Nanocomposite Films

Template Synthesis of Polypyrrole Nanofibers Insulated within One-Dimensional Silicate Channels: Hexagonal versus Lamellar for Recombination of Polarons into Bipolarons**

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The nanoscale orientation of conjugated polymers is an interesting subject for the development of the next-generation optoelectronic materials. In this respect, an attractive approach is to utilize unidirectionally aligned nanoscopic channels or pores as templates for the synthesis of conjugated polymers.[1] Martin and co-workers have utilized porous membrane filters for the polymerization of pyrrole to give a polymer composite material with oriented, submicron-scale tubular-shaped polypyrrole domains, whose electronic conductivity is an order of magnitude higher than those of unprocessed bulk polymers.[2] However, the fabrication and properties of "insulated polypyrrole nanofibers" have not yet been explored.

We have exploited a novel approach toward macromolecular synthesis by using porous silica with ordered hexagonal arrays of uniformly sized nanoscopic channels.[3] Recently, we and other research groups succeeded in the fabrication of mesostructured silica consisting of conjugated polymers within aligned silicate nanochannels by using a sol–gel-based approach with diacetylenic surfactants as templates.[4] In contrast with post-loading approaches,[5] this new method guarantees a dense filling of the silicate channels with conjugated polymers. Herein we report the synthesis of a novel polypyrrole/silica nanocomposite material (**3a**), templated by a pyrrole-containing surfactant (**1a**), where polypyrrole domains are segregated and insulated by one-dimensional silicate nanochannels (Figure 1). In particular, we highlight a "nanoscopic confinement effect" of the hexagonal silicate channels on the recombination of polarons into bipolarons.

Surfactant monomers **1a** and **1b** were synthesized by an alkaline-mediated coupling reaction of 1,12-dibromododecane and 1,10-dibromodecane, respectively, with pyrrole, followed by subsequent transformation of the terminal hydroxy group into a quaternary ammonium ion. Pyrrole-containing mesostructured silica **2a** was successfully synthesized using **1a** according to a method reported by Ogawa for

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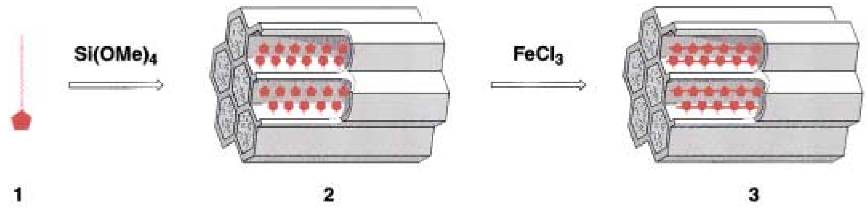
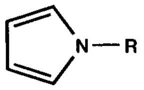


Figure 1. Schematic representation of the template synthesis of a polypyrrole/silica nanocomposite material (**3**) by oxidative polymerization of a pyrrole-containing surfactant (**1**) within a mesostructured silica (**2**).



$R = -\!(CH_2)_{12}\!-N^+Me_3\ Br^-$ **1a**

$R = -\!(CH_2)_{10}\!-N^+Me_3\ Br^-$ **1b**

the fabrication of mesoporous silica films.[6] Thus, tetramethyl orthosilicate (0.19 g) was added to 6 wt% of hydrochloric acid at 0 °C with magnetic stirring to hydrolyze the Si–O bonds, followed by partial condensation of the resulting silanol functionalities. After 10 min, **1a** (0.1 g) was added to the above solution, and the mixture, after sonication for 1 min at 20 °C, was spin-coated (3000 rpm) on a glass plate to afford a homogeneous, transparent film, which was then air-dried overnight at 25 °C to promote the formation of the silica framework. The X-ray diffraction (XRD) pattern obtained for **2a** was characteristic of a hexagonal silicate structure, with (100) and (200) diffraction peaks and a *d* spacing of the former of 29.7 Å.[7] This value is close to a diameter expected for a single rod micelle of **1a**. When **2a** was calcined at 450 °C for 8 h, the resulting material still showed a characteristic XRD pattern of the hexagonal structure, although the *d* spacing had decreased to 20.1 Å. Transmission electron microscopy studies on **2a** clearly showed regularly aligned hexagonal channels with a diameter of approximately 3 nm (Figure 2). The content of **1a** in the composite film was evaluated by thermogravimetric analysis (TGA) of **2a** to be 43 wt%,[7] which is as high as the values reported for ordinary mesoporous silica containing template surfactants. Therefore, the silicate channels of composite film **2a** are densely filled with **1a**. In contrast, when surfactant **1b**, which has a slightly shorter alkyl chain than **1a**, was used, the resulting composite film did not show any XRD diffractions.

