

Enhancement in the Raman Scattering of Polypyrrole Electrodeposited on Roughened Gold Substrates Coated with Gold Monolayers

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Received: September 30, 2003; In Final Form: December 3, 2003

In this study, polypyrrole (PPy) films were electrodeposited on gold substrates roughened by a triangular-wave oxidation–reduction cycle (ORC) in an aqueous solution containing 0.1 N HCl. Extending the applications of self-assembled monolayers, gold monolayers were then adsorbed onto PPy films by dipping the PPy-deposited gold substrates into Au complex-containing solutions, which were produced from the ORC procedure used in roughening the gold substrates. Encouragingly, the surface-enhanced Raman scattering (SERS) spectroscopy of PPy with this sandwiched structure, Au monolayers/PPy/roughened Au substrate, exhibits a higher intensity by 1 order of magnitude and a better resolution, as compared with the normal SERS of PPy electrodeposited on a roughened Au substrate. The enhanced SERS effects can be explained as the electromagnetic effect that correlates to both the Au monolayers above and the roughened Au substrate underneath. Moreover, the chemical effect, which is also contributive to the enhanced SERS effects, is first found from the phenomenon of charge transfer from the pyrrolylium nitrogen to the adsorbed Au-containing complex.

Introduction

In recent years, the structure situations of heterogeneous individual and double-wall carbon nanotubes were successfully investigated by Raman spectroscopies.^{1–3} However, only poor information can be provided because of a weak signal or interference from noise.^{4,5} On the whole, the Raman technique cannot be applied to the analysis of organic compounds that are present in a system at very low levels. However, resonance-enhanced Raman spectroscopy and surface-enhanced Raman scattering (SERS) are two useful exceptions to this rule.^{6,7} SERS occurring on roughened metal substrates in principle provides a powerful means of obtaining vibrational information on adsorbate–surface interactions in view of its unique sensitivity and excellent frequency resolution.^{8,9} Many techniques were used to obtain rough metals substrates, including plasma treatment,¹⁰ sputter coating,¹¹ mechanical polishing by using abrasives,¹² vacuum evaporation deposition,¹³ and electrochemical and laser deposition.¹⁴ However, a controllable and reproduced surface roughness can be generated through control of the electrochemical oxidation–reduction cycles (ORC) procedure.^{15,16} Much of the observed enhancement can be ascribed to the electromagnetic fields at the metals surfaces,^{17,18} which are quite well understood. The remainder can be ascribed to the chemical enhancement,^{19,20} concerning the charge transfer on the adsorbate–metal surface, which is poorly understood compared to the electromagnetic enhancement.

As shown in the literature,^{21,22} the molecules located between two nanoscale metallic spheroids should experience the highest electromagnetic field and, thus, contribute to the greatest SERS enhancement. This idea inspires new efforts on improving the SERS performance on the basis of nanoscale bimetallics. Up to the present time, the developed systems include metal/metal

alloy colloids,²³ metals coated to other metal colloids,^{24,25} and metal/adsorbate/metal sandwiches.^{26,27} Lu et al.²³ reported the SERS of Cu/Pd alloy colloids protected by poly(*N*-vinyl-2-pyrrolidone). The Raman signal intensities from the molecules adsorbed on the Cu/Pd (4:1, molar ratio) alloy colloids are about 10–10²-fold more intense than normal Raman scattering in an aqueous solution. Rivas et al.²⁴ studied the effects of Ag-coated Au and Au-coated Ag colloidal particles prepared by deposition of Ag or Au through chemical reduction on Au or Ag colloids, respectively, on SERS. The results indicated that the coverage of Au with Ag induces an increase of the enhancement factor corresponding to Au, although it does not reach the value corresponding to Ag. The Ag coverage by Au represents an improvement of the SERS activity of the deposited metal. Zhang et al.²⁶ studied the SERS of a sandwich structure of self-assembled monolayers (SAMs) of functionalized azobenzene thiols on gold to be further covered with a film of Ag mirror. The results revealed that the enhancement correlates to both the silver islands above and the gold substrate underneath.

