SYNTHESIS AND CHARACTERIZATION OF Ag-CEW CLUSTERS SHOWING AGGREGATION INDUCED EMISSION

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by

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2018-2020

CERTIFICATE

*This is to certify that the project report entitled "**SYNTHESIS AND CHARACTERIZATION OF Ag-CEW CLUSTERS SHOWING AGGREGATION INDUCED EMISSION"** is a bonafide work carried out by* **VIDHYA SHAJI,** *M.Sc. Chemistry student, under my supervision and guidance and that no part of this has been submitted for any degree, diploma or other similar titles of recognition under any university.*

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DECLARATION

I **VIDHYA SHAJI** hereby declares that this project report entitled "**SYNTHESIS AND CHARACTERIZATION OF Ag-CEW CLUSTERS SHOWING AGGREGATION INDUCED EMISSION**" is an authentic work carried out during my course of study under the guidance of **Dr. ANU GEORGE,** Associate professor Department of Chemistry, Bharata Mata College, Thrikkakara.

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VIDHYA SHAJI

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INTRODUCTION

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INTRODUCTION

Nanotechnology is an important field of modern research dealing with design, synthesis and manipulation of particles size ranging from approximately 1-100 nm. It also deals with nanomaterial manufacture using nanoparticles. Nanotechnology is rapidly gaining importance in a number of areas such as health care, cosmetics, mechanics, optics, electronics, catalysis, chemical industries etc. It is developed for use in bio sensing, bio- imaging, drug delivery and other biomedical applications. Metal nanostructures are one of the most developed and studied area in nanotechnology mainly nanoparticles and nanoclusters.[1-2]

Nanoparticle is a microscopic particle with a dimension less than 100nm. It has a special place in nanoscience and nanotechnology due to their wide variety of potential application in biomedical,optical and electronic field.They are the promising building block for more complex nanostructures.[3]

1.1 NANOCLUSTERS

Metal nanoclusters are ultra small microscopic particles with a dimension less than 2 nm. They possess unique geometric structures, discrete electronic states and exhibit extremely different chemical and physical properties from their larger counterpart nanoparticles.

Discovery of metal nanoclusters made great changes and extended the horizon of nanomaterial science. In recent years, metal nanoclusters received a great attention due to their excellent luminous and optical properties including large stokes shift, large two photon absorption cross section,good photostability, good biocompatibility and less toxicity.[4] The chemical and physical properties of metal nanoclusters mainly depend on their size, shape and composition. The intense light absorption and emission of nanoclusters is due to their discrete molecular like electronic energy bands.[5]

Recent studies show that among the newly developed metal nanoclusters, silver nanoclusters (AgNC) have a special interest because of their unique chemical, physical and biological properties which make it an excellent platform to develop theranostic agents for biomedical application.[6-8] AgNCs are a class of fluorophores with attractive properties including brightness, photostability etc. Proteins, polymers, dendrimers, DNA oligomers are different scaffolds used to stabilize AgNCs.[9] Proteins possess abundant binding sites that can potentially bind and can further reduce Ag ions, thus offering scaffolds for template driven formation of fluorescent AgNCs. They have a great potential for a variety of application in biosensing, biolabelling,biomedicines, photosensitizer, designing optical sensors.[10]

1.2 TYPES OF NANOCLUSTERS

1.2.1 MAGNETIC NANOCLUSTERS

Nanoclusters that are formed from inert gas atoms which are weakly bound by the vander waals forces are called van der waals nanoclusters. The long range atomic attraction is due to the induced dipole force. Short range repulsion is due to the quantum closed shell electronic interaction and the binding energy per atom is less than 0.3 eV. Rare gases form vander waals cluster with icosahedral shapes.

1.2.2 IONIC NANOCLUSTERS

Ionic nanoclusters are formed from ions which are attracted by the electrostatic force. NaCl is a typical example of an ionic cluster. Electrostatic bonds in ionic clusters are around 2-4eV per atom. It is ten times stronger than van der waals nanocluster. Ionic clusters tend to be more stable, if they have a completed cube shape.

1.2.3 METAL NANOCLUSTERS

Metal nanoclusters are ultra small particles with core size less than 2 nm. They are more complicated in their bonding. Some metals bond primarily by the outer valence sp electrons. Some others bond with d orbitals. These d orbital materials include Fe, Co and Ni.[11]

1.3 PROPERTIES OF METAL NANOCLUSTERS

1.3.1 MAGNETIC PROPERTIES

Metal nanoclusters possess magnetic properties. When atom combine together to form a nanocluster, their magnetic moment aligned to form a net magnetic moment for nanocluster. Since most of the atoms in nanoclusters are surface atoms, it is expected that the magnetic moment of an atom in a cluster will be larger than the bulk. The magnetic moment in nanoclusters are enhanced by the lower coordination and low dimensionality. The magnetic properties of metal nanoclusters show some variations.

