Synopsis of the Thesis Entitled

"Fabrication of Capped/Supported Nanosystems-Characterization and Applications."

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In

CHEMISTRY

By

Ms. Naznin Shaikh

Guided by: *Prof. P. Padmaja*

Department of Chemistry

Faculty of Science

M. S. University of Baroda,

Vadodara 390 002

INDIA

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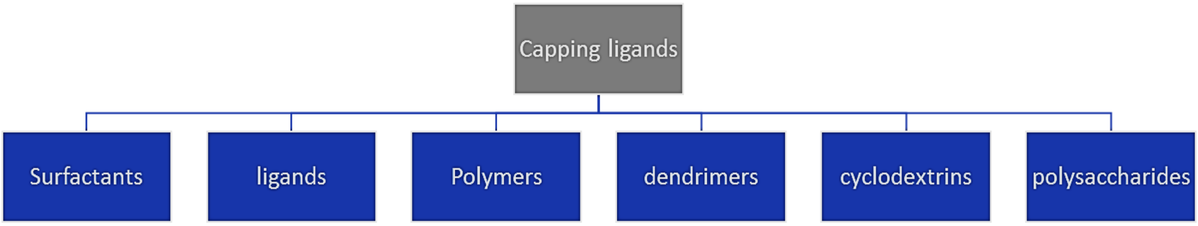
Introduction:

Nanoparticles are particles with a size between 1 and 100 nanometers. The small size in these materials confers new properties and opens up possibilities of novel applications.

Nanoparticles have been used in a variety of scientific applications throughout the last few decades. Usually, the nanoparticles are produced in large quantities on a commercial scale that are uncapped and having a larger size. When released in big aggregates, these nanoparticles become Hazardous to the environment. (***J Nanobiotechnol*** **18, 172 (2020)**). One of the key parameters to synthesize robust NPs of defined morphologies and function is the choice of capping ligand. The choice of capping agent for nanoparticles is crucial, because the capping agent often influences various properties of the nanoparticle, including its size, shape and interactions with surrounding solvent. The bonding between the chains of capping ligands and the nanoparticles surface leads to steric hindrance providing ultimate stability to the nanocomposite and the agglomeration of nanoparticles gets minimized for a longer period of time employing appropriate capping agents. Apart from their main role in stabilizing nanoparticles, some capping agents are capable of carrying out the additional role of reducing metal ions into metal nanoparticles**.** (***Chem. Rev.*** **2019, 119, 8, 4819–4880**)

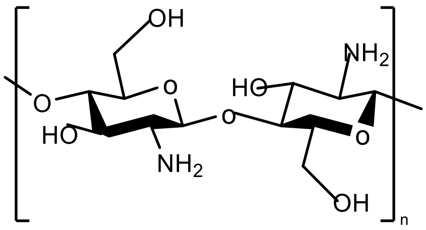
Different types of capping agents have been used in nanoparticles. (***Catalysts*** **2016, *6*(12), 185**)



Biopolymer (Chitosan) as a capping ligand

To prepare metal NPs by environmentally clean and sustainable way, researchers have begun to use biomolecules and bioorganism, such as bacteria, fungi, proteins, biopolymers and plant extracts. Biopolymers have been extensively used in the preparation of metal nanostructures, Such as starch, cellulose, chitosan, pectin and guar gum etc. Biopolymers contain abundant NH_2 and OH groups that can strongly chelate with metal ions and that can stabilize nanoparticles via electrostatic interaction with the nanoparticles and can also act as a reducing agent to form metal nanoparticles that are stabilised on the support. (***J Nanobiotechnol* 18, 172 (2020)**) (**Carbohydrate Polymers, 112, 2014, 539-545**)

Chitosan, a mouldable copolymer of d-glucosamine and N-acetyl-d-glucosamine obtained by alkaline deacetylation of chitin, has emerged as one of the most valuable polysaccharides. (**Carbohydrate Polymers, 207, 2019, 806-814**) Chitosan is an acid-soluble polymer. It's fascinating properties include biocompatibility, biodegradability, non-toxicity, and antimicrobial activity. Chitosan is a good option for stabilizing nanoparticles due to its polycationic nature and its conformation in solution (**Carbohydrate Polymers, 161, 2017, 63-70**)

