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Preparation and Electrochemically Catalytic Hydrogen Evolution of Co^{Ш}Corrole Copolymerized with Mono-, Bis- and Tri-Thiophenes

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Dedicated to the memory of Academician Oskar I. Koifman

A series of conductive polymers of thiophene-substituted Co^{Ш}corrole copolymerized with mono-, bis- and tri-thiophenes have been prepared by electrochemical polymerization. Compared with the Co^{Ш}corrole monomer, the electrocatalytic hydrogen evolution performance was significantly improved. In particular, when the molar ratio of Co^{Ш}corrole and bithiophene is 10:1, the conductive polymer prepared shows better electrocatalytic hydrogen evolution performance. In addition, when comparing the effect of chain length of thiophene, Co^{Ш}corrole-trithiophene showed the greatest improvement on the hydrogen evolution performance, followed by bis- and mono-thiophene.

Keywords: Co^{Ш}Corrole, thiophene, conductive polymer, hydrogen evolutions.

Получение и электрохимически катализируемое выделение водорода из Co^{III} коррола, сополимеризованного с моно-, бис- и три-тиофенами

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Электрохимической полимеризацией получен ряд проводящих полимеров тиофензамещенного Co^{III}-коррола, сополимеризованного с моно-, бис- и тритиофенами. По сравнению с мономером Co^{III}-коррола, электрокаталитические характеристики выделения водорода были значительно улучшены, в частности, когда молярное соотношение Co^{III}-коррола и битиофена составляет 10:1. Установлено, что улучшение характеристик выделения водорода увеличивается по мере удлинения цепи тиофена и максимальна в случае Co^{III}-коррол–тритиофен.

Ключевые слова: Co^{III}-коррол, тиофен, проводящий полимер, выделение водорода.

Introduction

Conductive polymer, a highly conjugated organic cojugated polymeric material, has the approximate metallic conductivity or semiconductor.[1-2] Importanly, the conductive polymer has the high electrical conductivity, but the mechanical properties are generally lack to other commercial polymers.[3] As the common methods, the conductive polymers could be well prepared by the regular organic synthesis methods and advanced dispersion technology to provide the fine-tune electrical properties,[4] and they also have the wide ranges of applications in energy storage, information technology, photovoltaic power generation, sensor technology and so on.[5-7] Based on the above advantages, conductive polymers have attracted the considerable attentions since Alan Heeger *et al.* Whi won the

Nobel Prize in Chemistry, and have been extensively studied by many scholars during the past 20 years.[8] In order to highly efficient prepare the conductive polymers, the chemical oxidation polymerization is one of the best strategies, which uses monomers to react with suitable oxidants.[9-10] For example, the reaction of aniline (monomer) with ammonium persulfate (oxidant) to give polyaniline with controllable molecular weight.[11] More interestingly, the conductive could also be efficient prepared through electrochemical polymerization by using simple device, easy control of conditions, uniform and controllable polymer film thickness and simultaneous and doping polymerizations.[12-14] In the case of electrochemical polymerization, we should use the functional monomers with electrochemically active sites which can be synthesized by electrochemical oxidation at room temperature, such as five-membered aromatic heterocyclic compounds (pyrrole and thiophene), or six-membered aromatic heterocyclic compounds (aniline).[15-18] For example, polythiophenes and their derivatives have been extensively studied due to their significant increase of the electrical conductivity that can be used as the conductive polymers by themselves or combined with other organic monomers.[19-20]

On the other hand, metalloporphyrins, the 18π conjugated molecules with the unique structures and the wide ranges of applications, have received considerable attention in the past decades. In particular, they have outstanding performances in the field of energy-related small-molecules activations including hydrogen evolution (HERs), oxygen evolution (OERs), oxygen reduction (ORRs), and even carbon dioxide reduction (CO_2RRs).[21-24] As the metalporphyrin derivative, metallocorrole, in the absence of a *meso*-site and a contracted macrocyclic ring compared to porphyrins, can stablize metal ions with specific oxidation states. Thus, metallocorroles were also widely applied for molecular or material catalysis. [25-27] Based on the same advantages, the researchers have succeeded in preparation and metallocorrole-based conductive polymers and they also have satisfied catalytic properties compared to a series of metal-containing catalysts.[28-29] Therefore, when with electrocatalytic active centers were polymerzied through electrochemical process, the conductive polymer significantly improves the catalytic performance than the monomer catalysts.[30-31] However, the current results are still lack of investigations on the copolymerization of metallocorroles with other functional molecules. Herein, we tested the copolymerization of Co^{III}corrole with mono-, bis- and tri-thiophenes through electrochemical processes, and the cobalt center could be rationally dispersed by copolymerized with thiophenes. Also, their electrochemically catalytic hydrogen evolutions will be investigated.

