

Strategy and Characteristics of Polypyrrole Deposited on Silver Substrates with Silver-Containing Nanocomplexes

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In this study, we provide a strategy to electrodeposit polypyrrole (PPy) on roughened silver substrates, which was accomplished by a triangular-wave oxidation–reduction cycle (ORC) for three scans in an aqueous solution containing 0.1 N KCl. This method overcomes the conventional limitation that silver, oxidizing more readily than the pyrrole monomer, would obviously not be a good choice for the anode in the electropolymerization of PPy. It was found that Cl- and Ag-containing nanocomplexes with grain sizes smaller than 100 nm were formed on the roughened Ag substrates after ORC treatment. Meanwhile, pyrrole monomers can form self-assembled monolayers (SAMs) and further autopolymerization on these nanocomplexes. As shown in the Fourier transform infrared (FTIR) spectrum, charge transfer occurs from electrodeposited pyrrolylium nitrogen to the roughened silver. The autopolymerized PPy owns a high conductivity, as confirmed by the analyses of X-ray photoelectron spectroscopy (XPS) and surface-enhanced Raman scattering (SERS).

Introduction

Recently, electrically conducting polymers (CPs) have attracted considerable attention because of their unusual electronic properties. Of all known CPs, polypyrrole (PPy) is the most frequently used in commercial applications, such as batteries,^{1,2} supercapacitors,^{3,4} sensors,^{5,6} anhydrous electrorheological fluids,⁷ microwave shielding, and corrosion protection,^{8,9} because of the fairly good environmental stability and the possibility of forming homopolymers or composites with optimal chemical and physical properties.^{10,11} There are two methods used to synthesize PPy, chemical and electrochemical polymerizations. The principal advantage of the electrochemical method is related to the better conducting properties and long-term stability of conductivities.^{12,13} However, in the electrochemical method, metals such as silver and aluminum, which oxidize more readily than the pyrrole monomer, would obviously not be good choices for the anode.¹⁴

Raman spectroscopy is an essential means to evaluate the structure situation of PPy in various states.^{15,16} Therein surface-enhanced Raman scattering (SERS) of nearly 10⁶-fold enhancement of Raman spectra of surface species provides a dramatic example for the modification of the optical properties of molecules near solid-state surfaces in view of its unique sensitivity and excellent frequency resolution.^{17–20} As shown in the literature,^{21–23} the technique of SERS depends critically on the presence of structural features of dimensions 10–100 nm. It is generally accepted that the enhancement of the Raman emission of molecules adsorbed on the metal surface has a double origin, the electromagnetic (EM) enhancement^{24,25} and the chemical (CHEM) enhancement.^{26,27} EM enhancement results from the enhancement of local electromagnetic fields at the surface of a metal, mainly confined to Ag, Au, and Cu, which can support surface plasma/optical conduction resonances. In contrast, CHEM enhancement is associated with the charge

transfer between the metal and adsorbate at atomic-scale roughness features. Bukowska et al.²⁸ reported that the change of the surface structure via oxidation–reduction cycles (ORC) treatment significantly influences the corresponding SERS effect. As reported in the literature,^{29,30} anion-containing complexes of metals, which were distinguishable from bulk metals, were easily formed during the ORC treatment. It was also found that the SERS activity is much more stable when the constituents of the complex are simultaneously present.³¹ Furthermore, it was believed that the SERS effect chiefly comes from the roughening procedure in ORC³² and the corresponding complex formed at the interface of roughened metal.³³ Henry et al.³⁴ reported that chlorauric acid can act as an oxidant to oxidize chemically polymerized PPy to produce composite PPy colloids. Burke and Hurley³⁵ reported that gold surfaces can be superactivated by a combination of thermal and cathodic pretreatment. They display inexplicably high catalytic activity for some reactions in the form of oxide-supported microparticles. All of these studies reveal that fine metals or metal-containing complexes with nanostructures demonstrate specially electrocatalytic activities. However, the detailed exploration and the mechanism of the catalytic activity for the electrooxidation pathway for the polymerization of conducting polymers were less observed in the literature.

