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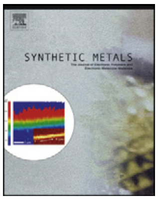

Polythiophene/SiO_2 nanocomposites prepared in the presence of surfactants and their application to glucose biosensing

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ABSTRACT

Conducting polythiophene/SiO_2 (PT/SiO_2) nanocomposites were prepared in the presence of three different surfactants (anionic, cationic and non-ionic) via chemical oxidative polymerization in an anhydrous medium to create an enzyme-immobilized polymeric amperometric biosensor. An anionic surfactant, sodium dodecylbenzenesulfonate (DBSNa), a cationic surfactant, tetradecyltrimethylammonium bromide (TTAB), and a non-ionic surfactant, poly(ethylene oxide) (20) sorbitan monolaurate (Tween 20), were used as additives. The properties of the nanocomposites were investigated, as a function of surfactant type and the amount of PT contained, by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The SEM results reveal that all PT/SiO_2 samples form nanometer-dimensioned globular structures. The highest conductivity obtained was $2.7 \times 10^{-2}\,S\,cm^{-1}$ for a PT/SiO_2-Tween 20 nanocomposite. Thermogravimetric analysis (TGA) shows that the residue decreases with increasing amount of PT. Glucose oxidase (GOX) was immobilized by crosslinking to the conducting PT/SiO_2 composites and was used for amperometric detection of glucose.

1. Introduction

During the past decade a new branch of materials science, nanostructured materials, has been developed, leading to the discovery of the special characteristics of nanosized solid materials [1,2]. These materials exhibit unique properties; for example, improved mechanical and thermal properties [3,4], gas permeability [5] and flame retardance [6] compared to the pristine polymers. These enhanced properties are achieved by dispersing nanoparticles or layered clay particles within a polymer matrix. One particular class of nanocomposite materials consists of conductive polymers that may contain conductive guest materials either dispersed in an inorganic host matrix [7] or, vice versa, the conductive organic matrix may incorporate the other phase. To create these nanocomposites, different conducting polymers can be synthesized by chemical and electrochemical routes [8,9] prepared in either aqueous or non-aqueous solutions [10,11].

Organic–inorganic nanocomposites can be prepared by directly mixing nanoparticles with organic compounds or by sol–gel processes. Commonly used inorganic nanoparticles include SiO_2, TiO_2 and ZnO. Nano-SiO_2 has been used specifically for the preparation of many polymer composites [12,13]. A number of different metallic and metal oxide particles have been encapsulated into the shell of conducting polymers, giving rise to a host of nanocomposites [14,15]. The direct mixing method is simple, fast and applicable to a variety of oxide particles of different grain size, from 10 nm to 5 mm, with various conducting polymers in organic and aqueous media. The resulting composites have been tested for several applications, such as photovoltaic devices and conducting pigments [16]. However, the conducting polymer composites have lower solubility in an aqueous solution in comparison with other polymer materials. To improve solubility, co-dopants and additives such as surfactants have also been used instead of inorganic acids for doping in the polymer chains. Camphorsulfonic acid, dodecylbenzenesulfonic acid and other acids with long alkyl chains and other kind of surfactants such as cationic and non-ionic have been used to modify properties of polymer materials.

Among conducting polymers composites, the polythiophene–metal oxide composites are attracting growing interest because of their advanced mechanical and chemical properties which are beneficial for many application fields [17–19]. The PT–metal interfacial structure is very important subject for various scientific and technological interests. Surfactants materials can modify the PT–metal or metal oxide interactions because the metal oxide particles can coalesce without surfactant during the polymerization process. They have been used also as soft templates for self-assemblies to control the size, shape and dispersion of nanoparticles for PANI/TiO_2, PANI/$PbTiO_3$, PANI/carbon nanotubes systems. Surfactants influ-

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enced the polymerization condition, kinetics, and final properties of the conjugated polymers.

Conducting polymers and their composites are attractive materials for the preparation of biosensors due to the considerable flexibility of their chemical structures and redox characteristics [20,21]. These characteristics are useful for the development of novel enzyme-based biosensors where rapid electron transfer at the electrode surface is required. Although nanostructured polythiophene and polythiophene nanocomposites have been used for gas and pH sensors [22,23], there are to date no reports of the use of such materials for glucose sensing.

In this work, we investigate the effect of surfactant additives on the properties of polythiophene chemically synthesized on a surface of nano-SiO_2 particles. Sodium dodecylbenzenesulfonate (DBSNa), tetradecyltrimethylammonium bromide (TTAB) and poly(ethylene oxide) (20) sorbitan monolaurate (Tween 20) were used as anionic, cationic and non-ionic surfactants, respectively. The properties of the nanocomposites were studied and compared with those of surfactant-free PT/SiO_2. They were characterized using different techniques: FTIR, elemental analysis, SEM, TGA, and conductivity measurements. A novel glucose biosensor was developed by immobilizing the enzyme glucose oxidase (GOX) on the nanocomposite surface by crosslinking via glutaraldehyde, to give an enzyme electrode which can be used for glucose determination at different glucose concentrations.