1.3.2 REACTIVITY PROPERTIES

Nanoclusters have a unique reactivity due to their large surface to volume ratios and low coordination of surface atoms. They are widely used as catalysts. AuNC is an excellent example of a commonly used catalyst. Bulk Au is chemically inert, when it is scale down to nanometer it becomes highly reactive. Electron affinity is the property that governs nanocluster reactivity.[12]

1.3.3 OPTICAL PROPERTIES

Nanoclusters potentially have unique optical properties. Optical properties of materials are determined by their electronic structure and band gap. Nanoclusters are made-up of few tens of atoms and hence the electronic band structure gets modified to discrete electronic states as a result of quantum confinement. As a result, the electronic structure and the optical properties of nanoclusters are entirely different from metallic nanoparticles of the same element. Metallic nanoparticles with size >3 nm (comparable to the de Broglie wavelength of the conduction electrons) show surface plasmon due to the excitation of metal surface electrons by electromagnetic radiation in the Visible region. But for the nanoclusters, the core size is around 1 nm, consequently the electronic bands will no longer exist and the band structure will resolve into discrete energy levels. These electronic energy levels resemble that of the organic molecules such as benzene and therefore the nanoclusters can be treated as molecular entities. Nanoclusters have outstanding optical properties including large stokes shift, large two photon absorption, good photostability and good biocompatibility.[13]

1.3.4 PHOTOLUMINESCENCE PROPERTIES OF NANOCLUSTERS

Luminescence from monolayer protected nanocluster in the Visible region of the electromagnetic radiation was first reported by Huang and Murray. The luminescence quantum yield of gold QCs synthesized so far ranges approximately from 70% to 0.1%. The emission wavelength of such QCs can be tuned by changing the core size, which can be can be modified by controlling the amount of gold to PAMAM ratio. Typically, smaller QCs emit in the lower wavelength and higher QCs emit in the higher wavelength with reasonably low quantum yield. The emission energies of these

QCs can be expressed by the Jellium model. Among the QC family, the monolayer protected QCs are known to show characteristic optical absorption features. In such QCs, there is a covalent linkage between metal core and ligands and they emit in the NIR region with relatively low quantum yield. In the case of monolayer protected QCs, the emission originates from radiative intraband transitions within the sp bands, across the HOMO–LUMO gap. And hence, as the size of the cluster decreases, the spacing between the discrete states increases.

Since the QCs are luminescent, they are promising candidates for biology-related experiments such as imaging. They have several advantages over other conventional imaging materials such as organic fluorophores and semiconductor quantum dots. While organic fluorophores are prone to photo bleaching, QCs are found to be highly photostable. Fluorescent semiconductor quantum dots are generally composed of toxic elements such as Cd and Pb. Hence, they have to be coated with other inorganic or biological molecules to reduce their toxicity. On the other hand, QCs that are composed of gold atoms are likely to be biocompatible. Moreover, the cytotoxicity of the QCs is very low due to their low metallic content.[14]

1.3.4.1 AGGREGATION INDUCED EMISSION

Most of the organic molecules due their strong pi pi interaction, undergo Aggregation induced quenching (ACQ) when their molecules are aggregated. The ACQ effect greatly limits their use in fields such as organic light emitting diodes (OLEDs) and organic nano-dots for bio-imaging, because the emission is often quenched when the organic dyes are used as solid films or in the aggregate state. Because conventional organic luminophores usually possess planar aromatic cores which favour the occurrence of pi–pi stacking when aggregated, the ACQ effect is very common and becomes the accepted belief. In 2001, a new concept called ‘‘aggregation-induced emission (AIE)’’ was first proposed by Tang *et al*.

Unlike conventional ACQ dyes, AIE luminogens (AIEgens) show weak or negligible emission in dilute solution but emit intensely in the aggregate or solid state AIE is thus the exact opposite of ACQ. AIE research has now gained extensive attention and AIEgens have been recognized as an important type of advanced functional material for a wide variety of applications. restriction of intramolecular motions (RIM) has been generally accepted as central to the AIE working mechanism. According to the RIM mechanism, it can be concluded that structural rigidification in high viscosity media, low temperature, and doping of chromophores in rigid matrices can also lead to strong emission. As AIEgens often show unique advantages such as high solid quantum yield, high photostability and no ACQ effect, they have been successfully applied in various fields such as OLEDs, stimuli responsive sensing, bioimaging and theranostics.