Besides roughening a metal surface to demonstrate SERS effects, self-assembled monolayers (SAMs) are generally used to modify metal substrates. SAMs form by the spontaneous adsorption of organic molecules onto a metal or metal oxide surface, especially for alkanethiols adsorbing on copper, silver, and gold.^{36,37} On these metals, thiols form a densely packed, oriented monolayer. The assemblies are the product of strong metal–sulfur interactions that are also responsible for the robust nature of the SAM in liquid. Silver substrates are most suitable for use in the SERS study of nitrogen-containing heterocycles with five- or six-membered rings because of their great enhancement effects, but their applications in electrochemistry are generally limited because of their narrow potential window

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available. By extending the idea of SAMs in this work, we provide a strategy to electrodeposit PPy on roughened silver substrates with nanostructures, which can be accomplished by a triangular-wave ORC in an aqueous solution containing 0.1 N KCl. Also, pyrrole monomers were originally autopolymerized and oxidized on the roughened Ag substrates.

Experimental Section

Chemical Reagents. Pyrrole (Py) was triply distilled until a colorless liquid was obtained and was then stored under nitrogen before use. KCl was used as received without further purification. The reagents (p.a. grade) were purchased from Acros Organics. All of the solutions were prepared using deionized 15 M Ω cm water.

Preparation of Roughened Ag Substrates. All of the electrochemical experiments were performed in a three-compartment cell at room temperature, 22 °C, and were controlled by a potentiostat (model PGSTAT30, Eco Chemie). A sheet of silver foil with bare surface area of 0.238 cm², a 2 \times 2 cm² platinum sheet, and silver–silver chloride (Ag/AgCl) were employed as the working, counter, and reference electrodes, respectively. Before the ORC treatment, the silver electrode was mechanically polished (model Minimet 1000, Buehler) successively with 1 and 0.05 μ m of alumina slurry to a mirror finish. Then the electrode was cycled in a deoxygenated aqueous solution containing 0.1 N KCl from -0.3 to $+0.3$ V vs Ag/AgCl at 5 mV/s for three scans without any duration at the cathodic and anodic vertexes. After the ORC treatment, the roughened Ag electrode was rinsed throughout with deionized water and finally dried in a vacuum-dryer with dark atmosphere for 1 h at room temperature for subsequent use.

Electropolymerization and Autopolymerization of Pyrrole on the Roughened Ag Substrates. A deoxygenated aqueous solution containing 0.5 M pyrrole was instantly dropped onto the as-prepared roughened Ag substrate. Then it was placed in a desiccator with nitrogen and dark atmosphere for 2 h. Finally the sample (called autopolymerized PPy) was rinsed throughout with deionized water and dried in a vacuum-dryer with dark atmosphere at room temperature before test. The electrochemical polymerization of PPy on roughened silver (called electropolymerized PPy) was carried out at a constant anodic potential of 0.85 V vs Ag/AgCl in a deoxygenated aqueous solution containing 0.1 M pyrrole and 0.1 N KCl. Before electropolymerization, ca. 15 min is necessary to wait for reaching a steady value of the open circuit potential (OCP). The charge passed was 25 mC cm⁻². To compare the characteristics of this kind of electropolymerized PPy on roughened Ag with that of the usual electrochemically polymerized PPy, the electrochemical synthesis of PPy on polished platinum without ORC treatment was also prepared with the similar condition.

Characteristics of Roughened Ag and Electropolymerized and Autopolymerized PPy. Raman spectra were obtained using a Renishaw 2000 Raman spectrometer employing an Ar laser of 1 mW radiating on the sample operating at 514.5 nm and a charge couple device (CCD) detector with 1 cm⁻¹ resolution. For the X-ray photoelectron spectroscopy (XPS) measurements, a Physical Electronics PHI 1600 spectrometer with monochromatized Mg K α radiation, 15 kV and 250 W, and an energy resolution of 0.1–0.8% $\Delta E/E$ was used. To compensate for surface charging effects, all XPS spectra are referred to the C 1s neutral carbon peak at 284.6 eV. The complex XPS and SERS peaks are deconvoluted into component Gaussian peaks using a peak separation and analysis software (PeakFit v4.0, AISN Software Inc.). In the XPS N 1s deconvolution, the four