SAMs can be formed by the spontaneous adsorption of organic molecules onto a metal or metal oxide surface, especially for alkanethiols adsorbing on copper, silver, and particularly gold.^{28,29} The ease and flexibility of the self-assembly process provides a convenient method for altering the properties of the metal as an electrode.^{30,31} On these metals, thiols and related molecules form a densely packed, oriented monolayer.^{32,33} As shown in the literature,^{26,27} most of the metals used in the outer and inner layers of a sandwiched structure were different, and the improved SERS effects were generally explained as the electromagnetic one. Because many nitrogen-containing heterocycles with five- or six-membered rings are known to give strong SERS spectra, we have published some SERS researches based on polypyrrole (PPy) films electrodeposited on electrochemically roughened Au substrates.^{9,19,34} In this study, PPy films were originally electrodeposited on gold substrates

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roughened by triangular-wave ORCs in 0.1 N HCl aqueous solutions and were further immersed in the Au complex-containing solutions, which are the products after roughening the gold substrates, to prepare sandwiched structures of the Au monolayers/PPy films/roughened Au substrate. Besides the electromagnetic effect, the improved SERS effect is also explained from the chemical effect.

Experimental Section

Chemical Reagents. Pyrrole (Py) was triply distilled until a colorless liquid was obtained and was then stored under nitrogen before use. HCl and LiClO₄ were used as received without further purification. The reagents (p.a. grade) were purchased from Acros Organics. All of the solutions were prepared using deionized 18 M Ω cm water.

Preparation of the Sandwiched Structure, the Au Monolayers/PPy/Roughened Au Substrate. 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 gold foil with a 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 gold 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 gold substrate was cycled in a deoxygenated 0.1 N HCl aqueous solution from -0.28 V (holding 10 s) to $+1.22$ V (holding 5 s) versus Ag/AgCl at 500 mV/s 25 times, which corresponds to the optimum roughening procedure for SERS.¹⁹ After the ORC treatment, the roughened Au electrode was rinsed throughout with deionized water and the used Au complex-containing solution was saved for subsequent use.

Then the electrochemical polymerization of PPy on the roughened Au substrate was carried out at a constant anodic potential of 0.85 V versus Ag/AgCl in a deoxygenated aqueous solution containing 0.1 M Py and 0.1 N LiClO₄.

For preparing a sandwiched structure, the PPy electrodeposited roughened Au substrate was further dipped into the solution containing Au complexes, which is the saved one mentioned previously, for 10 min to adsorb Au complexes onto the PPy film. Finally, the electrode was rinsed throughout with deionized water and dried in a vacuum dryer with a dark atmosphere for 1 h at room temperature for subsequent testing.

Characteristics of the Sandwiched Structure, the Au Monolayers/PPy/Roughened Au Substrate. Raman spectra were obtained using a Renishaw 2000 Raman spectrometer employing a He–Ne laser of 1 mW radiating on the sample operating at 632.8 nm and a charge-coupled device 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 referenced to the C(1s) neutral carbon peak at 284.6 eV. The complex XPS and SERS peaks are deconvoluted into component Gaussian peaks using peak separation and analysis software (PeakFit version 4.0, AISN Software, Inc.). In the XPS N(1s) deconvolution, the four component peaks are located at about 397.8, 399.8, and higher than 401 eV of about 401.5 and 402.9 eV with equal value of half width at half-maximum (hwhm). The Fourier transform infrared (FTIR) spectrum was recorded by using the mode of attenuated total reflectance (ATR, model DA 8.3, Bomem) with 2-cm⁻¹ resolution 512 times.

Thermogravimetric analysis (TGA) was performed using the Seiko SSC 5000 at a heating rate of 15 °C/min under nitrogen. The surface morphologies of the PPy-based films were examined by atomic force microscopy (AFM, Nanoscope III, Digital Instruments) in the mode of friction force.

Results and Discussion

Characteristics of the Sandwiched Structure. In a sandwiched structure, the Au monolayers on the PPy films deposited on roughened Au are not visible to the naked eye and even harder to be resolved on scanning electron microscopy. With the aid of AFM in the mode of friction force, a thin layer of Au particles coated on PPy can be distinguished, as shown in Figure 1. When the images of PPy films deposited on roughened Au substrates with and without the coating of Au monolayers are compared, it is found that the whole brightness is raised (the higher part increases on the topography image) and the corresponding friction force is decreased because of the coating of Au monolayers on PPy films due to the different adhesive forces between the tip and the studied film region characterized by surface tension.³⁵ The chemical composition of this sandwiched structure will be confirmed from the XPS analysis.

