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Chemical polymerization of pyrrole in the presence of L-serine or L-glutamic acid: Electrically controlled amoxicillin release from composite hydrogel

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ABSTRACT: Polypyrrole (PPy) was chemically prepared from aqueous solutions individually containing L-serine or L-glutamic acid, with the addition of ammonium persulfate as the oxidant. The electrical, XPS and FTIR characterizations indicated that the amino acids co-doped the PPy backbone. TEM revealed that PPy presented a quasi-spherical morphology with diameters in nanometric scale. The nanostructures of PPy-glutamic acid efficiently adsorbed therapeutic doses of amoxicillin. Composite hydrogels were obtained by the entrapment of amoxicillin-loaded PPy in polyacrylamide network. The antibiotic molecules can be subsequently released (or sustained) from composite hydrogel in response to application (or removal) of electrical stimulation. This tuning release profile can lead to promising drug delivery applications such as implantable devices and iontophoretic systems. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41804.

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INTRODUCTION

Polypyrrole (PPy) has been extensively studied due to its chemical and thermal stability, ease of preparation and electroactivity. Moreover, this polymer is known as biocompatible material, which has been used in some biomedical applications including biosensors,[1] tissue engineering,[2] neural implants,[3] and drug delivery devices.[4]

For the biomedical uses, the attachment of biomolecules or biologically active species to PPy is a critical step in order to accomplish its biofunctionality. Electrochemical polymerization is currently the most widely used method in PPy biomedical studies because it enables the control over the oxidation potential and hence, the integrity of incorporated bioagent may be retained.[5–7] However, the amount of polymer produced by an electrochemical technique is restricted to the electrode surface, which limits the versatility of its applications. In contrast, chemical method based on the initiation of polymerization by oxidative compounds allows the large-scale low-cost production of PPy. Thus, further studies related to the incorporation of biologically active species in PPy structures during its chemical preparation remains an important research task for its practical application in biomedical and biotechnological fields.

There are only few articles reporting the synthesis of PPy intentionally doped with simple amino acids. Most of works have focused on the preparation of molecularly imprinted PPy films using the amino acid as template molecule for its application in chiral discrimination of the target molecule. Nagaoka *et al.* galvanostatically deposited PPy films doped with glutamic acid (GA) for chiral recognition of the amino acid.[8] For similar purpose, Ling *et al.* reported the preparation of tyrosine imprinted PPy film by thermal polymerization and Syritski *et al.* electropolymerized pyrrole in the presence of L-aspartic acid.[9,10] Meteleva-Fischer *et al.* investigated the mechanism of the electrochemical deposition of PPy films doped with L-glutamic ions.[11] Their study showed that glutamic ions interact strongly with pyrrole molecules, apparently in form of a complex. Overall, studies have showed that polar/ionic nature of the amino acid molecule allows its incorporation to PPy structures in the role of dopant specie.

This study presents the chemical preparation of PPy nanostructures from aqueous solutions individually containing L-serine or L-glutamic acid. The reaction products were characterized by Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), conductivity measurements and

X-ray photoelectron spectroscopy (XPS). The capacity of the PPy-amino acid colloidal system for adsorption and release of drugs was evaluated *in vitro* using amoxicillin, an antibiotic of broad spectrum. The amoxicillin-loaded PPy particles were incorporated into polyacrylamide hydrogel and the feasibility of the composite hydrogel as electrically controlled release system was evaluated.

EXPERIMENTAL

Materials

Pyrrole (98%; Aldrich) was distilled under vacuum before use and stored in dark at about 3°C. Ammonium persulfate (APS, 98.7%; J. T. Bayer), L-serine (SER, 99%; Sigma), L-glutamic acid (GA, 98.99%; J. T. Bayer), ammonium hydroxide (98.6%; J. T. Bayer), acrylamide (AAm, ≥99%; Sigma), *N*,*N*′-methylenebis(acrylamide) (MBAAm, 99%; Sigma–Aldrich), *N*,*N*,*N*′,*N*′-tetramethyl-ethylenediamine (TEMED, 99%; Sigma–Aldrich) and amoxicillin (potency ≥900 μg per mg; Sigma–Aldrich) were used as received without further purification.

