In the Name of God

Razi University

Faculty of Chemistry
Department of Organic Chemistry

M. Sc. Thesis

Title of the Thesis:

Preparation, Characterization and Application of Multi-Walled Carbon Nanotubes and Boehmite Nanoparticles in Organic Synthesis and also Preparation of Amides from Nitriles in Water

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Mohsen Rostaei
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Dedicated to:

My Dear Mother

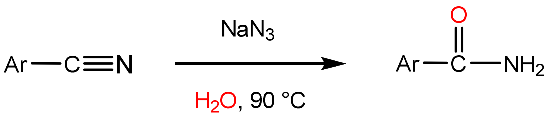
Who has always protected me

Abstract:

This thesis has been carried out in three parts:

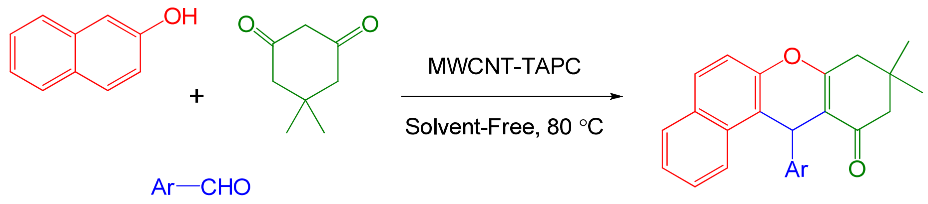
Efficient Preparation of Amides from Nitriles in Water

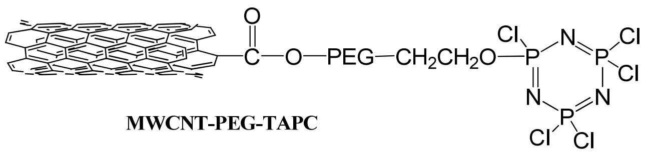
The selective conversion of aromatic nitriles has been accomplished using sodium azide. The corresponding amides were obtained efficiently and selectively in moderate to excellent yields. This reaction was carried out under eco-friendly conditions using water in the absence of organic solvents.



A Novel Practical Synthesis of 12-Aryl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-ones with MWCNT-PEG-TAPC System

A novel and efficient method is described for the preparation of 12-aryl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one derivatives using TAPC supported on multi-wall carbon nanotube as a reusable catalyst. Mild reaction conditions, shorter reaction times, high efficiencies, cost-effectiveness and facile isolation of the desired products make the present methodology a practical alternative.

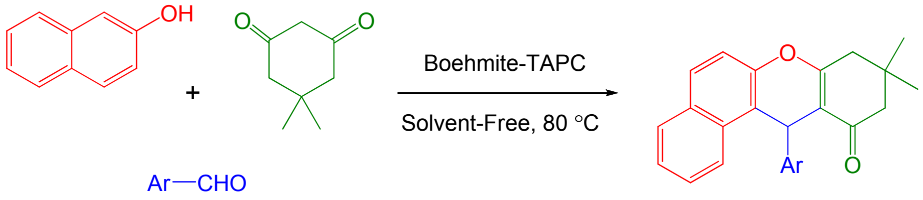


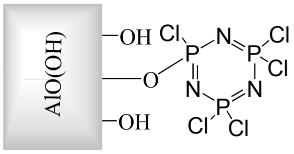


MWCNT-PEG-TAPC

Boehmite-TAPC Catalyzed Synthesis of 12-Aryl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one Derivatives

A novel and efficient method is described for the preparation of 12-aryl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-ones using boehmite-TAPC as a reusable catalyst. Mild reaction conditions, shorter reaction times, high efficiencies, cost-effectiveness and facile isolation of the desired products make the present methodology a practical alternative and will provide a valuable synthetic tool for various pharmaceutical applications.





Boehmite-TAPC

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List of Abbreviations

CNT	**Carbon nanotubes**
CVD	**Chemical vapor deposition**
d.c.	**direct current**
LiDDS	**Lithium dodecyl sulfate**
MAO	**Methylalumoxane**
MWCNT	**Multi walled carbon nanotubes**
n-MAO	**nanoparticle-based Methylalumoxane**
NaDDBS	**Sodium dodecylbenzene sulfonate**
NaDDS	**Sodium dodecyl sulfate**
PEG	**Polye ethylene glycol**
PHBA	***para*-Hydroxybenzoate-alumoxane**
PLV	**Pulsed laser vaporization**
PTC	**Phase transfer catalyst**
r.t.	**room temperature**
SDS	**Sodium dodecyl sulfate**
SEM	**Scanning electron microscope**
SWCNT	**Single walled carbon nanotubes**
TAPC	**Hexachlorocyclotriphosphazene**
TEM	**Transmission electron microscopy**

Chapter One

Introduction

Part A

Nanotechnology Definition

Nanotechnology is about making things, whether it be making things that are smaller,faster or making machines that will lead to new manufacturing paradigms.