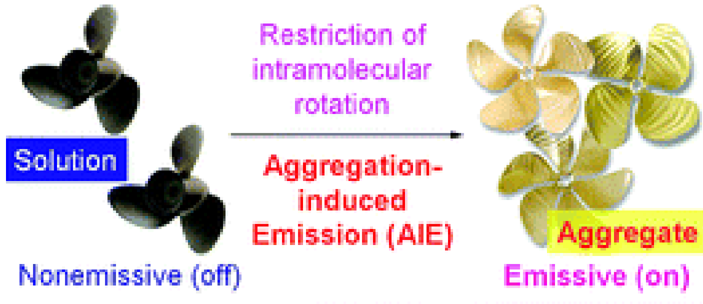

Figure 1.1: Schematic representation showing the mechanism od aggregation induced emission in organic fluorophores.[15]

Many nonconventional AIE systems have been reported to date, which is very interesting and greatly broadens the research scope of AIE. Auto-fluorescence in biological samples has long been thought to originate from proteins containing tryptophan, tyrosine and phenylalanine or the biomolecules such as NADPH and flavins. However, the studies of nonconventional AIE systems may suggest other probable origins. Novel concepts of CTE and ‘‘clusteroluminogens’’ have been proposed to describe these phenomena and materials. However, the mechanisms behind different nonconventional AIE systems are still not clear. Although the formation of new chromophores by through space conjugation after clustering provides a promising hypothesis to explain some of the systems

1.4 SYNTHESIS OF NANOCLUSTERS

Nanoclusters are synthesized by physical and chemical methods. Both methods have some advantages and disadvantages.

1.4.1 GAS AGGREGATION

This method is commonly used to synthesize large clusters of nanoparticles. In this method, the metal is vaporized and introduced into a flow of cold inert gas.Thus the vapors of metal become highly supersaturated.

1.4.2 LASER VAPORIZATION

Nanoclusters of various sizes and polarity can be synthesized by this method. Pulse laser is used to vaporize the target metal rod and the evaporated metal vapor is cooled by using He gas, which causes the cluster formation.

1.4.3 ION SPUTTERING

Ion sputtering source produces an intense continuous beam of small singly ionized clusters of metal. In this method, cluster ion beams are produced by bombarding the surface with high energetic inert gases such as Ar, Kr, Xe etc.

1.4.4 CHEMICAL REDUCTION METHOD

Nanoclusters can be prepared by reduction method. In chemical method, metal precursor, reducing agent and stabilizing/capping agents are used. The advantage of chemical method is high yield, ease of production and low cost.[16]

1.5 APPLICATIONS OF NANOCLUSTERS

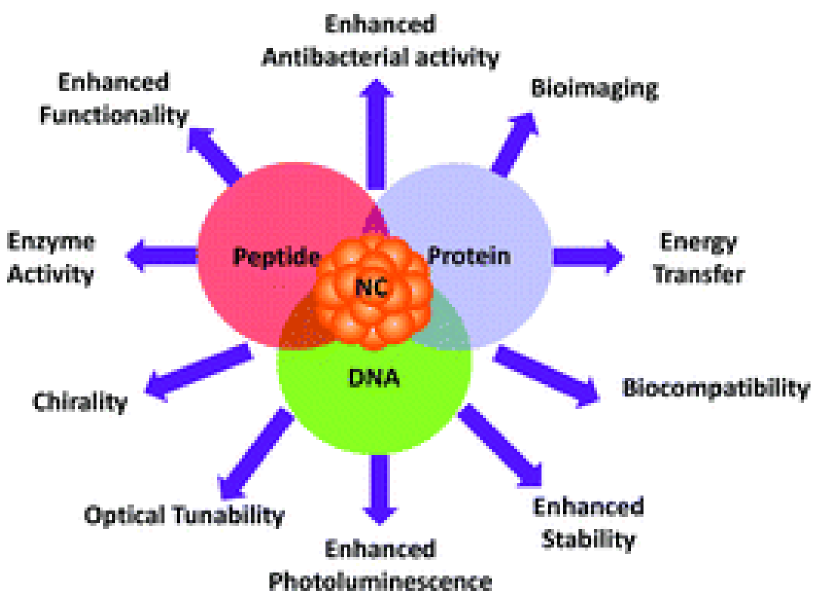

Figure 1.2: Schematic representation showing the various applications of nanocusters.[17]

1.5.1 BIOMEDICAL APPLICATIONS

*(a) **Antibacterial Activity***

Metal nanoclusters have been extensively developed to inhibit and reduce the growth of bacteria.