Experimental

Synthesis

$Co^{III}PPh_3$-5,15-bis(2-thiophenyl)-10-phenylcorrole (**1**). Firstly, 15-bis(2-thiophenyl)-10-phenyl-corrole (54 mg, 0.1 mmol) was put into a round-bottomed flask, and $Co(OAc)_2 \cdot 4H_2O$ (126 mg, 0.5 mmol) and PPh_3 (132 mg, 0.5 mmol) were added. Then, CH_2Cl_2 (10 mL) and MeOH (40 mL) were added and stirred at 75°C for 1 hour. After removal of the organic solvents, the products were purified by column chromatography (eluent: CH_2Cl_2/hexane (1:1, v/v)). The target compound $Co^{III}PPh_3$-5,15-bis-(2-thiophenyl)-10-phenylcorrole (**1**) was obtained as a deep-red solid state compound in a yield 61.85% (53.2 mg). ^1H NMR (400 MHz, $CDCl_3$) δ ppm: 8.72-8.60 (m, 4H), 8.31 (d, J = 4.4 Hz, 3H), 8.13 (d, J = 4.8 Hz, 2H), 7.64 (ddd, J = 28.2, 14.4, 6.2 Hz, 7H), 7.43-7.32 (m, 3H), 7.05 (t, J = 7.4 Hz, 3H), 6.77-6.62 (m, 6H), 4.77-4.56 (m, 6H).

Preparation and electrocatalysis of conductive polymers

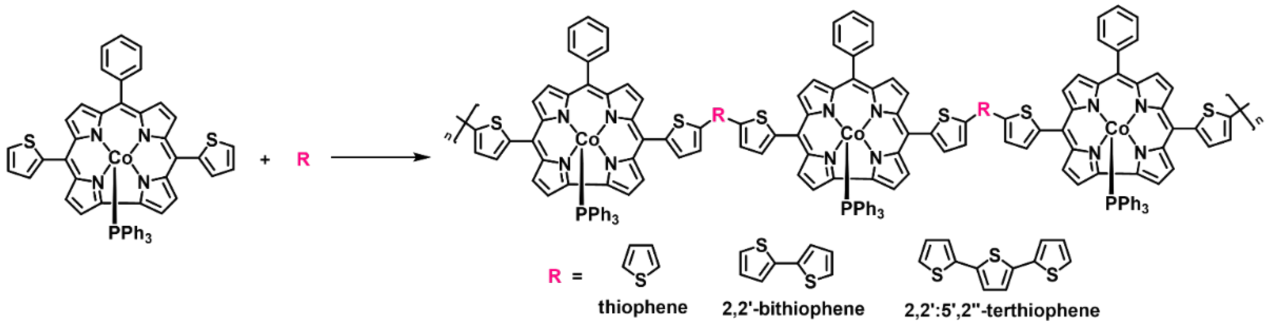
Electrochemical polymerization of the compound was carried out by a cyclic voltammetry, referring to the three-electrode system: carbon paper electrode (platinum clip), auxiliary electrode platinum wire, reference electrode Ag/AgCl electrode. Carbon paper electrode for polymerization (HCP030N) (thickness: 0.30±0.01 mm, area: 21.0×20.0 cm^2, mass per unit area: 0.78 $g \cdot cm^{-2}$, resistivity: 3 $m \cdot \Omega \cdot cm^{-2}$) was separated into 1.0×1.0 cm for electropolymerization and electrocatalysis. The actual area of the platinum clip carbon paper is 0.8 cm^2, and the carbon paper was cleaned with ethanol-acetone-ethanol ultrasonic and dried in N_2 before use. The polymeric solution was CH_2Cl_2/CH_3CN (3:2, v/v) mixed solution with tetraethyl ammonium tetrafluoroborate (TEAT) as the supporting electrolyte. After electropolymerization, the carbon paper electrode was directly used for electrocatalytic hydrogen evolution, unless otherwise indicated. Ag/AgCl and platinum wire were used as the reference electrode and the counter electrode, respectively, to electrocatalyze hydrogen evolution in 0.5 M H_2SO_4. The LSV curve was tested and the corresponding Tafel slope was fitted. To evaluate the catalytic reaction kinetics and electron transport rate of the materials, electrochemical impedance (EIS) was measured at 0.1 M Na_2SO_4 using the same three-electrode system.

