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One-step synthesis and self-organization of polypyrrole ultrathin films inlayed with Prussian blue nanoparticles induced by a drop of toluene solution on water surface

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ABSTRACT

A strategy was described for one-step synthesis and self-organization of polypyrrole (PPy) ultrathin films inlayed with Prussian blue (PB) nanoparticles. The formation of ultrathin films is induced by a drop of toluene solution on aqueous surface, and the organization process is accompanied by the shrinkage of organic layer area on water surface due to the evaporation of toluene. On the one hand, the combination of the downward gravity force from the toluene solution of pyrrole and its upward buoyancy force drives the toluene solution of pyrrole to collapse downwards and scatter outwards on water surface. On the other hand, the strong adhesion ability of PPy and the hydrophobic action between the toluene solution of pyrrole and water drives the upper organic layer to reunite. In addition, the dispersion of toluene solvent toward pyrrole monomers and the retraction of its evaporation kinetics toward the produced PPyPB nanocomposites play a great role here. All of these forces yield a close-packed ultrathin PPy films with inlayed PB nanoparticles. The suggested strategy for preparing ultrathin films of PPy inlayed with PB nanoparticles is very simple. Due to the existence of PPy, the obtained composite films could be easily transferred and anchored onto the solid surface.

1. Introduction

Prussian blue (PB) is a mixed valance hexacyanomatelate salt with a face-centered-cubic structure [1]. PB, its analogs and their various nanostructures have attracted growing concerns over the past few years due to their interesting photophysical, magnetic, electrochromic and electrochemical properties [2–7]. They show promising applications in various areas, such as molecular magnets, optomagnets, electrochromic devices, battery, chemical sensors and biosensors [8–14].

The organization of nanoparticles is considered to be important because of their potential use in nanodevices. Self-assembly at the liquid/liquid interface has been reported as a simple and flexible strategy for the organization of nanostructures which is driven by the reduction in interfacial energy/Helmholtz free energy [15]. The preparation of nanocrystal films of Au, Ag, and Cu at the liquid/liquid interface has been accomplished by taking a metallo-organic precursor in the organic layer and the appropriate reducing agent in the aqueous layer [16]. Despite the versatility of interfacial assembly, the creation of stable organized films remains a challenge since the competition between the interfacial energy and spatial fluctuations resulting from nanoparticles thermal energy causes instability in organized film [17]. Also, the immobilization of organized films onto the solid substrates is the key step for the real applications of nanoparticles.

Polypyrrole (PPy) or their various oligomers can adhere strongly onto the surface of many materials, which is employed to modify the surface of materials or nanoparticles [18]. Here we describe a strategy of one-step synthesis and self-assembly of PPy ultrathin films inlayed with Prussian blue (PB) nanoparticles induced by a drop of toluene solution on water surface. The formation of ultrathin films (PPyPB) was achieved by evaporation kinetics, PPy adhesion and other interaction forces at the air/liquid interface.

2. Experimental details

2.1. Reagent and materials

Pyrrole monomers were purchased from Sinopharm Chemical Reagent Co. Ltd. $K_3[Fe(CN)_6]$, $FeCl_3$ and toluene were from Aladdin Reagent Database Inc. (Shanghai, China). All the other chemicals were of analytical grade and used without further purification. The ultrapure water with resistivity of 18 MΩ from Milli-Q system was used to prepare all solutions and rinse the electrodes.

2.2. One-step synthesis and self-organization of PPy ultrathin films inlayed with PB nanoparticles induced by a drop of toluene solution on water surface

Typically, $FeCl_3$ solution was prepared firstly in 0.1 M HCl and $K_3[Fe(CN)_6]$ in 0.1 M KCl. Then 500 μL of 1% pyrrole solution in toluene

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Table 1
The PPyPB films were prepared in different condition[a].

	$FeCl_3$ 8 mL	$K_3Fe(CN)_6$ 8 mL	Pyrrole	Conditions
$PPyPB^{I}$	0.5 mM	0.1 mM	0.3% 100 μL	12 h at room temperature
$PPyPB^{II}$	0.1 mM		5% 500 μL	4 h at room temperature
$PPyPB^{III}$			1% 500 μL	12 h at 30 °C

[a] $FeCl_3$ solution was prepared with 0.01 M HCl for $PPyPB^{I}$ and 0.1 M HCl for $PPyPB^{II}$, $PPyPB^{III}$ and $PPyPB^{IV}$. $K_3Fe(CN)_6$ was dissolved in 0.1 M KCl.

was carefully dropped onto the surface center of 8 mL aqueous solution containing 0.1 mM $K_3[Fe(CN)_6]$ and 0.1 mM $FeCl_3$ in a small beaker of 50 mL. Immediately, a round and thin organic layer was observed which spreads on the water surface. At the interface of water/toluene, pyrrole and $FeCl_3$ reacted to produce PPy and $FeCl_2$ respectively, and nearly at the same time, the produced Fe^{2+} reacted with $K_3[Fe(CN)_6]$ to obtain PB. Accompanied with the evaporation of toluene, the round film retracted and finally the formation of a blue thin film was observed on the surface of aqueous solution. In order to obtain the complete volatilization of toluene and sufficient reaction between reactants, the reaction was allowed to last for 12 h. The PPyPB films were prepared in different condition listed in Table 1.