AgNCs with core size less than 2nm exhibit superior antibacterial activity towards a wide spectrum of bacteria. The high antibacterial efficacy of ultra small AgNCs,together with their unique chemical property could make them useful for disinfection application in variety of consumer products and medical devices.Compared to nanoparticles, AgNCs have high surface to volume ratio and more active atoms. So they possess higher antibacterial efficacy.

(b) ***Biosensing***

AgNCs exhibit strong luminescence and unique chemical properties.Due to this properties, AgNCs have recently emerged as a promising luminescent probe for optical sensor development. Red emitting AgNCs has a good luminescent probe to detect a biothiol, cysteine featuring selectivity and sensitivity.

(c) ***Bioimaging***

Bioimaging is a very powerful technique for localization and dynamic monitoring of biomolecules in living systems. The strong luminescence of AgNCs could also be used for bioimaging and biolabelling application. Luminescent AgNCs protected by GSH were used for the imaging of epithelial lungs cancer cells.The strong luminescence and good stability of AgNCs make them good luminescent probes for bioimaging and biolabelling application.

(d) ***Biological Analysis***

Metal nanoclusters can also be applied in detection of label free detection of small biomolecules such as urea, dopamine, glucose, biological thiols and also for protein detection, nucleic acid detection and microRNA detection.[18]

1.5.2 THERAPEUTIC APPLICATION

(a) ***Cancer Therapy***

Optical imaging guided cancer therapy is a promising technology for simultaneous tumor imaging and treatment. Metal nanoclusters have great potential for application in imaging guided cancer therapy, due to their excellent optical properties.

(b) Gene Therapy

Gene therapy also provides a promising paradigm for combating many serious diseases such as cancer and genetic disorder. Many metal nanoclusters have been successfully applied in gene therapy.

(c) Diabetes Treatment

Insulin directed fluorescent AuNCs show excellent biocombatibility and retained the insulin bioactivity. The excellent property of insulin-AuNCs to retain bioactivity in reducing blood glucose implied that insulin-AuNCs had the potential to be applied as diabetes medicine.[19]

1.6 AIMS AND OBJECTIVES

AIM

To synthesize silver nanoclusters using a protein mediated green protocol and to study the influence of the protein in the synthesis of silver nanoclusters and its optical and luminescent properties.

OBJECTIVES

The reduction and stabilizing property of Chicken Egg White (CEW) helps the synthesis of silver nanoclusters. Protein stabilized clusters are well known for their emission properties. These interesting properties can make these clusters an ideal candidate for several applications such as imaging, sensing etc. Moreover, the emission from these clusters in the solid state makes these clusters an interesting candidate for solid state device applications.

CHAPTER 2

EXPERIMENTAL SECTION

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EXPERIMENTAL SECTION

2.1 MATERIALS

Chemicals required for the synthesis of AgNCs were analytical grade and were commercially obtained.

- Silver Nitrate ($AgNO_3$)
- Fresh chicken egg white solution
- Sodium Hydroxide (NaOH)

2.2 SYNTHESIS OF PROTEIN STABILIZED SIVER NANOCLUSTERS

The synthesis of AgNCs was performed following a reported procedure related to the synthesis of gold nanoclusters.[20] In this typical experiment, 5.0 mL of 1mM $AgNO_3$ solution was added to 5.0 mL of fresh chicken egg white solution (diluted using H_2O, 1:1) at room temperature. The solution became turbidity immediately. It was then mixed for 2 minutes. Subsequently, 1.0 mL of 1.0 M NaOH was added into the reaction mixture and the colour became colourless immediately. Then, the resulting solution was left undisturbed at room temperature for 24 hours incubation and became light pale yellow. Clusters were precipitated using ethanol at low temperature. The as obtained precipitate was separated and dries for further analysis. This reaction was optimised by changing the metal concentration resulting in different coloured solution (Figure 2.1)

Samples	Metal Concentration	Colour Change
CEW@Ag I (a)	10 mM AgNO3	Reddish brown
CEW@Ag II (b)	5 mM AgNO3	Pale yellow
CEW@Ag III (c)	1 mM AgNO3	Light pale yellow

Table 2.1: Experimental parameters for the synthesis of silver nanoclusters.