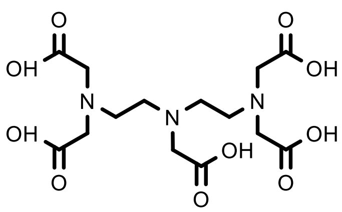


Chitosan

Diethylenetriamine pentaacetic acid (DTPA) as a capping ligand

DTPA contain five carboxyl groups, which can serve as effective capping ligands like citrate. DTPA can bind to NP surface due to the interaction between one carboxyl group of DTPA and metal surface and the negatively charged carboxyl group can stabilize the NPs against aggregation. DTPA can act as both reducing agent and capping agent for stabilization. (Sensors and Actuators B: Chemical, 258, 2018, 602-611)

It has been reported that amino polycarboxylic acids (APCAs) have good reducing and complexing properties. There are a number of reports in the literature wherein the metal NPs have been synthesized using complexes of APCAs which include Ag ethylenediamine tetraacetic acid (Ag-EDTA) and Ag- diethylenetriamine pentaacetic acid (Ag- DTPA).



DTPA

Nanosystems have been explored for numerous technical and biomedical applications in the last decade.

Application of Nanosystems

1. Organic Catalysis

Catalysis has changed and is still changing our world. The vital role of catalysis in modern society is shaped by transportation fuel supply, vehicle emissions control, production of low-toxic pesticide, artificial fertilizer, high-strength polymers, and various pharmaceuticals, as well as many other chemicals. A majority of industrial heterogeneous catalysts are small nanoparticles (less than 20 nm) that are highly dispersed on solid supports with high surface area. (*Chem. Mater.* 2014, 26, 1, 72–83)

Now a days, an important part of synthetic chemistry is established on the usage of valuable transition metal catalysts such as Ru, Co, Rh, Ni, Pd and Pt, mainly Pd which is widely used and highly valuable metal with high demand. Palladium catalyzed reactions are now recognized as very important toolbox in synthesis of many, medicinally important compounds, natural products, and synthesis of different building blocks for the development of many polymeric materials.

Although Pd catalyzed homogeneous reactions are beneficial in terms of increasing the reactivity of the system, some shortcomings include, large amount of wastes and imposing hazardous impact on the surrounding environment. As Pd and its complexes are very much expensive, its recovery and reuse are crucial for economic and environmental point of view.

One such method uses immobilization of PdNPs and Pd-complexes on suitable solid supports, such as organic polymers, zeolites, silicas, oxides, and carbon materials. (Current Organic Chemistry, 2015, 19, 2075-2121) However, Pd nanoparticles suffer from significant deterioration in catalytic activity owing to leaching or aggregation of the Pd species and to the formation of inactive Pd black particles. The search for more efficient separable catalysts has led to the development of catalysts with magnetic support/ magnetic properties.

2. **Surface enhanced Raman spectroscopy (SERS)**

The discovery of the enhancement of Raman scattering by molecules adsorbed on nanostructured metal surfaces is a landmark in the history of spectroscopic and analytical techniques. SERS is considered as one of the most powerful analytical methods to identify and to quantify trace amounts of analytes and provide structural information based on their unique vibrational Raman fingerprint. Significant enhancement of Raman signal arises from the localized electromagnetic field (localized surface plasmons) on metallic nanomaterial excited by laser. In SERS, the so-called hot-spots created in the gaps between nanoparticles or at the edges and tips of anisotropic nanoparticles provide sufficiently intense electromagnetic Fields to promote a tremendous increase in the Raman intensity of molecules located in these regions, making it possible to detect a SERS signal even from single molecules. Nanoscale, 2013, 5, 6013, Microchim Acta 186, 453 (2019)

3. **Environmental remediation**

Environmental pollution is undoubtedly one of the main problems that society faces today. New technologies are constantly being explored for the remediation of contaminants of the air, water, and soil. It relies mainly on using various technologies such as, adsorption, biological oxidation, chemical oxidation and incineration (Energy Environ. Sci., 2012,5, 8075-8109) The implication of nanotechnology in environmental applications has been a major focus of current research with a special emphasis on pollution prevention and the removal of environmental contaminants from various contaminated soils, sediments, solid wastes, air and water. (Environ. Sci.: Nano, 2018, 5, 2784)

The main objectives of present research are:

1. Synthesis of metallic and bimetallic nanostructures in aqueous phase.
2. Use different caping agents on the nanostructures.
3. Characterization of the synthesized nanostructures by UV-Vis spectroscopy, SEM, XRD, VSM, HRTEM, XPS, TGA, DSC, IR and by other required techniques.
4. Measurement of catalytic potential of these nanostructures for several organic transformations like nitro-, dye reduction and C-C coupling reactions.
5. Check the synergy between two metal components for different catalysis.
6. Investigate the potential of the nanostructures as SERS substrates.