Results and Discussion

Electropolymerization and characterization of conductive polymers

The conductive polymer was synthesized through electrochemical polymerization by using method from $E = -1.5 \sim 1.5$ V (V *vs*. Ag/AgCl, scanning speed: 50 mV/s, 100 cycles), and the ratios of Co^{III}corrole **1** and mono-, bis- and tri-thiophenes are all 10:1. As shown in Scheme 1 and Figure 1, the shape of CV curves have been significantly changed during the polymerization process, and the comparison of CV curves before and after polymerization was also obtained. Upon electropolymerization, the Co^{III}corrole-thiophene polymers were deposited on the surface of the carbon paper electrode that decreased the electron conductivity of carbon paper electrode. It should be noted here, all electrochemical polymerization processes are repeatable, and little or no changes were obtained for different measurements. Based on the above results and the established mechanism of thiophene polymerization through electrochemical process, we predict that the mechanism of Co^{III}corrole-thiophene copolymerization is similar to that of thiophenes electropolymerization themselves through the defined process of α-H oxidative coupling of thiophene. The electrochemical process leads to the separation of the α-site hydrogen atoms of thiophene to form a radical cation, and then the coupling of two thiophene corrole radicals to form a dimer, or continuous oxidative coupling between free radicals to form a polymer, in which the hydrogen radical cation attack other sites of thiophene will promote its irreversible oxidation process.

The morphologies of co-polymerized Co^{III}corrole-thiophenes modified carbon papers were clearly confirmed by the scanning electron microscope (SEM) and EDS mapping analysis. As shown in Figure 2, when Co^{III}corrole **1** copolymerized with mono- (up), bis- (middle) and tri-thiophenes (bottom), the uniform and dense nanosheets with regular and ordered structures were confirmed, and the average size was about 5 μm. This result suggested that the Co^{III}corrole-thiophene conductive polymers were successfully prepared, and the potential active surface area and electron transport rate can be inferred from their morphological characteristics, which is advantageous for electrochemical catalysis. In order to characterize the distribution of C, N, S and Co elements on carbon paper electrodes, the EDS mapping analysis of Co^{III}corrole-trithiophene conductive polymers were investigated. As shown in Figure 3, according to the density and distribution of the bright spots, the unique N and Co elements of Co^{III}corrole in the copolymer are shown. It is proved that the electrochemical copolymerization of Co^{III}corrole **1** and trithiophene is successfully carried out, and the conductive polymer modified electrode is prepared by loading on the surface of carbon paper electrode.



Scheme 1. The synthesis of Co^{III}corrole **1** copolymerized with mono-, bis- and tri-thiophenes.

