

Polymer Nanocomposites: Structure and Synthesis

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ABSTRACT

Nanotechnology may restructure the technological applications such as semiconductors, inorganic as well as organic materials, energy storage, and biotechnology. It integrates chemistry, physics, materials science, and biology to design and create new material properties of electronic devices, biomedical products, high performance materials and consumer articles. Composites or new product requires emphasis on new functionalities. Commercialization of nanotechnology based products and production of unique performance with customer benefits further puts challenge of reasonable cost, particle formation, precise processing, and desired fabrication of nanomaterial. The commercialization of nanotechnology will certainly boost technical development, improved quality of life and societal benefits. The paper describes new systematic approaches of synthesis and device formation of nanotechnology based composites: 1. Nano synthesis: making nanoscale building blocks including nanoparticles, nanotubes, and nanostructures; 2. Nano characterization: measuring and characterizing the basic properties of nanoscale building blocks, intermediate and final product forms; 3. Nano processing and nanofabrication: manipulating and processing nanoscale building blocks for a desired purpose and incorporating nanoscale building blocks. Organic conducting polymers or “synthetic organic metals” are p-doped polymers: polyaniline, polypyrrole, poly (p-phenylene vinylene), polythiophene and their derivatives. These composites display semi-conducting nature, electro-activity, and plasticity. Nanoconducting polymers are useful in electronic, optical and magnetic properties, self assemblies at the molecular level.

Key words: energy storage, nanocomposites, synthesis

1 INTRODUCTION

Polymer p-doped polymers are polyaniline (PANI), polypyrrole (PPy), poly (p-phenylene vinylene) (PPV), polythiophene (PTh) and their derivative polymer chains as nano conducting polymers have applications in light emitting diodes (LED), electrochromic displays, smart windows, field effect transistors (FET), electromagnetic interference (EMI) shielding devices, energy storage products such as batteries, super capacitors and fuel cells. Conducting polymers can be formed by chemical or electrochemical synthesis Traditional precipitation, crystallization, sol-gel transformation emulsion polymerization, molecular template nucleation for wires, tubes, globules and discs as attractive alternatives to silicon nanowires and carbon nanotubes because of their tunable

conductivity, flexibility, chemical diversity, and easy chemical synthesis, templated electrochemical synthesis, and electro-spinning to develop conducting polymer based nanocomposites in microelectronics [1].

2 SYNTHESIS OF NANOCOMPOSITES

2.1 Electrochemical Synthesis

The electrochemical method has been used for the synthesis of an array of nano-materials such as metals, inorganic composites, conducting polymer fibers or tubes and multi-metal striped rods, conductive polymer nanotubes and nanofibers such as polypyrrole (PPy), polythiophene(PTh), and polyaniline(PANI) in the pores of a polycarbonate (PC) or alumina membrane(AO).

2.2 Chemical Synthesis

Oxidative polymerization of aniline in an aqueous aniline is dissolved in 1N HCl at about 0°C for polymerization (Polyaniline nanofibers form) by adding an oxidant, ammonium peroxydisulfate with possibility of nanofibers polyaniline scaffold agglomerates containing nanofibers and particulates

2.3 Template Synthesis

It includes: surfactants, liquid crystals, nanowire seeds, aniline oligmers, and relatively complex, bulky organic dopants acting as templates (e.g., poly electrolytes) or ordered “soft templates” (e.g., micelles, emulsions). The templates technique can be classified as: Hard templates; Soft templates and Seed templates.

1. Hard Templates

The hard template polycarbonate (PC) or polyester (PE) membranes, anodic aluminum oxide (AAO) membranes, solid porous materials, such as zeolites, silica-based mesoporous molecular sieves, oxides, graphite composites, polyoxometallates, carbon nanotubes and Ag, Au, or Ni nanoparticles can be used in hard template synthesis of CP nanostructures.

