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Turkmenistan. Turkmenistan.***Samandarov E. Sh., Kodamboev P. K.,***Khorezm Mamun branch of Uzbekistan Academy of Sciences, Markaz-1, Khiva 220900, Uzbekistan.***MODIFICATION AND INTERCALATION OF CARBON NANOTUBES. CHEMICAL
MODIFICATIONS. SURFACE MODIFICATION OF CNTS BY AMIDATION AND
ESTERIFICATION**

Abstract. The impact of oxidation on the modification of single-wall carbon nanotubes (SWCNTs) through successive purification steps has been investigated. The efficient removal of metal impurities was monitored using inductively coupled plasma spectroscopy. Following acid treatment, Raman spectroscopy clearly demonstrated the intercalation of HNO_3 molecules into the bundles of SWCNTs. Simultaneously, SWCNTs underwent significant degradation and the introduction of defects. Subsequent thermal processes facilitated the removal of additional defective carbon materials and nearly complete de-intercalation of the HNO_3 molecules. Changes in the structure of SWCNT bundles were observed via transmission electron microscopy. While bundles tended to separate during acid treatment, the remaining SWCNTs tended to re-form thick bundles after the full purification process. The presence of functional groups in the initial raw single-wall carbon nanotube material, their modification, and near-complete removal after the final annealing step were analyzed using Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, and temperature-programmed desorption. Nitrogen adsorption isotherms, analyzed following the Brunauer–Emmett–Teller method, revealed significant alterations in pore volume and surface area throughout the purification steps.

Multiwall carbon nanotubes (MWCNTs) were non-covalently functionalized by a uniform layer of a porphyrin–Sn network (denoted as MPT) via a facile one-pot solvothermal synthesis for enhancing protein adsorption. The porphyrin–Sn network layer was assembled by meso-tetra(4-carboxyphenyl) porphine (TCPP) molecules cross-linked by SnCl_2 . The thickness of the shell layer can be precisely controlled by adjusting the precursor ratio of MWCNTs to TCPP. The structure and properties of the obtained MPT were fully characterized. Under the optimized shell thickness and adsorption conditions, MPT shows an ultrahigh adsorption capacity for proteins such as bovine serum albumin, cytochrome c, lysozyme, and bovine hemoglobin, due to the abundant uniformly distributed adsorption sites on the nanomaterials' surfaces.

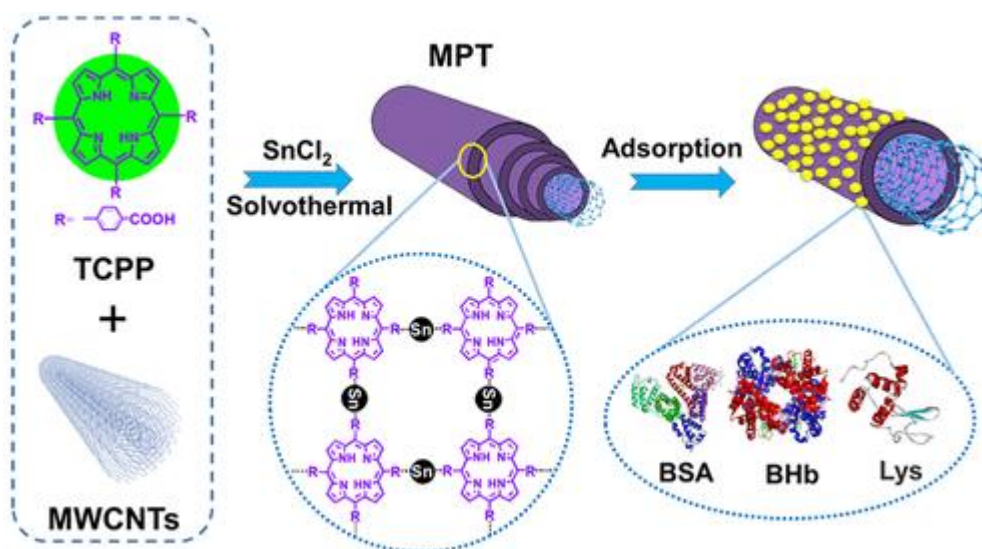


Figura-1

Key word: Carbon nanotubes; cytochrome c; Nickel; nanoelectronics; morphologies; nanometer-scale; allotropes; nanocomposite; Deposition of chemical vapors.

