

Hybrid Nanocomposites for Antimicrobial and Catalytic Purposes

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Abstract

This study investigates the synthesis and characterization of organic-inorganic hybrid nanocomposites, emphasizing their applications in catalysis and antimicrobial activity. It explores the multidisciplinary nature of nanocomposites, focusing on tuning molecular interactions at the nanoscale to create functional materials. By classifying nanocomposites into metal matrix, ceramic matrix, and polymer matrix types, the research highlights their unique advantages and technological applications. Special attention is given to polyaniline (PANI) for its easy synthesis, controllable conductivity, and stability, making it suitable for energy storage, biosensors, and anticorrosion coatings. The encapsulation of inorganic nanoparticles in conducting polymers is presented as a method for developing multifunctional materials. This study underscores the potential of hybrid nanocomposites in catalysis and antimicrobial treatments, paving the way for future innovations.

Keywords: Hybrid Nanocomposites, Organic-inorganic hybrids, catalysis, Antimicrobial Technology, Polyaniline (PANI)

Introduction

Design and synthesis of nanocomposite materials is an important area of research. This rapidly expanding field is generating many new high-performance materials with novel properties. Nanocomposite materials significantly encompass a large variety of systems such as one-dimensional, two-dimensional, three-dimensional and amorphous materials, made of distinctly dissimilar components and mixed at the nanometre scale. The study of nanocomposite materials requires a multidisciplinary approach. To exploit nanomaterials for technological applications it is very important to have them with good processability through a suitable matrix. The precise tuning of molecular level interaction in nanocomposites is a challenge. Indeed, this precise tuning of the molecular level interactions of dissimilar organic and inorganic components to form unique functional materials has generated a new theme of hybrid nanocomposite materials with several challenges and opportunities.

Significant effort is focused on the ability to obtain control of the nanoscale structures via innovative synthetic approaches. In general, these nanocomposites exhibit a core/shell or a binary nanostructure which can be modified with different charges, reactive groups or functional moieties on the surface with enhanced stability and compatibility. The advances in controlling functional peripheries can provide a platform for synthesizing nanocomposite materials. The successful application of such nanocomposites is highly dependent on their nanostructure, composition, stability, morphology, dispersity and interfacial characteristics under a range of different conditions. Therefore, many researchers have focused on the fabrication of different nanocomposite materials in order to develop novel multifunctional materials with unique properties. There is also the possibility of new properties which are unknown in the parent constituent materials.

1.2 Classification of Nanocomposites:

Depending upon the nature of continuous phase (matrix) used nano composite materials can be classified into three groups:

(a) Metal matrix nano composites (MMNC):

In these nanocomposites, metals or metallic alloys are used as matrices and fillers are generally ceramics. The fillers are in the form of particulates, whiskers or fibers. e.g., TiC, SiC or alumina particles in alumina metal matrix nanocomposites. In comparison with polymer matrix-based nanocomposites, they show superior mechanical properties, nonflammability, high electrical and thermal conductivities. These specific properties of MMNCs make them potential candidates for many technological applications.

(b) Ceramic matrix nano composites (CMNCs):

CMNCs are designed by combining a great variety of ceramic materials such as

polycrystalline ceramics, glass or their mixture with addition of materials. In general, monolithic ceramics such as alumina, silicon nitride, glasses, and carbon etc. have high strength and stiffness but brittle in nature. This limitation is overcome by combining them with particulate and fiber materials.

(c) Polymer matrix nano composites:

In materials research, development of polymer nanocomposites is rapidly emerging as a multidisciplinary research activity whose results could extend the applications of polymers to the benefit of many industries. In recent years, significant progress has been achieved in the synthesis of various types of polymer-nanocomposites, and in understanding their optical and electrical properties. As a result, organic nanocomposite devices, such as light emitting diodes, photovoltaic devices, and solar cells, have been developed using methods of thin organic films, such as chemical and electrostatic self-assembly, contact printing, and spin coating. Conventional polymers usually serve as the matrices, which reinforced with nanoscale fillers which results in a special class of hybrid materials termed "polymeric nanocomposites", which has shown enhanced optical, electrical and dielectric properties. However, nanostructured composite materials, when using organic polymer and inorganic fillers, represent a merger between traditional organic and inorganic materials, resulting in compositions that are truly hybrid. These polymer-based nanocomposites (PNCs), i.e. nanoparticles (spheres, rods, and plates) dispersed in a polymer matrix, have gained substantial academic and industrial interest since their inception, ca. 1990. The functional properties resulting from PNCs are due to the synergistic interaction between the dispersed phase and the polymer matrix. Incorporation of nanoscale constituents in organic polymeric materials has been extensively studied because they combine the advantages of the inorganic materials (high carrier mobility, band gap tunability, a range of magnetic and dielectric properties, mechanical strength, modulus and thermal stability) and those of the organic polymers - flexibility, dielectric, ductility and processibility), which are difficult to obtain from either of the individual components.

