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Amino Acid Mediated Synthesis of Nickel and Zinc Nanoparticles

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Abstract-- A simple one-step synthetic route was demonstrated for the synthesis of stable Ni and Zn nanoparticles by using L-Cysteine as reducing and stabilizing agent in aqueous medium. The synthesized nanoparticles were characterized by using UV-Vis, XRD, FT-IR and SEM analytical techniques. FT-IR spectrum confirmed the formation of thiol - metal bond indicating the capping of L-Cysteine on Ni/Zn metal. XRD analysis confirmed that the particles fall in nanometer range and the diameter of L-Cys capped Ni nanoparticle was 43 nm and the diameter of L-Cys capped Zn nanoparticle was 58 nm. The morphology of the synthesized nanoparticles was studied by SEM analytical technique.

Key words-- L-Cysteine, nanoparticles, thiol-metal bond, amino acid

I. INTRODUCTION

Nanoparticles are ultrafine particles having size in the nanometer range. They are important scientific tools because they have applications in various biotechnological, pharmacological and technological fields^{1,2}. They often possess unexpected physical and optical properties as they are small enough to confine their electrons and produce quantum effects. Even though they offer many advantages over other materials, nanoparticles have some serious limitations like aggregation, decomposition, chemical and colloidal instability in acidic or basic environment³. Organic molecules having thiol groups are most effectively used to stabilize the metal nanoparticles, because the sulphur atom present in the thiol group having the strong ability to bind the metal atoms^{4,5}.

L-Cysteine is a semi essential amino acid present in the human body contributing to build protein and includes the element sulphur appearing in its side chain. The sulfur atom of cysteine is involved in the formation of sulfhydryl group which is very reactive. The presence of sulfhydryl group where hydrogen can be easily replaced by radicals and other groups, makes it possible to form a covalent bond with the other molecules^{6-11[Ref. cited therein]}. The easiness of formation of such covalent bond depends on overall redox potential of environment as well as pH (at low pH, the equilibrium is shifted to the reduced form (-SH form) and under more basic conditions, the -SH group is more willing to be oxidized and replaced by -SR, where R is anything except for hydrogen)¹².

In the present work, it is proposed to synthesize L-cysteine capped Ni/Zn nanoparticles and the as-synthesized nanoparticles were characterized using FT-IR, XRD, SEM and UV-Vis spectral studies.

II. MATERIALS AND METHODS

L-Cysteine hydrochloride monohydrate was purchased from Loba chemicals. Zinc acetate Dihydrate, Nickel (II) Chloride hexahydrate and Sodium hydroxide were purchased from SRL chemicals. All the reagents used are of AR Grade. All aqueous solutions were made up of double distilled water.

A. Synthesis of L-Cysteine Capped Nickel nanoparticles

L-Cysteine hydrochloride monohydrate and metal salt were taken in 1:10 molar ratio. 0.5 M of L-Cysteine hydrochloride monohydrate (10 ml) was mixed with 0.05 M Nickel (II) chloride (10 ml). The pH of the solution was 1. Then the pH was adjusted to 9 with the use of Sodium hydroxide (0.1 M) under stirring condition. A white precipitate was formed. It was centrifuged at 2000 rpm for 10 minutes and then dried.

B. Synthesis of L-Cysteine Capped Zinc nanoparticles

L-Cysteine hydrochloride monohydrate and Zinc acetate dihydrate were taken in 1:5 molar ratio. 0.5M of L-cysteine hydrochloride monohydrate (10 ml) was mixed with 0.1M Zinc acetate dihydrate (10 ml). The pH of the solution was 1. Then the pH was adjusted to 5 with the use of Sodium hydroxide (0.1 M) under stirring condition. A white precipitate was formed. It was centrifuged at 2000 rpm for 5 minutes. Finally, the precipitate was dried at room temperature.

C. Characterization

Optical absorption spectra of the synthesized NPs were taken using UV-Vis Double Beam spectrophotometer 2201, Systronics using a quartz cuvette of 1 cm path length. FT-IR spectra of the nanoparticles prepared were recorded at room temperature on IR affinity (FT-IR spectrophotometer, Shimadzu) ranging from 4000 to 400 cm⁻¹. The synthesized CuO nanoparticle was analyzed by powder X-Ray diffraction technique using X-Ray Diffractometer (XPERT-PRO, Alagappa university, India) with the copper K_{a1} radiation (k = 1.54 A) in the 2h range of 10°–80°. The morphology of the synthesized nanoparticles was studied by Scanning Electron Microscopy (Jeol, Karunya University, India).