Introduction. Since their discovery in 1991, carbon nanotubes (CNTs) have been the subject of extensive research due to their exceptional electronic, mechanical, catalytic, and adsorption properties. These properties, including low densities and high surface areas, position CNTs as promising candidates for a wide array of applications in catalysis, energy storage, nanoelectronics, adsorption, and separation. However, the practical utilization of CNTs has been hindered by their limited dispersibility and challenging manipulation in solvents. To address this challenge, a crucial step involves the functionalization of CNTs through inorganic and/or organic methods to improve dispersibility while introducing new properties and functionalities. Novel hybrid nanomaterials with desirable structural and physicochemical characteristics have garnered significant attention in various fields, including environmental remediation, pharmaceutical treatments, sensing, catalysis, and energy storage. Among all types of nanomaterials, carbon nanotubes (CNTs), as one of the carbon allotropes, can be considered extraordinary materials. Primarily, CNTs have captured the interest of researchers due to their unique characteristics, such as excellent physical and chemical properties, large pore volumes, one-dimensional structures, and are deemed favorable building blocks for engineering hybrid nanomaterials. These attributes endow CNTs with tremendous potential for numerous applications in energy storage, air and water treatment, biological applications, catalyst supports, thermal interface materials, structural materials, ceramics, fibers, conducting plastics, field emission, conductive adhesives, thermal conductors, and more.

CNTs can be visualized as cylinders formed by rolling up graphene flakes on a nanometer-scale around a central hollow core structure. Typically, cylindrical nanotubes have at least one end capped with a hemisphere structure of fullerene. Based on the fabrication method, CNTs exist in two forms. The first type includes single-walled CNTs (SWNTs) with diameters ranging from 0.8 to 2 nm, comprising seamless cylinders of carbon atoms in single or multiple layers with open or closed ends. The second type consists of multi-walled CNTs (MWNTs) with diameters approximately between 5 to 20 nm, comprising two or more layers of assembled cylindrical shells of carbon atoms. The lengths of CNTs can vary from less than 100 nm to a few centimeters, spanning the molecular to macroscopic scales.

While there is no consensus on the absolute mechanical strength of nanotubes, experimental and theoretical findings have revealed exceptional mechanical properties, with a Young's modulus

reaching as high as 1.2 TPa and tensile strength ranging from 50 to 200 GPa. Due to these characteristics, CNTs can be considered among the stiffest and strongest materials known. Additionally, CNTs exhibit remarkable thermal conductivity, electrical conductivity, and an ultra-high surface area. The chemical interaction of nanotubes is predominantly composed of sp^2 C-C bonds, with layers of carbon atoms arranged coaxially around a central hollow core through van der Waals forces and π - π stacking interactions adjacent layers.

Chemical Modifications.

In this method, the modification of nanotubes is achieved through covalent bonding between small molecules and the layers of nanotubes. Typically, in chemical modification using polymer molecules, pre-modification of nanotubes with small molecules is necessary. This pre-modification process generates anchor sites that can be utilized for attaching polymer chains via covalent bonding. Moreover, the electrical, thermal, biological, and mechanical properties of the resulting composite materials are influenced by interfacial interactions, emphasizing the importance of compatibility between the fillers and the matrix.

One highly recognized approach for modifying CNTs involves oxidation reactions to introduce various oxygen-containing functional groups that can be further utilized for covalent functionalization. Commonly, carboxyl, epoxy, and hydroxyl groups are generated on the surface of nanotubes through diverse oxidation reactions using oxygen, aqueous hydrogen peroxide, concentrated nitric acid, and sulfuric acid. For instance, Xue et al. conducted a study where three functionalized MWNTs (-COOH, -NH, -OH) were added to an aqueous phase containing piperazine (PIP) to fabricate nanocomposite nanofiltration (NF) membranes via interfacial polymerization (IP) reaction. X-ray photoelectron spectroscopy (XPS) analysis confirmed the successful incorporation of these functional groups and their impact on the properties of the nanocomposite membrane.