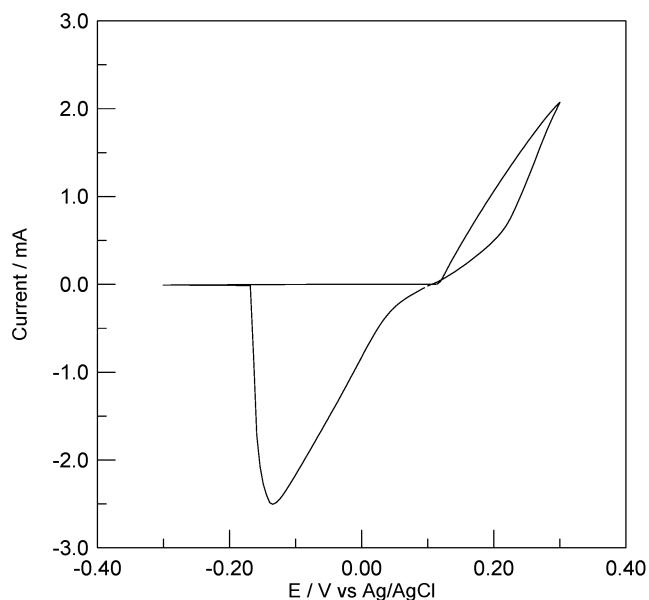


Figure 1. Cyclic voltammogram at 5 mV/s of the third scan for silver electrode in 0.1 N KCl.

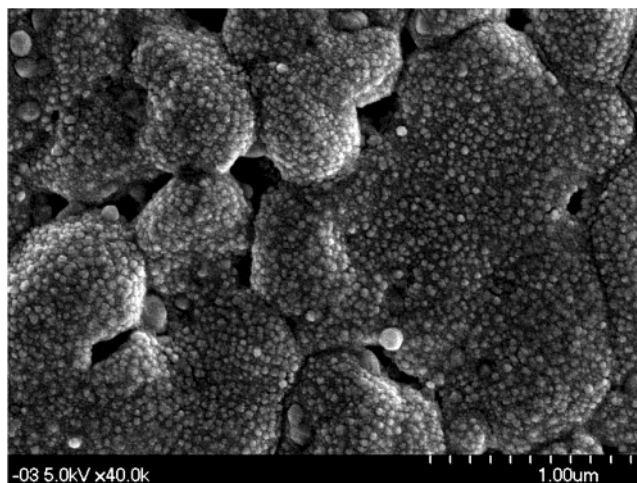


Figure 2. SEM image of silver substrate after ORC treatment.

component peaks are located at 397.3 and 399.8 eV and at higher than 401 eV of 401.3 and 402.8 eV with equal value of half width at half-maximum (HWHM) of 1.65 eV. The Fourier transform infrared (FTIR) spectrum was recorded by using the mode of attenuated total reflectance (ATR, model DA 8.3, Bomem) with 1 cm⁻¹ resolution for 256 times. The surface morphology of roughened silver was obtained from scanning electron microscopy (SEM, model S-4700, Hitachi). The surface morphologies of roughened silver and autopolymerized PPy on it were obtained from atomic force microscopy (AFM, Nanoscope III, Digital Instrument) experiments with the mode of friction force.