Polyaniline (PANI):

Polyaniline (PANI) has been known for more than one hundred years in its 'aniline black' form, an undesirable black deposit formed on the anode during electrolysis involving aniline. It was used as a dye to blacken cotton fabrics. At the beginning of the XX century number of works were realised with aim to resolve PANI structure. An important breakthrough in the polyaniline research took place in early 1980s, when polyaniline has been discovered as a member of a novel group of macromolecular compounds; namely intrinsic conductive polymers. Since then, it has become the most extensively studied polymer in this group. Among the ICPs, PANI is the most promising polymer due to its straightforward synthesis, controllable electrical conductivity, and good environmental stability. In addition, PANI has thermal stability, particularly in the conducting emeraldine salt form and is a candidate for potential commercial application, such as in light-emitting diodes, catalyst, lightweight battery electrodes, sensors, electro-optics, non-linear optics, electromagnetic shielding materials, biochemical capacitors, and anticorrosion coating. Besides these obvious advantages, there are certain fundamental issues that set PANI apart from other members of the conjugated polymer family.

Chemical structure of PANI:

A linear octameric structure for PANI as a chain of aniline molecules coupled head to-tail at the Para position of the aromatic ring. PANI, a typical phenylene based polymer, has a chemically flexible $-NH-$ group in the polymer chain flanked by phenyl rings on either sides. The general structure of the polymer is shown in Fig.1.

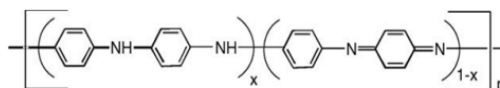


Fig. 1 The general structure of polyaniline



LITERATURE REVIEW

Shen, Z. X. (2016) review summarizes the recent progress in PANi based composites for energy storage/conversion, like application in supercapacitors, rechargeable batteries, fuel cells and water hydrolysis. Besides, PANi derived nitrogen-doped carbon materials, which have been widely employed as carbon-based electrodes/catalysts, are also involved in this review. PANi as a promising material for energy storage/conversion is deserved for intensive study and further development.

Rhee, K. Y. (2021) article, an in-depth overview of the synthesis methods of PANI-based composites, their biomedical applications as biosensors, current states, challenges, and the potential application of them in the future have been presented and discussed. Additionally, recent PANI-based biosensing devices for the detection of glucose, cholesterol, choline, virus, cancer, and bacteria have been described.

Lee, J. H. (2009) paper includes the advantages of the intrinsically conducting polymers (ICPs) over the other conducting polymers and the superiority of PANI among other ICPs. Details are provided of the different methods used for the synthesis of PANI along with a number of special methods used to obtain nanostructured PANI. A detailed discussion on the mechanism of electrical conduction in PANI and the factors those influence the conductivity of PANI is also included.

Kareem, Q. S. (2019) research polyaniline (PANI) was synthesized by using chemical oxidative polymerization method. The structural properties of polyaniline nano films pure and filled by graphene (GR) at different weight percentage of graphene like (1%, 3% and 5%) were investigated. The nano films prepared by using spin coating technique and deposited on glass substrate at room temperature. The structural and surface morphology of the nano films are evaluated by FT-IR, XRD and AFM. The results showed that FT-IR spectra of pure PANI is similar to the spectra of PANI/GR composites, While the results of XRD singular that the PANI has amorphous nature, As well as the results of AFM for all nano films of pure PANI and filled by graphene (PANI/GR) composites showed that Roughness average (Ra), Root mean square (Rms) value and average grain size (G.S) increase with increasing addition of GR ratio.

Synthesis of organic sulfonic doped PANI / Fe₃O₄ nanocomposites via self-assembly method

The DBSA doped PANI was synthesized via micelles assisted method using DBSA as dopant as well as surfactant. Typical synthesis involves dissolution of 0.0931 g of freshly distilled aniline and 5 ml of DBSA in 50 ml of distilled water in a round bottom flask at room temperature under magnetic stirring. The reaction mixture was quickly cooled to 0-5 °C using ice-water bath with constant stirring for 2 hours to disperse the aniline homogeneously and formed a milky dispersion of particles of anilinium-DBSA complex. Then a pre-cooled, 1 ml aqueous ammonium persulphate (APS) solution (0.02 mol L⁻¹) was added drop wise to the above under vigorous stirring. The colour of the reaction mixture slowly turned from colourless to light blue and eventually to a dark green. The reaction was allowed to proceed for 5 h at 0-5 °C, before warming it slowly to room temperature to obtain DBSA doped PANI green dispersion. Fe₃O₄ NPs were synthesized by co-precipitating Fe⁺² and Fe⁺³ ions by ammonia solution in presence of DBSA-PANI dispersion. Typical synthesis of PANI / Fe₃O₄ nanocomposite is as follows.

