DECLARATION

I, Mohammed Ali, hereby declare that the thesis entitled "**Self-Assembly of Nanoparticles at the Liquid-Liquid Interface**" has not been, either in whole or in part, previously submitted to any other institution for any other degree or qualification, and contains no material previously published or written by another person, except where due reference is made in the text.

Mohammed Ali

Course work Marksheet

Dedicated to my Parents

Mr. Azizur Rahman

&

Late Kohinoor Begum

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The information furnished herein is true to the best of my knowledge and belief.

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Preface

With an aim to exploit the unique physical and chemical environment at the liquid-liquid interface in designing nanoparticle decorated devices, the present Ph. D. thesis entitled "**Self-Assembly of Nanoparticles at the Liquid-Liquid Interface**" has been chosen, which includes fabrication of nanoparticle-decorated membranes, capsules, raspberry-like hollow spheres, giant supramolecular assemblies and nanorods by oriented attachment of primarily formed nanospheres at different aqueous-organic interfaces. Varieties of ligand cross-linking strategies, such as, ion-pair formation, diazo reaction, polymerization and click reaction have been adopted in order to impart mechanical strength and robustness to the as-synthesized assemblies. The assemblies so obtained have been characterized by transmission electron microscopy, scanning electron microscopy, atomic force microscopy, optical and fluorescence microscopy, absorption, fluorescence and Raman spectroscopy, energy dispersive X-ray analysis, Fourier transform infrared spectroscopy, X-ray diffraction and thermogravimetric analysis. Application of these nanoparticle-decorated superstructures has been envisaged in catalysis, electrochemical sensing and ultra-filtration. The thesis has been organized into seven chapters:

Chapter 1

Chapter 1 is the general introduction about the present state-of-the art research of interfacial assembly of nanoparticles at the liquid-liquid interface.

Chapter 2

This chapter gives a description of the reagents used and analytical instruments employed for the characterization of the assemblies.

Chapter 3

This chapter describes the formation of nanoparticle-decorated membranes by self-assembly of nanoparticles at the liquid-liquid interface. This chapter consists of three subunits: (i) fabrication of gold nanoparticle-decorated ultrathin membrane at the water/toluene interface by ion pair formation and study of permeability of the dyes for real-time applications; (ii) synthesis of Au-ZnO composite membrane at the water-CCl_4 interface using 'thiol-ene' click reaction as the ligand cross-linking strategy and study of charge-dependent permeability of the membrane using amino acids in different charge state and (iii) fabrication of magnetic Fe_3O_4 nanoparticle-decorated membrane at the water/chloroform interface by ligand polymerization and applicability of the membrane for electrochemical detection of L-Dopa (and also L-Dopa and ascorbic acid simultaneously) up to nanomolar level concentrations.

Chapter 4

This chapter has been assigned to describe the interfacial assembly of ZnO quantum dots into varieties of giant supramolecular architectures depending on the interfacial tension at aqueous-organic interface by diazo reaction and the assemblies exhibit different optical properties.

Chapter 5

This chapter describes the oriented attachment of primarily formed quasi-spherical ZnO nanoparticles to nanorods at a very low concentration of the precursor in a restricted environment created by a particular composition of polar/non-polar liquid pairs.

Chapter 6

This chapter highlighted the interfacial assembly of nanoparticles into robust hollow micro-capsules with ligand cross-linked nanoparticle shell. It consists of two subunits: (i) liquid−liquid interface has been exploited as a platform for devising gold and iron oxide nanoparticle-decorated composite microcapsules by ligand cross-linking and size-selective permeability across the capsule wall and (ii) synthesis of submicrometer-sized raspberry-like ZnO morphologies that have been envisaged as greener catalysts in Fries Rearrangement for the conversion of phenolic ester to o/p-hydroxyaryl carbonyl compound with high turnover frequency.

Chapter 7

Chapter 7 summerizes the important outcomes and highlights some of the future scope of this work.

Abbreviations

AFM…………………...Atomic Force Microscopy

aq.…………………………………………………………………………………...Aqueous

CPC……………………………………………………………………...Cetylpyridinium chloride

CdSe……………………………………………………………………………Cadmium Selenide

dil.…………………………… .. ………………………………………………………Dilute

DC……………………………………………………………………………..Direct Current

EDX……………………………………………………………………...Energy Dispersive X-ray

FTIR………………………………………………………………… Fourier Transformed Infrared

mg………………………………………………………………………………...Miligram

mL…………………………………………………………………………………Mililiter

nm………………………………………………………………………………….Nanometer

NMR…………………………………………………………...Nuclear Magnetic Rasonance

NPs…………………………………………………………………….…… Nanoparticles

SEM…………………………………………………………..Scanning Electron Microscopy

LSPR……………………………………………………....Localized Surface Plasmon Rasonance

TEM……………………………………………………….. Transmission Electron Microscopy

HRTEM…………………………………......High Resolution Transmission Electron Microscopy

UV-vis………………………...Ultraviolet and visible

XRD………………………………………………………………….X-ray Diffractometer

2-D…………………………………………………….……………………Two Dimensional

3-D…………………………………………………………………………...Three Dimensional

MC……………………………………………….…………………………Microcapsules meV……………………………………………………….………………………...Milielectron Volt

11-MUA……………………………………………………………11-Mercaptoundecanoic Acid

FITC…………………………………………………………………....Fluorescein Isothiocyanate

MW……………………………………………………………………..….Molecular Weight

IP……………………………………………………………………………………Isoelectric Point

mM…………………………………………………………………………….....Milimolar

PBS…………………………………………………………………..Phosphate Buffer Saline

TC………………………………………………………………………Terephthaloyl Chloride

CV………………………………… …………………………………Cyclic Voltammogram

DPV………………………………………………………………....Differential Pulse Voltametry

SAED…………………………………………………………. Selected Area Electron diffraction

mA…………………………………………………………………………………….Mili Ampere

nM…………………………………………………………………………………...Nanomolar

LOD……………………………………………………………………………..Limit of Detection

AA…………………………….. …………………………………………………Ascorbic Acid

µM……………………………………………………………………………………...Micromolar

QDs…………………………………………………………………………………Quantum Dots

DMF……………………………………………………………………Dimethyl Formamide

DMSO…………………………………………………………………....Dimethyl Sulfoxide

THF……………………………………………………………………………..Tetrahydrofuran

MRI………………………………………………………...……….Magnetic Rasonance Imaging

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