Polymerization of Pyrrole

Amount of 28.8 mmol of pyrrole was dissolved in 38 mL of aqueous amino acid (SER or GA) solution. The solution was cooled at 5°C in an ice bath under nitrogen atmosphere. Next, APS solution was slowly added to the monomeric solution after which the mixture was kept under moderate stirring for 24 h. The final molar ratio of pyrrole : amino acid : APS was 1 : 0.25 : 0.5. After polymerization, the reaction mixture consisting of dark-green suspension of PPy was rinsed thoroughly with deionized water in a Buchner funnel until the filtrate became neutral. A portion of washed PPy suspension was reserved for TEM and loading/releasing studies of amoxicillin. The precipitate cake was vacuum dried at room temperature and finally, it was pulverized using a mortar for FTIR, electrical and XPS characterizations. The samples of PPy were identified as PPy-SER and PPy-GA, in accordance of the amino acid used in the synthesis.

A portion of 100 mg of PPy was dedoped by dispersing the powder into 15 mL of aqueous ammonia 1*M* for 3 or 24 h. The treated particles were separated by filtration, repeatedly rinsed with deionized water followed by vacuum drying at room temperature.

Characterizations

FTIR spectra were recorded in a Perkin-Elmer Spectrum GX spectrometer (USA) by the KBr pellet technique. The morphology of samples was studied by TEM using a JEOL2010F (Japan) microscope. PPy suspensions were redispersed through sonication and adequate portion was transferred to copper grids for the analysis. The electrical conductivity of PPy samples was measured by the standard two-point method on pellets compressed with manual press. The measurements were done at room temperature using an Agilent multimeter model 34410A (Malaysia). Characterization by XPS was carried out on Perkin Elmer PHI5100 photoelectron spectrometer (Eden Prairie, MN) with MgK exciting radiation, 10 kV and 10 mA. The pressure in the analysis chamber was maintained approximately at 10^{-8} Torr during each measurement. To compensate for surface charging effects, all binding energies were referenced to the C1s neutral carbon peak at 284.6 eV.

Loading of Amoxicillin

For the loading of amoxicillin, 20 mL of PPy suspension (13.4 g L^{-1}) from the synthesis with GA were mixed with 5 mL of an aqueous solution of the drug (200 g L^{-1}). PPy suspension exhibited a pH value of 3.0 before mixing with amoxicillin solution. After stirring for 24 h, the resultant mixture was carefully transferred to dialysis tubing (acetate of cellulose, purification capacity M.W. > 12,000). The sealed dialysis tubing was then put into 500 mL of deionized water at room temperature for removing the drug that was not adsorbed on PPy structures. The dialysis solution was periodically replaced with fresh deionized water until the amoxicillin loss was below 0.1%.

The adsorption efficiency was calculated with the formula:

$$\text{Adsorption efficiency } (\%) = \frac{(a_0 - a)}{a_0} \cdot 100$$

where a_o is the total mass of amoxicillin in the solution placed in contact with PPy-GA particles (1 g) and a, the amount of amoxicillin removed during the dialysis process.

The concentration of amoxicillin was determined by recording the absorbance at 273 nm in the Perkin–Elmer Lambda 20 UV–vis spectrophotometer and the subsequent interpolation of the value in a calibration curve previously constructed from solutions of known concentrations.

Incorporation of Amoxicillin-Loaded PPy-GA into Polyacrylamide Hydrogel

In a cylindrical mold of 26 mm of diameter chilled in an ice bath, 10 mL of acrylamide (AAm)/bisacrylamide (MBAAm) aqueous solution (58 g of AAm and 1 g of MBAAm in 100 mL) was mixed with 8 mL of the amoxicillin-loaded PPy-GA suspension. Gelation process was initiated by adding 1 mL of APS solution (0.1 g mL^{-1}) and 50 μL of TEMED reactant. Before the gelation point was reached, a thin copper electrode with an active area of 40 mm × 15 mm was axially introduced in the center of the circular cross-section area of composite hydrogel. Finally, the composite hydrogel (PAAm/PPy-GA/amoxicillin) with the incorporated electrode was removed from the mold and it was immediately used in the experiment of electrically controlled drug release.