The main contents of the thesis entitled "**"Fabrication of Capped/Supported Nanosystems-Characterization and Applications"** consists of **seven** chapters.

Chapter 1: Introduction

Chapter 2: Chitosan supported monolayer assembly of silver nanostructures

Chapter 3 (A): Magnetic Chitosan stabilized Palladium Nanostructures

Chapter 3(B): Magnetic Chitosan stabilized Nickel-Palladium Nanostructures

Chapter 4: Recovery of Pd from Electroless Plating Solution using Cross- Linked Chitosan Derivatives and their valorization as efficient heterogeneous Catalysts for Organic Synthesis and Environmental Remediation

Chapter 5(A): Palladium Nanostructures Stabilized on Iron Oxide Nanoparticles Capped with Diethylenetriamine pentaacetic acid

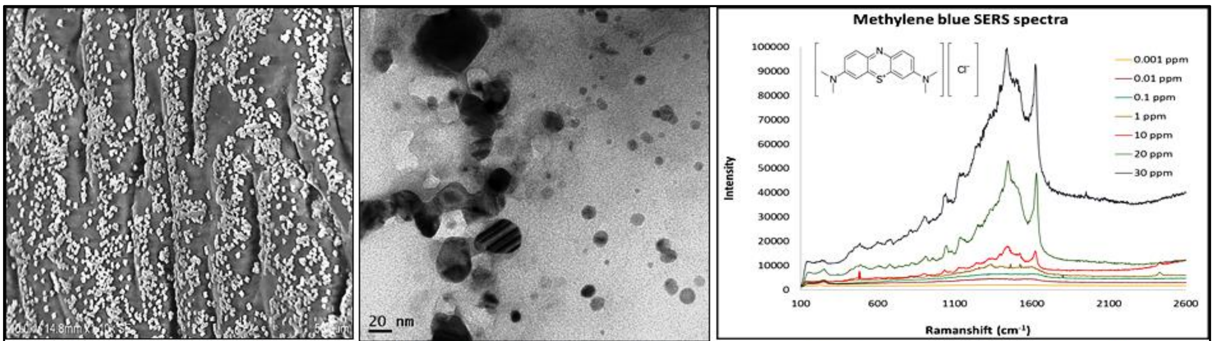
Chapter 5(B): Nickel-Palladium Nanostructures Stabilized on Iron Oxide Nanoparticles Capped with Diethylenetriamine pentaacetic acid

Chapter 6: DNA based magnetically separable hybrid Nanocatalyst

Chapter 7: conclusions

The First chapter presents: an introduction to Nanosystems and capping agent and a detailed review of the biopolymers and capping agents used for fabrication of magnetic palladium and Nickel based catalysts for Suzuki reactions and environmental remediation. An attempt was also made to present a detailed review of the biopolymer based SERS substrates

The second chapter (Chitosan supported monolayer assembly of silver nanostructures). discusses the preparation of wrinkled chitosan supported silver nanostructures (Ag@Ch) by self-assembly in order to provide a roughened surface, avoid aggregation, and improve the stability of Ag NPs as well as to avoid dissociation of Raman probe molecules. Synthesized nanostructures were characterized by UV, IR, XRD, XPS, TGA, SEM, EDS, HRTEM techniques. The potential of Ag@Ch as SERS substrates was investigated by monitoring the progress of catalytic reduction of p-Nitrophenol and by detection of Crystal Violet (CV), Methylene blue (MB) and p-Nitrophenol(p-NP) as model analyte probes.



