



Historical perspective

Interfacial polymerization of conductive polymers: Generation of polymeric nanostructures in a 2-D space

Panagiotis Dallas^{a,*}, Vasilios Georgakilas^b^a Department of Materials, University of Oxford, Oxford OX1 3PH, UK^b Materials Science Department, University of Patras, Patras, Greece

ARTICLE INFO

Available online 29 July 2015

Keywords:

Interfacial polymerization
 Conductive polymers
 Nanofibers
 Sensors
 Conductivity

ABSTRACT

In the recent advances in the field of conductive polymers, the fibrillar or needle shaped nanostructures of polyaniline and polypyrrole have attracted significant attention due to the potential advantages of organic conductors that exhibit low-dimensionality, uniform size distribution, high crystallinity and improved physical properties compared to their bulk or spherically shaped counterparts. Carrying the polymerization reaction in a restricted two dimensional space, instead of the three dimensional space of the one phase solution is an efficient method for the synthesis of polymeric nanostructures with narrow size distribution and small diameter. Ultra-thin nanowires and nanofibers, single crystal nanoneedles, nanocomposites with noble metals or carbon nanotubes and layered materials can be efficiently synthesized with high yield and display superior performance in sensors and energy storage applications. In this critical review we will focus not only on the interfacial polymerization methods that leads to polymeric nanostructures and composites and their properties, but also on the mechanism and the physico-chemical processes that govern the diffusion and reactivity of molecules and nanomaterials at an interface. Recent advances for the synthesis of conductive polymer composites with an interfacial method for energy storage applications and future perspectives are presented.

© 2015 Elsevier B.V. All rights reserved.

Contents

1.	Introduction	47
2.	The boundary between two immiscible liquids	47
2.1.	Overview and theoretical background	47
2.2.	Electron and mass transfer in the boundaries of two immiscible liquids	48
2.3.	Mass diffusion in the interface (molecular recognition at an interface)	48
2.4.	Surface tension at the liquid–liquid interface	49
3.	Interfacial polymerization of aniline and pyrrole	49
3.1.	Aniline	49
3.1.1.	Formation mechanism of nanofibers at the interface	49
3.1.2.	Other morphologies that can be generated at an interface	51
3.2.	Interfacial polymerization of pyrrole	51
3.3.	Conductive polymer nanocomposites	51
3.3.1.	Noble metal nanocomposites	51
3.3.2.	Carbon nanotubes and graphene nanocomposites	52
4.	Properties and applications	52
4.1.	Sensors: importance of the fibrillar network	52
4.2.	Single crystalline polymers: ordering of polyaniline chains	54
4.3.	Electronic and magnetic properties	55
4.3.1.	Transport mechanism	55
4.3.2.	Metallic polyaniline	56
4.4.	Energy applications: composite anode catalysts, self-assembled monolayers and capacitive storage	56

* Corresponding author. Tel.: +44 1865273724; fax: +44 1865273789.
 E-mail address: panagiotis.dallas@materials.ox.ac.uk (P. Dallas).

5. Outlook and perspectives	58
References	58

1. Introduction

Interfaces have a fundamental role in life function and the understanding of their structure, composition and functionality is an important challenge for biomedical engineering, biology, materials science and biomimetics. The most typical example is the living cell membrane. Cell membranes were formed through the assembly of amphiphilic lipopolysaccharides or phospholipid molecules and they enable the selective transport of molecules and ions through them. To that end, biological systems can be viewed as advanced models for the synthesis and construction of numerous biomimetic monolayers, functional materials and devices since they provide an un-paralleled, example of self-assembled functional structures. In the laboratory, lipid bilayer systems can be readily constructed with the droplet interface approach that can even enable the incorporation of ion channels and pores [1a]. This involves the injection of liposomes in oil films where lipid bilayers spontaneously form. In summary the study of the biological two phase systems presents an important challenge in the field of biomimetics [1,2]. Furthermore, and this is a key aspect in polymer chemistry, at the two dimensional (2-D) liquid–liquid interface boundary, completely different properties compared to the separate aqueous and organic phases can be found. In fact, the interface can be considered as a separate and new entity, with a complex structure and a thickness of less than 1 nm where electron and mass transfer can take place [3].

