Progress in Polymer Science xxx (2013) xxx–xxx

Contents lists available at ScienceDirect

Progress in Polymer Science

journal homepage: www.elsevier.com/locate/ppolysci

Carbon nanotube–polyaniline composites

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ARTICLE INFO

Article history:
Received 20 March 2013
Received in revised form 18 August 2013
Accepted 22 August 2013
Available online xxx

Keywords:
Carbon nanotubes
Polyaniline
Nanoparticles
Synthesis
Application

ABSTRACT

The last decade has seen a growing interest in hybrid electrically conducting nanocomposites. This article aims to provide a detailed overview of the present status of research in carbon nanotube–polyaniline (CNT/PANI) composites, from processing to structural and property evaluations. CNT/PANI are synthesized by electrochemical and chemical processing. When chemical methods are used, the main challenge is to obtain processable CNT/PANI in the emeraldine salt (ES) form composites. Stable dispersions of ES–CNT in organic media are prepared using the post doping method, inverse emulsion polymerization, or ex situ polymerizations. On the contrary, stable water dispersions of CNT/ES are prepared using hydrophilization of a preformed CNT/ES composite, direct synthesis of micelle–CNT hybrid templates, interfacial polymerization, covalent functionalization of CNT with a water soluble polymer, or using electrostatic interactions between two oppositely charged ES and CNT aqueous colloids. Moreover, the strategies for the synthesis of ternary CNT/PANI composites incorporating noble metal nanoparticles, metal oxide, or graphene sheets are also presented and analyzed in depth. Finally, we give a review of potential applications, including chemical sensors, capacitors, fuel cells and electronic devices.

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Abbreviations: a-CNT, acylchloride functionalized CNT; AChE, acetylcholine esterase; AsOx, ascorbate oxidase; APS, ammonium peroxydisulfate; Ani, Aniline; β CD, β-cyclodextrin; CNT, carbon nanotubes; c-MWCNT, carboxylized-carbon nanotubes; S-CNT, sulfonized-carbon nanotubes; CNTA, CNT array; CDI, 1,4-carbonyldiimidazole; ChOd, choline oxidase; ChOx, cholesterol oxidase; CS-CNT, chitosan-coupled CNT; CS-GA, chitosan coupled glutaraldehyde; CTAB, cetyltrimethyl ammonium bromide; CTA, cetyltrimethylammonium; CV, cyclic voltage; CE, carbon electrode; CPE, carbon paste electrode; Cyt c, cytochrome c; DBSA, dodecyl benzene sulfonic acid; DNNDSA, dinonylnaphthalene disulfonic acid; DMPU, N,N′-dimethyl propylene urea; ES, emeraldine salt; EB, emeraldine base; ECD, enzyme catalytic deposition; EDC, N-ethyl-N′(3-dimethylaminopropylcarbodiimide); EP, electropolymerization; EPh, electrophoretic method; FTIR, Fourier transform infrared; GA, glutaraldehyde; GO, graphite oxide; GOD, glucose oxidase; GSHOx, glutathione oxidase; GCE, glassy carbon electrode; GN, graphene; HCSA, (S)-(+)-10-camphorsulfonic acid; HA, hexanoic acid; HRTEM, high resolution transmission electron microscopy; IL, ionic liquid; IP, interfacial polymerization; ITO, indium tin oxide; MIP, molecularly imprinted polymer; MWCNT, multi-wall carbon nanotubes.

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http://dx.doi.org/10.1016/j.progpolymsci.2013.08.009

1. Introduction

In 2000, Heeger, MacDiarmid and Shirakawa were awarded the Nobel Prize in chemistry for their discovery and development of the conducting polymers [1–3]. Among the conducting polymers, polyaniline (PANI) and polypyrrole (PPy) are the most popular. According to the *Web of Science*, more than 10,000 papers appeared in the past 30 years on various aspects of chemistry, physics, and engineering of PANI. This is due to the cheapness and easy availability of raw materials, ease of synthesis, good environmental stability, high electrical conductivity and simple doping/dedoping chemistry [4]. PANI has the general formula $[(\text{—B—NH—B—NH—})_n(\text{—B—N=Q=N—})_{1-n}]_m$ in which B and Q denote the rings in the benzenoid and quinonoid forms, respectively. PANI is found in three idealized oxidation states: the fully reduced form, leucoemeraldine ($n = 1$) and the fully oxidized form, pernigraniline ($n = 0$) are poor conductors. In contrast, emeraldine which correspond to the partially oxidized polymer ($n = 0.5$) is the most attractive form due to tunable states: emeraldine salt (ES) and emeraldine base (EB). The conductive salt form of PANI (ES, green color) is not soluble, however dedoping the salt form with ammonium hydroxide yields the soluble EB, blue color [5]. The PANI synthesis by chemical and electrochemical methods has been reviewed [6]. The typical chemical oxidative polymerization methods of aniline include solution blending [7,8], emulsion [9], dispersion [10,11], in situ polymerization [12,13] and enzymatic polymerization [14,15]. The genesis of nanostructures (granules, nanofibers, nanotubes, nanospheres, . . .) produced during the preparation of PANI has been recently reviewed [16,17].

Soft micellar template [18,19], the in situ formation of anilinium-peroxydisulfate ion clusters aggregates [20] and the model of phenazine nucleates are generally offered to explain the various supramolecular nanostructures produced by PANI. Carbon nanotubes (CNT), discovered by Iijima [21] in 1991, are one of the four well-known organized carbon states on Earth, with graphite, diamond and fullerenes. CNT are cylindrical shells made by rolling graphene sheets of sp^2 bonded carbon atoms into a seamless cylinder. Single-wall carbon nanotubes (SWCNT) consist of a single graphite sheet wound on itself that can be closed at both ends with a semi-fullerene molecule. Multi-wall carbon nanotubes (MWCNT) comprise a central tube of nanometric diameter surrounded by graphitic layers that are concentrically nested like the rings of a tree trunk with an intertube spacing roughly equal to the van de Waals graphite interplane distance, 0.34 nm [22]. The

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