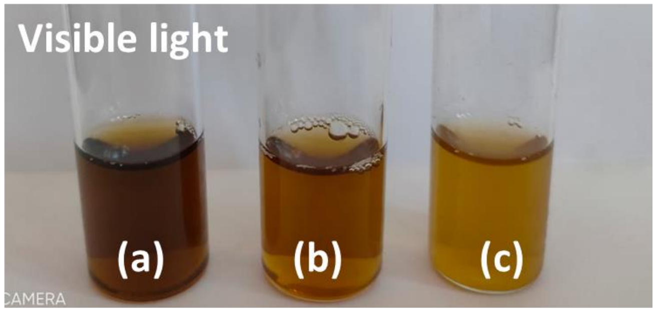

Figure 2.1: Photograph of silver nanoclusters prepared at different metal concentrations

2.3 CHARACTERIZATION TECHNIQUES

Various high- techniques have been used for the optical characterization of synthesized metal nanoclusters. The characterization techniques including UV-Visible spectroscopy and photoluminescence spectroscopy.

2.3.1 UV- VISIBLE SPECTROSCOPY

Ultraviolet-Visible spectroscopy (UV-Vis) refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet-Visible spectral region. This means it uses light in the Visible and adjacent (near-UV and near-infrared (NIR)) ranges. The absorption or reflectance in the Visible range directly affects the perceived color of the chemicals involved. In this region of the electromagnetic spectrum, molecules undergo electronic transitions. This technique is complementary to fluorescence spectroscopy, in that fluorescence deals with transitions from the excited state to the ground state, while absorption measures transitions from the ground state to the excited state.

It measures the intensity of light passing through a sample (I), and compares it to the intensity of light before it passes through the sample (Io) according to the Beer-Lambert's law.

$$A = \log_{10} (I_0/I) = \epsilon.c.L$$

where A is the measured absorbance, I_0 is the intensity of the incident light at a given wavelength, I is the transmitted intensity, L the pathlength through the sample, and c the concentration of the absorbing species. For each species and wavelength, ε is a constant known as the molar absorptivity or extinction coefficient. Absorbance usually ranges from 0 (no absorption) to 2 (99% absorption), and is defined in context with spectrometer operation.

Optical absorption spectra were collected in Perkin-Elmer Lambda 25 spectrophotometer. The experiments were carried out at room temperature and the absorption spectra were recorded. from 200 to 1100 nm.

2.3.2 PHOTOLUMINESCENCE SPECTROSCOPY

Fluorescence spectroscopy is a type of electromagnetic spectroscopy which analyzes fluorescence from a sample. It involves using a beam of light, usually ultraviolet light, that excites the electrons in molecules of certain compounds and causes them to emit light of a lower energy, typically, but not necessarily, Visible light. It is primarily concerned with electronic and vibrational states. Generally, the species being examined has a ground electronic state (a low energy state) of interest, and an excited electronic state of higher energy. Within each of these electronic states are various vibrational states. The molecule then drops down to one of the various vibrational levels of the ground electronic state again, emitting a photon in the process. As molecules may drop down into any of several vibrational levels in the ground state, the emitted photons will have different energies, and thus frequencies.

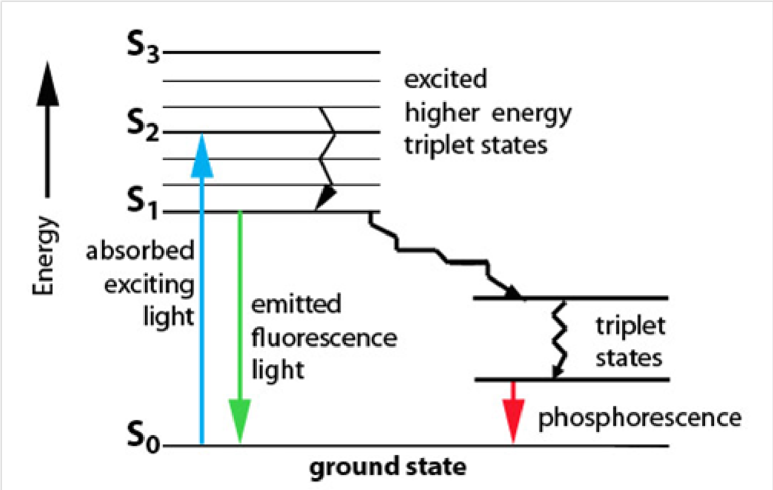

Figure 2.2: Schematic of the electronic processes responsible for the fluorescence.

The different wavelengths of fluorescent light emitted by a sample are measured using a monochromator, holding the excitation light at a constant wavelength. This is called an emission spectrum. An excitation spectrum is the opposite, whereby the emission light is held at a constant wavelength, and the excitation light is scanned through many different wavelengths (via a monochromator).