2.3. Apparatus

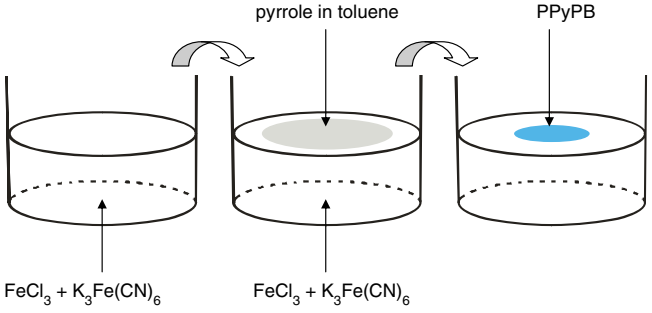
The self-assembled PPyPB nanocomposite films were carefully transferred from above and from below respectively onto the surface of a carbon plate whose morphology was studied by scanning electron microscopy (SEM, S-4800 UHR FE-SEM) operating at 5.0 kV. The formers yield films with PB on the top of PPy which is defined as PPyPB–PB/PPy, and the latter does with PPy on the top of PB which is defined as PPyPB–PPy/PB.

A transmission electron microscope (TEM, JEM-2100F) was used to observe the morphological characteristics of PPyPB operating at 200 kV.

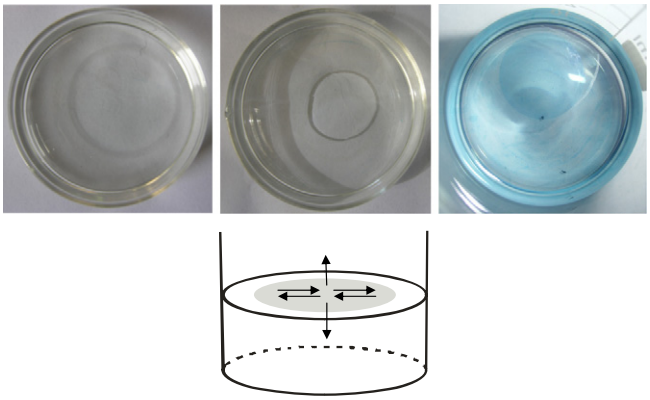
Fourier transform infrared spectroscopy (FTIR) was recorded on a NEXUS 670 FTIR spectrometer at wavenumbers 490–4000 cm^{-1}.

A Lambda 950 UV/VIS spectrometer (Perkin Elmer) was used to study the LBL assembly of close-packed PBPPy nanocomposites.

Cyclic voltammetry (CV) was conducted using CHI 842B electrochemical workstation (CH Instruments, Shanghai, China) with conventional three-electrode setup. A PPyPB nanocomposite film modified glass carbon electrode (GCE) was employed as working electrode, an Ag/AgCl as reference electrode and a platinum wire as counter electrode. The supporting electrolyte is 0.1 M KCl. All experiments were carried out at room temperature.



Scheme 1. Schematic representation for the one-step synthesis and self-assembly of PPy ultrathin films inlayed with PB nanoparticles induced by a drop of toluene solution on water surface.



Scheme 2. Photo for the one-step synthesis and self-assembly of PPy ultrathin films inlayed with PB nanoparticles induced by a drop of toluene solution on water surface, and schematic representation for the involved driving forces.

2.4. Modification of GCE with PPyPB nanocomposite films

Prior to use, the surface of GCE with a diameter of 3 mm was carefully polished with 0.3 and 0.05 μm alumina slurry in turn, rinsed thoroughly with water and sonicated in ethanol, 1:1 HNO_3 solution, water for 1 min, successively. After 12 h of synthesis and self-assembly, the formed PPyPB nanocomposite films were transferred onto the GCE surface by using the pretreated GCE to touch slantways the PPyPB nanocomposite film from the underwater. The modified electrode was dried at room temperature for use.

3. Results and discussions

For the organization of PPyPB nanocomposite films, a small volume of pyrrole solution in toluene was dropped onto the surface of aqueous solution containing $K_3[Fe(CN)_6]$ and $FeCl_3$. Immediately, a round and thin organic layer was observed which spreads on the water surface. With the evaporation of toluene and the process of

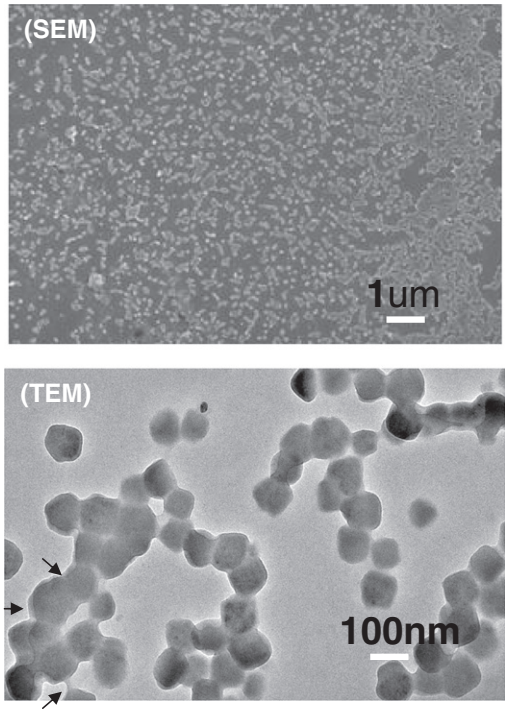


Fig. 1. SEM and TEM images of $PPyPB^{I}$.