Swelling studies of PAAm/PPy-GA/amoxicillin hydrogel were also carried out in order to determine the mass swelling ratio in phosphate-buffered saline (PBS, 200 m*M*, pH 7, 25°C). Immediately after the cross-linking process, hydrogel samples were placed in the buffer solution where they were allowed to swell to equilibrium. The masses of swollen hydrogels were measured periodically, removing the excess of solution. The equilibrium swelling was reached at 96 h. Once equilibrium was attained, the hydrogels were weighed, dried at vacuum and then reweighed. The study was done in triplicate and it was found a mass swelling ratio of 155.4% (standard deviation 0.8%), calculated as mass ratio of absorbed solution at equilibrium and the dried gel.[12]

Controlled Release of Amoxicillin by Electrical Stimulus

The composite hydrogel-coated electrode was immersed in 80 mL of PBS (200 m*M*, pH 7, 25°C) together with an

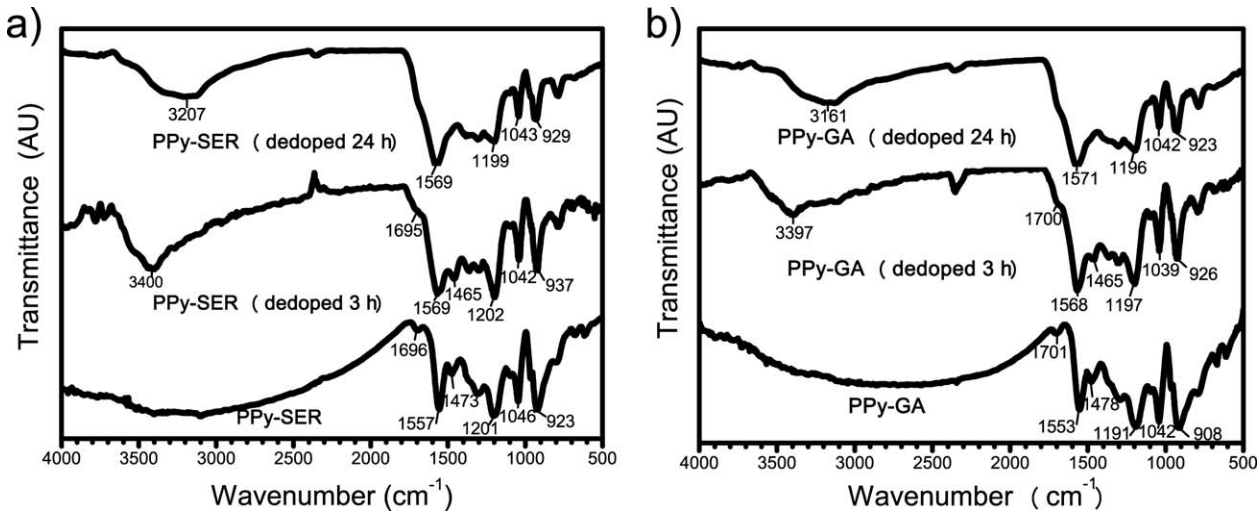

Figure 1. FTIR spectra of (a) as-synthesized and ammonia treated PPy-SER and those of (b) as-synthesized and ammonia treated PPy-GA.

uncoated identical electrode. The distance between the hydrogel surface and coplanar free electrode was ~4 mm. The hydrogel-coated electrode was connected to the negative pole of a DC power supply Agilent, model E3632A. For the release study, potentials of 5 V were applied for 2 min between the two electrodes in intervals of 30 min. Samples of 1 mL were withdrawn at specific time intervals for measuring the released amoxicillin. Sink condition was maintained by replacing equal volume of buffer. The release studies were performed in triplicate and the average results were plotted versus time.