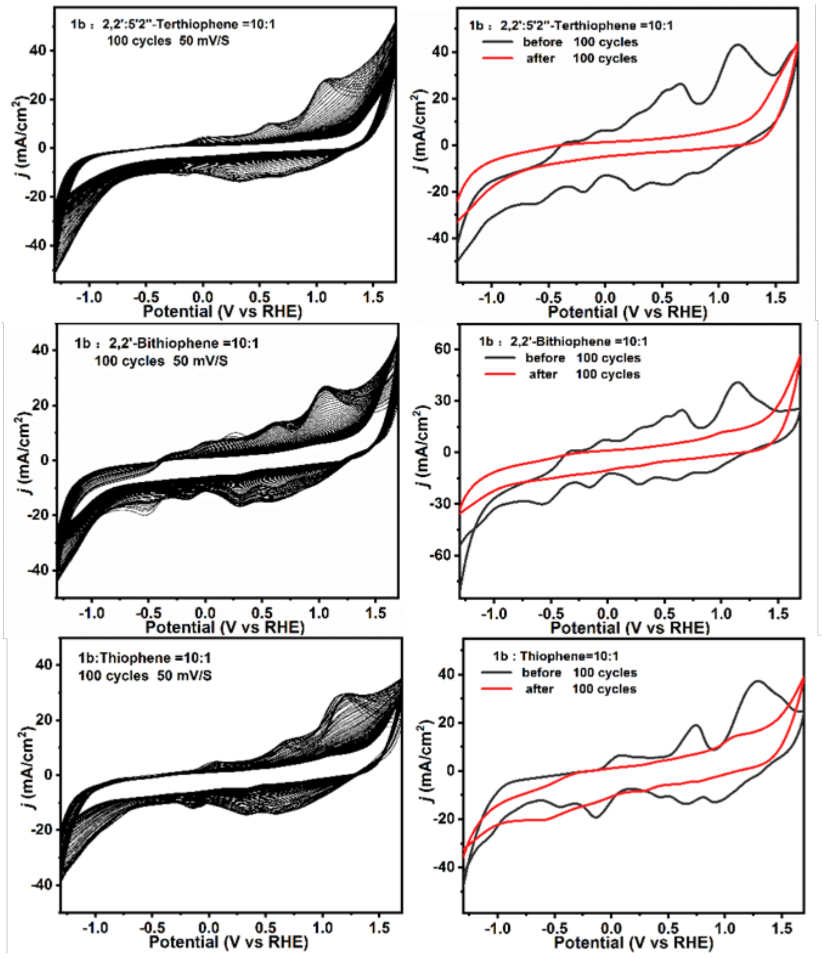


Figure 1. The CV polymerization curves of Co^{III}corrole **1** copolymerized with mono-, bis- and tri-thiophene (left) and CV comparison chart before and after 100 cycles electropolymerizations (right).

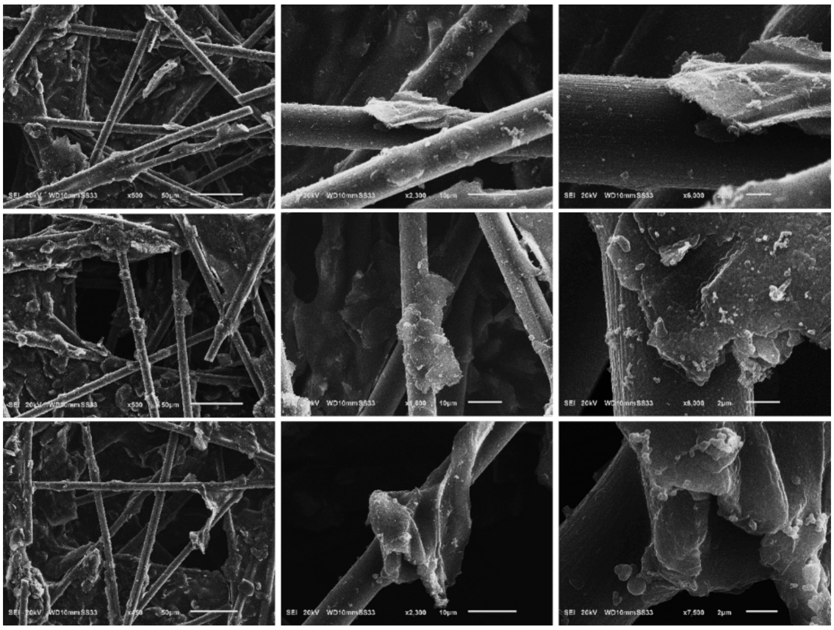


Figure 2. The SEM images of Co^{III}corrole **1** copolymerized with mono- (first row), bis- (second row) and trithiophene (third row) modified carbon papers.

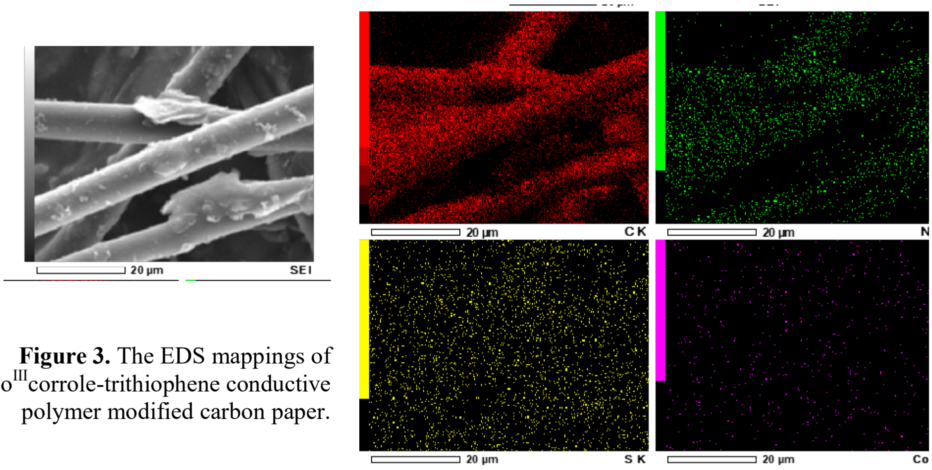


Figure 3. The EDS mappings of Co^{III}corrole-trithiophene conductive polymer modified carbon paper.

