

# A Heterostructure Composed of Conjugated Polymer and Copper Sulfide Nanoparticles

Riccardo Narizzano,<sup>†</sup> Victor Erokhin,<sup>‡</sup> and Claudio Nicolini<sup>\*,†,‡</sup>

Nanoworld Institute and Biophysics Division, University of Genova, Corso Europa, 30, 16132 Genoa, Italy, and Fondazione Elba, Via delle Testuggini snc, 00100 Rome, Italy

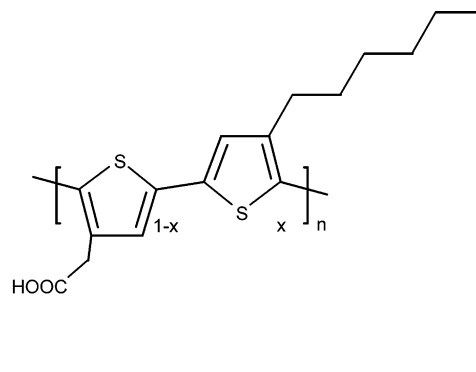
Received: April 15, 2005; In Final Form: June 30, 2005

A heterostructure formed by a conjugated polymer and semiconducting nanoparticles was produced. The conjugated polymer was synthesized by oxidative copolymerization of 3-thiopheneacetic acid and 3-hexylthiophene, thus obtaining an amphiphilic polythiophene that allows the formation of a stable polymer layer at the air–water interface. Different numbers of monolayers were deposited on solid substrates. CuS nanoparticles were grown directly in the polymeric matrix using the carboxylic groups as nucleation centers. The reactions were monitored by quartz crystal microbalance, Brewster angle, and fluorescence microscopy. The heterostructure showed increased conductivity as compared to the pristine polymer.

## Introduction

Assembly of nanoparticles in organic conjugated heterostructures or superlattices is of great importance in current material science, as well as in molecular electronics.<sup>1</sup> Controlled thickness and order of these ultrathin structures play a crucial role in obtaining high-quality molecular films.<sup>2</sup> One of the most promising techniques, which allows us to obtain molecular controlled architectures, is the Langmuir–Blodgett (LB) deposition technique.<sup>3,4</sup>

A method for preparing CdS particles in LB matrix was suggested by Smotkin et al. in 1988.<sup>5</sup> An LB film of cadmium arachidate was exposed to an atmosphere of H<sub>2</sub>S gas. During the reaction, carboxylic groups of arachidic acid were protonated, and CdS was produced. Several experimental techniques were applied to characterize these objects,<sup>6,7</sup> and it was found that CdS was formed as nanometer size particles inside LB film. It was possible to aggregate these particles in ultrathin layers by selective removal of the organic matrix.<sup>7</sup> The technique allowed us to obtain very good resolution of inorganic layer formation, 0.6 nm for each precursor bilayer. The methodology was employed to prepare PbS, CuS, HgS, and so forth layers. It was found that the technique does not yield continuous semiconductor monolayers, and for films less than 25-nm thick,<sup>8</sup> low conductivity is observed. The aim of this study was to obtain a heterostructure based on a polythiophene derivative and CuS nanoparticles. The use of a conjugated matrix should result in conductive connection of the semiconductor islands and, therefore, in the formation of a continuous conductive layer at film thickness less than 25 nm. A conjugated polymer with amphiphilic properties, that allowed the formation of a stable monolayer at the air–water interface, was needed<sup>9</sup> to achieve structures with controlled thickness, by means of the LS technique. This was obtained by chemical copolymerization of two different monomers: the 3-thiopheneacetic acid (3TAA) and 3-hexylthiophene (3HT) (Figure 1). The former allows for reaction with copper ions, and consequently the formation of nanoparticles, and it has a hydrophilic character. The latter has a hydrophobic character and makes the final polymer soluble



**Figure 1.** Molecular structure of the amphiphilic polythiophene derivative.

in common organic solvents. In this paper, we present a study of LS multilayers of a soluble polythiophene derivative and semiconducting CuS nanoparticles. Chemical, morphological, and electrical studies have been performed on various structures and for different numbers of layers.