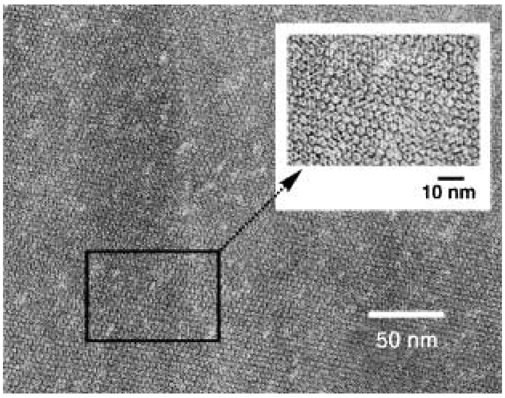


Figure 2. Transmission electron micrographs of pyrrole/silica nanocomposite film **2a**.

When spin-coated film **2a**, after being air-dried overnight, was dipped for 1 min in a solution of anhydrous FeCl$_3$ (2 M) in diethyl ether at 20 °C it immediately stained brown (Figure 3a), as a consequence of the oxidative polymerization of included **1a**.[8] The colored material **3a** thus obtained was found to retain essentially the same XRD profile[7] as that of **2a**. The absorption spectrum of **3a** showed a broad band centered at 1200 nm, which is characteristic of an electronic transition from a valence band of doped polypyrrole to a bipolaron (dication) band (Figure 4a). Etching the silica framework of **3a** with HF allowed isolation of the included polymer as a highly insoluble black precipitate, whose IR spectrum[7] over the range 900–1400 cm^{-1} was identical to that reported for a doped polypyrrole.[9] The complete polymerization of **1a** in composite film **2a** was confirmed by the absence of ^{1}H NMR signals arising from **1a** in the supernatant solution of the above extract.[7] All these observations demonstrate the formation of a nanocomposite material, in which each silicate channel contains a single, nanoscopic bundle of doped polypyrrole chains. Such a rapid, complete polymerization of **2a** is interesting, when the limited accessibility of included **1a** to the initiator (FeCl$_3$) is considered.

It is understood that oxidative polymerization of pyrrole derivatives is accompanied by the initial formation of polarons (radical cation species), which are then transformed into bipolarons (dicationic species) by recombination.[10] Each polypyrrole domain in composite material **3a** is nanoscopically segregated and insulated by the silicate channel, hence the transformation of polarons to bipolarons must occur within the individual silicate channels. We were motivated to explore the effects of this "nanoscopic segregation" on the recombination of polarons. Thus, **1a** was diluted with a nonpolymerizable surfactant (dodecyltrimethylammonium bromide, DTAB) at molar ratios of [**1a**]:[DTAB] = 1:3 and 1:6, and the mixtures were utilized for the sol–gel process. Consequently, transparent, thin films $\mathbf{2}_{\mathbf{1a}/\mathrm{DTAB}}$ were obtained by spin coating which showed XRD patterns characteristic of hexagonal structures with *d* spacings of 32.3 and 32.6 Å.[7] These films, like **2a**, immediately stained brown when dipped in a solution of FeCl$_3$ (2 M) in diethyl ether for 1 min (Figure 3b,c). XRD analysis of these colored materials indicated the successful retention of their hexagonal silicate structures upon oxidative polymerization. Etching these nanocomposite silica films with HF allowed the isolation of insoluble black precipitates, whose IR spectra were characteristic of polypyrrole derivatives.[7] The polypyrrole-containing nanocomposite films ($\mathbf{3}_{\mathbf{1a}/\mathrm{DTAB}}$) obtained at molar ratios [**1a**]:[DTAB] of 1:3 and 1:6 both exhibited two absorption