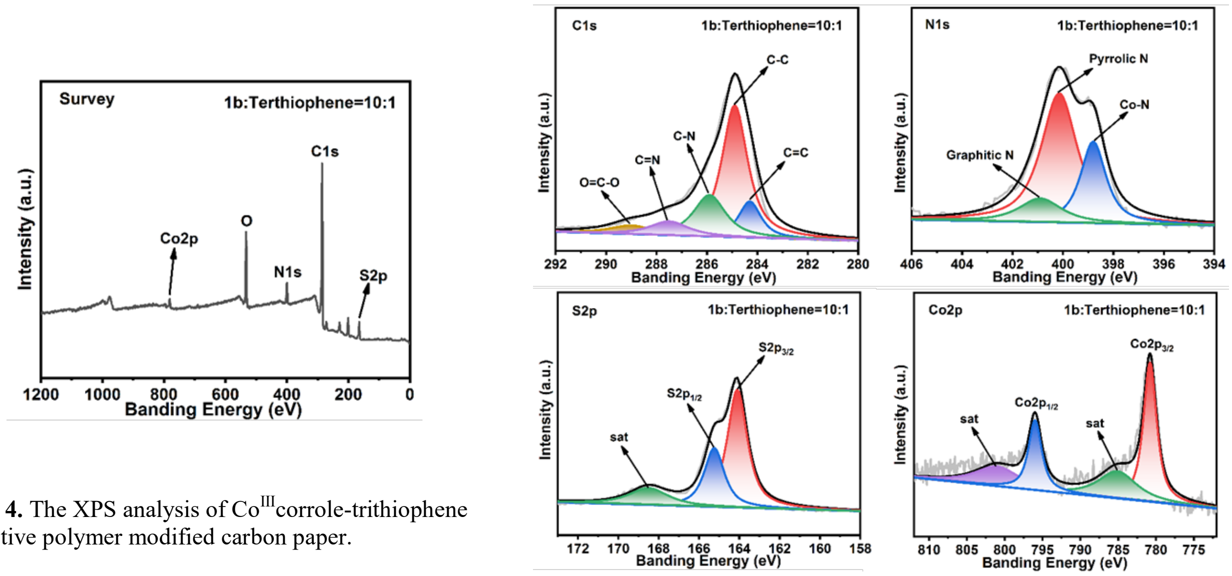


Figure 4. The XPS analysis of Co^{III}corrole-trithiophene conductive polymer modified carbon paper.

In addition, to further explore the electronic states of C, N, S and Co of co-polymerized Co^{III}corrole-trithiophenes (10:1 ratio) modified carbon papers, X-ray photoelectron spectroscopy (XPS) analysis was performed. As shown in Figure 4, the full spectra shows that Co, S and N atoms are successfully dispersed on the surface of the carbon paper electrode upon electropolymerization. Firstly, the XPS analysis of C1s orbital has five peaks assigned as: 284.3 eV (C=C), 284.9 eV (C-C), 285.9 eV (C-N), 287.5 eV (C=N) and 289.0 eV (O=C-O), where the C-C and C=C bonds are attributed to carbon materials and corrole conductive polymers, the C-N and C=N bonds are attributed to the corrole conductive polymer, and O=C-O is attributed to the hydrophilic groups in the hydrophilic carbon paper. Secondly, the XPS analysis of N1s has three peaks which assigned as: 398.8 eV (Co-N), 400.2 eV (Pyrrolic N) and 400.9 eV (Graphitic N), which were all attributed to the Co^{III}corrole-thiophene conductive polymer on the surface of carbon paper. On the other hand, the XPS data of S2p has three peaks at 164.1 eV (S2p3/2), 165.2 eV (S2p1/2) and 168.5 eV (satellite peaks), and Co2p has four peaks at 780.8 eV (Co2p3/2), 796.0 eV (Co2p1/2), 785.1 eV and 801.0 eV (satellite peaks). It should be noted here, all peaks from S and Co elements were attributed to Co^{III}corrole-trithiophene conductive polymers.

