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In situ electrochemical SERS studies on electrodeposition of aniline on 4-ATP/Au surface

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Abstract The electrochemical polymerization of 0.01 M aniline in 1 M H₂SO₄ aqueous solution on roughened Au surface modified with a self-assembled monolayer (SAM) of 4-aminothiophenol (4-ATP) has been investigated by in situ electrochemical surface-enhanced Raman scattering spectroscopy (SERS). The repeat units and possible structures of the electrodeposited polyaniline (PANI) film were proposed; i.e., aniline monomer is coupled in head-to-tail predominately at the C₄ of aniline and amine of 4-ATP, and the thin PANI film is orientated vertically to substrate surface. Simultaneous Raman spectra during potential scanning indicate clearly that the ultrathin PANI film (in initial growth of the film) consists of semiquinone radical cation (IP⁺), para-disubstituted benzene (IP and IP⁺) and quinone diimine (NP) while it is oxidized, and without quinone diimine and semiquinone radical cation while reduced. Meanwhile, the results confirm that 4-ATP monolayer shows a strong promotion on the electrodeposition of aniline monomer, and a possible polymerization mechanism was proposed.

Keywords Aniline · Electrodeposition · Self-assembled monolayer · In situ electrochemical SERS

Introduction

Self-assembling technique, as a promising method of interfacial modification in the scale of molecules, has received great interest within past decade. Self-assembled monolayers (SAMs) have been used to tailor solid surfaces at the molecular level and have various applications, such as in biomimetic films, chemical sensors, nonlinear optical materials, high-density memory devices, protective coatings, lubricants, photopatterning substrates, etc [1–7]. Although a wide variety of substrates and functional groups are known to form SAMs, the thiol/disulfide monolayer on Au has received considerable attention due to its simplicity and ease of preparation [8]. The SAMs of aromatic thiols are also widely used because they have several features: highly anisotropic, the strong intermolecular interactions due to neighbor π - π conjugation and overlap, and so on, which is much advantageous than alkanethiols, may lead into different molecular packing structure and interfacial reactivity [9]. Moreover, higher electrical conductance would be expected in the aromatic thiol, as the electrons are delocalized around the benzene ring [10].

Polyaniline (PANI) is one of the most promising electronically conductive polymers. It has potential applications in secondary batteries, electrochromic displays, nonlinear microelectronic devices, etc [11–13]. It can be usually used in the form of films, bulk, thin or ultrathin films, in both basic researches and practical applications.

Surface-enhanced Raman Scattering Spectroscopy (SERS) is a versatile and powerful tool for illustrating the detailed structural information of those polymer films, especially at quite low coverage of organic ultrathin films, such as self-assembled monolayer and submonolayer, layer-by-layer multilayer (LBL), etc., which play a key role in the improvement of interfacial adhesion, stability, uniformity, morphology, surface grafting and modification, etc [14–17, 24]. So, herein, in situ electrochemical SERS plays an important role to eluci-

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date the possible structure of polyaniline during the initial potential scanning, especially at variously modified surfaces.

4-ATP SAM has received considerable attention. T. Ohsaka et al. [9] studied the electrochemical transformation of the 4-ATP SAM on Au electrode in neutral solution by means of electrochemical and in situ FTIR measurements. The electrochemistry of 4-ATP SAM in acidic aqueous perchlorate solutions has also been investigated [18, 19]. Mandler et al. [20] have investigated the electrochemistry and structure of the isomers of aminothiophenol (including 4-ATP) absorbed on gold. The template-directed growth of polyaniline nanostructures at Au electrodes modified with two-component self-assembled monolayers consisting of 4-aminothiophenol (4-ATP) and *n*-octadecanethiol (ODT) has been reported by Shannon et al. [21]. Rubinstein et al. have used 4-aminothiophenol (4-ATP) monolayers to increase the density of polyaniline electrodeposits on Au [22, 23].

In this work, 4-ATP is used to modify the roughened Au electrode due to not only a close-packed and oriented monolayer on Au surface but also a higher electrical conductance originated from the delocalized benzene ring. In situ electrochemical SERS studies on the electrodeposition of aniline during potential scanning are investigated, and SERS bands in different range are recorded and assigned in detail. The possible composition of polyaniline films and the polymerization mechanism are proposed.

Experimental

4-aminothiophenol was purchased from Aldrich and was used as received. Aniline monomer was distilled prior to use. All other chemicals used in this work were of analytical grade and used without further purification. All aqueous solutions were prepared with ultra pure water obtained from a Millipore System ($> 18 \text{ M}\Omega \text{ cm}$).

Electrochemical measurements were conducted with CHI660A Electrochemical workstation (CHI, USA) using a conventional three-electrode one-compartment cell with a polycrystalline Au working electrode (3 mm diameter), a spiral Pt wire counter electrode, and Ag/AgCl reference electrode (in saturated KCl solution).

