Synthetic Metals 221 (2016) 67–74

Contents lists available at ScienceDirect

Synthetic Metals

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

Colloids of polypyrrole nanotubes/nanorods: A promising conducting ink

Yu Li[a,b], Patrycja Bober[a,*], Dogukan H. Apaydin[c], Tomáš Syrový[d], Niyazi Serdar Sariciftci[c], Jiřina Hromádková[a], Irina Sapurina[a,e], Miroslava Trchová[a], Jaroslav Stejskal[a]

[a] Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague 6, Czech Republic
[b] Department of Applied Chemistry, School of Science, Xi'an Jiaotong University, Xi'an 710049, People's Republic of China
[c] Linz Institute for Organic Solar Cells, Physical Chemistry, Johannes Kepler University of Linz, 4040 Linz, Austria
[d] University of Pardubice, Faculty of Chemical Technology, Department of Graphic Arts and Photophysics, 533 53 Pardubice, Czech Republic
[e] Institute of Macromolecular Compounds, Russian Academy of Sciences, St. Petersburg 199004, Russian Federation

ARTICLE INFO

Article history:
Received 18 July 2016
Received in revised form 30 September 2016
Accepted 6 October 2016
Available online 19 October 2016

Keywords:
Colloids
Polypyrrole
Nanotubes
Nanorods
Conducting polymers
Stability
Coating

ABSTRACT

Stable colloidal dispersions of polypyrrole (PPy) nanotubes/nanorods were obtained by the chemical polymerization of pyrrole in the presence of methyl orange and poly(*N*-vinypyrrolidone). Due to extended morphology of colloidal particles, the films deposited from colloids with PPy nanotubes/nanorods had conductivity two orders of magnitudes higher than those from colloids of ordinary PPy nanoglobules. Dynamic light scattering measurement demonstrated that PPy nanotubes/nanorods have average particles sizes around 500 nm with a dispersity index around 0.3. The PPy colloids were stored over 3 months without visible agglomeration or precipitation. UV–vis spectra of PPy nanotubes/nanorods were recorded both in acidic or alkaline media. Raman spectra excited with 785 nm excitation laser confirmed the same mechanism of protonation of nanoglobular and nanotubular PPy. The colloid of PPy nanotubes/nanorods also exhibited good electrochemical redox activity, which makes them promising for the deposition of thin conducting layers used in sensors or energy-storage devices. The dispersions were used for the coating of films on poly(ethylene terephthalate) foils.

1. Introduction

Among all conducting polymers, polypyrrole (PPy) is probably the most attractive due to its good environmental stability and biocompatibility [1–3] in addition to a considerably high conductivity [4], which does not decrease significantly even after alkaline treatment associated with the conversion of PPy salt to a corresponding base [5]. Polypyrrole has widely been used in the field of chemical sensors [6] and biosensors, platforms for tissue engineering, and devices for energy conversion or storage [7]. In addition, PPy nanotubes with the one-dimensional morphology and internal cavities provide good possibility to load noble metals, such as silver [8,9], gold [10], or palladium [11] nanoparticles, which made them candidates for antibacterial or catalytic materials [12]. Unfortunately, similarly to other conducting polymers, poor processing ability of PPy due to its insolubility in common solvents, seriously hinders a further exploration of its application. Researchers have therefore put efforts to synthesize PPy-based composites [13,14] or hydrogels [15] in order to make good use of its application advantages.

The colloidal dispersions of nanostructured conducting polymers, which maintain the nanoscale morphology of conducting polymers while at the same time exhibit a liquid character, provide pathways to process conducting polymer nanostructures [16] and to prepare their composites [17,18]. For example, polypyrrole colloids decorated with silver nanoparticles were used to fabricate an enzymeless hydrogen peroxide sensor, which showed a fast response towards peroxide reduction [19]. A xanthine biosensor was similarly prepared by using stable colloids of PPy/gold nanocomposites, which provide sensitive and reliable biocompatible environment for the xanthine oxidase [20].

Especially in recent years, with the increasing interest on flexible, wearable and smart electronic devices, effective technologies producing films of conducting polymers are highly desirable. The colloids of conducting polymers can be used as conducting inks, which are fit for printing and coating technologies. Therefore,

* Corresponding author.
E-mail address: bober@imc.cas.cz (P. Bober).

http://dx.doi.org/10.1016/j.synthmet.2016.10.007
0379-6779/

such low-cost and large-scale production of conducting films or layers on versatile substrates with pre-designed geometry can be practical [21]. This kind of easy-processed conducting films is attractive when small-sized, high-efficient electronic devices are developed. For instance, polyaniline colloid in xylene or chloroform has recently been used for gravure printing of ammonia sensors [22]. A biosensor was also prepared by inkjet printing of colloidal polypyrrole dispersions blended with horseradish peroxidase and glucose oxidase onto flexible poly(ethylene terephthalate) substrate coated with carbon paste [23].

Polypyrrole or polyaniline colloids have typically been prepared by the oxidation of respective monomers in aqueous solutions of water-soluble polymers [24]. The polymer particles had a size 100–400 nm, and spherical, globular or rice-grain morphology with low aspect ratio [25]. The films obtained after drying are composed of conducting-polymer particles embedded in a matrix of non-conducting polymer [26]. Such morphology does not favour high conductivity. For that reason, the present paper reports the synthesis of polypyrrole colloids based on extended polypyrrole nanostructures composed of nanotubes and nanorods prepared at low concentration of supporting water-soluble polymer. The morphology is typical of PPy prepared in the presence of sulfonated dyes such as methyl orange (MO) [27–31]. We shall refer to corresponding colloidal forms as to nanotubular PPy colloids. They are expected to contain conducting objects with high aspect ratio, which would produce an effective conducting network after drying at low fraction of non-conducting component. There is additional reason for the expected conductivity improvement. Nanotubular PPy prepared with MO has a typical conductivity $\approx 50\ S\ cm^{-1}$ [32], which is significantly higher than conductivity of globular PPy, $1.7\ S\ cm^{-1}$ [33]. This fact should also be reflected in the conductivity of films prepared from colloidal forms. These hypotheses have been tested in the present communication.