Three factors define nanotechnolgy: small size, new properties and the integration of the technology in to materials and devices. Nanotechnology covers a broad range of science, drawing concepts, knowledge and expertise, skills and materials from all the three classical sciences, physics, chemistry and biology. In fact, Nanotechnology (sometimes shortened to "nanotech") is the study of manipulating matter on an atomic and molecular scale. Generally, nanotechnology deals with structures sized between 1 to 100 nanometre in at least one dimension, and involves developing materials or devices possessing at least one dimension within that size.

1.1. Carbon Nanotubes

Carbon nanotubes (CNT) are formed by rolling graphene sheets of hexagonal carbon rings into hollow cylinders that was accidentally discovered by Sumio Iijima in1991 and can be classified into either multi-walled or single-walled CNT (MWCNT or SWCNT)

1.1.1. Types of Carbon Nanotubes

1.1.1.1. SWCNT

Single-walled carbon nanotubes (SWCNT) are composed of a single graphene cylinder with a diameter in the range of 0.4–3 nm and capped at both ends by a hemisphere of fullerene. The length of nanotubes is in the range of several hundred micrometers to millimeters.

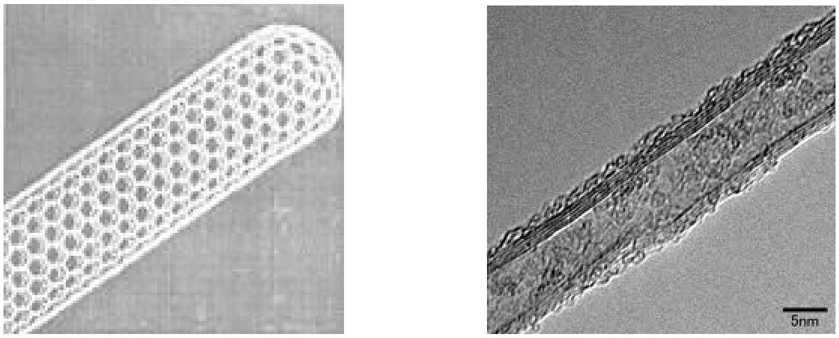

Figure 1.2. Ends of SWCNT like a hemisphere of fullerene (left) and TEM image of SWCNT (right)

1.1.1.2. MWCNT

Multi-walled carbon nanotubes (MWCNT) comprise 2 to 50 coaxial cylinders with an interlayer spacing of 0.34nm The diameter of MWCNTs generally ranges from 4 to 30 nm.

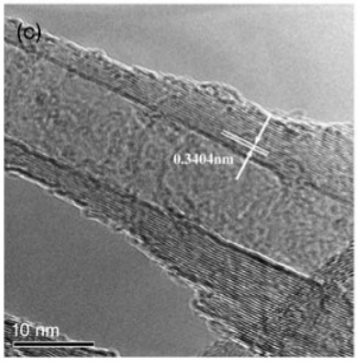

Figure 1.3. TEM image of MWCNT

1.1.2. Types of Carbon Nanotubes Based on "Roll Up" the Graphene Sheet

The graphene sheets can be rolled into different structures, that is, zig-zag, armchair and chiral. Accordingly, the nanotube structure can be described by a chiral vector ($\vec{C}_h$) defined by the following equation:

$$\vec{C}_h = n\vec{a}_1 + m\vec{a}_2$$

Where $\vec{a}_1$ and $\vec{a}_2$ are unit vectors in a two-dimensional hexagonal lattice, and n and m are integers. Thus, the structure of any nanotube can be expressed by the two integers n, m and chiral angle, Θ (Figure 1.4).