Figure 2 shows the Raman spectra of the PPy-based sandwiched structure and the PPy electrodeposited on a roughened Au substrate for comparison. Obviously, the PPy spectrum obtained on the sandwiched structure exhibits both a higher intensity, more than 1 order of magnitude, and a better resolution. This increase in intensity is significant in comparison with the report of polyaniline chemically deposited on various rough metals by Baibarac et al.³⁶ These phenomena of higher intensity and better resolution of the PPy spectrum obtained from this sandwiched structure may correspond to the electromagnetic coupling effect between two metal layers, as generally proposed in the literature.^{26,27} However, the contribution from the chemical effect will be discussed later.

Besides the enhanced SERS spectroscopy of PPy, much-oxidized PPy can also be observed on the Raman spectrum as a result of the coating of Au monolayers. As shown in the previous study,³⁷ the peak shown at the higher frequency of the double peaks at about 1052 and 1083 cm⁻¹ in SERS is assigned to be the C–H in-plane deformation of oxidized PPy. Thus, the broader Raman peaks of PPy appearing in the range of 1020–1120 cm⁻¹ shown in Figure 2 were further deconvoluted into their individual reduced and oxidized component peaks, which are located at 1053 and 1086 cm⁻¹ and 1054 and 1086 cm⁻¹ for PPy films with and without the coating of Au monolayers, respectively, as demonstrated in Figure 3. Here, we use the oxidation degree (which is defined as the ratio of the area of oxidized PPy to that of the total component peaks in this region of C–H in-plane deformation) to quantitatively relate the corresponding oxidation of PPy. The calculated oxidation degrees are 0.45 and 0.36 for PPy films with and without the coating of Au monolayers, respectively. This phenomenon may come from the electron transfer from PPy to the Au monolayers. The higher oxidation degree would be consistent with the corresponding oxidation level in XPS analysis.

Chemical Effect on the Improved SERS. Figure 4 shows the XPS N(1s) spectra of PPy films electrodeposited on roughened Au substrates with and without the further coating of Au monolayers onto PPy films. Generally, the XPS N(1s) spectrum of PPy is deconvoluted into four component peaks with equal values of hwhm. One is a larger peak at 399.8 eV, which is assigned to the amine (–NH–) nitrogen. Another is a