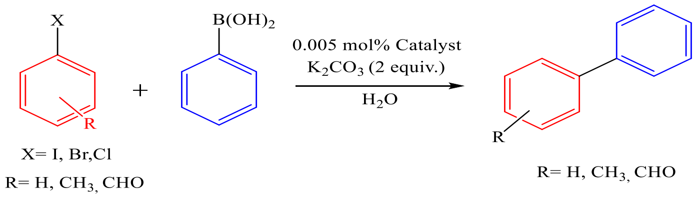
SEM image of Ag@Ch | HRTEM image of Ag@Ch | SERS spectra of Methylene blue

The Third chapter discusses the fabrication of **3(A)** Magnetic Chitosan stabilized Palladium Nanostructures and **3(B)** Magnetic Chitosan stabilized Nickel-Palladium Nanostructures

Magnetic nanoparticles were prepared using iron oxide and chitosan under ambient conditions (IO-Chitosan). This was followed by in situ reduction of Ni and palladium ions by IO-Chitosan to form magnetically separable palladium nanostructure (Pd@IO-Chitosan) and Pd@Ni@IO-Chitosan. The Synthesized nanostructures were characterized by Infrared spectroscopy, transmission electron microscopy, scaning electron microscopy, energy-dispersive X-ray spectroscopy, Thermo gravimetric analysis, X-ray diffraction, vibrating sample magnetometer, electron spin resonance spectroscopy, X-ray photoelectron spectroscopy and X-ray absorption near edge structure techniques. The catalytic efficiency of the synthesized Pd@IO-Chitosan and Pd@Ni@IO-Chitosan in P-Nitrophenol reduction and in Suzuki coupling reaction of aryl halides with arylboronic acid in water has been demonstrated. Magnetically separable catalyst (Pd@IO-Chitosan) was isolated and reused for 12 cycles. Recycled catalysed was characterized by different by Infrared spectroscopy, scaning electron microscopy, Thermo gravimetric analysis, vibrating sample magnetometer and X-ray photoelectron spectroscopy.

This chapter also reports the optimisation of reaction parameters and substrate scope of this methodology. The detail experimental procedure of the performed reactions, results and the supporting data of the prepared compounds (physical data, spectroscopic data etc.) are also reported in this chapter

Suzuki coupling reaction catalysed by Pd@IO-Chitosan at different temperatures



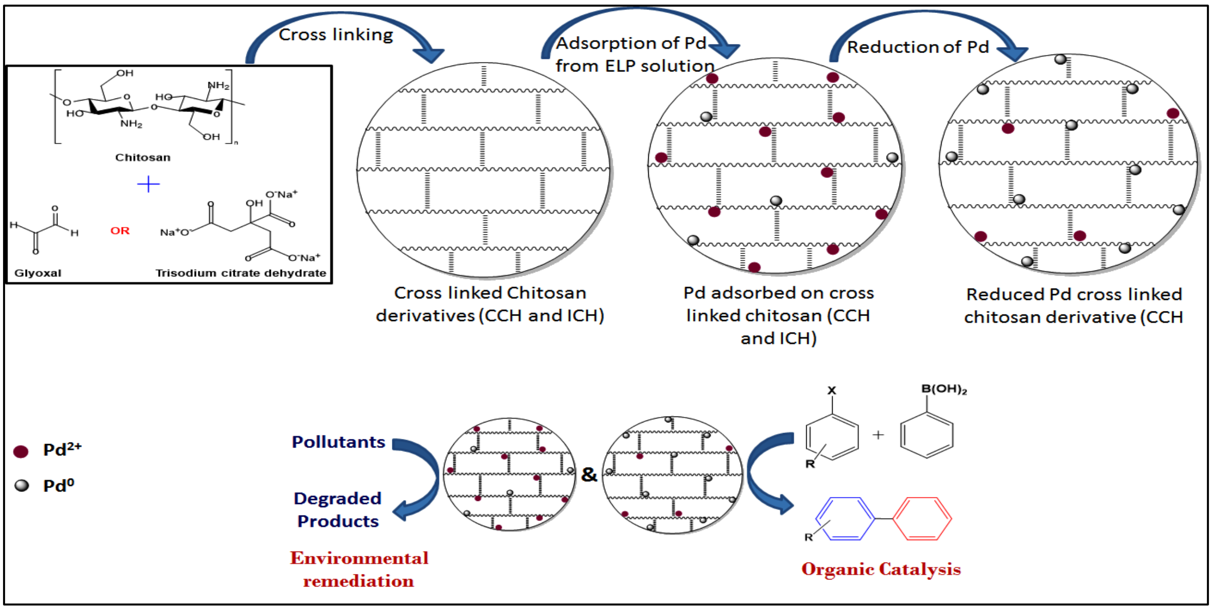
TON: 1.85×10^4

Recyclability: 12 cycles

Sr. No.	X	R	Temperature (°C), Time (h.)	GC-MS Yield (%)	Temperature (°C), Time (h.)	GC-MS Yield (%)	Temperature (°C), Time (h.)	GC-MS Yield (%)	Isolated Yield (%)
1	I	H	35°C,6 h	99.99	65 °C, 6 h	99.99	100 °C, 6 h.	99.99	99