Results and Discussion

Characteristics of Redeposited Ag. In ORC treatment, the chloride electrolyte was selected because, as for silver, this facilitates the metal dissolution–deposition process that is known to produce SERS-active roughened surfaces.³⁸ Figure 1 shows the typical triangular voltammetry curve obtained at 5 mV/s on silver in 0.1 N KCl. Clearly, the roughened Ag electrode is unsuitable for depositing PPy on it at anodic potential more positive than 0.15 V vs Ag/AgCl because of its

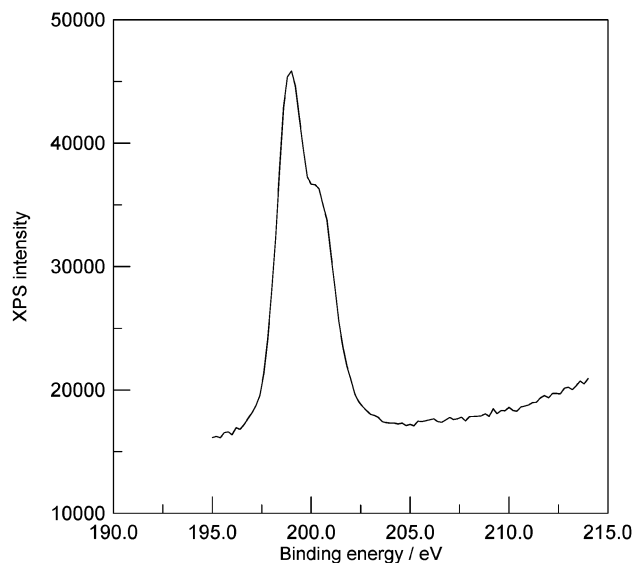


Figure 3. XPS Cl 2p core-level spectrum of the roughened silver substrate.

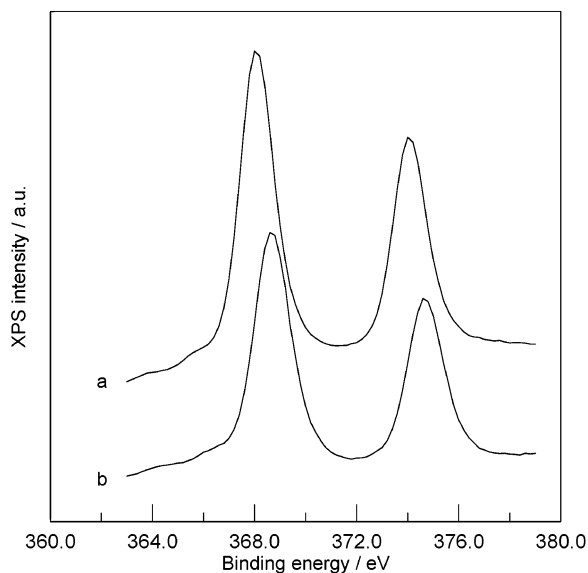


Figure 4. XPS Ag 3d_{5/2-3/2} core-level spectra of the silver substrates (a) before and (b) after roughening by ORC treatment of 3 scans.

narrow polarizable potential window. Figure 2 shows the surface image of the roughened Ag substrate. It is a typical aspect of a rough surface with a good Raman activity, which demonstrates a microstructure smaller than 100 nm.²¹⁻²³

The components formed on the roughened Ag can be confirmed via XPS analyses. Figure 3 shows the XPS Cl 2p core-level spectrum of the roughened Ag substrate. The main peak of the chloride-containing complexes is located at 199 eV, which can be assigned to Cl (-1).³⁹ Figure 4 displays the XPS Ag 3d_{5/2-3/2} doublet region of roughened Ag compared to that of the same Ag substrate before roughening. A positive shift of 0.6 eV of binding energy of the Ag 3d_{5/2-3/2} doublet region after ORC treatment reveals that the roughened Ag is of oxidized state according to the XPS handbook. The oxidized Ag can be primarily assigned to trivalent Ag(III) at 367.6 eV, as usually shown in the Cl- and Ag-containing complex.^{40,41} Combining the electronic configuration of Cl shown in Figure 3, we can assign the complexes to AgCl₄⁻ formed on the Ag substrate.

