. The SPR peaks are found to be blue shifted with decrease in the size of the

nanoparticles irrespective of the shapes, which is attributed to the increase of Kubo gap. This blue shift of SPR peak is also correlated with surface effect shift due to surface reconstruction during NP formation. As the shape of NP changes the related symmetry and S/V ratio also changes. Lowering of symmetry leads to splitting of degenerate energy levels. This is the reason behind the systematic change in optical response in between nanosphere and nanocube following the symmetry trend. The anomalous nature of optical response in case of cylinder can be explained from the enhancement of the band gap due to the inclusion of significant contribution of S/V ratio. The band gap varies linearly with S/V ratio. As a consequence the cylinder symmetry of Cu_2O NPs are following completely different trend. Irrespective of diameter, the surface plasmon wavelength maximum (λ_{max}) of the cylinder is completely blue shifted compared to sphere and cube. This is due to the largest band gap of the cylinders among the three shapes of same volume.

TDDFT computation is also performed to explore the phenomena of tuning optical response through surface structure reconstruction. The effect of size is traced by increasing the size of $(Cu_2O)_n$ with $n = 1$, 2 and 3, keeping the C_{2v} symmetry intact. On the other hand, the effect of symmetry on absorption is studied for a specific cluster $(Cu_2O)_3$ varying its symmetry from C_{2v} to D_{3h}. The energy gap between occupied and virtual MOs ($\Delta E_{occ\text{-}vir}$), increases with decrease of cluster size from $(Cu_2O)_3$ to $(Cu_2O)_1$. Increase of symmetry leads to the blue shift of peaks, which is realized due to a increase in $\Delta E_{occ\text{-}vir}$. The reconstruction of surface induces the variation in structural parameters due to change in coordination number of the surface atoms. The nature of electronic transition depends on the coordination number of surface atoms. On this account, two types of absorption occur on the surface of Cu_2O NPs. As the coordination number of O atom decrease the absorption becomes LMCT type and with decrease of coordination number of Cu atoms the absorption becomes MMCT type. A similar result of the increase in the size of NP is also tested with clusters of larger and more realistic sizes. The results invariably show the same trend as is observed for smaller clusters. The blue shift in peaks with decrease in size is attributed to the increase of $\Delta E_{occ\text{-}vir}$. Therefore we can conclude that with change of size and symmetry the variation of two major factors play an important role to tune the absorption as well as surface plasmon resonance of Cu_2O nanoclusters.

In the present work, it has been systematically shown that the optical property, i.e., SPR, absorption, and scattering can be tuned by manipulating size and symmetry of Cu_2O nanostructures. Hence, these observations find sophisticated applications in the fields of biosensors, solar cells, photodiodes, photo catalysts etc. With the increment of size of Cu_2O nanospheres the values of scattering coefficients become larger than the gold sphere, which is already employed for the selective imaging of cancer cells. The Cu_2O nanospheres of $D = 140$ nm, 160 nm, 180 nm, 220 nm, and 240 nm have ε_{sca} greater than that of gold NPs. So these size ranges for Cu_2O nanospheres can be used as cell imaging and detection of proteins as reported earlier. Therefore, this work can also guide the selection of appropriate size and shape of nanoclusters with desired band-gap for some specific application.

In the sixth chapter the entire analysis imprints the spectral shift of photoisomerization of 11-*cis* retinal while conjugated to Au_{14} nanoclusters of different symmetries. The red shift in the absorption wave lengths of the conjugates recommends for the photoisomerization occurring in the IR region. This red shift is attributed to the decrease of $E_{occ-vir}$ value in retinal-gold conjugates with respect to free retinal. Furthermore the excited state estimation of the retinal-cluster conjugates warrants for the occurrence of photoisomerization in the IR region. Being the triggering step of the entire mechanism of vision, the red shifting of this photoisomerization process highlights the possibility of vision enhancement to the IR region. The analysis of major excitations reveals that the absorption in retinal-gold conjugates is due to the charge transfer from gold cluster to retinal part. Among all the gold-retinal conjugates, maximum red shifting of the absorption occurs in case of retinal-Au_{14} (O_h). On the other hand, the retinal-Au_{14} (D_{2h}) shows the most intense peak in the absorption profile due to the constructive interference of individual transitions dipole moments. Hence, one can infer this retinal-Au_{14} (D_{2h}) conjugate to be the preeminent elevator of photoisomerization process. The vibrational and subsequent thermochemical analysis of ground states along with the excited states of the conjugates have verified the occurrence as well as spontaneity of photoisomerization of retinal despite of its conjugation with Au_{14} cluster. Finally the speculation of enhancement of vision through the spectral shift of photoisomerization has emerged as the consequence of the entire write up.