RESULTS AND DISCUSSION

When pyrrole was dissolved in the aqueous solution of SER and GA prior to polymerization, the pH of the resultant solutions were around 6.4 and 3.3, respectively. In both cases, neutral pyrrole molecules coexist with the amino acid in zwitterionic form; SER ($-NH_3^+$, $-COO^-(C_\alpha)$) and GA ($-NH_3^+$, $-COO^-(C_\alpha)$, $-COOH(C_\beta)$). Such conditions allow the molecules of pyrrole and the amino acid to held together through supramolecular interactions (e.g., NH from pyrrole as proton donor and carbonyl oxygen from the amino acid as proton acceptor) to form a kind of complex preceding the polymerization reaction. This assumption is supported by previous reports of polymerization of pyrrole in the presence of simple amino acids. Specifically, the finding of strong interaction between glutamic ions and pyrrole moieties during the electrochemical deposition of PPy films and the glycine inclusion in PPy matrix when the polymer was prepared by chemical oxidation of pyrrole with APS in the presence of this amino acid.[11,13]

Figure 1 shows the FTIR spectra of as-synthesized (a) PPy-SER and (b) PPy-GA samples. The spectra of PPy-SER and PPy-GA depict the spectral contributions of polymer and amino acids units. The position of the typical bands of PPy is quite similar in both spectra. The band at 1557 cm^{-1} in the spectrum of PPy-SER is assigned to the C—C stretching vibration of pyrrole ring.[14] A slight shift to 1553 cm^{-1} of this band is detected in the spectrum of PPy-GA. The bands at 1473 cm^{-1} in the spectrum of PPy-SER and at 1478 cm^{-1} in the spectrum of PPy-GA correspond to C—N stretching vibration in the ring.[15] For PPy-SER sample, the signal with minimum at 1310 cm^{-1} is attributed to C—H or C—N in-plane deformation modes.[15] This minimum is shifted to 1291 cm^{-1} for PPy-GA. A strong band is observed in the region from 1250 to 1100 cm^{-1} that corresponds to the breathing vibration of the pyrrole ring.[15] The minimum is situated at 1201 and 1191 cm^{-1} for PPy-SER and PPy-GA, respectively. The sharp peak at 1046 cm^{-1} in the spectrum of PPy-SER and at 1042 cm^{-1} in that of PPy-GA is correlated to the C—H in plane deformation vibration of PPy.[14] The band of C—H out-of-plane deformation vibration of the ring has a minimum at 923 cm^{-1} for PPy-SER and at 908 cm^{-1} for PPy-GA.[15]

It is important to note the spectral contribution at 1696 cm^{-1} in the spectrum of PPy-SER and at 1701 cm^{-1} in the spectrum of PPy-GA. This band can be assigned to the C=O stretching vibration of carboxylic moiety which strongly suggest the presence of the amino acids.[13] A broad band above 2000 cm^{-1} is visible in both spectra. This feature is attributed to an intra-chain (free-carrier) excitation associated with the doped form of PPy.[15]

Figure 1 also includes spectra of ammonia treated (a) PPy-SER and (b) PPy-GA. PPy samples were treated with an excess of aqueous ammonium hydroxide solution during 3 and 24 h. The most pronounced change after the dedoping process was the reduction of the free-carrier band as indication of deprotonation of PPy in both samples.

After 3 h of ammonium treatment, the main band associated with the ring stretching vibration of PPy blue-shifts to 1569 and 1568 cm^{-1} for PPy-SER and PPy-GA, respectively. The signal attributed to the C=O vibration of amino acids is still detected as a shoulder of the band of ring stretching vibration of PPy in samples treated for 3 h. A resolved band with minimum around 3400 cm^{-1} appears in both spectra, which is