Electropolymerization of Pyrrole on the Roughened Ag Substrates. Figure 5 records the cyclic voltammograms of

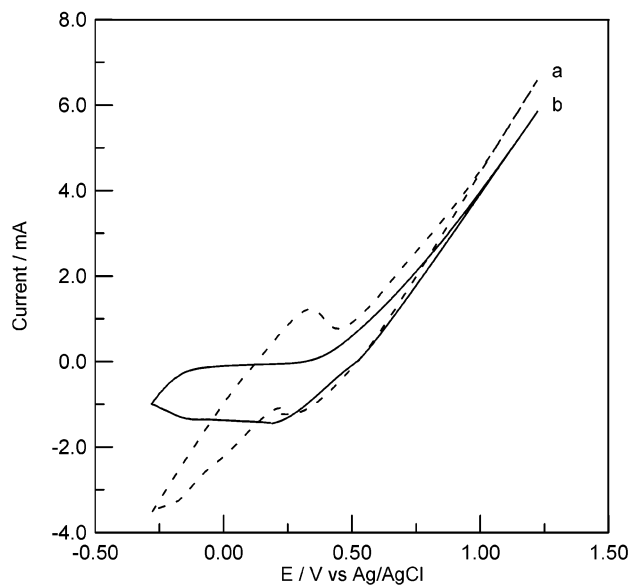


Figure 5. Cyclic voltammograms at 50 mV/s of the first scan for roughened silver electrodes in 0.1 N KCl and 0.1 N pyrrole performed (a) before (dashed line) and (b) after (solid line) the open-circuit potential is steady.

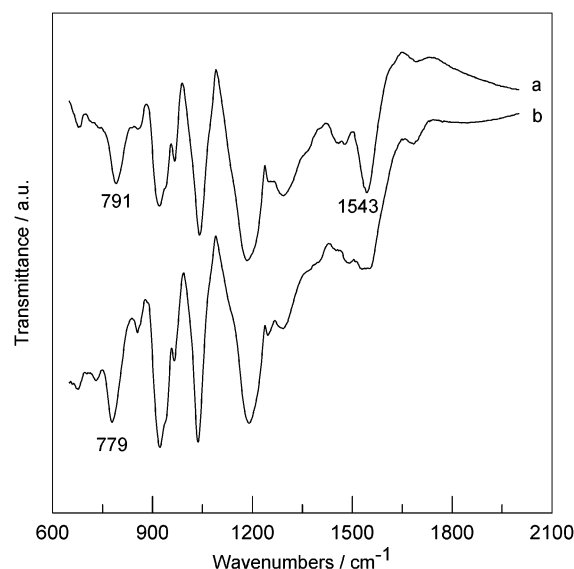


Figure 6. FTIR spectra of PPy films electrodeposited (a) on electrochemically roughened Ag and (b) on mechanically polished Pt substrates.

pyrrole oxidized on roughened Ag substrates in 0.1 N pyrrole and 0.1 N KCl performing before and after the OCP is steady. Obviously, the redeposited AgCl₄⁻ complexes are easily dissolved with the anodic scan if this experiment starts immediately after the circuit is connected without waiting for an equilibrium state at the electrode interface. In this situation, oxidized polymerization of PPy on silver substrates is also difficult to occur. However, an interesting phenomenon is observed on the contrary experiment after the OCP is steady. The dissolution of the redeposited AgCl₄⁻ complexes, which would interfere with the pyrrole oxidation, is depressed in the anodic scan. This can be ascribed to the pyrrolylium nitrogen readily adsorbing on the AgCl₄⁻ complexes to form ordered SAMs in the period of the equilibrium time as amine assembles onto Au surfaces.^{42,43} Thus the redeposited AgCl₄⁻ complexes are protected from dissolution. Furthermore, as shown in curve b of Figure 5, the onset potential of pyrrole polymerized on the roughened Ag