The photo excitation and luminescence studies were done using a NanoLog HORIBA JOBINYVON spectrofluorimeter.

CHAPTER 3

RESULTS AND DISCUSSION

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Silver nanoclusters were synthesized using a chemical reduction method using egg white acting as both stabilizing and reducing agent. The as synthesized cluster was dissolved in water and characterized using UV Visible spectroscopy. The cluster solution shows a weak absorption at around 300 nm and a strong absorption at 275 nm from the cluster and the protein respectively.

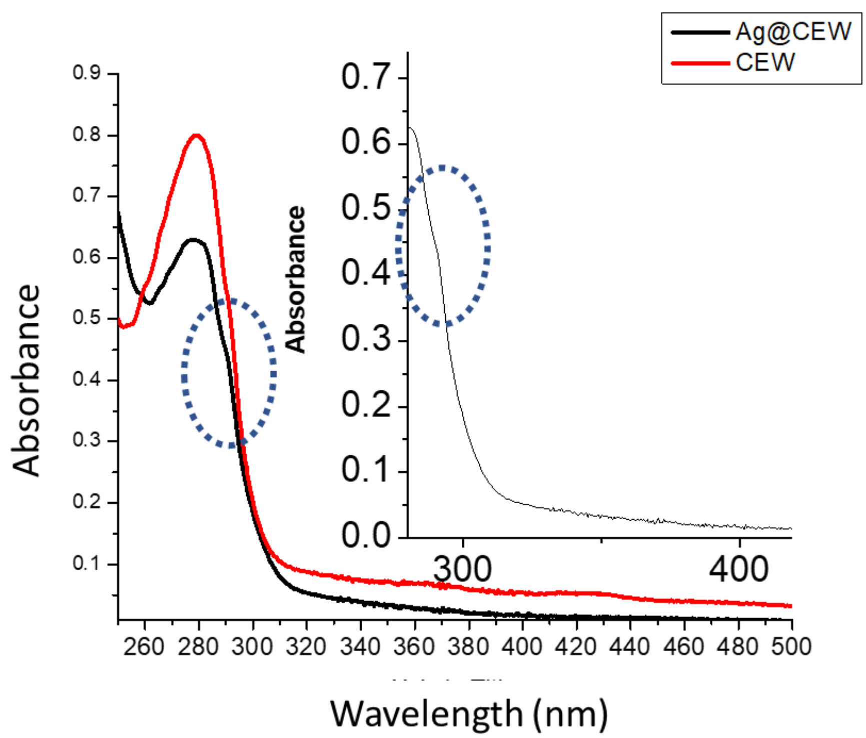

Figure 3.1: UV Visible spectrum of Ag@CEW and CEW (Inset shows the absorption from the cluster).

Another interesting property of these clusters was their highly emissive nature. The as synthesized nanoclusters show green emission in the solution as well as solid state. This emissive property was tuned by changing the metal concentration of the nanocluster. The emission intensity was enhanced on decreasing the concentration of the metal ion which was taken for further luminescence studies (Figure 3.2).

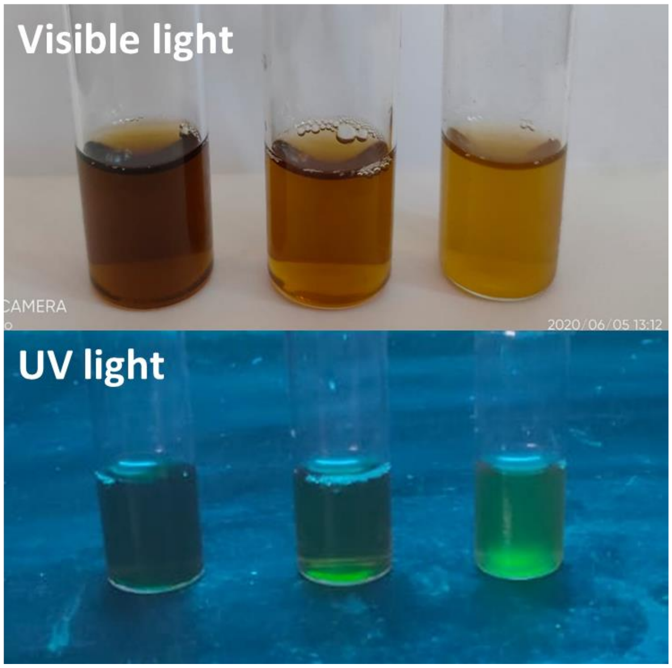

Figure 3.2: Photograph of the silver cluster at different concentration of metal ion (Metal ion concentration decreases from left to right)