Co^{III}corrole-thiophene copolymers for HERs

Considering the introduction of mono-, bis- and trithiophenes to Co^{III}corrole-thiophene conductive polymers will enhance the atom dispersion of cobalt center, we firstly tried to investigate the optimal molar ratio of Co^{III}corrole **1** and different thiophenes. As shown in Figure 5 and Table 1, we choose 2,2-bisthiophene as the example to test the effect of molar ratio on the electrocatalytic behaviors, and all of them have satisfied performance on the LSV measurements in 0.5M H_2SO_4. When we tested the ratio from 10:10, 10:5, 10:3, 10:1, 10:0.5 (**1**:bisthiophene), the best results were obtained as the 10:1 and 10:0.5 ratios with overpotential E=0.078 and 0.081 V, and Tafel slop values 98 and 87 mV/dec. Thus, we can easily determined that the copolymerization of thiophene can easily enhance the electrochemically catalyzed hydrogen evolution behaviors of pure Co^{III}corrole-polymers, but the excess amount of 2,2-bisthiophenes may further decrease the catalytic ability probably due to the lack of electron conductivity. Meanwhile, we also tested the EIS measurements of Co^{III}corrole-trithiophenes with different molar ratios, and the similar trends were clearly obtained when we compared with the results we obtained from LSV measurements.

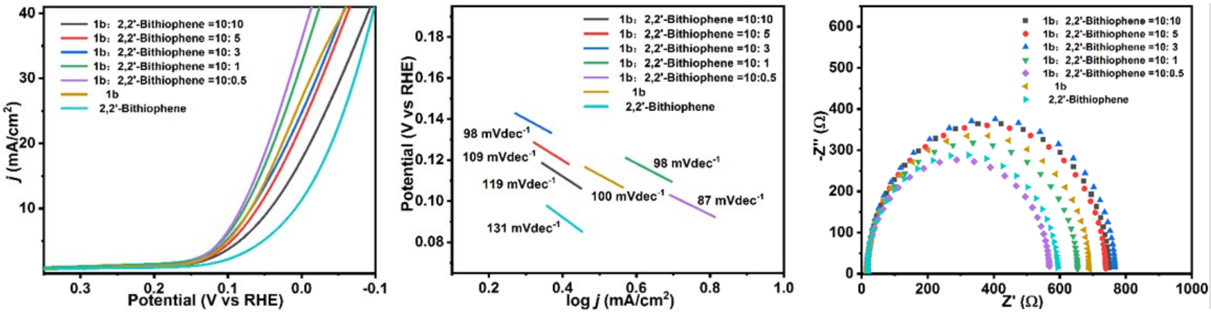


Figure 5. LSV measurements, the calculated Tafel slope and EIS diagram of Co^{III}corrole-bisthiophene copolymers with different molar ratios modified carbon papers.

Table 1. Summary of overpotential and Tafel slope of Co^{III}corrole **1** copolymerized with different thiophene molecules in different molar ratios modified carbon papers in 0.5 M H_2SO_4.

Monomer	Overpotential (V) ($|j|$ = 10 mA/cm^2)	Tafel (mV/dec)
1	0.069	100
2,2'-Bithiophene	0.009	131
1:2,2'-Bithiophene = 10: 10	0.043	119
1:2,2'-Bithiophene = 10: 5	0.060	109
1:2,2'-Bithiophene = 10: 3	0.069	98
1:2,2'-Bithiophene = 10: 1	0.078	98
1:2,2'-Bithiophene = 10: 0.5	0.081	87
1:2,2':5'2"-Trithiophene = 10:3	0.082	126
1:2,2':5'2"-Trithiophene = 10:1	0.107	87
1:2,2':5'2"-Trithiophene = 10:0.5	0.090	106
1:Thiophene = 10:3	0.059	104
1:Thiophene = 10:1	0.080	92
1:Thiophene = 10:0.5	0.069	99

In addition, when 2,2':5',2"-trithiophene (trithiophene) was used instead, the effect of chain length of Co^{III}corrole-trithiophene copolymers on the electrochemically catalyzed hydrogen evolutions was investigated. As shown in Figure 6 and Table 1, the extension of the chan in length may continually increase the electrocatalyzed hydrogen evolution behaviors, and the most satisfied results were observed when the 10:1 ratio was used (**1**:trithiophene; $E = 0.107$ V, Tafel slop: 87 mV/dec). On the other hand, Co^{III}corrole-trithiophene copolymers also have tunable EIS radius from 460 Ω (10:1) to 820 Ω (10:3). In contrast, we also tested the electrochemically catalyzed hydrogen evolution behaviors of Co^{III}corrole-thiophene copolymers. As shown in Figure 7 and Table 1, we received the similar results that we obtained from Co^{III}corrole-thiophene copolymers. When 10:1 molar ratio was applied, we received the positive-shift of the overpotentials ($E = 0.08$V), the decreased Tafel slope and EIS radius (92 mV/dec and 740 Ω), respectively.