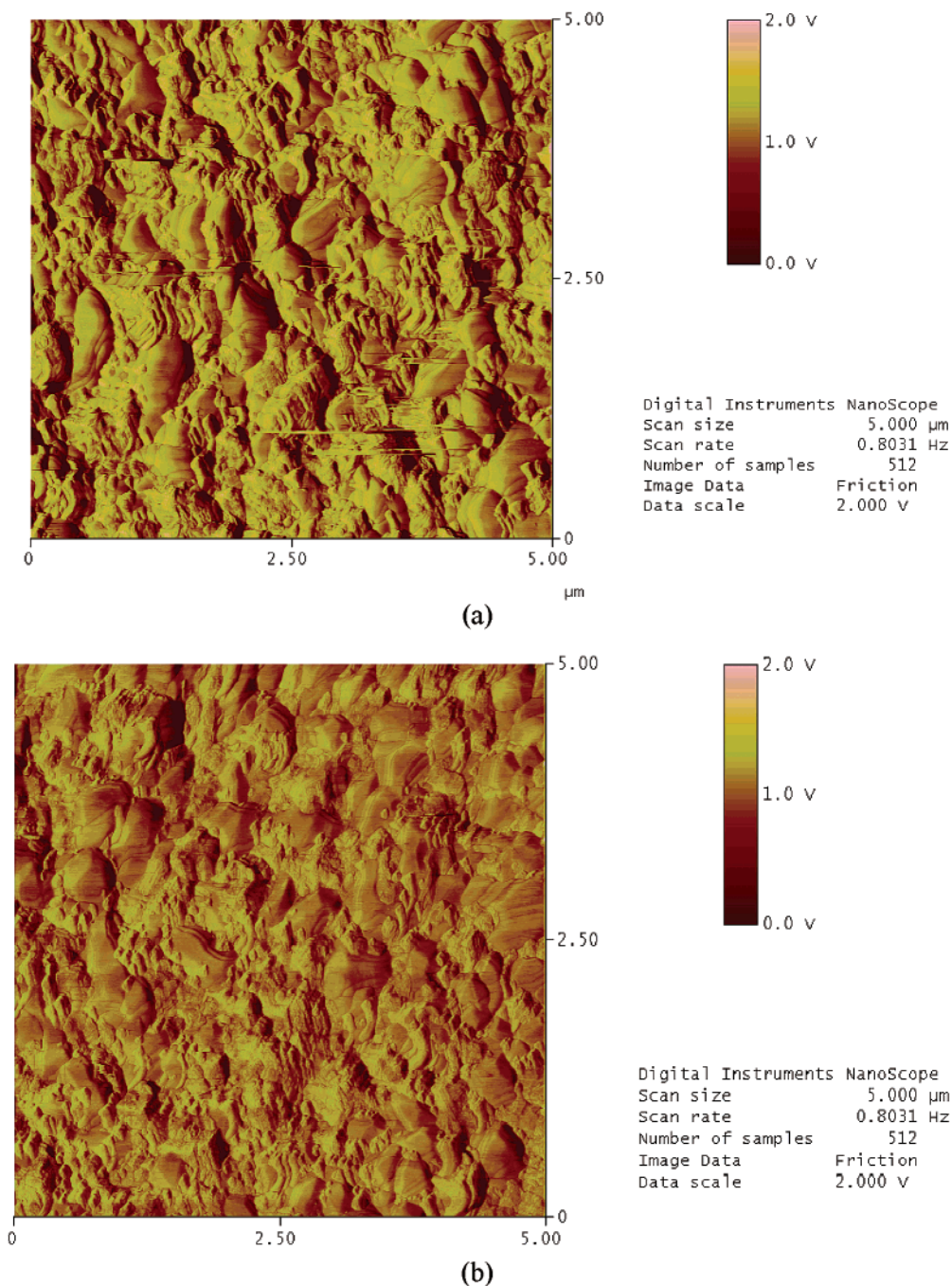


Figure 7. AFM friction force images of (a) roughened Ag substrate and (b) PPy autopolymerized onto it because of the electrochemical activity of Ag-containing nanocomplexes.

substrate is ca. 0.5 V vs Ag/AgCl, which is a significantly cathodic shift from the general value of 0.65 V vs Ag/AgCl.^{27,44} It is generally accepted that the mechanism for polymerization of pyrrole is the oxidation of pyrrole monomer to the radical cation as the first step. Coupling of a pyrrole radical cation with a neutral monomer forms a radical cation dimer and further reaction continuous the chain-forming sequence.⁴⁵ Before the electrooxidation of pyrrole, electron transfer from pyrrole to AgCl_4^- , as confirmed later, occurs immediately following the formation of SAMs. Dimers or oligomers of PPy can precipitate onto the electrode surface to form nucleation sites. This would contribute to the subsequent electropolymerization of pyrrole and contribute to the lower anodic onset potential for the polymerization of pyrrole. It clearly explicates that the AgCl_4^- complexes formed on the roughened Ag substrate demonstrate

a catalytic electrooxidation pathway for the pyrrole polymerization. Therefore, the electropolymerization of pyrrole on the Ag substrate is both accessible and even ready.