Raman spectra were obtained using a JY-T64000 Raman Scattering Spectrometer (Jobin-Yvon, France) equipped with a Ti:Sapphire CW Tunable Laser (model 3900 S, and 798.447 nm excitation in our use) and a multichannel CCD (charge couple device) detector cooling with liquid nitrogen (to 139 K).

Prior to 4-ATP monolayer modification, electrodeposition of aniline, and SERS measurements, the working Au electrode should be cleaned and roughened. At first, it was polished successively with 1.0 and 0.3 μm of alumina slurry to a mirror-like substrate, and was rinsed copiously with water, and then was scanned in

1 M H_2SO_4 solution until a stable and standard cyclic voltammogram was obtained. After that, the cleaned Au electrode was roughened in a separate cell using a traditional oxidation-reduction cycling (ORC) similar to previous report by Liu [24], and was immersed immediately in ethanol solution of 1 mM 4-ATP for 10 h. After this immersion, the roughened Au substrate modified with a 4-ATP monolayer was cleaned completely with ethanol and water to remove unreacted thiol component and dried.

The in situ electrochemical SERS measurement was performed in a homemade spectroelectrochemical cell filled with 0.01 M aniline in 1 M H_2SO_4 aqueous solution (purged with nitrogen flow before use). The potential was scanning between -0.2 and 0.9 V .

Results and discussion

4-aminothiophenol can form a close-packed and oriented monolayer spontaneously on Au surface based upon the strong covalent bonding between the thiol group and the Au substrate. The physical and chemical properties will change so much after this monolayer adsorption, such as in interfacial capacitance and impedance, electrochemical activities, and so on, which have been used to explore the formation, kinetics, grafting, templating synthesis, assembly and immobilization, etc. Here, Raman spectroscopy with an excellent surface enhancement is used to investigate the presence and structure of 4-ATP monolayer on a roughened Au surface. The SERS spectrum of 4-ATP on the roughened Au substrate is shown in Fig. 1. A strongest band can be observed at ca. 1081 cm^{-1} , which is assigned to C(benzene ring)-S stretching vibration, while the relational band located at 1590 cm^{-1} is assigned to C-C stretching vibration of benzene rings. The band at 1007 cm^{-1} is

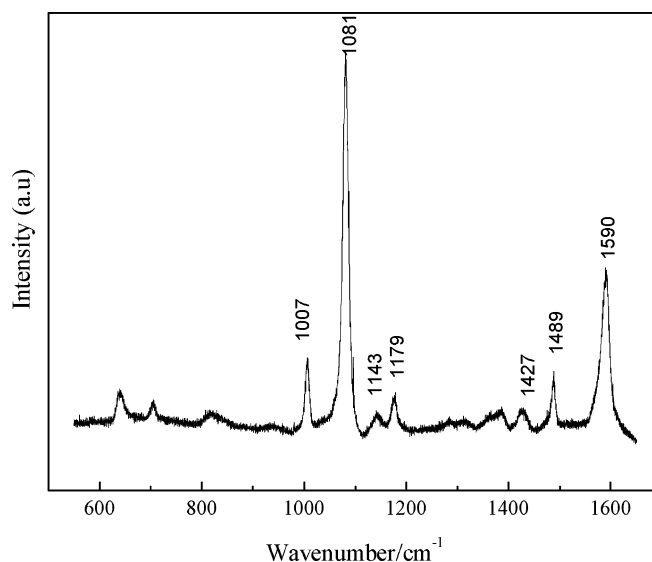


Fig. 1 SERS spectrum of 4-ATP monolayer on a roughened Au

originated from C–C bending vibration; and 1179 cm^{-1} and 1489 cm^{-1} bands correspond to C–H bending vibration and a combination of C–C stretching and C–H bending vibration, respectively. Moreover, the bands located at 1141 cm^{-1} and 1427 cm^{-1} , ascribed to the charge transfer of the metal to the adsorbed molecules, can also be seen clearly, where it suggests a perpendicular orientation of 4-ATP unit to the metal surface [25–27]. The detailed assignment of those Raman bands is listed in Table. 1 and 2.