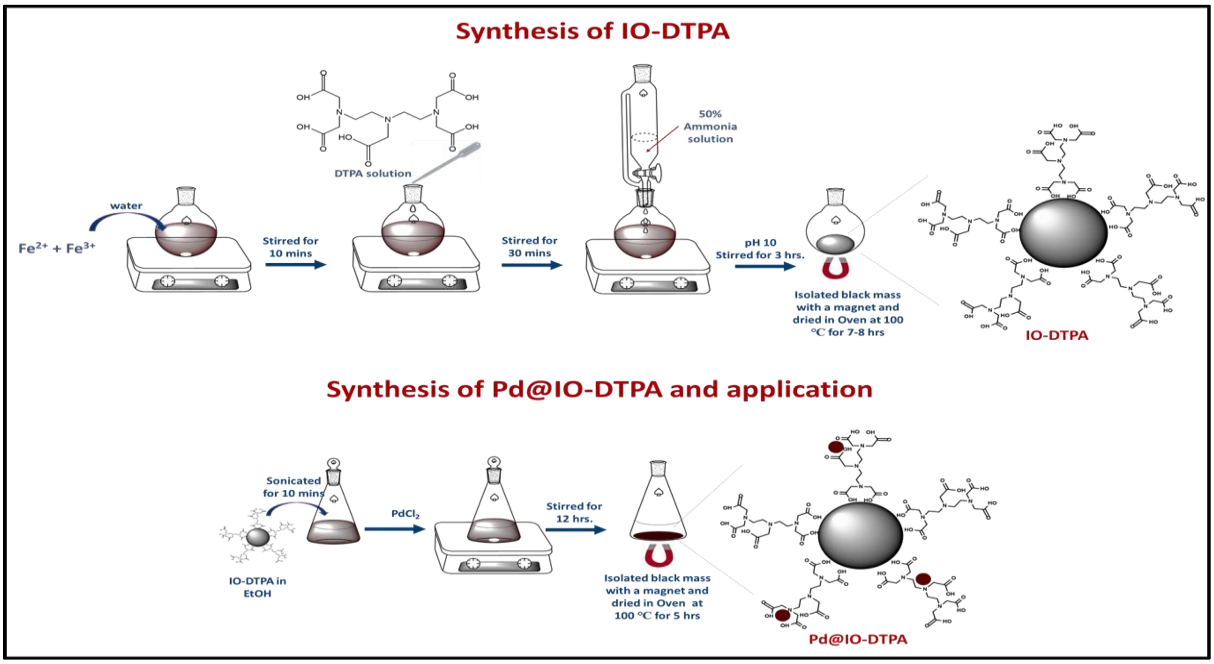
2	I	p-CH_3	35°C, 12 h	14.91	65 °C, 12 h	58.4	100 °C, 8 h	85.58	85.3
3	I	o-CH_3	35°C,12 h	7.93	65 °C, 12 h	76.4	100 °C, 9 h	83.10	83.05
4	I	o-CHO	35°C,20 h	4.52	65 °C, 15 h	78.38	100 °C,12 h	99.99	99
5	I	p-CHO	35°C, 12 h.	68.66	65 °C, 12 h	93.2	100 °C, 11 h	99.99	99
6	Br	H	35°C, 10 h	53.41	65 °C, 8 h	99.5	100 °C, 7 h	99.99	99
7	Cl	H	35°C,12 h	10.19	65 °C, 12 h	92.41	100 °C, 11 h	93.65	93.2