From the overpotential and Tafel slope, it can be determined that the introduction of mono-, bis- and tri-thiophenes with molar ratio of 10:1 are more appropriate, and all of them have the enhanced hydrogen evolution performance. Upon increasing the amount of thiophenes, the hydrogen evolution performance gradually decreases, due to the introduction of excess amount of thiophenes which block the electron transfer on the carbon paper electrodes. When we combined the electrocatalytical results, it has been well indicated that Co^{III}corrole-trithiophene with larger length of copolymerization linkers has the accelerated electrochemically catalyzed hydrogen evolution behaviors and smaller EIS radius.

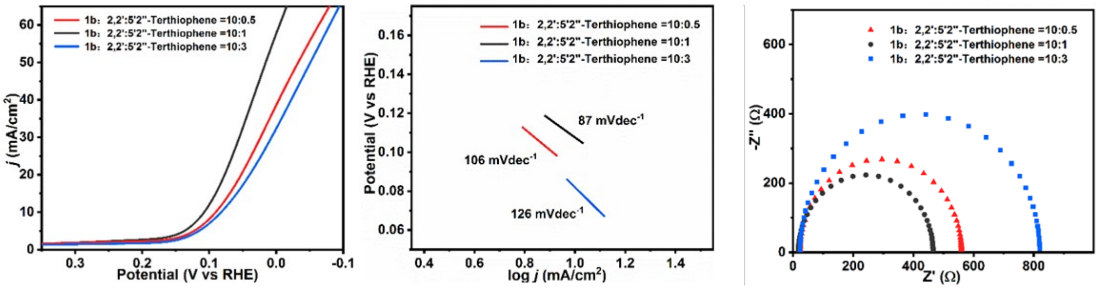


Figure 6. LSV plot, Tafel slope and EIS diagram of Co^{III}corrole **1** copolymerized with 2,2':5'2"-trithiophene in different molar ratios modified carbon papers.

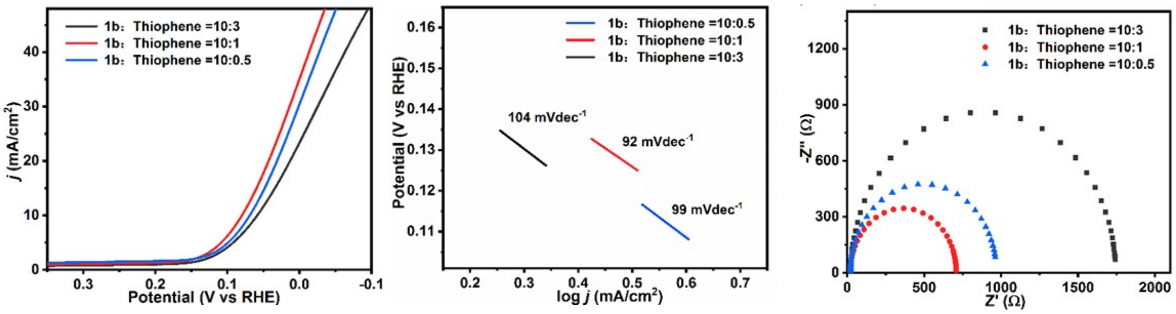


Figure 7. LSV plot, Tafel slope and EIS diagram of Co^{III}corrole **1** copolymerized with thiophene in different molar ratios modified carbon papers.