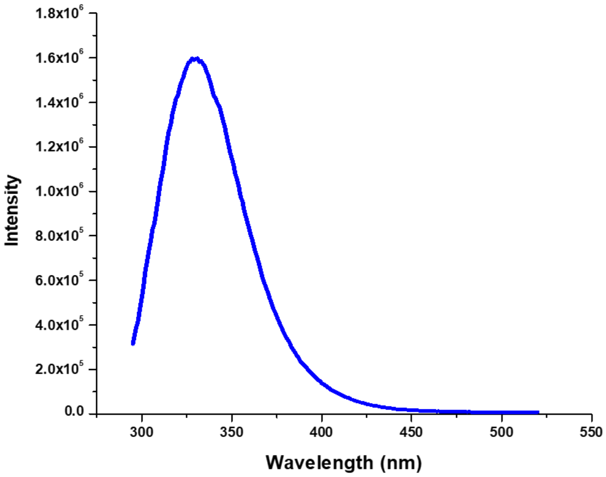

Figure 3.3: Fluorescence spectrum of Ag@CEW clusters

Florescence spectra of the as synthesized cluster was collected which shows a broad emission at around 340 nm (Figure 3.3) for an excitation at 280 nm.

As mentioned earlier, these clusters were highly emissive even in the solid state which was quite interesting property useful for solid state applications.

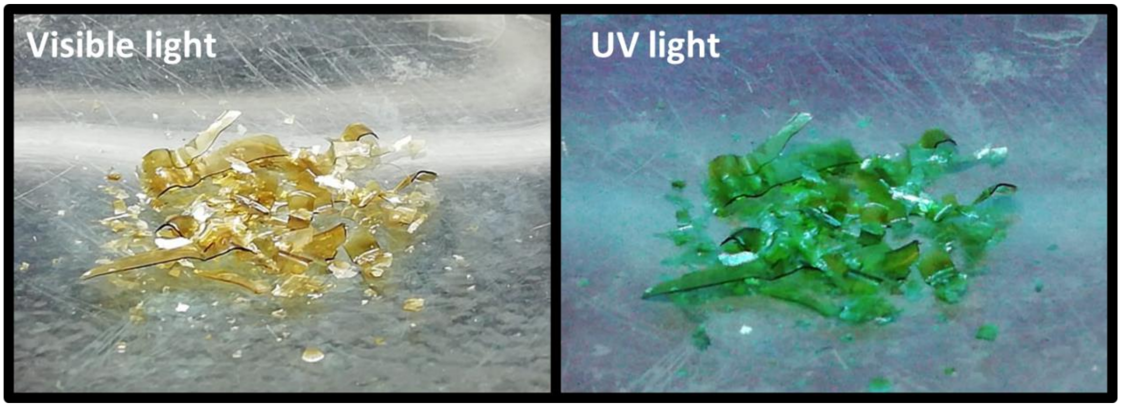

Figure 3.4: Photograph of Ag@CEW clusters in the solid state

Solid state emissions contradict the normal aggregation induced quenching (ACQ) phenomenon. Aggregation Induced Emissive luminogens (AIEgens) are a class of materials that are weakly emissive or non-emissive in dilute solutions (i.e., isolated molecular species) but emit particularly strong fluorescence in the aggregated and solid states. So far, the restriction of intramolecular motions (RIM), including both the restriction of intramolecular rotations (RIR) and the restriction of intramolecular vibrations (RIV), is regarded as the primary mechanism to interpret the AIE phenomenon.

To study the aggregation phenomenon in the solution state, the emission behaviour of these clusters was observed at different concentrations. As the concentration of the as synthesized cluster increases, the emission intensity also increases. Generally, when the concentration increases, the molecules come closer and the emission from one molecule can be reabsorbed by the adjacent molecule. This process is known as self-quenching. Due to self-quenching, the emission intensity decreases as the concentration increases. But in the case of Ag@CEW clusters, reverse phenomenon was observed due to aggregation induced emission property.