Feel free to explore the intriguing world of chemical modifications of nanotubes and their applications based on the revised text. Let me know if you require further assistance or detailed explanations.

In addition to successful encapsulation of modified MWCNTs in the active layer of the fabricated NF membranes (refer to Figure 4 II), the researchers highlighted that the improved dispersibility of modified MWNTs was attributed to the presence of active functional groups (-COOH, -NH, -OH). These functional groups played a crucial role in creating distinct nodular surface morphologies, varying hydrophilicities, and thicknesses of the NF membranes, as depicted in Figure 4 III. Notably, all the manufactured NF membranes demonstrated a molecular weight cutoff of up to 300 Da and exhibited enhanced functional stability.

The incorporation of modified MWNTs and the subsequent effects on the properties of the NF membranes showcase the intricate interplay between nanotube functionalization, membrane morphology, and performance characteristics. This successful functionalization and encapsulation process offer promising avenues for advancing the field of nanocomposite membranes for various applications.

Table-1. Summary of Modification of Nanotubes and Their Derivatives by Small Molecules via Non-covalent and Covalent Methods.

Nanotube	Interacting molecule	Method	Mode of attachment	Application	Ref
MWCNT	Octadecylamine	Covalent	Nucleophilic addition	Enhanced solubility/dispersibility	(34)
MWNT	Pyrene	Non-covalent	π - π interaction	Glucose sensing	(35)

MWCNT	Ethylendiamine	Covalent	Acylation reaction	Electrochemical detection of double stranded-deoxyribonucleic acid (dsDNA)	(36)
MWNT	Porphyrins	Non-covalent	π - π interaction	Biofuel cell applications	(37)
MWNT	Horseradish peroxidase	Covalent	Amidation reaction	Enzymatic degradation	(38)
SWNT	Reactive red 195	Non-covalent	π - π interaction	Water-soluble CNT	(39)
SWCNT	Alkyne-focal dendrons	Covalent	1,3 Dipolar cycloaddition	Cell culture	(40)
SWNT	Nile blue	Non-covalent	π - π interaction	Electrochemical catalysis	(41)
MWNT	fluorine	Covalent	Halogenation	Enhanced water dispersibility	(42)
SWNT	Tertiary phosphines	Non-covalent	π - π interaction	Stable dispersions	(43)
SWNT	Succinic or glutaric acid acyl peroxides	Covalent	Free radical addition	Enhanced solubility in polar solvents	(44)
MWNT	Rosemary acid	Non-covalent	π - π interaction	Enhanced mechanical properties	(45)

