Journal of Research in Chemistry 2021; 2(2): 86-89

Journal of
Research in Chemistry

E-ISSN: 2709-9423
P-ISSN: 2709-9415
JRC 2021; 2(2): 86-89

www.chemistryjournal.net
Received: 09-01-2021
Accepted: 17-02-2021

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Preparations and applications of polypyrrole nanomaterial: A review

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Abstract
Although nanostructured polypyrrole (PPy) offers so many unique features and so many advantages over bulk-structured PPy, it has been extensively explored in the last ten years. The primary structures, techniques of preparation, physicochemical characteristics, possible uses, and prospects for the future of PPy nanoparticles are described in this paper. The hard physical template method, the template less method, and the soft micellar template method are the preparation techniques. In the areas of energy storage, biomedicine, sensors, adsorption and impurity removal, electromagnetic shielding, and corrosion resistance, PPy nanomaterials have potential uses because of their exceptional electrical conductivity, biocompatibility, environmental stability, and reversible redox properties. Lastly, a discussion of the challenges and prospects facing this field of study is held.

Keywords: Polypyrrole, nanostructures, synthetic methods, properties, applications

Introduction

Conventional polymers are among the most widely used materials in the world today and have high insulating qualities. A. J. Heeger, A. J. MacDiarmid, and H. Shirakawa did, however, create a novel kind of polymer material in 1977. Iodine-doped polyacetylene showed a substantial improvement in conductivity, reaching 10^3 S cm^{-1} (Shirakawa *et al.*, 1977) [26]. The discovery of a number of polymers with related characteristics, including polyaniline, polythiophene, and polypyrrole, later on, served as a major impetus for the creation of conductive polymers (CPs). The benefits of PPy-simple preparation, nontoxicity, outstanding stability, superior mechanical qualities, and high conductivity-have drawn a lot of interest. These attributes could make PPy the next conductive polymer that can be produced industrially and used in a variety of applications. Unfortunately, traditional PPy with an amorphous phase lacks mechanical ductility and solubility, which makes it difficult to form into precise geometries and causes insolubility and infusion in the majority of organic solvents. More importantly, because of its amorphous morphology, standard bulk PPy lacks good electrical, optical, and biological properties; therefore, to get optimal performance, the structure and size must be adjusted. When compared to bulk PPy, nano-PPy exhibits exceptional biocompatibility, superior optical qualities, and unique electrochemical activity because of its well-defined nano-topography and greater surface area (Jang, 2006). It is important to understand the preparation strategy, morphology control, and the relationship between structure and performance for nano-PPy because it can be fabricated into a wide range of nanostructures, including zero-dimensional nanoparticles, one-dimensional nanotubes/nanowires, two-dimensional nanosheets, and three-dimensional nanonetworks. This will help to advance research and develop high-performance applications for PPy nano-materials (Li *et al*., 2009; Oh *et al*., 2013) [41, 29].

Seizing the chance, this paper describes the development of PPy nanomaterial research since 2010, with a primary emphasis on three areas: PPy nanomaterial preparation, PPy nanomaterial application, and PPy nanomaterial structure and characteristics. Four different forms make up the structure of PPy nanomaterials: PPy nanoparticles (Hao *et al.*, 2016; Zhou *et al*., 2017; Zhou *et al*., 2019) [17, 36, 40], PPy nanotubes (Bober *et al.*, 2015; Ying *et al.*, 2016) [20, 24], PPy nanowires (Lee *et al.*, 2014; Ramirez *et al.*, 2019) [8, 2], and PPy nanosheets (Jha *et al*., 2013; Liu *et al*., 2015) [21, 23]. Three primary techniques are used in the creation of PPy nanomaterials: the templateless method, the hard physical template method, and the soft micellar template method. Potential uses for PPy nanoparticles include energy storage, biomedicine, sensors, adsorption and contaminant removal, corrosion resistance, and electromagnetic shielding.

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Energy storage, biomedicine, sensors, adsorption and impurity removal, electromagnetic shielding, solid-phase extraction, and actuators are the main areas in which PPy nanoparticles are used.