2. Soft Templates

Oxidative polymerization of aniline in the presence of nonionic surfactants (Triton X-100), anionic surfactants (sodium dodecylsulfate), cationic surfactants (cetyltrimethyl ammonium bromide), mixture of ionic surfactants (cetyltrimethyl ammonium bromide and sodium dodecylbenzene sulfonate), amphiphilic ionic liquid (1-hexadecyl-3-methylimidazolium chloride), and amphiphilic acids e.g., 4-{n-[4-(4-nitrophenylazo)-phenoxy] propyl,

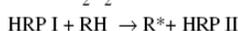
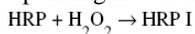
amino benzenesulfonic acid where n = 2, 3, 4, 6, 8, or 10, 77, 78 azobenzene sulfonic acid, naphthalene sulfonic acid (NSA), dodecyl benzene sulfonic acid, *p*-aminobenzene sulfonic acid, *p*-toluene sulfonic acid, CSA, 4-[4-hydroxy-2-pentadec-8-enyl]phenylazo] benzenesulfonic acid, Allura Red AC, cardanol and sulphonated dendrons make 3-D conducting polymer network, nanofibers, cylindrical micelles, helical PANI nanostructures, chiral PANI nanorods and gold microspheres.

3. Seed Template Method

Seeding single-walled carbon nanotube (SWNT) conjugate with PANI to make nanofibers 20–60 nm seed (nanofibers vs nanospheres).

2.4 Biocatalytic Approach

Biocatalytic enzyme is biocatalyst for polymerization of phenols and anilines by *horseradish peroxidase* (HRP) for polymerization in the nanocomposites, PAA/PANI/(+)CSA, and PAA/PANI/(-)CSA. HRP catalyzes the oxidation to generate corresponding free radicals:



2.5. Chemical Vapor Deposition

The thermal chemical vapor deposition polymerization (CVD) is an effective top-down method to fabricate nano-materials, nano-composites, and conformal coating on nano-structures.

2.6 Electro Spinning Process

Electrostatic spinning or “electrospinning” is a process capable of producing polymer fibers in the nanometer diameter range.

2.7 Mechano-Chemical Synthesis

Copper, nickel, and other metal powders are obtained by mixing ultrafine metal powders with liquid metal eutectics. The Cu–Bi and Fe–Bi ‘immiscible’ systems make nanocomposites.

2.8 Vapor-Phase Assisted Surface Polymerization (VASP)

Micro architectures on solid substrate surfaces by VASP technique is useful for the construction of fine structured composites and coatings at the gaps and spaces within the solid substrate “pseudo-grafting” give anchoring effect, with excellent binding strength at the polymer/ substrate interface.

7.4 Intercalation Techniques

In *in-situ* polymerization, monomers are intercalated into layered clays and subsequently polymerized within the gallery via heat, radiation, pre-intercalated initiators or catalysts.

3 STRUCTURE OF NANOCOMPOSITES

Polymer based nanocomposites can have structures as:

- 1) Layered like inorganic media and porous hosts
- 2) Nano-scale metal nanoparticles
- 3) Nano-scale metal oxide nanoparticles
- 4) Carbon nanotubes

3.1 Inorganic Media and Porous Hosts

Silicate clay structures are briefly described in Fig.6.1 (i) built up from combinations of tetrahedral and octahedral

sheets Si–O tetrahedron and Al–O octahedron, built up from combinations of tetrahedral and octahedral sheets basic units are usually Si–O tetrahedron and Al–O octahedron.

Table.6.1. Montmorillonite, kaolinite & kanemite silicates.

Type of clay	Formula	Origin	Substitution	Layer charge
<i>2:1 type</i>				
MMT	$M_1(\text{Al}_2, \text{Mg})\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$	N	Octahedral	Negative
Hectorite	$M_1(\text{Mg}, \text{Li})\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$	N	Octahedral	Negative
Saponite	$M_2\text{Mg}_2(\text{Si}_4, \text{Al})\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$	N	Tetrahedral	Negative
Fluorhectorite	$M_1(\text{Mg}, \text{Li})\text{Si}_4\text{O}_{10}\text{F}_2 \cdot n\text{H}_2\text{O}$	S	Octahedral	Negative
Laponite	$M_1(\text{Mg}, \text{Li})\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$	S	Octahedral	Negative
Fluoromica (Somasil)	$\text{NaMg}_{2.5}\text{Si}_4\text{O}_{10}\text{F}_2$	S	Octahedral	Negative
<i>1:1 type</i>				
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_7(\text{OH})_4$	N	—	Neutral
Halloysite	$\text{Al}_2\text{Si}_2\text{O}_7(\text{OH})_4 \cdot 2\text{H}_2\text{O}$	N	—	Neutral
<i>Layered silicic acid</i>				
Kanemite	$\text{Na}_2\text{Si}_4\text{O}_9 \cdot 5\text{H}_2\text{O}$	N/S	Tetrahedral	Negative
Makaitite	$\text{NaHSi}_2\text{O}_7 \cdot 7\text{H}_2\text{O}$	N/S	Tetrahedral	Negative
Octasilicate	$\text{Na}_2\text{Si}_4\text{O}_{17} \cdot 9\text{H}_2\text{O}$	S	Tetrahedral	Negative
Magadite	$\text{Na}_2\text{Si}_4\text{O}_{17} \cdot 10\text{H}_2\text{O}$	N/S	Tetrahedral	Negative
Kenyaite	$\text{Na}_2\text{Si}_4\text{O}_{17} \cdot 10\text{H}_2\text{O}$	S	Tetrahedral	Negative