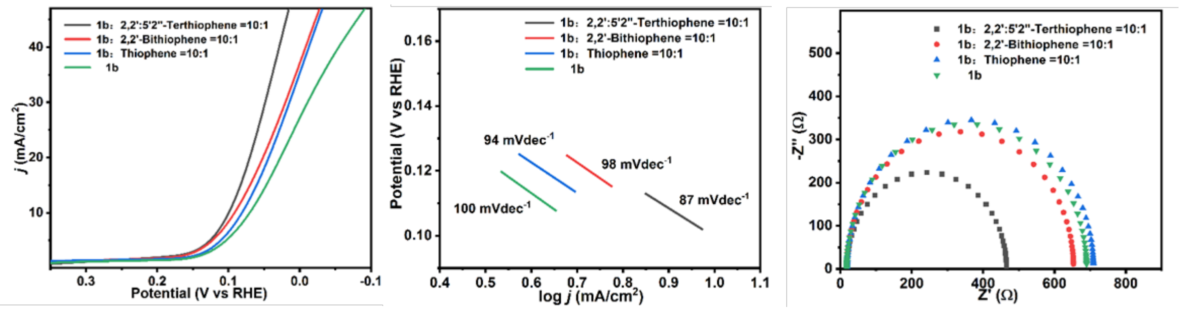


Figure 8. LSV plot, Tafel slope and EIS diagram of Co^{III}corrole **1** and three thiophenes in a molar ratio of 10:1 modified carbon papers.

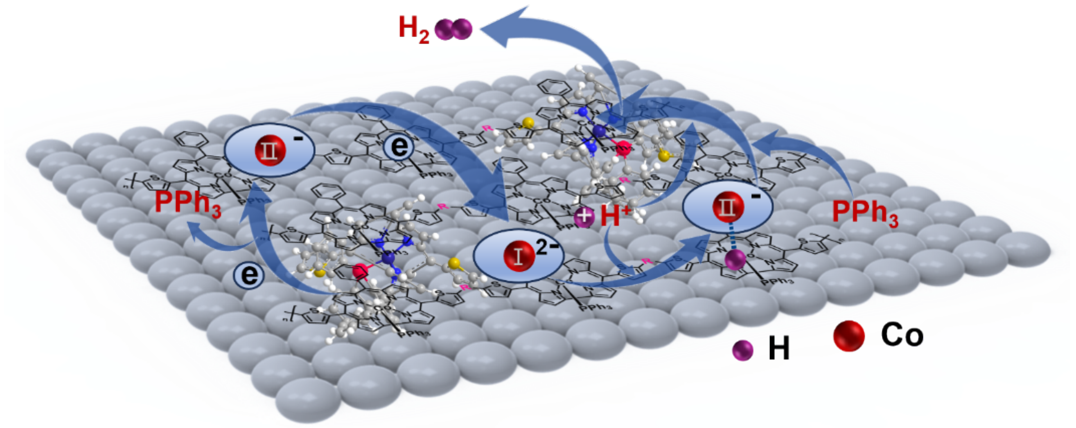


Figure 9. Catalytic hydrogen evolution mechanism of Co^{III}-corrole **1** copolymer conductive polymer.

The proposed mechanism

The mechanism of hydrogen evolution is shown in Figure 9. First, Co^{III}-PPh_3 loses an electron to $[Co^{II}]^-$, which is accompanied by the dissociation of PPh_3, and then $[Co^{II}]$ continues to lose an electron and is reduced to $[Co^{I}]^{2-}$, which combines with H^+ to form $[Co^{II}$**-**$H]^-$, and $[Co^{II}$**-**$H]^-$ continues to react with H^+ to release H_2. It then recombines with PPh_3 to form C_O^{III}-PPh_3. The preparation of conductive polymer can improve its catalytic hydrogen evolution performance mainly due to its long-range ordered structure, which increases the electron transport rate, exposes more metal active centers, and has a larger active surface volume.

Conclusions

In summary, three thiophene molecules including mono-, bis- and tri-thiophenes were successfully copolymerized with $Co^{III}PPh_3$-5, 15-bis(2-thiophenyl)-10-phenylcorrole, through electrochemical polymerizations. The structural information was investigated by SEM, EDS and XPS analysis. Interestingly, these Co^{III}corrole-thiophene-copolymers have the significant increase of the electrochemically catalyzed hydrogen evolutions compared with pure Co^{III}corrole-polymer, and their catalytic abilities could be tunable modulated by the length of thiophene chain and the amount of thiophene molecules. Considering the Co^{III}corrole-trithiophene-copolymers have the better performance, the higher dispersion of cobalt catalytic center is an effective strategy for enhancing the electrochemical catalytic behaviors. Considering highly conjugated conductive polymers have a wide range of potential applications, the current investigations may provide useful information for future porphyrin and material science investigations.

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