Preparation of PPy Nanomaterials

Nano-PPy exhibits superior electrochemical activity, shorter ion migration distance, increased specific surface area, and improved conductivity when compared to traditional PPy. The soft micellar template method, the hard physical template method, and the template less approach are the preparation techniques for nano-PPy.

Soft Micellar Template Method

The hydrophobic and hydrophilic groups in the amphiphilic molecule interact to form a specific micelle in the solvent, and the monomer takes on a specific morphology inside or on the surface of the micelle, according to the soft micellar template method, also known as the self-assembly method. Typically, microemulsion polymerization is used to create these nanomaterials, yielding polymer nanostructures with tunable sizes. The materials for PPy NPs and NTs are typically prepared using the soft template approach. The primary determinants of product morphological characteristics are the composition and concentration of surfactants and monomers.

Han *et al*. (2010) [31] synthesised a hierarchical nanostructured PPy in an aqueous solution with potential applications in the field of supercapacitor materials, using CTAB as a template and 1, 5-naphthalene disulfonic acid (1,5-NDA) as a dopant. Triton X100 micelles helped Chen's group (Li *et al*., 2013) [32] create nanoscale PPy particles through a soft templating technique. Acetone can be detected by the surface acoustic wave sensor that has the nano-PPy particles in it. Moreover, his group created ultralong linked PPy NWs using an organic phase (pyrrole)/aqueous phase (oxidant) interfacial interaction (Lei *et al*., 2014) [30] by employing CTAB as a soft template.

Hard Physical Template Method

The hard physical template method fills the polymer monomer into a material with a specific inner or outer surface, which serves as a template. Then, by adjusting the reaction conditions, the polymer with the appropriate morphology is synthesised. Typical templates typically consist of fibres, colloidal particles, porous membrane materials, and so forth. The creation of PPy hollow particles, NTs, and NWs materials is the primary usage of this technique. Anodized aluminium oxide (AAO) was used as a template to fabricate PPy tubes for the first time, as described by Martin *et al*. (1990) [6]. However, the diameter of the finished tubes was micrometer-sized, and removing the template proved to be challenging. Hydroquinone monosulfonate-doped PPy NW arrays were successfully manufactured by Sulkaa *et al*. (2013) [13] utilising a potentiostatic technique on AAO membranes with an aperture of 80 nm. The arrays were then utilised as potentiometric pH sensors. Another popular hard template for creating PPy nanoparticles is V_2O_5 (Zhao *et al*., 2015; Zhan *et al*., 2018) [35, 34]. Furthermore, it has been documented that TiO_2 (Kowalski *et al*., 2011) [7], MnO_2 (Dubal *et al*., 2015) [11], and Fe_2O_3 with various morphologies can also be used as sacrificial templates to create 1D PPy nanostructures.

Template less Method

The template less method uses weak interactions like hydrogen bonds, electrostatic interactions, and coordination bonds between molecules to control the diffusion of monomers and oxidants in two incompatible phases and control the polymerization reaction conditions through interface action. This allows the polymer to self-assemble into tubes, spheres, films, and other special morphologies. Electrochemical control (Chebil *et al*., 2014; Fakhry *et al*., 2015) [22, 1], lithography (Rickard *et al*., 2016) [15], radiation (Cui *et al*., 2014), and other techniques (Monfared *et al*., 2019) [19] are examples of template-free technologies.

Application of Polypyrrole

PPy's exceptional electrical, optical, and biological qualities make them suitable for use in energy storage, biomedicine, sensing, and other domains.

1. Energy Storage

The synthesis of PPy is essential to the fabrication of energy storage devices because PPy nanoparticles can be employed as the electrodes of energy storage devices (Peng *et al*., 2014) [27]. The production of PPy-based nanomaterials is comparatively advanced, and various techniques (such as radiolysis polymerization, electrospraying, greener mechanochemical routes, etc.) can be used to prepare nanomaterials with the necessary size and morphology to produce electrode materials with exceptional performance (Karim *et al*., 2010; Monfared *et al*., 2019) [28, 19].