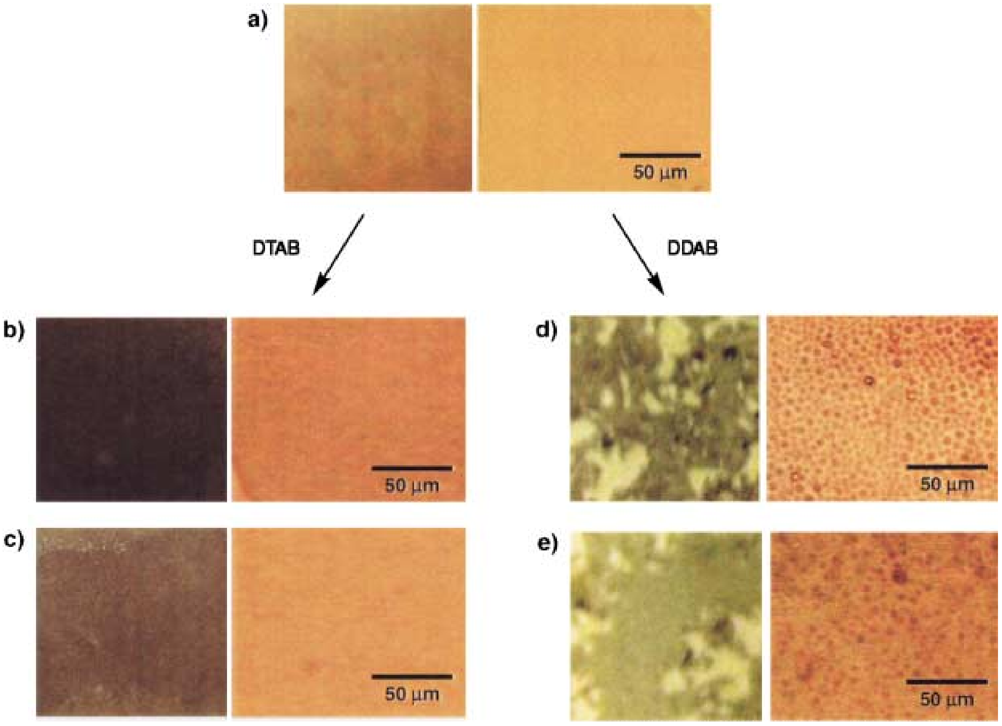


Figure 3. Pictures (left) and optical micrographs (right, ×400) of polypyrrole/silica nanocomposite films **3a**, $\mathbf{3}_{1a/DTAB}$, and $\mathbf{3}_{1a/DDAB}$. Compounds **3a** and $\mathbf{3}_{1a/DTAB}$ were prepared at [**1a**]:[DTAB] molar ratios of: a) 1:0, b) 1:3, and c) 1:6, while $\mathbf{3}_{1a/DDAB}$ were prepared at molar ratios [**1a**]:[DDAB] of: d) 1:3 and e) 1:6.