The aniline monomer can be oxidized into aniline radical cation at a little high potential, then coupled each other and deposited on the electrode surface by such potential cycling, which has been reported a lot before [29, 34]. The monomer-like 4-ATP layer should conduct a different coupling and growth of PANI on such a 4-ATP/Au substrate. Also, 4-ATP cation radical could be electrogenerated at the surface in aqueous media [21]. The CV curves in Fig. 2 clearly shows the initial oxidation of aniline monomer and growth of PANI film on

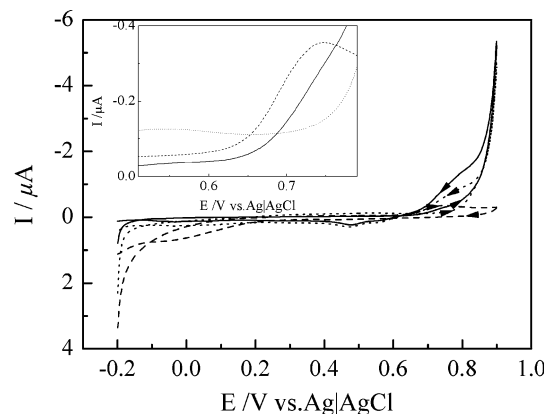


Fig. 2 CV curves of aniline oxidation in 1 M H_2SO_4 aqueous solutions of 0.01 M aniline on 4-ATP-modified roughened Au electrode (*solid*) and on bare Au electrode (*dash*), and on 4-ATP-modified roughened Au electrode without aniline monomer (*dotted*) at scan rates of 1 mV s^{-1} . Inset: local magnification of potential range from about 0.5–0.8 V

Table 1 Vibration modes observed by SERS spectroscopy on 4-ATP-modified Au

Wavenumber (cm^{-1})	Assignments [31]
1591	$\nu(\text{CC})$
1489	$\nu(\text{CC}) + \delta(\text{CH})$
1428	$\nu(\text{CC}) + \delta(\text{CH})$
1386	$\delta(\text{CH}) + \nu(\text{CC})$
1180	$\delta(\text{CH})$
1141	$\delta(\text{CH})$
1082	$\nu(\text{CS})$
1007	$\gamma(\text{CCC}) + \gamma(\text{CC})$
817	$\pi(\text{CH})$
805	$\pi(\text{CS}) + \pi(\text{CH}) + \pi(\text{CC})$
639	$\gamma(\text{CCC})$

ν stretching; δ and γ bending; π wagging

Au electrode modified by 4-ATP monolayer in 1 M H_2SO_4 solution of 0.01 M aniline. Meanwhile, the initial electrochemistry of 4-ATP in 1 M H_2SO_4 solution is also shown.

As is shown, it does not change in current on the onset potential from -0.2 V to 0.65 V for the 4-ATP modified Au electrode in 1 M H_2SO_4 solution of 0.01 M aniline. The anodic current increases over ca. 0.65 V (solid curve in Fig. 2). This potential is quite consistent with that corresponding to the formation of 4-ATP cation radical (dotted curve in Fig. 2). While for bare Au (dash curve in Fig. 2), the onset potential, where anodic current increases, is about 0.75 V . Thus we can conclude that 4-ATP can be oxidized easily compared with aniline. After the formation of 4-ATP cation radical, the radical cation of aniline monomer can also be formed as

Table 2 Assignments of PANI vibration modes recorded by in situ SERS spectroscopy

	Wavenumber (cm^{-1})		Assignments [27,28,32, 34, 35]
	Exp.	Cal.	
	1625	1628	CC stretching (SQ)
	1589	1592	CC stretching (B)
	1574	1570	C=C stretching (Q)
	1514	1532	NH bending
	1478	1500	C=N stretching (Q)
	1320	1308	
	1340	1342	CN ⁺ Stretching (SQR)
	1380	1376	
	1235	1234	In-plane ring deformation (Q) + CN stretching of polaronic units
	1175	1170	In-plane CH bending (Q+B)
	1125	1112	In-plane CH bending (Q)
	1080		CS stretching (B)
	870	888	In-plane ring deformation (B)
	815	828	Out-plane CH deformation
	750	762	Imine deformation (Q)
	594	611	In-plane amine deformation + ring deformation
	520	514	Out-plane CNC deformation

(Q) quinoid ring; (B) benzene ring; (SQ) semiquinone structure; (SQR) semiquinone cation radical

the potential scanning. Then aniline monomer is coupled in head-to-tail predominately at the C₄ of aniline and at N position of 4-ATP, which can be further confirmed by in situ SERS spectra and by electrochemical results.

In situ SERS spectra during the electrodeposition of PANI on the 4-ATP/Au electrode were obtained by recording different wavenumber centers at 570, 815, 1080, 1200, 1350, 1580, and 1610 cm⁻¹, respectively, and the integration time was 60 s for all. The spectra are shown in Fig. 3a–d for the positive scan from –0.2 to 0.9 V and in Fig. 4a–d for the reversal scan from 0.9 to –0.2 V. The curves 1–12 were recorded at different potentials of –0.2, 0.2, 0.62, 0.7, 0.8, 0.9, 0.8, 0.7, 0.56, 0.48, 0.03, and –0.05 V, respectively. The detailed assignment of those Raman bands is listed in Table 1 with a comparison with the result from theoretical calculation.