## Experimental Section

**General Information.** 3HT, iron(III) chloride, 3TAA, and chloroform were purchased from Aldrich and were used with no further purification.

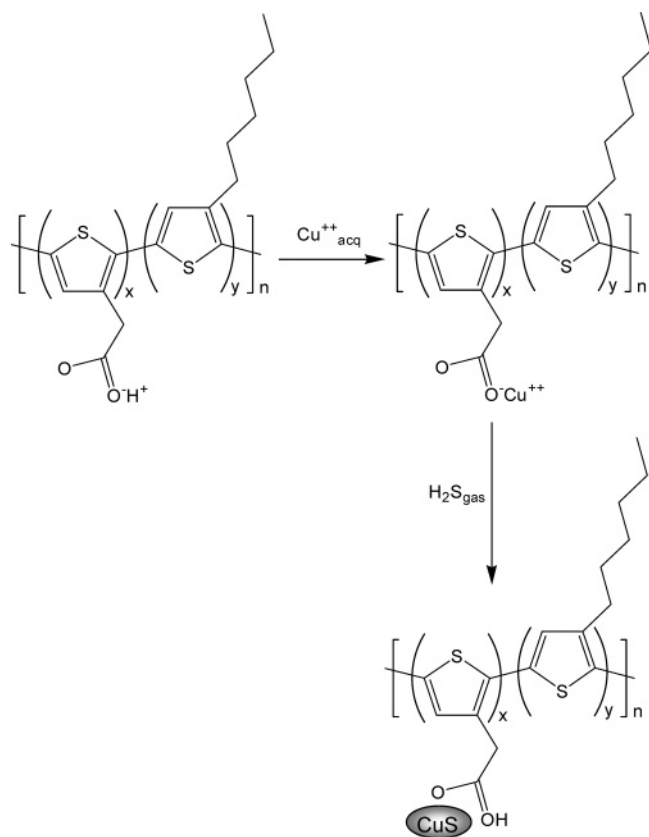
**Polymer Synthesis.** The amphiphilic polymer (PAET) was prepared by chemical oxidative copolymerization of 3TAA and 3HT monomers in equal molar ratio. Polymerization was performed by slowly adding a chloroform slurry of FeCl<sub>3</sub> into a monomer chloroform solution over a period of 8 h in nitrogen atmosphere at room temperature. The final concentrations of the monomers and FeCl<sub>3</sub> were 0.1, 0.1, and 0.6 M, respectively. The black mixture that was obtained was stirred for 3 additional hours and then was poured into methanol to get a dark green-black polymer precipitate. The solid was filtered and dedoped by repeated treatment with methanol and 0.05 M aqueous EDTA solution. Afterward, the precipitate was washed several times with diethyl ether and dried at 60–70 °C under vacuum.

**NMR Spectroscopy.** The final structure of the polymer was determined by <sup>1</sup>H NMR spectroscopy. The NMR spectra of the

\* Author to whom correspondence should be addressed.

<sup>†</sup> University of Genova.

<sup>‡</sup> Fondazione ELBA.

**SCHEME 1: Illustration of the Different Steps of the Copolymer/CuS Heterostructure Formation**

polymer were measured in  $\text{CDCl}_3$  solution using a Bruker AMX 500 instrument.

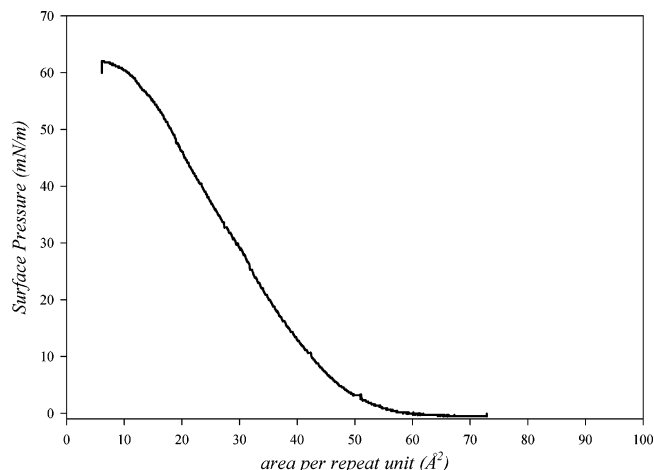
**Film Formation.** Films were deposited by the horizontal lift technique, also known as the Langmuir–Schaefer (LS) method. LS films of copper polymer were deposited with a Langmuir trough (MDT, Russia) ( $237 \times 100$  mm). Layers were formed by spreading a filtered 10% (m/v) solution of copolymer in chloroform at the subphase, which contains  $10^{-4}$  M of  $\text{CuSO}_4$  in water purified by Milli-Q system ( $18.2 \text{ M}\Omega\text{cm}$ ). Glass plates were used as substrates for the deposition of thin films