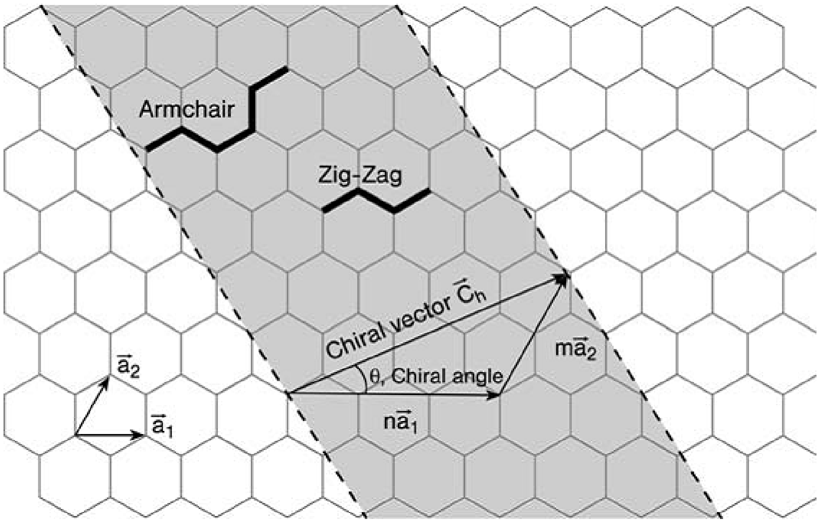

Figure 1.4. Schematic diagram showing chiral vector and chiral angle in a rolled graphite sheet with a periodic hexagonal structure

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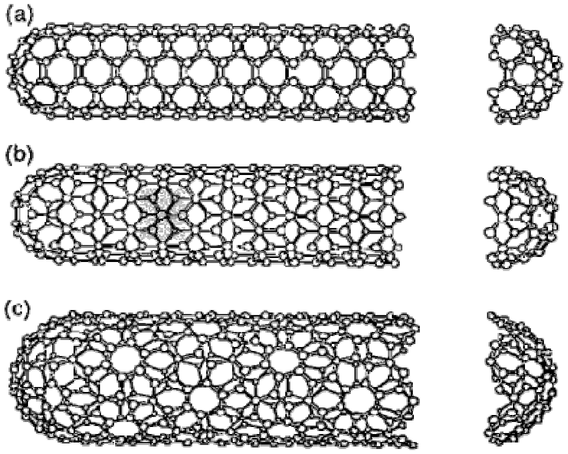

a) When $n = m$ and $\Theta = 30^\circ$, an armchair structure is produced

b) When m or $n = 0$ and $\Theta = 0^\circ$, zig-zag nanotubes can be formed

c) Any other values of n and m, $0^\circ < \Theta < 30^\circ$ is a chiral nanotubes

1.1.3. Synthesis of Carbon Nanotubes

1.1.3.1 Electric Arc Discharge

In the process, an electric (d.c.) arc is formed between two high purity graphite electrodes under the application of a larger current in an inert atmosphere (helium or argon). The high temperature generated by the arc causes vaporization of carbon atoms from anode into a plasma. The carbon vapor then condenses and deposits on the cathode to form a cylinder with a hard outer shell consisting of fused material and a softer fibrous core containing nanotubes and other carbon nanoparticles.It is worth noting that SWNTs can only be synthesized through the arc discharge process in the presence of metal catalysts. Typical catalysts include transition metals, for example, Fe, Co and Ni, rare earths such as Yand Gd, and platinum group metals such as Rh, Ru and Pt. In this respect, the graphite anode is doped with such metal catalysts.

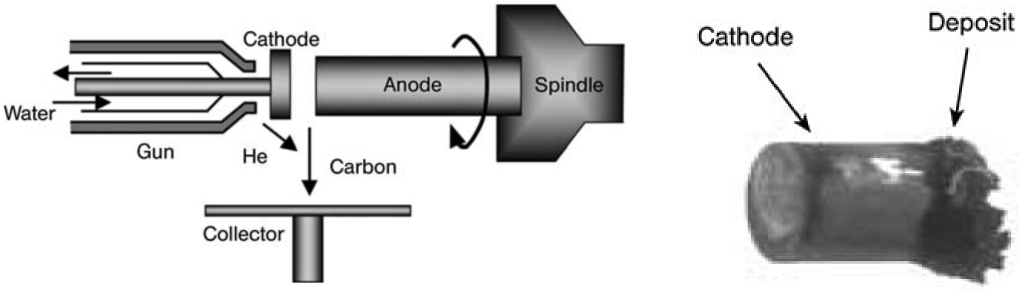

Figure 1.5. Schematic drawing of the arc discharge apparatus and side image of the MWNTs rich material deposited on the cathode

1.1.3.2. Laser Ablation

Laser ablation involves the generation of carbon vapor species from graphite target using high energy laser beams followed by the condensation of such species. In the process, graphite target is placed inside a quartz tube surrounded by a furnace operated at 1200 °C under an inert atmosphere. The target is irradiated with a laser beam, forming hot carbon vapor species (e.g. C_3, C_2 and C). These species are swept by the flowing gas from the high-temperature zone to a conical copper collector located at the exit end of the furnace.