As can be seen from these in situ electrochemical SERS spectra (curves 1 and 2 in Fig. 3), almost none of any such change is observed in the anodic scan while the applied potential is lower than 0.62 V, which is consistent with our CV result in Fig. 2. With the increase of applied potential over ca. 0.62 V, a few new Raman bands which are derived from the aniline oxidation are observed. The intensity of those Raman bands are changing regularly with the anodic (shown in Fig. 3) and cathodic (shown in Fig. 4) scans due to the effect of electrical field.

The electrodeposited PANI film on 4-ATP layer consists of four possible structural units as illustrated in Scheme 1 during electro-oxidation: imino-1,4-phenylene (IP), imino-1,4-phenylenesalt (IP⁺), nitrilo-2,5-cyclohexadiene-1,4-diylidene nitrilo-1,4-phenylene (NP), radical cation of imino-1,4-phenylene (IP^{•+}) [28], which are listed in the Scheme 1.

It has been widely accepted that the initial step of aniline polymerization is characterized by the removal of electrons of the amine nitrogens between two benzene rings [29–31]. This process leads to the formation of a “modified quinone diimine” structure [29], i.e., semiquinone radical cation (IP^{•+}). In our case, many Raman bands corresponding to the semiquinone radical cation have been obtained, confirming its presence during the electropolymerization of PANI.

Strong broad Raman bands located in the range of 1320–1380 cm⁻¹ (Figs. 3c, 4c) are the key bands of semiquinone radical cation which are assigned to C–N⁺ stretching vibrations. At first, when the potential is between 0.62 and 0.68 V, the bands at 1320, 1340 and 1370 cm⁻¹ can be seen respectively. Later a broad peak ranging from 1320 to 1380 cm⁻¹ appears. The assignment of 1380 cm⁻¹ is consistent with the results in literatures [28] and [32].

The bands at 520 and 815 cm⁻¹ (see Figs. 3a, 4a), which have been assigned to out-plane CNC deformation and CH out-plane deformation vibrations of benzene ring, respectively, are characteristic of para-substitution. Thus these bands reflect the substitution. Para-disubstituted benzene mainly takes the form of IP

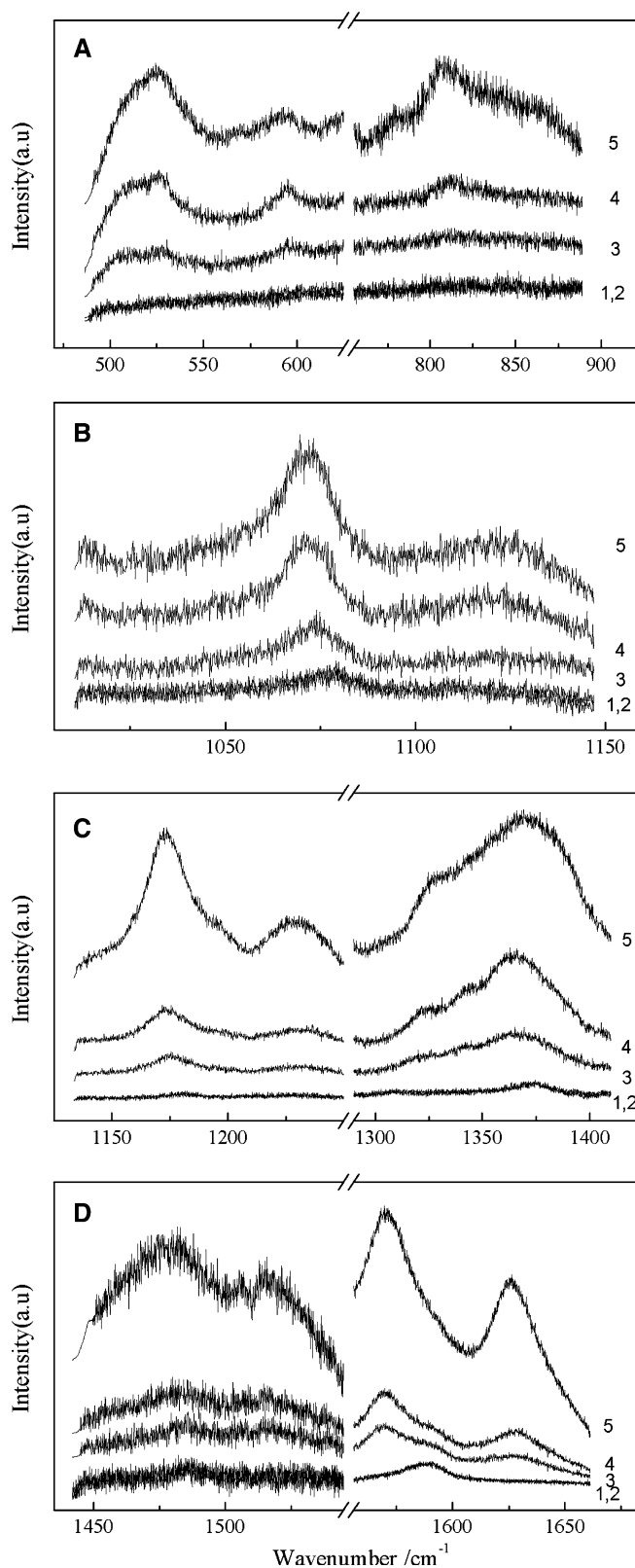


Fig. 3 In situ SERS spectra of ultrathin PANI film on 4-ATP/Au substrate. Potential (positive scanning): from 1 to 5 corresponding to –0.2, 0.2, 0.62, 0.7, and 0.8 V, respectively