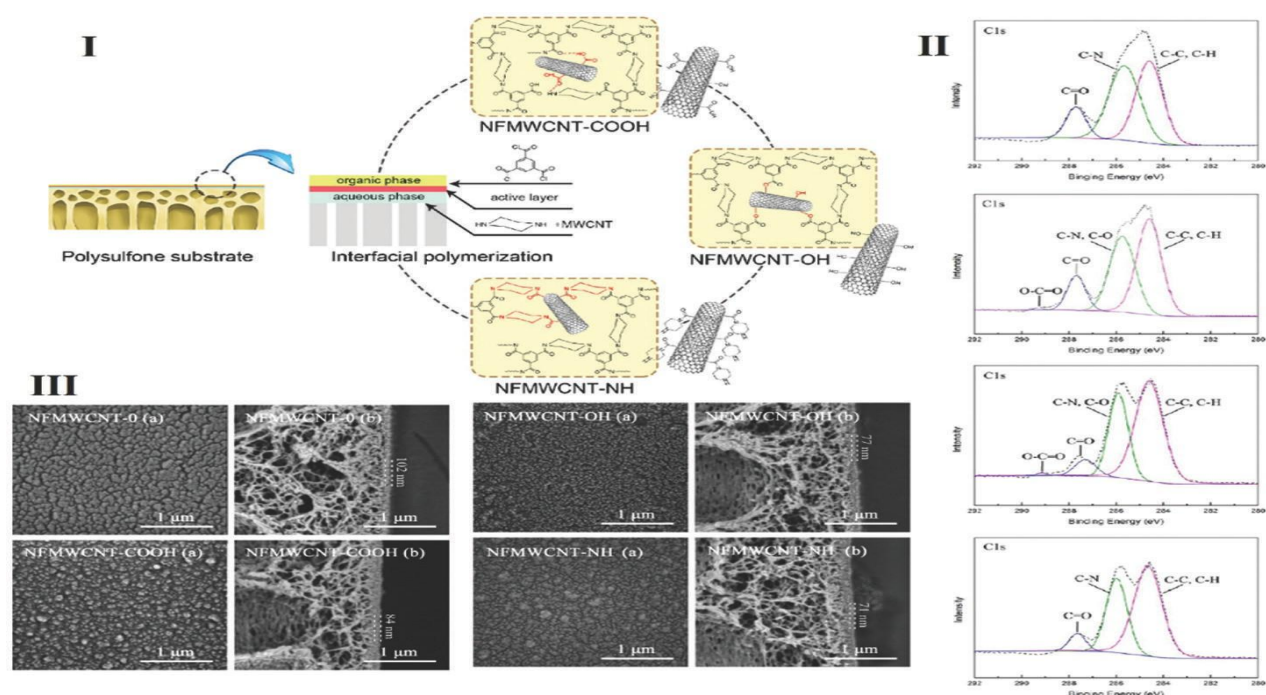


Figure-2..

(I) A graphical representation illustrating the preparation of various NF membranes through the IP approach,
 (II) Surface morphology images displaying (a) top surfaces and (b) cross sections of both pristine and functionalized MWNTs integrated NF membranes, and
 (III) XPS response for (a) NFMWNT-0, (b) NFMWNT-COOH, (c) NFMWNT-OH, (d) NFMWCNT-NH. The proportion of functionalized MWNTs in the NF membrane was 0.01% (w/v). This figure has been adapted with permission from reference (47), Copyright 2016 American Chemical Society.

Carbon nanotube synthesis and modification.

Nickel plates containing 99% Ni, with a maximum concentration of non-Ni elements at 0.4% Fe, 0.25% Cu, 0.15% C, 0.35% Mn, 0.35% Si, and 0.01% other elements, were used to grow UNNs. The plates, 0.5 cm wide and of various lengths, underwent initial mechanical polishing with P#60, #400, and #1200 SiC papers, followed by ultrasonic degreasing with ethanol for 30 minutes. Each sample was then placed inside a 25 mm inner diameter and 410 mm long quartz tube, heated to the desired temperature of $685 \pm 2^\circ\text{C}$ in a tube furnace under Ar (O_2 below 3 ppm, H_2O below 5 ppm, and THC below 0.5 ppm) at a flow rate of 637 ± 5 SCCM. The samples were held at this temperature for 5-10 minutes to ensure uniform heating before the injection of ($\text{C}_{14}\text{H}_{10}\text{Fe}_2\text{O}_4$). The content of ($\text{C}_{14}\text{H}_{10}\text{Fe}_2\text{O}_4$) was 7% by volume at a total flow rate of 685 ± 5 SCCM. The flow of ($\text{C}_{14}\text{H}_{10}\text{Fe}_2\text{O}_4$) was stopped after specific durations of 2 and 10 minutes. The Ar flow was maintained at the same temperature for an additional 30 minutes. Subsequently, the heating was turned off, and the furnace was allowed to cool under a nitrogen gas flow (with the Ar flow rate reduced to 25% of the initial value). An extra 30 minutes of thermal CVD revealed the essential role of the Ar flow in the growth and crystallization of the UNNs under the specified temperature conditions. Figure-3.

The synthesized carbon nanotube was modified with NLO synthesized based on tin metal. Figure-4.