SWNTs can also be produced by laser ablation but require metal catalysts as in the case of electric arc discharge. Pulsed laser beam with wavelengths in infrared and visible (CO_2, Nd:YAG) or ultraviolet (excimer) range can be used to vaporize a graphite target. This is commonly referred to as pulsed laser vaporization (PLV) technique Moreover, CO_2 and Nd:YAG lasers operated in continuous wave mode have been also reported to produce nanotubes.

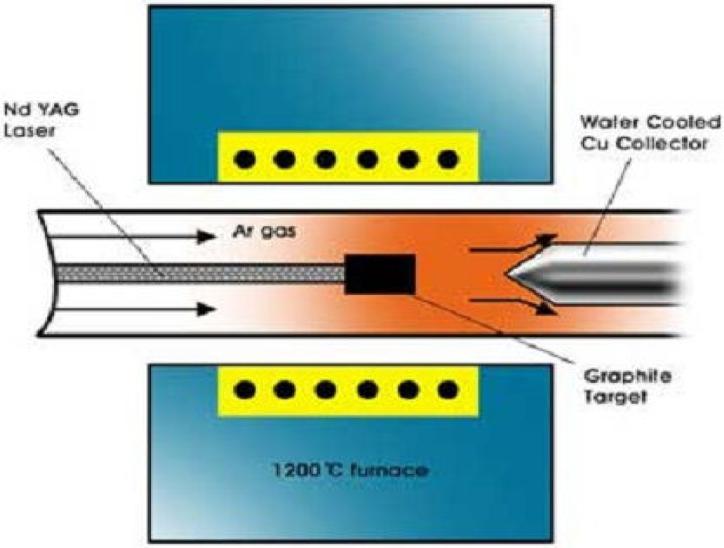

Figure 1.6. Schematic drawings of a laser ablation apparatus

1.1.3.3. Chemical Vapor Deposition

The CVD process involves chemical reactions of volatile gaseous reactants on a heated sample surface, resulting in the deposition of stable solid products on the substrate. The process involves the decomposition of hydrocarbon gases over supported metal catalysts at temperatures much lower than the arc discharge and laser ablation. The type of CNTs produced in CVD depends on the synthesis temperatures employed. MWNTs are generally synthesized at lower temperatures (600–900 °C) whereas SWNTs are produced at higher temperatures (900–1200 °C). Film formation during CVD process includes several sequential steps

(a) transport of reacting gaseous from the gas inlet to the reaction zone;
(b) chemical reactions in the gas phase to form new reactive species;
(c) transport and adsorption of species on the surface;
(d) surface diffusion of the species to growth sites;

(e) nucleation and growth of the film;
(f) desorption of volatile surface reaction products and transport of the reaction by-products away from the surface.

CVD can be classified into thermal and plasma-enhanced and vapor phase growth and laser-assisted processes depending upon the heating sources used to activate the chemical reactions.

1.1.3.4. Carbon Monoxide Disproportionation

In 1999, Smalley's research group at Rice University developed the so-called high pressure CO disproportionation (HiPCo) process that can be scaled up to industry level for the synthesis of SWNTs. SWNTs are synthesized in the gas phase in a flow reactor at high pressures (1–10 atm) and temperatures (800–1200 °C) using carbon monoxide as the carbon feedstock and gaseous iron pentacarbonyl as the catalyst precursor. Solid carbon is produced by CO disproportionation that occurs catalytically on the surface of iron particles via the following reaction.[1]

$$CO + CO \longrightarrow C_{(s)} + CO_2$$

1.1.4. Special Properties of Carbon Nanotubes

1.1.4.1. Chemical Reactivity

The chemical reactivity of a CNT is, compared with a graphene sheet, enhanced as a direct result of the curvature of the CNT surface. Carbon nanotube reactivity is directly related to the pi-orbital mismatch caused by an increased curvature. Therefore, a distinction must be made between the sidewall and the end caps of a nanotube. For the same reason, a smaller nanotube diameter results in increased reactivity. Covalent chemical modification of either sidewalls or end caps has shown to be possible.

1.1.4.2. Electrical Conductivity

Carbon nanotubes with a small diameter are either semi-conducting or metallic. The differences in conducting properties are caused by the molecular structure that results in a different band structure and thus a different band gap.

The differences in conductivity can easily be derived from the graphene sheet properties. It was and n and m are defining the nanotube. The resistance to conduction is