III. RESULTS AND DISCUSSION

A. Optimization



Figure 1: Absorption spectra of synthesized Ni nanoparticles at (1:3, 1:5, 1:7 and 1:10) molar ratios.

The synthesis of L-Cysteine capped Nickel nanoparticles was optimized by varying the concentrations of metal to amino acid

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ratio such as 1:3, 1:5, 1:7 and 1:10. Figure 1 showed the absorption spectra of synthesized Ni nanoparticles at various molar ratios. Among the molar ratios, the absorption spectrum of L-Cys capped Ni NPs synthesized from 1:10 molar ratio showed a shift in peak at 291 nm indicating the formation of Cysteine capped Ni nanoparticles¹⁰ thereby the concentration was optimized as 1:10 molar ratio.

A. UV-Vis absorption spectra of L-Cys capped metal nanoparticles

The UV-Vis spectra of L-Cys capped Ni and Zn nanoparticles were shown in Fig. 1 & 2. L-Cysteine hydrochloride monohydrate showed absorption maximum at 223 nm (Fig. 2 a). When Zinc was capped with L-Cysteine, the absorption wavelength was shifted from 223 nm to 263 nm indicated the formation of Zn-Cys nanoparticles (Fig. 2 b). When Nickel was capped with L-Cysteine, the absorption wavelength showed a characteristic red shift from 223 nm to 291 nm indicated the formation of Nickel nanoparticles capped with L-Cysteine¹⁰ (Fig. 1).



Figure 2: UV-Vis spectra of a) L-Cysteine hydrochloride b) Zn-Cys NPs





Figure 3: FT-IR spectra of L-Cysteine, L-Cys capped Ni and Zn nanoparticles

Fig. 3 (a) showed the FT-IR spectrum of L-Cysteine hydrochloride monohydrate which was used as the reducing and capping agent to synthesize nanoparticles. Fig. 3 (b) showed the FT-IR spectra of synthesized L-Cysteine capped Ni nanoparticles and Fig. 3 (c) showed the FT-IR spectrum of L-Cys capped Zn nanoparticles. Absorption peak at 2550 cm⁻¹ is assigned due to an S-H stretching vibration of standard L-cysteine. This band disappears on encapsulation of Ni/Zn NPs with L-Cysteine molecule, reporting the strong surface binding interactions of L-Cysteine through thiol linkage to the particle surfaces.

C. XRD Spectra of synthesized Cysteine capped metal nanoparticles

Fig. 4 showed the XRD spectrum of L-Cys capped Ni/Zn nanoparticles. The diffraction peaks observed are sharp and they fall in nanometer range. The particle size of the synthesized nanoparticles was calculated using Debye Scherrer formula. The particle size of the Nickel-Cys nanoparticles was 43 nm and the size of the Zinc-Cys nanoparticles was 58 nm.



Figure 4: XRD spectrum of l-Cys capped Ni/Zn nanoparticles *D. SEM analysis*



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Figure 5: SEM images of (a) Ni-Cys NPs (b) Zn-Cys NPs

The surface morphology of the synthesized nanoparticles was studied by Scanning Electron Microscopy. Fig. 5 (a) showed the SEM images of Nickel nanoparticles capped with L-Cysteine biomolecules indicating that the particles were in flower like shape. Fig. 5 (b) showed the SEM images of Zinc nanoparticles capped with L-Cysteine indicated that the particles were in distorted spherical shape.

CONCLUSION

A simple chemical method was demonstrated for the synthesis of stable Nickel and Zinc nanoparticles with the size of 43 nm and 58 nm respectively using L-Cysteine as a reducing and stabilizing agent. This method was simple, one-step and requires less time. FT-IR analysis confirmed the linkage of Ni/Zn through sulfhydryl group of the L-Cysteine. The synthesis of L-Cysteine capped Metal nanoparticles can easily be prepared at low cost and can be applicable in the fields of sensors and catalysis in future.

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