

**SYNTHESIS AND CHARACTERIZATION
OF FLUORESCENT COPPER NANOCLUSTER**

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In

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By

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Under the Guidance of

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DEPARTMENT OF CHEMISTRY
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2017 - 2020



**DEPARTMENT OF CHEMISTRY
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THRIKKAKARA**

CERTIFICATE

This is to certify that the project report entitled “**SYNTHESIS AND CHARACTERIZATION OF FLUORESCENT COPPER NANOCLUSTER**” is a bonafide work carried out by **ANJANA JOY** B.Sc. Chemistry Student in partial fulfilment of the requirement for the award of the degree of Bachelor of Science in Chemistry

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**DEPARTMENT OF CHEMISTRY
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This is to certify that the dissertation entitled “**SYNTHESIS AND CHARACTERIZATION OF FLUORESCENT COPPER NANOCLUSTER**” submitted in partial fulfilment of the requirement for the award of the degree of Bachelor of Science in chemistry to Mahatma Gandhi University, Kottayam is authentic record of work carried out by **ANJANA JOY** under my guidance and supervision.

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DECLARATION

I **ANJANA JOY** hereby declare that this project report entitled “**SYNTHESIS AND CHARACTERIZATION OF FLUORESCENT COPPER NANOCUSTER**” is bonafide work carried out during my course of study under the guidance of **Dr. ANU GEORGE**, Assistant Professor , Department of Chemistry , Bharata Mata College , Thrikkakara

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1. INTRODUCTION

1.1 NANOSCIENCE AND NANOTECHNOLOGY

Nanotechnology, in its traditional sense, means building things from the bottom up, with atomic precision. This theoretical capability was envisioned as early as 1959 by the renowned physicist Richard Feynman. Nanotechnology deals with small structures or small-sized materials. The typical dimension spans from subnanometer to several hundred nanometers. Nanotechnology is very diverse, ranging from extensions of conventional device physics to completely new approaches based upon molecular self-assembly, from developing new materials with dimensions on the nanoscale to investigate whether we can directly control matter on the atomic scale. Materials in the micrometer scale mostly exhibit physical properties the same as that of bulk form. However, materials in the nanometer scale may exhibit physical properties distinctively different from that of bulk, such as a transition from atoms or molecules to bulk form takes place in this size range. Two principal factors cause the properties of nanomaterials to differ significantly from other materials are increased relative surface area, and quantum effects. These factors can change or enhance properties such as reactivity, strength and electrical characteristics.¹

1.2 NANOPARTICLES

Nanoparticles are particles between 1 to 100 nm size ranges. They display properties different from atomic and bulk matters. The unique physical properties shown by nanoparticles are often dictated by their size, shape and surface characteristics, for example lower melting points, higher specific surface areas, and specific magnetizations. Metal nanoparticles are efficient candidates as catalysts; their small size and particular electronic configuration make them extremely active catalysts. In general, nanoparticles have different physical and chemical properties from bulk metal (e.g. lower melting point, higher specific surface areas, specific optical properties, mechanical strength and specific magnetizations) properties that might prove attractive in various industrial applications.²⁻⁵ So far, numerous wet-chemistry methods, including the reduction of metal precursors in solution-phase, in microemulsions, or in the sol-gel process, have been developed to obtain metallic nanoparticles with well-defined morphologies. Metal nanoparticles may be stabilized by the addition of polymers, surfactants or ligands which allows controlling of their size, shape and dispersion and also their surface state. Consequently, an adequate choice of the stabilizer should allow the tuning of the surface properties and therefore, the catalytic reactivity.

1.3 NANOCLUSTERS

Nanoclusters come under the umbrella of nanoparticles. Nanoclusters are known as the bridging link between atoms and nanoparticles. Metal nanoclusters consist of a small number of atoms, at most in the tens these nanoclusters can be composed either of a single or multiple element, and typically measure less than 2nm.⁶⁻⁹ Such nanoclusters exhibit attractive electronic, optical and chemical properties compared to their

larger counterparts. Due to the very small size, they exhibit molecular transitions in absorption and emission and are totally different from the conventional metallic nanoparticles possessing surface plasmon resonance, and different synthetic approaches have been followed to make them. The concept of atomic nanoclusters dates to prehistoric times. The formation of stable nanoclusters such as Buckminsterfullerene (C_{60}) has been suggested to have occurred during the creation of the universe. The first set of experiments to form nanoclusters can be traced back to the 1950s and 1960s. During this period, nanoclusters were produced from intense molecular beams at low temperature by supersonic expansion. The development of laser vaporization technique made it possible to create nanoclusters of a clear majority of the elements in the periodic table. Since the 1980s, there has been tremendous work on nanoclusters of semiconductor elements, compound clusters and transition metal nanoclusters. Nowadays nanoclusters are synthesized using a wet chemical method by optimising the experimental parameters such as concentration of metal, ligand and reducing agent. Temperature is also a crucial parameter to control the formation of nanoclusters in the sub nanometre range.