2. Experimental

2.1. Preparation

Poly(*N*-vinylpyrrolidone) (PVP; molecular weight 360,000), iron(III) chloride hexahydrate, methyl orange (MO; sodium 4-[(4-dimethylamino)phenylazo]benzenesulfonate) and pyrrole were of analytical purity from Sigma-Aldrich. They were all used as received. Solutions with different concentrations of PVP, *viz.* 0, 0.2, 0.4, 0.6, 0.8, 1.0, 2, 4, and 10 wt.%, were prepared by dissolving a defined amount of PVP powder in Milli-Q water. To each of the PVP solution, 0.335 g of pyrrole (5 mmol) and 0.082 g MO (0.25 mmol) were added, and the total volume was adjusted to 50 mL. The mixture of PVP, pyrrole and MO were put under ultrasonic treatment for *ca.* 30 min to obtain a solution. Each solution was mixed with 50 mL solution of iron(III) chloride (1.352 g; 5 mmol) in Milli-Q water. The concentrations thus were 0.05 M pyrrole, 0.05 M iron(III) chloride and 0.0025 M MO. The mixture was kept undisturbed at room temperature for 24 h. The produced colloidal dispersions were poured into dialysis tube (Visking Dialysis Membrane, supplied by Carl Roth GmbH, Germany, molecular-weight cut-off 14,000) and dialyzed against large volume of 0.1 M hydrochloric acid to remove the residual methyl orange, any unreacted monomer, and oxidant ions. Stable PPy colloids were obtained. As a comparison, PPy samples in the powder form were prepared at exactly the same conditions as colloids only in the absence of stabilizers. After 24 h at room temperature, the solids were separated from reaction mixture by filtration, rinsed with 0.1 M hydrochloric acid followed by ethanol, and dried until the weight became constant.

2.2. Characterization

The morphologies of globular and nanotubular PPy powders prepared in the absence of PVP were characterized with the scanning electron microscopy (SEM) using a JEOL 6400 microscope, and morphology of PPy colloids was assessed with a transmission electron microscope (TEM) JEOL JEM 2000 FX.

The colloidal particle size was determined with a dynamic light-scattering apparatus AutoSizer Lo-C (Malvern, UK). The colloidal dispersions were diluted 200× with 0.1 M hydrochloric acid before such experiments. At least five determinations of particle sizes have been done and the results were averaged. The dispersity index (DI), a relative width of the particle-size distribution, has also been obtained by assuming the logarithmic-normal distribution of particle sizes.

The UV–vis spectra of PPy colloids were recorded with a Lambda 950 spectrometer (Perkin Elmer, UK). The colloids were diluted 200× times with 0.1 M hydrochloric acid for the spectra of PPy salts or with 0.1 M ammonium hydroxide for corresponding PPy bases.

Raman spectra of the dried PPy colloids were recorded with a Renishaw InVia Reflex Raman microspectrometer. The spectra were excited with a 785 nm diode laser. The scattered light was analyzed by the spectrograph with holographic grating 1200 lines mm^{-1}. A Peltier-cooled CCD detector (576 × 384 pixels) registered the dispersed light.

In order to assess the electrochemical characteristics of the PPy colloids, cyclic voltammetry was carried out. One-compartment electrochemical cell with three-electrode configuration was used. A glassy carbon rod served as working electrode, platinum plate was used as counter electrode and a silver chloride electrode was used as the reference. Electrolyte solution was 0.1 M hydrochloric acid. The cell was purged with argon for 15 min prior to experiments in order to have an inert atmosphere in the cell. Potential was cycled between −400 mV and 800 mV *vs.* reference with a scan rate of $25\ mV\ s^{-1}$.

Four-point probe method was employed for determining the conductivity of the PPy films cast from colloids. For that purpose, $2.5 \times 0.7 \times 0.1\ cm^3$ glass slides were coated with the PPy colloids via drop casting and left for drying overnight. A Signatone Corporation manual four point resistivity probing equipment with a Signatone SP4 head was used along with a Keithley 2700 for the conductivity measurements. For the films which showed measureable conductivity, the thickness of the film was determined with a Bruker Dektak XT Profilometer. The thicknesses of films cast from globular PPy colloid (with 0.2 wt% PVP), PPy nanotube colloid (with 0.2 wt% PVP) and PPy nanorods colloid (with 1 wt% PVP) are 0.54 μm, 1.38 μm and 4.09 μm, respectively. Thus the volume conductivity of the film was calculated according to the standard correction equations.

The flexible layers were deposited from PPy colloids by spiral-bar coating technique on poly(ethylene terephthalate) foil Melinex ST504. The layers were prepared on plasma treated side. Dispersions was homogenized by ultrasonic bath Sonorex Digitec DT 103H for 10 min, and then filtered by a polytetrafluoroethylene syringe filter (0.45 μm). Filtered dispersions were deposited with an automatic film applicator (TQC AB3120) using a 30 μm spiral bar. Wet samples were dried in hot-air oven at 100 °C for 15 min.

3. Results and discussion

3.1. Morphology

The chemical polymerization of pyrrole without any templates usually produces irregular globules (Fig. 1a) [30,32,34]. Methyl orange (MO) has been found to be an effective structure-directing