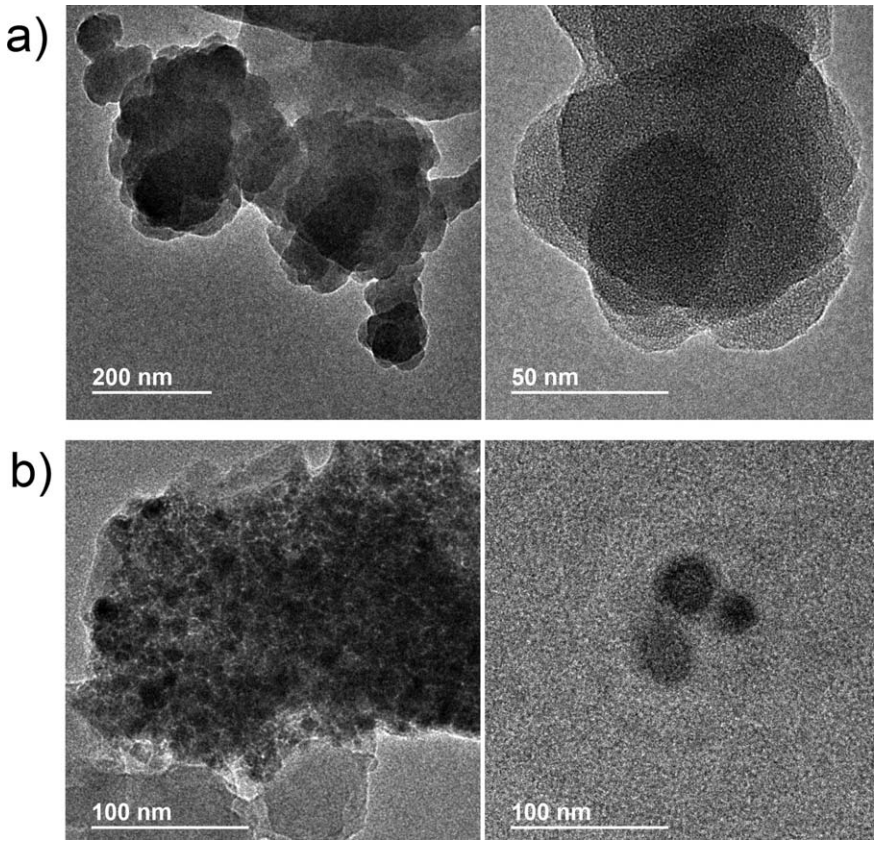

Figure 2. TEM images of PPy structures formed from the polymerization of pyrrole with APS in the presence of (a) SER and (b) GA.

attributed to the overlapping of N—H stretching band of PPy/amino acid and O—H stretching contribution of the amino acid.[16,17]

In the spectra of samples treated for 24 h, the contribution of C═O group is virtually suppressed. The broad band with minimum around 3400 cm^{-1} in samples treated for 3 h is replaced with a narrower band centered at 3207 cm^{-1} in PPy-SER spectrum and at 3161 cm^{-1} in that of PPy-GA. These features suggest a drastic reduction of amino acid content when the dedoping treatment was extended from 3 to 24 h.

Figure 2 depicts TEM images of PPy structures formed from the polymerization of pyrrole with APS in the presence of (a) SER and (b) GA. The particles of both samples were mainly found in aggregated form. The primary particles exhibited a quasi-spherical morphology with diameters <50 nm. Moreover, PPy particles of smaller sizes were found in sample synthesized in the presence of GA compared with those obtained in the presence of SER.

Table I summarizes the conductivities and atomic compositions determined by XPS of PPy-SER and PPy-GA samples. The results for samples treated with aqueous ammonia were also

Table I. Electrical Conductivities and XPS Data of As-Synthesized Samples of PPy and Those Treated with Ammonia

		XPS results			
		Atomic composition (%)			
	Electrical conductivity (S cm^{-1})	N	S	C	Atomic ratio S : N
PPy-SER	1.3×10^{-2}	8.9	1.9	59.2	0.21
PPy-SER (dedoped 3 h)	1.1×10^{-5}	12.9	0	76.0	0
PPy-SER (dedoped 24 h)	1.7×10^{-7}	16.5	0	72.2	0
PPy-GA	1.5×10^{-2}	14.9	2.1	69.4	0.14
PPy-GA (dedoped 3 h)	1.1×10^{-5}	13.1	0	76.6	0
PPy-GA (dedoped 24 h)	1.8×10^{-7}	15.2	0	73.0	0