1.4 APPLICATIONS OF NANOCLUSTERS

Nanoclusters have many areas of application as they have unique optical, electrical, magnetic and reactivity properties. Nanoclusters are biocompatible, ultrasmall and exhibit bright emission, hence promising candidates for fluorescence bioimaging or cellular labelling.¹⁰ Nanoclusters along with fluorophores are widely used for staining cells for study both in vitro and in vivo. Furthermore, nanoclusters can be used for sensing and detection applications. They can detect metal ions in an aqueous solution based on fluorescence quenching. Also, many small molecular biological entities such as biomolecules, proteins, DNA, RNA can be detected using nanoclusters. The unique reactivity properties and the ability to control the size and number of atoms in nanoclusters have proven to be a valuable method for increasing activity and tuning the selectivity in a catalytic process.

1.5 COPPER NANOCLUSTERS

Non-noble metal Cu is earth-abundant, much lower cost and widely used in industry. Thereby, development of copper nanoclusters has been attracting more and more attention. Copper nanoclusters (Cu NCs) have emerged as a valuable member of the family of ligand-protected few-atomic metal nanoparticles and show fascinating properties of colour-controlled light emission, combined with the advantages of versatile solution-based chemical synthesis at low cost. Synthetic methods of Cu NCs using various types of functional ligands and scaffolds allow tuning their emission wavelength and improving their environmental stability. Depending on the method of preparation and the ligands used, Cu NCs have already been applied for a wide variety of applications in catalysis, sensing, bioimaging, theragnostic and optoelectronics. Recently, several studies have been successfully proposed for the synthesis and application of CuNCs.^{11,12} For example, a polyethyleneimine (PEI)-coated CuNCs was prepared in water solution and further employed

for the quantification of Sudan dyes.¹³ Moreover, tannic acid capped CuNCs and their application for Hg²⁺ sensing was reported.¹⁴ Similarly, L-cysteine protected CuNCs was employed for assaying Fe³⁺.¹⁵ Again, D-penicillamine (DPA) stabilized CuNCs with an aggregation induced emission feature has been explored for pH sensing and catalysis applications.¹⁶

1.6 OBJECTIVES

Glutathione (GSH), playing roles as both a reducing reagent and protecting ligand, can be successfully employed for synthesizing Cu nanoclusters (CuNCs@GSH) on the basis of a simple and facile approach. This helps to synthesize Cu nanoclusters by a one pot wet chemical method. The emission from these clusters at longer wavelength is very important for applications like fluorescence imaging, metal sensing etc. In an acidic environment, glutathione can effectively reduce and stabilize the copper nanoclusters.

2. EXPERIMENTAL SECTION

2.1 MATERIALS

- Copper sulfate (CuSO₄)
- Reduced Glutathione
- Sodium Hydroxide

2.2 SYNTHESIS

The synthesis of copper nanoclusters was performed following a reported procedure.¹⁷ As a typical experiment, 5.0 mL of GSH solution (50 mg mL⁻¹) was added into 5.0 mL of CuSO₄ solution (10 mM). The transparent solution changed to white suspension liquid. Then, a NaOH solution (1M) was added dropwise until the turbid liquid turned to transparent light yellow, and the corresponding pH value was 4-5. Subsequently, the solution was stirred vigorously at 37 °C for 1 h and the products were centrifuged. The white powder was separated and repeatedly washed.

2.3 CHARACTERIZATION TECHNIQUE

2.2.1 Optical Absorption Spectroscopy (UV/VIS)

UV/VIS spectroscopy is one of the most widely used techniques for structural characterization of silver nanoparticles. The UV/VIS spectrometer consists of light source, monochromator, detector, amplifier and

recording devices. A spectrophotometer can be either single beam or double beam. Most commonly double beam instruments are used. In a double-beam instrument, the light is split into two beams before it reaches the sample. One beam is used as the reference; the other beam passes through the sample. The reference beam intensity is taken as 100% transmission (or zero absorbance), and the measurement displayed is the ratio of the two beam intensities. Some double-beam instruments have two detectors (photodiodes), and the sample and reference beam are measured at the same time. In other instruments, the two beams pass through a beam chopper, which blocks one beam at a time. The detector alternates between measuring the sample beam and the reference beam in synchronism with the chopper. The spectrum usually plotted is absorbance versus wavelength.

3. RESULTS AND DISCUSSION

Copper nanoclusters were synthesized using glutathione as both stabilizing and reducing agent. Glutathione is a tri-peptide (L-g-glutamyl-L-cysteinyl-glycine) that acts as both reducing agent and capping agent, which assemble on the surface of copper nanoclusters via a stable copper-thiol linkage (from cysteine) and imparts the nanoclusters with a net negative surface charge due to the presence of terminal carboxylic acid functional groups. The reaction completed in one hour resulting in a red emissive copper nanocluster dispersion. These clusters appear pale yellow in the visible light but are red emissive under the UV light. (Figure 1) This emissive behaviour confirms the formation of the copper nanoclusters due to the sub nanometre size range.