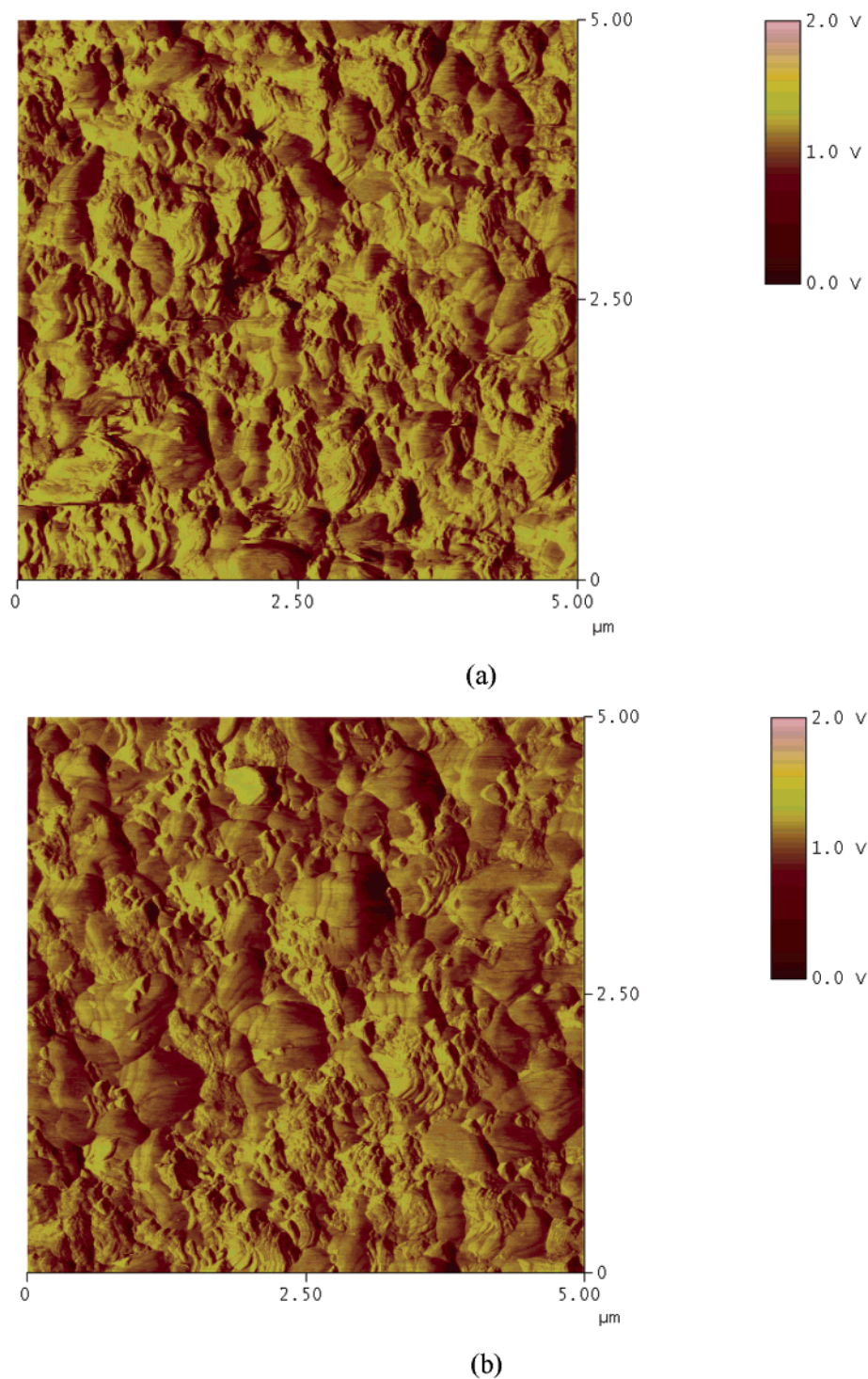


Figure 1. AFM friction force images of (a) PPy electrodeposited on the roughened gold substrate and coated with gold monolayers and (b) PPy electrodeposited on the roughened gold substrate.

smaller peak at 397.8 eV, being attributable to the imine (—N=) nitrogen. The others attributed to the positively charged nitrogen ($\text{—N}^+\text{H—}$) species are shown in the higher binding energy (BE) tail ($\text{BE} > 401$ eV), which can be used to define the oxidation level of PPy.^{38,39} This oxidation level is calculated from the ratio of the peak area of N^+ ($\text{BE} > 401$ eV) to that of the total $\text{N}(1s)$ shown in the XPS spectrum. The results indicate that the oxidation level significantly increases from 0.23 to 0.34 as a result of the adsorption of Au-containing complexes on PPy during the dipping procedure in preparing the sandwiched structure. The increased oxidation level indicates that an electron

transfer indeed occurs from the pyrrolylium nitrogen to the adsorbed Au-containing complex, which is consistent with the change of the oxidation state of the adsorbed Au-containing complex.

Figure 5a displays the XPS $\text{Au}(4f_{7/2-5/2})$ core-level spectrum of Au-containing complexes after roughening the Au substrate in 0.1 N HCl. When comparing this spectrum with that of Figure 5b, representing the elemental $\text{Au}(0)$ monolayers adsorbing onto PPy with the doublet peaks located at 84 and 87.7 eV,⁴⁰ it is found that there are extra oxidized components of Au shown in the higher BE side. The oxidized Au shown in Figure 5a can

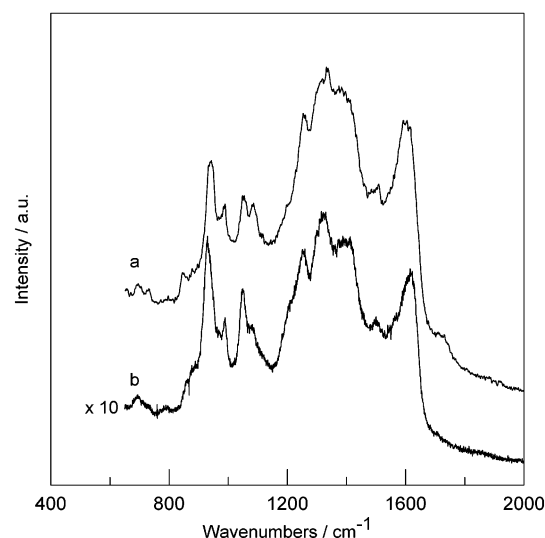


Figure 2. SERS spectra of (a) PPy electrodeposited on the roughened gold substrate and coated with gold monolayers and (b) PPy electrodeposited on the roughened gold substrate; the intensity was magnified 10-fold.