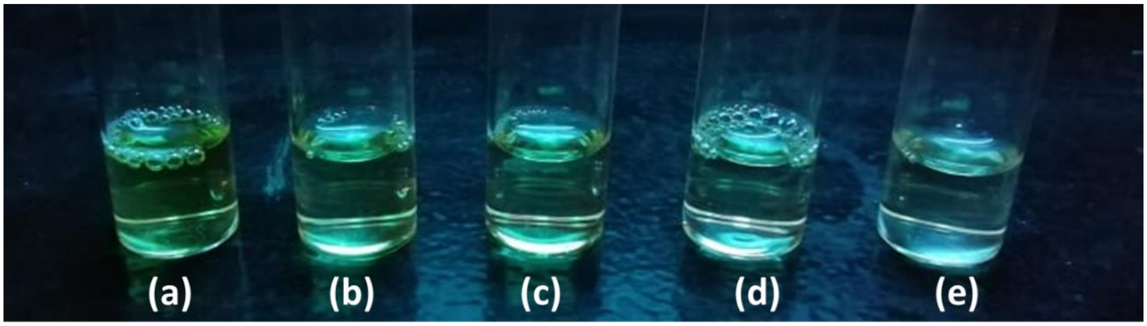

Figure 3.5: Photograph of Ag@CEW cluster at different concentration under UV light.

In order to examine this phenomenon, the as synthesized cluster was dissolved in water in five different concentrations. The concentration of the solution decreases from (a) to (e) as shown in figure 3.5. As the concentration decreases from (a) to (e), the emission also decreased. This resulted in the high emissive nature of these clusters in solid state. This emission property can be utilized for various applications such as light emitting diodes, luminescent concentrators etc.

CHAPTER 4

CONCLUSION

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CONCLUSION

Egg white protected silver nanoclusters were synthesized using a facile green protocol. The egg white protein helps the stabilization and the reduction of the cluster. This dual property of egg white overcome the adverse effects of using toxic reducing agents. The clusters were characterized using UV Visible and fluorescence spectroscopy. Ag@CEW shows a broad absorption at around 300 nm and a broad emission at around 340 nm. This green emission was observed both in the solution state as well as the solid state. The highly emissive nature of these clusters on increasing the concentration due to aggregation induced emission property makes these clusters a suitable candidate for solid state applications.

BIBLIOGRAPHY

1. M. Shellaiah, K.W Sun, *chemosensors.* 5 (2017) 36-40.
2. D.J.Barber, I.C.Freestone, *Archaeometry*. 32 (1990) 33-45.
3. H.Xu, K.S.Suslick, *ACSNano.* 4 (2010) 3209-3214.
4. T.Q.Yang, B. Q. Shan, Y. X. Zong, J. G. Jiang, P. Wu, K. Zhang, *Nanomaterial*. 10 (2020) 261-264.
5. I.Diez, R. H. Ras, *Nanoscale*. 3 (2011) 1963-1970.
6. L.Shang, S. Dong, G. U. Nienhaus, *Nano Today*. 6 (2011) 401-418.
7. L.Zhang, E. Wang, *Nano Today*. 9 (2014) 132-157.
8. B.Han, X. Hu, M. Yu, T. Peng, Y. Li, G. He, *RSC Adv*. 8 (2018) 22748-22752.
9. I.Diez, M. I. Kanyuk, A. P. Demochenko, A. Walther, H. Jiang, D. Ikkula, R. H. Ras, *Nanoscale*. 4 (2012) 4434-4437.
10. R. Lu, D. Yang, D. Cui, Z. Wang, L. Guo, *Int. J of nanomedicine.* 7 (2012) 2101-2107.
11. Bondybey, V. E, J. H. English, *J. Chem. Phys.* 76 (1982) 2165-2168.
12. Y. Z. Lu, W. T. Wei, W. Chen, *Sci. Bull.* 57 (2012) 41-47.
13. M. Liu, W. Chen, *Nanoscale.* 5 (2013) 12558-12564.
14. K. Zheng, X. Yuan, N. Goswami, Q. Zhang, J. Xie, *RSC Adv.* 4 (2014) 60581-60596.
15. Y. Hong, J. W. Y. Lam, B. Z. Tang, *Chem. Commun.* (2009) 4332-4353
16. A. V. Rane, K. Kanny, V. K. Abitha, S. Thomas, *J. Mater. Sci.* 9 (2004) 3211-3212.
17. Nirmal Goswami, Kaiyuan Zheng, Jianping Xie, *Nanoscale*, 6 (2014), 13328-13347.
18. S. H. Lee, B. H. Jun, *Int. J. Mol. Sci.* 20 (2019) 865-869.
19. Y. Tao, M. Li, J. Ren, X. Qu, *Chem. Soc. Rev.* 44 (2015) 8636-8663.
20. M. Li, D. P. Yang, X. Wang, J. Lu, D. Cui, *Nanoscale Research Letters.* 8 (2013) 182-186.