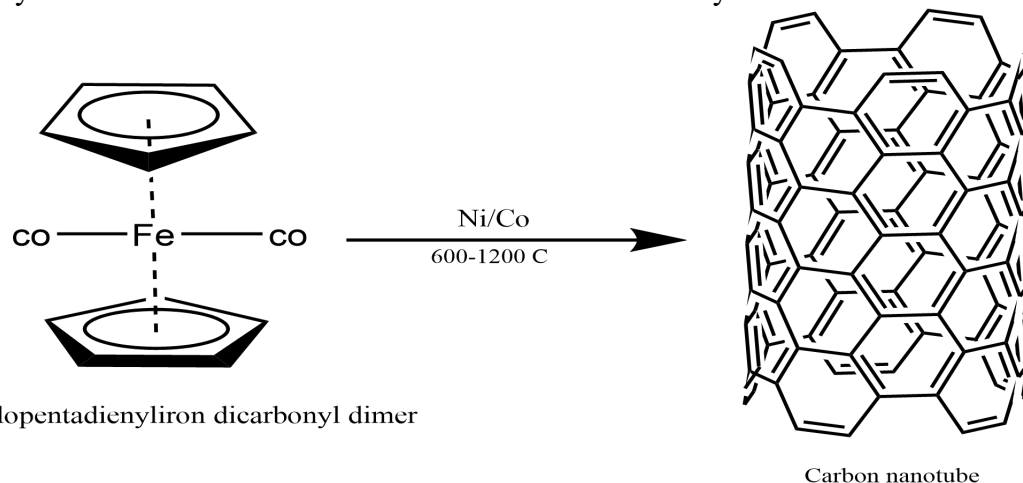


Figura-3. Synthesis carbon nanotube.