M indicates exchangeable ions represented by monovalent ions. Symbols: N (nature) and S (synthetic).

Nanocomposites N-heterocyclic polymers like polypyrrole (PPy), poly(N-vinylcarbazole) (PNVC), and polyaromatics such as polyaniline (PANI), poly(p-phenylene vinylene)(PPV) display electric conductivity and PNVC is well known for its high thermal stability and characteristic optoelectronic properties. PANI-MMT, poly(styrenesulfonic acid-co-amino styrene) (P(SSA-co-AMS) / clay nanocomposite) or by simple blending of poly(styrene sulfonic acid-g-aniline) [PSSA-g-PANI], PSSA-g-PANI, show thermal stability and compatibility of the nanocomposite improved with PSSA-g-PANI.

3.2 PANI-Silica Nanocomposites

The glass-PANI nanocomposites need polymerization of aniline, adsorbed in its protonated (i.e. positively charged) form via an ion-exchange process within the pores of porous vycor glass by the use of ammonium persulfate acidic solution as oxidant by Cu^{2+} ions.

3.3 PANI-Silane Nanoparticles

In graft polymerization, nanoparticles were hydroxylated and reacted with (3-bromopropyl) trichlorosilane to form a dense bromopropylsilane monolayer → reacted with aniline to displace the bromine atoms in polymerization of PANI, Fig. 1.

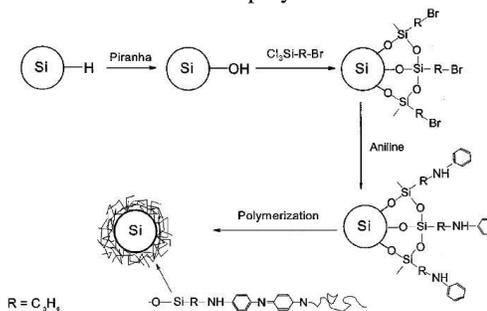


Figure 1. Grafting of PANI on Si nanoparticles through self-assembly method, consisting of formation of Si–OH groups.

3.4 Nano-Scale Metal Particles

Nanocomposites such as polyaniline and metal can have metal oxide embedded in matrices of conductive polymers, as conductor and binder; or guest-host compounds (macromolecules of conductive polymers are inserted into the interlayer galleries or channel of inorganic particles). For illustration, 3 types of intercalates are shown:

- ❖ Intercalation of monomers into the host matrix followed by polymerization due to an external effect (e.g. interaction with an oxidant).
- ❖ Redox based host intercalation of the monomers and in-situ polymerization.
- ❖ Direct intercalation of polymer macromolecules into the host particles.

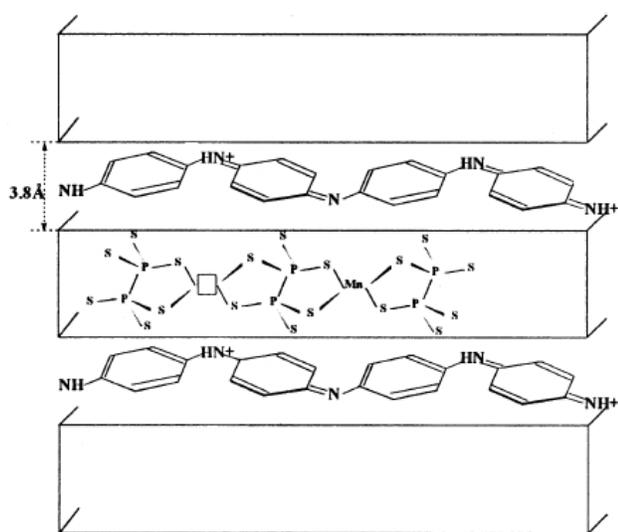


Figure 2. PANI-MnP₃ intercalates.