The chemical and physical processes that occur in the interface between an organic and an aqueous solution can be substantially different than those occurring in a homogeneous, single-phase, reaction mixture [4]. The interface can be considered as an imaginable membrane through which selective flow and transitions can take place. Consequently, the reactions at the boundary between two immiscible liquids play an important role in fields such as analytical chemistry, organic chemistry and biochemistry [5]. Reactions at the liquid/liquid (denoted as L/L) interface have been reported in various systems. Typical processes include photo-induced electron transfer [6], organic synthesis [7], charge transfer even between photosensitizers and quenchers [8], and phase-transfer catalysis [9] and ion-pair extraction [10]. Noteworthy is the phase-transfer catalysis (PTC), which facilitates chemical reactions between reactants in two immiscible phases and is one of the most important techniques in organic synthesis [11]. By the virtue of supramolecular interactions the liquid–liquid interfaces [12a] offer an important scaffold for the organization of nanomaterials, typically inorganic nanoparticles and viruses [12b] by exploiting the different hydrophobic or hydrophilic characters of the constituent members of the reaction.

In polymer science the interfacial polymerization method is already known to produce relatively high molecular weight products for a series of conventional polymeric materials like polyamides, polyesters and polyurethanes which are synthesized through radical mediated addition or condensation polymerization [13,14]. Compared to these polymers, the unique characteristic of conductive polymers is their charged macromolecular chains, their oxidative polymerization mechanism and the constant need for the synthesis of ultra-small nano-structures and fibrillar, elongated morphologies that can conduct electricity and also exhibit a rapid and reversible response as sensors. As such, the interfacial polymerization of conductive polymers creates a common ground of nanoscience, materials science, polymer chemistry and physics, and organic chemistry.

The characteristics of the interfacial reactions have extensively been studied from the viewpoint of physical chemistry and electrochemistry. The electron, ion and mass transfer as well as the polarity and thickness of the interface between these two immiscible liquids have been the

focus of intense research. In these two-phase systems diffusion phenomena between the immiscible phases, a slow reaction rate and a restricted reaction space govern the formation of various products. The technique has been studied in the context of numerous applications in membrane and polymer science. Examples include the bulk polymer synthesis of polycarbonates [15,16] and other polymeric materials [17], a range of different applications and families of materials such as micro/nano-encapsulation [18,19], thin film composite and nanocomposite membranes [20–25], polyamides reinforced with carbon nanotubes for reverse osmosis [25b] and other polymer nanocomposite formation [26,27]. It has also attracted attention in the context of surface modification of fibers [28,29], micro-units [30,31] and self-healing materials [32].

The discovery of conductive polymers has opened up many new possibilities for electronic devices and sensors due to the combination of a range of controllable and exciting, optical, electrochemical, and conducting properties. These polymers demonstrate instant and easily detectable electrical and optical changes when they are chemically treated with oxidizing or reducing agents. After chemical treatment with redox active agents, conductive polymers immediately change from an insulating to an electrically conducting state and vice versa [33,34]. These transitions between different states can be particularly useful in applications such as optical sensors [35] chemical sensors [36] and biosensors [37]. The most widely studied conductive polymers include polyaniline (PANI), polypyrrole (PPY), and poly-(3,4-ethylenedioxythiophene) (PEDOT). They have been synthesized through oxidative interfacial polymerization, utilized as matrices for the incorporation of numerous nanostructures and have found applications in many and diverse areas. In all these applications the uniformity of the polymers morphology and the specific morphological characteristics are playing a vital role making the interfacial polymerization a versatile tool for the synthesis of conductive polymers fibers, films and composites.

We will firstly present an overview of the characteristics of the L/L interface. As a second step we will critically discuss how it influences the formation of elongated nanostructures and the advantages it represents in terms of conductivity, crystallinity and sensor applications. Our discussions are focusing on the oxidative polymerization of conductive polymers. We will close our review with presenting and critically addressing the recent progress in the field of energy storage applications.

2. The boundary between two immiscible liquids

2.1. Overview and theoretical background

In the field of materials science and nanotechnology, the liquid–liquid medium has been employed for the synthesis of polymeric nanoparticles, films of metallic nanoparticles in the interface including highly crystalline and photoluminescent metal chalcogenides, metal oxides, and noble metal nanoparticles [38a]. The process involves the assembly of the inorganic nanoparticles at an oil–water interface, localized in a place where the interfacial tension is high. In this system, the self-organization is a highly dynamic process, the particles move rapidly and try to self-assemble and equilibrate and this enables errors to be corrected immediately. Similar processes have been known and studied for over 100 years and have been denoted as “Pickering emulsions” in which large particles, for example silicon oxide (diameter, $d > 1$ nm), stabilize emulsions efficiently by adsorption to a liquid–liquid interface [38b]. The high interfacial energy between oil and water can be decreased by the assembly of the NPs at the interface; in fact it is interesting

Download English Version:

<https://daneshyari.com/en/article/590624>

Download Persian Version:

<https://daneshyari.com/article/590624>

[Daneshyari.com](https://daneshyari.com)