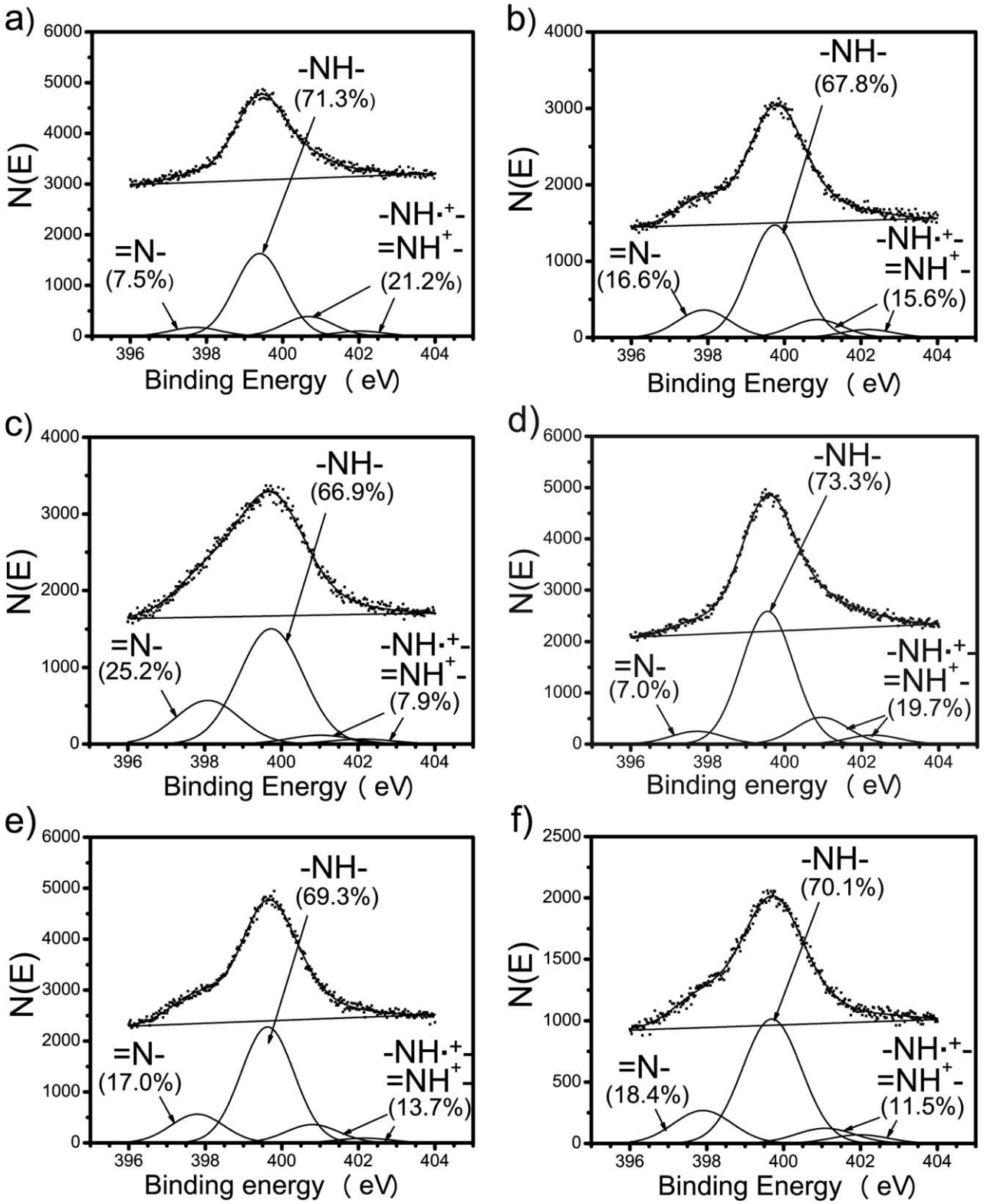

Figure 3. High-resolution XPS spectra of N 1s regions for (a) as-synthesized PPy-SER, (b) PPy-SER after 3 h of ammonium treatment, (c) PPy-SER after 24 h of ammonium treatment, (d) as-synthesized PPy-GA, (e) PPy-GA after 3 h of ammonium treatment and (f) PPy-GA after 24 h of ammonium treatment.