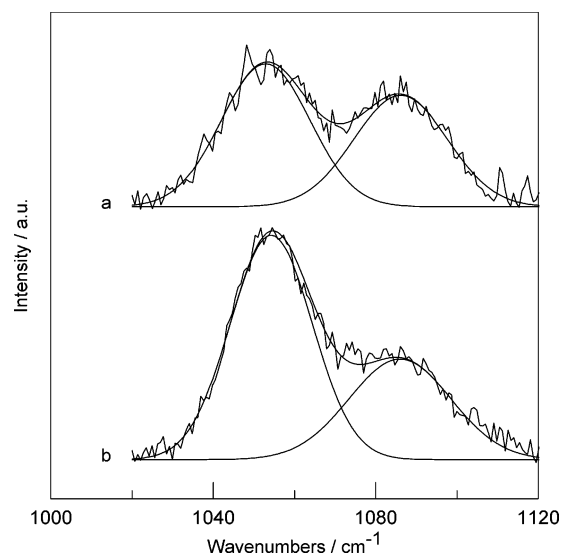


Figure 3. Raman double peaks of C—H in-plane deformation in the range of 1020–1120 cm^{-1} of (a) PPy electrodeposited on the roughened gold substrate and coated with gold monolayers and (b) PPy electrodeposited on the roughened gold substrate.

be assigned to monovalent Au(I) and trivalent Au(III) at 85.2 and 86.7 eV, respectively.⁴¹ No further deconvolution was made here. Obviously, the adsorption of Au-containing complexes on the PPy film would be accompanied with the gain of electrons from PPy and, thus, results in the reduced Au monolayers observed.

Figure 6 demonstrates the IR spectra of PPy films electrodeposited on roughened Au substrates with and without the Au monolayer adsorptions on PPy. It is encouraging that the broad peak, occurring at 3100–3400 cm^{-1} corresponding to the N—H stretching in the PPy ring,^{42,43} markedly appears for PPy in the sandwiched structure. To observe the chemical effect of the improved SERS due to the coating of Au monolayers on PPy and the PPy-based composites with sandwiched structures that are deposited on Au substrates, the FTIR spectrum was measured by using the suitable ATR mode and was collected for 512 scans. Thus, both the intensity and the resolution are not comparable with the normal absorption spectrum with

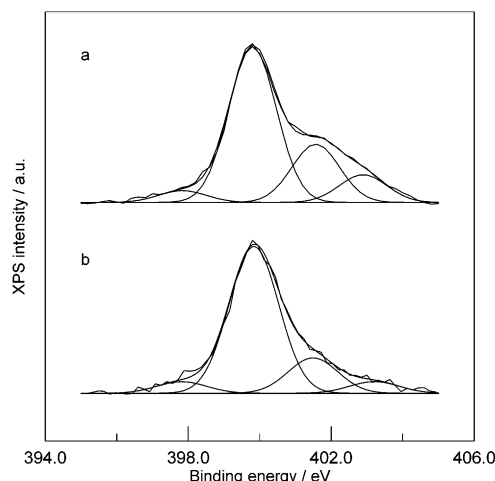


Figure 4. XPS N(1s) core-level spectra of (a) PPy electrodeposited on the roughened gold substrate and coated with gold monolayers and (b) PPy electrodeposited on the roughened gold substrate.

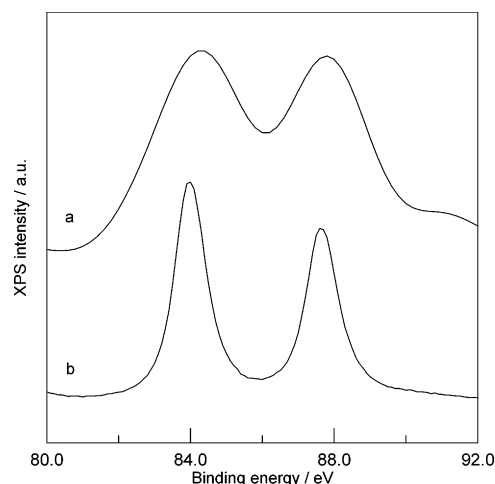


Figure 5. XPS Au(4f_{7/2–5/2}) core-level spectra of (a) Au-containing complexes in solutions after roughening the Au substrates and (b) gold monolayers adsorbing on PPy, which is electrodeposited on the roughened Au substrates, after the dipping of the PPy-electrodeposited gold substrate.

samples dispersed in KBr pellets. Plays et al.⁴⁴ also found that three peaks markedly appear in the 3100–3500 cm^{-1} N—H stretching region in the study of the oxidation of 1,8-diaminonaphthalene on roughened copper. Therefore, the marked appearance of N—H stretching of PPy means that charge-transfer indeed occurs from the pyrrolylium nitrogen to the Au-containing complex to form chemical adsorptions. It increases the possibility of transition of the N—H stretching mode when excited by the laser beam, and, hence, it results in the strong enhanced Raman intensity obtained.