Other intercalates are with host layers of MPS₃ (M = Mn, Cd) and guest layers of PANI, MPS₃, PANI-NMP, PANI-CSA_{0.124}),_{1.06}MoO₃, PANI-CSA, PANI with MoO₃ using ammonium vanadate ([AV], V⁵⁺) as the oxidant.

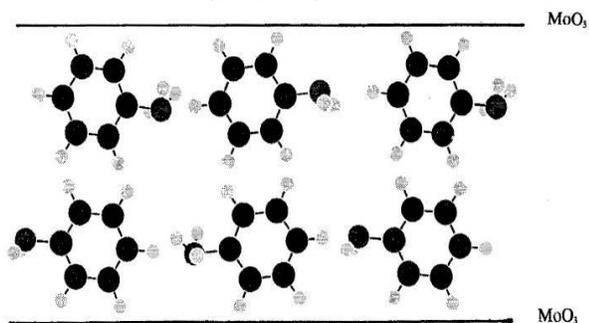


Figure 3. Arrangement of the aniline bilayer in MoO₃,

For illustration, the interlayer distance increases by 6.6 Å after aniline intercalation and returns to its original value after

polymerization. Cyclic voltammetry experiments hint further to the existence of highly linear chains with negligible crosslinking in the nanocomposite materials. The α-RuCl₃ is other example of host matrix for the in-situ redox intercalative polymerization of aniline resulting in a nanocomposite material with a positive Seebeck effect suggesting that holes were the dominant carriers in the electrical transport. Recently, new information has become available on successful synthesis with their detail structures based on PANI nanocomposites as shown below:

- 1.PANI-Au; 2.PANI-Ag Nanoparticles; 3. PANI-Pt Nanoparticles;4. PANI-Pd Nanoparticles;5 PANI-Ni And PANI-Sn Nanoparticles;6 PANI-Cu Nanocomposites ;7 Oxides Based Nanocomposites (1.PANI-V₂O₅ Nanocomposites;2.PANI-TiO₂ Nanocomposites ;3.PANI-Ferrite Nanocomposites ; 4.Pani- Al₂O₃; 5.PANI-Sno₂ Nanoparticles ;6.PANI- PANI-Zno and PANI-CeO₂ Nanocomposite ;7.PANI-Mno₂ Nanocomposites ; 8.PANI-Phosphate Nanocomposites ;9.PANI-Cds Nanocomposites ;10.PANI-Tin Nanocomposites;11.Pani-Zeolite ;12.PANI- CNT and PANI - Graphite Nanocomposites including Carbon Black

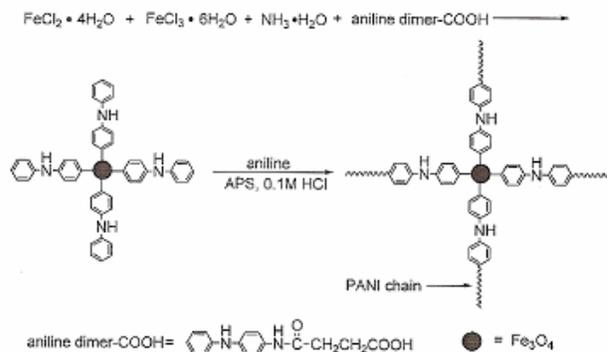


Figure 4. Fe₃O₄-PANI nanoparticles synthesis by aniline dimer-COOH assisted polymerization.

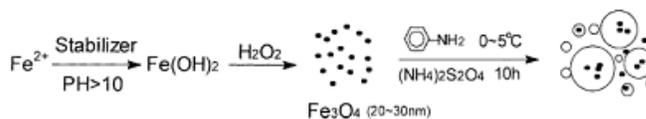


Figure 5. Synthesis of magnetic and conducting PANI-Fe₃O₄ particles.

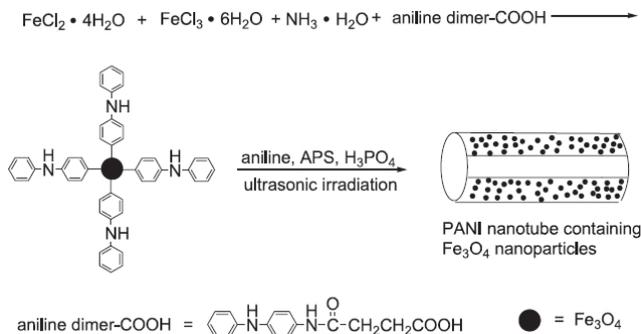


Figure 6. Fe_3O_4 -PANI nanotubes synthesis assisted by ultrasonic irradiation.