2. Battery

The application of PPy nanoparticles to batteries has been concentrated on three areas: fuel cells (Xia *et al*., 2013; Wu *et al*., 2014) [38, 39], dye-sensitized solar cells (Jeon *et al*., 2011; Hwang *et al*., 2014) [25, 10], and lithium and sodium batteries (Ma *et al*., 2015) [12].

3. Supercapacitor

In addition to their high specific electric capacity, PPy-based supercapacitors have drawn a lot of interest in the supercapacitor community. Researchers have worked tirelessly to improve the electrical performance and stability of PPy-based supercapacitors due to their low stability (Wang *et al*., 2014) [16]. Using a modified gas phase polymerization, Santino *et al*. (2014) [42] coated a high aspect ratio bristle-like nano-PPy continuous network on a graphitic hard carbon paper current collector. High discharge rates show good performance from electrodes based on nano-PPy. PPy nanoparticles have been reported for use in flexible supercapacitor applications, in addition to their traditional use as supercapacitors (Shi *et al*., 2014; Wei *et al*., 2017) [33, 4]. A straightforward and adaptable synthesis method for employing PPy hydrogels with adjustable 3D microstructures as electrically active components for high-performance, flexible solid-state supercapacitors was published by Shi *et al*. in 2014 [33]. During extended cycling, the flexible symmetric PPy hydrogel-based supercapacitors demonstrated strong electrochemical stability and capacitive performance.

4. Drug Delivery and Release

The benefits of PPy-based polymers and nanomaterials include facile drug loading, minimal impact on drug activity, and a regulated rate of drug release. Using a straightforward microemulsion polymerization method, Samanta *et al*. (2015) [9] created PPy NPs with a good drug loading capacity (15 wt %) and stable dispersion in solution. Drug release from the manufactured PPy NPs can be controlled by varying the pH, the drug's charge, and the addition of a little quantity of charged amphiphiles.

5. Photoacoustic and Photothermal Therapy

With its exceptional photostability, photothermal conversion capabilities, and strong biocompatibility, PPy nanoparticles have a wide range of potential applications in the photothermal therapy space. The most popular and original PPy nanomaterial for photothermal therapy is PPy NPs (Zhang *et al*., 2018; Theune *et al*., 2019) [5, 18].

Conclusions

PPy nanoparticles exhibit numerous qualities, including strong conductivity and huge surface area. As this paper explains, numerous novel fabrication techniques, such as electrochemical polymerization, emulsion polymerization, interfacial synthesis, radiation-initiated surfactant-assisted polymerization, polymerization, gas-phase polymerization, electrospinning, etc., have been developed for the preparation of spherical, tubular, wire, rod, sheet, helical, and other PPy nanomaterials. The numerous appealing characteristics of functional PPy nanoparticles created in this way have been thoroughly investigated in the fields of energy storage, biomedicine, sensors, adsorption and impurity removal, microwave absorption, solid-phase extraction, and actuators.

Future perspectives

PPy nanoparticles research is moving along quickly, but there are still a lot of tasks to be accomplished. First off, one of the biggest obstacles in this industry is still accurately managing the size and morphology of PPy nanoparticles. The application of PPy can be expanded by precisely manipulating the size and morphology of PPy nanoparticles to produce a variety of materials with superior optical, thermal, and electrical properties. In order to better regulate the size and structure, future improvements should concentrate on refining synthetic techniques and developing innovative assembly processes. Furthermore, it is anticipated that the characterization accuracy will increase, and this will require improvements in both repeatability and precision. These developments will have an effect on the mechanism study. Finally, only a small percentage of PPy nanoparticles can be employed in commercial applications, and there are still a lot of significant issues with their utilisation. The environmental stability of PPy nanomaterials needs to be strengthened, new environmentally friendly PPy nanomaterials need to be developed, and the application fields of PPy nanomaterials need to be further expanded in order to realise commercial application as soon as possible. It is anticipated that PPy nanoparticles combined with another appropriate component will be a very promising material for a variety of applications. Studying fresh approaches to this material's preparation, finding intriguing and improved qualities, and broadening its uses are still necessary.

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