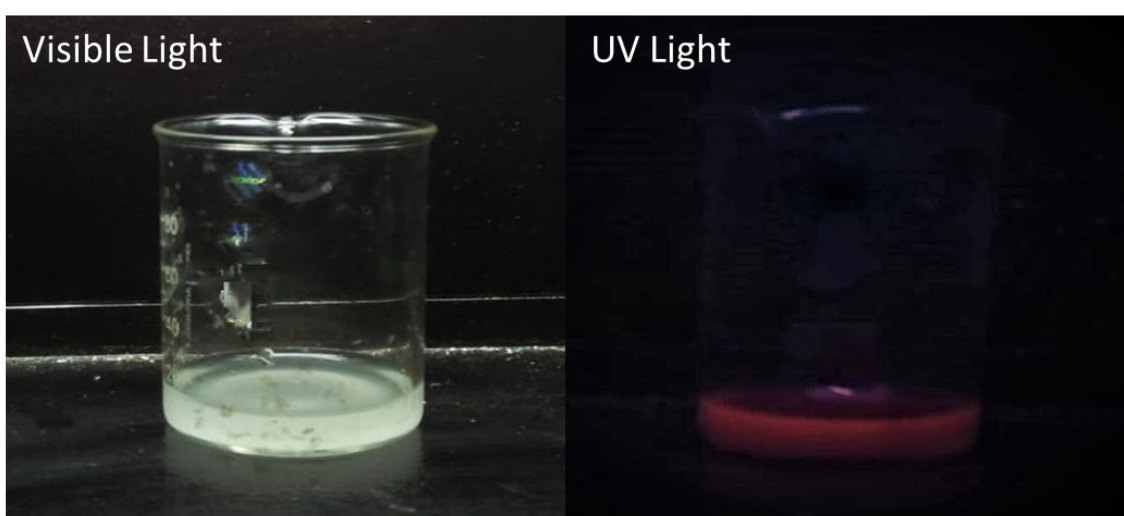


Figure 1: Photograph of glutathione stabilized copper nanoclusters under visible and UV light.

The UV Visible absorption spectrum of the synthesized Copper nanoclusters were recorded. The nanocluster dispersion was diluted with water and transferred to a 3 ml cuvette. The sample was placed in a UV Visible spectrophotometer and the spectrum was recorded from 230 to 500 nm. The copper nanoclusters show an absorption peak at around 275 nm. (Figure 2) The stabilizing ligand, glutathione does not show any absorbance in this particular spectral window.

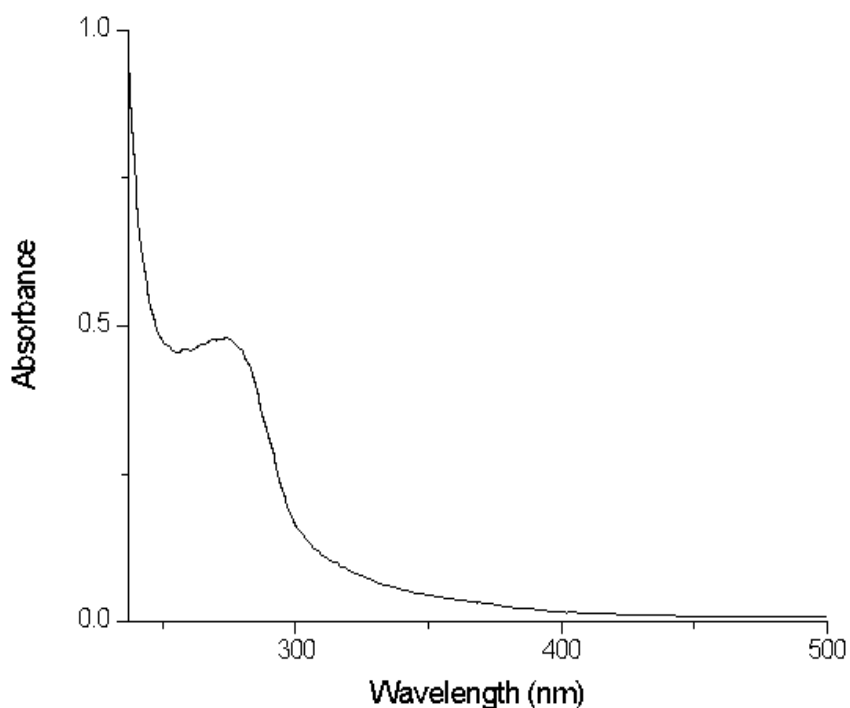


Figure 2: UV-Vis spectrum of glutathione stabilized Copper nanoclusters

4. CONCLUSION

Glutathione stabilized copper nanoclusters were synthesized using a one pot wet chemical method. Glutathione acts as both a reducing agent as well as a capping agent. This is a very facile approach for the synthesis of copper nanoclusters. These clusters are red emissive under the UV light. The synthesised copper nanoclusters show an absorption at around 275 nm. The emission property of these clusters can be utilized for various applications like metal sensing, bio-imaging etc.

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