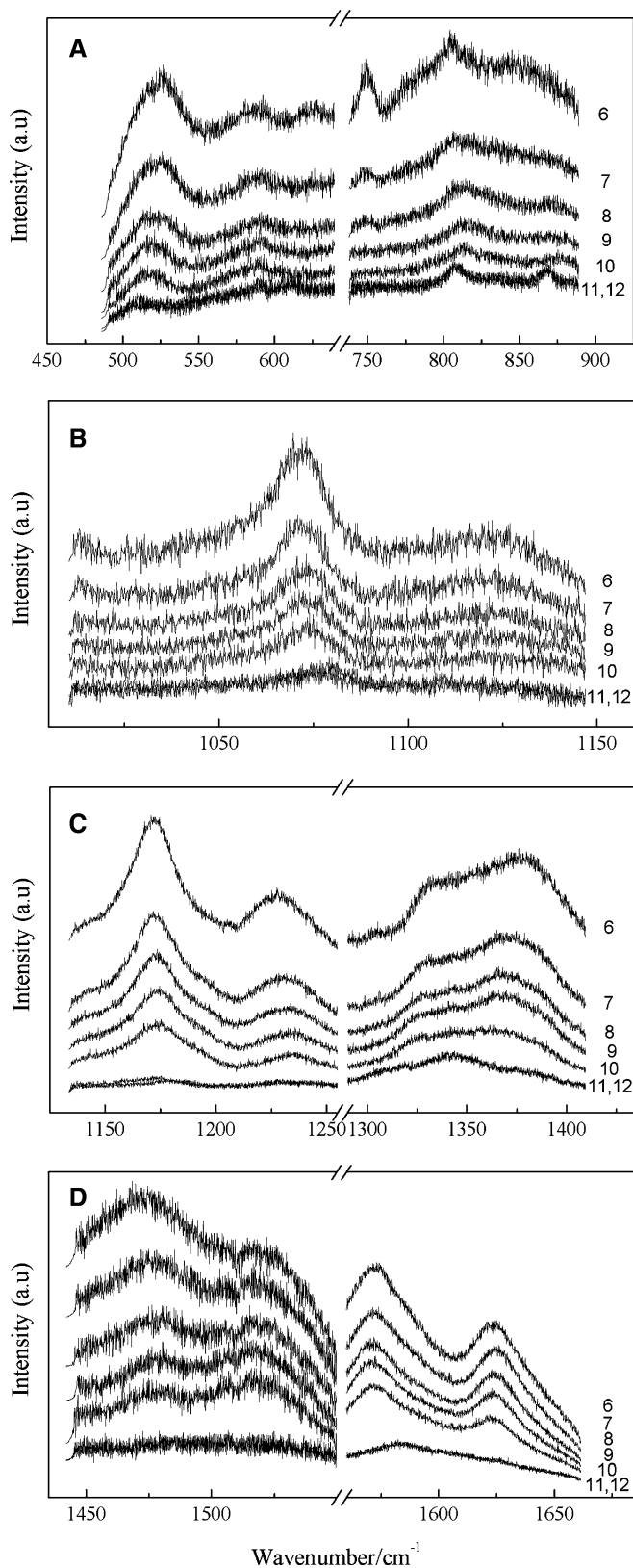


Fig. 4 In situ SERS spectra of ultrathin PANI film on 4-ATP/Au substrate. Potential (negative scanning): from 6 to 12 corresponding to 0.9, 0.8, 0.7, 0.56, 0.48, 0.03, and -0.05 V, respectively

and IP^+ units. The result, which is consistent with that of previous reports [28, 32], indicates that aniline monomer is polymerized through head-to-tail coupling at the C_4 and N position of 4-ATP. The bands located at 594 and 750 cm^{-1} are associated with the in-plane amine deformation of benzene ring and imine deformation of quinoid ring, respectively. The evolution of these two bands indicates that the polyaniline thin film that has been formed is oriented [38]. The surface morphology of this polymer film of 4-ATP/PANI has been studied by Zhang et al. [32]. They have shown by STM investigation that such films are close-packed, homogeneous, and flat in two-dimension. Meanwhile, the band at 594 cm^{-1} , which is also assigned to ring deformation, is another evidence of para-disubstituted benzenes. A new band at 870 cm^{-1} , which is assigned to in-plane deformation of benzene ring, appears when the potential is below 0 V. Thus it is a characteristic of the reduced polyaniline film.