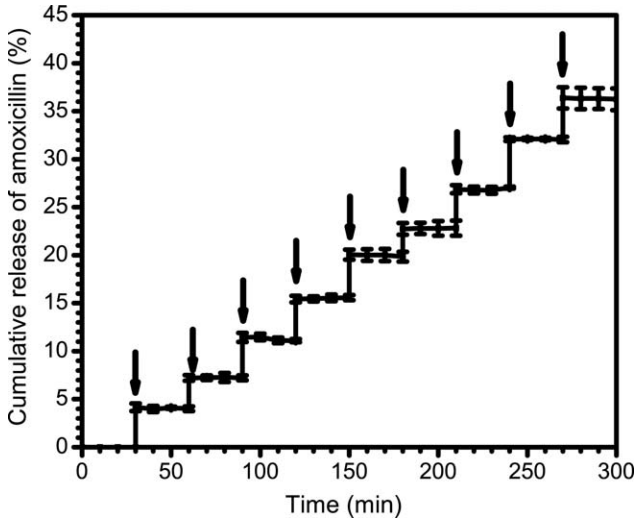

Figure 4. Release of amoxicillin from composite hydrogel of PAAm/PPy-GA under electrical stimulation (5 V). The arrows indicate when the voltage was applied.

included in Table I. The conductivities of as-synthesized samples were lower than those reported for PPy prepared in the presence of strong acids and similar to those reported by our research group for PANI prepared from solutions containing L-glutamic acid.[15,18]

The presence of sulfur in as-synthesized PPy samples suggests that sulfur containing anions were incorporated as counterions, i.e. sulfate and hydrogensulfate ions were generated from decomposition of APS during the oxidation of pyrrole. The S : N atomic ratio in PPy-SER indicates that PPy chains contain a minimum of one sulfur per five pyrrole units; whereas in PPy-GA, the polymer chains contain a minimum of one sulfur containing specie per seven monomer moieties. When samples were treated with aqueous ammonia for 3 h, sulfur containing species were eliminated; however, the resultant conductivities in the order of 10^{-5} S cm^{-1} pointed to an incomplete dedoping process. These features strongly suggest the role of the amino acid as co-dopant specie of PPy, which is consistent with FTIR results that indicated an incomplete removal of amino acids after 3 h of ammonium treatment.

Moreover, conductivity decreased by two order of magnitude when dedoping treatment was extended from 3 to 24 h. This result is in good correlation with the drastic reduction of amino acids due to the further dedoping treatment accompanying the deprotonation of PPy backbone.

Figure 3 shows the high-resolution XPS spectra of N 1s regions of as-synthesized PPy-SER and those of PPy-SER after ammonium treatments. The spectra of analogous samples of PPy-GA are also included. The N1s core-level spectrum of PPy-SER and PPy-GA displayed the lowest binding energy (BE) component at 397.9 eV that was attributed to the neutral imine nitrogen (—N═) followed by the signal of amine nitrogen (—NH—) at 399.6 eV with the strongest intensity. The two components above 400 eV were attributed to positively charged nitrogen atoms from conductive state of PPy.[19,20]

After 3 h of ammonium treatment, a decrease of the contribution of positively charged nitrogen with a concomitant increase of the signal of neutral imine nitrogen were observed for both samples of PPy, as indication of deprotonation of polymer backbone. When dedoping treatment was extended from 3 to 24 h, a further decrease of components above 400 eV was observed while the contribution of neutral imine nitrogen became higher. The analysis of N1s core-level spectra are in accordance with the conductivity results and this also supports the above-mentioned idea of the role of amino acids as co-dopant species of PPy.

The effectiveness of PPy structures for amoxicilin adsorption was studied for PPy-GA, which was the sample with lowest content of sulfur. A therapeutic dose of the drug was added to 20 mL of PPy-GA suspension. Un-bonded amoxicillin was removed by dialysis against deionized water and the adsorption efficiency was founded to be 42.5%.

The amoxicillin-loaded PPy particles were incorporated into PAAm hydrogel in order to evaluate its potential as electrically controlled release system. The drug release profile from composite hydrogel under electrical stimulation is shown in Figure 4. The first 30 min without electrical potential exhibited no burst release. The application of voltage produced an immediate release of 4.2% of amoxicillin. Negligible amount of drug was delivered in the next 30 min at 0 V. Similar "ON–OFF" release pattern was observed at least in the eight subsequent cycles of application and removal of the electrical potential difference. The average amoxicillin release with the electric impulse was 4.1% (standard deviation of 0.6%).

