ABSTRACT

Nanoparticles are extensively studied for their unique properties which become predominant at length scales that occur at the interface between bulk materials and molecules. They may be synthesized by physical, chemical or biological processes. In this study, gold and semiconductor nanoparticles were synthesized using the green microalga *Chlamydomonas reinhardtii*. These photosynthetic microalgae are easy to culture, can be grown in abundance and are safe for handling.

The focus of this thesis has been to use safe, bio-inspired methods for nanoparticles synthesis. Gold nanoparticles were synthesized by the reduction of aqueous chloroaauric acid with algal cell extract at room temperature. The reaction proceeded to completion within two and half hours leading to the formation of gold nanoparticles with characteristic Surface Plasmon Resonance (SPR) absorption at 540 nm. The effect of reaction conditions like pH, temperature and cell extract concentration was studied. Gold nanoparticles were formed even at low pH and at temperatures as high as $100^\circ\text{C}$; increasing the volumes of cell extract produced particles of different sizes. The gold nanoparticles synthesized by this method were largely spherical ranging from 9-40 nm with few particles having hexagonal and triangular morphologies as observed by High Resolution Transmission Electron Microscopy (HRTEM) and High Resolution Scanning Electron Microscopy (HRSEM). The elemental composition of the nanoparticles was identified by Energy Dispersive X-ray Spectroscopy (EDX). X-Ray
Diffraction (XRD) studies showed that the gold nanoparticles had a Face-Centered-Cubic (FCC) structure. The average crystallite size as measured by Scherrer's equation was 14 nm. Particles size analysis by Dynamic Light Scattering (DLS) revealed that the average hydrodynamic radius was larger than the sizes estimated by electron microscopy. The stability of the nanoparticles was studied by measuring its zeta potential and was measured to be -21mV. The Fourier Transform Infrared Spectroscopy (FTIR) results indicated that the algal proteins may have played a key role in the synthesis and stabilization of the nanoparticles; this result was confirmed by running a Sodium Dodecyl Sulphate (SDS) Poly Acrylamide Gel Electrophoresis (PAGE). Four proteins with molecular weights ranging from 26-32 kDa were likely to be involved in gold nanoparticle biosynthesis.

The second part of this work describes the use of these gold nanoparticles as catalysts. Bulk gold is known for its chemical inertness, however, gold nanoparticles are surprisingly good catalysts due to their large surface to volume ratio. The synthesized gold nanoparticles were found to catalyze the reduction reaction of 4-nitrophenol a toxic environmental pollutant to 4-aminophenol. The rate of the reaction at room temperature was determined to be $2.02 \times 10^{-2} \text{ min}^{-1}$. The effect of temperature on the catalytic reaction was studied and increase in temperature was found to increase the rate of reaction. Similarly, the influence of catalyst concentration was investigated and the reaction rate was found to increase with catalyst concentration.
The versatility of this method was used in the synthesis of a number of semiconductor nanoparticles, namely, zinc sulphide (ZnS), cadmium sulphide (CdS) and zinc oxide nanoparticles (ZnO). Because of their unique size-dependent properties, these nanoparticles have applications in a number of fields.

Zinc sulphide nanoparticles were synthesized at room temperature using *Chlamydomonas reinhardtii* cell free extract. The morphology of the particles as observed by HRSEM and HRTEM was found to be spherical. Particle sizes ranged from 8-12 nm with an average size of 10 nm. EDX confirmed that the nanoparticles were composed of zinc and sulphur. The fluorescence spectrum of ZnS nanoparticles showed visible emission. Structural analysis revealed that the nanoparticles possess a cubic zinc blende phase and the average crystallite size was determined to be ~7 nm. DLS and zeta measurements for the nanoparticles were 68 nm and -21.1 mV respectively. The variation in sizes could be due to the capping agent surrounding the nanoparticle. FTIR analysis showed the characteristic bands of peptides and this was responsible for capping the nanoparticles.

Cadmium sulphide nanoparticles were synthesized using the algal cell free extract at 65°C. The formation of a yellow solution indicated nanoparticle formation, with maximum absorption at 430 nm which is blue-shifted in comparison with bulk material. The photoluminescence (PL) spectrum showed a broad green emission. The nanoparticles were observed to have a spherical morphology and its size ranged from 6-10 nm as measured by HRTEM. The nanoparticles possessed a cubic zinc blende structure when
analysed by XRD with an average crystallite size of 6 nm. The nanoparticles were found to be very stable in solution with a zeta potential of -30.7 mV and an average hydro-dynamic radius of 38 nm. FTIR studies showed that algal proteins and peptides are involved in nanosynthesis.

Zinc oxide nanoparticles with distinctive nanoarchitectures were synthesized by a similar approach. Usually zinc oxide nanoflowers are synthesized using hydrothermal methods at elevated temperatures of upto 200°C. In this study the nanoparticles were formed under alkaline conditions at 80°C within an hour. Porous nanoflowers and nanorods were observed using HRSEM. The nanorods appeared to be bundled together and some were forming flower like structures. The rods approximately measured 330 nm in length and 43 nm in breadth. HRTEM analysis revealed that the nanostructures had a porous sheet like morphology, however in some places rods were observed indicating that the rods may have aggregated together to form the nanosheets. ZnO showed maximum absorption around 360 nm while the PL spectrum showed enhanced near band edge emission in the blue region. XRD analysis suggested that the nanoparticles had a hexagonal structure with an average crystallite size of 21 nm. The DLS results showed two peaks corresponding to 370 nm and 4 µm; these corresponded to the sizes of the nanorods and the porous nanostructures. A relatively low zeta potential of -15.3 mV was observed and could be indicative of the large size of the nanostructures.