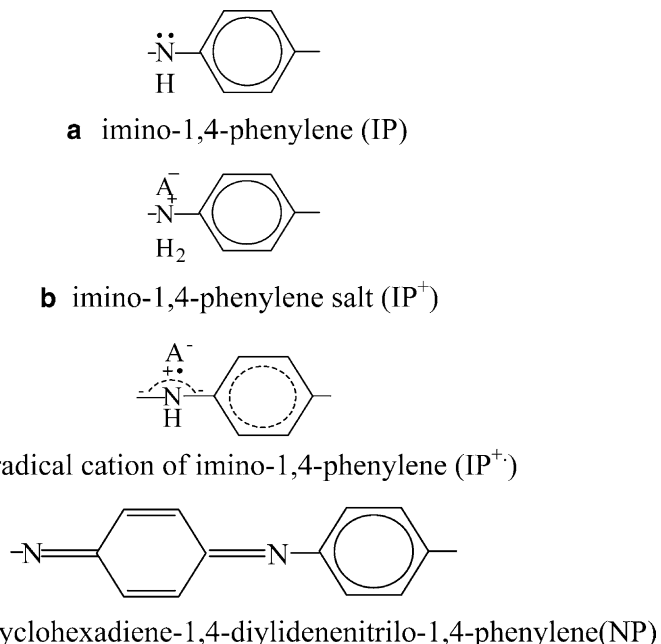
Noticeably, in Figs. 3b and 4b, the band at 1080 cm^{-1} is assigned to C(aromatic ring)-S stretching vibration. Its intensity increases and shifts to low wavenumber when aniline begins to oxidize. This should be originated from the delocalization of benzene ring and the Raman enhancement in the electric field. However, its intensity decreases dramatically when the cathodic scan is over because the 4-ATP monolayer has been covered totally by the PANI thin film. Meanwhile, a weak peak at about 1125 cm^{-1} is assigned to the in-plane CH bending vibration of quinone and it is characteristic of oxidized form of PANI.

A very strong band at about 1175 cm^{-1} appears when the potential is above 0.62 V in the anodic scan (Figs. 3c, 4c). This band has been assigned to CH in-plane bending mode of quinoid and semiquinoid rings. Tagowska et al. [33] believe that it belongs to the CH bending deformation of benzene, which is characteristic of reduced semiquinone structures. In this case, it is a mixed mode according to the experiment results. Moreover, this band is another evidence of para-disubstituted benzene rings [28]. Simultaneously, the band at ca. 1235 cm^{-1} can be assigned to CN stretching mode of polaronic units and in-plane deformation of quinone ring.

The strong Raman band at 1478 cm^{-1} , shown in Figs. 3d and 4d, is assigned to C=N stretching mode which is one of the key bands of quinone diimine structure. At the same time, it is also characteristic of semiquinone radical cation structure [28]. Further, the 1514 cm^{-1} band, corresponding to the N-H bending deformation band of protonated amine, is also a key band of the semiquinone radical cation. So, it can be concluded that these bands are markers of the presence of both quinone diimine (NP) and semiquinone radical cation structures.

As can be seen from Figs. 3d and 4d, a band at 1589 cm^{-1} exists at the beginning of the anodic scan. This band has been assigned to C-C stretching vibration of benzene rings. However, when the potential is above

Scheme 1 Constitutional units of polyaniline: here A^- is HSO_4^-



0.62 V in the anodic scan, a new band at about 1574 cm^{-1} , which is assigned to C=C stretching vibration of quinone rings, appears at a lower wavenumber. This should be derived from the π electron delocalization. Meanwhile, when aniline begins to oxidize, a shoulder peak at 1625 cm^{-1} corresponding to C-C stretching of bipolarons can be seen. This band can be proposed as a characteristic of oxidized form of PANI and of para-disubstituted benzene rings [28] as well.