Furthermore, the adsorption of Au monolayers on PPy in the preparation of a sandwiched structure shall contribute to the stable thermal property of PPy. Figure 7 shows the TGA analyses for PPy films with and without the adsorptions of Au monolayers on them. A serious degradation of pure PPy is observed, and the weight loss reaches 72% at the ending temperature of 800 °C. Encouragingly, for PPy with the adsorption of Au monolayers, the degradation is depressed. At the ending temperature of 800 °C, the weight loss is just 35.0%. Also, the temperatures at the 10% weight loss for PPy films with and without the adsorptions of Au monolayers on them are 340 and 175 °C, respectively. Clearly, the PPy film with the chemical adsorption of Au monolayers becomes more stable.

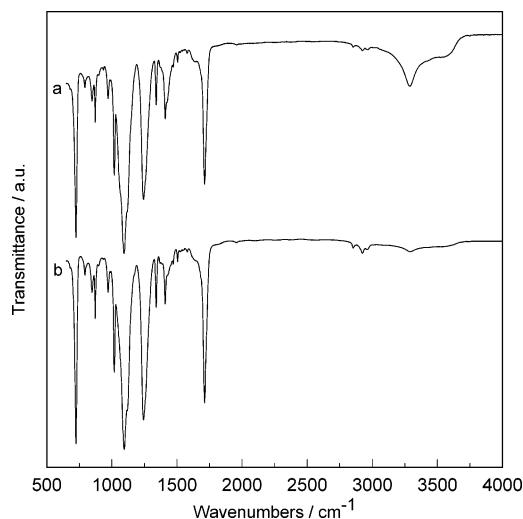


Figure 6. FTIR spectra of (a) PPy electrodeposited on the roughened gold substrate and coated with gold monolayers and (b) PPy electrodeposited on the roughened gold substrate.

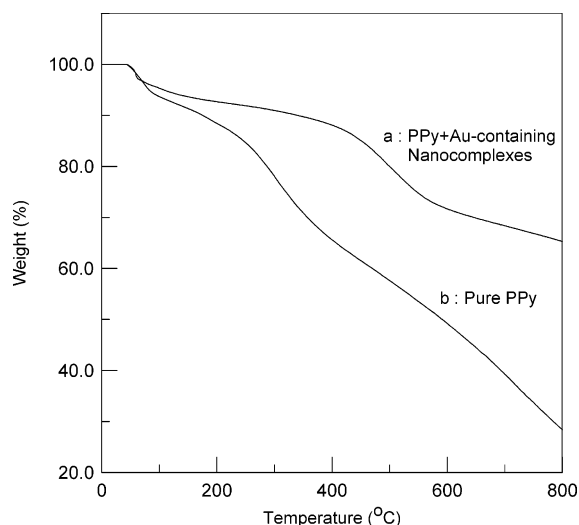


Figure 7. TGA curves of (a) PPy electrodeposited on the roughened gold substrate and coated with gold monolayers and (b) PPy electrodeposited on the roughened gold substrate.

Conclusion

Extending the applications of SAMs, a sandwiched structure of the Au monolayers/PPy films/roughened Au substrate was successfully prepared on the basis of the electrochemical technologies in this study. Encouragingly, the SERS spectroscopy of PPy with this sandwiched structure exhibits a higher intensity by 1 order of magnitude and a better resolution, as compared with the normal SERS of PPy electrodeposited on a roughened Au substrate. Besides the contribution of the electromagnetic effect, as generally shown in the literature, to the improved SERS, the chemical effect is first found from the phenomenon of charge transfer from the pyrrolylium nitrogen to the adsorbed Au-containing complex. The present method can be extended to other SERS studies of S- or N-containing heterocycles with five- or six-membered rings.

Acknowledgment. The author thanks the National Science Council of the Republic of China (NSC-91-2214-E-238-001) and Van Nung Institute of Technology for their financial support.

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