Figure 6 demonstrates the IR spectra of PPy films deposited on the roughened Ag and on the polished Pt substrates. Each spectrum shown here is the sum of 256 individual scans to obtain better resolutions. As shown in spectrum a of Figure 6, the characteristic bipolaron bands at ca. 923 and 1203 cm^{-1} indicate that the formation of PPy on the roughened Ag is in its doped state.⁴⁶ Because the PPy film electrodeposited on Pt is free-standing, the peak shift of C–H out-of-plane bending⁴⁷ at 779 to 791 cm^{-1} and marked appearance of N–H bending vibration⁴⁸ at 1543 cm^{-1} for PPy electrodeposited on roughened Ag are meaningful. The appearance of N–H bending vibration of PPy means that charge-transfer indeed occurs from the deposited

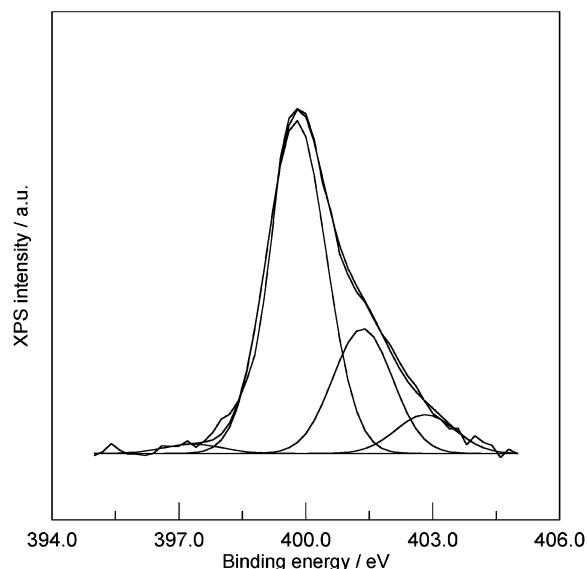


Figure 8. XPS N 1s core-level spectrum of autopolymerized PPy.

pyrrolylium nitrogen to the metal-containing complex formed on the bulk metal. Because PPy is a conjugated polymer with an aromatic-like structure and the delocalized π electrons, which come from both the C and N atoms, this effect of charge transfer would be responsible for the change of C–H out-of-plane bending.

Autopolymerization of Pyrrole on the Roughened Ag Substrates. The polymer layer of autopolymerized PPy on roughened Ag is not visible to the naked eye and even hard to resolved on SEM. With the aid of AFM with the mode of friction force, a thin layer of PPy coated on the nanoparticles can be distinguished, as shown in Figure 7. Comparing the images of roughened Ag substrates with and without autopolymerization of PPy deposited on them, it is found that the whole brightness is reduced (the lower part increases on the topography image) and the corresponding friction force is increased because of the autopolymerization of PPy on roughened Ag coming from the electrochemical activity of Ag-containing nanocomplexes. For organic films with similar elastic modulus, the main contribution to the friction comes from adhesive force between the tip and the studied film region characterized by surface tension.⁴⁹ This interesting phenomenon would be further confirmed via XPS and SERS.