2. Experimental

2.1. Materials

Thiophene (Merck) was purified by vacuum distillation before use. Ferric chloride ($FeCl_3$, Aldrich), chloroform ($CHCl_3$, Aldrich), methanol (CH_3OH, Aldrich), and surfactants: sodium dodecylbenzenesulfonate (DBSNa, Fluka), tetradecyltrimethylammonium bromide (TTAB, Fluka) and poly(ethylene oxide) (20) sorbitan monolaurate (Tween 20, Merck) were used as received. Surfactant formulas are listed in Table 1. Nanodimensioned SiO_2 particles (average size was 7 nm in diameter) were purchased from Aldrich.

The buffer solution, which was used as supporting electrolyte in electrochemical measurements, was prepared using $NaH_2PO_4{\cdot}2H_2O$ (Riedel De Haen). 25% Glutaraldehyde (GA) water solution (Aldrich) was used as crosslinking agent. All other compounds were analytical reagent grade. De-ionised doubly distilled water was used for preparation of the solutions.

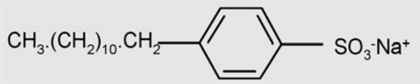
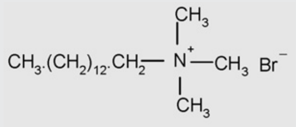
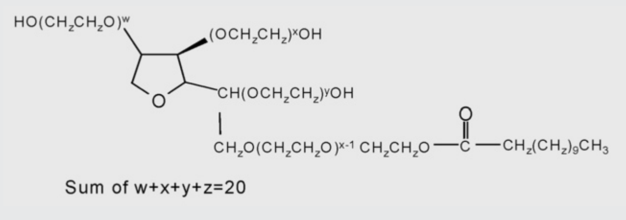
2.2. Synthesis of PT/SiO_2 nanocomposites

The synthesis of PT/SiO_2 composites was carried out in a 250 mL three-neck round-bottomed flask equipped with a magnetic stir bar, by the oxidation of thiophene monomer with ferric chloride ($FeCl_3$) used as oxidant. 1.0 g of SiO_2 was dispersed in 100 mL of $CHCl_3$, then thiophene (5.3 mmol, 0.45 g; 12 mmol, 1.0 g; and 15.9 mmol, 1.34 g) under N_2 atmosphere. These amounts correspond to the different sample numbers (from 1 to 3) labelled later as PT*x*/SiO_2-surfactant. The molar ratio of thiophene to surfactant was 7 in all experiments. The solution was mixed for 10 min, subsequently one of the chosen s surfactant was added to this solution and stirred for an additional 15 min. Finally, appropriate amount of $FeCl_3$ in $CHCl_3$ solution was added dropwise to start chemical polymerization of the monomer. The molar ratio of $FeCl_3$ to thiophene was 2.3. Polymerization was carried out at 15–20 °C under N_2 with 24 h stirring. Brown PT/SiO_2-surfactant nanocomposite suspensions were filtered out, washed with methanol and then dried at 50 °C under vacuum for 24 h. For comparison, a PT/SiO_2 nanocomposite was synthesized in $CHCl_3$ under the same conditions without any surfactant.

2.3. Instrumental

Fourier transform infrared (FTIR) spectra of prepared materials in KBr pellets were recorded between 400 and 4000 cm^{-1} with 4 cm^{-1} resolution on a Perkin Elmer Spectrum BX FTIR system (Beaconsfield, Bucks HP91QA, England). Prepared composite powders were compressed into 13-mm diameter pellets using a hydraulic press at 700 MPa. Direct electrical conductivity was measured using a PCI-DAS6014 (Measurement Computing) as a current source, voltammeter and temperature controller following a standard four-point probe method. Samples for scanning electron microscopy (SEM) analysis were sputtered with gold; photographs were taken with a XL-30S FEG (Philips FEI) model SEM device. Thermograms of the composites were recorded on a Perkin Elmer thermogravimetric analyser (Beaconsfield, Bucks HP91QA, England) in the presence of O_2 atmosphere from 50 to 900 °C with a heating rate of 10 °C min^{-1}. Sample composition was determined by elemental analysis using a CHNSO Flash EA 1112 analyser (Ankersmid GmbH, Germany).

Table 1
Surfactants and their formulas.

Structure	Abbreviation	Type
 Sodium dodecylbenzensulfonate	DBSNa	Anionic
 Tetradecyltrimethylammonium bromide	TTAB	Cationic
 Poly(ethyle oxide) (20) sorbitan monolaurate	Tween 20	Non-ionic