To further confirm the polymerization of aniline, we also conducted similar experiments in which 4-ATP was oxidized in 1 M H_2SO_4 aqueous solution in the absence of aniline monomer. The first two cycles were recorded in Fig. 5. After that, the SERS spectra was obtained and compared with that of electropolymerization of aniline on the 4-ATP/Au electrode. The results are listed in

Fig. 6. Though the two spectra are seemingly similar, obvious difference can also be seen. The band located at 1175 and 1478 cm^{-1} after the oxidation of 4-ATP is rather weak compared with that after the polymerization of aniline, which means the contents of quinoid and semiquinoid rings in the products after the oxidation of 4-ATP in 1 M H_2SO_4 aqueous solution without aniline monomer are relatively fewer. Moreover, after slow scanning, relatively fast scan in 1 M H_2SO_4 aqueous solution was performed and the difference is overt, which can be seen in Fig. 7, and a CV characteristic of polyaniline was obtained after the aniline electropolymerized on the 4-ATP/Au electrode. From these, it can be confirmed that the in situ SERS results were derived from the electropolymerization of aniline on 4-ATP/Au electrode and a possible mechanism is that after the

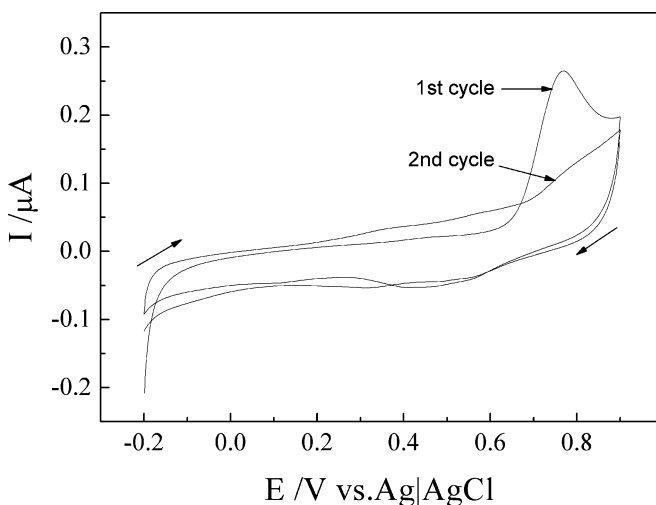


Fig. 5 CV curves of 4-ATP/Au in 1 M H_2SO_4 aqueous solutions (first two cycles). Scan rate: 1 mV s^{-1}

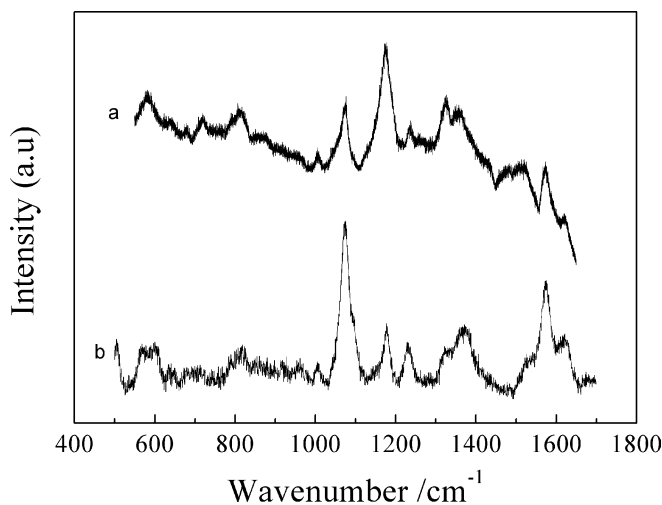


Fig. 6 SERS spectra of (a) ultrathin PANI film on 4-ATP/Au substrate; (b) 4-ATP/Au substrate after the first two potential cycles