**Quartz Crystal Microbalance System.** The kinetics of copper ion reaction with the carboxylic groups of the polymer was monitored by a quartz crystal microbalance mass sensor (QCM).<sup>10,11</sup> The QCM sensors we employed were the commercially available 10 MHz AT-cut unbonded quartz crystals with gold electrodes on both sides. The polymer was cast on the electrodes and the reaction of copper ions with the carboxylic groups of the polymer was obtained by vertical dipping of the coated QCMs in a milli-Q water solution of copper sulfate ( $10^{-4}$  M). Frequency data were recorded every 2 min. The mass changes were calculated on the basis of the Sauerbrey equation

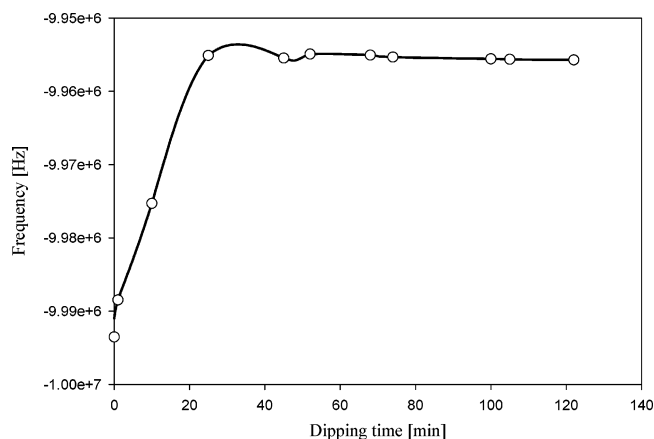
$$\Delta f = -K\Delta m$$

where  $\Delta f$  is the measured frequency change of the quartz resonator simply related to the change in mass,  $K$  is the constant, and  $\Delta m$  is the mass change.<sup>12</sup>

**Nanoparticle Growth.**  $\text{H}_2\text{S}$  gas was prepared by the reaction of FeS with diluted  $\text{H}_2\text{SO}_4$ . Samples were placed into the chamber and were exposed to the  $\text{H}_2\text{S}$  atmosphere for 12 h, that is, a time interval long enough to complete the reaction even for rather thick films of the precursor (200 monolayers).<sup>13</sup> Morphology of the films was studied by Brewster angle



**Figure 2.** Compression isotherm of the amphiphilic polymer.



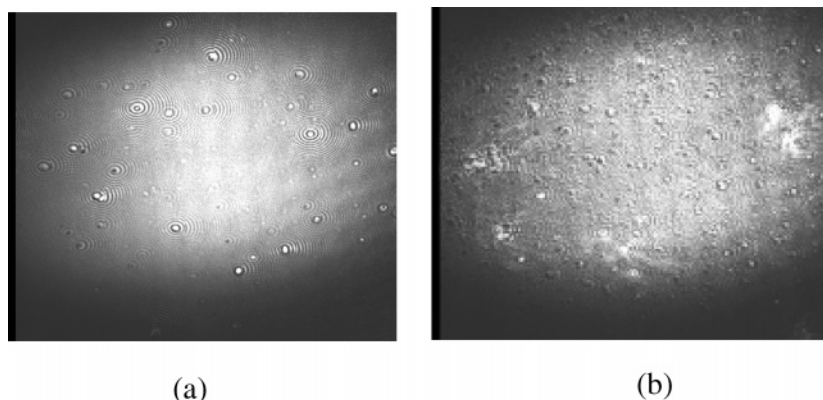
**Figure 3.** QCM measurements. Copper ion absorption kinetics on copolymer surface: frequencies as a function of dipping time.

microscopy (BAM 2, Nanofilm Technologie GmbH, Germany) at each step, that is, after deposition and after the particle formation process.