Figure 8 shows the XPS N 1s spectra of autopolymerized PPy deposited on roughened Ag. With further deconvolution of N 1s spectra into four component peaks, the positively charged nitrogen ($-N^+H-$) species with the higher binding energy (BE) tail (BE > 401 eV) can be used to determine the oxidation level of PPy. This oxidation level is calculated from the ratio of the peak area of N^+ (BE > 401 eV) to that of the total N 1s shown in the XPS spectrum.^{50,51} The result shows that the oxidation level of autopolymerized PPy is 0.33, which is significantly higher in comparison with that of as-grown PPy, generally ranging from 0.25 to 0.33.⁵²

Figure 9 shows the SERS spectrum of the autopolymerized PPy deposited on the roughened Ag substrate. It is a typical Raman spectrum of polypyrrole deposited on metal substrates, as shown in the literature.^{27,53} The appearance of the peak shown at the higher frequency side of the double peaks of C–H in-plane deformation of PPy⁵⁴ located at about 1081 cm^{-1} indicates that the autopolymerized PPy is oxidized and doped.⁵⁵ As described in the Experimental Section, the sample is free of pyrrole monomers in the SERS analysis. Thus, it certifies that

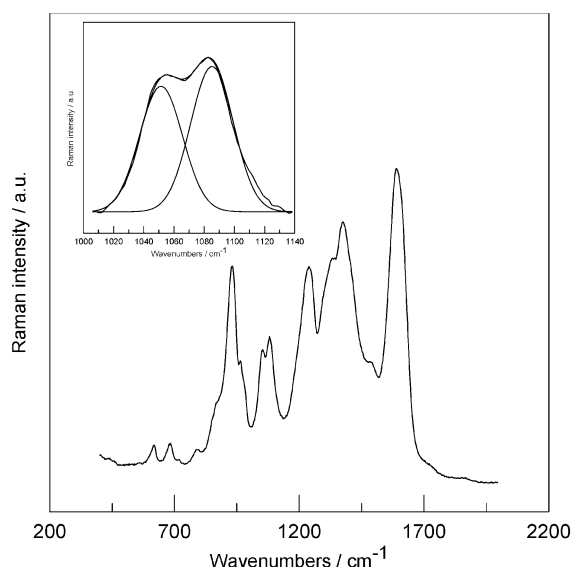


Figure 9. Raman spectrum of autopolymerized PPy on roughened Ag substrate. Insert of figure displays the Raman double peaks of C–H in-plane deformation in the range of 1000–1150 cm^{-1} .

the oxidized PPy can be produced, which is distinguishable from the known chemical or electrochemical method, on the roughened Ag because of the special activity of the complexes. As shown in the previous study,^{11,55} the conductivity of PPy is strongly related to and increases with this Raman peak of C–H in-plane deformation of oxidized PPy. Thus the broader Raman peaks of PPy appearing in the range of 1000–1150 cm^{-1} were further deconvoluted into their individual reduced and oxidized component peaks, which are located at 1054 and 1081 cm^{-1} , respectively, as demonstrated in the insert of Figure 9. Here, we use the oxidation degree¹¹ (which is defined as the ratio of the area of oxidized PPy to that of total component peaks in this region of C–H in-plane deformation) to qualitatively relate the corresponding conductivity of PPy. The calculated oxidation degree is 0.54. The high oxidation degree, as the high oxidation level calculated from XPS N 1s spectrum, demonstrates a positive effect on more electron holes available, which are favorable for the electron hopping along the polymer chains.

Due to the quantity limitation of the forming autopolymerized PPy films on the roughened Ag substrate, the real conductivity cannot be directly obtained by using the four-probe technique measuring on the pellets of the samples. However, XPS and SERS results of the high oxidation level of 0.33 and the high oxidation degree of 0.54, respectively, show that the autopolymerized PPy owns an extremely high conductivity.

Conclusion

With the extending application of SAMs in this study, PPy films can be successfully electrodeposited on roughened silver substrates without the conventional limitation that silver, oxidizing more readily than the pyrrole monomer, would not be a good choice for the anode. In the electropolymerization, charge transfer occurs from electrodeposited pyrrolylium nitrogen to the roughened silver. Furthermore, the Cl- and Ag-containing nanocomplexes formed on the roughened Ag with grain sizes smaller than 100 nm demonstrate special electrochemical reactivity. It is encouragingly found that pyrrole monomers can form SAMs and further autopolymerization on these nanocomplexes. The autopolymerized PPy owns a high conductivity.

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