The Fourth chapter describes the recovery of Pd from Electroless Plating Solution using Cross- Linked Chitosan Derivatives and their valorization as efficient heterogeneous Catalysts for Organic Synthesis and Environmental Remediation) investigates the Pd(II) adsorption characteristics on covalently and ionically crosslinked chitosan derivatives (CCH and ICH) using synthetic electroless plating solutions. The chitosan derivatives CCH and ICH were characterized by scanning electron microscopy, energy dispersive X-ray spectroscopy, Fourier transform infrared spectroscopy, Thermo gravimetry, Differential scanning calorimetry and X-Ray Diffraction techniques. Quantitative adsorption of Pd^{2+} was achieved independent of pH conditions (1-10) in 120 minutes using 0.2 g and 0.4g of CCH and ICH respectively. Attempts were further made to reduce the adsorbed Pd^{2+} (CCH-Pd^{2+}) to Pd^0(CCH-Pd^0). The catalytic potential of CCH-$Pd^{2+}$and CCH-Pd^0 towards organic synthesis and environmental remediation was studied.

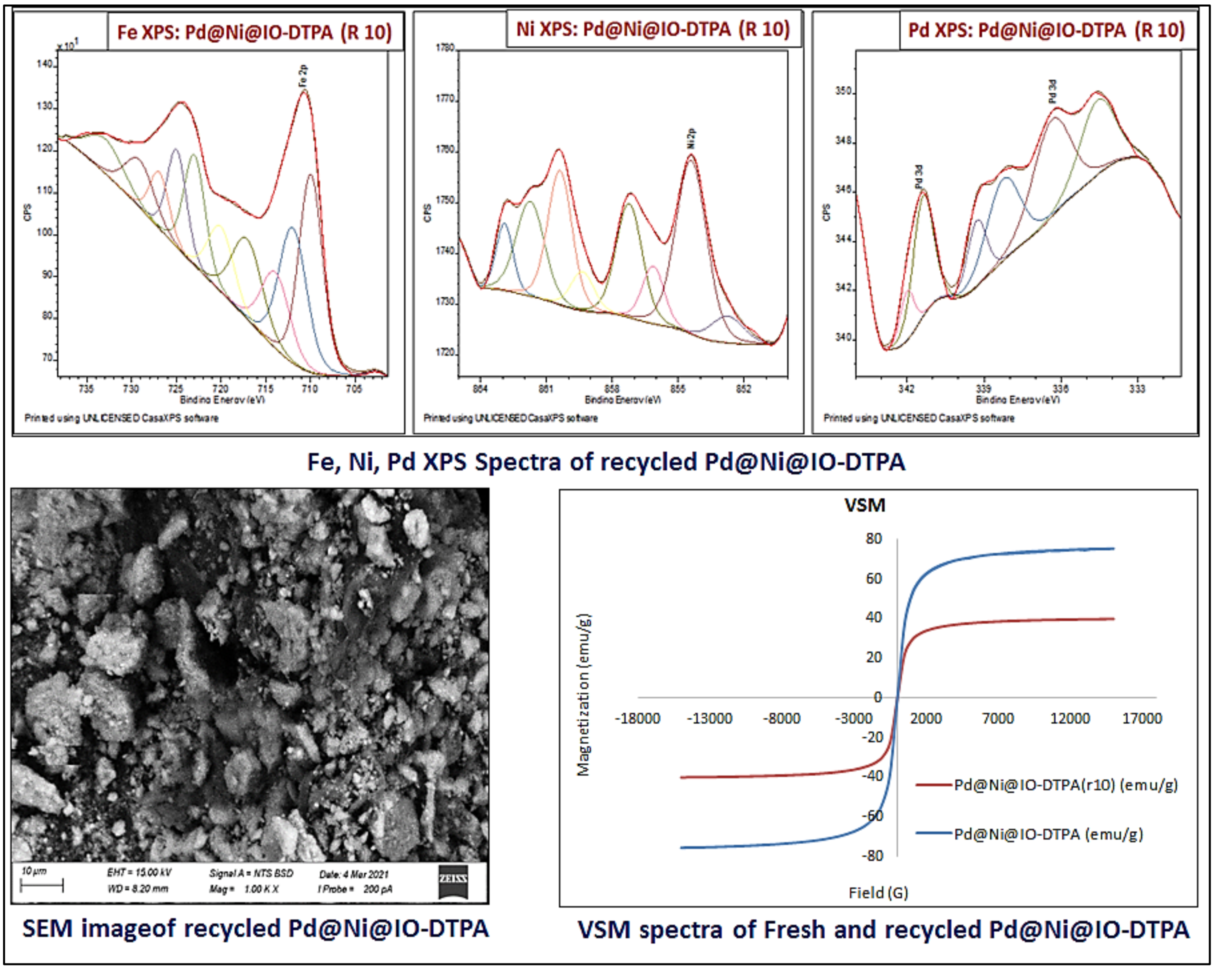


The fifth chapter describes the fabrication of: Palladium Nanostructures Stabilized on Iron Oxide Nanoparticles Capped with Diethylenetriamine pentaacetic acid and Nickel-Palladium Nanostructures Stabilized on Iron Oxide Nanoparticles Capped with Diethylenetriamine pentaacetic acid