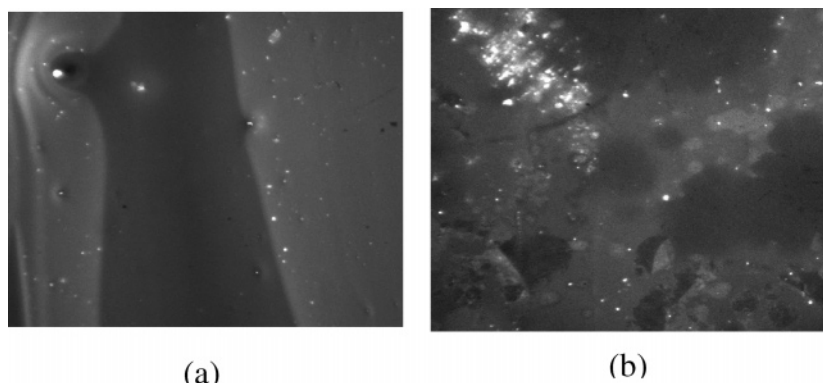
Brewster angle microscopy images were acquired with an Instrument BAM-2 (Nanofilm Technologie GmbH, Göttingen, Germany).<sup>14</sup> The standard laser of the BAM is a diode laser with wavelength of 690 nm. The high-power laser diode has 30 mW primary output.

Local distribution of nanoparticles in polymeric matrix was monitored by fluorescence microscopy using a Zeiss Axioplan light microscope (Zeiss, Oberkochen, Germany) modified for computer-controlled stage, shutter, and focus, and data acquisition was used<sup>15,16</sup> with a Zeiss Plan-Neofluar  $40\times/\text{NA} = 0.75$  lens. The standard epifluorescence setup was employed, and the sample was excited at 450 nm and was observed at wavelengths of  $>500$  nm. Digital pictures were obtained with an air-cooled ( $-50^\circ\text{C}$ ) scientific grade charged coupled device (CCD) camera (ORCAII, Hamamatsu Photonics, Japan) with a dynamic range of 14 bits (gray levels from 0 to 16383). The optical resolution element (pixel), at our level of magnification, corresponds to the  $0.167 \mu\text{m} \times 0.167 \mu\text{m}$  area in the object plane. The image covers the sample area of  $214 \mu\text{m} \times 171 \mu\text{m}$ .

**Electrical Measurements.** Electrical properties of thin films of the resulting materials were performed with a Keithley model 6517 electrometer (Keithley Instruments, Inc., U.S.) in a shielding box. Contacts to the sample were made with the indium or silver paint Electrodag1415M (Acheson Colloids B.V., The Netherlands).



**Figure 4.** BAM images of 20-layer films of copolymer. (a) Before exposure to  $\text{H}_2\text{S}$ ; (b) after exposure to  $\text{H}_2\text{S}$ . The image size is  $0.3 \text{ mm} \times 0.2 \text{ mm}$ .



**Figure 5.** Images taken by fluorescence microscopy of 20-layer films of copolymer. (a) Before exposure to  $\text{H}_2\text{S}$ ; (b) after exposure to  $\text{H}_2\text{S}$ .