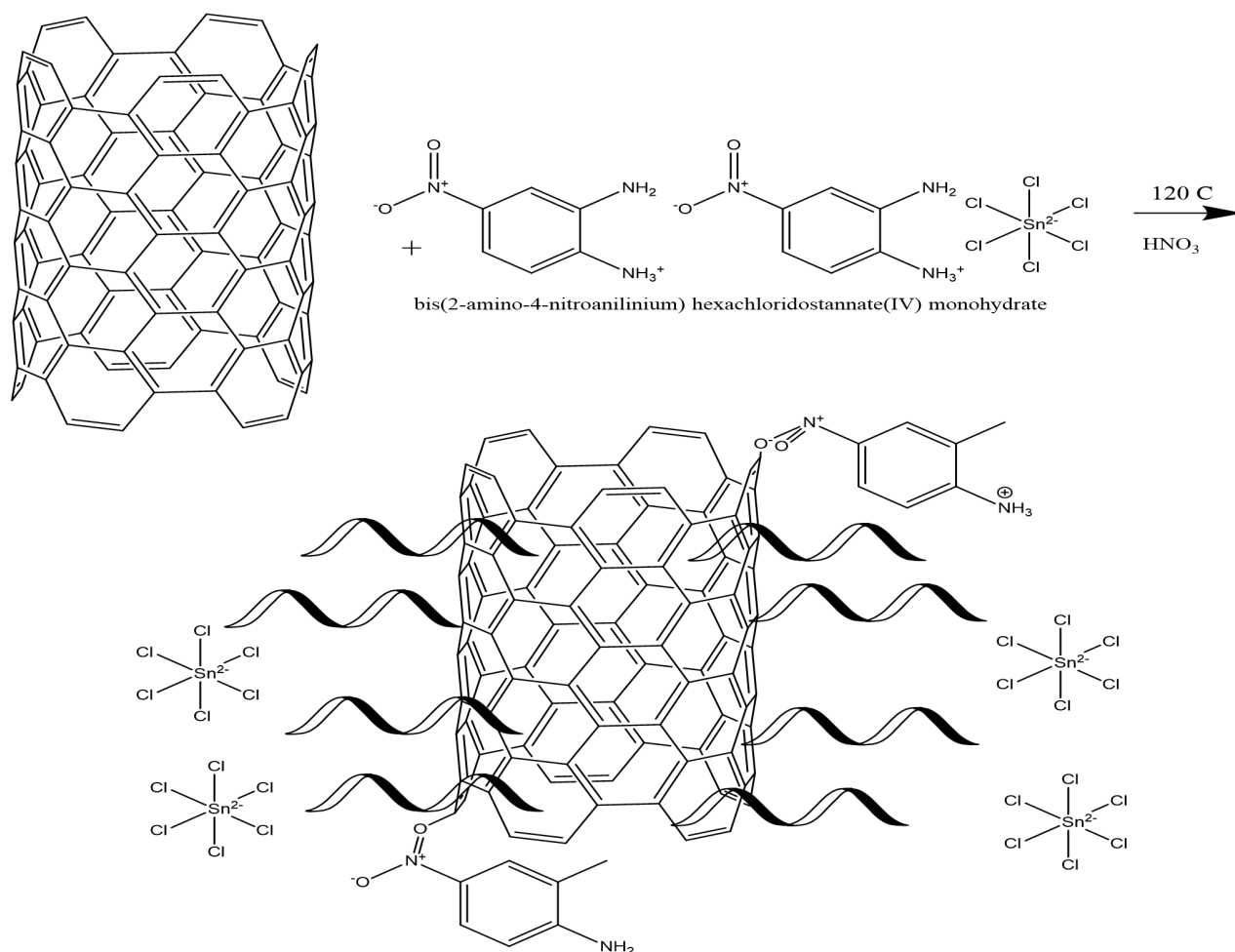


Figura-4. Carbon nanotube modification

Surface Modification of CNTs by Amidation and Esterification.

Surface modification of carbon nanotubes (CNTs) through amidation and esterification processes enables the construction of water-soluble organic compounds such as conjugates with nucleic acids, proteins, and polymers. The $-\text{COOH}$ groups on the surface of oxidized CNTs serve as active sites for further functionalization, enhancing their potential for diverse applications. Amidation of CNTs is influenced by factors like the type of amine and catalysts, facilitating substantial surface modification by incorporating active functional groups. Structural analysis of amidated CNTs reveals the covalent bonding of amine nitrogen to the nanotube surface.

Researchers have demonstrated the creation of hydrophilic multi-walled carbon nanotubes (MWNTs) through amidation of oxidized MWNTs followed by Michael addition reactions with various compounds. Spectroscopic analyses confirm the presence of functional groups like $\text{C}=\text{O}$, $-\text{OH}$, $\text{C}-\text{N}$, $-\text{NH}$, and amid groups on the CNT surface. Incorporating these functionalized MWNTs as fillers in waterborne polyurethane (WPU) composites enhances interfacial adhesion and dispersion within the matrix, leading to improved electrical conductivity, hydrophilicity, and mechanical properties.

Amidation of multi-walled carbon nanotubes (MWNTs) involves attaching amine ($\text{N}-\text{H}$) and carboxylic (COOH) groups to the outer tube of MWNTs at temperatures below 600°C . This process results in improved dispersion of amino-modified MWNTs in water. Additionally, Abjameh et al. (55) conducted research on the modification of single-walled carbon nanotubes (SWNTs) with amide

groups using NH_3 and thionyl chloride (SOCl_2). Chemical characterization via FTIR analysis confirmed the presence of amide groups and $-\text{COOH}$ groups, indicated by the broad band of the amide and specific bands related to carbon-nitrogen (C-N) and amine (NH) groups of the amid group, respectively.

Furthermore, Mallakpour et al. (56) described the functionalization of MWNTs with amino acids under microwave irradiation, followed by a reaction with a carboxylic acid. The resulting functionalized MWNTs (f-MWNTs) were dispersed within a thiadiazol and amino acid-based poly(amide-thioester-imide) (PATEI) as shown in Figure 5a. They observed homogeneous dispersion of f-MWNTs in the PATEI matrix without any macroscopic aggregation.