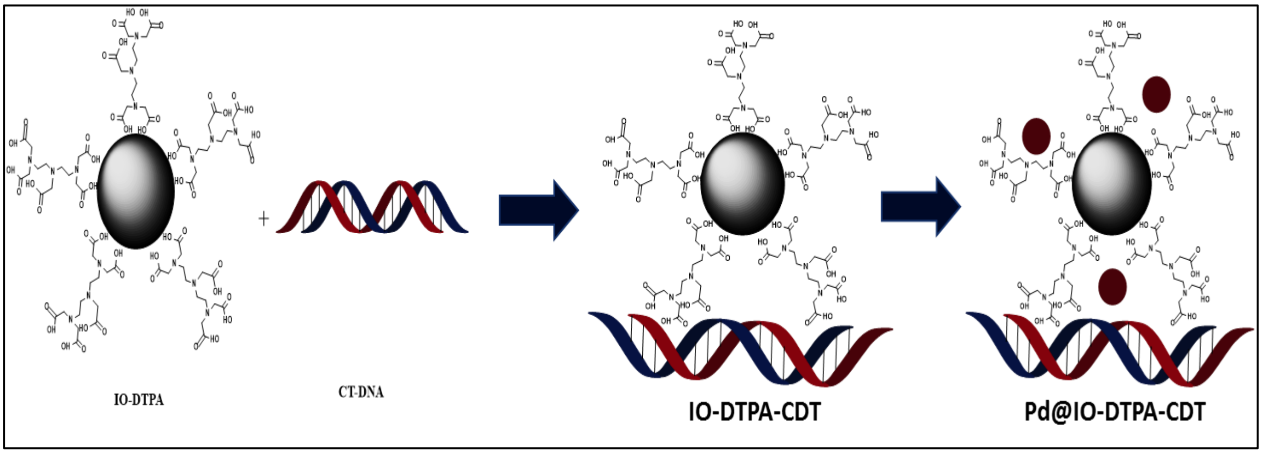
The use of DTPA with multiple carboxyl groups has not only facilitated the fabrication of capped iron oxide nanoparticles (IO- DTPA) but also provided active sites for the further immobilization of Pd to fabricate a magnetically recoverable nanocatalyst (Pd@IO-DTPA) and Pd@Ni@IO-DTPA. Synthesized (Pd@IO-DTPA) and Pd@Ni@IO-DTPA nanocatalysts were characterized by Infrared spectroscopy, transmission electron microscopy, scaning electron microscopy, energy-dispersive X-ray spectroscopy, Thermo gravimetric analysis, X-ray diffraction, vibrating sample magnetometer, electron spin resonance spectroscopy, X-ray photoelectron spectroscopy and X-ray absorption near edge structure techniques. The effectiveness of Pd@IO-DTPA and Pd@Ni@IO-DTPA as catalysts was investigated with P-Nitrophenol reduction and Suzuki cross coupling reaction of aryl halides and aryl boronic acids and the catalyst could be recovered using a simple magnet.



. The XPS analysis demonstrated the presence of Pd, PdOx, Ni and NiO species. The superparamagnetic properties of the catalyst and strong metal support interactions facilitated the separation of the catalyst using a simple magnet and its reuse over several cycles.



The Sixth chapter discusses the synthesis of (DNA based magnetically separable hybrid Nanocatalyst). The same have been characterised by SEM (Scanning electron microscope), FTIR (Fourier transform infrared) spectroscopy, XRD (X-ray Diffraction), BET surface area analysis, XPS (X-Ray photoelectron spectroscopy), TGA (Thermogravimetric analysis) etc. this nanostructure was used for Suzuki coupling reaction.



The chapter seven of the thesis summarizes the work presented in the thesis. Brief conclusions with future scope of the study are also included in this chapter.

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