## Results and Discussion

The  $^1\text{H}$  NMR spectra revealed that the polymer contains 20% of 3HT. The molar fraction of HT was calculated by integrating the peak areas of methyl protons ( $\sim 0.9 \text{ ppm}$ ), which are only present in the 3HT units, and of aromatic protons ( $\sim 7.0 \text{ ppm}$ ). The normalized areas were 0.52 for the methyl group and 1.00 for the aromatic protons, respectively. The smaller molar fraction of 3HT in the polymer could be due to the high steric effect of alkyl chain during polymer formation<sup>17</sup>. The polymer exhibits good solubility in  $\text{CHCl}_3$ , maintaining the typical absorption peak of 3-alkyl-substituted polythiophenes which is obtained via the  $\text{FeCl}_3$  method at about 431 nm. This absorption, which is detected in the UV–visible spectrum of the nondoped sample in chloroform solution, corresponds to the typical  $\pi$ – $\pi^*$  transition of the conjugated backbone.<sup>18</sup>

Pressure–area isotherms were measured at  $25^\circ\text{C}$  with a compression speed of  $1.0 \text{ mm s}^{-1}$  (Figure 2). The compression proceeded smoothly until the film collapsed at a surface pressure corresponding to  $63 \text{ mN m}^{-1}$ .

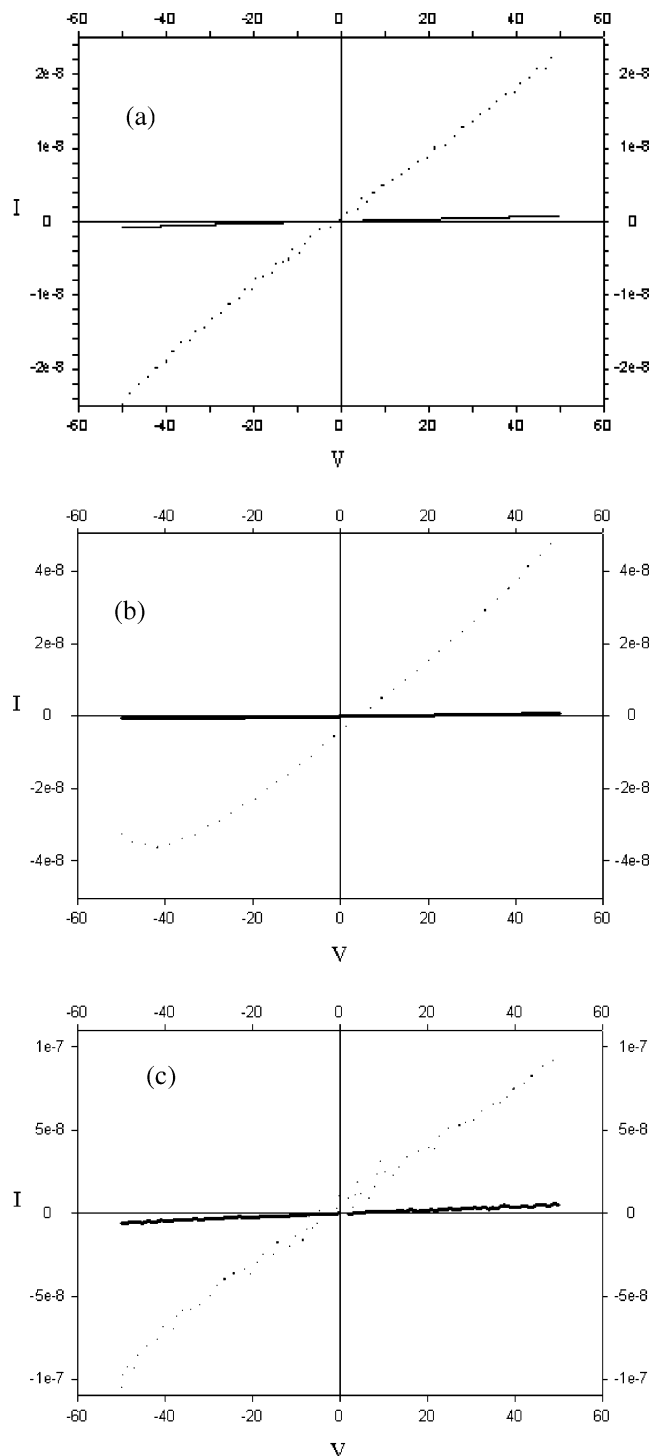
Two different processes govern the kinetics of the reaction between copper ions and carboxylic groups of the polymer (Figure 3). The first is fast and takes place in about 20 min, while the second is slower and is over in about 25 min. The shape of the compression isotherm curve and the amount of deposited copper ions allow us to attribute a chemical reaction nature to the first process and a physical adsorption one to the second. Furthermore, there is no desorption of copper ions from the polymeric matrix after repeated washing in water.