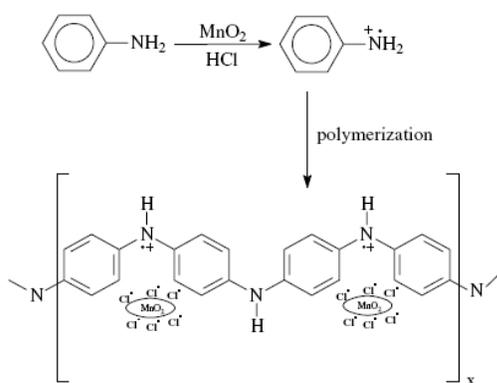


Figure 7. PANI- MnO_2 composite, made by polymerization of aniline in aqueous acidic (HCl) medium with MnO_2 as oxidant.

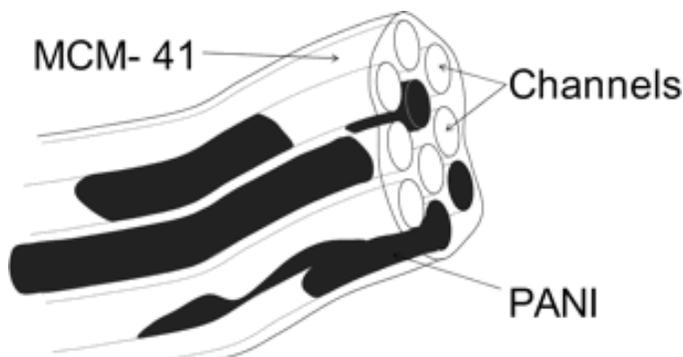


Figure 8 PANI-(MCM-41) composite particle.

PANI-(MCM-41) composites display also semiconductor behaviour besides paramagnetic characteristics. Readers may find interesting nanocomposites with variety of other applications.

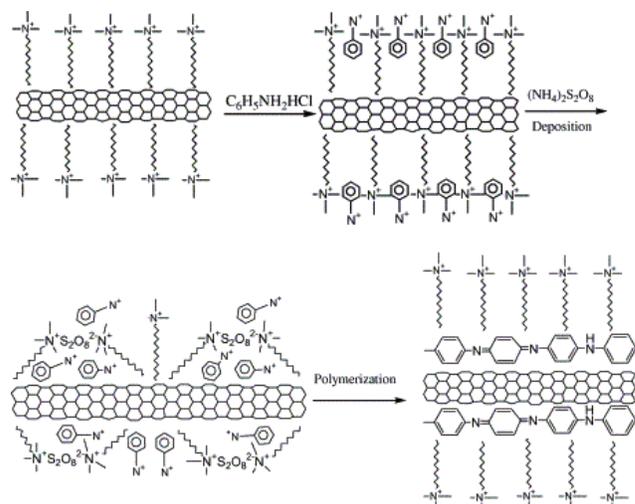


Figure 9. Dispersion of CNTs using CTAB and subsequent coating via in-situ synthesis of PANI.

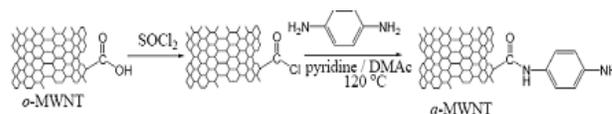


Figure 10. Conversion of carboxylated CNTs to amine-functionalized CNTs.

4 CONCLUSION

The potential of nano conducting polymers: Biodegradable polymer-based nanocomposites in sectors such as aerospace, automotive, packaging (particularly food but also solar cells), electrical and electronic goods, household goods etc. may include inkjet markets, nanoparticles in cosmetics, and automotive applications such as body moldings, engine covers and catalytic converts, batteries, computer chips, memory devices, biosensors for diagnostics. The time-scale for automotive, aerospace, bio-nanotechnology. These composites display semi-conducting nature, electro-activity, and plasticity. Nanoconducting polymers are useful in electronic, optical and magnetic properties, self assemblies at the molecular level[1].

5 REFERENCES

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