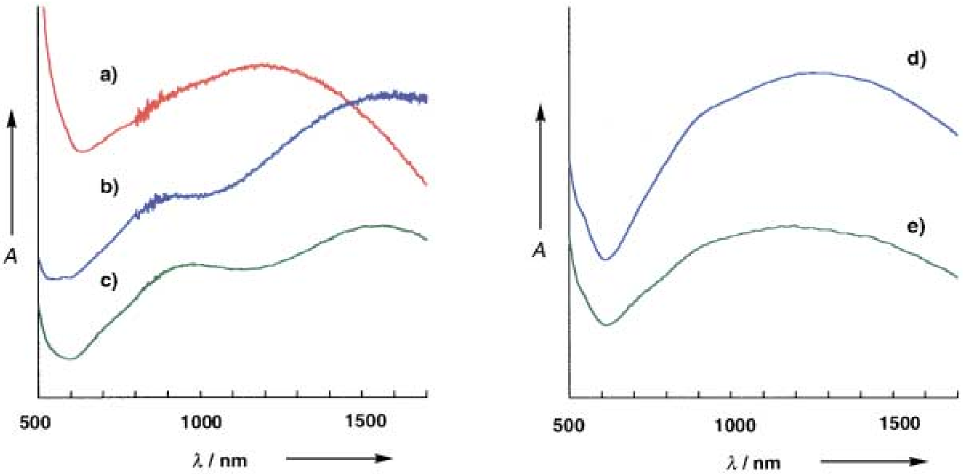


Figure 4. Electronic absorption spectra of polypyrrole/silica nanocomposite films **3a**, $\mathbf{3}_{1a/DTAB}$, and $\mathbf{3}_{1a/DDAB}$. Compounds **3a** and $\mathbf{3}_{1a/DTAB}$ were prepared at [**1a**]:[DTAB] molar ratios of: a) 1:0, b) 1:3, and c) 1:6, while $\mathbf{3}_{1a/DDAB}$ films were prepared at [**1a**]:[DDAB] molar ratios of: d) 1:3 and e) 1:6. All the spectra were taken 30 min after being dipped in a solution of $FeCl_3$ (2 M) in diethyl ether for 1 min at 20°C. No spectral change occurred thereafter. The absorbance is given in arbitrary units.

bands centered at 900 and 1500 nm, with a small shoulder at 700 nm[11] (Figure 4b,c), which are typical of those reported for EPR-active polarons.[10] In sharp contrast, when the concentration of **1a** was higher (for example, [**1a**]:[DTAB] = 1:2), the resulting composite film $\mathbf{3}_{1a/DTAB}$, similar to **3a**, showed an absorption spectrum characteristic of bipolarons.[7]

We found that pyrrole-containing nanocomposite "lamellar" films $\mathbf{2}_{1a/DDAB}$ can be prepared by using didodecyldimethylammonium bromide (DDAB) as a co-template at [**1a**]:[DDAB] = 1:3 and 1:6. These composite films displayed characteristic XRD peaks with *d* spacings of 34.7 and 34.0 Å, respectively.[7] Similarly to hexagonal **2a** and $\mathbf{2}_{1a/DTAB}$, lamellar films $\mathbf{2}_{1a/DDAB}$ immediately stained black when dipped in a solution of $FeCl_3$ (2 M) in diethyl ether, thus indicating the successful polymerization of included **1a**. However, in sharp contrast to $\mathbf{2}_{1a/DTAB}$ ([**1a**]:[DTAB] = 1:3 and 1:6), the resulting polymeric composites ($\mathbf{3}_{1a/DDAB}$) both displayed only a broad absorption band centered at 1200 nm, which arises from bipolarons (Figure 4d,e). Analysis of these films by optical microscopy showed a macroscopic phase separation consisting of black-colored, doped polypyrrole domains dispersed in a continuous phase of nonpolymerizable DDAB (Figure 3d,e). These contrasting results clearly indicate that doped polypyrrole chains are highly constrained and insulated when incorporated within hexagonal nanoscopic channels and lose the possibility of the polarons (radical cations) recombining into bipolarons (dications), whereas those in two-dimensional lamellar interlayers possess a certain freedom for this electronic event.

In conclusion, we succeeded in the fabrication of a novel composite material (**3a**) consisting of "polypyrrole nanofibers" segregated and insulated by hexagonal silicate channels by using a sol–gel-based template polymerization of a pyrrole-containing surfactant monomer (**1a**). The dilution experiments with nonpolymerizable surfactants as co-templates with **1a** demonstrated an essential difference between one-dimensional and two-dimensional nanospaces for the electronic confinement of doped polypyrrole chains. The sol–gel-based synthetic approach reported herein in combination with lithographic technologies[12] would allow the nanoscopic patterning of aligned conductive cables with an insulating coat. Toward this end, studies on the electronic conductivity of the insulated polypyrrole nano domains would be one of the challenging subjects worthy of further investigation.

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