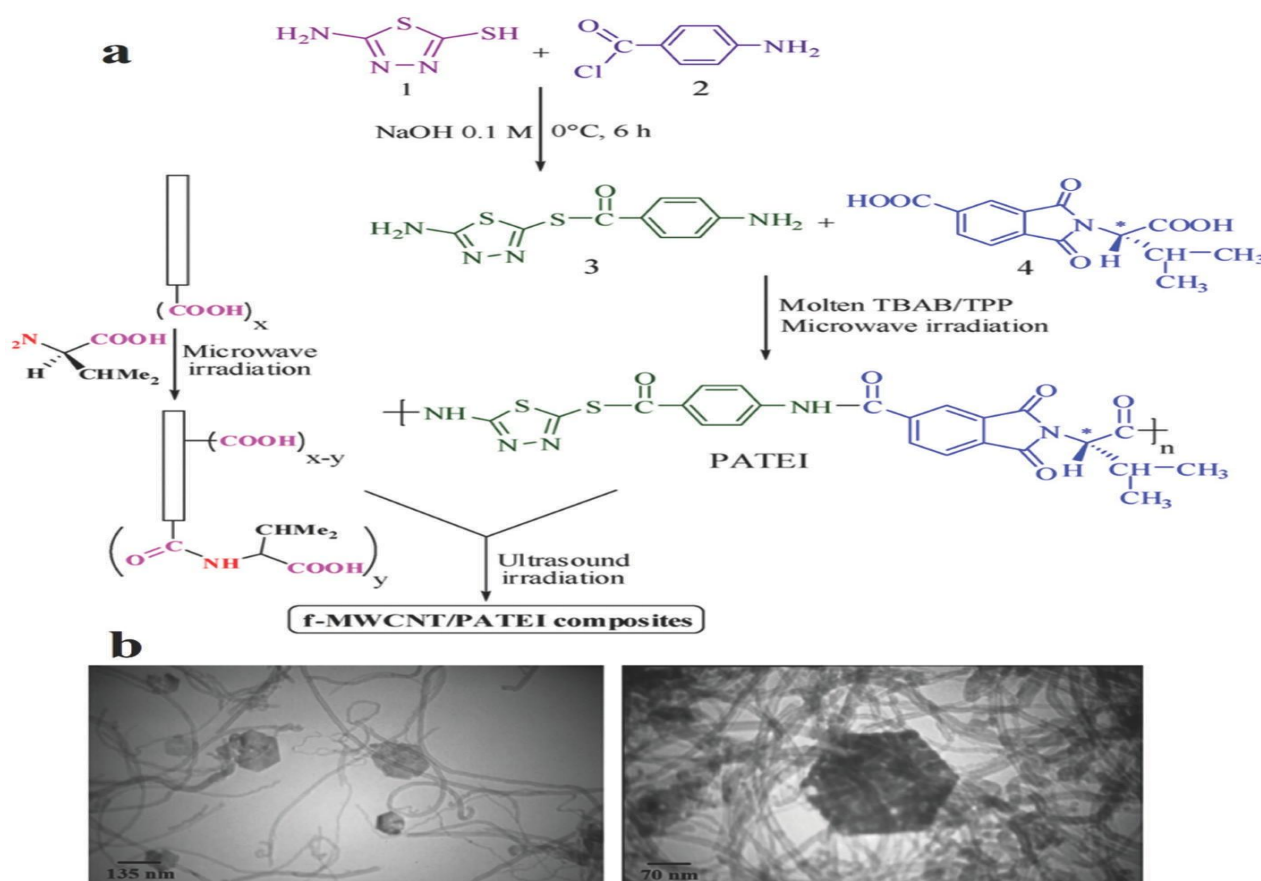


Figure-5

(a) A schematic depiction of the manufacturing process of PATEI, and f-MWNT/PATEI composites, and

(b) TEM micrographs demonstrating the well-dispersed f-MWNTs within the composites. This figure has been adapted with permission from reference (56), Copyright 2013 Elsevier.

Summary and Outlook

The unique structure and properties of carbon nanotubes (CNTs) make them highly promising materials in various research fields for diverse applications. However, their utility is limited by challenges such as compatibility with polymer matrices, processability constraints, and solubility issues in both water and organic solvents. Functionalization or modification of CNTs is crucial for addressing these limitations, enhancing their selectivity, sensitivity, and solubility. Various methods of

modifying the surface of CNTs have been explored, showing the ability to introduce different active chemical sites that alter their surface properties effectively.

Surface modification of nanotubes holds significant promise for creating stable CNT suspensions with high dispersibility, paving the way for a wide range of applications. Functionalized CNTs have demonstrated solubility in polar solvents like dimethylformamide, ethanol, and even water, depending on the type and extent of functional groups attached. Both non-covalent and covalent interaction-based techniques are being investigated for CNT functionalization. Non-covalent modifications, such as hydrogen bonding and π - π interactions, involve adsorbing interacting moieties onto the nanotube surface without disrupting their extended π conjugation. While these interactions may be weaker than covalent bonds, they preserve the electronic structure of CNTs, leading to enhanced electronic, mechanical, and physical properties.

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