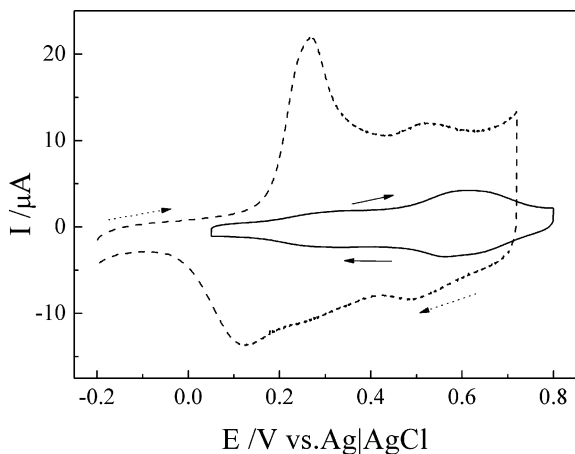
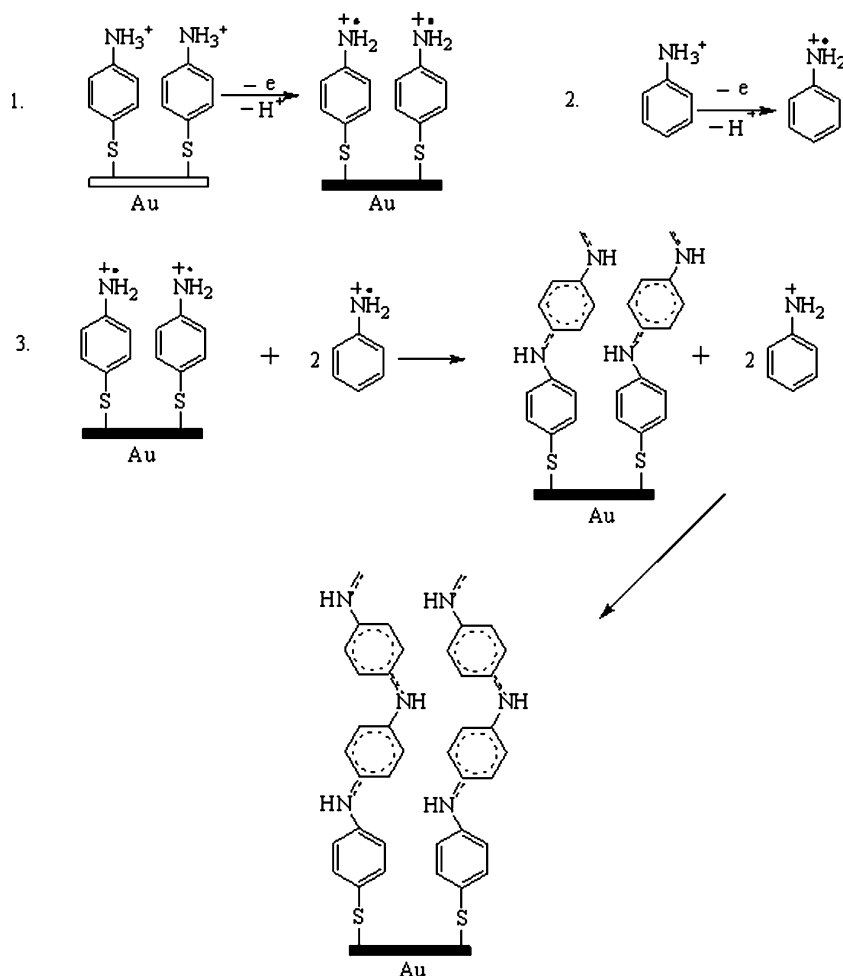


Fig. 7 CV curves of 4-ATP/Au substrate after the first two slow potential cycles (*solid line*) and of ultrathin PANI film on 4-ATP/Au substrate (*dash line*) in 1 M H₂SO₄ aqueous solutions. Scan rate: 100 mV s⁻¹

formation of 4-ATP cation radical, cation radical of aniline is also formed. Then aniline polymerizes through head-to-tail coupling at the C₄ and N position of 4-ATP, as this head-to-tail coupling reaction is favorable in acidic solutions [37]. The representation of this mechanism is shown in Scheme 2.

Scheme 2 Schematic representation for the electropolymerization of aniline on 4-ATP modified gold electrode



The electrochemical polymerization of aniline on roughened Au modified with self-assembled monolayer of 4-aminothiophenol (4-ATP) in aqueous solution containing 1.0 M H₂SO₄ and 0.01 M aniline has been investigated. From the cyclic voltammetry and in situ SERS measurements, the following results can be concluded:

- (1) Aniline begins to oxidize at a potential of ca. 0.65 V compared to ca. 0.75 V on the roughened gold electrode without 4-ATP SAM. Thus, the 4-ATP monolayer shows a promotion on the polymerization of aniline.
- (2) Aniline polymerizes through head-to-tail coupling at the C₄ and N position of 4-ATP. The evolution of the bands located at 594 and 750 cm⁻¹ indicates that the polyaniline thin film formed is oriented.
- (3) In the initial stage of electropolymerization of aniline, when the polymer is in oxidized form at high potential, three units including semiquinone radical cation (IP⁺), para-disubstituted benzene (IP and IP⁺) and quinone diimine (NP) are all present. However, the quinone diimine and semiquinone radical cation structures disappear, which is of reduced form, when the potential is below 0 V.

Conclusions

Many investigations have been made to explore the exact mechanism of polymerization of aniline on electrode, especially on SAMs-modified electrode, but it is still not fully elucidated. Here, in this work, some preliminary results of the correlation between the electrochemical response and polyaniline structure by means of in situ cyclic voltammetry–SERS are obtained, which can provide some valuable information about redox reactions and the initial stage of electrodeposition. Furthermore, modification on the aimed surface shows a stronger promotion on electrodeposition of PANI.

In this work, 4-ATP is used to modify the roughened Au electrode due to not only a close-packed and oriented monolayer on Au surface but also a higher electrical conductance originated from the delocalized benzene ring. The SERS spectrum of 4-ATP with a high S/N ratio has been obtained. Meanwhile, in situ electrochemical SERS studies on the electrodeposition of aniline during potential scanning have been investigated. Surface-enhanced Raman bands in different range have been recorded and assigned in detail. The possible composition of polyaniline films is proposed. In addition, the results indicate that 4-ATP-modified surface exhibits a strong promotion on electrodeposition of PANI, which is useful and promising in possible selective deposition and patterning.

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