Last, the semiconductor particles were grown directly on LS films of copolymer with copper ions by exposure to  $\text{H}_2\text{S}$  atmosphere. The morphology of the films, studied by Brewster angle microscopy, undergoes evident changes upon exposure

to the  $\text{H}_2\text{S}$  atmosphere. In fact, the formation of  $\text{CuS}$  nanoparticles causes increased layer corrugation. As can be observed in Figure 4 (BAM image), the rather good homogeneity of the pristine film surface changes drastically after the reaction. Distribution of nanoparticles observed by CCD camera, shown in Figure 5, reveals their random growth resulting in the formation of isolated islands.

The electrical behavior of the films was studied by  $I$ – $V$  measurements. After the formation of nanoparticles in the polymeric matrix, the conductivity of LS films was changed, increasing by about 2 orders of magnitude. Conductivity shows a linear dependence on the film thickness. In fact, Figure 6 demonstrates the electrical behavior as a function of a number of monolayers. The relatively low value of the conductance depends on the limited number of polymeric layers and, as a consequence, on the low number of  $\text{CuS}$  nanoparticles as well as on their random distribution.

What is interesting is the dependence of the specific conductance ( $\sigma$ ) of the polymer, with and without nanoparticles, as a function of the monolayer number (see Figure 7). As a consequence of the increase in the number of monolayers, we observed a net and linear increment of  $\sigma$  in the PAET/ $\text{CuS}$  heterostructure, while in the pristine polymer  $\sigma$  remains almost unchanged, going from 5 to 10 monolayers, with a slight increment for the 20 monolayer system. This could be due to the structural reorganization of the polymer that usually occurs as the number of monolayers increase, thus leading to a longer conjugation length. Nanoparticle formation is responsible for a monotonic increase. The noticeable change brought about by increasing the number of monolayers suggests that particles are able to move and to rearrange themselves within the films, leading to a structural reorganization of the PAET/ $\text{CuS}$  system.<sup>19</sup>

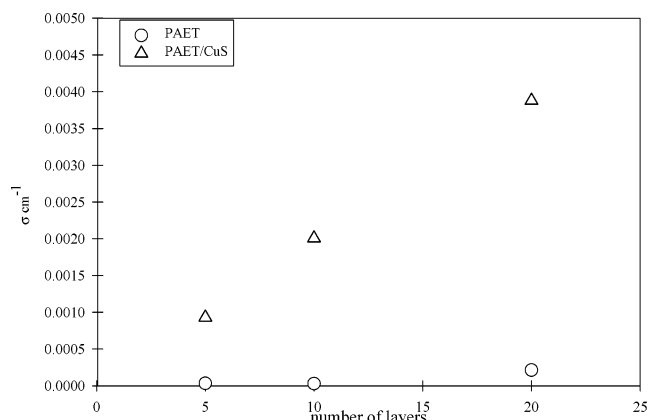


**Figure 6.** I–V curves as a function of the number of layers of copolymer/CuS nanoparticles: (a) 5 layers; (b) 10 layers; (c) 20 layers. The solid lines refer to the polymer alone, and meanwhile the dotted lines refer to polymer/CuS nanoparticle composites.

In thicker film, large nanocrystal domains grow at the expense of smaller ones. Such behavior may reflect a three-dimensional diffusion mechanism of individual particles from smaller to larger domains.<sup>20</sup> This is driven by a decrease in the surface-free energy as larger domains grow, since only few nanoparticles remain in energetically unfavorable sites.

## Conclusions

In this paper, we report the synthesis and the characterization of a new conjugated polymer, whose amphiphilic character



**Figure 7.** Specific conductance ( $\sigma$ ) as a function of the number of monolayers: (○) PAET; (▲) PAET/CuS.

allows for the formation of a densely packed monolayer at the air–water interface and for its easy transfer to solid substrates by the LS technique. The polymer acts as a growth matrix for semiconducting CuS nanoparticles in which they form randomly distributed islands/domains.