The electrically triggered release of molecules from conductive polymers is directly associated to (1) the electric-field-driven movement of the charged molecules and to (2) the change of the overall net charge within the polymer upon reduction or oxidation.[21] In our case, the first effect is discarded because amoxicillin mainly exists as zero net charge molecule at neutral pH (pK_a values of 2.4, 7.4, and 9.6).[22] Thus, the drug delivery can be associated to the electrochemical reduction of PPy, which causes changes in the

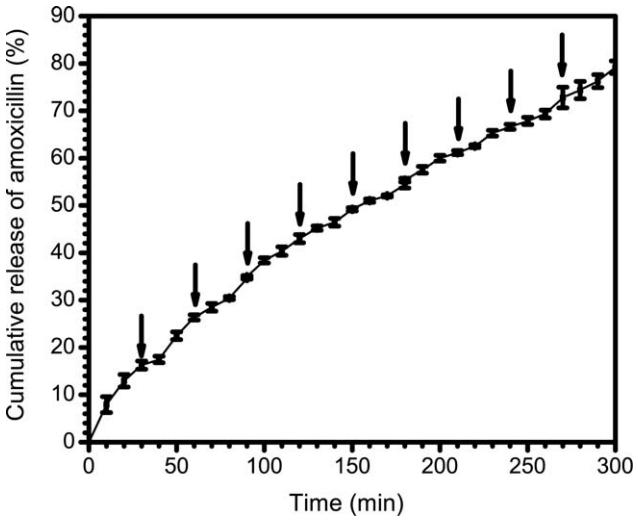

Figure 5. Release of amoxicillin from PAAm hydrogel under electrical stimulation (5 V). The arrows indicate when the voltage was applied.

charge density of the particles, with the concomitant volume contraction and synergistically release of noncovalently bonded amoxicillin molecules. It is important to mention that no erosion was detected in any composite hydrogels; their physical integrity was preserved during the experiments.

PPy-free hydrogels were prepared in order to evaluate the effect of conductive polymer on the electrical control of the drug release. It also allows studying the amoxicillin delivery feature of the PAAm hydrogel at its specific crosslinking condition, in a similar experiment of drug release using electrical stimulus of 5 V.

Hydrogels without PPy (PAAm/amoxicillin) were prepared following an identical procedure used to prepare composite hydrogels (PAAm/PPy-GA/amoxicillin), but without adding PPy particles. The amount of amoxicillin loaded to PAAm hydrogel was also the same of that incorporated to composite hydrogel.

The drug release profile from amoxicillin-loaded PAAm hydrogel under electrical stimulation is shown in Figure 5. PPy-free hydrogel did not show the "ON–OFF" release pattern observed in PPy-containing hydrogel. This result corroborated that the electrochemical properties of PPy and the association PPy-drug play a determining role for the tunning release delivery of amoxicillin from hydrogel system by electrical stimulus.

CONCLUSIONS

Polypyrrole was synthesized by chemical polymerization with ammonium persulfate in aqueous solutions individually containing L-serine or L-glutamic acid. The results of FTIR, conductivity measurements and XPS proved that the amino acids were incorporated into the polymer structure as dopant specie similarly to sulfur containing anions produced from decomposition of ammonium persulfate. Polypyrrole structures exhibited a quasi-spherical morphology with diameters <50 nm. The particles of polypyrrole prepared in the presence of L-glutamic acid efficiently adsorbed therapeutic doses of amoxicillin. Composite hydrogel can be obtained by the entrapment of amoxicillin-loaded polypyrrole in polyacrylamide network. The drug release profile from composite hydrogel under electrical stimulation showed an "ON–OFF" release pattern in cycles of application and removal of the electrical potential. Drug delivery behavior was associated to the electrochemical reduction of polymer, which produced the synergistically release of noncovalently bonded amoxicillin molecules. Hybrid system of polypyrrole and such amino acids combines the electrical properties of the polymer with the biofunctionality of the amino acid, therefore it can be considered as a potential platform for biomedical applications. Further studies are in course in order to optimize the incorporation of the amino acids to polypyrrole structures by chemical procedures.

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