The 10 ml of 1 mol L⁻¹ FeCl₃·6H₂O and 10 ml of 0.5 mol L⁻¹ FeSO₄·7H₂O aqueous solution were rapidly injected into the above polymerization reaction mixture followed by slowly heating up to 65 °C under continuous stirring. Then, 5 ml of 25% NH₄OH was rapidly injected into above reaction mixture. The entire reaction system became black. The reaction was allowed to proceed for 5 h under vigorous stirring until a viscous PANI/Fe₃O₄ nanocomposite was obtained. The resulting mixture was centrifuged to separate the byproducts and un-reacted reagents, and the residue was washed with distilled water and methanol. Finally, the pure dark residue was dried under vacuum for 12 h.



The same procedure has been adopted for the synthesis of all other DBSA doped PANI / Fe₃O₄ nanocomposites except for varying the molar ratio of DBSA to aniline. All other reaction parameters such as monomer to APS molar ratio, Fe²⁺ /Fe³⁺ molar ratio, temperature and reaction time were kept constant.

1.3 A brief overview of Intrinsic Conducting Polymers (ICPs)

An organic polymer that possesses the electrical, electronic, magnetic and optical properties comparable to that of a metal while retaining the mechanical properties, processibility etc. commonly associated with a conventional polymer, is termed an “intrinsically conducting polymer” (ICP) more commonly known as “synthetic metal”. Since the discovery of (ICPs) in 1976, a tremendous amount of research has been carried out in the field of conducting polymers and many new conducting polymers have been synthesized. The ICPs have been emerging as important potential materials due to their applications in multidisciplinary areas such as electrical, electronics, thermoelectric, electrochemical, electromagnetic, electromechanical, electro-luminescence, electro-rheological, chemical, membrane, and sensors.

ICPs are inherently conducting in nature due to the presence of a conjugated π electron system in their structure. ICPs have a low energy optical transition, low ionization potential and a high electron affinity. A high level of conductivity (near metallic) can be achieved in ICPs through oxidation–reduction as well as doping with a suitable dopant. The first ICP to be discovered was polyacetylene, synthesized by Shirakawa Louis et al. and these investigations found that the conductivity of polyacetylene could be increased by several orders of magnitude through chemical doping and in reality, it can be converted from an insulator to a metal like conductor. The most common examples of ICPs are Polyacetylene (PA), Polyaniline (PANI), Polypyrrole (PPY), Polythiophene (PTh), Poly (phenylene), Poly (phenylene vinylene) and their derivatives.

1.4 Intrinsic conducting polymer Nanocomposites:

Intrinsic conducting polymers (ICPs) have emerged as an important class of electronic materials because of their potential applications in solid state batteries, electrochromic displays, microelectronic devices, chemical sensors, catalyses, drug delivery and energy storage systems. Electrically conducting polymers, termed as “fourth generation polymeric materials” with their unique redox properties, when doped appropriately, can have electrical conductivity over the full range from insulator to metallic. The properties of conducting polymers such as non-corrosiveness, light weight, mechanical strength, and the possibility to tune electrical conductivity and dielectric behaviour, can be utilized along with other properties of inorganic nanoparticles to developed multifunctional materials for many technological applications. However, conducting polymers are not molten in nature and generally insoluble in common solvents, thus it is difficult to prepare conducting polymer/inorganic nanoparticle composites by conventional blending or mixing in solution or melt form. Encapsulation of inorganic nanoparticles inside the shell of conducting polymers is a feasible way of preparing conductive polymer/ inorganic particle nanocomposites.

CONCLUSION

This study has demonstrated the significant potential of organic-inorganic hybrid nanocomposites in catalysis and antimicrobial applications. Through innovative synthesis methods, it is possible to precisely tune the molecular interactions between organic and inorganic components, leading to the creation of unique materials with enhanced properties. The classification of nanocomposites into metal matrix, ceramic matrix, and polymer matrix types reveals the distinct advantages and wide-ranging technological applications of each category. Polyaniline (PANI) stands out as a particularly promising material due to its straightforward synthesis, controllable electrical conductivity, and environmental stability. The incorporation of inorganic nanoparticles within conducting polymers further enhances the functionality and applicability of these materials.

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