Electrical properties of the heterostructure strongly depend on the formation of nanoparticle islands in the conjugated polymer, suggesting that the nanoparticle organization arises from a three-dimensional diffusion of the particle in the polymeric matrix. Future development of the investigation will be the study of heterostructures with other metal ions, in particular, with the monovalent ones. The dependence of conductivity on frequency of applied electrical field will also be investigated.

**Acknowledgment.** The authors gratefully acknowledge Mr. Nozza for his technical assistance. This work was supported by a FIRB-MIUR grant on Organic Nanoscience and Nanotechnology to the Nanoworld Institute, namely to the Fondazione EL.B.A. and to the Centro Interuniversitario di Ricerca sulle Nanotecnologie e Nanoscienze Organiche e Biologiche of Genova University.

## References and Notes

- (1) Mingyuan, G.; Bernd, R.; Stefan, K. *Adv. Mater.* **1997**, *9*, 802.
- (2) Nicolini, C. *Thin Solid Films* **1996**, *1*, 284–285.
- (3) Roberts, G. G. In *Langmuir–Blodgett films*; Plenum Press: New York, 1990.
- (4) Ulman, A. In *An introduction to ultrathin organic films from Langmuir–Blodgett to self-assembly*, 1st ed.; Academic press: Boston, MA, 1991.
- (5) Smotkin, E. S.; Lee, C.; Bard, A. J.; Campion, A.; Fox, M. A.; Mallouk, T. E.; Webber, S. I.; White J. M. *Chem. Phys. Lett.* **1988**, *152*, 265.
- (6) Facci, P.; Erokhin V.; Nicolini, C. *Thin Solid Films* **1993**, *230*, 86.
- (7) Facci, P.; Erokhin, V.; Tronin, A.; Nicolini, C. *J. Phys. Chem.* **1994**, *98*, 13323–13327.
- (8) Erokhina, S.; Erokhin, V.; Nicolini, C. *Colloids Surf., A* **2002**, *198*–200, 645–650.
- (9) Bjornholm, T.; Greve, D. R.; Reitzel, N.; Hassenkam, T.; Kjaer, K.; Howes, P. B.; Larsen, N. B.; Bogelund, J.; Jayaraman, M.; Ewbank, P. C.; McCullough, R. D. *J. Am. Chem. Soc.* **1998**, *120*, 7643.
- (10) Erokhin, V.; Facci, P.; Carrara, S.; Nicolini, C. *J. Phys. D: Appl. Phys.* **1995**, *28*, 2534.
- (11) O’Sullivan, C. K.; Guilbault, G. G. *Biosens. Bioelectron.* **1999**, *14*, 663.
- (12) Sauerbrey, G. *Z. Phys.* **1959**, *155*, 206.
- (13) Facci, P.; Erokhin, V.; Tronin, A.; Nicolini, C. *J. Phys. Chem.* **1994**, *98*, 13323–13327.

- (14) Honig, D.; Overbeck, G. A.; Möbius, D. *Adv. Mater.* **1992**, 4, 419.
- (15) Mascetti, G.; Vergani, L.; Diaspro, A.; Carrara, S.; Radicchi, G.; Nicolini, C. *Cytometry* **1996**, 23, 110–125.
- (16) Hiraoka, Y.; Sedat, J. W.; Agard, D. A. *Science* **1987**, 238, 36–41.
- (17) Odian, G. In *Principles of Polymerization*, 3rd ed.; Wiley-Interscience: New York, 1991.
- (18) Skotheim, T. A.; Elsenbaumer, R. L.; Reynolds, J. R. In *Handbook of conducting polymers*, 2nd ed.; Marcel Dekker Inc.: New York, 1988.
- (19) Liu, Z.; Pappacena, K.; Cerise, J.; Kim, J.; Durino, C. J.; O'Shaughnessy, B.; Levicky, R. *Nano Lett.* **2002**, 2, 219.
- (20) Voorthees, P. V. *Annu. Rev. Mater. Sci.* **1992**, 22, 197.